IAEA-TECDOC-1419

Treatment of liquid effluent from uranium mines and mills

Report of a co-ordinated research project
1996–2000

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FOREWORD

Increased environmental awareness has made control and treatment of liquid effluents generated during mining and processing an integral part of all uranium operations, both during production and reclamation/decommissioning. Their potential to negatively impact aquatic ecosystems and drinking water resources necessitates that all effluents either be recycled back to processing circuits for reuse or treated prior to disposal or release to the environment.

Uranium production occurs in diverse physical and climatic settings, which, when combined with different production technologies, necessitate unique combinations of effluent control and treatment. However, though each uranium operation has unique environmental protection issues, they also share many problems in common. Therefore, in 1996, the IAEA initiated a coordinated research project (CRP) to facilitate exchange of ideas and experience among Member States in the expanding field of control and treatment of liquid effluents generated by uranium production facilities.

During their production phase, uranium mining and processing operations typically use active liquid effluent treatment. Water treatment systems are integrated into operations to treat effluent from processing circuits and liquids from tailings management facilities and waste rock storage areas. The transition to reclamation and decommissioning is usually accompanied by increased use of passive effluent treatment techniques, which include construction of wetlands, natural geochemical attenuation, permeable reactive walls and use of micro-organisms.

Both active and passive treatment techniques are based on a solid body of science and both have been extensively field-tested. At the same time, effluent treatment technology continues to evolve, as mining operations look for better treatment strategies to control costs and still meet increased environmental requirements. This CRP, which was completed in November 2000, provided a forum in which case histories from active mining operations and effluent treatment research could be discussed and documented. The case histories provide examples of how individual mining operations have dealt with effluent control and treatment under a wide range of operating conditions. Documentation of effluent treatment research offers operational personnel access to new ideas and technologies that could potentially apply to their operations.

The IAEA wishes to express its appreciation to all participants in the CRP. Special gratitude is extended to R. Ring (Australia), J. Jarrell (Canada) and M. Csövári (Hungary) who provided advice and guidance to the CRP. The IAEA staff member responsible for the CRP was J.-P. Nicolet of the Division of Nuclear Fuel Cycle and Waste Technology. The IAEA officers responsible for this publication are C. Ganguly and K. Wenrich of the Division of Nuclear Fuel Cycle and Waste Technology.

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SUMMARY

1. Introduction

Treatment and control of liquid effluents are required throughout the uranium production and reclamation cycle. Effluents generated during uranium mining and processing contain radioactive and non-radioactive elements and compounds that, if not properly contained, can contaminate drinking water resources or enter the food chain, potentially harming the environment and endangering the health and well being of human populations. Accordingly, regulatory standards have been established that set maximum levels of contaminants that can be released to the environment. The objective of effluent treatment and control is to ensure that these limits are met so that uranium mining operations and reclamation sites do not endanger surrounding populations.

Effluent treatment and control is a concern of every mining operation, and a large body of science and experience has been built up around these activities. As regulatory requirements become more rigorous, however, improved technologies will be required. In addition to being driven by the regulatory environment, new technologies will also focus on cost containment and water conservation. Uranium mining takes place in a variety of physical and climatic conditions, which necessitate design of site specific effluent control and treatment systems. At the same time, the chemical and physical characteristics of the effluents from operation to operation are broadly similar, which means that uranium production facilities worldwide share many common control and treatment problems. Therefore, the purpose of this co-ordinated research project (CRP) was to facilitate exchange of ideas and experience in the field of treatment and control of liquid effluents generated during uranium mining and processing. Representatives from ten countries participated in the CRP: Australia, Canada, China, Germany, Hungary, India, Kazakhstan, Portugal, Turkey and Ukraine. This TECDOC includes research results compiled from these countries along with case histories of operating experience with various treatment and control technologies.

2. Effluent characterization

Liquid effluents are generated at all stages of the uranium production cycle that use process water and chemicals, including crushing, grinding, leaching, precipitation and tailings disposal and management. In addition, leaching of ore and mineralized waste rock by groundwater and surface water, respectively, can result in generation of acid mine water, which must also be contained and treated. Containment and treatment of liquid effluents does not stop when production ceases, but must continue through decommissioning and reclamation. The effectiveness of the containment strategies must continue to be monitored even during the long term monitoring phase of a reclaimed operation.

Liquid effluents typically contain both radioactive contaminants namely uranium and radium (^{226}Ra) and non-radioactive contaminants, including nickel, arsenic, manganese, magnesium, molybdenum, selenium, fluorides and sulphates. Because of the diversity of operating environments and potential contaminating elements and compounds, a single treatment technology may not work for all potential contaminants. Therefore, different combinations of treatment strategies may be required depending on the chemical composition of the effluents. During uranium production, active effluent treatment is usually the dominant technology, with utilization of passive technologies increasing during reclamation and long term monitoring.

However, both active and passive technologies have application during operations and decommissioning. The following summaries highlight current research into active and passive technologies and operating experience that help quantify their effectiveness. The results of the research and case histories on which these summaries are based are well documented and include very specific and detailed illustrations and tables.

3. Active treatment systems

The characteristics of uranium liquid effluents depend on composition of the ore and the type of mining and processing used to extract the uranium. Local climate can also play a role in treatment and control of effluents. The effectiveness of treatment depends on maintaining optimum physical and chemical conditions that facilitate removal of contaminants. Most conventional uranium mills use acid leach systems, and neutralization of acidic slurries/liquors with lime before discharge is the preferred method for initial acid effluent treatment. With the exception of ^{226}Ra, removal of radionuclides is typically greater than 99%. Similarly, heavy metals and dissolved salts are also removed from the effluents. However, the resulting precipitate or sludge contains concentrations of heavy metals, radionuclides and dissolved salts that exceed regulatory standards. In addition the sludge, which requires large storage volumes, retains moisture, which limits the quantity of water available for recycle. In Australia, research has shown that recycling of the sludge and blending it with lime slurry results in high-density sludge with 50 to 65% volume reduction and recovery of up to 16% more neutralized water for reuse.

Neutralization results in precipitation of most contaminates, but radium as ^{226}Ra is still present in the effluent that overflows from the neutralization process. Most operations use barium chloride to remove the radium. As is the case with sludge from the neutralization process, however, barium-radium sulphate sludge resulting from radium removal also has high water content and needs large storage cells. In China, research has been conducted that suggests that recycling the sludge from barium chloride treatment reduces reagent consumption and improves settling properties so that less water is retained, reducing storage requirements and improving availability of water for recycling. Research in China has also shown that aerating neutralized sludge that contains manganese oxide from the leaching process, results in formation of manganese hydroxide that absorbs radium, thus eliminating the barium chloride step and saving on reagent costs. In effect, waste treatment is accomplished by using modified waste from the leaching process.

Not all effluents require neutralization such as that required for effluents generated by acidic leaching processes. Therefore, other treatment methods may be more suitable for effluents such as mine water, drainage from waste dumps and contaminated surface waters. In Australia, for example, research has shown that nanofiltration, a membrane separation technique that depends on molecule size and charge, is effective in removing ions from contaminated water. Nanofiltration is between ultrafiltration and reverse osmosis (RO) in terms of species separated, and is potentially more cost effective than RO where removal of multivalent rather than monovalent ions is important.

Similarly, research has been conducted in China on use of macropore resins to remove uranium from mine water. The macropore resins are shown to have better adsorption properties than strong base ion exchange resins currently used in most mine water treatment systems. One of the four resins tested (D263B) is particularly effective in recovering uranium from very dilute uranium effluent, which makes it ideal for use in decommissioning projects.

4. Passive treatment systems

Wismut in Germany is arguable the world's largest uranium reclamation/decommissioning project, involving effluent treatment related to mine flooding, mine dumps and mill tailings remediation. Because of the diversity of remediation at Wismut several passive treatment systems have been evaluated in order to lower costs and still meet regulatory standards. Wismut has tested such passive systems as:

- In situ microbial treatment of contaminated groundwater;
- Permeable reactive walls for groundwater remediation;
- Biological treatment of mine water in a constructed wetland.

The goal of passive systems research at Wismut is to identify and test systems that can be used to replace conventional treatment plants where long-term reclamation will be required such as the Helmsdorf site where treatment of seepage water from a tailings pond could be required for 200 years.

The Ranger uranium mine-mill complex in northern Australia has used wetlands to treat ore stockpile run off and water from the open pit for 10 years. The principle solutes of concern are UO_2, Mn, NO_3 and SO_4 and with the exception of sulphates all are effectively removed in the wetland environment. Carbon limitation of bacterial activity has been identified as the cause of poor sulphate removal efficacy. Addition of biomass from a specific species of green algae (*Scenedesmus* sp.) has, however, proven effective in promoting sulphate removal.

India has conducted research into biogenic treatment of uranium mill effluents, which is a combination of active-and passive-state effluent treatment. This research was initiated to address India's concerned about the long term stability of barium-radium sulphate sludge due to re-dissolution of radium when contacted by fresh water. Indian researchers have found that the microbe *Penicillium chrysogenum* is a ^{226}Ra biosorbent. Biomass from this species in the form of granules can be used in columns to remove ^{226}Ra, similar to ion exchange resins used in conventional water treatment. This process is being evaluated as a substitute for the barium chloride treatment of mill effluents.

In situ leach (ISL) uranium extraction utilizes either acid or alkaline leach systems to remove uranium from porous sandstone deposits. Acid leach systems are more widely used, particularly where the water quality in the leach aquifer is unsuitable for human or agricultural use because of high natural radionuclide levels or high levels of other dissolved compounds. Regardless of the ultimate suitability of the aquifer for post-leach use, the return of water quality to pre-mining conditions is a goal of all in situ leach operations to ensure that leach solutions do not migrate laterally or vertically beyond the leach fields.

Kazakhstan has taken a leading role in research in self-remediation of groundwater in in situ leach aquifers. Core samples taken after leaching has been completed show that certain minerals in the aquifer sandstones have adsorptive properties that allow them to remove impurities. Acid leach solutions seem to enhance the adsorptive properties of some of these minerals. Once leaching is complete and the leach aquifer is allowed to achieve equilibrium groundwater flow rates, these minerals begin to adsorb minerals from the leach solutions. Similarly, the sorption characteristics of the host sands help reduce the toxicity of leach solutions as they gradually migrate beyond the leach field perimeter. Self-remediation of ISL operations may, however, require several tens of years, so monitoring must continue vertically and horizontally away from the leach operation to ensure that leach solutions do not impact adjoining aquifers.

5. Economics

Control and treatment of liquid effluents is an integral part of uranium production and site reclamation and must be factored into total production costs. In turn, treatment costs must consider not only the treatment process itself, including manpower, reagents, power, etc., which can extend decades beyond closure of production operations, but also immobilization and disposal of contaminated residues such as sludges. The Wismut project puts the significance of the cost of effluent treatment and the need for comprehensive effluent treatment strategies into perspective. Water treatment costs at Wismut are expected to total approximately 15% of total reclamation costs, which in turn are expected to total more than US$6 billion.

6. Conclusions

Control and treatment of liquid effluents is a well-recognized aspect of environmental protection related to uranium mining and processing. Accordingly, a large body of science and operating experience has been built up to support liquid effluent control and treatment. Uranium production facilities worldwide share many common control and treatment problems and this CRP has afforded experts an opportunity to share research and experience related to these problems, which in turn has lead to new information on the following treatment and control technology:

- High-density sludge from effluent neutralization (Australia);
- Aerated manganese hydroxide for removal of radium (China);
- Nanofiltration and macropore resins to treat mine water (Australia and China);
- In situ microbial treatment and permeable reactive walls for treatment of contaminated groundwater (Germany);
- Construction of wetlands to treat mine water runoff (Australia and Germany);
- Biogenic granules to remove ^{226}Ra from mill effluent (India);
- Self-remediation of acidic in situ leach aquifers (Kazakhstan);
- Sorption characteristics of soil for self-remediation of contaminated groundwater (Hungary).

These and other topics presented in this TECDOC will be of interest to technical personnel who deal with day-to-day practical aspects of liquid effluent control and treatment at uranium production facilities worldwide.

7. List of related IAEA publications

The following IAEA publications help define the many environmental issues that face all environmental protection aspects of uranium mining, processing and reclamation. While they focus on broader issues facing the uranium production industry, this TECDOC concentrates on a specific activity within the uranium production-reclamation cycle — control and treatment of liquid effluents.

INTERNATIONAL ATOMIC ENERGY AGENCY, In Situ Leaching of Uranium: Technical, Environmental and Economic Aspects, IAEA-TECDOC-492, Vienna (1989).

INTERNATIONAL ATOMIC ENERGY AGENCY, Guidebook on Design, Construction and Operation of Pilot Plants for Uranium Ore Processing, IAEA Technical Report Series, STI/DOC/10/314, Vienna (1990).

INTERNATIONAL ATOMIC ENERGY AGENCY, Uranium Extraction Technology, IAEA Technical Report Series, STI/DOC/10/359, Vienna (1993).

INTERNATIONAL ATOMIC ENERGY AGENCY, Decommissioning of Facilities for Mining and Milling of Radioactive Ores and Closeout of Residues, IAEA Technical Report Series, STI/DOC/10/362, Vienna (1994).

INTERNATIONAL ATOMIC ENERGY AGENCY, Environmental Impact Assessment for Uranium Mine, Mill and In Situ Leach Projects, IAEA-TECDOC-979, Vienna (1997).

INTERNATIONAL ATOMIC ENERGY AGENCY, Guidebook on Good Practices in the Management of Uranium Mining and Mill Operations and the Preparation for their Closure, IAEA-TECDOC-1059, Vienna (1998).

OECD NUCLEAR ENERGY AGENCY, A Joint OECD-NEA/IAEA Report, Environmental Activities in Uranium Mining and Milling, OECD-NEA, Paris (1999).

INTERNATIONAL ATOMIC ENERGY AGENCY, Impact of new Environmental and Safety Regulations on Uranium Exploration, Mining, Milling and Management of Waste, IAEA-TECDOC-1244, Vienna (2001).

INTERNATIONAL ATOMIC ENERGY AGENCY, Technologies for the Treatment of Effluents from Uranium Mines, Mills and Tailings, IAEA-TECDOC-1296, Vienna, (2002).

INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Radioactive Waste from the Mining and Milling of Uranium and Thorium Ores, IAEA Safety Guides No. WS-G-1.2, Vienna (2002).

INTERNATIONAL ATOMIC ENERGY AGENCY, Monitoring and Surveillance of Residues from the Mining and Milling of Uranium and Thorium, IAEA Safety Report Series No. 27, IAEA, Vienna (2002).

INTERNATIONAL ATOMIC ENERGY AGENCY, The Long Term Stabilization and Isolation of Uranium Mill Tailings, IAEA-TECDOC-1403, Vienna (2004).

Treatment of liquid effluent from uranium mines and mills during and after operation

R.J. Ring, P. Holden, J.K. McCulloch, G.J. Tapsell, D.E. Collier, R. Russell, S. Macnaughton, K. Marshall, D. Stimson

Australian Nuclear Science and Technology Organization (ANSTO),
Ore Processing Group, Menai, NSW, Australia

Abstract. The Australian research programme examined three separate topics, all related to the processing of uranium mill effluents. The topics covered conventional line treatment of process liquor and the application of the emerging technologies, nanofiltration and wetlands, to the treatment of higher quality run-off waters. The investigation of the lime treatment processes focused on changes in operating strategies to increase the density of the resulting sludge. The wetland study examined factors potentially limiting bacterial sulphate reduction, namely carbon limitation and competition with iron reducing bacteria for carbon and energy. For the wetland sediment used in the experimental programme, it was found iron reduction activity was not likely to significantly limit sulphate reduction. Carbon limitation of bacterial activity was, however, found to be a significant factor in poor sulphate removal efficiency. The use of green algae as a low cost, rapidly produced carbon source to promote sulphate reduction was then investigated. Reduction of sulphate by bacteria grown on algeal biomass was demonstrated at benchscales less than 10 kg of biomass was required to drive bacterial reduction of 1t of sulphate. The final topic investigated the potential of nanofiltration to remove dissolved species from typical uranium mill effluents. The separation performance was found to vary significantly with membrane type, but rejection of divalent methods ions was generally high, with good selectivity over single valent iones

1. Background

The control and treatment of liquid effluents from uranium milling operations have assumed greater importance because of increased environmental awareness and more stringent regulatory requirements. Conservation of water has also placed more pressure on mill operators to recycle water, which both minimises usage and limits quantities requiring disposal.

In Australia, the two operating uranium mines are in diverse environments. The Ranger mine is located in a tropical zone, with wet and dry seasons, and management of excess water is a key issue. The other site, Olympic Dam, is semi-arid with low ground water quality, and water utilisation/recycle is a major consideration. Although both of these mills have established water management strategies, changes are being implemented as part of recent expansions and as a result of operating experience.

Neutralisation of acidic slurries/liquors with lime before discharge is the current preferred method of effluent treatment for operating plants. However, the volume of the sludge produced requires large storage volumes and the sludge retains a significant moisture fraction, which promotes seepage and limits the quantity of water available for recycle. In addition, lime treatment produces concentrations of heavy metals, radionuclides and dissolved salts, which do not meet all regulatory requirements. There is a need for improved technologies to meet these standards, particularly cost-effective methods for reduction of sulphate, which is present at the saturation level of gypsum after lime treatment.

Residual sulphate is a significant problem in regard to impacts on aquatic ecosystems and the quality of drinking water resources. Bacterial sulphate reduction offers the potential to remove sulphate, as well as decreasing acidity and precipitating soluble heavy metals (if present). However, the problem currently confronting investigators seeking to utilize bacterial sulphate reduction for treatment of mine effluents is the requirement to supply carbon and energy to drive the sulphate reduction process, whether it be in artificial wetlands or in plantless treatment systems.

Over the last few years, there have been major advances in the use of membranes in the water treatment industry. Membrane filtration processes are finding increasing application to the treatment of waste streams because of their ability to separate the contaminants into a small volume for subsequent disposal. However, there have been very few applications in the mining/mineral industries, apart from some very recent installations of RO plants to treat mine water.

Nanofiltration separates chemical species based on their molecular size and/or charge. These characteristics make nanofiltration ideal for many applications, especially for recovery of valuable components from process streams. Currently such separations are affected by chemical processes (eg. precipitation, ion exchange), which involves the use of chemicals and the production of wastes.

The objectives of the ANSTO project were to:

- Improve the efficiency of water treatment processes, particularly with regard to reduction of sludge volumes;
- Investigate factors limiting bacterial sulphate reduction in constructed wetlands; and
- Examine the potential for use of low-pressure membrane processes to remove specific contaminants (radionuclides, heavy metals) from process and treated liquors.

2. Research on recycle of process water

2.1. Introduction

Neutralization of acidic effluents is required to allow either the recycle of the treated water to the process or discharge of the treated water to an evaporation pond or a local water system. For the latter, additional treatment to further reduce contaminant concentrations may be necessary. In conventional lime neutralisation circuits, a low density sludge is produced which occupies large storage volumes and retains large quantities of water that could be recycled. ANSTO has undertaken an extensive laboratory study of neutralisation processes with the aim of developing a more efficient process for water recycle [1].

2.2. Neutralization of acidic process liquors

In lime neutralization circuits treating acidic waste liquors, such as acid mine drainage (AMD), efficient sludge collection is the most critical part of the process. In a conventional liming process, thickening of the neutralised slurry produces an underflow density of typically 3wt%. Because of the low density, it remains uncompacted for a considerable time and requires a large retention volume or further treatment (e.g. pressure filtration).

These problems have been overcome by the high density sludge (HDS) version of the basic lime process [2] and [3]. The HDS process recycles a substantial proportion of thickener underflow sludge, which is blended with lime slurry prior to the main reaction vessel. The pre-mix is the major factor in achieving a dense particulate material compared to the fluffy precipitate normally obtained. The HDS process has produced underflow densities of 15–30% and as an additional benefit of the higher solids loading, near complete control of gypsum scaling. Although the HDS process has been applied to the treatment of acidic waste liquors (TDS = 2 g L^{-1}), to our knowledge, it has not been used for neutralisation of more concentrated process liquors (TDS = 40 g L^{-1}) and its potential effect on radionuclide concentrations has not been determined.

Recent publications [4] have claimed significant advantages for a staged neutralization process. The essential feature of the process is to control the reagent addition to each neutralization vessels so that heterogeneous precipitation occurs, which favours the formation of dense crystalline particles, rather than a fluffy amorphous precipitate. A key aspect of the process is the selection of the optimum pH profile.

The mechanism of precipitation (heterogeneous versus homogeneous) is controlled by the level of supersaturation. The above work has found that heterogeneous reactions can be obtained provided that the supersaturation ratio is controlled below a critical level.

2.3. Experimental studies of neutralization processes

2.3.1. Scope

The scope of the experimental studies was to compare the performances of four treatment processes for the neutralization of acidic tailing waters from two uranium mills. The performance criteria were:

- effluent composition;
- reagent consumption; and
- settled sludge density.

The circuits examined were:

- a conventional circuit where the bulk of the neutralising reagent is added together with the feed water to the first tank in the cascade;
- a staged addition circuit where the feed water is added to the first tank, but the neutralising reagent is added to all tanks in the circuit to maintain a carefully selected pH profile; and
- an HDS circuit where thickener underflow sludge is recycled to a conditioning tank and mixed with the neutralising reagent. The conditioned slurry flows by gravity to the first neutralisation reactor to react with the incoming feed water; and
- staged HDS where conditioned slurry is added to all tanks in the circuit.

2.3.2. Circuit flowsheets

Figure 1 shows the conventional, staged and HDS neutralisation circuits used for the tests. The neutralisation tanks had a total working volume of 11.3 L. The overflow from the final tank was flocculated and gravity fed a 0.1 m diameter high rate thickener. The thickener bed height was controlled at a fixed level by pumping underflow to a sludge storage tank. For the HDS circuit, the conditioned slurry flowed by gravity to the first tank. In all circuits the flow rate of the neutralising reagent was controlled to achieve a desired effluent pH from the thickener, and in the case of the staged process, the target pHs for the individual tanks.

2.4. *Feed water and reagent compositions*

Waters originating from two different sites were used (Table 1 for compositions). Waters 1 and 2 differed significantly in terms of pH, total dissolved salts and ferrous ion concentration. Water 1 also contained significantly more uranium because of process conditions at the time of collection.

Two series of tests were carried out in the continuous circuit described in Figure 1. In the first series of tests (Table 2), a single addition of reagent was made to the first tank. Two feed waters were examined. The neutralising reagent used for water 1 (W1) was a hydrated dolomitic slurry. The calcined solids contained of 49 wt% $Ca(OH)_2$, 35 wt% $Mg(OH)_2$. For water 2 (W2), a high grade hydrated lime slurry was used. Both slurries were made up to a concentration of 30 wt% solids.

In the second series, staged addition was examined. However, to obtain the desired pH profile, the number of circuit tanks was increased to four. Air sparging for oxidation of ferrous ion was carried out in tanks 3 and 4. Water 1A was used in this series and some single addition tests were also repeated.

During the HDS trials, the solids recycle ratio, defined as the mass of solids recycled to new solids precipitated, was varied to determine the effect on thickener underflow density.

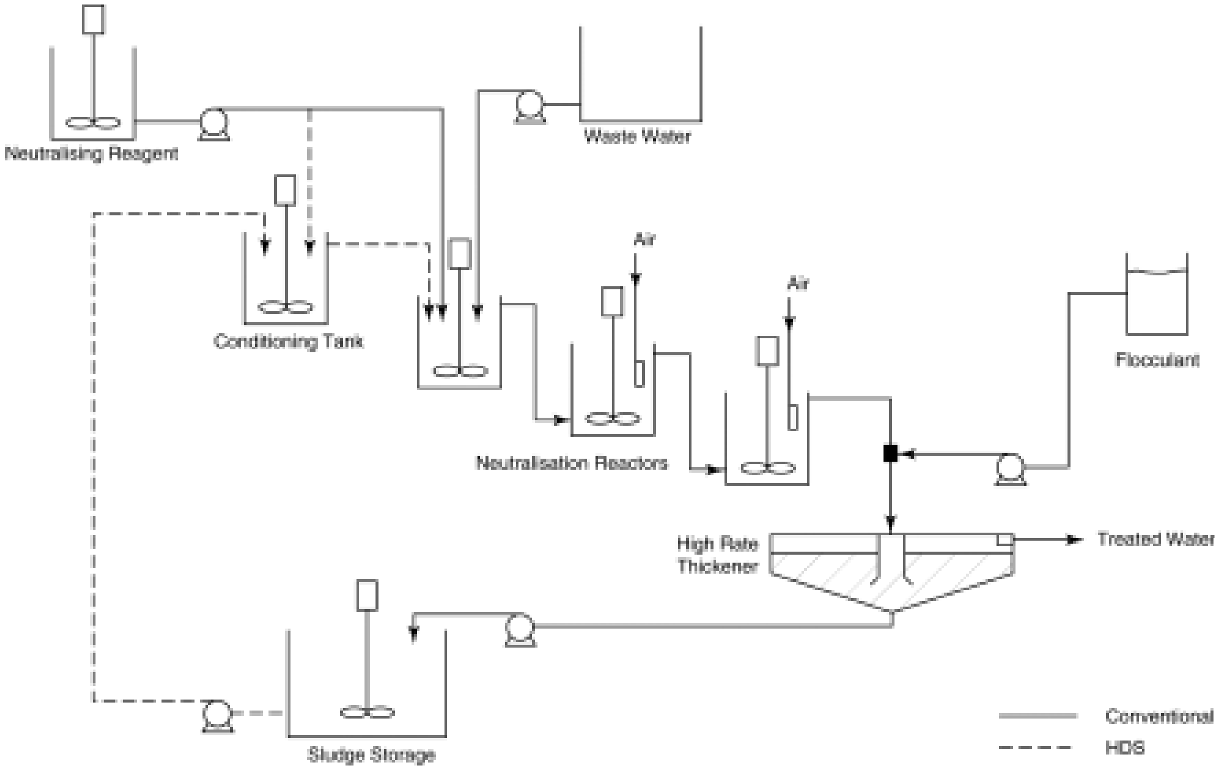

FIG. 1. Conventional/Staged/HDS neutralization processes.

Table 1. Composition of feed waters[#]

		Water 1	Water 1A	Water 2
pH		1.16	1.17	1.66
Fe^{2+}	g L^{-1}	3.9	2.4	< 0.1
Fe^{3+}	g L^{-1}	1.3	3.6	2.6
Fe (total)	g L^{-1}	5.2	6.0	2.6
Al	g L^{-1}	1.27	1.43	1.47
SO_4	g L^{-1}	29.1	33.3	39.6
Si	Mg L^{-1}	102	110	510
U	Mg L^{-1}	233	271	8.2
Cu	Mg L^{-1}	705	1040	17.6
Ca	Mg L^{-1}	669	721	490
P	Mg L^{-1}	42	25	103
Mg	Mg L^{-1}	251	278	3810
Mn	Mg L^{-1}	78	95	2040
Co	Mg L^{-1}	9	8.1	2.8
Zn	Mg L^{-1}	9	17.2	1.1
Pb	Mg L^{-1}	0.93	0.45	3.2
Mo	Mg L^{-1}	0.37	0.53	0.043
V	Mg L^{-1}	0.56	0.87	8.8
Th	Mg L^{-1}	2.4	2.6	1.1
Cr	Mg L^{-1}	4	5.8	4.4
Zr	Mg L^{-1}	7	9.9	0.054
Se	Mg L^{-1}	0.53	0.81	0.87
Bi	Mg L^{-1}	0.18	0.21	0.0067
F	g L^{-1}	1.81	nm	nm
K	Mg L^{-1}	500	nm	66.2
^{230}Th	Bq L^{-1}	2770	2730	11 200
^{226}Ra	Bq L^{-1}	5.4	2.1	6.0
^{210}Pb	Bq L^{-1}	514	420	350

[#] waters 1 and 1A were from the same site, but were collected at different times

Table 2. Test parameters

Waste Liquor	Reagent	Type	Target pH	Circuit Residence Time (h)	Reagent Addition
Series 1					
W1	Dolime	Conventional	7.5	3.0	Single
W1	Dolime	HDS	7.5	2-3	Single
W2	Lime	Conventional	7.0	1.5	Single
W2	Lime	HDS	7.0	2-3	Single
Series 2					
W1A	Dolime	Conventional	7.5	3.0	Single
W1A	Dolime	Conventional	7.5	3.0	Staged
W1A	Dolime	HDS	7.5	2.3 – 2.4	Single
W1A	Dolime	HDS	7.5	2.3 – 2.4	Staged

2.5. *Experimental results*

2.5.1. *Sludge densities – Single addition of reagent*

For all feed waters, HDS operation produced significantly higher thickener underflow densities, as shown in Table 3. For HDS, these results were achieved at a solids recycle ratio of only 2–3/1. The net solids production for all waters was 40–45 g L^{-1}.

The data also confirm that the HDS process is effective for a reagent other than lime, which has been used in all other HDS applications.

Table 3. Underflow densities

Feed water	Reagent	Type	Underflow Density (wt%)
W1	Dolime	Conventional	23.5
W1	Dolime	HDS	41.7
W2	Lime	Conventional	12.6
W2	Lime	HDS	25.5
W1A	Dolime	Conventional	25
W1A	Dolime	HDS	36.8

The underflow density was greatest for water 1, which contained the smallest proportion of iron as ferric ion. Density was least for water 2, in which all the iron was present as ferric ion. This is consistent with trends observed for AMD waters. The high underflow densities were achieved at low solid recycle ratios, in contrast to AMD applications where recycle ratios of 20–30 are typical.

Recycle ratio was not optimised in this work programme, but it was clearly demonstrated for water 1A, that the underflow density improved as the recycle ratio was increased. These trends, illustrated in Figure 2, suggest that greater recycle rates should be investigated, but there is clear trade-off between a higher density and the need to construct a larger capacity circuit to handle the higher total flow. For example, at a recycle ratio of 2.5/1, the total feed (water plus recycle) was increased by 20%.

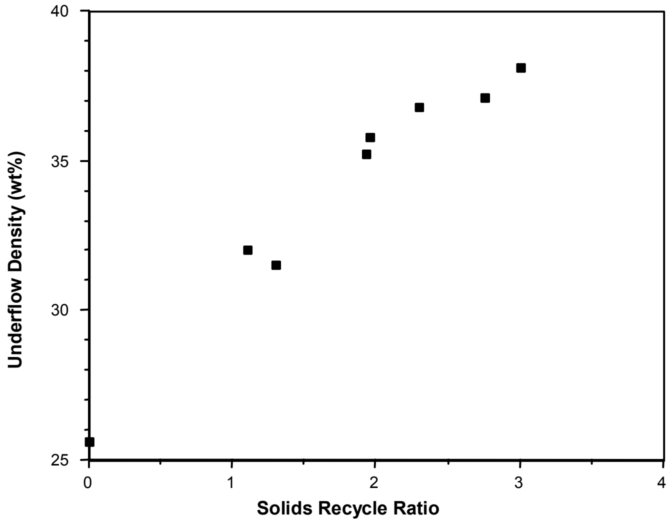

FIG. 2. Effect of recycle ratio on underflow solids content for water 1A.

The effects on underflow density of recycle ratios significantly greater than 3 were examined for water 2. Higher densities were achieved, but only at impractical recycle rates for these liquors [1].

About 2 days were required to reach a steady state sludge density, which is much less than for AMD liquors. Figure 3 illustrates the variation of sludge density with time for feed water 1. The reason for the better response is probably due to the high total dissolved salts. A typical AMD water typically produces a solids concentration of less then 5 g L^{-1}. For the test liquors, the greater concentration of solids both precipitating and in the recycle stream would allow greater particle interaction, contributing to a faster response of the system.

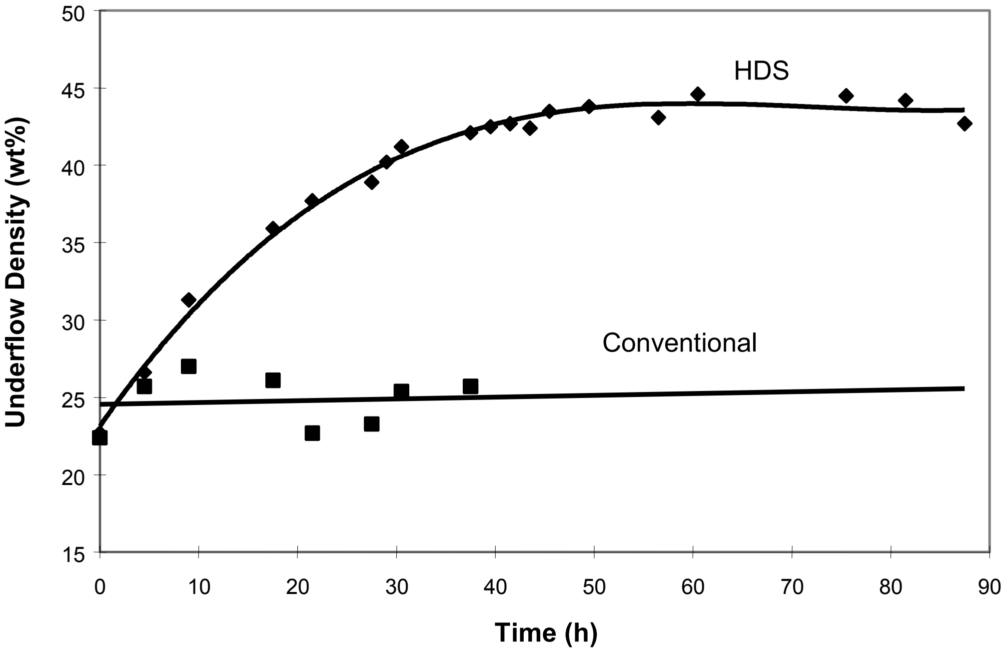

FIG. 3. Feed water 1 underflow density.

2.5.2. Sludge densities – Staged addition of reagent

For non-HDS operation, staged addition of reagent produced lower thickener underflow densities compared to a single addition to the first tank. For HDS operation, staged addition of reagent offered no advantages in terms of sludge density. Results are summarised Table 4.

Table 4. Underflow densities

Feed	Reagent	Operation	Reagent addition	Underflow Density (wt%)
W1A	Dolime	Conventional	Single	25.6
W1A	Dolime		Staged	21.0
W1A	Dolime	HDS (~2.5/1)	Single	36.8
W1A	Dolime		Staged	37.1

2.5.3. pH Profiles

Conventional versus HDS - The pH profiles for conventional and HDS operation for water 2 are compared in Figure 4. At the lower recycle ratio, the HDS profile is quite similar to the conventional circuit. For the high ratios, the impact of the high pH slurry (~pH 9–10) steam entering tank 1 from the conditioning tank is apparent. Under these conditions elements such as Mn and Mg are precipitated in the conditioning tank, but then redissolve in tank 1.

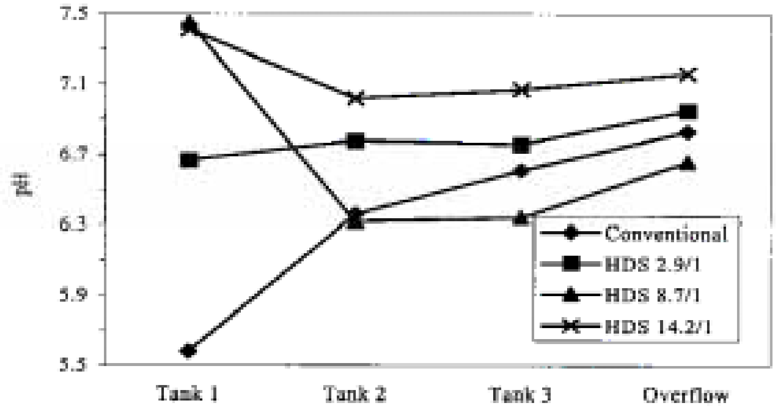

FIG. 4. pH Profiles for treatment of water 2.

Conventional single versus staged addition — The pH profiles for conventional single and staged addition operation for water 1A are compared in Figure 5. Obviously, the staged profile is considerably different as it was controlled at the selected values. For water 1A (and water 1) the conventional and HDS profiles are even closer than observed for water 2.

2.5.4. *Treated liquor compositions*

The composition of thickener overflow liquors was determined for the full range of circuit configurations. Overflow concentrations of major elements for all waters are compared in Table 5. The main findings are as follows:

- there was no essential differences between conventional, HDS, and the staged conventional processes in the removal of most major ions;
- the use of dolime, as expected, resulted in a higher concentration of Mg compared to the feed water; and
- for water 2 and using lime as the neutralising agent, the HDS process yielded lower concentrations of Mn and Mg, and consequently sulphate ions.

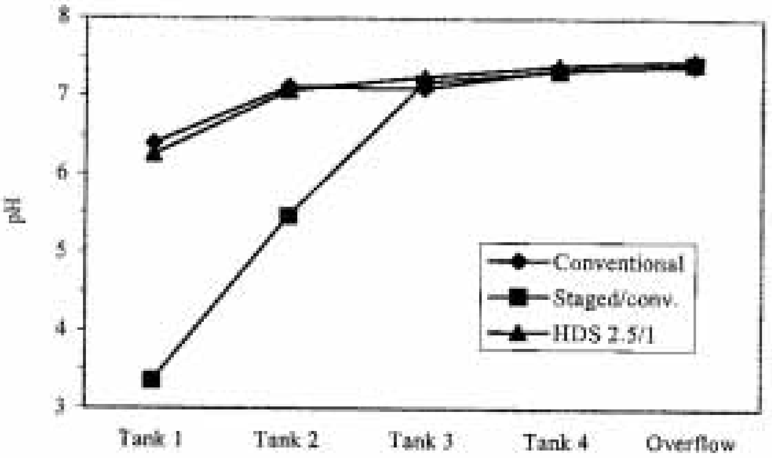

FIG. 5. Circuit pH profiles for treatment of water 1A.

Table 5. Concentration of major ions in thickener overflow

Conditions	pH	SO_4 g L^{-1}	Mn mg L^{-1}	Mg mg L^{-1}	Ca mg L^{-1}	Si mg L^{-1}	Cu mg L^{-1}	Fe mg L^{-1}	Al mg L^{-1}
Feed water 2	1.66	39.6	2040	3810	490	510		2610	1470
Conventional	6.83	22.3	1480	3880	371	< 0.1		1.1	4.7
HDS - 2.9/1	6.95	17.3	820	3250	427	4.5		< 1	< 1
Batch	7.12	23.7	1470	3970	442	0.1		< 1	< 1
Feed water 1A	1.17	33.3	95	278	720	110	1040	6000	1430
Conventional	7.40	14.9	62	2830	583	1.3	2.3	< 1	1.8
Staged conventional	7.44	14.2	70	2800	503	1.3	2.2	< 1	1.9
HDS - 2.5/1	7.47	17.2	48	3240	499	< 0.1	0.61	< 1	< 1

The lower concentrations of Mn and Mg produced by the HDS process result from the almost complete precipitation of these elements under the high pH conditions in the conditioning tank. Redissolution occurred in the lower pH tanks of the main circuit, but some precipitates must remain inaccessible to the bulk solution. Element profiles for the complete circuit for water 2 are compared in Table 6.

Overflow concentrations of minor elements and radionuclides for water 2 are compared in Table 7. For all waters and neutralisation processes, there were no significant differences in minor element concentrations.

With the exception of ^{226}Ra, removal of radionuclides was greater than 99% in all runs. The data for ^{226}Ra are consistent with the findings from many other uranium operations where it has been established that secondary treatment (*eg*. barium chloride addition) is necessary to reduce radium in neutralised liquors to <0.1 Bq L^{-1}. The removal of ^{226}Ra achieved at pH 7.5 was 94%.

Table 6.Circuit profiles

Sample	pH	SO_4 g L^{-1}	Mn mg L^{-1}	Mg mg L^{-1}
Feed	1.66	39.6	2040	3810
Conventional neutralization				
T1	5.58	21.2	1670	3370
T2	6.36	21.8	1670	3500
T3	6.61	22.4	1570	3860
O/F	6.83	22.3	1480	3880
U/F	--	22.7	1620	3830
HDS 2.9/1				
Cond.	10.9	1.7	0.57	14.3
T1	6.67	15.7	660	3030
T2	6.78	15.3	695	2930
T3	6.76	17.0	805	3240
O/F	6.95	17.3	820	3250
U/F	--	16.4	775	3080

Table 7. Concentrations of minor ions in overflow for W2# (MG L^{-1})

	Feed water composition	Conventional neutralization	HDS treatment recycle: 2.9/1
pH	1.66	6.83	6.95
Bi	0.0067	0.0003	0.0003
Co	2.8	1.8	0.11
Cr	4.4	0.046	0.057
Mo	0.043	0.020	0.026
P	103	< 0.01	< 0.01
Pb	3.2	0.0088	0.0057
Se	0.87	0.94	0.60
Th	1.1	<0.0001	<0.0001
U	8.2	0.13	0.26
V	8.8	0.067	0.053
Zn	1.1	0.57	< 0.01
Zr	0.054	<0.0001	<0.0001
^{230}Th	11 200	0.079	0.82
^{226}Ra	6.0	0.22	0.19
^{210}Pb	350	0.12	0.90

Radionuclides in Bq L^{-1}

2.5.5. Reagent consumptions

Reagent consumptions for conventional neutralisation and the HDS process at a recycle ratio of 2–3/1 are compared in Table 8. Staged operation did not result in any increase in the efficiency of reagent usage. HDS operation increased usage by 12–14% for waters 1 and 3 and by 17% for water 2. At recycle ratios greater than 3, there was not any further increase in consumption.

As discussed, the increase in reagent consumption for HDS operation for water 2 is related to the precipitation of additional Mn and Mg. The reason for the increases for water 1A are not as obvious. In all runs, including batch tests, the utilisation of the MgO component in the calcined dolomite was 60–70%. In all the HDS tests, it would appear that the CaO component was less reactive.

Table 8. Reagent consumptions (g L^{-1})

Feed water	Reagent	Type	Reagent consumption
W1	Dolime	Conventional	25.1
		HDS 2.7/1	28.2
W2	Lime	Conventional	16.3
		HDS 2.9/1	19.1
W1A	Dolime	Conventional	29.3
		Staged/conventional	28.7
		HDS 2.3/1	33.1
		Staged/HDS 2.75/1	32.3

2.5.6. Precipitated solids

The compositions of the underflow solids for conventional neutralisation and HDS are compared in Tables 9 and 10. All solids were predominantly gypsum.

Table 9. Composition of underflow solids (wt %)

Operation	Mg	Al	Si	P	SO_4	Ca	F	Mn	Fe	U	Cu
					Water 1						
Conventional	3.04	2.66	1.70	0.11	26.4	13.4	2.18	0.11	10.7	0.44	1.35
HDS 2.7/1	2.32	3.20	1.81	0.13	28.9	15.5	2.92	0.11	12.8	0.54	--
					Water 2						
Conventional	0.09	4.43	1.49	0.36	41.5	18.7	nc	0.70	5.9	0.014	0.053
HDS 2.9/1	1.29	3.80	1.28	0.31	42.4	18.2	nc	1.82	5.1	0.012	nc

nc: not calculated

Table 10. Concentration of radionuclides in underflow solids (Bq g^{-1})

Operation	^{230}Th	^{210}Pb	^{226}Ra
	Water 1		
Conventional	67	13.3	
HDS	70	13.3	
	Water 2		
Conventional	463	10.3	
HDS	391	8.6	
	Water 1A		
Conventional	85	15	0.28
Staged	70	13	0.39
Staged HDS	88	15	0.43
HDS	86	15	0.36

For water 1, the presence of unreacted dolime is the reason for the high Mg concentrations. Another factor affecting solids composition is the form of the calcium sulphate precipitate, determined by XRD, which was present as both gypsum ($CaSO_4.2H_2O$) and bassanite ($CaSO_4.0.5H_2O$) for the conventional solids and only bassanite in the HDS solids.

For water 2, the greater Mg and Mn contents in the HDS solids reflect the almost complete precipitation in the conditioning tank, but only the subsequent partial dissolution in the circuit proper. Bassanite was the only crystalline phase identified in the sludges from water 2.

The activities of the sludges were independent of the neutralisation process. In terms of solids disposal, it should be noted that the ^{230}Th content of the dry solids was considerably greater than the typical tailings that would be produced in the corresponding milling operation.

2.6. Implications of HDS for water recycle

The application of the HDS process for the treatment of liquors from a uranium milling operation has major implications in terms of the water recovered and the volume of the sludge requiring disposal. Consider the case of the new HDS installation treating 200 m^3 h^{-1} of water 1. Comparative design flows for a conventional and HDS plant are compared in Table 11. At the higher underflow density, liquor recovery is about 94%, compared to 87% for a conventional neutralisation circuit.

For a plant treating water 2, the savings would be even greater with the HDS process increasing water recovery by 16% and yielding a reduction in sludge volume of 58%.

Table 11. Plant outputs for treating 200 $m^3 h^{-1}$

Water 1			
Underflow density (wt%)		23.5	41.7
Dry solids production	$t h^{-1}$	8	8.0
Sludge production	$t h^{-1}$	34.0	19.2
Sludge production	$m^3 h^{-1}$	28.1	13.8
Water lost with sludge	$m^3 h^{-1}$	26	11.2
Water 2			
Underflow density (wt%)		12.6	33.4
Dry solids production	$t h^{-1}$	7.6	8.4
Sludge production	$t h^{-1}$	60.4	25.0
Sludge production	$m^3 h^{-1}$	54	18.8
Water lost with sludge	$m^3 h^{-1}$	52.8	16.6

2.7. *Conclusions*

The main conclusions from the ANSTO research programme are:

- the high density sludge process offers significant improvements for the neutralisation of acidic process waters arising from uranium milling operations;
- compared to a conventional neutralisation circuit, the HDS process was effective in significantly increasing the underflow density of thickened sludge. For the liquors tested, this increase resulted in reductions in sludge volumes of 50–65%;
- the use of the HDS process resulted in an increase of 7–16% in the recovery of neutralized water, which both reduces the potential for seepage from the sludge after disposal and provides a greater volume of water for recycle;
- the HDS process was effective on uranium process waters at a much lower recycle ratio than is required for the treatment of acid mine drainage waters, which contain much lower levels of dissolved salts than uranium process waters;
- the HDS process consumed slightly (5–10%) more lime than conventional treatment but final dissolved salts in the effluent were lower for the same pH;
- staged addition of reagent, for both conventional and HDS circuit configurations, offered no advantages in terms of final sludge density; and
- all neutralisation methods examined were equally effective in removing metal ions and radionuclides from process waters.

3. Factors limiting bacterial sulphate reduction in a constructed wetland

3.1. *Introduction*

The treatment of mine drainage containing heavy metals and sulphate using artificial wetlands is a technology that has been applied over the last 20 years with varying degrees of success [6]. Whilst the metal and sulphate removal mechanisms were originally thought to be plant mediated, it is now recognised that bacterial sulphate reduction (BSR) is a key process in effluent treatment [7]. The Ranger mine operated by Energy Resources Australia Ltd (ERA) was amongst the first in the world to use wetlands to treat drainage from a uranium mine. The RP1 constructed wetland is used to treat up to 450,000 m^3 of water annually. The principal solutes of concern are UO_2, Mn, NO_3, and SO_4 and, with the exception of sulphate, they are effectively removed [8] and [14].

Factors potentially limiting bacterial sulphate reduction were investigated, namely carbon limitation and competition with iron reducing bacteria for carbon and energy. Bacterial sulphate reduction is a process undertaken by heterotrophic bacteria which require an organic source of carbon and energy [13] and [12]. If such organic carbon is limited in availability, competition with iron reducing bacteria could also be significant as they are more efficient competitors for available electron donors and carbon than sulphate reducing bacteria [9]. The work was conducted as part of a larger collaborative project with the Commonwealth Science and Industrial Research Organization, the Northern Territory University and the Environmental Research Institute of the Supervising Scientist on performance of the wetland, funded by ERA. ANSTO also independently conducted investigations of the use of algal biomass to drive bacterial sulphate reduction as a potential solution to carbon limitation in BSR systems.

3.2. Wetlands at the Ranger mine

The water management system used at Ranger segregates water according to its degree of contamination and all rainfall run-off on the site is collected in one of four retention ponds (RP1 to RP4). Research into the use of wetlands to improve water quality has been conducted at Ranger for more than ten years and their application has been gradually phased in. The RP1 Constructed Wetland is used to treat ore stockpile run-off and water from the pit and was constructed in two stages. It holds 50 000 m^3 of water in 9 cells varying in size from 2050 to 17 500 m^2. The dominant plants in the wetland are *Eleocharis* (spike rush) and *Nymphya* sp. (water lilies). A detailed account of the wetland's construction is given by Shinners (1996). The composition of water entering the wetland changes from year to year, and seasonally. However, the data given in Table 12 was typical of water treated in the wetland at the time the studies reported here commenced.

3.3. Sulphate vs iron reduction

The literature suggests that bacteria capable of reducing certain forms of Fe[III] compete more efficiently for electron donors and carbon than sulphate reducers and that, under carbon-limited conditions, iron reduction processes will predominate at the expense of sulphate reduction [9]. Therefore, chemical and microbiological investigations of core samples from the constructed wetland were undertaken to quantify the amount of microbially reducible Fe[III] present, and whether iron or sulphate reduction predominates in the wetland or whether they co-occur.

Table 12. Composition of water entering ranger experimental wetland

Parameter	Units	Dissolved	Particulate
pH		7.5	
Conductivity	µS/cm	1440	
Sodium	mg/L	11	
Potassium	mg/L	3	
Magnesium	mg/L	190	
Calcium	mg/L	27	
Chloride	mg/L	4	
Bicarbonate	mg/L	31	
Sulphate	mg/L	711	
Iron	µg/L	14	44
Manganese	µg/L	15	8
Uranium	µg/L	983	6

(from Jones *et al.*, 1996)

The hydroxylamine/HCl assay of Lovley and Phillips [10] was used to estimate the amount of microbially reducible iron. The reducible iron concentrations in a 23 cm core taken from the wetland and sectioned in 2 cm segments under anaerobic conditions ranged from 78 to 536 mg/kg and decreased rapidly with depth (Fig. 6). The latter value was 10-fold less than that observed by Lovley and Phillips [10] in sediments with high Fe reduction activity, suggesting the capacity for iron reduction to compete with sulphate reduction in the sediment may be limited. The relatively constant ratio of Fe[III] to Fe[II] suggests that the majority of Fe is attributable to HCl-soluble solid forms of Fe rather than to Fe[II] produced from microbial reduction.

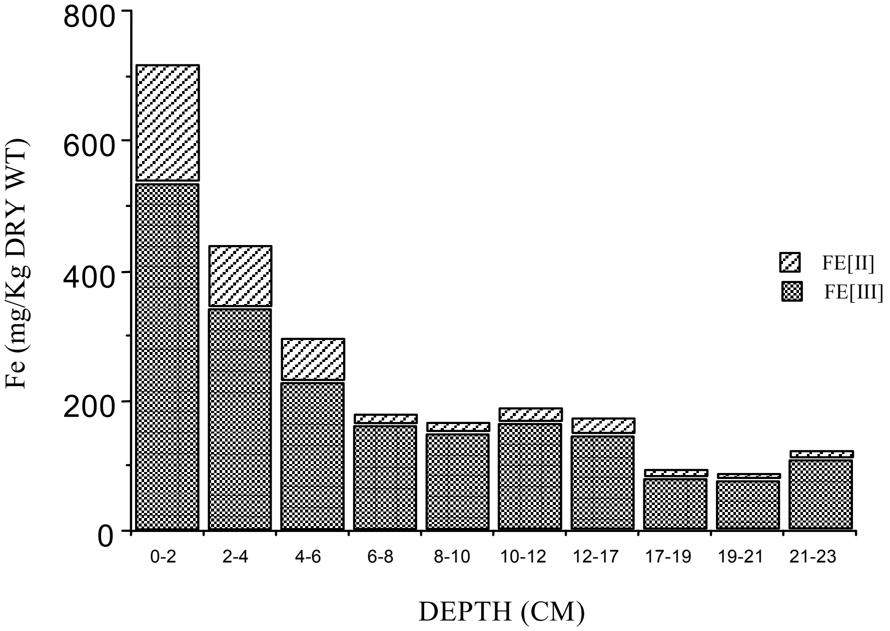

FIG. 6. Depth profile of FE[II] and FE[III] in wetland sediment.

3.3.1 Microbial assays

Duplicate samples of core segments were incubated with Artificial Wetland medium containing 710 mg/L sulphate, with and without the addition of 100 mg/L acetate, to determine whether iron or sulphate reduction, or both, would take place. After three weeks incubation, iron reduction was determined by hydroxylamine/HCl assay of the sediments and the medium was analysed for sulphate by Ion Chromatography (IC). Sulphate reduction was most pronounced in the 0–4 cm segments with added acetate (Fig. 7). Lower activity was observed in the absence of added acetate in this zone with some marginal activity apparent in the 4–6 cm horizon and below. The increase in sulphate reduction obtained in the top two segments by the addition of 100 mg/L acetate was 86% and 114% respectively. It was concluded that the 0-4 cm zone contained the most sulphate reducing bacteria.

Fe[III] reduction took place in the top 2 cm with or without added acetate, the latter producing more Fe[II] (Fig. 8). Below 2.0 cm, Fe reduction only took place when acetate was added and the amount decreased with depth (as did the available iron), most activity being observed in the 0–6 cm zone. It was apparent from total iron values that microbial action increased the solubility of iron in the sediments. It was concluded that although in the absence of added carbon substrate Fe reduction was a competing process, insufficient Fe[III] was present for this to be a major limitation.

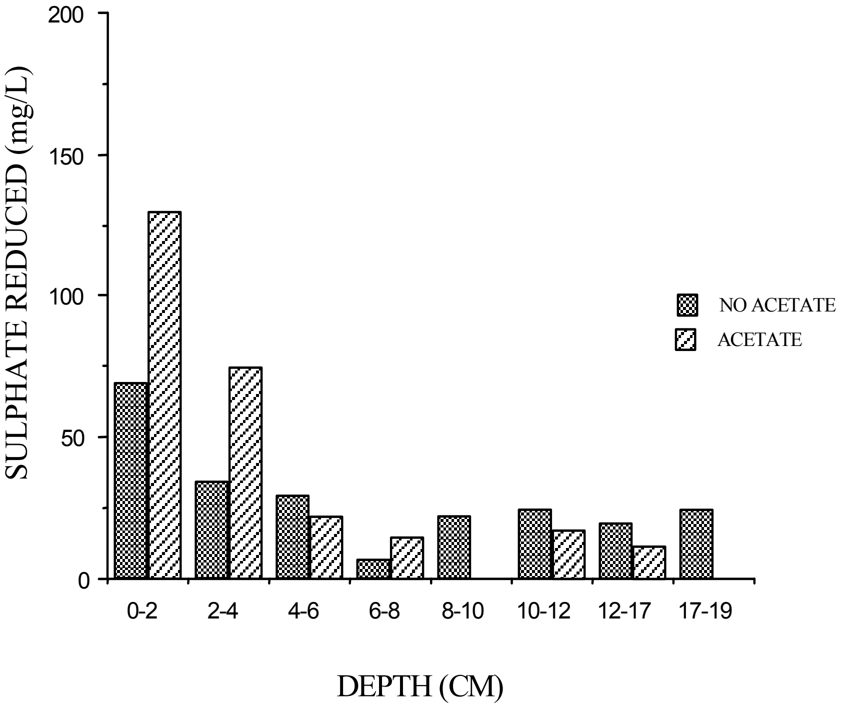

FIG. 7. SO_4 reduction in microbial assays of core segments.

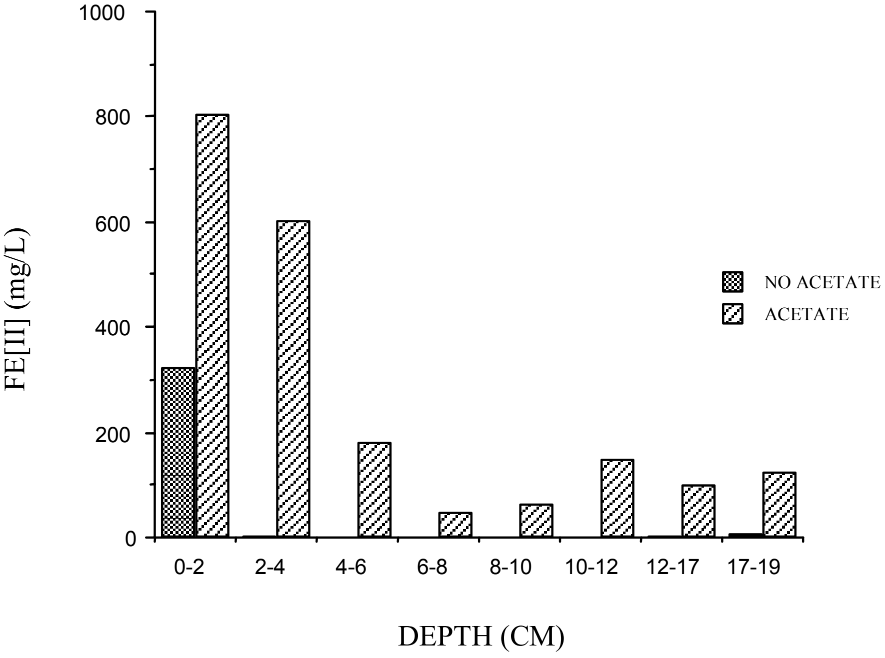

FIG. 8. FE[II] Production in microbial assays of core segments.

3.4. Carbon limitation

At the time of commencement of the studies, the relative immaturity of the wetland was thought to limit the amount of carbon and energy available to drive the process of sulphate reduction. Investigations focussed on the amendment of wetland sediments with carbon substrates to determine the effect on sulphate reduction rates. Communities of sulphate reducing bacteria, isolated from Ranger wetland sediments by acetate enrichment, were used in studies using batch or continuous flow reactors (2 L) containing wetland sediment (1 kg) and medium amended with compost or acetate. Compost is a relatively cheap source of organic carbon that can be mixed or added to wetland sediments to provide a long-term growth substrate in the anoxic zone. It could be prepared from local plant materials to minimise risk of importing unwanted plant species into a sensitive area.

Studies were conducted with acetate as it is considered one of the primary soluble substrates supporting bacterial sulphate reduction in natural sediments, being one of the main intermediates of detrital decomposition processes. Also, unlike compost, which was provided as a one-off addition of carbon at the beginning and which was degraded by indigenous microflora to compounds utilisable by the sulphate reducers, acetate could be provided at a constant concentration and so its use would facilitate achievement of steady state conditions in relation to carbon concentration. It is not, however, a substrate that would be practical to add to full scale or field applications of wetlands due to cost and availability.

3.4.1. Batch composite amendment

In a preliminary study, the effect on sulphate reduction rates of amending sediment with compost was investigated. Sediment from the constructed wetland was amended with compost at 0, 5, 20 and 100% w/w, to give a bed depth of 4 to 5.5 cm, and covered with 1500 mL of medium simulating water received by the wetland. Samples of the aqueous phase were filtered and analysed for sulphate by Ion Chromatography.

Sulphate reduction rates improved with increasing compost concentration in the sediment (Fig. 9). Approximately linear rates of sulphate reduction were observed after 9 days and reduction rates were calculated over the period 9 to 18 days. The reactor containing unamended wetland sediment contained sufficient organic material to support some sulphate reduction. The addition of 5, 20 and 100% compost (no sediment) improved sulphate reduction by 17, 31 and 72% respectively.

3.5. Continuous flow studies

3.5.1. Acetate amendment

Acetate addition was investigated in reactors containing sediment covered by Artificial Wetland medium containing 0, 500 and 2000 mg/L acetate. This was pumped over the sediment at a rate consistent with a 15 day residence time. The sediment without acetate addition supported an initial decrease in sulphate concentration (Days 0-3), which subsequently varied but showed no net increase (Fig. 10). The addition of acetate at 33 and 133 mg/L/day produced similar rates of net sulphate reduction of approximately 9 mg/L/day, suggesting acetate was in excess at both concentrations. The results for 2000 mg/L acetate addition are shown in Figure 11. However, the reactor had not reached equilibrium and a longer time frame was needed to determine the steady state.

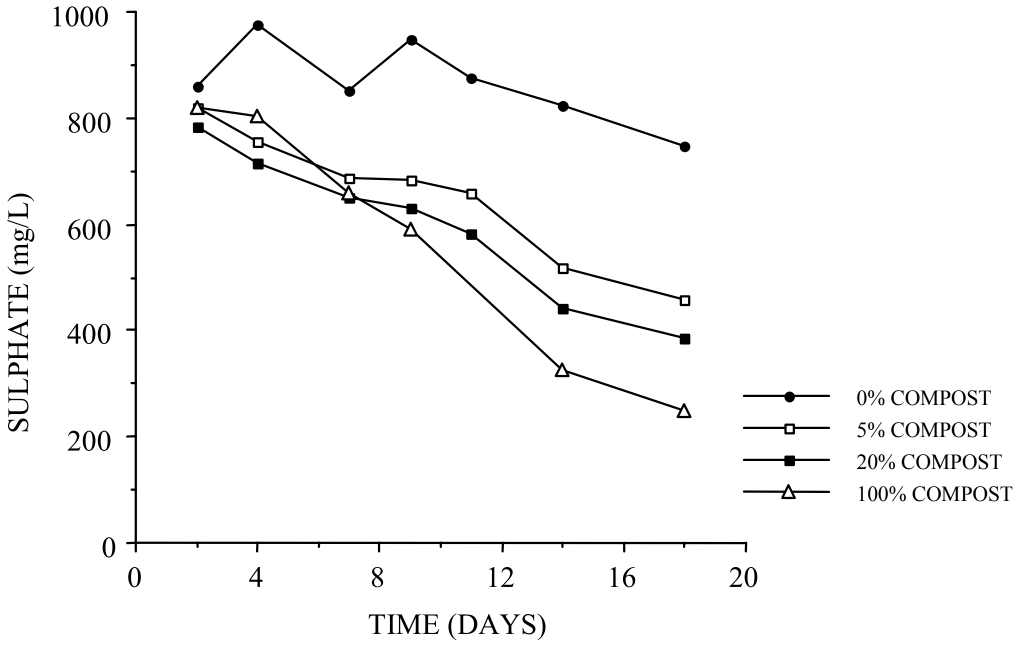

FIG. 9. SO_4 (mg/l) in reactors containing compost and sediment.

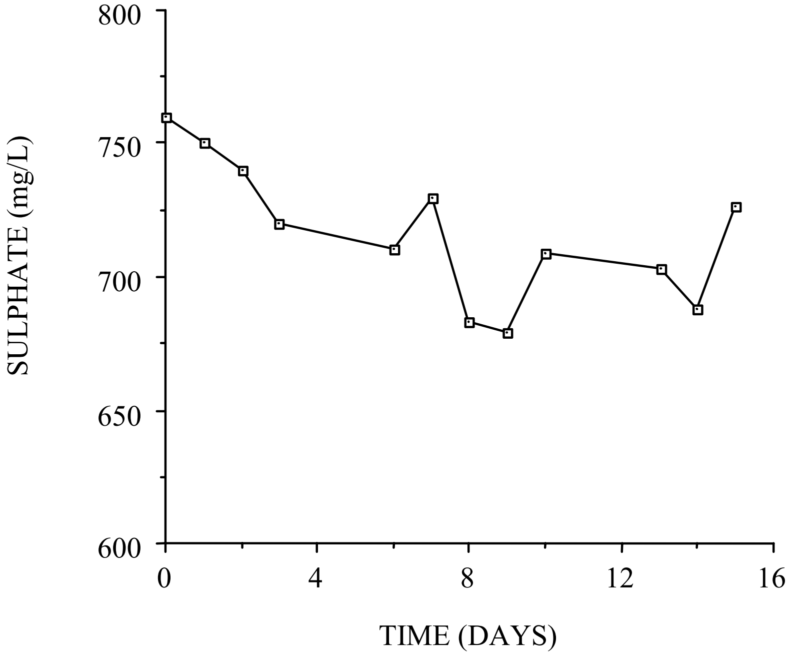

FIG. 10. Continuous sulphate reduction-0 mg/L acetate.

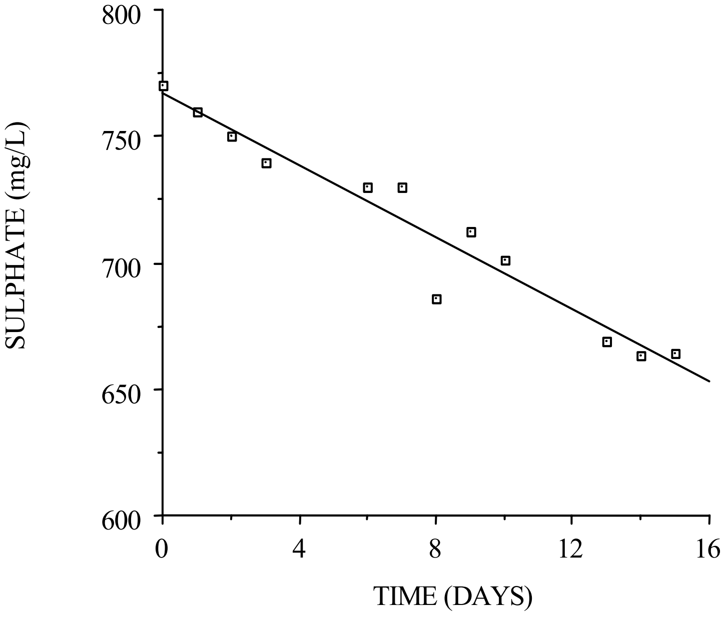

FIG. 11. Continuous sulphate reduction - 2 g/L acetate.

3.5.2. Compost amendment

Amendment of sediment with compost was investigated in a continuous flow system over five months. Compost was added at 2.5, 5, 10 and 20% w/w of sediment. The aim was to establish equilibrium conditions in the reactors, and to determine minimum effluent sulphate concentrations. With an input sulphate concentration of 710 mg/L, unamended sediment showed a reduction of sulphate of 0.4 mg/L/day. Amendment with 2.5, 5, 10 and 20% w/w compost produced rates of 2.2, 4.9, 5.5 and 8.0 mg/L/day, respectively (Fig. 12). The maximum rate of sulphate reduction was twenty times the unamended rate.

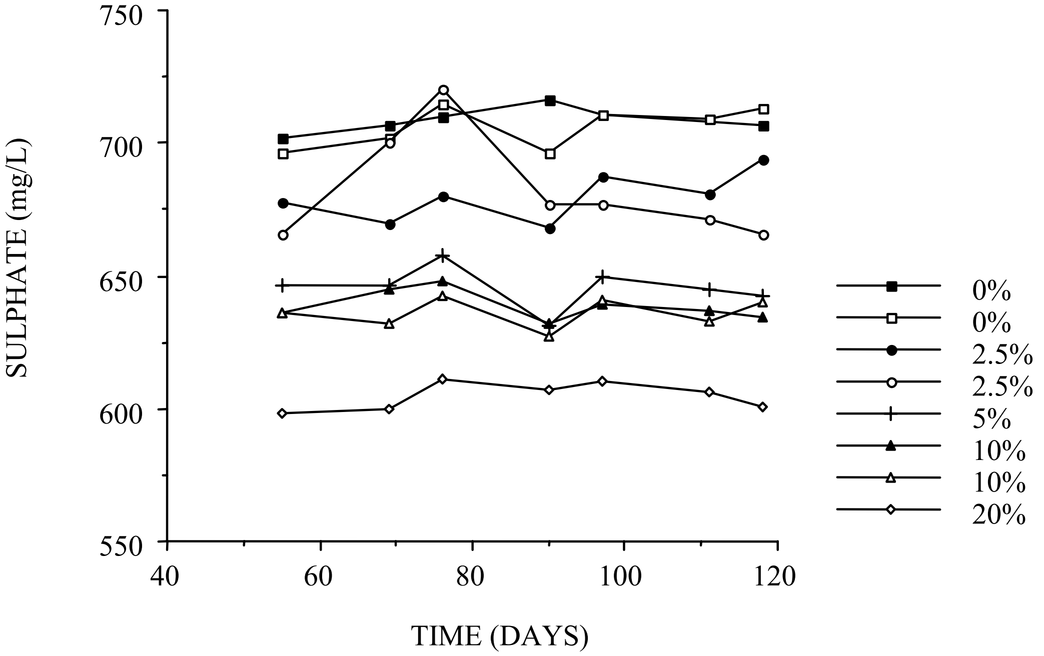

FIG. 12. Continuous sulphate reduction - compost amended sediment.

The smaller than expected improvement in sulphate reduction rates implies that some limiting factor other than carbon concentration was of significance. Blackening of the sediment, due to precipitation of sulfides with iron, provided visual evidence that sulphate reduction was established. Diffusion of sulphate from the water column into the active reduction zone in the sediment may be a limiting factor. Further investigation of solid and liquid substrates is required to assess their potential for improving wetland performance. Investigation of other factors such as flow rates, diffusion rates, and whether the active zone of sulphate reduction can be deepened and rates improved, may improve treatment of high sulphate concentrations.

3.6. Demonstration of use of algal biomass to support bacterial sulphate reduction

The investigations described above identified carbon limitation of bacterial activity as a significant factor in poor sulphate removal efficacy. The provision of organic carbon to drive bacterial growth and sulphate reduction is potentially a significant operational cost with attendant technical issues. As they are solar driven, photosynthetic processes to produce biomass as feedstock for the bacteria are likely to be a cheap option. Although plants are part of the usual wetland design, their tissues contain lignified polymers that are only partly biodegradable. The use of green algae as a low cost, rapidly produced, carbon source to promote sulphate reduction was investigated at bench scale.

Two algal cultures, each dominated by a species of algae designated A3 and N9 (subsequently identified as *Carteria* sp. and *Scenedesmus* sp., respectively), were isolated from the constructed wetland at Ranger uranium mine in Northern Territory, Australia. These algae were cultivated in the laboratory and harvested on an 8 µm membrane (Millipore Corporation, Bedford, MA) under vacuum in order to provide biomass as a carbon/energy source for bacterial sulphate reduction. The algal cells were resuspended in Postgate's Medium C (Atlas 1993), modified by reducing sulphate to 350 ppm and omitting carbon sources, and inoculated with bacteria.

The sulphate reducing bacterial culture (AWF6) used in these tests was isolated from the Ranger wetland using *Scenedesmus* as sole carbon source. It was subsequently shown by 16S rRNA gene sequencing to be dominated by a novel spirilloid sulphate reducing bacterium most closely related to the *Clostridia* assemblage (results not shown). Controls were prepared excluding algae or sulphate reducing bacteria, and all treatments were incubated in darkness at 28°C under anaerobic conditions. Samples were filtered through 0.45 µm membranes and analysed by Ion Chromatography for sulphate concentration.

Algal biomass was added to 30 mL basal medium at different concentrations to determine the amount of organic carbon necessary for sulphate reduction. Sulphate reduction proceeded virtually to completion in all *Scenedesmus* amended treatments after 25 days (Fig. 13). Faster reduction was observed in treatments containing at least 40 mL algae. This equates to a sulphate reduction yield of 3.6 mg/mg dry weight of *Scenedesmus* algae.

Conversely, sulphate concentration only decreased to between 100 and 150 ppm in media amended with *Carteria* algal culture (Fig. 14). The process was substrate dependent only at low concentrations (1 & 5 mL) above which some unknown limitation prevented further sulphate reduction. Possibilities include that some end product of catabolism of the algae by the bacteria accumulated to a level producing partial inhibition at the higher algal concentrations.

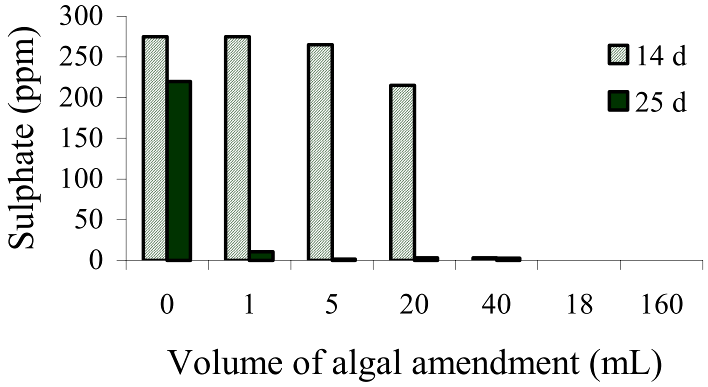

FIG.13. Reduction with Scenedesmus.

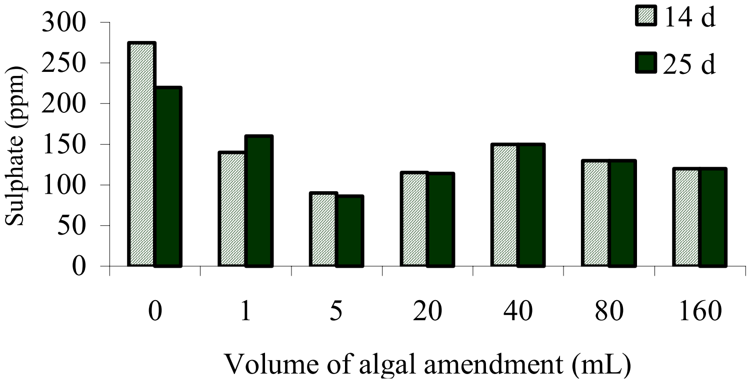

FIG. 14. Reduction with Carteria.

Figure 15 shows the yield of sulphate reduced per mg of algal biomass. Some sulphate reduction was observed in controls without algal amendment. Given the small inoculum size (0.3%), carry-over of carbon in the inoculum is unlikely. Residual endogenous activity of sulphate reducers in the inoculum was probably responsible. *Carteria* and *Scenedesmus* algal cultures had similar cell concentrations prior to harvesting, but the dry weight of a given volume of *Scenedesmus* was approximately double that of *Carteria*. Each treatment contained 10 mg sulphate which was completely reduced by 0.36 mg *Scenedesmus* algal biomass (dry weight). The maximum sulphate reduction achieved by *Carteria* amended medium in 25 days was approximately 7 mg and required 0.175 mg dry weight algal biomass. Only 0.07 mg of *Scenedesmus* biomass was required to reduce this quantity of sulphate. *Scenedesmus* strain N9 produced a maximum specific yield of 94.3 mg sulphate reduced per mg algal biomass added compared with 43.5 for *Carteria* strain A3. For *Scenedesmus,* this yield indicates that less than 10 kg of biomass is required to drive the reduction of 1 t of sulphate and demonstrates potential as a cheap feedstock to drive bacterial sulphate reduction for water treatment. In an area such as the World Heritage listed Kakadu National Park, which surrounds the Ranger mine, it has the added advantage that it is a natural indigenous substrate without the attendant risks of importing exotic plant biomass or synthetic feedstock.

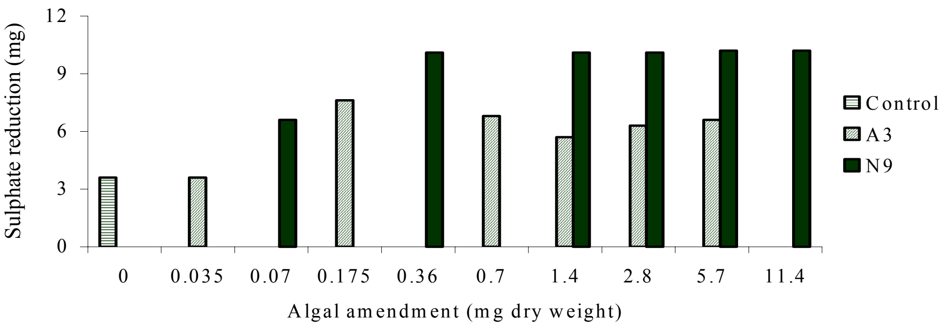

FIG. 15. Specific yield of sulphate reduced with each alga.

3.7. Conclusions

The major findings from this investigation are as follows:

- The wetland sediment used in these experiments was able to support some limited sulphate reduction.
- Little microbially reducible iron was available in the wetland sediments.
- Both iron and sulphate reduction took place in sediment core segment assays and the addition of acetate extended the activity deeper in the profile and increased the amount reduced.
- It was therefore concluded that iron reduction activity was not likely to significantly limit sulphate reduction in these sediments.
- The amendment of sediment with compost improved sulphate reduction by up to 20 times the unamended level.
- Carbon amendment did not improve rates sufficiently to remove >700 mg/L sulphate in a 15 day residence time.
- Reduction of sulphate by bacteria grown on algal biomass as carbon/energy source was demonstrated at bench scale using both *Scenedesmus* and *Carteria* algal cultures.
- The amount and rate of sulphate reduction was dependent on algal concentration.
- The use of *Scenedesmus* produced a higher specific yield of sulphate reduced per mg algal biomass.
- <10 kg of algal biomass would be required to drive bacterial reduction of 1 t of sulphate.

4. Research on the application of Nanofiltration

4.1. Introduction

There are numerous reports of applications of nanofiltration in water treatment and softening plants [23]. Nanofiltration is a membrane separation technique falling between ultrafiltration and reverse osmosis in terms of the species separated. Reported pore diameters for these membranes range from around half a nanometre to several nanometres, and the membranes are charged when in contact with aqueous solutions. Separation takes place on the basis of charge and size.

Nanofiltration in general will remove species in solution which have an effective diameter of around one nanometre or greater. Multivalent ions are removed to a greater extent than singly charged ions. In contrast, reverse osmosis removes almost all ions. Under circumstances where removal of multivalent rather than monovalent ions is important, nanofiltration offers a more cost-effective option than reverse osmosis, as equipment may be operated at significantly lower pressures to obtain the same permeation rates.

In this investigation, the potential of nanofiltration to remove dissolved species from typical uranium mill effluents and process liquors has been studied.

4.2. Theory

This investigation tested polymeric nanofiltration membranes. These can be simple polymers or composite membranes, and have either a positive or negative charge. Membranes which are negatively charged in neutral solutions are more commonly used, as they are less easily fouled by negatively charged colloidal particles often found in water [23]. The membrane charge depends on the solution conditions and the isoelectric point (IEP) of the membrane, where the membrane has a zero net charge. At solution pH levels above the IEP the membrane is negatively charged, and below it is positively charged. Negatively charged membranes generally contain sulfonic acid groups, while those positively charged contain amine or imine groups.

Nanofiltration membranes are used for the separation of a wide range of organic and inorganic solutes. Inorganic solutes such as Ca^{2+} and Na^{+} are separated on the basis of charge and size, while organic materials, *e.g.* humic and fulvic acids, are mainly separated on the basis of size. The degree to which material passes through the membrane is generally evaluated in terms of rejection of a fraction of a solute by the membrane. The factors which influence rejection are the size and charge of the ion, the pore size of the membrane, the membrane material and surface charge, the solution conditions (pH, ionic strength), the nature of the counter ions, and the operating conditions (membrane flux, cross flow velocity, pressure).

4.3. Metal separation

Literature in this area was summarised in an earlier publication [20]. A recent paper describes the application of the technique to the recovery of uranium. The removal of uranyl carbonate complexes from solution has also been reported [22]. The membranes used were the Desal series from Osmonics as well as the NF 45 and NF90 membranes. Uranium rejections were mostly above 95% however performance was heavily dependent on solution pH and the speciation of the uranyl carbonate complexes.

4.4. Experimental plan

The programme for this study was in two stages. The first stage was to undertake a quick evaluation of the separation potential of a wide cross-section of commercial membranes. The target liquor for the first stage of experiments was a uranium mill effluent (UME). The composition is shown in Table 13. The effluent originated from a retention pond at an operating uranium mill. The pond collects rain that falls on ore stockpiles, the mine pit and other areas around the process plant. Current practice is to pass the effluent through wetlands before release. This has been efficient for U and Mn removal, but not sulphate.

The so-called dead-end filtration mode was used in stage 1 because it is simple to operate and uses a small volume of feed liquor. However, this procedure has several disadvantages and it is not used for large-scale nanofiltration operations, where instead the feed stream is passed, under pressure, across the surface of the membrane.

On completion of stage 1, two of the best-performed membranes were selected for further evaluation. A bench scale cross-flow filtration rig was constructed to evaluate performance under more realistic conditions. The performance of this cell can be correlated with the performance of industrial spiral wound membrane elements. This apparatus was used to determine whether the separation potential shown in the early experiments can be converted into a technically feasible separation process.

Two solutions were used for stage 2, the UME and a typical process solution, an acidic raffinate from uranium solvent extraction (Table 13). The pH of the raffinate was around 1.2, which means that the charge of the membranes will be positive in this solution, compared to a negative charge in the UME.

Table 13. Composition of feed solutions

Species	Uranium mill effluent (mg L^{-1})	Acidic raffinate (mg L^{-1})
Al	-	431
Ca	10.8	128
Fe	-	663[#]
K	1.72	-
Mg	84.5	1040
Mn	0.777	83.2
Na	4.9	-
P	-	18
Ra (Bq L^{-1})	2.7	14.7
S	118	4720
Si	-	134
U	0.28	0.03
V	-	1.64
Zr	-	0.06
Acid (g L^{-1} H_2SO_4)	-	4.4

[#] Around 98% of the iron in the raffinate is present as ferric.

4.5. Experimental procedures

Both liquors were passed through a 1 μm filter prior to the nanofiltration tests to remove particulates, which could rapidly foul the membranes. In any industrial application feed pre-treatment such as microfiltration would be used to minimize particulate fouling of the nanofiltration membranes.

The percentage rejection, R, of species by the membranes is defined as

$$R = \left(1 - \frac{C_p}{C_f}\right) x100 \qquad (1)$$

Where C_p is the permeate concentration, and C_f is the feed concentration and is calculated from analysis of feed and permeate samples.

4.5.1. *Batch filtration experiments*

Experiments were performed in a Kiryat Weizmann stirred cell of 30 ml capacity (Fig. 16). A 25 mm diameter disc of each membrane was placed on a porous stainless steel support and held in place with a teflon gasket. The cross sectional area available for flow in the stirred cell was 3.80×10^{-4} m. The experimental set-up is described by [20]. The 18 membranes, which were studied, are listed in Table 14 along with the operating pressure and initial flux of the UME.

4.5.2. *Cross-flow filtration experiments*

The main feature of this rig is a cross-flow cell, which is capable of taking a 190 × 140 mm membrane sheet and delivering the feed stream at pressure across the surface of the membrane. The surface area of the membrane used in the cell was 0.0155 m^2. The apparatus allows the pressure, flow rate and membrane type to be studied independently. Performance data from the apparatus may be easily scaled up and used for preliminary process design.

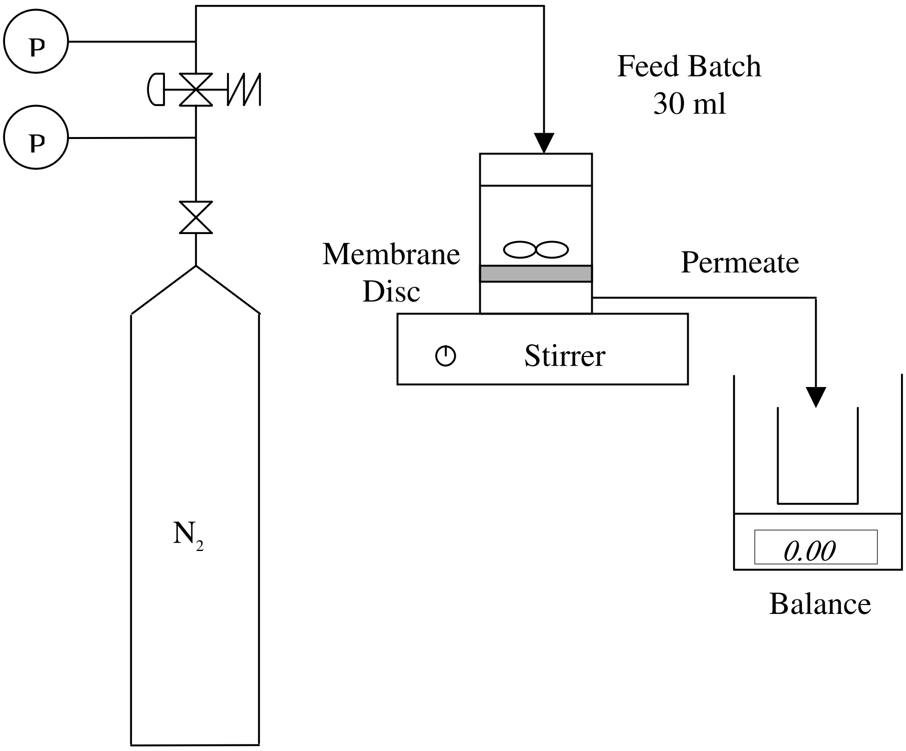

FIG 16. Batch filtration experimental apparatus.

Table 14. Membranes and operating conditions

Membrane				Pressure	Flux
Supplier	Designation	Composition	IEP	(kPa)	(L m^{-2} h^{-1})
Filmtec/Dow	NF 45	TF composite polyamide	6.05	1730	48
Hydranautics	ESNA 1	TF composite polyamide		520	42
Hydranautics	ESNA 2	TF composite polyamide		520	37
Hydranautics	PVD 1	Polyvinyl alcohol derivative	4.0	1030	34
Osmonics	DL	Proprietary thin film	4.0	690	17
Osmonics	DK	Proprietary thin film	4.0	690	16
Millipore	Nanomax 50	Polyamide/polysulfone TFC		690	38
Trisep	TS 40	Aromatic Polyamide		690	25
Trisep	TS 80	Proprietary composite		690	17
Trisep	ACM 4	Aromatic Polyamide		1550	39
PTI	ASP 10	Sulfonated polysulfone		1380	861
PTI	ASP 20	Sulfonated polysulfone		1380	177
PTI	ASP 30	Sulfonated polysulfone		1380	75
PTI	ASP 50	Sulfonated polysulfone		1380	61
PTI	ATF 50	TF composite polyamide		1380	67
PTI	ATF 60	TF composite polyamide		1380	109
Pall Gelman	NOVA	Polyethersulfone		380	43
Pall Gelman	OMEGA	Modified polyethersulfone		380	41

TF: thin film

The concept of cross-flow filtration is shown in Figure 17.

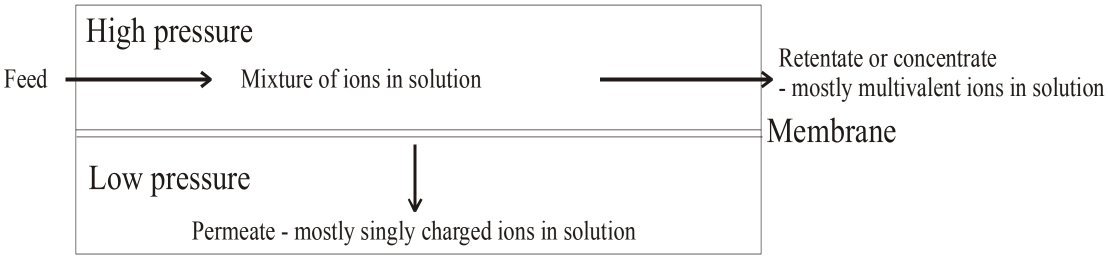

FIG. 17. Cross-flow filtration.

A schematic diagram of the cross-flow rig is shown in Figure 18. The cell and tubing were constructed from 316 stainless steel, the feed and permeate spacers were polypropylene.

The feed pump is a piston metering pump which pressurises the system. Valve V5 (the concentrate bleed) is adjusted to control the pressure in the filtration stage. The recycle loop in the filtration stage enables the cross-flow velocity to be varied independently of the feed flow rate and the pressure by adjusting the variable speed pump in the loop.

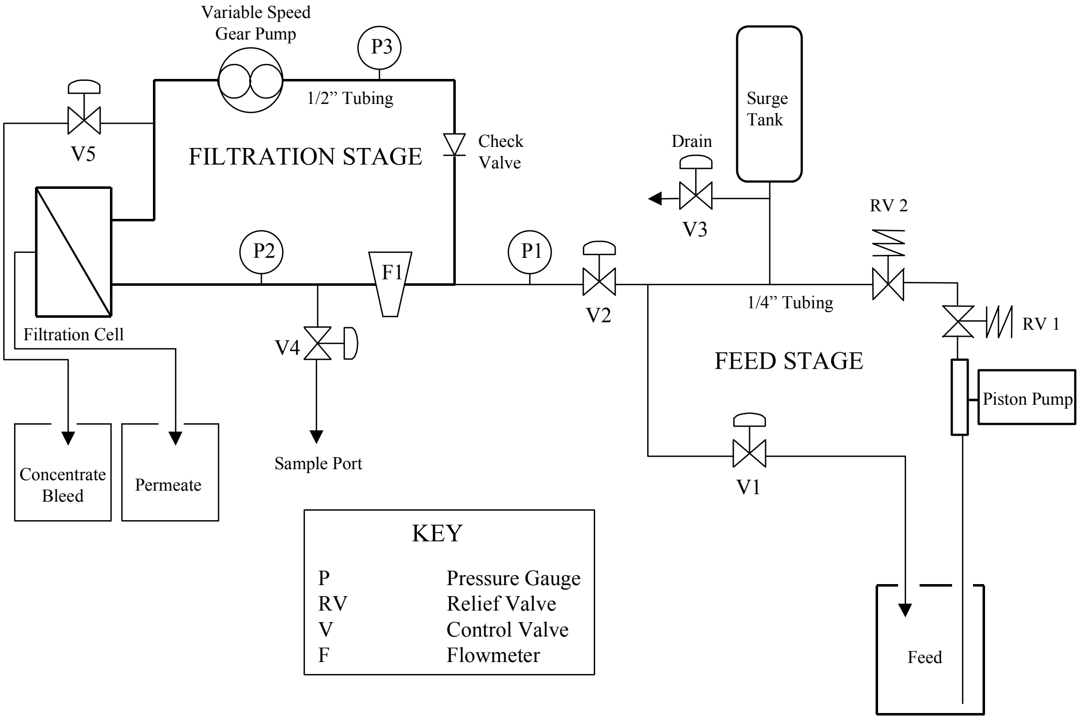

FIG. 18. Schematic diagram of cross-flow filtration apparatus.

A feed sample (from sample port V4, Fig. 18) and a permeate sample were taken for each set of conditions, and the permeate flux and concentrate bleed flow rates were measured. The flow of fresh feed solution into the filtration circuit can be determined from the flow rates of the permeate and the concentrate bleed. The experiments were performed at ambient temperature, which was 20 ± 2°C.

4.6. Results

4.6.1. Batch filtration tests

A more detailed description of results is given by Macnaughton et al [20].

Membrane Evaluation: In all 18 membranes were tested. The flux of UME was measured, with permeate samples being analysed for target elements. The initial rejections achieved with each membrane were calculated according to Equation 1, and are listed in Table 15.

These values correspond to the rejection achieved when a permeate volume equal to 20% of the feed volume has been produced. The data in Table 15 provide an overview of the separation potential for these membranes for removing the target species of U, Mn and SO_4. The rejection of uranium was consistently high (>73%) with two membranes achieving rejections of 99%. The reason for this is most likely due to the physical size of the uranyl sulphate complex, which is actually hindered from passing through the membrane pores.

Table 15. Initial solute rejections from batch cell

Membrane	Rejection (%)						
	Ca	K	Mg	Na	Mn	SO_4	U
NF 45	86	43	88	23	84	88	90
ESNA 1	20	22	18	18	15	18	86
ESNA 2	27	26	23	23	25	20	76
PVD 1	64	44	64	<5	55	63	74
DL	86	66	87	50	87	87	88
DK	87	62	86	47	84	87	91
TS 40	44	28	45	17	42	43	85
TS 80	95	68	95	52	95	93	99
Nanomax 50	83	31	90	6	77	81	93
ACM 4	82	59	84	58	70	83	99
ASP 10	6	8	11	<5	18	10	81
ASP 20	7	11	14	<5	13	10	87
ASP 30	9	9	14	<5	10	9	84
ASP 50	19	22	24	12	14	20	84
ATF 50	33	26	32	18	33	31	82
ATF 60	7	10	11	8	10	8	73
NOVA	17	17	15	13	9	16	79
OMEGA	20	24	19	18	10	19	73

The rejection of the other target elements is considerably more variable with values ranging from 9% up to 95%, which is not unexpected, given the intrinsic complexity of nanofiltration separation processes.

The solution pH was 7.4, which was greater than the IEP of most of the membranes. The membranes would therefore be negatively charged and tend to reject sulphate. Electro-neutrality considerations would then require that cations were rejected as well. The monovalent cations (K and Na) were most easily passed through the membranes and have the lowest rejections. This effect may be due to ion-pairing effects with sulphate ions or may be due to the smaller size of the hydrated cations when compared to hydrated divalent cations. Of the divalent cations in this solution Ca, Mg and Mn generally behaved in a similar way with rejections within a few percent of each other.

***Effect of Pressure**:* A series of experiments were done using the ATF 50 membrane in which the flux and rejection profiles were measured under three applied pressures. As expected the flux increased linearly with pressure and there was a corresponding increase in rejection. Figure 19 illustrates the rejection behaviour for uranium. The increase in rejection at higher pressures is generally explained by a shift in the transport mechanism across the membrane. At lower pressures a diffusive transport of salts occurs, which accounts for the lower rejections, and at higher pressures convective transport of salts through the membrane becomes dominant. If the applied pressure was increased further it would be expected that rejections would stabilise as concentration polarisation effects start to become significant [21].

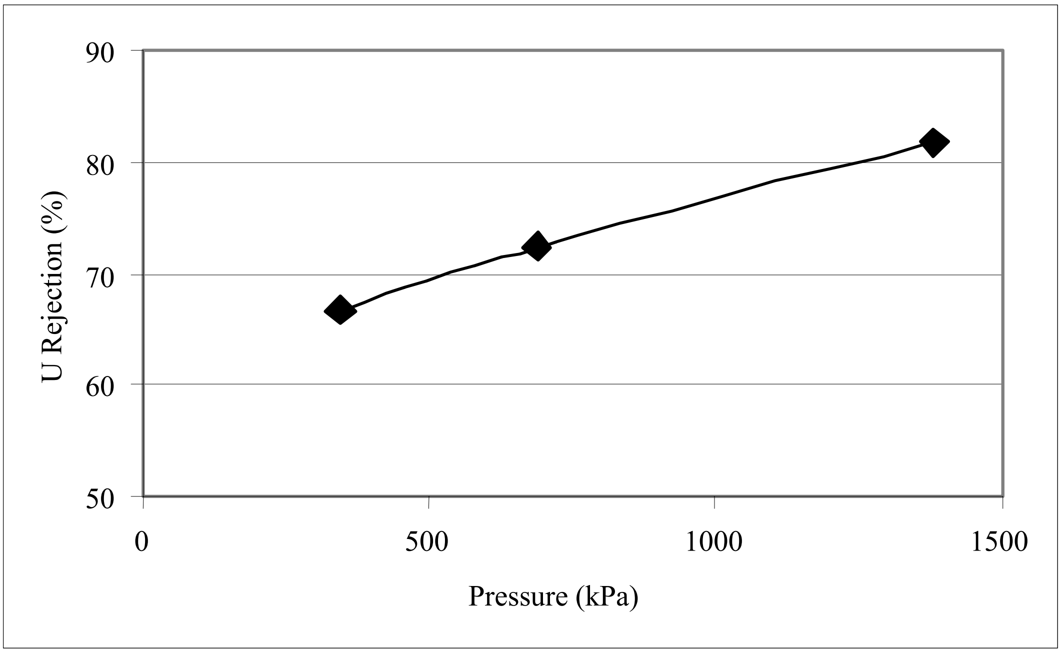

FIG. 19. Uranium rejection versus pressure for 20% permeate (Membrane ATF 50 (PTI)).

Selectivity*:* The rejection that could be achieved with each membrane for uranium, the di-valent species and the mono-valent species varied widely and there was also a significant variability in the selectivity between species. This is best illustrated in Figures 20a-c. The Osmonics and the Trisep membranes both show high rejections for U, Mn, and SO_4, however there is poor selectivity between these species.

The PTI membrane was quite different. Although the rejection of U was only modest (~75%) the selectivity between U and the other species was quite significant. There is clearly potential for the selective separation of uranium from this mixture with this membrane. Of interest also is the poor selectivity between K and Mn and SO_4, which is in contrast to Figures 20a and 20b. These examples highlight the variable behaviour of the different membrane systems and also the potential for designing selective metal separations.

Radium Rejection**:** In Table 16, data are presented for permeate flows equal to 80% of the feed volume. The purpose of this experiment was to obtain enough permeate to facilitate analysis for radium. As would be expected, the rejections for each solute have reduced, however the trends are similar to those presented in Table 15.

High rejections were obtained for ^{226}Ra with the Osmonics DK membrane whereas the results were less impressive with the two Trisep membranes. As a divalent ion with similar hydrated ionic radii, it would be expected that radium would be rejected in a similar fashion to Ca, Mg and Mn. This is not the case for all three membranes with radium rejections clearly different from the other three ions. The reasons for this are difficult to determine without further experiments, however the extremely low mass concentration of radium in the UME could be partially responsible.

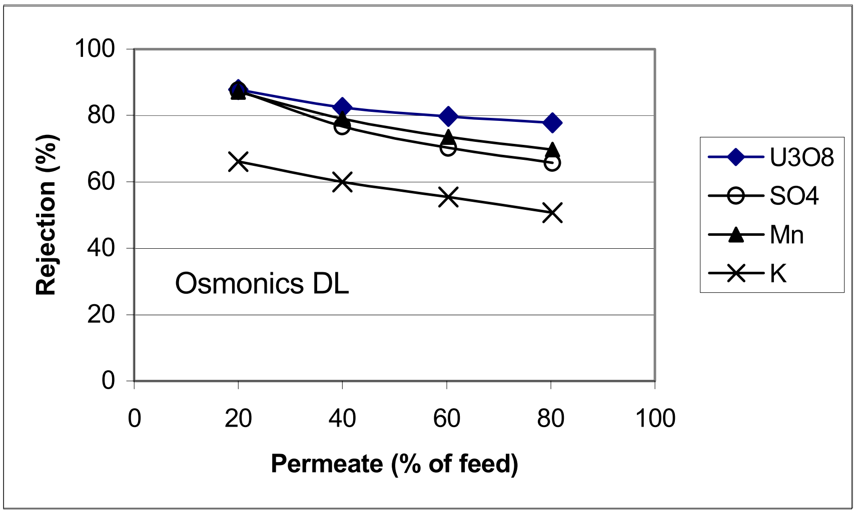

FIG. 20A. Selectivities using the Osmonics DL membrane.

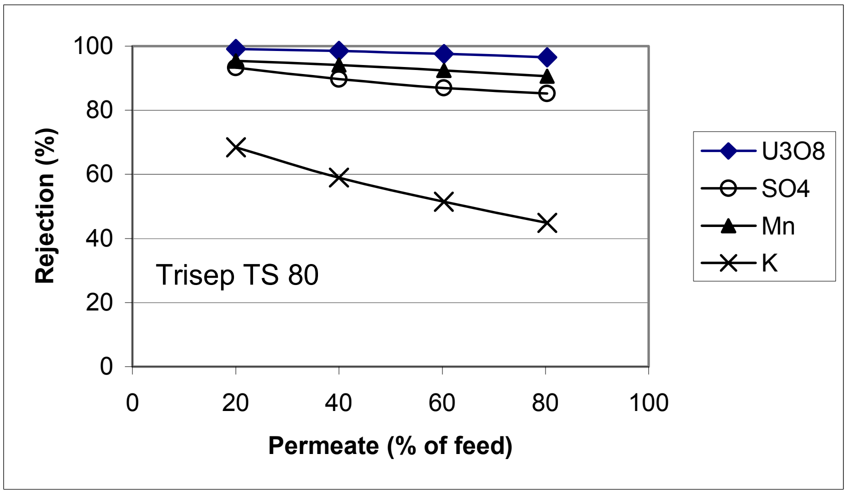

FIG. 20B. Selectivities using the Trisep TS 80 membranes.

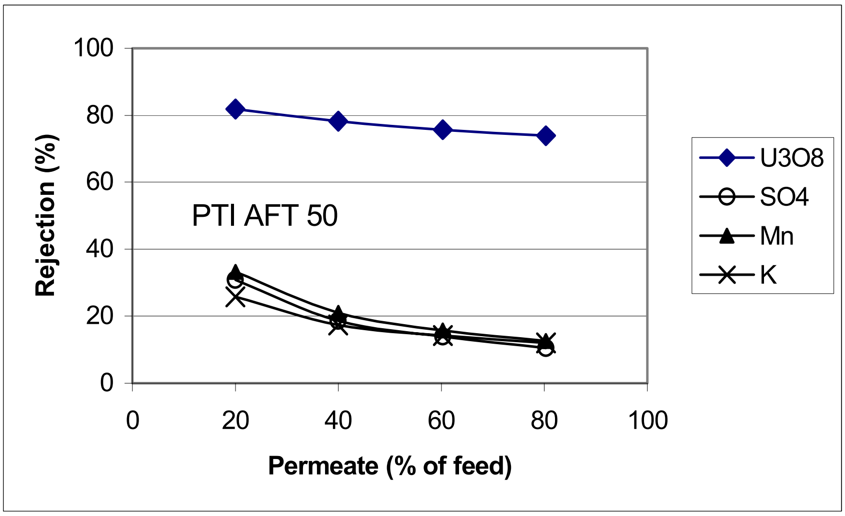

FIG. 20C. Selectivities using the PTI AFT 50 membrane.

Table 16. Overall rejections for 80% permeate for batch cell

Membrane	Rejection (%)							
	Ra	Ca	K	Mg	Mn	Na	SO_4	U
DK[#]	87	61	36	59	64	16	61	82
DK[#]	79	70	47	70	72	26	72	90
TS 40	45	29	17	30	33	8	28	69
TS 80	58	85	45	86	91	25	85	97

duplicate experiments with separate membranes.

Variability: Duplicate experiments showed some variability. This topic is summarised further in the test work on the cross-flow rig.

Conclusion: The results obtained with the 18 commercial membranes highlight the complex nature of nanofiltration separations and also confirm the potential for this technique to be applied to a treatment of uranium mill effluent. The target species for removal, uranium, manganese, sulphate and radium, were all rejected by some of the membranes.

4.6.2. Cross-flow cell

The two membranes chosen for this work were the Desal DK, a proprietary thin film membrane, and the Nanomax 50, polyamide/polysulfone thin film composite. As the cross-flow cell uses a larger section of membrane, the effect of flaws or inconsistencies in the membrane sheets should be less significant than when the small discs are used, although some variation would still occur.

UME Filtration

The species of interest were uranium, manganese, sulphate and radium.

Uranium, radium, manganese and sulphate data: Uranium rejection was very high for both membranes. Rejections greater than 99% were calculated for all conditions. Radium was determined in the feed and permeate solutions only for some of the operating conditions. This showed that the radium rejection was also high, and the data are tabulated below.

Table 17. Radium rejection from UME

Pressure (kPa)	Velocity (m s^{-1})	Desal DK	Nanomax 50
1000	0.169	98.6	94.4
1000	0.339	98.9	97.4
1300	0.169	96.5	98.8
1300	0.339	97.1	95.6

Manganese rejection levels were high overall, being above 95% for both membranes. Data for manganese and sulphate rejection are presented in Figure 21. Generally, there was a trend of increasing rejection with increasing pressure for most ions, although the effect was often very slight. The data for sulphate with the Nanomax membrane show a more significant pressure dependence than, for example, the manganese data.

Other species: The rejection of calcium and magnesium was over 95% for all the measurements with the UME (Fig. 22). The singly charged ions, sodium and potassium, were not as efficiently removed from the solution, as expected. The rejection of these two species also showed a higher dependence on the flow rate than did the multivalent ions, which were rejected more strongly. Sodium and potassium rejection also decreased with increasing pressure, which is the opposite of the behaviour of the other species in the UME.

Variability: Measurements were carried out at 1300 kPa and 0.339 m s^{-1} with two separate membrane sheets. Rejections for a number of key species are shown in Table 18. The variation for sulphate is the most significant, while the metal ion rejections were fairly reproducible. Some variability is expected as membrane sections are cut from larger sheets, which may contain flaws or irregularities.

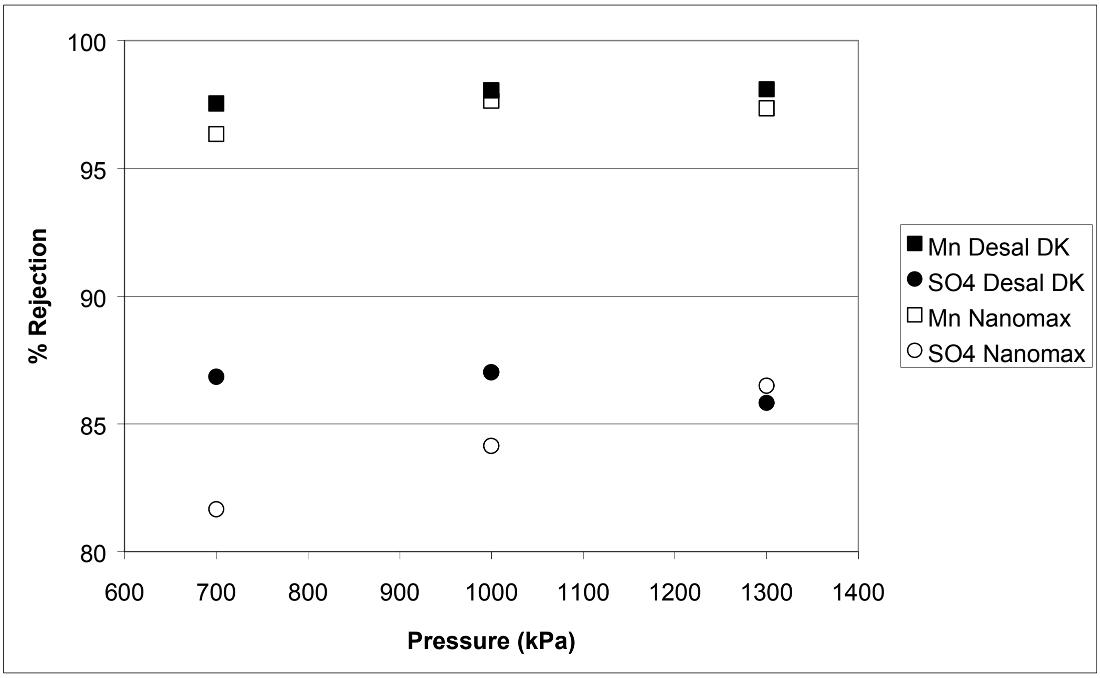

FIG. 21. Sulphate and manganese rejection - Cross-flow velocity 0.339 m s^{-1}

Table 18. Variability between cut sheets of membrane

Membrane	Rejection at 1300 kPa, 0.339 m s^{-1}			
	Mn	Ra	SO_4	U
Desal DK 1	98.1	99.3	85.8	99.3
Desal DK 2	98.6	98.2	96.7	99.6
Nanomax 1	97.4	98.7	86.5	99.3
Nanomax 2	99.0	95.6	98.4	99.6

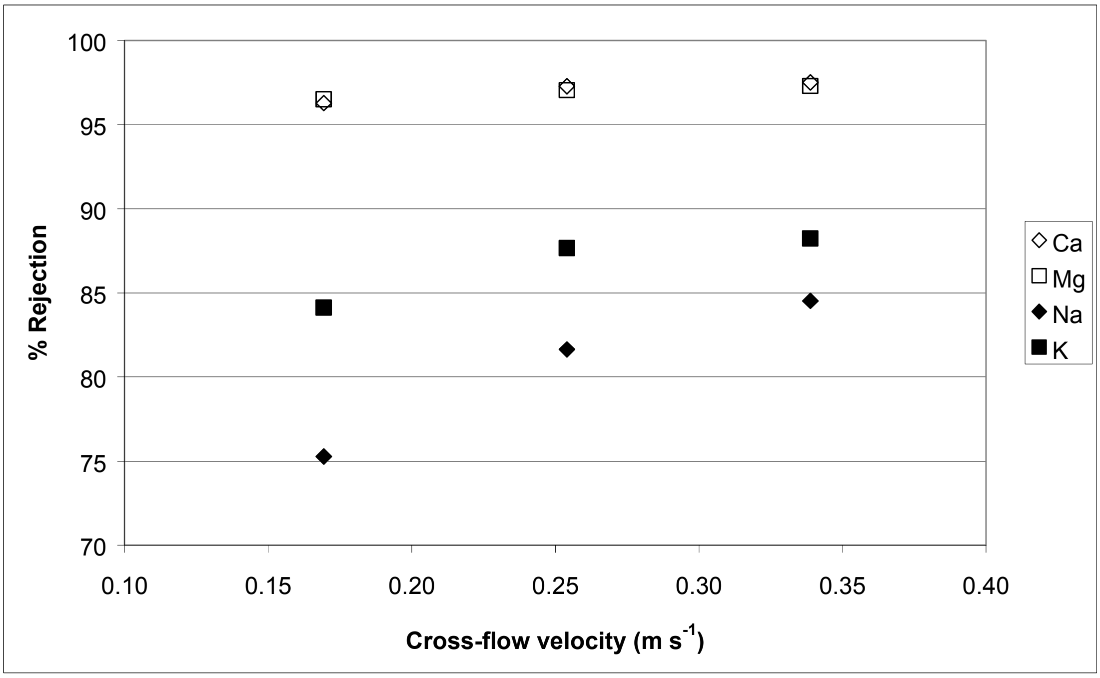

FIG. 22. Ca, Mg, Na and K, rejection at 700 kPa, Desal DK membranes.

Raffinate filtration

The raffinate contains a number of the same ions as the UME, but because the raffinate has a low pH, a comparison of results will indicate the effect of membrane charge on the rejection of these ions. The concentrations of the uranium, manganese, radium and sulphate are quite different in the raffinate solution. The uranium concentration is an order of magnitude lower than in the UME, while manganese, radium and sulphate are all significantly higher. Concentration will have an effect on the rejection of ions, however the positive charge on the membrane is likely to be the most significant factor determining the separation of ions.

Uranium, radium, manganese and sulphate data: The uranium was mostly below the detection limit in the permeate, so that the rejection could not be calculated accurately. Radium rejection data are presented in Table 19. The radium concentrations in the raffinate were almost an order of magnitude higher than in the UME, although the mass concentrations are still very low.

Table 19. Radium rejection from raffinate

Pressure (kPa)	Velocity (m s^{-1})	Desal DK	Nanomax 50
1000	0.169	98.9	99.0
1000	0.339	98.9	99.2
1300	0.169	85.9	99.5
1300	0.339	98.2	99.6

Manganese rejection was slightly higher from the raffinate than from the UME (Fig. 23). Although the higher concentration of this ion in the raffinate means that the rejection would be expected to be lower, the electrostatic repulsion between the cations and the positively charged membrane leads to higher rejections. This was observed for all the metal cations in the raffinate solution.

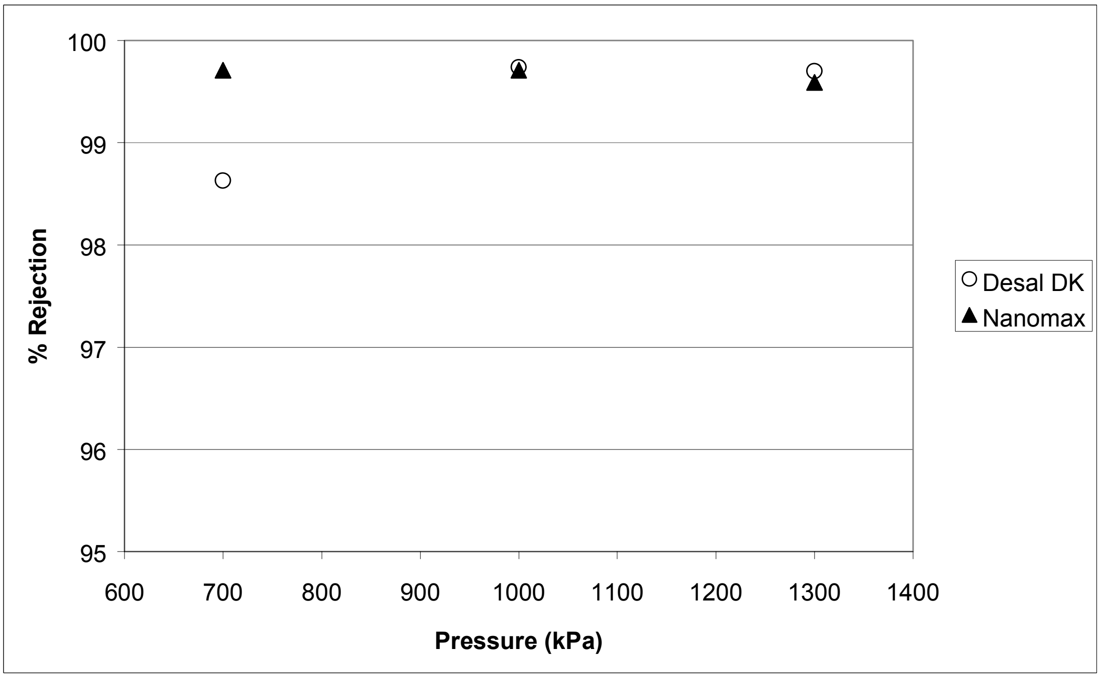

FIG. 23. Manganese rejection - cross-flow velocity 0.339 m s^{-1}

The rejection of sulphate was generally lower than for the UME and shows a stronger dependence on the operating pressure. A comparison of the sulphate rejection for both solutions is shown in Figure 24. The lower rejections are due to the higher concentration of the sulphate in the raffinate solution, and the positive charge on the membrane.

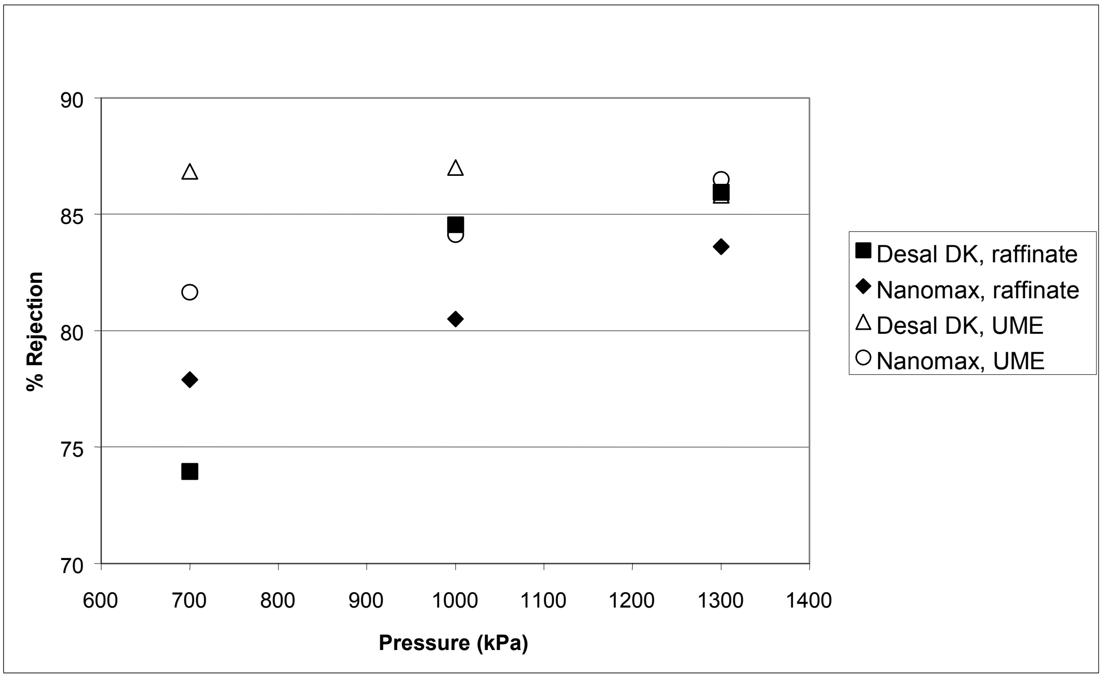

FIG. 24. Sulphate rejection at 0.339 m s^{-1} *- comparison of UME and raffinate.*

Sulphuric acid: Data from the raffinate give an opportunity to evaluate the potential of these membranes for acid recovery. The Desal DK membrane has been reported for use in recovery of acid from waste solutions [18]. Although the acid concentration is low (4.4 g L^{-1}) in the feed solution, the data show that the acid is poorly rejected by both membranes, and also that acid conditions give high rejections of metal cations.

The removal of sulphuric acid from the raffinate solution shows more variation with operating conditions than do some of the metal ions. The acid is not strongly rejected by the nanofiltration membranes, with all rejection levels below 60%, as shown in Figure 25.

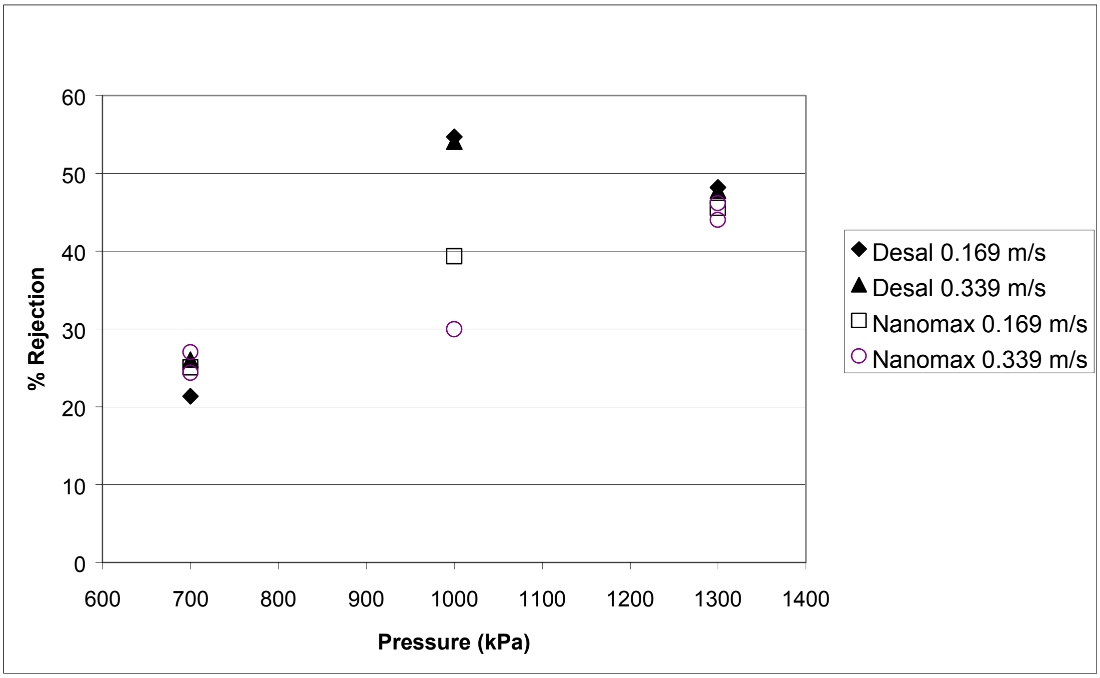

FIG. 25. Acid rejection with pressure for raffinate filtration.

Other species: Rejection data for aluminium, phosphorus and iron from the raffinate is presented in Figure 26. Overall, more than 95% of the aluminium, calcium, iron, magnesium and manganese was removed over the full range of pressures and flow rates examined. Over 90% of the phosphorus and silicon were also removed except at the lowest pressure. Overall, these results show a greater dependence on pressure than do those from the UME filtration.

Variability: Measurements were carried out using two separate sheets of membrane, as described for the UME filtration. The rejection levels of some species are shown in Table 20. Some variability is apparent in the uranium results, although the error in these may be quite high as the concentrations were very close to detection levels. There is also some variation for silicon and sulphate, while the other ions were fairly consistent.

Table 20. Variability between cut sheets of membrane (0.0155 m^2)

Membrane	Rejection[#]				
	Mn	Ra	S	Si	U
Desal DK 1	99.7	99.3	85.9	95.3	94.3
DESAL DK 2	99.6	98.2	78.4	95.1	73.7
Nanomax 1	99.6	99.4	83.6	89.8	94.1
Nanomax 2	99.5	99.6	80.4	95.1	77.5

[#] 1300 kPa and 0.339 m s^{-1}

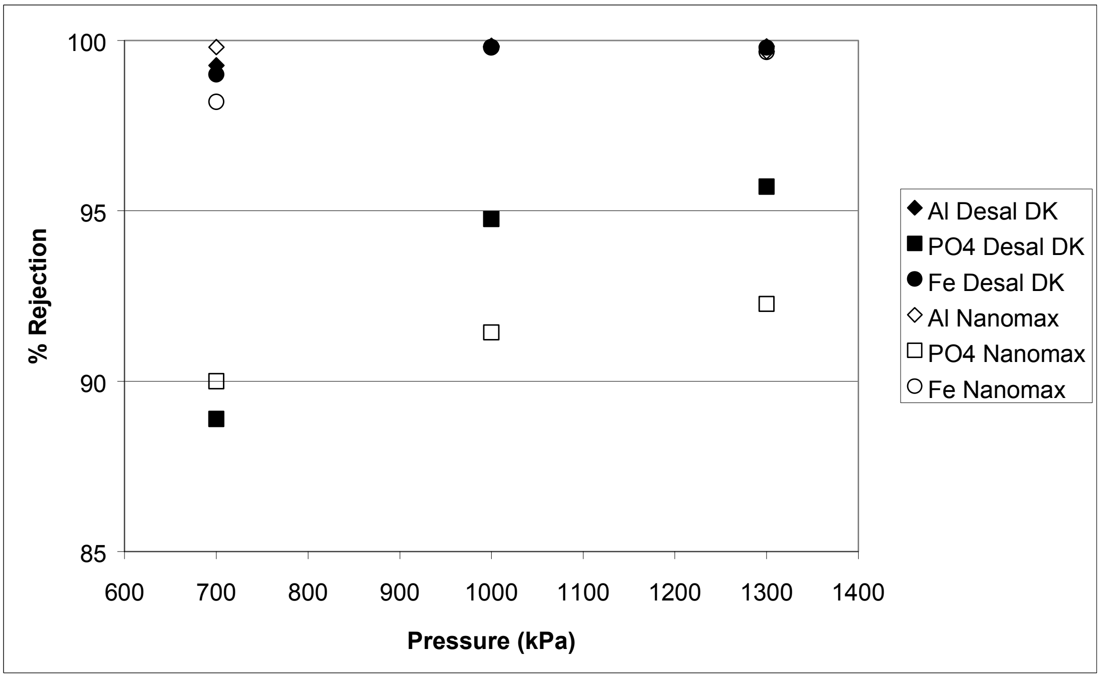

FIG. 26. Rejection of aluminium, phosphate and iron: cross-flow velocity 0.339 m s^{-1}

4.6.3. Overall membrane performance with cross-flow cell

Higher permeate production rates were achieved for the UME filtration, compared to the raffinate because of the lower osmotic pressure of the solution. The maximum rate for both solutions was measured at 1300 kPa with a cross-flow velocity of 0.339 m s^{-1}. From these measurements the rate of permeate production from the commercial spiral wound cartridges Helicon RO-300 (Nanomax 50 membrane) and DK 8040C (Desal DK membrane) was calculated, and are tabulated below. The membrane surface area for each of these cartridges is 32 m^2. The production of permeate from the UME is around 75% faster than from the raffinate. Permeate recoveries shown in Table 21 are around 9% for the UME and 5% for the raffinate. This is typical, or even quite high, for a single-stage bench scale cross-flow filtration apparatus, while recoveries for a multi-stage full scale operation would be expected to be around 70-90% [17].

Table 21. Calculated permeate production rates at 1300 kpa and 0.339 m s^{-1}

Feed solution	Membrane	Maximum permeate flux (m^3 m^{-2} s^{-1})	Production rate from SW cartridge (kL day^{-1})	Permeate recovery (%)
UME	Nanomax 50	1.40×10^{-5}	38.7	9.0
	Desal DK	1.30×10^{-5}	35.9	8.9
Raffinate	Nanomax 50	0.80×10^{-5}	22.1	5.5
	Desal DK	0.73×10^{-5}	20.2	4.7

The permeate composition from each of the solutions is given in Tables 22 and 23. Both membranes used in these tests showed good separation characteristics for the multivalent metal ions under both neutral and acid solution conditions. The removal of uranium, radium and manganese, which are of particular interest, was very effective, while high levels of sulphate removal were also attained for the UME. Acid permeated the membranes quite easily and cation rejection was very high under acid conditions, indicating the possibility of using these membranes for acid recovery from solutions contaminated with metal ions.

Table 22. Composition of permeate solution from UME filtration#

Species	Feed (mg L^{-1})	Desal DK permeate (mg L^{-1})	Nanomax 50 permeate (mg L^{-1})
Ca	10.8	0.25	0.39
K	1.72	0.25	0.60
Mg	84.5	2	2.36
Mn	0.78	0.018	0.025
Na	4.9	1.08	2.05
S	118	20	20
U	0.28	0.002	<0.002
Ra (Bq L^{-1})	14.7	0.04	0.11

\# 1300 kPa and 0.339 m s^{-1}

Table 23. Composition of permeate solution from the raffinate filtration#

Species	Feed (mg L^{-1})	Desal DK (mg L^{-1})	Nanomax 50 (mg L^{-1})
Al	431	0.76	1.58
Ca	128	0.42	0.66
Fe	663	1.35	2.64
Mg	1040	2.60	4.59
Mn	83.2	0.23	0.39
P	18	1.10	1.70
S	4720	782	885
Si	134	9.18	0.18
U	0.03	<0.002	<0.002
V	1.64	0.003	0.007
Zr	0.06	<0.002	<0.002
H_2SO_4	4.4	2.21	2.44
Ra (Bq L^{-1})	2.7	0.11	0.05

\# 1300 kPa and 0.339 m s^{-1}

4.7. Discussion and conclusions

The initial screening experiments with the batch cell showed that the type of separation achieved for the UME was very dependent on the membrane type. The two membranes chosen for the cross-flow cell work showed good potential for the separation of sulphate, manganese, uranium and radium. The performance was influenced by a number of factors, including membrane charge, ion speciation, and the operating conditions of the cross-flow rig.

4.7.1. Membranes and ion speciation

The rejection levels achieved for all the multivalent cations in solution were generally above 95%. The Desal DK and Nanomax 50 membranes gave very similar results for these species, with differences between the two less than half a percent with few exceptions. For these solutions there were, however, differences observed for the rejection of other cations. The rejection levels of sodium and potassium from the UME solution were lower for the Nanomax 50 membrane by around 20%.

For raffinate, there was some difference in the rejection results for phosphorus and silica, which may be due to a slight difference in the membrane pore size. In the raffinate at pH 1.2, the speciation of these two elements is probably H_3PO_4 and $Si(OH)_4$. Phosphoric acid has a pKa of 2.13, so the ratio of $H_3PO_4:H_2PO_4^-$ is around 11:1. Since both H_3PO_4 and $Si(OH)_4$ have no net charge in solution, rejection takes place on the basis of size. Slightly larger pores in the Nanomax 50 membrane would result in lower rejection levels for the neutral species, although both species were retained over 90% for both membranes.

Rejection levels differ between the UME and raffinate, due to the differing charge on the membrane. Cation rejection was enhanced in the raffinate filtration at pH 1.2, for the same pressure, due to the high repulsive forces between the ions and the positively charged membrane surface. This effect counters the decrease in rejection that would be expected due to the significantly higher concentrations in the raffinate solution. Rejection of sulphate was much lower in the raffinate filtration as a result of a number of factors. Firstly, the membrane charge in the UME filtration is negative, and the electrostatic repulsion between the membrane and the sulphate ions ensures high rejection of these ions, while in the raffinate solution, the membrane is positively charged. The speciation of the sulphate changes as the pH changes. At neutral pH, the sulphate will be present as SO_4^{2-}, while at pH 1.2 the ratio of SO_4^{2-}: HSO_4^- is around 1:6.6, and hydrogen ions, which permeate the membrane more easily than metal cations, perform the role of counter ions for these anions. The higher concentration in the raffinate solution also leads to lower rejection.

4.7.2. Operating conditions

The driving force for the solute across the membrane has two components: convective (solute carried through by the solvent flux) and diffusive (solute diffusing through the pores of the membrane. At low fluxes, that is, low pressures, the diffusive component, which is driven by the concentration gradient, increases relative to the convective component. This results in lower solute rejections.

Increasing operating pressure and cross-flow velocity resulted in an increase in the rejection levels in most cases, although the dependence on pressure was less for the species in the UME. The effect of pressure was most apparent in the sulphate rejection data for both solutions. There was a higher dependence of rejection on pressure for the raffinate solutions, than for the UME solution, and the rejection at the lower pressures was much lower for sulphate in the raffinate. As the sulphate concentration is much higher in the raffinate, it would be expected that the diffusive component of the solute permeation driving force would be proportionately larger for the raffinate than for the UME. This would lead to the lower rejections observed at lower pressure for the raffinate, and also to the higher dependence of rejection on operating pressure as the concentration driven diffusive transport mechanism is reduced relative to the convective component. Increasing rejection at higher fluxes (that is, at higher pressures) is generally reported. However, increasing flux through the membrane promotes concentration polarisation. For this condition and low cross-flow velocities, low rejection of ions is observed, which decreases with increasing pressure (Afonso & de Pinho, 1998). The rejection of acid by Desal DK membranes shows a decrease in rejection from 1000 kPa to 1300 kPa for all flow rates.

There are two mechanisms by which increasing concentration at the membrane surface, induced by concentration polarisation, affects solute rejection. As the concentration increases, the electrostatic forces between the membrane and the ions in solution become weaker. Also, the concentration driving force for solute transport increases, increasing the diffusive component of the transport through the membrane. Both of these can lead to decreased solute rejection. The increased osmotic pressure may also lead to lower permeate fluxes. Concentration polarision may be minimized by enhancing the mixing in the cell, by increasing the flow rate or modifying the feed spacer, to promote turbulent flow. Variation of the rejection levels with cross-flow velocity is most apparent in this work at lower pressures, that is, where the rejections are lower.

The separation properties of these membranes for metal ions in these solutions are good and the low acid rejection, coupled with high cation rejection under acid conditions, shows great potential for acid recovery from process streams. Further work needs to be carried out to determine the long-term membrane performance, water recovery and fouling characteristics in order to properly evaluate nanofiltration as a treatment method.

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Liquid effluent treatment initiatives at the Key Lake uranium mine, Saskatchewan, Canada, 1996–2000

J.P. Jarrell

Environment and Safety, Cameco Corporation,
Saskatoon, Saskatchewan, Canada

Abstract. The Canadian paper focuses on liquid effluent-related work at the Key Lake mine in Northern Saskatchewan. Over the 1996-2000 period covered under this CRP, the work at Key Lake focused primarily on better understanding how the mine site's effluents impact the near-field aquatic environment. Three separate projects were tracked in this paper: i) an assessment of the significance of elevated nickel and molybdenum concentrations in the mine dewatering and mill effluents; ii) a report on efforts to determine and eliminate the cause of fish toxicity in Key Lake mill effluent; and iii) a report on efforts made to reduce nickel loadings to the environment from Key Lake mine dewatering effluent. The paper also provides a history of the Key Lake site as it relates to liquid effluent, describes the effluent treatment processes, reviews current environmental impact against original predictions made in the Environmental Impact Statement written in 1979 prior to start-up, and finally, reviews some of the wider issues facing Canadian uranium producers. In terms of nickel toxicity, a series of four studies over the past eight years have essentially not found significant environmental impact in the near-field receiving environment. However, the studies also essentially site-validated the receiving water quality objective established for nickel to protect the most sensitive species from biological harm (in their early life cycles). With respect to molybdenum toxicity, site-specific laboratory studio concluded that waterborne Mo was not toxic to any life stage of any fish species tested. Field-based early life cycle testing showed sore response in Mo-containing waters, however dietary selinium toxicity is the suspected cursitive agent, despite very low waterborne Se levels. The overall conclusion on early life cycle toxicity testing, particularly using indigenous fish species, is that they are difficult to conduct, easy to critique, can generate variable results, and do not necessarily provide much insight into the likely cost-benefit of modifying environmental performance.

1. Scope of the report

Cameco Corporation is the world's largest uranium producer, currently accounting for about 26% of the western world production, or about 20% of the production for the world. Its operations include the world's largest, high-grade uranium mines, located in Saskatchewan, and Canada's only uranium processing facilities, located in Ontario. Cameco also obtains uranium from *in-situ* leach operations in Wyoming and Nebraska in the United States. Uranium exploration activities currently focus on the uranium-rich Athabasca Basin in northern Saskatchewan and the Arnhem Land region of the Northern Territory in Australia. The company is also actively involved in the Inkai *in situ* leach project in Kazakhstan.

The focus of the work covered by this IAEA Co-ordinated Research Project (CRP) is the Key Lake mine in northern Saskatchewan. It is the largest high-grade uranium milling operation in the world, with a licensed annual production capacity of 7.2 million kilograms of uranium, or 18.7 million pounds U_3O_8. This operation is a joint venture, currently owned 83% by Cameco, and 17% by Cogema Resources Inc.

In 1996, we set the following long-range objectives for this CRP:

- Report on efforts to assess the significance of elevated molybdenum concentrations in Key Lake mill effluent (subsequently expanded to include nickel as well);
- Report on efforts to determine and eliminate the cause of fish toxicity in Key Lake mill effluent; and
- Report on efforts to reduce nickel loadings to the environment from the Key Lake mill dewatering systems.

These three objectives for the CRP show that the priority at Key Lake is to better understand how the site's effluents impact the near-field aquatic environment. This is the main liquid effluent treatment issue at Key Lake: better understanding impacts before steps are taken to consider significant changes to these effluent treatment systems.

The purpose of this final report is to provide a summary of Cameco's efforts in dealing with these three identified issues over the past four years, comment on our current understanding of the level of environmental impact related to liquid effluent, and offer comments on expected effluent-related developments at this site early in this new millennium. More detailed information on this project, including information on related activities at other Cameco-operated Canadian uranium developments may also be found in the following earlier progress reports prepared in conjunction with this CRP:

- Liquid Effluent Treatment Status Report and Current Research Initiatives – presented at the First Research Co-ordination Meeting December 2-5, 1996, Vienna, Austria; and
- 1998 Status Report: Liquid Effluent Treatment and Current Research Initiatives – presented at the Second Research Co-ordination Meeting October 19-22, 1998, Pécs, Hungary.

2. Key Lake site history

A series of site maps, showing the regional setting and main features of the Key Lake mine site are provided in Figures 1, 2 and 3. Exploration work on the Key Lake site began in 1968, leading to the discovery of the Gaertner deposit in 1975 and the Deilmann deposit in 1976. Production began in 1983. The Gaertner open pit was mined out in 1987, and the larger Deilmann pit was mined from 1989 to 1997. Cameco acquired the one-third interest in the mine held by Uranerz Exploration and Mining Limited in 1998, and sold a 16.66% interest to Cogema in 1999.

The mine currently employs about 300 people including on-site long-term contractors. It is located 570 kilometres north of Saskatoon by air on the southern rim of the uranium-rich Athabasca sandstone basin. It is 80 kilometres south-west of the McArthur River mine by road. The nearest village by road is Pinehouse (population 922), 220 kilometres south of Key Lake.

Starting in January 2000, Key Lake is now processing McArthur River ore, along with relatively small remaining reserves of stockpiled Key Lake ore (which amount to 2.2 million lbs. U_3O_8 at 0.46% average grade). From 1983 to the end of 1999, Key Lake produced 207.7 million pounds of U_3O_8.

From 1983 to 1995, tailings generated by the Key Lake mill were placed in a purpose-built, above-ground storage facility (which is approximately 45 hectares at its top). This tailings facility has a bentonite-amended glacial till bottom seal and partial embankment seals, along with a sand drain and collection system to return supernatant and drainage waters back to the mill. The design volume of the tailings facility is 5.8 million m^3, with about 0.6 million m^3 capacity remaining, based on current tailings consolidation characteristics. Interestingly, about 200 000 m^3 of residual storage capacity has come from thaw-consolidation over the past two years.

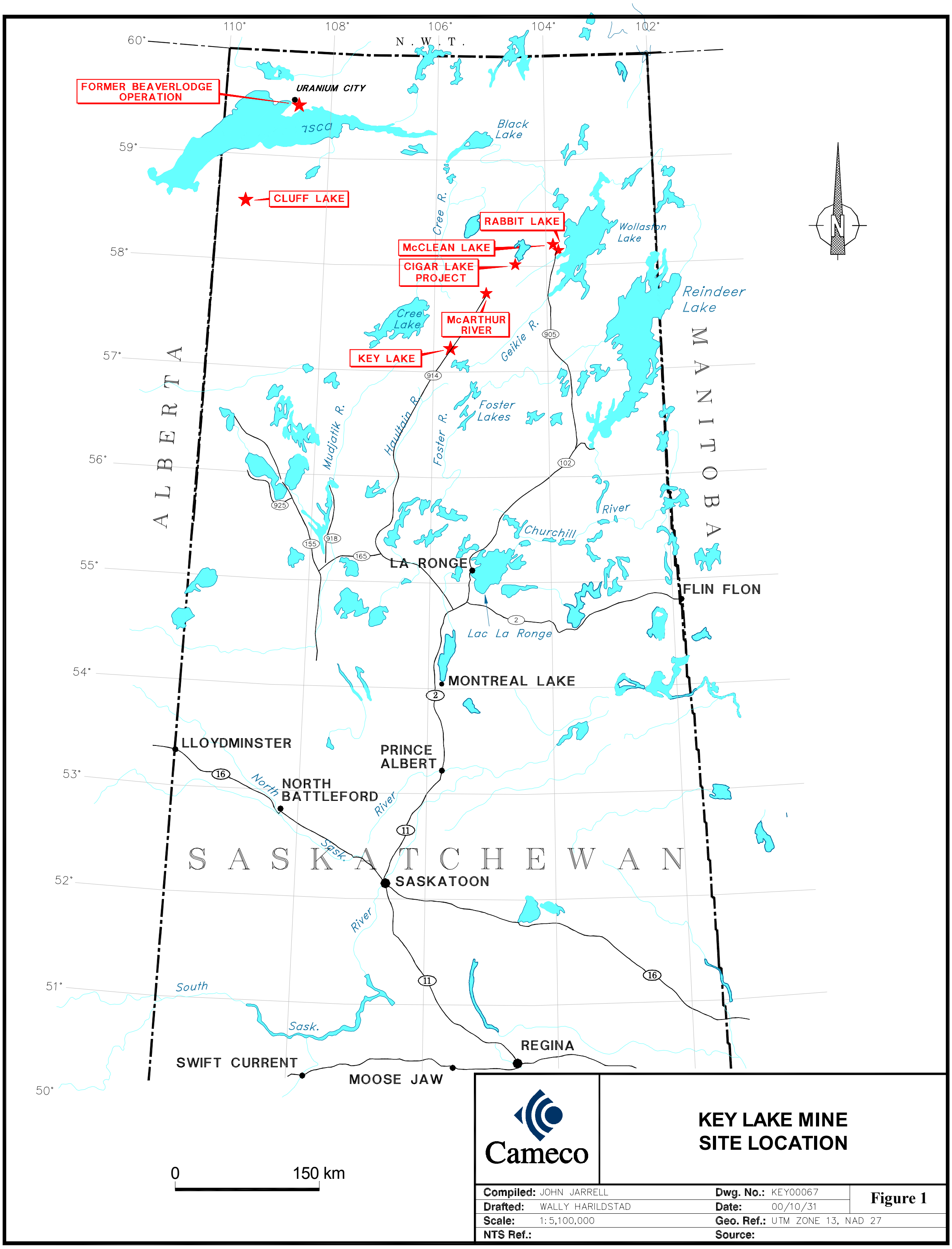

FIG. 1. Key Lake mine site location.

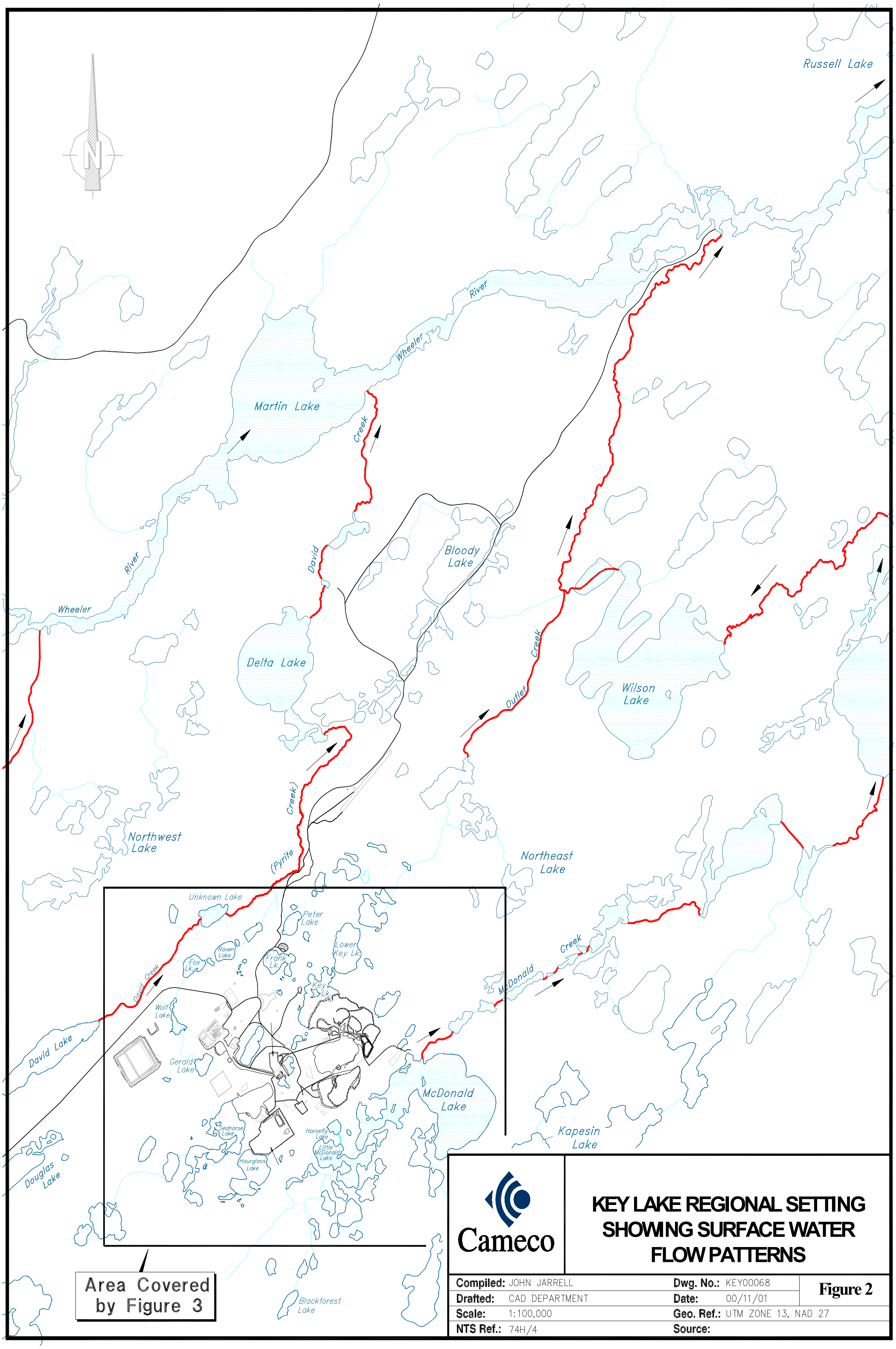

FIG. 2. Key Lake regional setting showing surface water flow patterns.

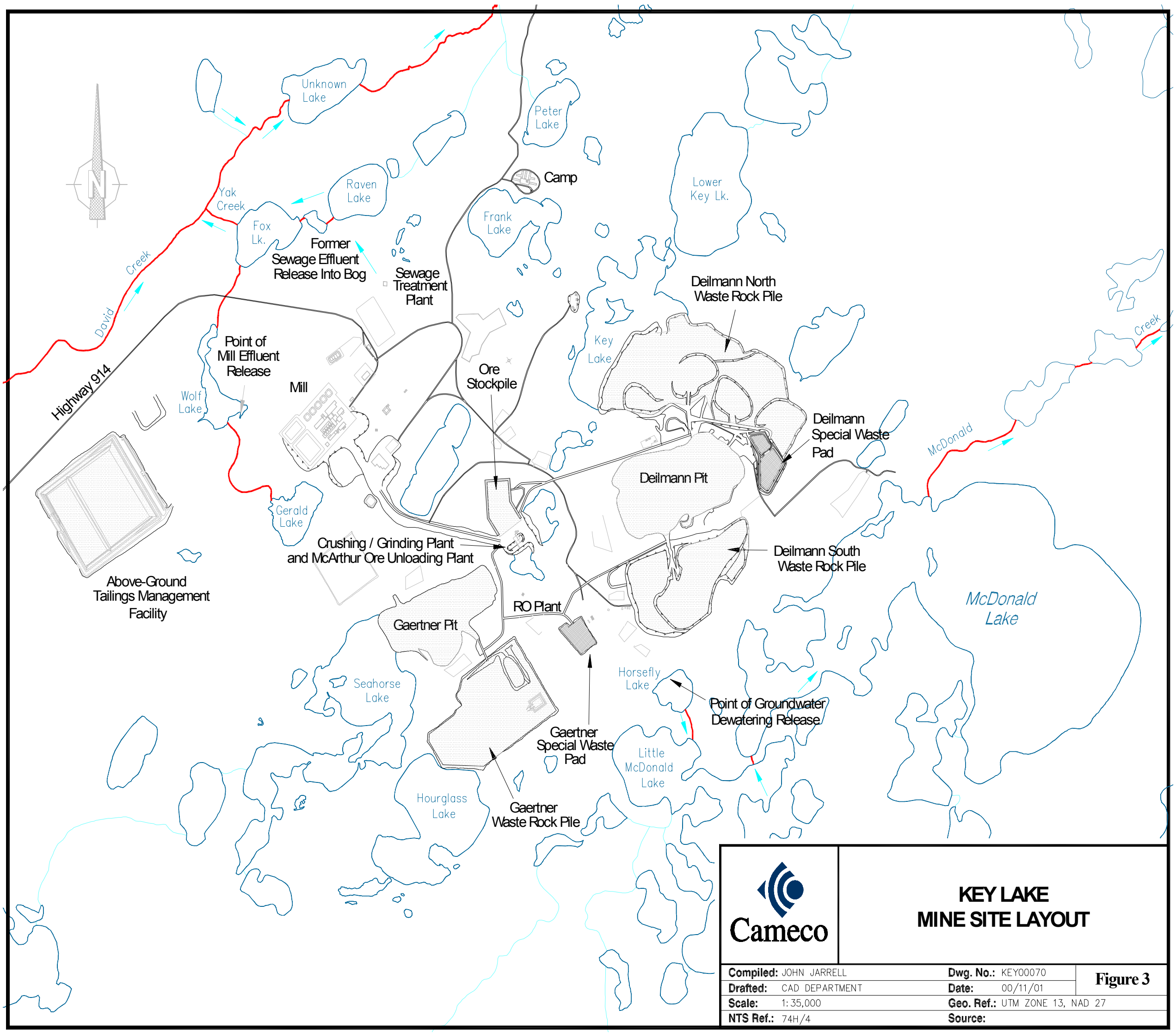

FIG. 3. Key lake mine site layout.

In December 1995, tailings deposition was successfully changed over from the above-ground tailings facility to an in-pit facility in the Deilmann pit. The overall pit capacity to store tailings will be a function of the criteria used to select the final permitted deposition horizon. This will be a function of pit geology and ongoing post-operational modelling projections. If tailings deposition was restricted to the basement rock horizon, the Deilmann In-Pit Tailings Management Facility (DTMF) could contain about 5 million m^3. Deposition to the lowest sandstone/overburden sand horizon would add about 10 million m^3 (to 476 masl), and a complete fill to the groundwater-rebound horizon (520 masl) would add another 15 million m^3. This in-pit facility initially operated using subaerial tailings deposition. The Deilmann pit required an extensive dewatering system to be mined. A portion of the same dewatering system, which remains in use, coupled with a bottom drain beneath the tailings to promote tailings consolidation both serve to provide ongoing hydraulic containment around the DTMF. The conversion to subaqueous deposition commenced in December 1998 (sealing the top of the side-drain constructed between the tailings and pit walls). This allowed water to begin ponding on the surface. Partial flooding of the DTMF began in June 1999, and in July 2000, a more complete flooding of the facility commenced.

The Gaertner pit is in the same hydraulic regime (cone of depression) as the Deilmann pit. Therefore decisions to flood one pit means the other pit also becomes flooded. After near-complete flooding, which should be completed in mid-2003, water levels in the two pits will be controlled to levels about 10 m below their natural rebound level (to 510 masl), therefore providing ongoing hydraulic containment for tailings leachate collection and for any leachate from waste rock deposited near the two pits.

3. Effluent treatment processes at the Key Lake mine

There are two water effluent discharges from the Key Lake mine:

(i) Effluent discharge from the dewatering system that was installed around the Gaertner and Deilmann open-pit mines; and
(ii) Treated mill effluent discharge, which includes water returned from the tailings facilities and contaminated water from the dewatering system.

The Deilmann/Gaertner dewatering system has evolved over time. About thirty dewatering wells were originally installed in the Gaertner dewatering system, and approximately one hundred dewatering wells were installed in and around the Deilmann pit between 1983 and 1995. In addition, about 120 horizontal drain holes were installed in the Deilmann pit to depressurize the pit slope in 1993, to compliment about 180 horizontal drains previously installed prior to 1993. This overall dewatering system was divided into two parts. A contaminated water system, which collected and transported water to the mill, and a clean water system, which was allowed to discharge directly to the environment (Horsefly Lake/Little McDonald Lake/McDonald Lake system), under site-specific, regulatory-controlled water quality objectives (Table 1).

Table I. Key Lake effluent water quality criteria

Contaminant	Dewatering Effluent Quality Objectives*	Mill Effluent Quality Limits**
Arsenic	0.05 mg/L	0.5 mg/L
Copper	0.02 mg/L	0.3 mg/L
Lead	0.05 mg/L	0.2 mg/L
Nickel	0.10 mg/L	0.5 mg/L
Selenium	-	0.6 mg/L
Uranium	0.08 mg/L	2.5 mg/L
Vanadium	-	0.5 mg/L
Zinc	0.05 mg/L	0.5 mg/L
Radium-226	0.11 Bq/L	0.37 Bq/L***
Thorium-230	-	1.85 Bq/L
Lead-210	-	0.92 Bq/L
Total Suspended Solids	-	25.0 mg/L
Ammonia	-	0-30 mg/L for pH 2
pH	-	5.0-7.0****

* Allowable Maximum Monthly Arithmetic Mean Concentration.

** Maximum Monthly Arithmetic Mean Concentration (Also regulated by Grab and Composites sample concentration).

*** Provincial limit on total radium, Federal limit on dissolved radium.

**** Federal limits only specify minimums (6.0 monthly, 5.5 composite, 5.0 grab).

Following completion of a pre-mining surface drainage programme, it was estimated that approximately 72 million m^3 of static groundwater needed to be removed from the mining area, and about 15.4 million m^3 would need to be pumped to the surface on an annual basis. Historically (1982–1998), discharge rates to the Horsefly Lake/McDonald Lake system have averaged 10.9 million m^3/y, ranging from a peak of 15.7 million m^3 in 1986 to a low of 7.8 million m^3 in 1998. Over the period 1994–1998, about 84% of the overall volume of dewatering water was released to Horsefly Lake and 16% was sent to the mill. The clean dewatering water contributes 32-90% of the pre-mining flow in the Horsefly Lake/McDonald Lake drainage system, tending to produce more uniform flow conditions relative to pre-mining conditions. The first of these lakes (Horsefly) is very small, at 480 000 m^3. The next lake, Little McDonald Lake is approximately 4.3 million m^3, and McDonald Lake is approximately 25.6 million m^3 in volume.

While the pit dewatering volumes have decreased with time, nickel concentrations and loadings began to generate interest in 1991 when the request for the first nickel-specific dewatering environmental assessment was received from our regulatory agencies.

Nickel loadings to Horsefly Lake started to increase, particularly starting in 1994, peaking in 1995. The peak annual loading of nickel was about 2800 kg/y, increasing from about 370 kg/y in 1982. In 1996, a reverse-osmosis (RO) plant was commissioned to reduce this nickel loading to the environment. Table 2 shows the history of nickel concentrations in the clean dewatering effluent discharge. As previously noted, studies into the environmental significance of this increased nickel loading (as a supplement to the initial intent to study the environmental significance of molybdenum discharges) and efforts to reduce the nickel loading formed a core of the work being documented in this CRP, as discussed in more detail later in this report. In 1999, efforts to flood the Deilmann and Gaertner pits, coupled with good operation of the RO plant generated much reduced flows to the Horsefly/McDonald Lake system (2.0 million m^3), much lower nickel loadings (107 kg) and nickel concentrations (0.053 mg/L) which were equivalent to those seen in the early years 1982-85 (0.026, 0.054, 0.052, and 0.055 respectively). In 2000, even lower flows and loadings are expected because more dewatering water is being pumped back into the Deilmann pit to enhance slope stability during flooding of the pit. In fact, the main current reason to operate the RO plant is to provide clean industrial water for the mill (for fire water make-up, pump gland water, reagent mixing, and for water coolers in the Powerhouse which cannot be fouled, etc.).

The mill effluent treatment consists of four main sections: solvent extraction raffinate neutralization, radium removal, pH adjustment and tailings neutralization. A schematic is provided in Figure 4.

The raffinate neutralization circuit consists of four neutralization pachucas and a thickener. The radium-removal circuit has three-mechanically agitated reactors, flash mix tanks and a thickener. The pH adjustment section consists of two small agitated tanks and a discharge launder system to four monitoring ponds (5000 m^3 each). The tailings neutralization section consists of a small splitter box and two large agitated holding tanks connected to the tailing pumps.

Table II. Average nickel concentration in Key Lake dewatering system effluent

Year	**Nickel Concentration (mg/L)**
1990	0.170
1991	0.172
1992	0.144
1993	0.189
1994	0.228
1995	0.292
1996	0.262
1997	0.250
1998	0.134
1999	0.053

Raffinate from the solvent extraction circuit is pumped into pachuca #1 at the head end of the neutralization train. The raffinate flows by gravity through each of the pachucas in series with lime being added to progressively raise the pH from one to seven. Each of the pachucas is connected by a launder and the lime is added to the launder. Slurry from either pachuca #3 or #4 is pumped back to pachuca #2 to provide a seed material for precipitate formation. In 1995, airlifts were installed on each pachuca to remove oversize from the bottom of the vessels, thereby reducing plugging problems. In 1997, the raffinate line was re-routed from a central front-end feed box to flow directly to #1 pachuca while the recycle was directed from the front-end feed box to #2 pachuca. This permitted aeration of the raffinate prior to neutralization in order to improve arsenic and organic levels in the final effluent. Steps were also made to permit higher temperature operation to promote organic removal. In other modifications to help reduce final effluent toxicity, the overflow launders on the bulk neutralization thickener were resealed to trap entrained organics and a removal system was installed to facilitate the removal of these organics. Scrap steel may be dissolved in #1 pachuca to improve contaminant precipitation by increasing the iron concentration. The overflow from pachuca #4 is fed into the bulk neutralization thickener where the solids are separated and removed as a 25% solids slurry. The thickener underflow is pumped to the tailings splitter box for disposal at the DTMF. The overflow from the thickener flows to the radium-removal circuit.

Contaminated water from reservoir 1 or 2 that has to be treated over and above process water requirements and other sources of contaminated mine water are fed into the circuit in the bulk neutralization thickener feed well. This mixes with the slurry from neutralization pachuca #4 before going into the neutralization thickener.

Reservoirs 1 and 2 provide much of the storage capacity within this effluent treatment system. Reservoir 1 tends to be used for non-sulphate saturated water storage (such as runoff, RO plant reject water) while reservoir #2 holds sulphate rich water (return water from the tailings management facilities and recycle effluent for re-treatment).

In the radium-removal circuit, barium chloride is added to the bulk neutralization thickener overflow stream before it flows into reactor #1. The discharge from reactor #1 is treated with lime in a small flash mix tank then fed into reactor #2. The pH is maintained at 10.5 to 11.0. The overflow from reactor #2 goes through another flash mix tank to which further lime can be added if required to maintain the pH and then into reactor #3.

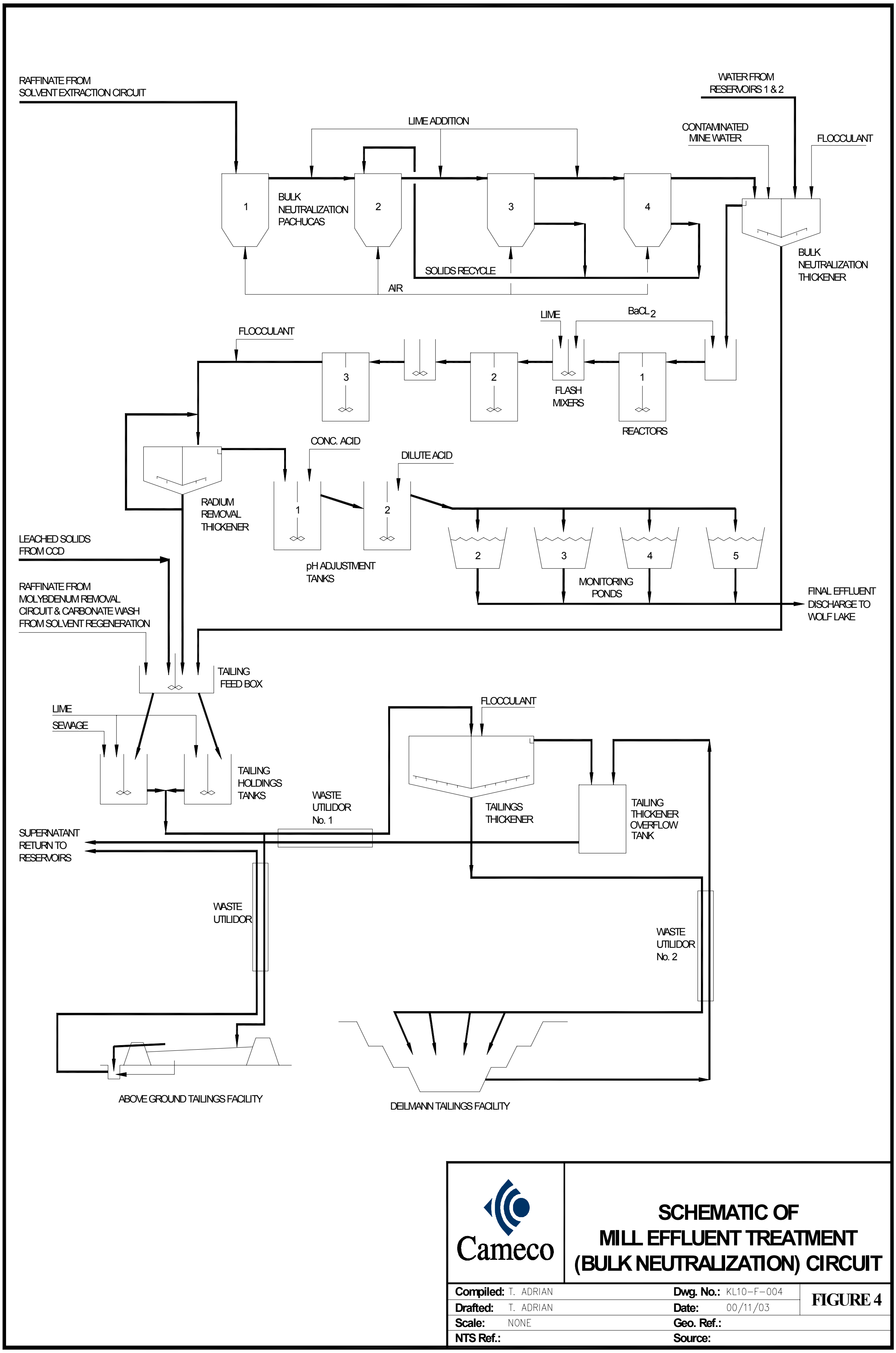

FIG. 4. Schematic of mill effluent treatment (bulk neutralization) circuit.

The discharge from reactor #3 goes into the radium-removal thickener for separation of the solids from the solution. The underflow solids are pumped to the tailings tanks and the solution flows to the effluent pH adjustment mixing tanks. Sulphuric acid is added in two stages to reduce the pH too slightly below neutral to control ammonia toxicity. It then flows by gravity through an open launder system to one of the four monitoring ponds located along the north side of the mill terrace.

The effluent is sampled while a pond is filling and the sample is analysed by the laboratory when the pond is full. The pond is held until the results are available at which time a decision is made by comparing the analysis results with the licence parameters. The pond is either released to Wolf Lake or recycled to reservoir 2. When a pond is batch released to Wolf Lake, a discharge composite sample is collected from the discharge pipeline. The discharge composite analysis results are reported as the final analysis of the monitoring pond's quality.

In the tailings neutralization circuit, the tailings from the counter-current decantation (CCD) circuit and the underflow streams from the two bulk neutralization thickeners are fed to a mix box. The combined slurry flows to the two tailings holding tanks where it is adjusted to pH 10.5 to 11.0 with lime and pumped to the tailings thickener by either a three stage centrifugal pump installation or two positive displacement diaphragm pumps. Domestic sewage (including camp sewage since early 1998), raffinate from the molybdenum removal circuit and carbonate wash from solvent regeneration are also added to the tailings hold tanks.

In 1996, a new tailings thickener system was commissioned. Combined tailings slurry from bulk neutralization is thickened to 35-40% solids in a 30-metre diameter thickener. Underflow is transferred by a two-stage centrifugal pump installation or two positive displacement pumps to the DTMF. Raise water from the DTMF is combined with thickener overflow in a storage tank prior to being recycled to reservoir #2.

Because Key Lake mill circuit employs a conventional ammonia strip and precipitation process, effluent ammonia control is necessary. Control has been good, so the next contingent level of control has not been installed (zeolite adsorption or some combination of strong and weak acid cationic ion exchange on the ammonium sulphate vapour condensation system). Also note that supplemental ferric sulphate addition is not required to control dissolved arsenic. Driving effluent to pH 10-10.5, with solids removal prior to final neutralization has effectively controlled effluent arsenic concentration. The switch to the arsenic/nickel-free McArthur River ore as prime mill feed further controls this contaminant.

4. Environmental significance of Nickel and Molybdenum discharges

As noted in Section 1, the initial intent of this CRP was to report on efforts to assess the significance of elevated molybdenum in mill effluent. However, in practice, this component of the work, studying the impact of specific contaminants, also included significant studies of nickel impact as well.

The nickel work began first, in 1993 [1]. Relatively low concentrations of nickel have been shown to exhibit an impact on early larval development of fish in the very soft waters endemic to northern Saskatchewan. The first study was to field-truth this finding, under site-specific conditions. These tests showed that the Saskatchewan surface water quality nickel objective for nickel to protect aquatic life and wildlife (Saskatchewan Surface Water Quality

Objectives, or SSWQO, equal to 0.025 mg/L where water hardness is ≤ 100 mg/L $CaCO_3$) was in the same range as NOEC/LOEC determinations (no/lowest observed effect concentration). This was measured by embryonic hatching success, survival, and growth for indigenous bottom-feeding white suckers. At the time, it was felt that the 1993 study was complicated by the presence of iron hydroxide precipitation in the dewatering effluent. Field investigations carried out in 1994 [2], revealed little evidence of adverse effects on native fish populations, but it was also concluded that the quality of pre-operational baseline data mediated the degree to which any significant change in 1994 could be detected.

Despite effluent performance improvements demonstrated in 1996 and 1997, nickel concentrations in the dewatering effluent remained above the site-specific end-of-pipe objective which had been established for this dewatering effluent. Namely, 0.1 mg Ni/L or five times less than the general Canadian Metal Mining Liquid Effluent Regulation limit for nickel. Consequently, a follow-up study was carried out in 1998, to further assess the environmental impact of elevated nickel levels in the McDonald Lake drainage basin [3]. The 1998 study assessed the spatial extent of current impacts based on phytoplankton community composition and water quality, studied fish recruitment in near-field waters within this drainage basin, expanded fish growth rate assessments carried out in the 1994 study, and assessed the bioavailability of the elevated nickel through additional site-specific early-life stage toxicity assessments. The conclusions from this work are summarized below:

- Water transparency improvements were noted at the point of discharge (Horsefly Lake), due to reduced iron loading (pre-treatment requirement for the RO plant);
- Phytoplankton abundance measurements showed decreases near the point of discharge relative to 1993/94, but showed overall increases in the 1990’s relative to the pre-operational 1970’s data. Measurable species diversity impact was restricted to the near-field Horsefly and Little McDonald lakes;
- Biological impacts of the dewatering effluent on the McDonald Lake fish community was minimal as measured by fish recruitment. However, in the closer Little McDonald Lake, few younger fish were captured possibly due to the impact of nickel but also possibly because of a confounding factor, namely, limited availability of spawning habitat. General fish community structure was consistent between 1994 and 1998; and
- After several unsuccessful attempts to conduct Early Life Cycle tests on white suckers (high transportation mortality and timing issues), successful tests were completed on long nose suckers. These studies showed time to egg hatch was similar in all test waters, egg hatch success rates were similar, but larval survival was a function of nickel concentration (>90% survival at 0.005 mg/L, <5% survival at >0.100 mg/L), and median effects in McDonald Lake water with larval survival of 40.3% at 0.040 mg Ni/L. This was a similar result to the 1993 work which showed 40% larval survival at 0.056 mg Ni/L. For reference, in nature, which obviously does not have the controls afforded laboratory tests, it is expected that 3% of longnose sucker embryos survive from egg to migrant fry.

On a parallel track, Dr. Gregory Pyle was completing his Ph.D. research work at the Department of Biology, University of Saskatchewan. This work, partially funded by Cameco which began in the summer of 1996, looked at the toxicity and bioavailability of nickel and molybdenum to standard toxicity-test fish species and fish species found in the Key Lake area [4]. He looked at egg hatchability, time-to-hatch, larval mortality and growth rate. Some of the main findings from his work, related to nickel, are summarized below:

- Nickel toxicity was found to be dependent upon fish species. In terms of species tested, the order was fathead minnow > northern pike > white sucker > alevin rainbow trout > juvenile rainbow trout. The minnows and trout are standard laboratory surrogates with trout being a common species used in Canada to monitor fish toxicity. Therefore cultured trout studies do not necessarily provide adequate toxicological information to protect indigenous fish;
- Relative 96h LC50 concentrations for minnows, northern pike, and suckers at the larval stage were 2.4, >3 and 17.9 mg Ni/L respectively. For reference, the alevin and juvenile trout concentrations were >20 and 51.2 mg Ni/L respectively;
- Nickel toxicity is reduced by increased hardness, pH, and water total suspended solids content;
- The most sensitive end point for detecting nickel toxicity was the time required for fathead minnow eggs to hatch. (LOEC of 0.75 mg Ni/L). However, this early hatch phenomenon was not seen in the indigenous white sucker species. Time to hatch is an ecologically important end point often not considered in more conventional toxicity-characterization programmes;
- The concentrations of nickel required for toxicity to occur are higher than those observed in receiving waters. The MATC (Maximum Acceptable Toxicant Concentration – geometric mean between NOEC and LOEC) to protect minnow eggs was estimated at 0.14 mg Ni/L. This MATC is four times higher than the SSWQO of 0.025, but in the range of observed effluent and very near-field environmental concentrations; and
- Larval fathead minnow tests carried out *in situ* in Little McDonald Lake (0.116 mg Ni/L) and McDonald Lake (0.054 mg Ni/L) generated results which were not significantly different from mortality observed at the reference site (0.0005 mg Ni/L).

Slight variations can be seen in comparing the methodologies for the 1993, 1998, and 2000 studies. All were 24-hour static renewal tests, but exposure times varied (7–32 days), as did the life cycle timing for first nickel exposure (for example, from within 24-hours of egg fertilization to four days post-fertilization). Nevertheless, all three studies generated estimates close to the current SSWQO.

In 1999, another Key Lake environmental effects monitoring programme was carried out, this time to document baseline conditions prior to the start of McArthur River ore processing. The study was based around the following core components:

- A deep water sediment coring programme;
- A detailed sediment quality triad (SQT) investigation incorporating a benthic macroinvertebrate assessment, sediment chemistry, and sediment macroinvertebrate toxicity assays in an integrated manner; and
- A fisheries component investigating species relative abundance and fish bioaccumulation in a number of fish tissues (flesh, bone, liver and kidney).

With respect to the McDonald Lake drainage, the 1999 report concluded:

- The weight-of-evidence provided by the sediment coring, SQT and fish tissue investigations indicates that there have been some near-field impacts in Little McDonald Lake and McDonald Lake relating to the release of dewatering water. There is no evidence of ecological effects further downstream (i.e., Wilson Lake);

- The sediment coring programme indicates that dewatering related contaminants, especially uranium and nickel have been loading to the system (indicated by increased concentrations in the upper sediment horizons). This shows that a significant portion of the elevated concentrations in Little McDonald Lake is partially due to dewatering releases. The weight-of-evidence suggests that a weak effluent effect may have influenced the Little McDonald Lake benthic community abundances, however exposures have not altered community composition from that documented in communities in the region exposed to naturally elevated metal concentrations (i.e., Zimmer Lake);
- There is no strong weight-of-evidence for further downstream effects in the McDonald drainage. High abundances, number of taxa, and the presence of suspected sensitive species such as Sphaerid clams in McDonald and Wilson lakes indicate no significant negative effects, despite the uranium and nickel accumulation in McDonald Lake. The results of the toxicity assays were highly variable and did not correlate with sediment contaminant concentrations, hence, based on the SQT data there is no evidence of a biological contaminant effect related to dewatering releases beyond Little McDonald Lake; and
- The fish tissue programme indicates that bioaccumulation of dewatering related contaminants has occurred in McDonald Lake but there is no evidence of bioaccumulation further downstream (i.e., Wilson Lake).

Regulatory critiques of the current work tend to focus on the need for:

- Sediment toxicity identification evaluation (TIE) studies;
- Sediment collection technique improvements and reduced sample variability;
- Increased frequency and expanded analysis of track improvements made in the dewatering aquatic receiving environment, as a result of the RO plant and pit reflooding, and;
- The need for yet lower analytical detection limits to detect changes.

Triggers for future environmental effects monitoring programmes also continue to be debated.

At present, no further nickel studies are contemplated. Construction of the RO plant, and re-flooding of the Deilmann/Gaertner system have reduced the nickel load at least for the time being, and four studies over the past eight years have essentially not found significant environmental impact in the near-field aquatic receiving environment. We have also essentially site-validated the SSWQO for nickel. The cost-benefit of intervening with a treatment plant to reduce nickel loadings to the environment has not been carried out. At this stage, we would be hard-pressed to justify the necessary cost-benefit study, since it would likely require yet another field study to evaluate fish population change in the McDonald Lake system. One aspect which will be interesting to follow in the future is the potential for a transitory nickel rebound from the sediment in Horsefly Lake. The discharge objective of 0.1 mg Ni/L was largely set to achieve a value of ≤0.06 mg Ni/L in Little McDonald Lake. In part, this reduction was due to co-precipitation of nickel with iron hydroxide in Horsefly Lake. Addition of iron removal in the RO plant pre-treatment process increased residence times in Horsefly Lake due to lower flows, and reduced end-of-pipe concentrations have all potentially changed the equilibrium. However laboratory studies and literature data indicate that the nickel in the sediments should be relatively stable.

With respect to the toxicity of molybdenum, Dr. Pyle [4] concluded that at Key Lake concentrations, waterborne Mo was not toxic to any life stage of any fish species tested. Concentrations up to 2 g/L were not sufficient to cause any detectable effects on fathead minnows, rainbow trout, northern pike, or white suckers. Molybdenum concentrations in dewatering effluent are low. However, Mo can be found in treated mill effluent, as shown in Table 3. Analysis of field toxicity studies showed a strong correlation between Mo concentrations and larval fathead minnow mortality in near-field mill effluent receiving water. However, association does not prove causation, and in fact, Dr. Pyle came to the conclusion that dietary selenium, which co-varied with molybdenum was the probable cause of toxicity. Selenium is felt to be more toxic to fish through diet as opposed to waterborne exposure. Although effluent selenium levels are low (Table 3), literature suggests that Se concentrations in food organisms inhabiting water containing 2-3 μg Se/L can be sufficient to cause toxicity. Laboratory attempts to determine if dietary Mo, as opposed to Se was the cause of elevated level of toxicity failed due to cadmium contamination of the Mo salts used as toxicant.

Our overall conclusion on early life cycle toxicity tests, particularly using indigenous fish species, is that they are difficult to conduct, easy to critique, can generate variable results, and do not necessarily provide much insight into the likely cost-benefit of modifying environmental performance. They nevertheless do provide a window into the chronic, low-level impact of our effluent in near-field waters.

Table III. Key Lake mill effluent molybdenum and selenium level

Year	**Concentration (mg Mo/L)**	**Concentration (Mg Se/L)**
1990	0.79	0.010
1991	0.81	0.026
1992	1.12	0.036
1993	1.46	0.021
1994	2.37	0.017
1995	2.27	0.022
1996	4.23	0.023
1997	3.24	0.020
1998	3.46	0.044
1999	3.29	0.053
2000*	2.06	0.025

* (Jan. – Sept. only)

5. Mill effluent fish toxicity, toxicity reduction and aquatic effects studies

Routine, semi-annual, 96-hour static acute lethality tests have been carried out on mill effluent for many years. Rainbow trout fry (0.5 - 10 g) are the standard reference fish, selected because they are generally available throughout Canada, their responses to most metals are fairly well known, and the water which they inhabit are representative of good water quality in Canada. In November 1993, the Key Lake mill effluent failed one of these routine tests (>50% mortality). This prompted an investigation, which ultimately rectified the acute toxicity problem. A Toxic Identification Evaluation (TIE) study was carried out. This study involves a systematic fractionation of the effluent mixture in order to characterize, isolate, and identify the toxic constituent(s). Isodecanol, which is added to the kerosene/tertiary amine solvent to assist in organic/aqueous phase separation in solvent extraction, was identified as the substance responsible for rendering the effluent marginally toxic to trout, despite its relative insolubility in water. The problem was eventually traced to a change in ore mineralization in the deeper reaches of the Deilmann deposit (basement rock hosted vs. sandstone hosted mineralization). This ore change increased silica and calcium inputs to solvent extraction, which in turn, led to higher raffinate organic losses. The processing problem was resolved in 1994, through better silica/calcium control in solvent extraction feed, lower isodecanol levels in solvent, reduced raffinate organic loss and organic removal from effluent during treatment by aeration and heat.

The investigation also showed that for the toxicity problems encountered at Key Lake, there was a defined relationship between 96-hour rainbow trout tests and a 15-minute microbioassay test (Microtox), which measures the inhibition of light production from a strain of luminescent bacteria as a sign of toxic response. This quick biological test is now used on all pond releases to control the effluent acute toxicity.

Follow-up investigations were carried out, and formed one of the issues tracked in this CRP. It was decided to assess the environmental effect of the 1994 problem on the near-field mill effluent drainage system. A study was designed with the following objectives:

- Review known literature on the ecological fate and effects of isodecanol in aquatic systems;
- Verify the conclusions of this literature-based evaluation using appropriate field measurements; and
- Document any shift in the aquatic biological resources of the near-field drainage. This aspect had been extensively documented in 1993 as baseline work for the proposed McArthur River development.

The literature review concluded that the levels of isodecanol in the effluent discharge in 1994 probably had little or no measurable effect on the receiving aquatic system. It was felt that isodecanol would likely be lost through co-precipitation, vaporization, non-specific adsorption and bio-degradation. The bio-accumulation potential was considered small, perhaps non-existent. Field water-quality measurements failed to find differences in isodecanol concentrations between reference and effluent receiving waters (to a 0.2 mg/L detection level). Water quality and limnological data were similar to previous operational investigations, being consistent with known effluent influences. Macroinvertebrate community structure and composition changes were evident between 1993 and 1995; however, these differences were judged minor and of little significance to the overall functioning of the aquatic ecosystem. Fish studies were purposefully restricted in the study due to a desire to use non-destructive sampling methods. Concerns had been raised that the limited fish population needed time to recover from extensive fish sampling programmes conducted in 1993 and 1994, given the relatively low productivity of the small, shallow, cold, nutrient poor, sandy substrate lakes found in the area. Spawning site assessments were generally inconclusive, and lake fish population presence was only determined by indirect evidence (fish sounders). Nevertheless, fish avoidance of the area due to increased pollutant presence in the receiving water was not evident.

Attempts to conduct sediment toxicity tests using non-standardized procedures proved somewhat problematic. Benthic macroinvertebrate testing showed no discernible impact on sediment dwelling organisms. Fathead minnow larvae tests initially showed a difference from controls, believed due to pH suppression during the test. Follow-up tests had control problems due to turbidity. Therefore, minnow tests were judged inconclusive. Rainbow trout tests showed no transfer of contaminants at toxic concentrations to the water column.

The 1995 programme would likely have brought closure to the issue; however, in the last field investigation in September 1995, a relatively high incidence of skin lesions was found in fish populations within the drainage, particularly in near-field bottom-feeding white sucker populations. This brought a new dimension to the follow-up study.

Follow-up investigations in late 1995 and 1996 focused on fish disease epidemiology. Pathological examinations defined the problem as an outbreak of a haemorrhagic ulcerative skin disease, associated with the presence of elevated levels of certain bacterial strains. Literature reviews showed that the type of problems encountered at Key Lake have been seen elsewhere, in relation to deteriorating water quality, high stocking densities in farmed fish, reduced dissolved oxygen levels, high organic loading, parasitic infections, domestic sewage, other pollutants and prior disease outbreaks (i.e., primary pathogen vs. secondary or opportunistic pathogen). A variety of hypotheses were formed for the site-specific Key Lake outbreak of disease:

- Presence of treated domestic sewage effluent in the same lakes which receive the mill effluent;
- Elevated water temperatures during the summer of 1995;
- Outbreak of a particularly virulent strain of previously benign bacteria in the drainage;
- General immuno-suppression or chronic stress in resident fish populations from some as yet unidentified substance or condition, leading to opportunistic bacterial infections be it effluent related or natural in origin (such as spawning stress); and
- An artifact of generally low pH within the focal lakes. Receiving waters have very low buffering capacity, and ammonia control dictates lower-end pH discharges to mediate ammonia toxicity (average pH of 6.31 in 1995, with total ammonia levels averaging 12.8 mg/L).

The focal point of the disease was located in near-field lakes, which received mill effluent and domestic sewage effluents, and it was primarily associated with white suckers. Disease incidence and severity further downstream appeared to be significantly lower. Bacterial densities in water were similar in effluent-exposed and reference lakes, suggesting water-borne bacteria densities were not a primary factor. Host susceptibility differences between the reference and influenced water bodies, for an as-yet undetermined causal agent, seemed likely.

In 1997, it was concluded that the initial disease outbreak likely occurred sometime between mid-1994 and mid-1995. The disease has been identified as a bacterial haemorrhagic septicemia (red-spot) with evidence supporting a specific diagnosis of Motile Aeromonad Septicemia (MAS). The disease progression is different from other reported MAS outbreaks in that death of the fish was not the disease outcome. Cold water temperatures may have provided the fish with a temporary respite from the disease, leading to a chronic disease with late stage lesions, showing evidence of cycles of healing and reactivation. It is believed that this disease outbreak resulted when the chronically immuno-suppressed fish population experienced an additional stressor(s) in 1994/95 that overcame the capabilities of the fish to manage bacterial pathogens shown to be present in both reference and exposed fish populations. Some combination of chemicals in the mill effluent, sewage effluent or natural environmental factors precipitated the problem. This conclusion led to the decision to divert the sewage effluent (to the mill effluent treatment and tailings management circuit) in a further attempt to reduce fish stress (commencing January 1998).

Ongoing non-fatal visual fish health surveys and a tagging programme (199 fish) were implemented in June 1997 to track disease progression and a multi-year monitoring programme was implemented to gauge the impact of sewage discharge into the same drainage system.

In 2000, reports were filed on these two 1997 monitoring initiatives [6,7]. Results are briefly summarized below:

- The data from the three-year monitoring survey continues to support the conclusion that the fish populations in the near-field waterbodies of the David Creek drainage experienced a severe bacterial disease outbreak some time in 1995. Previous findings and the results of the three-year survey suggest that the population has been gradually recovering from this initial outbreak of ulcerative skin disease as both disease intensity and prevalence have markedly decreased;
- Comparisons restricted to the spring portion of the three-year monitoring period show that the percent disease incidence has declined from 25% in 1997 to a low of 3.3% in 1999. The severity of lesions has also markedly decreased as shown by comparisons of the intensity of the ulcerations in the early outbreak years relative to those observed in 1999. This decrease in disease incidence and intensity corresponds to the increase in overall fish health over the last two years. In the last two years, the overall physical condition of individuals in the population has improved;
- The low capture mortality (especially for white suckers) and high recapture success within and between sample years indicate that the programme was successful in minimizing study related mortality and that fish with ulcerations can recover from the disease. The number of fish with scars from previous disease expression has fluctuated, but provides clear evidence that fish with lesions can recover and survive through multiple years. Some of these healed lesions were quite large indicating that individuals recover from severe ulcerations;
- Despite this evidence of recovery this population is likely still at risk of another bacterial disease outbreak should they be exposed to any additional stressors, whether anthropogenic or natural; and
- Raven Lake, which received the treated sewage effluent prior to diversion in January 1998, is expected to recover very slowly, due to the low flushing rate for the lake. Availability of nutrients from sediments results in substantially higher phytoplankton productivity relative to a nearby reference lake. The zooplankton community in Raven Lake has responded with a complimentary increase in its own productivity along with a corresponding decrease in community complexity. The benthic macroinvertebrate community also exhibited the increased productivity/decreased community complexity trend. The only biotic component that does not show increased productivity in Raven Lake is the aquatic macrophyte community, likely due to dense algae blooms which are limiting summer time light penetration. This current work was done primarily to provide baseline for future decommissioning phase recovery evaluation.

Studies of fish health in the near-field waters receiving mill effluent have not yet been brought to closure. In July and August 2000, monthly rainbow trout acute toxicity tests of the discharge from Wolf Lake (the small, 50 000 m^3 lake which first receives treated mill effluent) failed, despite the fact that actual end-of-pipe effluent samples passed both trout and

Microtox tests. This apparent anomaly is pH-related. Wolf Lake shows pH depression from about six in the winter to four in the summer. These were the first toxicity failures in five years of data collection from this point in the near-field receiving environment. Ammonia oxidation (nitrification) from NH_3 and NH_4^+ to nitrate/nitrite is undoubtedly a major factor in pH depression in the summer months. However, pH starts to drop in the March-May period, when water temperature is too low for rapid ammonia oxidation to occur. Therefore it appears that there might be more than one factor involved. Acid-rain spring melt runoff, low pH releases from the vicinity of the above-ground tailings management facility, and sediment degradation have all been suggested as possible additional causative agents.

The fact that we are currently studying pH suppression was expected. In our 1998 progress report to this CRP, we predicted follow up on the following two issues in relation to fish health:

(i) Investigation of the cause of pH suppression in the receiving water. Natural pH levels in these waters are in the pH 6–7 range. Values as low as 3.65–3.75 have been recorded in effluent receiving water bodies. Acidic water conditions of less than five are known to be stressful to white suckers. A pH data logging system was proposed to monitor seasonal effects. The water appears to drop in pH downstream from the effluent discharge point. Effluent is typically discharged at pH 6-6.5; and

(ii) Sediment contaminant bioavailability studies. In light of as-yet unexplained pH effects, and likely impact on sediment contaminant behaviour, further study was felt warranted.

We were unable to carry out the pH work in 1999. The Key Lake mill was shut down (for retrofitting to receive McArthur River ore), thus it was an atypical year. It was however noted that pH data in the summer of 1999 was not as depressed as previous summer periods when full volume mill effluent was being discharged. Formal regulatory requests for additional sediment toxicity testing as follow up to the 1997 – 1999 work have recently been received. The 1999 sediment toxicity work [5] looked at the small lake downstream of Wolf Lake, where the near-field benthic macroinvertebrate community has been impacted by treated mill effluent. The next step is likely a sediment TIE study.

6. Nickel loading reduction initiatives

6.1. Overview

As previously mentioned, a reverse-osmosis (RO) plant was installed in 1996, to reduce nickel loadings in the dewatering effluent. The work began in 1994/95, when a large-scale pilot test was carried out to examine the relative merits and drawbacks of ion exchange and reverse-osmosis technologies to lower nickel levels in this discharge. Confounding factors were as follows:

- The majority of dewatering wells also contain iron, which can foul ion-exchange resins and require pre-treatment for RO;
- The system should be capable of removing other impurities. Wells containing elevated uranium and radium-226 concentrations were being diverted directly to the mill effluent treatment system. Water requiring U, Ra-226, and Ni treatment should not require different treatment from water elevated only in Ni concentration; and

— The system should be compatible with future, decommissioning phase water treatment requirements, which will involve "pump and treat" of flooded pits, possibly coupled with heap leach of surrounding waste rock piles to accelerate recovery processes.

Although both treatment alternatives produced excellent nickel removal rates, it was concluded that RO was a better fit for these requirements, despite higher capital and operating costs, and arguably, a higher level of technical risk (primarily fouling risk).

The RO plant was constructed in 1995/96, and operational approvals were received in April 1996. The plant technical specifications are summarized below:

Number of Units	4
Type	Single Pass
Configuration	3 stage 12:5:2
Vessels	Osmonics 8"
Elements per Vessel	6
Type of Element	Polyamide Thin Film
Manufacturer	Dow-Filmtec
Model	BW30-400
Feed water	Groundwater at 160-300 mg/L TDS
Pre-treatment	Potassium permangenate/manganese greensand pressure filter system to oxidize and remove iron and manganese. Also a cartridge polishing filter to remove fine particulate not removed by the greensand filters. In 1999, a caustic addition system was added to control raw water pH to 6.2 – 6.5
Typical RO Feed	TDS at 160-240 mg/L; TSS at 0.1-0.4 mg/L
RO Recovery	85%
Typical Salt Rejection	94-98%
Feed Capacity Per Unit	450-600 USgpm/102-135 m^3/h
Product Capacity @ 85%	383-510 USgpm/87-116 m^3/h

The new plant was housed in a 720 m^2 building, which also housed a pH adjustment system (sodium carbonate) since RO tends to depress pH in the permeate, and greensand filter backwash and RO membrane cleaning systems.

In 1999, the RO plant supervisor prepared an overview of operation and experience over the first three years of operation [8]. This overview formed the majority of the summary of plant operation provided below:

6.2. Raw water

Raw water feed to the plant comes from a number of deep and shallow wells. These wells feed a 50 000-gallon storage tank which in turn supplies feed water to the pre-treatment process. The main operational problem at first was highly variable feed water quality, specifically iron precipitate suspended solids and general turbidity. Previously deposited iron precipitate and silty material in the dewatering well supply network and header became mobilized by flow changes when the RO plant was brought on-line. Other disturbances such as temporary power failures and well servicing requirements have more pronounced effects under RO than under straight discharge to the mill effluent circuit or Horsefly Lake. A decision to re-route contaminated water from the Deilmann dewatering system to the Gaertner pit (which acts as a very large settling pond) and feeding the RO plant exclusively from a limited number of Gaertner area wells (which in effect sand-filters the Gaertner pond water) effectively stabilized feed water quality.

6.3. Pre-Treatment

The dominant feature required in the pre-treatment process is the removal of ferric iron (Fe^{+3}). The RO membranes have the ability to reject ferrous iron (Fe^{+2}) but not ferric iron. Much of the feed water has been exposed to air so the process of completing the oxidization to Fe^{+3} must be undertaken.

Oxidation is achieved by injecting a potassium permanganate solution ($KMnO_4$) into the feed stream at an approximate ratio of 1 ppm $KMnO_4$ to 1 ppm Fe in feed water. This oxidized feed water is pumped through nine manganese greensand filters which are 10 feet in diameter. The internal media of these tanks are stratified layers of anthracite, manganese greensand and various layers of sand and gravel. The anthracite and sand are effective at filtering out the suspended solids while the greensand removes the iron. As the feedwater comes in contact with the greensand it is further oxidized and the soluble iron is precipitated within the greensand layer.

The post greensand water then passes through a polishing filter or cartridge filter system. These filters are a disposable extruded polypropylene microfibre with a nominal pore size of 5.0 microns. These filters are key in maintaining Silt Density Index (SDI) of <5.0 in the RO feedwater.

Many of the initial start-up problems centred on the pre-treatment circuit. For example: rapid pressure build-up on the greensand filters from previously deposited iron precipitate in the supply piping, generating excessive backwash requirements and resulting in greensand media attrition; fouling with fine well sand; greensand bleeding due to improper support bed media; $KMnO_4$ injection rate control problems due to low pH (about 5.3) cold groundwater conditions; and post-greensand iron oxidation fouling of downstream pre-filters and RO membranes.

6.4. Reverse-Osmosis units

Each of the four RO units has a single pass, three stage 12:5:2 configuration. Pressure vessels are Osmonics 8" diameter × 21.5' long. Each vessel contains 6-40" elements. In the original RO plant design and construction, no consideration was given to the piping arrangements with respect to the cleaning process. The feed line from the cleaning solution pump entered the RO unit at virtually the same location as the feed water and at no other locations. What this allowed was flow control of cleaning solution to the first array only. To clean the second or third stage, the solution had to pass through the first stage, and with little or no instrumentation at interstage locations, proper cleaning flow rates were difficult to achieve.

As part of the automation project, a major re-plumbing was done. Upon completion, the option of cleaning any individual array became available. Strategically placed vortex flow meters and pressure transducers monitor all flows and pressures at interstage locations.

6.5. Reverse-Osmosis membranes

The plant was originally commissioned with 100% Dow-Filmtec membranes. Over the years, approximately 105 of them have been replaced due to damage and/or scaling. Dow Filmtec BW30-400 elements are typically, but not exclusively used. The Dow element is designed for brackish water with polyamide thin film construction. The benefits of the polyamide membrane is the broad pH range allowable for operating and cleaning. The one drawback of polyamide membrane is that they are chlorine intolerant. Chemical attack to the membrane will occur with chlorine or any other oxidizing agent and salt rejection will decrease.

6.6. Recovery

The current recovery, or production rate is 80–85% of raw water input rate. The primary balance is to produce the required amounts of product while maintaining sufficient flow in the concentrate stream to carry remaining ions and solids. All this must be done while ensuring that the concentrate stream does not reach 100% saturation of any scaling ions. To determine allowable recovery rates, a detailed water analysis must be done to project operating concentration levels. Saturation limits can be overcome with the injection of antiscalants and/or silt dispersants.

6.7. Feed rates

Each of the four units had a design feed rate of 450 USgpm (102 m^3/h) at 85% recovery. For extended periods of time (1 month plus) units have been run with a feed rate of 600 USgpm (136 m^3/h). At these increased feed rates (near the maximum pressure differential across the membranes), increased fouling is experienced, requiring more frequent cleaning.

6.8. Key contaminant removal

The main objective of the RO plant is the removal of Ni from minewater for discharge to the environment. It is not possible to design an RO unit to remove one particular element from the feedwater. A 96-99% rejection rate of all ions is generally obtained based upon:

— Ionic charge	- The higher the charge, the greater the rejection.
— Size	- The larger the size (molecular weight), the better the rejection.
— Combinations	- Mixtures of different ions are rejected differently by membranes.

Removal efficiencies in 1998 and 1999 are provided in Table 4.

6.9. Fouling tendency

Fouling is defined as the accumulation of suspended material on the RO membrane or associated equipment within an RO unit. Fouling can further be broken down into two separate groups. Colloidal fouling, which is the accumulation of TSS within the unit and bio-fouling, which is the growth of bacteria within the unit. Fouling should not be confused with scaling, which is an entirely different set of circumstances.

Fouling has been an ongoing problem with the main foulant being iron and/or filter media from the greensand filters. If the pre-treatment is not operated properly or the downstream cartridge filters have lost capacity, then this type of fouling can occur.

Table IV. Key Lake reverse-osmosis plant

Parameter	Water quality		Removal efficiency %
	Raw water	Product water	
Raw Water vs. Product Water Quality – 1998			
U (µg/L)	151.71	2.73	98.52
Ra-226 (Bq/L)	0.19	0.011	95.29
Ni (mg/L)	1.202	0.024	98.39
Zn (mg/L)	0.234	0.013	95.48
Cu (mg/L)	0.026	0.006	81.89
Raw Water vs. Product Water Quality - 1999			
U (µg/L)	222.96	2.86	98.91
Ra-226 (Bq/L)	0.43	0.017	96.66
Ni (mg/L)	1.455	0.023	98.69
Zn (mg/L)	0.149	0.007	95.91
Cu (mg/L)	0.009	0.007	37.39

Typical performance – other parameters

	Feed Water	Post Greensand	Product
PH	5.7-7.0	6.2-6.5	5.2-6.0
TSS	0.1-2.4 mg/L	0.1-0.4 mg/L	--
TDS	160-300 mg/L	160-240 mg/L	0.1-20.0 mg/L
As	0.0005-0.0120 mg/L	--	<0.0005 mg/L
Fe	0.070-1.20 mg/L	0.005-0.07 mg/L	<0.0005 mg/L
Pb	0.01-0.06 mg/L	--	0.01-0.03 mg/L
Mn	0.01-0.20 mg/L	0.01-0.06 mg/L	<0.0005 mg/L
Mg	9.0-20.0 mg/L	--	--
Ca	8.0-24.0 mg/L	--	--
Na	5.0-20.0 mg/L	--	--
SiO_2	9-15 mg/L	--	--
Al, K	2-12 mg/L	--	0.2-3.0 mg/L

6.10. Cleaning fouled unit

If filter media is causing a problem within the unit it will likely be on the lead end of the first elements. This is easily remedied by simply removing the end caps and hosing particles off the elements. If iron fouling is causing third array pressure problems, the cleaning of this is done with a high temperature, low pH solution. The low pH is obtained by mixing a cleaning solution utilizing citric acid based on membrane manufacturers specifications.

6.11. Scaling tendency

Scaling is defined as the precipitation of previously-dissolved substances on the RO membrane or other components within an RO unit.

In the Key Lake case, the scaling is usually associated with silica and barium sulphate. With respect to silica, the units operate just at or near saturation limits. The barium sulphate poses a different problem. Concentration levels of barium sulphate are at super saturation levels, and deposits on the membrane can be severe, rendering the elements useless. Cleaning of barium sulphate is not an option as any chemical used to dissolve barium sulphate also harms the membrane. Costs incurred to purchase equipment and chemicals to install a scale inhibitor injection system were judged not economic when compared to treating membranes as a disposable item. Interestingly, membranes can develop low gamma radiation fields (up to 30 µSv/h contact at the back end of the module, 3 µSv/h at the front end). We have also had to modify the plant's heating and ventilating system to prevent minor radon problems (excursions to 0.1 – 0.2 working levels).

6.12. Cleaning scaled unit

The type of scale will determine the cleaning chemical to be used. Generally high temperature, high pH solutions are used. The high pH is obtained by mixing a 50% sodium hydroxide solution based on membrane manufacturers specifications.

6.13. Membrane life

The current rule of thumb is that membrane life should be three to five years. This is a very rough estimate as each unit will be subject to different chemicals, feedwater quality, operating extremes, pH and operator errors which will all affect membrane life and product water quality.

6.14. Automation

From plant commissioning in March 1996 to June 1998, operation of the plant was strictly manual. Twenty-four hour coverage was required due to the backwashing demand of the manganese greensand tanks. Starting in approximately June 1998, an automation project was initiated. Included in the project was automation of the pre-treatment circuit and RO units. Operation of these two circuits can now be done within the RO plant as well as from workstations throughout the property.

The plant is still manned 24 hours but with better automation, the operator is not bound to the RO plant. Remote monitoring frees up the operators, allowing them to leave the plant but still be able to monitor and perform some plant functions.

6.15. Other Ni reduction initiatives

Addition of the RO plant was the most significant, most immediately beneficial step taken to reduce nickel loading to the environment. However, it was not the only step taken. Other longer term measures are briefly summarized below.

- In 1995, Cameco began to segregate nickel-rich basement waste rock (at 200 mg Ni/kg) while it was being excavated during mining of the Deilmann ore body. Approximately 1.2 million m^3 of rock were segregated and temporarily stockpiled on top of the general Deilmann north waste dump. Some of this material was used to construct the DTMF bottom drain, and in 1998, the remaining material was relocated to the adjacent Gaertner pit. About 1 million m^3 of rock was relocated to Gaertner and covered with 325,000 m^3 of filter sand prior to pit reflooding. Ongoing pump-and-treat operations via the RO plant, subaqueous disposal to prevent nickel oxidation, and material compaction and cover all combine to control the impact from this problematic material;
- Starting in 1997, efforts are being made to both identify and remediate sources of the increased nickel loading in the dewatering system. Problems were found with the bentonite liners under the special waste pad constructed near the Deilmann pit and under

the ore pad located near the satellite crushing and grinding plant. Repairs have been made to both, and we are currently in the process of evaluating conditions under the other special waste pad, located near the Gaertner pit. While steps have been taken to reduce seepage losses from these storage facilities, it must also be borne in mind that we have preserved environmental containment (within the dewatering system hydraulic cone of depression). These waste and ore materials will also eventually be fully consumed as diluent for McArthur River ore (to maintain a nominal 4% mill head grade); and

— Substantial efforts have been, and continue to be placed on better characterizing the general waste rock piles around the Deilmann and Gaertner pits. Both in-house and university-based research programmes are in place. The broad objective is to better understand pile leachate characteristics and consequently develop better, or validate current long-term decommissioning projections. In the mid-term, placement of the waste rock in the vicinity of the mined-out pits, within the hydraulic containment provided by the dewatering system, provides containment of any impact. Since this containment is needed to use the Deilmann pit as a tailings facility, and since McArthur River can reasonably be expected to have a long life, we have a good, well-integrated mid-term waste rock management plan.

Detailed description of these other nickel reduction initiatives is well beyond the scope of the current report.

7. Conclusion and future outlook

7.1. Focus of current Cameco work

The current Co-ordinated Research Project focuses on the treatment of liquid effluent from uranium mines and mills. As evidenced by the contents of this report, Cameco's work in this area increasingly seems to focus on the quantification and assessment of environmental impact arising from effluent release rather than the study of ways to provide either lower cost treatment methods or even lower levels of contaminants in effluents. In part, this shift in priority may be because the time period of this CRP coincided with the assessment and licensing of a new generation of uranium facilities in northern Saskatchewan. That said, the trend towards more assessment is expected to continue.

In 1996, at the start of this CRP, we noted that the assessment work is becoming increasingly dominated by identification and research into the causes of biological impact from effluents. While one cannot disagree with a biological basis for environmental assessment and establishment of performance criteria, the lines of distinction between compliance requirements, standards setting requirements and basic biological research are becoming increasingly blurred. The necessary investigations to address these biological issues are lengthy, costly and can lead to expensive retrofits for very modest effluent improvements if measured on a concentration basis. Major contaminants of concern are typically measured in the ppm to sub-ppm range. Treatment processes employed are arguably at or near known BATEA levels – best available technology economically achievable. If required levels of performance were to increase further, we would expect the costs to be significant, as demonstrated by the reverse-osmosis work. Effluent discharge limits set beyond those dictated by equilibrium chemical solubility limits or the capabilities of biological processes, such as wetland polishing, will likely be expensive propositions, and for what degree of benefit? By studying environmental effects, we hope to show that current behaviour is reasonably well understood, generating impacts of limited range, magnitude, and duration.

7.2. Current assessment of Key Lake performance

As we study environmental interactions, it is instructive to compare current conditions against those originally predicted. This is one of the main purposes of regulatory-required state of the environment (SOE) reports for existing uranium operations. The Saskatchewan provincial regulatory agency requires such studies on a regular basis, nominally every five years. The second such report for Key Lake has recently been published [9]. The main conclusions from this work are provided below to give an overall perspective on the Key Lake Operation:

- Environmental baseline studies were conducted from 1976 to 1978 and were presented in an Environmental Impact Statement (EIS) published in 1979. Therefore over 20 years of data can be assessed at this point;
- In the current study, the state of the air quality in the Key Lake operational area was found to be relatively uninfluenced by mining activities and within the predictions provided in the original EIS. Radon levels were identified as exhibiting an increasing trend since the last SOE in the immediate vicinity of the above-ground tailings management facility. It is believed that this is primarily a result of the tailings becoming unsaturated. This increase is restricted to the immediate area of the tailings facility and has, as was originally predicted, not impacted the surrounding Boundary Lake radon monitoring stations (Northwest, Northeast, Douglas, Kapesin, and Blackforest lakes);
- In assessing surface hydrology impact, it was concluded that actual dewatering discharges were lower than predicted and as a result, measured mean annual flow at McDonald Creek is also lower than originally predicted. A comparison of predicted changes to lake elevations and present observed lake elevations indicated that early predictions were generally quite close to existing conditions and predicted boundaries for the zone of influence have proven to be quite accurate;
- Overall, the EIS accurately or over-predicted effluent concentrations and under-predicted effluent flows. The net result is that effluent loadings were accurately predicted for three analytes (Ba, Cl, K), over-predicted for 13 analytes (mostly heavy metals) and under-predicted for six analytes relative to the 93/98 period (Ca, Na, NH_3, Mo, SO_4, and Mg). Arsenic and selenium, which are both important from an ecological perspective, were over-predicted in the original EIS;
- The basic predictions of the original EIS relating to the treated mill effluent receiving environment were relatively accurate. Substantial near-field impacts have been documented in the David Creek system, as was predicted in the EIS. There is evidence of possible pH depression at the near-field sampling points of Yak Creek and possibly David Creek downstream, although it is not known if this depression is mill related or naturally occurring within the drainage. Biological effects have been documented in Fox Lake and to a lesser extent in Unknown Lake. There was evidence of contaminant loading and bio-accumulation in Delta Lake, though the ecological integrity of Delta Lake does not appear to have been affected. The EIS prediction that ammonia could produce a measurable biological effect at the inflow of David Creek to the Wheeler River was not supported as no evidence of biological effects have been found in the Wheeler River;
- The potential impact from the treated sewage release was not adequately addressed in the EIS and these releases have resulted in eutrophication of Raven Lake. No predictions

were made in the EIS with respect to Raven Lake water quality. Steps have been taken to alleviate this problem by altering the sewage handling procedures; and

- The dewatering releases to the McDonald Lake system have resulted in substantial impacts to Horsefly Lake, as was predicted in the original EIS. However, the EIS did not foresee the elevated nickel concentrations that arose in the dewatering water, and therefore did not predict any of the associated impacts. In the near-field, nickel continues to be the analyte of most concern, with exceedances of SSWQO noted up to the outlet of McDonald Lake in recent years. Nickel concentrations further downstream in Outlet Creek and the Wheeler River tend to fluctuate near the detection limit and are not a concern. Dewatering impacts on the Wheeler River were found to be minimal, with few changes noted between the current SOE review period and the preceding five-year period. The EIS accurately predicted that the Wheeler River biological community would not be measurably impacted by the dewatering activities. This remains true despite the elevated nickel releases and resulting near-field nickel water and sediment concentrations.

The overall conclusion is as follows:

> *"The present state of the environment for the Key Lake operational area falls within the environmental predictions documented in the original EIS. Air and terrestrial impacts have been minimal and been restricted to immediate near-field locations. Changes in water quality and aquatic impacts were predicted in David Creek, near-field sites in the McDonald Lake system, and in the Wheeler River immediately downstream of the David Creek inflow. However, water quality and aquatic ecological effects have been restricted to David Creek and the near-field waterbodies of the McDonald system with no evidence of impacts within the Wheeler River. The elevated nickel concentrations in the dewatering water were not foreseen by the EIS and therefore the associated near-field effects were not predicted. There is no evidence of dewatering related effects occurring downstream of McDonald Lake. The overall conclusion is that the Key Lake facility is operating as predicted and within the environmental boundaries of the original EIS"[9].*

7.3. Future outlook

Finally, as we continue to assess current operations, practice ongoing continual environmental improvement, develop and implement decommissioning plans, and work on forecasting environmental performance for new facilities, a number of wider issues will have to be addressed. In no particular order of importance, they can be summarized as follows:

Environmental effects monitoring. As documented in this report, there appears to be a shift in regulatory assessment, away from the more conventional measurements of environmental performance such as adherence to a predetermined set of chemically-based performance criteria and the effluent's acute toxicity to fish. The esoteric nature of more wide-ranging environmental effects monitoring has been well demonstrated. What is unknown is how such analysis can (or should) be used to regulate the uranium mining and milling industry. Clearly if one examines any effluent in enough detail, one will find some measure of impact. To bring manageable scope to the process, the environmental effects monitoring requirement must be defined in terms of such things as class(es) of organisms to be studied (i.e., fish, benthos, zooplankton, phytoplankton, macrophytes and/or bacteria), sampling methodology to be employed, the structural levels to be studied in each selected class of organism (i.e., intracellular, tissue, population and/or community level) and the end point of the work. End points could range from such things as developing a database on current performance for future reference, defining the zone of influence of the operation's effluent, documenting sublethal toxicity impacts of effluents, or to effect a higher level of regulatory control. Detectable change, in and by itself, is insufficient grounds for performance improvements. In Canada, there is a wide range of opinion on such matters. The debate also delves into the area of cumulative effects monitoring. Specifically, accumulative effects of a single operation over time and/or possible overlapping effects of several operations at a particular location in any given time. It is our view that these studies should focus on higher trophic levels, and deal with population-based impacts.

Sediment-based ecological assessment. Effluent systems can operate within an accepted standard of performance, yet over time, create enhanced concentrations of metallic impurities in the sediment of near-field receiving waters. The biological impact of elevated metal levels in sediment during operation and upon decommissioning is a topic which is difficult to assess. Intuitively, it seems unlikely that the biochemical/geochemical/physical processes which lead to sediment enrichment will be completely reversed once the operation ceases. However, the long-term fate of these sediment-based metals, involving bio-mineralization, geochemical immobilization and biological/chemical cycling to and from the sediment matrix are difficult to assess. Basic research, most likely site-specific, is needed to effectively address these issues, provided a case can be made that these enriched sediments create important, long-term effects. This is a debatable point. The issue is to what extent these "research" questions should impact the regulatory licensing/de-licensing process.

Potentially incompatible environmental goals. Current Canadian engineering thinking on the best way to handle disposal of problematic waste rock and tailings involves subaqueous disposal, provided the resulting drop in oxidation rate of contaminants has net environmental benefit. Deeper water disposal can also provide contaminant isolation, depending upon the water body's limnological characteristics. However, subaqueous waste disposal can also affect fish habitat and increase the risk of interaction between the waste material and aquatic organisms, all in the name of reducing overall impact. Some favour isolation in a sterile ecological compartment. Others favour integration into the natural environment, within the "carrying capacity" of that environment. To this list of potential incompatible goals could be added the inherent conflict between initiatives to reduce water use and the use of performance indicators such as concentration limits and end-of-pipe toxicity criteria. A compromise between these polar positions is routinely needed to advance the licensing process.

Application point for environmental performance standards. During operations, effluents must meet chemical performance standards that represent a compromise between what is achievable, size of the negotiated "mixing zone", cost, and environmental consequence. Upon decommissioning, the reference point and performance standard must be redefined. There is clear expectation that the environmental loadings from a facility should be less upon close-out than those accepted during operation. In Canada, surface water quality objectives have been established, typically based on such concepts as lowest observable effect concentration. The location at which the performance of the facility will be judged against either current or future surface water quality objectives can have pronounced effect on the scope of decommissioning. For example, simple accumulations of surface deposited piles of sub-economic grades of waste rock (typically 300–500 μg U/g in Saskatchewan) are unlikely to be compatible with surface water quality objectives for most metallic and radiological parameters, if judged at seeps from the toe of the waste rock pile. An impervious cap over the entire pile would be required in this instance. Site-specific negotiation of the location of the performance monitoring stations is a critical component in any decommissioning plan, probably requiring some re-negotiation once actual close-out performance can be measured.

Conservatism in establishing environmental performance standards. One of the federal regulators, Environment Canada, is in the process of assessing radionuclide releases under the Canadian Environmental Protection Act (CEPA). In it's recently published draft assessment report, Environment Canada have proposed that uranium generally, and radionuclides from uranium mines and mills specifically, be considered toxic elements with respect to "non-human biota". As such, they would warrant additional risk assessment to determine if additional controls are necessary. The CEPA process is a structured evaluation process which initially uses "hyperconservative" analysis. As the process evolves, the layers of conservatism are meant to be moderated. We have developed a number of concerns with this methodology:

- The approach of building conservatism upon conservatism in developing criteria puts the industry in a defensive position. One can well imagine how this leads to ever-lower criteria and ever-evolving research programmes;
- It is far from clear what we should be studying and what the criteria should be based on - which trophic level, and at what biological organization level (cellular, individual or population); and
- By starting with ultra-conservatism, one can easily be convinced to retain multiple margins of safety, following the "precautionary principle" promoted by some.

The approach being taken to assess radionuclides is being used elsewhere. In 1997, the Canadian Water Quality Guideline to protect freshwater life from arsenic was lowered from 50 to 5 μg/L. Arsenic toxicity data were found for 21 species of fish, 14 species of invertebrates and 14 species of plants. The most sensitive organism tested was described in a 1980 study of phytoplankton which showed 14-d EC-50 (growth) values of 0.05–30.76 mg/L for As (V). EC-50 refers to the concentration which produced 50% of the control response, as measured by chlorophyll-a concentration. The lower bound value was multiplied by a safety factor of 0.1, generating the new objective of 5 μg/L. This is likely too conservative for most applications, yet generates an onus to prove that this factor of safety is not needed, rather than an onus to prove that this level of conservatism is in fact needed.

Balanced regulation of non-radiological parameters. In many countries, Canada included, specialized regulatory agencies, or departments of more general environmental agencies are established to oversee nuclear facilities. The required expertise in these matters formed the basis for this regulatory specialization, and is both a strength of the system and a potential weakness in regulating the non-radiological aspects of the operation. For example, it is now quite apparent that arsenic and nickel control rather than uranium and radium control will be the main driver in decommissioning planning for the Key Lake Operation. It is important that the level of control afforded nickel at Key Lake is compatible with that applied to a nickel mine elsewhere in the country. The use of 10,000 year modelling by nuclear regulators versus simpler performance criteria in conventional mining is a good example of different approaches to a common issue.

Impact assessment of decommissioning works. Experience has shown that the process of disturbing identified problem areas in a reclamation programme (excavation, recontouring) can have significant short- to mid-term impacts on environmental performance. These short-term negatives must be weighed against potential longer-term benefits.

Forward-looking regulatory approval process. Canada has produced an effective, thorough environmental assessment and licensing process for uranium developments. As time goes on, there is undoubtedly merit in judging modifications to a project against original predictions. However, there must be room to evolve within this regulatory environment in an efficient manner. Only significant modifications should warrant detailed examination and comparison to past assessment/licensing decisions to generate a time-efficient regulatory process.

As we look into the future, we expect that we will eventually develop consensus on the ecological assessments for major contaminants of concerns like arsenic, nickel, Ra-226 and uranium. We will also complete study on the next tier of contaminants of concern, which currently include molybdenum and selenium. Finally, the focus will likely shift to the impact of relatively benign constituents of effluent, specifically, the principle components of total dissolved solids loading. Mill effluents are at, or close to, being saturated gypsum solutions. Total dissolved solids levels are typically about 3000 mg/L with the major ions being SO_4 and Ca along with some Na, Mg, K and Cl in that order. We expect to eventually be asked to study this impact on the aquatic environment, as a precursor to discussions on the pros and cons and technical feasibility of lower TDS levels.

One comes to the conclusion that any enterprise, if studied in sufficient detail, will demonstrate some level of impact identification. In dealing with these issues, the question correctly becomes one of balancing the costs of studies and the costs and benefits of potential solutions against the relative degree of environmental risk. What seems lacking at this point is an effective cost-benefit methodology.

There is much left to study and undoubtedly we are further along the path of sustainable mine development as a result of these efforts.

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Study on the technology for the development of macroporous resin adsorption for high purification of uranium effluent

Zhang Jianguo, Chen Shaoqiang, Qi Jing, Rao Song

Beijing Research Institute of Chemical Engineering and Metallurgy,
Beijing, China

Abstract. Evaluating macropore resins for high purification of uranium effluent from uranium mines and mills is presented in this paper. Compared with the currently used 201 × 7 strong base anion ion exchange resin, macropore resin TS-25 and medium pore resins D263B show better adsorption properties. Adsorption rate is fast (Macropore>Medium>Gel-type). In acidic medium when adsorption reaches equilibrium, the uranium total distribution coefficient of TS-25, D263, 201 × 7 and hydroxyoxime resin is 6.33×10^3, 2.78×10^3, 1.42×10^3, 2.1×10^2 respectively. TS-25 resin, D263 resin, D263B resin and 201×7 resin can be used in a wide pH range from 1.8 to 10, but hydroxyoxime resin can only be used in weak alkali or alkaline solution. When the concentration of uranium in effluent is between 5.4~11.2 mg/l and the contact time is between 2~5 minute, breakthrough point of TS-25 resin and D263B resin is 2000~2500 and 250~500 bed volume number respectively while saturation bed volume number is 4000~7600 and 1100~2700 respectively. The D263B resin shows a better improvement in operation properties for dilute uranium solution. It also shows the best elution properties among the four resins tested. TS-25 resin shows a good adsorption property.

1. Introduction

Ion exchange, using solid resins, is one of the best methods to reduce heavy metal concentration in waste streams to levels meeting the every day stringent regulatory requirements for the disposal of wastewater and for environmental protection.

There are significant number of electroplating, mining and other industries that produce large volume of liquid waste containing heavy metals. In some instances, these waste effluents are discharged to river streams or to the ocean with no control. Frequently, these waste streams are diluted to meet regulations, which requires a substantial increase in water consumption. On the contrary, these liquid wastes may be treated by ion exchange in order to remove heavy metals allowing treated water to be recycled [1, 2].

A large number of ion exchange plants are now in operation in various parts of the world. Interest in treating effluents, uranium leach liquors and uranium bearing mine waters for example is becoming widespread, so any possible improvements in equipment and technology are worthwhile.

Ion exchange techniques have been successfully used in the uranium industry in China. Uranium is leached from ores and leach liquors are absorbed by ion exchange resins to concentrate and purify uranium. In the earliest uranium plants, concentration and purification of solutions was achieved by selective adsorption of uranium by an ion exchange resin in fixed-bed columns. The development of the continuous ion exchange system has been a big breakthrough in uranium extraction technology. This is particularly important for unclarified leach liquors and when large volumes of solutions with low uranium concentration are to be treated. The fluidized bed technique has been studied and applied in the uranium industry from 1970 and now research and application of the densely packed-moving bed techniques in uranium industry are in progress.

Ion exchange has been used to recovery uranium from mine water in China, beginning in the late seventies. Type 201×7 resin has been used since then, and fixed bed and fluidized bed techniques are all in use now. They have made significant contributions to processing a large volume of uranium bearing water. Some problems still exist from discharged tailing waters. This current project can solve some of these problems and purify uranium effluent to meet more stringent regulation of environmental requirements.

As part of the development of equipment and innovative technology for the process flow-sheet, study on the preparation and selection of good resin for uranium processing is ongoing. The objective of our work in this section is to select a good resin to recover uranium while purifying mine water to meet regulatory requirements and generally develop the technology. The discharge standards for effluents in the uranium industry to protect the environment in China are shown in Table 1.

Table I. The discharge standard of the liquid effluent from uranium industry [3]

Element	U	Th	Ra^{226}	Pb	Hg	Cd	Cr	As	Cu	Zn	Mo	Ni	F	PH
Standard, mg/l	0.05	0.1	1.11 Bq/l	0.1	0.05	0.1	0.05	0.5	0.1	1.0	0.5	0.5	10	6.5-8.5

2. Experiments

2.1. Equipment and chemicals

Equipment:

1) Ion exchange column	3 pcs
2) Automatic sampling collector	2 pcs
3) HL-2 Peristaltic pump	3 pcs
4) pHS-3C acidimeter	1 pc
5) Thermostatic shaker	1 pc

Chemicals:

1) CaO	C.P (Chemical Grade)
2) NaOH	C.P
3) H_2SO_4	C.P
4) $(NH_4)_2SO_4$	C.P
5) Ion exchange resin	

The type and properties of resins used in this work are shown in Table 2.

Table II. The properties of ion exchange resins

Type	TS-25 resin	201×7 resin	D263 resin	Hydroxyoxime resin
Skeleton	Styrene-divinylbenzene	Styrene-divinylbenzene	Styrene-divinylbenzene	
Pore size	Macropore	Gel-type	Medium pore	Macropore
Group	$-^{+}N(CH_3)_2OH^-$ $-N(CH_3)_2$	$-N^+(CH_3)_3Cl^-$	$-N^+(CH_3)_3Cl^-$	$-P-NHOH$ $\diagdown NH_2$
Mechanical strength	95%	> 98 %	>98 %	
Granular size	0.55mm	0.6~1.2 mm	0.6~1.2 mm	0.35~1.0 mm
Water content	~65%	40~50 %	50~55%	56%
Bulk Density, g/ml	0.73	0.725	0.72	0.72
Total exchange capacity milli-equivalent/g (dry)	5.5	3	3.8	4.0

2.2. Adsorption solution

The adsorption solution is shown in Table 3.

Table III. The composition of adsorption solution

U mg/l	F^- mg/l	SO^{2-}_4 mg/l	Mg^{2+} mg/l	Ca^{2+} mg/l	Na^+ mg/l	pH
11.2	81.0	3120.0	182.0	600.0	780.0	1.84

2.3. Experimental methods

Experiments on adsorption equilibrium; effect of acidity on adsorption and measurement of adsorption kinetics etc. were carried out in static adsorption conditions in a thermostatic shaker. The adsorption equilibrium experiment was carried out by varying the ratio of resin and adsorption solution. Different pH adsorption solutions were prepared by addition of sulphuric acid or sodium hydroxide.

Resin adsorption and elution tests were carried out in a glass column with fibre on top and bottom. Adsorption solution flowed through the column from bottom to top and elution solution flowed through the column from top to bottom by pump. Breakthrough point was defined as 0.05 mg uranium per litre in column effluent. Saturation point is the point at which outlet solution concentration equals the inlet solution concentration.

3. Results and discussion

3.1. pH influence on adsorption of uranium

In uranium extraction by ion exchange, there are many factors that influences the resin adsorption, such as the composition of the solution, uranium concentration, solution pH, impurities, temperature. The pH is a very important factor in the adsorption process. Therefore, study of pH influence on adsorption of uranium by different resins was carried out firstly by contacting one-gram resin (wet) with100 ml uranium effluent for 6 hours. The results are shown in Table 4 and Figure 1.

Table IV. pH influence on adsorption of uranium by difference resin

	pH	2.01	5.03	7.00	8.52	10.55
D263, after adsorption	U in solution, mg/l	0.456	0.477	0.394	0.207	0.249
	U in resin, mg/l	2.191	2.187	2.204	2.240	2.232
201 × 7, after adsorption	U in solution, mg/l	0.394	0.332	0.498	0.270	0.187
	U in resin, mg/l	1.845	1.855	1.828	1.865	1.878
TS-25 after adsorption	U in solution, mg/l	0.270	0.124	0.124	0.124	0.187
	U in resin, mg/l	2.834	2.870	2.870	2.870	2.855
Hydroxyoxime resin, adsorbed	U in solution, mg/l	4.540	1.200	0.270	0.187	0.187
	U in resin, mg/l	1.677	2.458	2.675	2.695	2.695

It can bee seen from Table 4 and Figure 1 that pH has a great influence on resin adsorption properties.

In summary:

- D263 resin, 201×7 resin and TS-25 resin can adsorb uranium at all pH values; but the hydroxyoxime resin only adsorbs uranium in weak alkali or alkali-solution;
- Among the four kinds of carefully chosen resin for the experiment, TS-25 resin shows the best adsorption property in acidic, weak acidic and alkali solution;
- The higher pH value favours uranium adsorption.

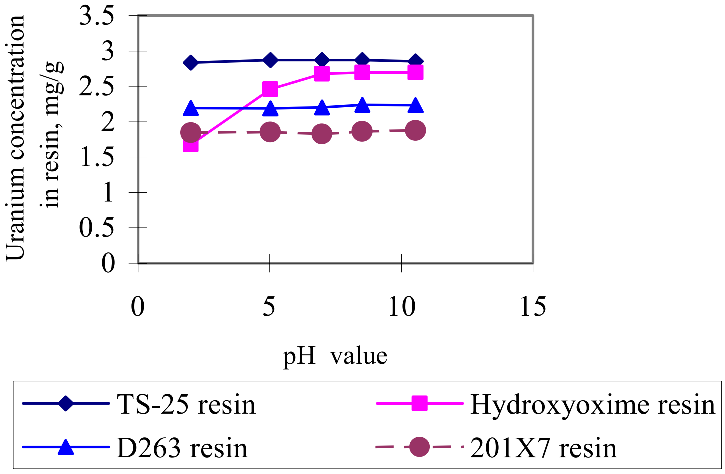

FIG. 1. pH influence on the adsorption of uranium by different resins.

3.2. Ion exchange adsorption equilibrium

When anion ion exchange resin is used to adsorb uranium from the uranyl sulphate solution at pH<2, two kinds of complexes $UO_2(SO_4)_2^{2-}$, $UO_2(SO_4)_3^{4-}$ are adsorbed on the resin as well as

HSO_4^- and SO_4^{2-} ions. Under this condition, there exists the following equilibrium between resin and adsorption solution [4].

$$R_2SO_4 + 2HSO_4^- \quad = \quad 2RHSO_4 + SO_4^{2-} \qquad (1)$$

$$R_2SO_4 + UO_2(SO_4)_2^{2-} \quad = \quad R_2UO_2(SO_4)_2 + SO_4^{2-} \qquad (2)$$

$$2R_2SO_4 + UO_2(SO_4)_3^{4-} \quad = \quad R_4UO_2(SO_4)_3 + 2SO_4^{2-} \qquad (3)$$

When ion exchange reaches equilibrium, the adsorption contents of HSO_4^-, SO_4^{2-}, $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ on the resin depend on the composition of the adsorbed solution. The total distribution coefficient is employed to express the equilibrium results of uranium adsorbed on the resin, i.e. the ratio of uranium concentration on the resin to uranium concentration in the adsorbed solution when adsorption research the equilibrium.

$$K_{D,total} = \frac{\sum \overline{C_u}(resin\ phase)}{\sum C_u\ (liquid\ phase)} \qquad (4)$$

The experiment results are shown in Table 5, which show that the relative total distribution coefficient is TS-25 resin > D263 resin > 201×7 resin > hydroxyoxime resin. The adsorption capacity sequence in acidic solution is therefore TS-25 resin > D263 resin > 201×7 resin > hydroxyoxime resin.

Table V. The equilibrium test results

Test conditions: 100 ml effluent, U=11.2 mg/l, pH =1.84, 96 hours contact time. All resin in SO_4^{2-}.

	Resin quantity, mg	10	20	30	60	120	200	300
D263	U in solution, mg/l	9.80	9.10	8.50	6.90	6.39	4.09	3.48
	U in resin, mg/g	27.24	20.42	17.73	13.96	7.80	6.92	5.0
	Distribution Kd	2.78×10^3	2.25×10^3	2.06×10^3	2.02×10^3	1.22×10^3	1.69×10^3	1.44×10^3
201×7	U in solution, mg/l	10.3	8.19	7.98	6.74	4.48	3.57	2.84
	U in resin, mg/g	14.66	24.51	17.48	12.11	9.12	6.21	4.54
	Distribution Kd	1.42×10^3	2.99×10^3	2.19×10^3	1.80×10^3	2.0×10^3	1.74×10^3	1.6×10^3
TS-25	U in solution, mg/l	8.92	7.83	6.69	4.98	3.53	1.06	0.975
	U in resin, mg/g	56.436	41.709	37.21	25.66	15.821	12.55	8.436
	Distribution Kd	6.33×10^3	5.33×10^3	5.56×10^3	5.15×10^3	4.48×10^3	1.18×10^4	8.65×10^3
Hydro-xyoxime	U in solution, mg/l	11.1	11.0	10.9	10.9	10.7	10.3	10.2
	U in resin, mg/g	2.376	2.336	2.336	1.168	0.974	1.051	0.779
	Distribution Kd	2.1×10^2	2.12×10^2	2.14×10^2	1.07×10^2	9.1×10^{-1}	1.02×10^2	1.64×10^1

3.3. Adsorption dynamics experiment

Normally, a good resin not only has a large capacity, but also has a fast adsorption speed. In practice, such a resin has a lower inventory with high operation performance. Thus the operating costs will be lower. To obtain enough data to evaluate the resin operation properties, the adsorption dynamics experiment was done. The results are shown in Figure 2.

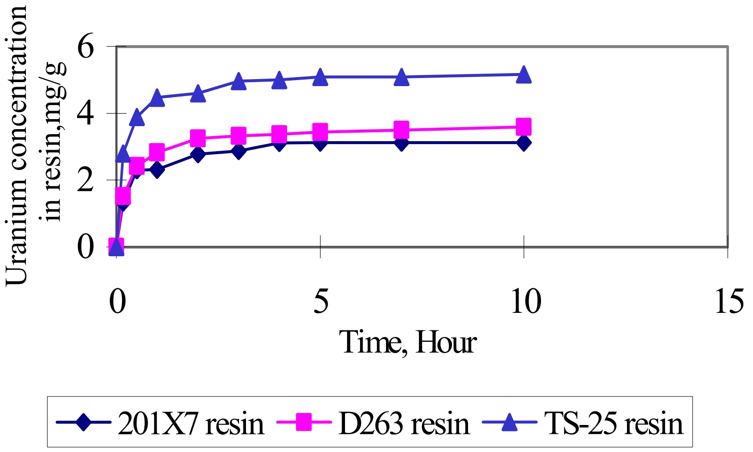

FIG. 2. Adsorption kinetics.

Figure 2 shows that in about three hours, all three kinds of resin reach their adsorption equilibrium points. As time goes on, there is little increase to their capacity. Macropore TS-25 resin and medium pore resin D263 have better adsorption dynamics than gel-type 201×7 resin. At the first 10 minutes of adsorption time, adsorption speed is very fast, then it becomes very slow. This suggests that during the first 10 minute, the adsorption mechanism is controlled by particle diffusion, then, it becomes film diffusion controlled. Accordingly, a fluidized bed will be of benefit to the resin adsorption.

3.4. Adsorption saturation curve

The total amount of uranium that may be absorbed is a function of the anionic complex present in solution. For the uranyl anionic complexes, the main interest is the total operation capacity of the resin. So, the performance of the four kinds of resin (TS-25 resin, D263 resin, D263B (an improved version of D263) and 201×7 resin) are evaluated by the adsorption saturation load curve. The results are shown in Figure 3.

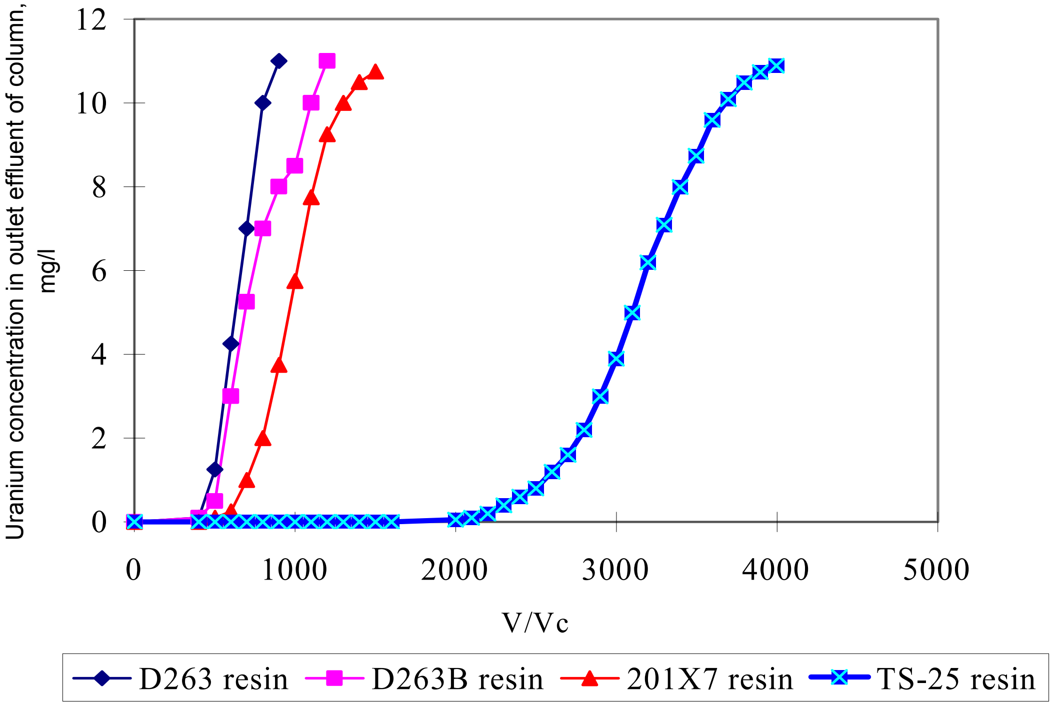

FIG. 3. Adsorption saturation curve. Contact time 5 minute.

From this experiment, the breakthrough point volume of TS-25 resin, D263 resin, D263B and 201×7 resin are 2000, 250, 250 and 450 bed volumes (discharge liquid effluent volume/resin bed volume) respectively. The saturation bed volume numbers for TS-25 resin, D263 resin and 201×7 resin are 4000, 920, 1100 and 1550 respectively. The resin saturation capacity values are shown in Table 6.

Table VI. Resin saturation capacity

201×7 resin	D263 resin	D263B resin	TS-25 resin
26.9mg/g	20.0mg/g	23.2mg/g	117.1mg/g

3.5. Elution results

The elution agent 1mol/l H_2SO_4 +1.5 mol/l $(NH_4)_2SO_4$ was used. Saturated resin (all 10 ml) was prepared in the experiments described above. Liquid flows were from top to bottom by peristaltic pump. The contacted time are 24 minutes. The results are shown in Figure 4.

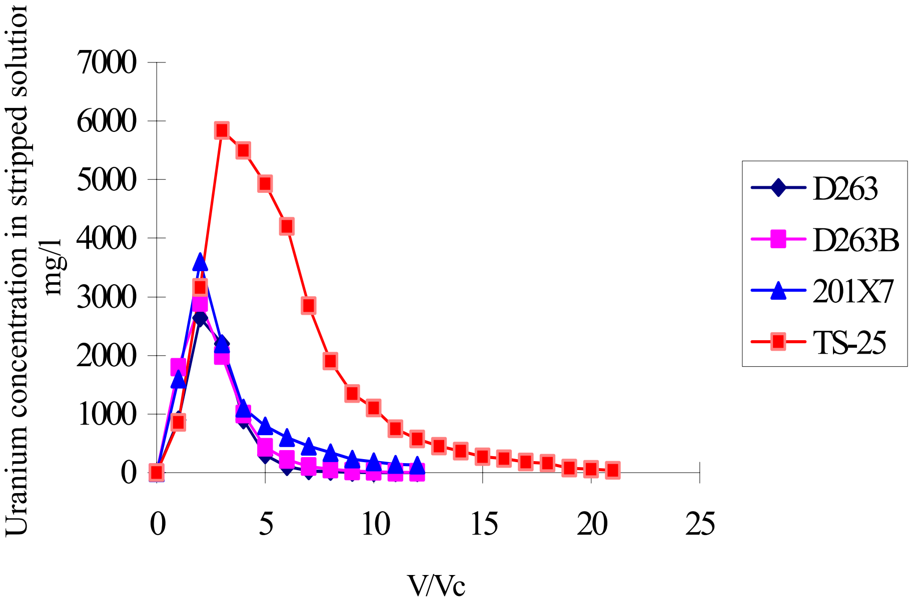

FIG. 4. Stripping curve.

This experiment indicates that:

- D263 and D263B resin have the best elution properties of the four resins tested;
- A very good pregnant uranium solution was obtained from eluting TS-25 resin;
- The elution reagent was not optimized. This is because of two factors. One is the need to avoid introduction of other ions such as Cl^- by the elution reagent, and the other is the fact that the better intense fraction process [5] will be employed in this step, which would generate much better results.

3.6. Influence of uranium concentration in effluent and contact time on the adsorption property

Uranium concentration of the effluent has a great influence on resin adsorption. Generally, resin capacity is proportional to concentration of the adsorption solution. Also, the contact time is a very important variable in the resin adsorption practice. This is especially true for column operation. Therefore, proper contact time is necessary to achieve effective adsorption. Also, the lower the contact time, the better the operational performance of the resin provided it does not affect the resin loading capacity. In this section, the effect of the concentration of uranium and contact time influence on resin adsorption was examined by column operation.

Former experiments were carried out using a uranium concentration of 11.2 mg/l and contact time that was 5 minute. In this experiment, the uranium concentration was 5.4 mg/l and contact time was 2 minute. The other conditions are as before. The adsorption results and the loaded resin elution results are shown in Figures 5 and 6 respectively.

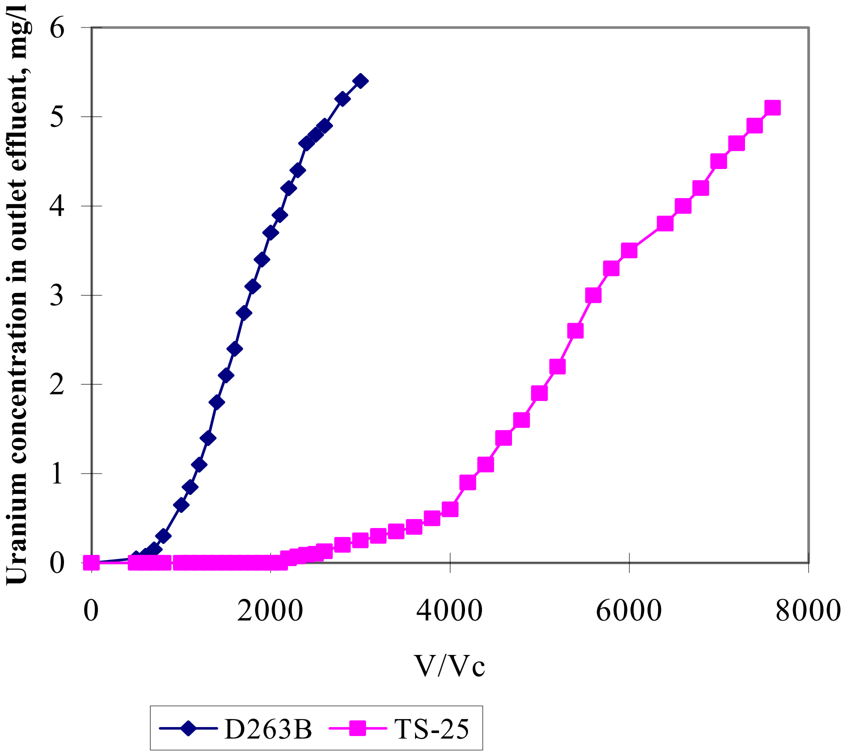

FIG. 5. Adsorption saturation curve. U=5.4mg/l, contact time 2 minutes.

As shown in Figure 5, under diluted uranium concentration, a 2-minute contact time can generate good adsorption results. The breakthrough point of D263B resin and TS-25 resin were 500 and 2300 bed volume number respectively. Saturation bed volume numbers were 2700 and 7600 respectively. The uranium saturation capacity of D263B and TS-25 resin are about 30 mg U/g, R(dried) and 98 mg U/g, R(dried) respectively. Figure 6 shows that a good elution is also achieved. Compared with the 5-minute contact test, this indicates that these two kinds of resin have good operational properties, which can be used to recover uranium from discharged effluent and mining water. Furthermore, D263B resin shows better operational properties in dilute solution than in higher uranium solution. It is common that uranium concentration in mining water is about 2 mg/l. Consequently by using D263B and TS-25 resin adsorption with 2-minute contact time, good adsorption results will be achieved.

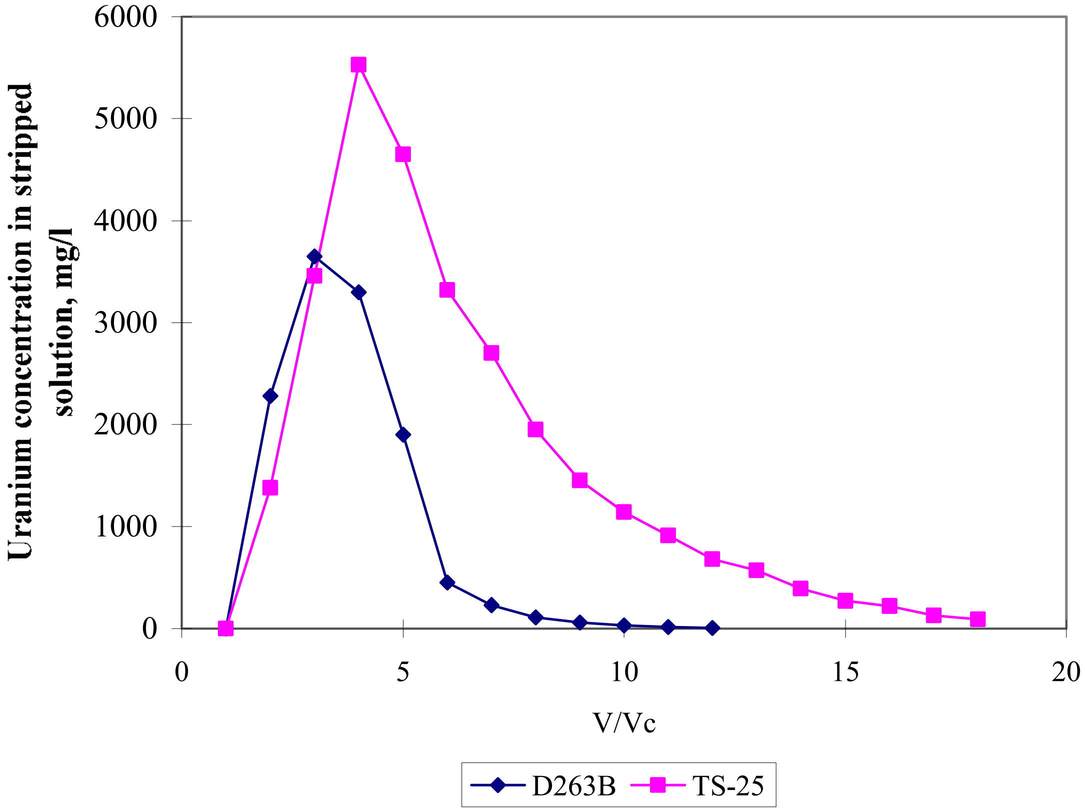

FIG. 6. Stripping curve.

3.7. Bench test

Based on the earlier experiments, a bench test was carried out with 200 ml volume of D263B resin packed in a column, processing 540 liter of uranium effluent that contains 6.5 mg/l uranium. The average contact time is 3 minute. The other operating conditions are as used in previous experiments. The adsorption result is shown in Figure 7. The test indicates that the breakthrough point is 510-bed volume number and saturation capacity of the resin is 27.57 mg U/g, R(dried). This is in agreement with the former experiments.

3.8. Elution technology

There are many research investigations and reports about stripping uranium from uranyl sulphate solution-saturated resin. The most commonly used stripping agents are chloride, nitrate, dilute sulphuric acid (or addition sulphate) and carbonate. When chloride and nitrate is used to strip uranium from loaded resin, the resin is converted to Cl^- or NO_3^- type. After the elution, resin is transferred back to the adsorption phase and in the next adsorption, the Cl^- or NO_3 will be passed back into barren solution. When discharged, the ions can cause environment pollution. If the barren solution is directed back to the leach section, a lot of Cl^- and NO_3^- ions will accumulate in the leached liquor. This sort of leach liquor will greatly reduce the resin loading capacity in the adsorption process. When sulphuric acid and sulphate is used as the elution agent to strip uranium from loaded resin, the adsorbed solution can be recycled totally to the leach process. The intense fractional process can be used in this elution system to improve the stripping efficiency. The intense fraction process is carried out in a fixed-bed column. In this process, the loaded resin is contacted with eluents containing different uranium contents, from higher to lower in the last elution process, and additional new eluent is added when necessary. With this technology, a very high pregnant solution concentration is achieved compared with the conventional stripping process. This is very effective in treatment of the lower loading uranium resin obtained by ion exchange recovery of uranium from uranium effluent and mining water. The elution agent was 1 mol/l H_2SO_4 + 1.5 mol/l $(NH_4)_2SO_4$. The elution contact time was 24 minute. The results are shown in Figure 8 and Table 7.

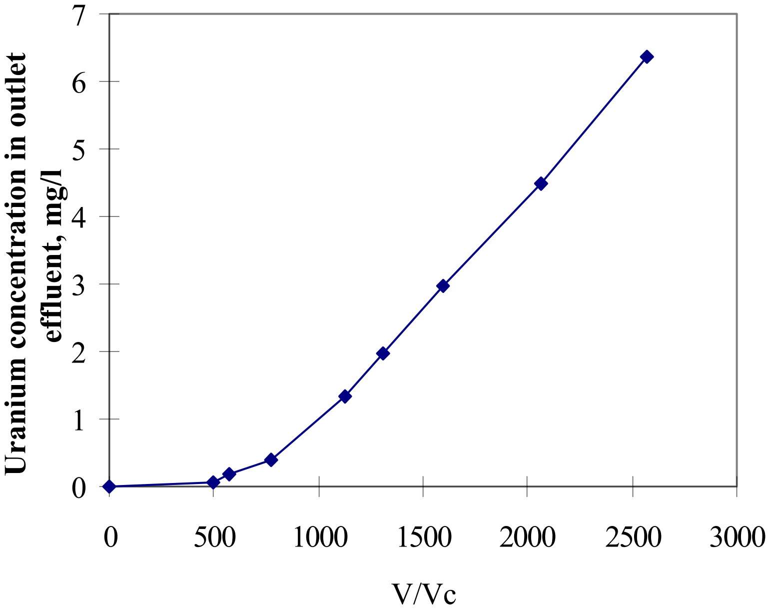

FIG. 7. Bench test adsorption curve for D263B resin.

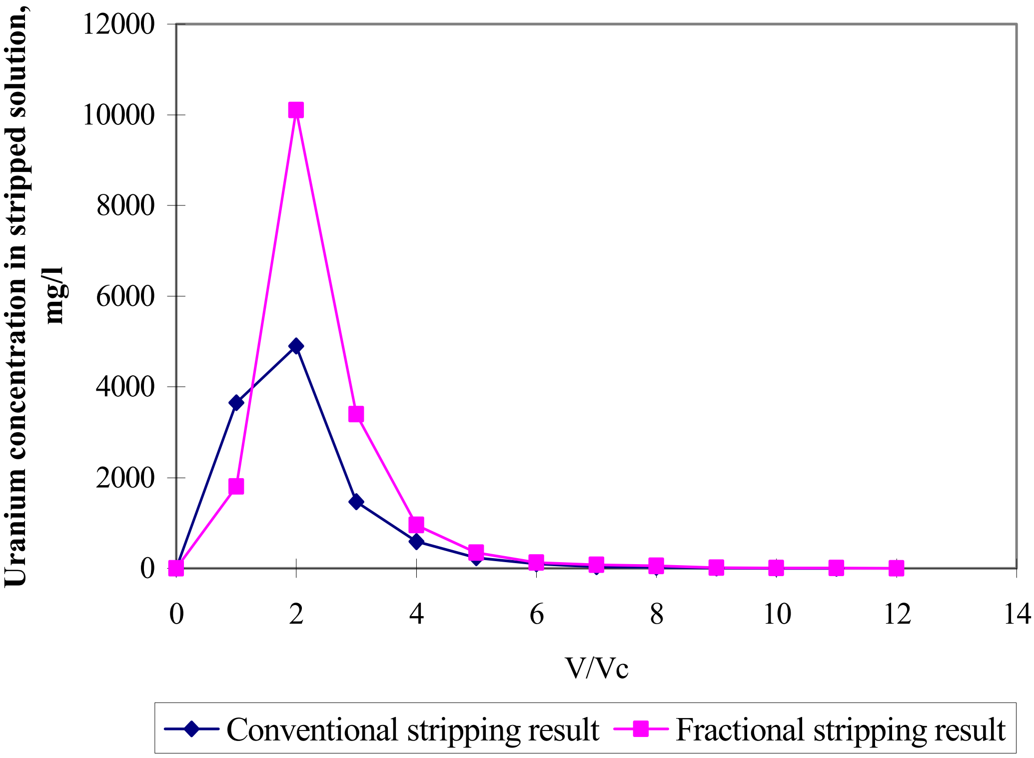

FIG. 8. Intense fractional process stripping results.

Table VII. Intense fractional process stripping results with conventional stripping results

Elution methods	Eluent's acidity	Elution peak BV*	[U], g/l	Elution termination [U], mg/l	Total elution BV*	Eluted resin [U], mg/g, R	Pregnant liquor BV*	[U], mg/l
Conventional elution	2.1 N	1	4.9	1.90	11	0.2	2	4.27
Intense fractional process	2.1 N	1	10.10	2.97	12	0.2	1	10.10

* Bed volume

It can be seen from Figure 8 and Table 6 that by using the intense fractional process, the elution peak uranium concentration is much higher than that of the conventional elution process and the pregnant liquor volume is half that of the conventional elution process. When elution termination uranium concentration is about 5-mg/l uranium, the elution bed volume is about equal in both process. This result indicates that the intense fractional process is very effective.

In these experiments eight time recycling was carried out. The system reached equilibrium in the fourth recycle. The later five-recycle experimental results are shown in Table 8.

Table VIII. Results of the intense fractional process, effluent acidity 2.10 N

Recycle Time	Stripping peak liquor			Eluted Resin		End [U] mg/l	Recycle BV*	New eluent BV*	Total elution BV*
	BV*	[U] g/l	$[H_2SO_4]$ g/l	[U] mg/g, R	Elution efficiency, %				
4	1.0	10.1	74.9	0.2	99.27	2.97	7.37	4.63	12
5	1.0	8.25	52.1	0.2	99.27	2.75	8.22	3.78	12
6	1.0	8.75	96.0	0.2	99.27	4.38	8.38	3.62	12
7	1.0	10.1	50.4	0.2	99.27	3.82	9.15	3.85	13
8	1.0	8.75	75.6	0.2	99.27	2.49	9.10	3.90	13
average	1.0	9.19	69.8	0.2	99.27	3.28	8.44	3.96	12.4

*Bed volume

It is indicated by Table 8 that the average pregnant liquor uranium concentration was 9.19 g/l when stripping peak liquor bed volume was 1.0. Average total elution bed volume was 12.4 which is about equal the conventional stripping process. The elution efficiency was 99.27%. In the end, the compositions of elution liquor in 8th recycle time of different bed volume are shown in Table 9.

It can be seen from Tables 8 and 9 that acidity is lower in the stripping peak liquor. After the peak liquor bed volume, the acidity is basically stable in 3~13 bed volume. This is beneficial for maintaining high intense fractional process efficiency as well as for recovering uranium in the later precipitation process. The sulphate ion has some accumulation in the process that did not influence the stripping efficiency.

Table IX. The compositions of elution liquor in 8th recycle

Bed volume Number	[H_2SO_4] g/l	[U] mg/l	[SO_4^{2-}] g/l
1	34.3	2300	146.4
2	84.3	8750	213.6
3	101.9	4600	237.6
4	104.8	2000	242.4
5	102.9	950	242.4
6	102.9	414	242.4
7	102.9	240	238.8
8	101.4	112.9	236.4
9	101.4	59.3	235.2
10	104.4	18.7	232.8
11	103.9	12.4	236.4
12	102.9	5.81	240.5
13	101.4	2.49	240.0

In general, the intense fractional process can be employed to strip uranium from the lower loading uranium resin, which achieves higher pregnant elution liquor. The pregnant liquor is reduced to one bed volume, and uranium concentration is increased two times. Over 50% of the eluent agent is saved compared with the conventional stripping process. This is also beneficial in the following neutralization process in uranium precipitation. So, when ion exchange resin is used to purify uranium effluent, the intense fractional process is a better and very effective way to recovery uranium.

4. Conclusions

From the study on the adsorption and elution property of four kind resins, the following points can be made:

- Acidity of adsorption solution has a great influence on resin adsorption of uranium. TS-25 resin, D263 resin, D263B resin and 201×7 resin can be used in a wide pH range from 1.8 to 10.But hydroxyoxime resin can only be used in weak alkali or alkaline solution. The higher the pH value, the better the adsorption.
- In acidic medium when adsorption reaches equilibrium, the uranium total distribution coefficient of TS-25, D263, 201×7 and hydroxyoxime resin is 6.33×10^3, 2.78×10^3, 1.42×10^3, and 2.1×10^2 respectively. The resin adsorption capacity sequence is TS-25 resin > D263B resin > 201×7 resin.
- Adsorption dynamics experiments show that TS-25 resin and D263 resin have good adsorption properties. Adsorption rate is very fast (macropore> medium pore> Gel-type). The adsorption mechanism in the beginning is controlled by particle diffusion and later becomes film diffusion limited.
- Breakthrough point volume of TS-25 resin and D263B resin are 2000~2500, and 250~500 bed volume number (liquid effluent volume/resin bed volume) respectively when uranium is between 11.2 mg/l and 5.4 mg/l and the contact time between 5 and 2 minute. The saturation bed volume number of TS-25 resin and D263B resin is 4000~7600 and 1100~2700, respectively. But the D263B resin shows a better improvement in operating properties for dilute uranium solutions.

- Of the four kind of resins tested, D263B resin shows the best elution property under the experiment conditions. The intense fractional process is very effective for stripping uranium from the lower loading uranium resin. The pregnant liquor is reduced to one bed volume, and the uranium concentration is increased two times. Over 50% of the eluent agent is saved compared with the conventional stripping process.

So, in general, macropore resin TS-25 and medium pore resin D263B show better adsorption properties compared with 201×7 resin. In practice, the mining water normally contains about 2 mg/l uranium and process water contains about 5 mg/l uranium. TS-25 and D263B resin can be used to adsorb uranium for purifying these effluents. In decommissioned uranium mines and mills areas, D263B resin is a good choice because it not only shows better adsorption property, but also shows the best stripping property. With the intense fractional process, D263B can effectively recovery uranium from very dilute uranium effluent.

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Barium chloride precipitation-sludge recycle to treat acidic uranium industrial effluent

Zhang Jianguo, Chen Shaoqing, Rao Sun, Qi Jing

Beijing Research Institute of Chemical Engineering and Metallurgy,
Beijing, China

Abstract. Barium chloride precipitation and sludge recycle to treat acidic uranium industrial liquid waste is described in this paper. It is found that the barium chloride precipitation sludge recycle method to process acidic uranium effluent can save reagent exceeding 10% and improve the sludge precipitation property.

1. Introduction

There are many reports about the application of the barium chloride precipitation process to treat acidic uranium industrial effluent. It is one of the classical methods to treat uranium effluent and is used extensively in uranium industry [1].

The principle of this method takes the use of sulphate ions in liquid effluent, with the addition of barium chloride to form barium sulphate precipitate, then the radium provides isomorphous replacement with the $BaSO_4$ to form co-precipitation $Ba(Ra)SO_4$ [2]. The natural radionuclides uranium, thorium, in effluents was reduced to discharge standards by adjusting the effluent pH by lime milk. In this operation the manganese and magnesium etc. cations also form flocculent deposits. It takes the action of flocculation and carriage roles for $Ba(Ra)SO_4$ precipitation. This accelerates the precipitation process. The barium chloride method is easily operated and has good results to remove the radium. The disadvantage of this method is higher water content in sludge and difficulty to compress the sludge. Settling rates are lower and normally needed large settling cells.

The recent research reports about barium chloride treatment are concentrated on its application and improvement of the technology. The sludge recycle of barium chloride precipitation shows some development. It saves reagent costs and produces less sludge, and improving the sludge precipitation and filtration properties [3]. There are also reports about improvement of the sludge deposit properties by adding flocculant in the treatment process to haste the precipitation rate and increase the process capacity of deposit cells [4]. P.M. Huck et al reported that a new process for treating uranium mining effluent was developed [5]. It involves the use of a fluidized bed to facilitate $Ba(Ra)SO_4$ co-precipitation on a granular medium of high surface area. No solids separation step is required, as the granular material is free draining. The new process has been demonstrated to provide radium-226 removal efficiencies consistently exceeding 90% in contact times of about 20 seconds. These short times are in contrast to times on the order of days for conventional pond systems or hours for mechanical systems involving stirred tank precipitation reactors.

In this paper, a barium chloride precipitation sludge recycle process to treat the acidic uranium industrial liquid waste is described. It is found that the barium chloride precipitation sludge recycle method to process acidic uranium effluent can save reagent exceeding 10% and improve the sludge precipitation properties.

2. Experiment

2.1. The composition of the effluent

The composition of the effluent is shown as in Table 1.

Table I. Composition of effluent

U	mg/l	5.8	F	mg/l	40
Th	mg/l	1.7	$SO^{2}{}_{-4}$	mg/l	1560
As	mg/l	1.0	Ca^{2+}	mg/l	300
Ra	Bq/l	31	Al^{3+}	mg/l	90
Cd	mg/l	<0.02	SiO_2	mg/l	80
Cr	mg/l	0.05	COD	mg/l	102
Mn	mg/l	41.0	pH		1.54

2.2. Experimental operation

First, the effluent pH is adjusted to 8 by adding 10% w/w lime milk. Then, barium chloride is added and stirred for about 20 minutes. Then, the pH of the effluent is adjusted to 11. After that, clarification takes over one hour. Finally the supernatant solution is taken for analysis of the natural radionuclides and other elements.

2.3. Analysis methods

Uranium measurement:	1)	Normal amount uranium by capillary tube titrimetric method.
	2)	Trace amount uranium by resin separation and luminosity.
Radium measurement:		By radon emanation technique.
Fluorine measurement:		Fluoride ion selective electrode.
Thorium measurement:		TBP eluex resin separation-arsenazo luminosity.

3. Results and discussion

3.1. pH value effects on the purifying treatment

pH value is a very important factor in processing the acidic uranium effluent. So experiments were carried out first with pH effect on the removal of elements from effluent. Taking one litre effluent, the pH is adjusted to different value by lime milk. Then clarification is over one hour. The result is shown in Table 2.

Table II. pH effects on the removal of natural radionulides and other harmful elements from acidic uranium effluent

PH	2.63	5.25	6.05	7.64	8.60	8.93	9.02	9.84	10.01	10.40	11.03	11.83
U, mg/l	4.91	0.93	0.51	0.367	0.327	0.314	0.293	0.119	0.059	0.039	0.05	0.053
Th, mg/l	0.3	0.02	0.01	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ra, Bq/l	30	23	19	10	8.0	9.0	7.0	8.0	7.0	8.0	.0	10.0
F, mg/l	25	20	15	5.0	4.75	5.0	3.5	3.5	3.5	3.0	3.5	3.0
Cr, mg/l	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
As, mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mn, mg/l	2.0	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

The results indicated that the pH has a great influence on processing acidic uranium effluent. When the effluent pH is adjusted to 7~8, the non-radioelements can meet the required discharge standards. Fluoride concentration in pH adjusted effluent reaches the industrial effluent discharge standards. As pH increase, the fluoride content is maintained at about 3 mg/l. If the content of fluoride would be farther reduced, aluminum sulphate must be added in the process. The natural long life radionuclide thorium can easily be removed from the effluent and uranium can meet the discharge standards at pH over 10.40. Radium content exceeds the discharge standards.

3.2. The relationship of CaO consumption with pH and sludge production

Disposal and management of the processed uranium effluent sludge is very important to environmental protection because it contains long life radionuliclides. So, sludge production is as low as possible in order to reduce solid waste pollution to the environment. The experimental result for a 1 litre sample are shown in Table 3.

Table III. Relationship of CaO consumption with pH and sludge production

PH	2.65	5.25	7.64	8.60	10.0	10.4	11.03	11.86
CaO consumption, g/l	0.65	0.93	1.10	1.15	1.30	1.32	1.40	1.53
Sludge volume, ml	13	35	60	67	94	107	107	130

The sludge volume in Table 3 is the natural deposit volume with 24 hours free precipitation. There is no compression occurring. CaO consumption and sludge volume accrue as the pH increases. pH 11 was selected to process the acidic uranium effluent according to the purifying requirements and the relation between the CaO consumption and sludge volume production.

3.3. Barium chloride content influences on the results of removal of radium

One litre of effluent was measured, its pH adjusted to 8. Different amount barium chloride is added into the effluent. Stirring takes 30 minutes, then the pH is adjusted to about 11 and continue stirring 20 minutes. After classification for one hour, the sample was taken for analysis. The result is shown in Table 4.

Table IV. Barium chloride concentration effect on the removal of radium

$BaCl_2$ consumption mg/l	5.0	8.0	10.0	13.0	15.0	20.0
U, mg/l	0.057	0.039	0.028	0.027	0.044	0.027
Ra, Bq/l	1.0	0.8	0.8	0.3	0.4	0.1
F, mg/l	3.5	3.0	3.0	3.0	2.7	2.7

It is indicated by the result from Table 4 that the barium chloride for removal of radium is very effective under this test condition and reagent consumption is low maybe due to higher content of aluminum and magnesium existing in this effluent. 5 mg barium chloride for one litre liquid effluent can meet the removal of radium requirement to reduce the radium to discharge standards. 10 mg barium chloride would be added as an additional safety factor.

3.4. Stirring time influences on the removal of radium

Other conditions are as described in Section 3, pH 11, 10 mg/l $BaCl_2$. When barium salt is added, after stirring different time, the sample is taken to measure radium in effluent. The results are shown in Table 5.

Table V. Stirring time influence on the removal of radium

Stirring time, minute	Ra content in processed effluent, Bq/l
5	0.13
10	0.21
15	0.26
20	0.25
30	0.11

It can be seen from Table 5 that co-precipitation of radium with barium sulphate is fast. A stirring time is between 20~30 minutes can meet the requirement of removal of radium with a safety factor.

3.5. Sludge recycle experiment

The flowsheet of sludge recycle technique is shown in Figure 1.

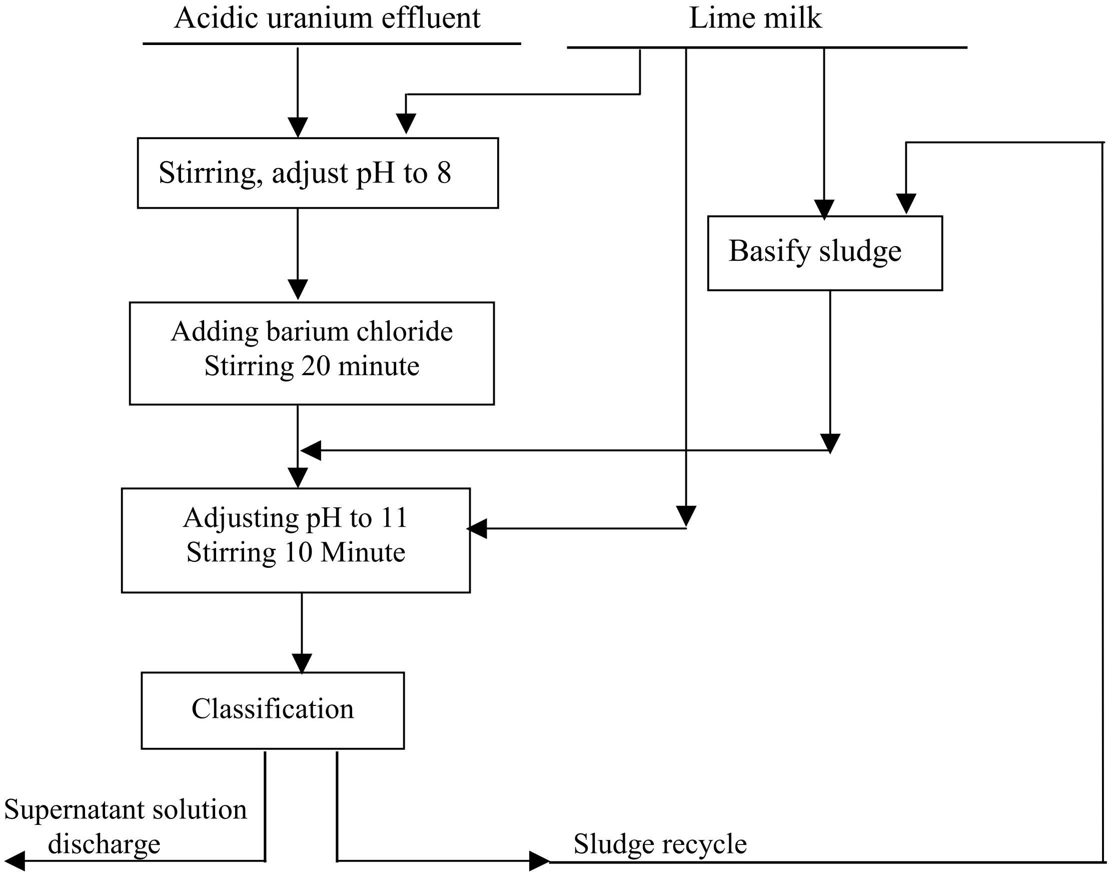

FIG. 1. Sludge recycle diagram.

The effluent pH is adjusted to 8 by lime milk, then barium chloride is added in the process, stirring takes 20 minute. After that, recycle sludge is added in the effluent. Stirring continues. Furthermore, the pH value of the processed effluent is adjusted to 11 by lime milk. After one hour clarification, the supernatant solution is discharged. The most freshly deposited sludge is recycled. By this method the consumption of calcium oxide can save over 10% and the sludge precipitation properties are improved.

3.6. Settling curve

The settling curve for processed effluent is shown on Figure 2. In order to meet the required discharge standard for the uranium waste liquid, one-hour clarification time is necessary to achieve the majority of the settling.

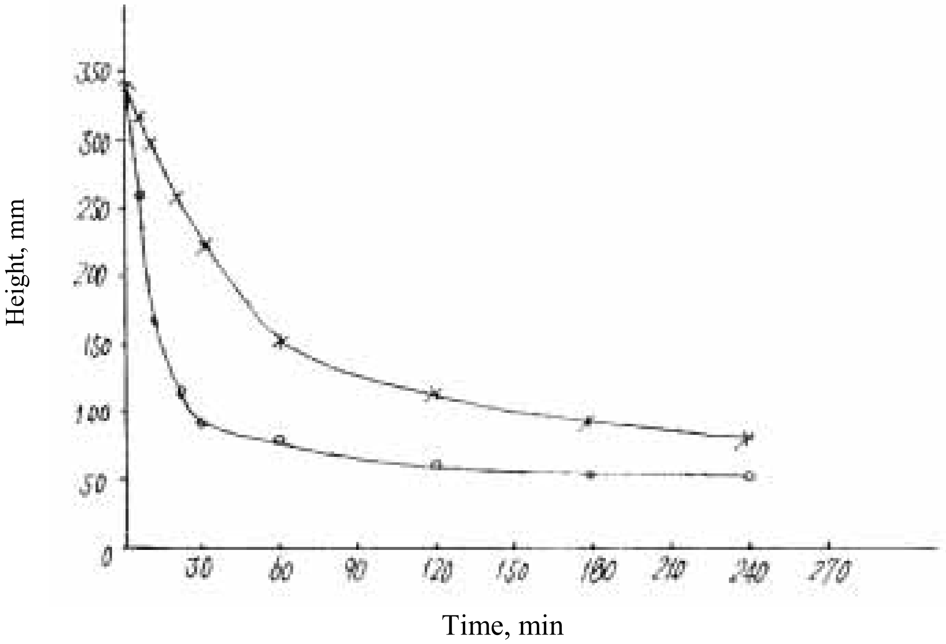

FIG. 2. Settling curve.

4. Conclusions

Barium chloride precipitation-sludge recycling is an effective method for the treatment of acidic uranium effluent to achieve high removal of radium. The sludge precipitation property is improved and this method also saves reagent.

- The acidity is a very important parameter in the neutralization precipitation process for acidic uranium effluent. By control the proper pH value, radionuclides elements uranium and radium as well as other non-radionuclides in the waste liquor can be removed.
- In this experiment, the consumption of barium chloride was determined to be 5 mg/l. But for safety, 10mg/l barium chloride would be recommended. And a stirring time of about 20 minutes would be recommended. Because the barium chloride is expensive, reducing its consumption can save reagent cost.
- The recycling of the sludge can improve the properties of processing acidic uranium effluent. Over 10% of CaO and can be saved by the sludge recycling. The sludge settling properties are improved. It contains little water and is easily compressed.

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Analysis and evaluation of water coming from several uranium processing areas

Zhang Jianguo, Chen Shaoqing, Rao Sun, Qi Jing

Beijing Research Institute of Chemical Engineering and Metallurgy,
Beijing, China

Abstract. Treatment of liquid effluent from uranium mines and mills in China during operation is described in this paper. Analysis and evaluation of water types coming from different sources of polluted areas are also presented in this paper. From this study, several methods for processing liquid effluents were chosen for study to improve current practice. In this work, three uranium mines and mills were carefully chosen for investigation. One is located in the north west of China. The other two are located in the southern part of China.

1. Analysis and evaluation of liquid effluent pollution from Mine 1#

1.1. Introduction

Mine 1# is located in Shannxi Province in the north west of China. The main type of uranium ore exists as uraninite, micro-particle uranium oxide minerals (in pyrite, hematite, clay and fluorite) and dispersed state uranium minerals (in clay, hematite and fluorite). The ore mainly consists of breccia, gangue and disseminated mineralization type. Secondary uranium ore is mainly uranium black, dauberite, zippeite, uranotilite, uranothallite and crandallite.

The mine is located in the continental dry weather zone. Annual rainfall is 525~836 mm, average 681 mm. The water evaporation is greater than the rainfall. The highest temperature is 43.3°C. The average humidity is 68.5%. The mine is in a high mountain area with strong relief. Ground water system is well developed. Three water ravines are through all the mining areas. Underground water is not well developed. The groundwater flow is 0.0001~0.001 l/s.m. The pH is 6~8. The TDS is 0.2~0.5 g/l with HCO_3^- – Ca, Mg, Na.

1.2. Technology flow sheet

Ore → Grinding → Heap leaching → Ion-exchange adsorption → Elution → Precipitation → Product.

The mineral composition is simple with few harmful elements. Leaching is good with low consumption of acid. The ore is well suited for heap leaching. Heap weight of ore is 1843 ton. Original ore grade is 0.369%. The consumption of sulphuric acid is 23.2 kg/t ore. The leaching rate is 95.7% and recovery rate is 93.1%.

1.3. Environmental impacts

The discharged uranium effluent contains natural uranium, ^{226}Ra, ^{210}Po, ^{210}Pb etc. as well as other non–radiative materials which may cause the pollution of natural water system in the long term. Internal radiation danger to inhabitants may be caused by drinking and food, if the effluent is not processed and managed properly.

1.4. Liquid effluent process

There are two sources of liquid effluent from the heap leach process scheme; the barren liquor from ion exchange effluent and the barren precipitation liquor. There is no pit water effluent problem because all the pit water is used to prepare leaching solution. The effluent from ion-exchange section is 15 times greater than the effluent from precipitation section.

Two effluents are combined for treatment by lime neutralization → barium chloride precipitation in one step. The main constituents and concentrations in original effluent and after treatment are shown in Table 1.

Table I. Main constituents and concentration in effluent before and after treatment

Conditions Element	Original effluent, mg/l		Treated effluent, mg/l
	IX Barrens	Precipitation Barrens	
Natural U	10	6.6	<0.05
Natural Th	9.14	<0.1	<0.1
^{226}Ra	80.66Bq/l	1.11Bq/l	<1.11Bq/l
Hg	<0.001	<0.001	--
Cd	<0.01	<0.01	<0.002
As	<0.04	<0.04	<0.04
Pb	<0.10	<0.10	--
Cu	<0.1	<0.1	<0.002
Zn	3.25	<0.1	<0.01
Mn	133~200	0.24	<0.01
F^-	20~70	3.6	<10
Cr	--	--	<0.005
Ni	--	--	<0.04
Mo	--	--	<0.05
pH	1.5~2.0	7~8	8~9

It can be seen from Table 1 that after treatment all nuclides and harmful elements are under the limit concentrations for ground water requirements and meet the industrial effluent discharge standards; U<0.05 mg/l, Th<0.1 mg/l, 226Ra<1.11 Bq/l, F<10 mg/l and other non-radionuclides in the requirements.

1.5. Environment monitoring measurement results of uranium in water system from different pollution area in Mine 1# (Table 2)

Table II. Environment monitoring measurement results of uranium in water system from different points in the polluted area, Unit: g/l

Date	30/01/96	29/02/96	29/03/96	29/04/96	31/05/96	28/06/96	27/07/96
Under Wangchuan bridge	1.17×10^{-6}	3.50×10^{-6}	1.05×10^{-6}	1.57×10^{-7}	9.85×10^{-8}	5.46×10^{-6}	1.04×10^{-6}
Under industrial bridge	4.20×10^{-6}	4.36×10^{-6}	3.03×10^{-6}	5.43×10^{-7}	9.76×10^{-6}	1.27×10^{-5}	1.01×10^{-6}
Yan village	6.7×10^{-6}	4.26×10^{-6}	4.62×10^{-6}	2.30×10^{-6}	1.15×10^{-5}	2.40×10^{-5}	1.43×10^{-5}
Xue village	6.60×10^{-6}	5.21×10^{-6}	7.74×10^{-6}	2.65×10^{-5}	1.27×10^{-5}	2.15×10^{-5}	9.66×10^{-6}
Jiandi Shaku	1.75×10^{-4}	2.42×10^{-4}	1.31×10^{-4}	1.67×10^{-4}	1.69×10^{-4}	2.08×10^{-4}	2.69×10^{-4}
No.1work section boiler house	1.76×10^{-4}	1.86×10^{-4}	1.33×10^{-4}	2.03×10^{-4}	2.08×10^{-4}	1.62×10^{-4}	4.38×10^{-4}

Date	30/01/96	29/02/96	29/03/96	29/04/96	31/05/96	28/06/96	27/07/96
Chenjia Gou	2.84×10^{-5}	3.37×10^{-5}	1.71×10^{-5}	1.83×10^{-5}	2.52×10^{-5}	2.36×10^{-5}	1.89×10^{-5}
Anjia shan	4.13×10^{-5}	1.19×10^{-5}	1.03×10^{-5}	1.69×10^{-5}	3.27×10^{-5}	2.12×10^{-5}	1.63×10^{-6}
Weijia Gou	1.63×10^{-5}	5.02×10^{-5}	5.43×10^{-5}	4.04×10^{-5}	1.35×10^{-5}	3.67×10^{-4}	2.44×10^{-5}
Small drill hole 1#dam			3.18×10^{-4}	3.89×10^{-4}	7.37×10^{-5}	3.03×10^{-4}	9.36×10^{-5}
No2 work section well water	5.34×10^{-5}	5.75×10^{-5}	3.53×10^{-5}	3.63×10^{-5}	3.73×10^{-5}	2.56×10^{-5}	3.29×10^{-5}
Under Lantian bridge			1.81×10^{-7}			3.73×10^{-7}	2.37×10^{-7}
Joint point			1.17×10^{-6}			4.58×10^{-7}	--
Ba river			4.32×10^{-6}			2.46×10^{-6}	--
Wei river			1.79×10^{-6}			4.64×10^{-6}	--
1# dam	1.54×10^{-2}	1.60×10^{-2}	1.08×10^{-2}	1.68×10^{-2}	2.80×10^{-2}	2.25×10^{-2}	2.80×10^{-2}
451# pit water	1.38×10^{-2}	1.66×10^{-2}	2.06×10^{-2}	4.07×10^{-2}	2.04×10^{-2}	9.15×10^{-3}	2.04×10^{-2}
Large drill hole 1# dam				1.15×10^{-4}	2.88×10^{-5}	1.12×10^{-4}	2.88×10^{-5}

Date	30/08/96	23/09/96	25/10/96	22/11/96	28/12/96	28/01/97	28/02/97
Under Wangchuan bridge	2.36×10^{-7}	1.61×10^{-6}	3.76×10^{-7}	1.04×10^{-6}	1.09×10^{-12}	3.89×10^{-7}	3.22×10^{-7}
Under industrial bridge	2.58×10^{-7}	8.43×10^{-6}	2.64×10^{-6}	5.78×10^{-6}	1.18×10^{-12}	7.98×10^{-6}	8.24×10^{-7}
Yan village	1.14×10^{-5}	5.97×10^{-6}	6.60×10^{-6}	7.80×10^{-6}	1.56×10^{-12}	1.17×10^{-5}	2.53×10^{-6}
Xue village	1.29×10^{-5}	7.56×10^{-6}	9.88×10^{-6}	7.67×10^{-6}	1.46×10^{-12}	1.19×10^{-5}	3.25×10^{-6}
Jiandi Shaku	9.90×10^{-5}	2.95×10^{-4}	1.02×10^{-4}	1.12×10^{-4}	1.47×10^{-12}	1.86×10^{-4}	1.57×10^{-4}
No.1work section boiler house	1.09×10^{-4}	3.09×10^{-4}	1.35×10^{-4}	1.08×10^{-4}	1.69×10^{-12}	2.12×10^{-4}	4.95×10^{-4}
Chenjia Gou	2.80×10^{-5}	2.71×10^{-5}	2.96×10^{-5}	2.04×10^{-5}	1.30×10^{-12}	2.39×10^{-5}	3.81×10^{-5}
Anjia shan	9.90×10^{-6}	1.63×10^{-5}	8.36×10^{-6}	1.13×10^{-5}	7.33×10^{-13}	7.36×10^{-6}	1.25×10^{-6}
Weijia Gou	1.87×10^{-5}	1.39×10^{-5}	1.27×10^{-5}	7.86×10^{-6}	9.77×10^{-13}	2.92×10^{-5}	2.30×10^{-5}
Small hole 1#dam	4.78×10^{-5}	4.44×10^{-5}	2.72×10^{-4}	2.28×10^{-5}		1.19×10^{-4}	2.95×10^{-4}
No2 work section well water	4.78×10^{-5}	1.37×10^{-5}	5.35×10^{-5}	1.14×10^{-5}		4.50×10^{-5}	4.65×10^{-6}
Under Lantian bridge		1.58×10^{-6}			2.27×10^{-13}		
Joint point		4.14×10^{-7}			4.28×10^{-13}		
Ba river		2.17×10^{-7}					--
Wei river		2.56×10^{-6}			1.06×10^{-13}		--
1# dam	5.90×10^{-2}	1.16×10^{-2}	8.0×10^{-3}	2.0×10^{-3}	6.98×10^{-12}	1.09×10^{-3}	1.68×10^{-2}
451# pit water	3.36×10^{-2}	3.26×10^{-2}	2.04×10^{-2}	5.45×10^{-3}		1.54×10^{-2}	2.78×10^{-2}
Large drill hole 1# dam	$6.47\times10\text{–}^{3}$	4.64×10^{-6}	5.15×10^{-6}	2.28×10^{-5}	6.98×10^{-12}		

1.6. Problem and treatment

a) From the analysis results in environment monitoring from different populated areas, the uranium in water system can meet the demand of ground water requirement (0.05 mg/l). But in mining and milling production area, uranium concentration sometimes is over the requirement. These liquid effluents containing uranium must be managed properly. Otherwise they may cause the environment pollution.

b) It can be seen from the Table 3 that radium in water system is quite low and under the requirement (1.11 Bq/l). But as all the water flows through a high densely populated area, the radium discharge must be under stringent control.

c) In Table 4, uranium in the discharged effluent is under the limit of groundwater requirement. However, radium is greater than the industrial standard, as is also the pH value. All these are diluted by natural water system to meet the requirement.

d) Lime neutralization and barium chloride precipitation produced a sludge which consists of fine particle with high water content. It is difficult to compress and the settling rate is poor.

e) In Mine 1#, fluorine content is generally between 20~70 mg/l. When the fluorine is over 40 mg/l, the aluminum sulphate must be added to the effluent 60 times the fluorine content by weight, and the consumption of lime is also increased. This will result in the increase of the effluent treatment cost.

Table III. Environment monitoring measurement results of radium in water system from different points in the polluted area, Unit: Bq/L

Date	29/03/96	23/09/96	30/12/96
1# dam	0.432	0.396	0.714
Big drill hole in 1# dam		0.448	
Small drill hole in 1# dam	0.34	0.206	
Weijia Gou	0.1	0.086	0.016
Anjia Shan	0.095	0.149	0.032
Chenjia Gou	0.058	0.256	0.006
Boiler house in No1 work section	0.027	0.144	0.068
Jiandi Gou		0.102	0.081
Under industrial bridge	0.029	0.036	0.005
Yanjia village	0.018	0.069	0.013
Xuejia village	0.063	0.044	0.013
Under Lantian bridge	0.161	0.027	0.115
Joint point	0.008	0.099	0.02
Wei river	0.272	0.059	0.027
Ba river	0.014	0.058	0.007
Under Wangchuan bridge	0.022	0.027	0.007
Well water in No2 work section	0.286		

Table IV. Analysis results of elements in discharged effluent, (annual average value)

Date	1995	1996	1977
U	0.027 mg/l	0.016 mg/l	0.019 mg/l
Ra	2.59 Bq/l	3.37 Bq/l	0.51 Bq/l
F	9.5 mg/l	11.33 mg/l	10.47 mg/l
pH	9.98	8.51	9.0

2. Analysis and evaluation of liquid effluent pollution at Mine 2#

2.1. Introduction

Mine 2# is located in Jiangxi province in south part of China. The wastewater contains uranium with high concentrations of ^{226}Ra, ^{210}Po and ^{210}Pb. These waters must be treated properly before release into natural water system.

2.2. Pit water treatment

There are four pit water treatment stations in Mine 2#. The total process capacity is 5000 m^3/day. Because of the limitation of production, water changes and other factors, the process now treats 3500 m^3/day. Uranium mine pit water is processed by ion exchange. In the pit water, uranium and total α activity are over the discharge standards. Other elements are within the limits of the requirement. Thus, the main purpose of liquid effluent treatment is to remove and recover uranium from the effluent and reduce the uranium in the discharged effluent to below 0.05mg/l. If this is achieved, the total α activity will be greatly decreased. Figure 1 shows one pit water effluent monthly quantity and the relationship with uranium content.

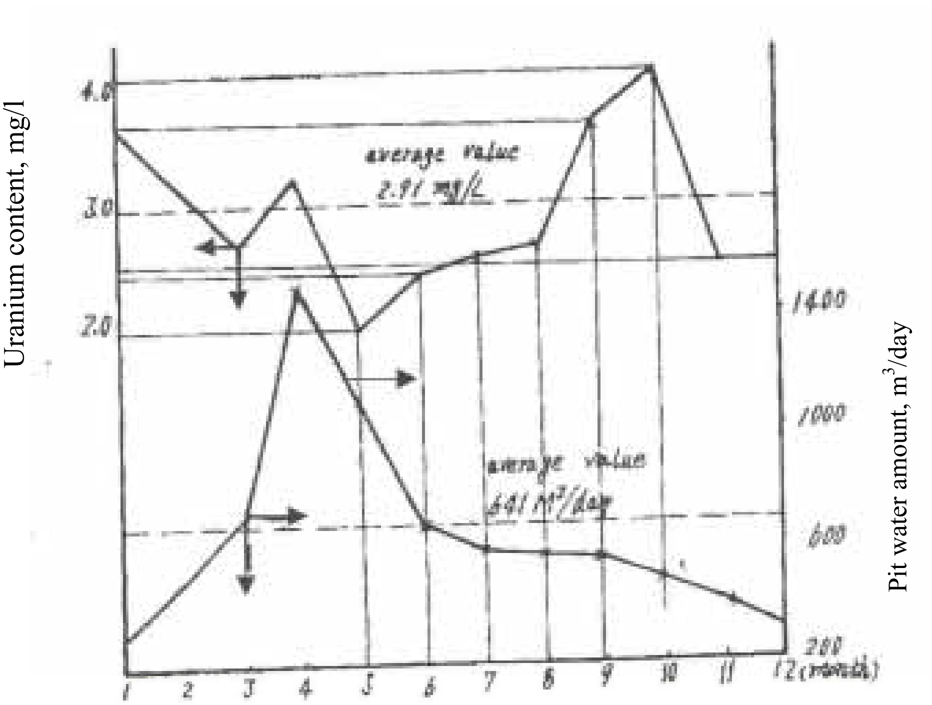


FIG. 1. The relationship of uranium contents and water amount in one pit.

201×7 strong base anion ion exchange resin is used in the process to recover uranium from liquid effluent. The pH value of the liquid effluent is about 6.9~7.1. The results of the effluent process station are shown in Table 5 and the process technology flow sheet is shown in Figure 2.

Table V. The operation results of effluent process stations

Items / Station	Technology	U in pit water mg/l	U in treated water, mg/l	Adsorption time, h	Purifying rate, %	Date
I	Fixed bed, 201×7resin NaCl+$NaHCO_3$ elution	3.5	0.08	1	97.7	12/1991
II	Fluidized bed, 201×7resin 10% H_2SO_4 elution	7	0.2	0.2	97.1	11/1991
III	Fluidized bed, 201×7resin 10% H_2SO_4 elution	2.2	0.07	0.25	96.8	11/1991
IV	Fluidized bed, 201×7resin 10% H_2SO_4 elution	2.1	0.05	0.25	98	11/1991

2.3. Tailings effluent treatment

The tailings effluent mainly comes from lime neutralization of the acidic milling wastewater. Every year about 1.42×10^6 ton acidic water are discharged into the tailings dam. The composition of tailings water is described in Table 6.

It can be seen from Table 6 that the uranium content in the tailings water meets the State regulatory discharge standard. Fluorine content and pH almost meet the requirement, but ^{226}Ra content is over the State standard. The highest level is 9.6 times and the average level is 3.12 times higher than the State standard.

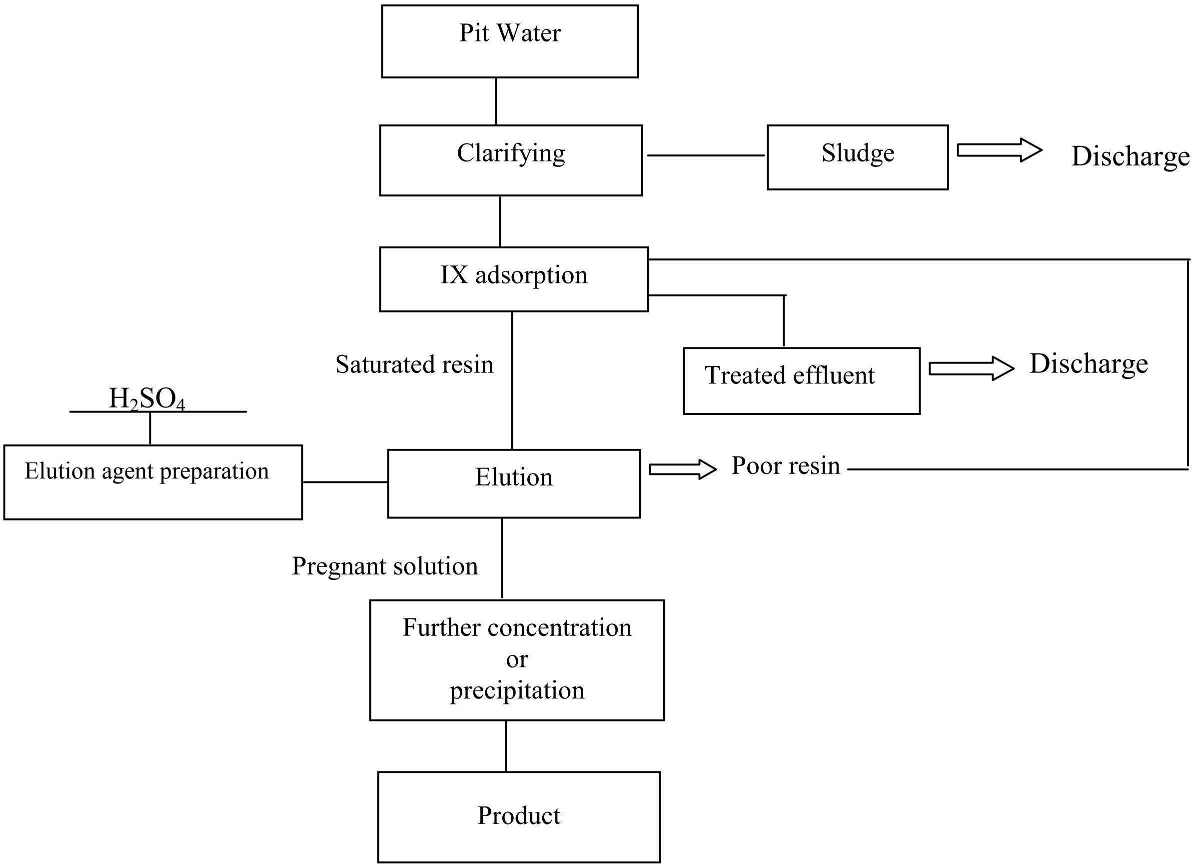


FIG. 2. Pit water process flow sheet.

Table VI. The composition of tailings water

Elements / Location	U Mg/l	^{226}Ra Bq/l	Mn mg/l	F mg/l	pH
Highest	3.60×10^{-2}	10.73	16.05	24.0	8.00
Lowest	7.23×10^{-4}	0.26	0.40	1.0	5.00
Average	1.38×10^{-5}	3.47	4.71	5.90	6.69
Standard difference	$\pm0.948\times10^{-2}$	±4.33	±4.49	±3.57	±0.57
Sample number	51	56	44	40	48
Meeting standard requiring number	51	3	6	37	46
Qualified rate, %	100	5	14	93	96
State standard	5×10^{-2}	1.11		10	6~9

The effluent from the tailings dam passes through a pyrolusite adsorption cell to remove ^{226}Ra and Mn content. The effluent pH is 6~7 before the adsorption cell. The particle size is 0.5~1.5 mm. MnO_2 content is 40~50%. The bed thickness is 1000 mm. Bed voidage is about 50%. Contact time is 5 minutes. When it reaches the breakthrough point (^{226}Ra=1.11Bq/l), the pyrolusite capacity of radium is < 74 Bq/g, MnO_2.

After the treatment by pyrolusite cell adsorption, ^{226}Ra and Mn contents are greatly decreased in the treated effluent, and the ^{226}Ra conformity rate reaches 94%. It is indicated that the pyrolusite cell adsorption is very effective, economic and practical because the used pyrolusite can be transferred to the leaching section for use as an oxidizing reagent. The pyrolusite cell adsorption results are shown in Table 7.

Table VII. Pyrolusite cell adsorption results

Elements / Location	Tailings dam effluent					After treatment				
	U mg/l	^{226}Ra Bq/l	Mn mg/l	F mg/l	pH	U mg/l	^{226}Ra Bq/l	Mn mg/l	F mg/l	pH
Average value	1.38×10^{-2}	3.47	4.71	5.90	6.69	6.56×10^{-3}	0.43	2.72	6.29	6.28
Standard difference	$\pm0.948\times10^{-2}$	±4.33	±4.49	±3.57	±0.57	$\pm4.96\times10^{-3}$	0.39	±3.69	±4.39	±0.78
Sample number	51	56	44	40	48	85	88	70	61	81
Sample number meeting requirement	51	3	6	37	46	85	83	16	56	79
Qualified rate %	100	5	14	93	96	100	94	23	92	98

2.4. Analysis results of hazardous elements in different polluted area in Mine 2#

The environmental monitoring results from different polluted area are shown in Table 8.

Table VIII. Environmental monitoring results of hazardous elements from different polluted areas (Average value, 1996)

Elements / Location		U mg/l	226Ra	Total α Bq/l	^{210}Po Bq/l	Th Bq/l	Cd mg/l
Mill area water channel		2.39	6.46×10^{-1}			2.37×10^{-2}	
Location	1#gate bridge	6.79	3.92×10^{-1}	7.94	8.32×10^{-2}	5.71×10^{-2}	1.86×10^{-2}
	Tailing dam outlet	5.90	4.81	9.70	8.11×10^{-2}	7.46×10^{-2}	2.67×10^{-2}
	I station	2.78	0.825	7.75	1.52×10^{-1}	3.33×10^{-2}	2.14×10^{-2}
	II station	7.44	0.336	3.02×10^{1}	3.73×10^{-2}	5.16×10^{-2}	1.19×10^{-2}
Water channel in mine area		1.49	1.23	5.77			
Water channel out mine area		1.69×10^{-2}	1.16×10^{-2}	8.29×10^{-2}			
Join point outlet water		1.81×10^{-1}	7.86×10^{-2}	0.437	9.39×10^{-3}	2.22×10^{-2}	
Reference		1.27×10^{-2}	1.43×10^{-2}	3.29×10^{-2}			

Location	Elements	Ca mg/l	Mg mg/l	Pb mg/l	SO^{2-}_4	F mg/l	Mn mg/l	As mg/l	Cr mg/l	pH
Mill area water channel		11.2	2.37	20.1		0.5	0.168			6.94
Location	1#gate bridge			0.1	1350	0.606	0.257	0.0162	5.84×10^{-3}	7.10
	Tailing dam outlet			0.322	588	2.06	3.68	0.027	7.14×10^{-3}	6.30
	I station			0.104	180	1.74	0.0286	0.0594	1.10×10^{-2}	7.54
	II station	81.8		0.117		1.27	0.754	0.0383	7.79×10^{-3}	6.94
Water channel in mine area										
Water channel out mine area										
Join point outlet water								0.0106	4.76×10^{-3}	

3. Analysis and evaluation of liquid effluent pollution in Mine 3#

3.1. Introduction

Uranium mine 3# is located in Zhejiang province in the south east of China. The weather is a sub-tropical monsoon climate and has the characteristics of basin meteorology. The highest temperature is 45ºC and lowest is –10.4ºC. Annual average temperature is 17.3ºC. Annual rainfall is 1726 mm and always has storms in summer. Water resource is rich in this region. Uranium orebody is mesozoic igneous rock, meso-epithermal deposit. The composition of the ore is simple. Metal minerals consist of uraninite, pyrite and hematite. Gangue minerals consist of feldspar, quartz, fluorite and mica etc.

3.2. Technology flow sheet

The technology flow sheet to process uranium is shown in Figure 3.

3.3. Pollution problems caused by process liquid effluent

The process effluents described in section 3.2 mainly contain the radionuclides uranium, radium etc. and other hazardous elements. Their concentrations depend on the characteristics of orebody. By a variety of way, these elements will increase the whole region radiation level and cause water and environmental pollution.

3.4. Pit water effluent treatment

Effluents from the heap leach operation are combined with pit water and treated in a dedicated effluent plant. The combined effluent is processed by ion exchange to recovery uranium. The technology flow sheet is shown in Figure 4 and the results of effluent treatment are shown in Table 9.

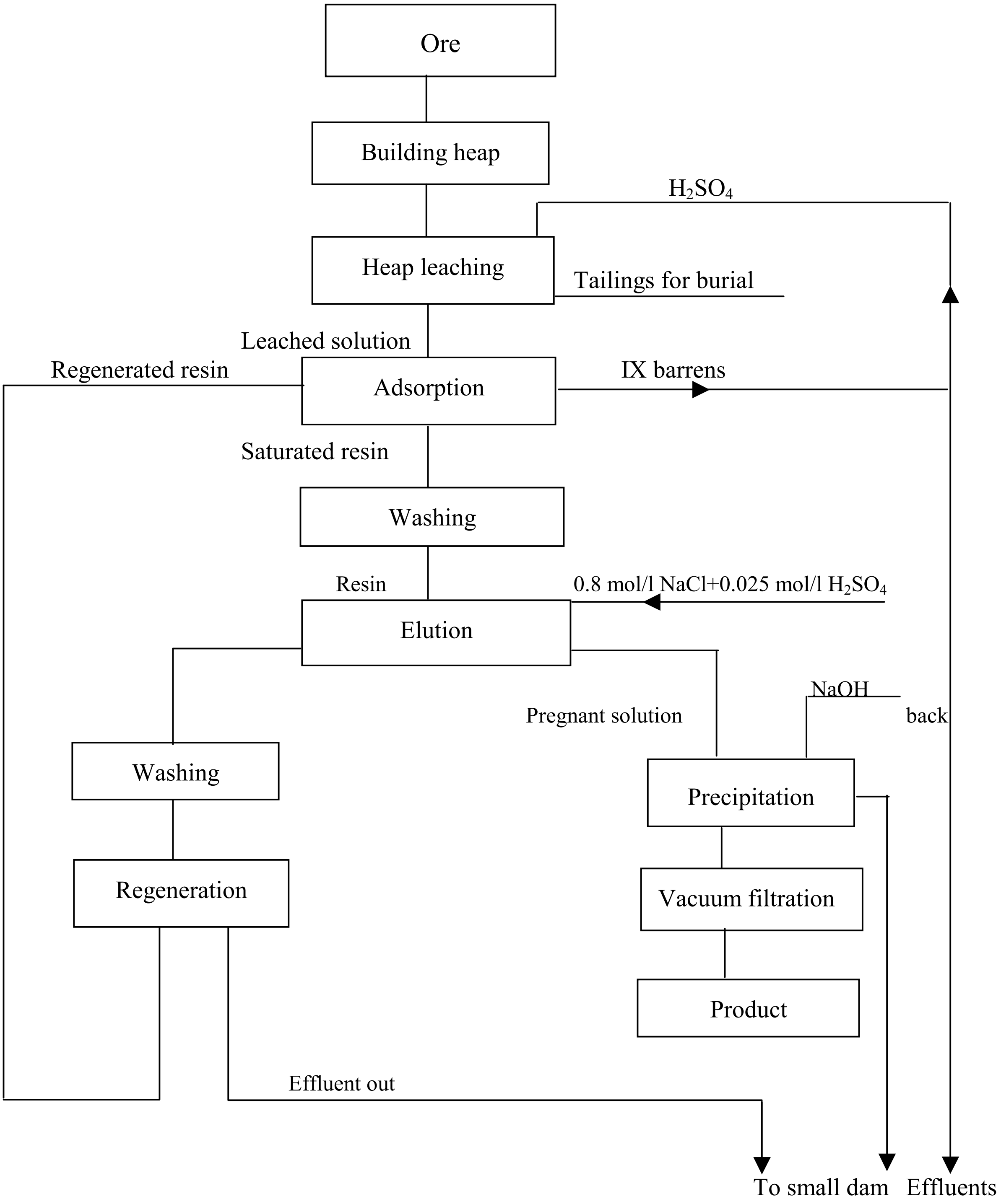
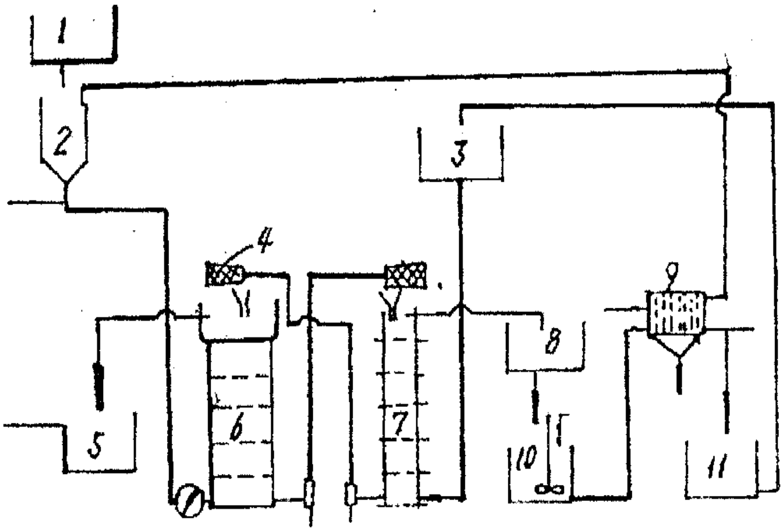


FIG. 3. Flow sheet of processing technology in Mine 3#.



1. pit water, 2. clarifying, 3. elution agent, 4. screen, 5. recovery resin,
6. adsorption column, 7. elution column, 8. pregnant solution,
9. filtration, 10. precipitation, 11. prepare elution reagent.

FIG. 4. Technology flowchart of recovery uranium by ion exchange system.

Table IX. The results of pit water effluent treatment by ion exchange adsorption (U mg/l)

		1984	1985	1986	1987	1988	1989	1990
Working Section 1	Original Water	1.55	1.43	1.34	1.79	1.12	1.13	1.56
	after process	0.162	0.24	0.22	0.79	0.27	0.28	0.59
Working Section 2	Original water	4.74	3.60	2.81	5.66	3.25	4.93	4.56
	after process	1.83	0.24	0.45	0.79	0.64	1.34	2.14
Working Section 3	Original Water	2.29	1.93	2.39	1.33	1.41	1.20	1.07
	after process	0.30	0.31	0.26	0.17	0.31	0.44	0.24
Working Section 4	Original Water	2.51	2.82	3.88	1.90	1.87	2.67	4.39
	after process	0.97	0.64	0.56	0.83	0.77	1.62	1.83
Annually average adsorption rate of whole mine		71.9%	85.8%	84.7%	71%	73.9%	69.8%	58.7%

3.5. Environmental monitoring results

The environmental monitoring data of uranium and radium are shown in Tables 10 and 11.

Table X. Environmental monitoring results of uranium in liquid effluent from different polluted areas in Mine 3#, Unit: mg/l, 1996

Location	Annual average value
Under bridge of No.2 working section	2.09×10^{-1}
Under Chejian bridge	2.25×10^{-1}
Under Huayuangeng bridge	1.75×10^{-1}
Joint point	5.67×10^{-2}
Under Dazhou bridge	5.71×10^{-2}
Under Qingshui bridge	3.60×10^{-2}
No.3 work section washing house	4.96×10^{-2}
Under Lishe bridge	3.37×10^{-2}
No.4 work section effluent channel	1.19×10^{-1}
Douzeshuiku joints	1.66×10^{-1}
Under Douze bridge	6.32×10^{-2}
Chemical works gate	7.60×10^{-2}
Water pond in leach work section	1.01

Table XI. Environment monitoring results of radium in liquid effluent from different polluted area in Mine 3#, Unit: Bq/L, 1996.

Location	Annually average value
Under bridge of No.2 working section	1.57×10^{-2}
Under Chejian bridge	2.38×10^{-2}
Under Huayuangeng bridge	1.98×10^{-2}
Joint point	1.04×10^{-2}
Under Dazhou bridge	7.42×10^{-3}
Under Qingshui bridge	7.15×10^{-3}
No.3 work section washing house	8.54×10^{-3}
Under Lishe bridge	6.54×10^{-3}
No.4 work section effluent channel	6.98×10^{-3}
Douzeshuiku joints	5.83×10^{-3}
Under Douze bridge	8.16×10^{-3}
Chemical works gate	9.17×10^{-3}
Water pond in leach work section	6.73×10^{-2}

4. Conclusion

As the data for the three-mine areas show, environmental pollution from the uranium industry is strictly controlled according to the discharge standards for the relevant elements. Many ways have been adopted in uranium industry to process the uranium effluent; lime neutralizing, barium chloride precipitation, resin adsorption and pyrolusite adsorption etc. So, generally speaking, environmentally harmful elements such as uranium, radium, Cd, Mn^{++}, Cr^{6+}, Th, $SO^{=}_4$, F^-, As and acidity etc. all can meet the industrial discharge standards. This industry has a strong and strict monitoring system to prevent environmental pollution.

Research on the removal of radium from uranium effluent by air-aeration hydrated manganese hydroxide adsorption

Zhang Jianguo, Chen Shaoqing, Qi Jing

Chinese National Nuclear Corporation (CNNC),
Beijing Research Institute of Chemical Engineering & Metallurgy,
Beijing, China

Abstract. In the acidic leaching uranium process, pyrolusite or manganese oxide (MnO_2) powder is often used as an oxidizer. In the resulting effluent, manganese ion is present as a contaminant in addition to U, Ra, Th, As, Zn, Cu, F^-, SO_4^{2-}, etc. Manganese ion content is about 100~200 mg/l in effluent. In this case, a new process technique can be developed to treat the effluent using the Mn^{2+} present in the effluent. The approach is as follows: The effluent is neutralized by lime milk to pH about 11. As a result, most contaminants are precipitated to meet the uranium effluent discharge standards (U, Th, Mn, SO_4^{2-} etc), but radium is still present in the effluent. In this process, manganese ion forms manganese hydroxide $Mn(OH)_2$. The manganese hydroxide is easily oxidized to form $MnO(OH)_2$ by air aeration. This hydrated manganese hydroxide complex can then be used to adsorb radium in effluent. The experiments show: (1) Effluent pH, manganese concentration in effluent, and aeration strength and time etc. influence the radium removal efficiency. Under the test conditions, when manganese in effluent is between 100~300 mg/l, and pH is over 10.5, radium can be reduced to lower than 1.11 Bq/l in the processed effluent. Higher contents of impurity elements such as aluminum, silicon and magnesium in the effluent affect the removal efficiency, (2) Under the experimental conditions, the lime precipitation-air aeration formed hydrated manganese hydroxide complex sludge is stable. There is no obvious release of radium from the adsorbed hydrated manganese hydroxide complex sludge, (3) the current experiments show that hydrated manganese hydroxide complex sludge has very good re-adsorption ability for removal of radium from uranium effluent. Some experimental parameters have been measured, (4) Compared with other process methods, such as neutralizing effluent without aeration; or neutralization with barium chloride addition at pH 5, 8, and 11, the removal of radium from uranium effluent by air aeration hydrated manganese hydroxide adsorption can effectively remove radium from effluent. Under the study conditions, air aeration formed hydrated manganese hydroxide pulp needs a longer time for clarification.

1. Introduction

A significant quantity of uranium effluent can be produced during uranium mining and milling operations. The natural radionuclide radium is a normal element existing in uranium effluent. It can have a great influence on the environment. The content of radium in effluent depends on the processed uranium ore grade and the processing technology. Generally, higher contents of radium always exist in association with higher grades of uranium ore. As environmental awareness increase and more stringent environmental protection requirements develop, the demand for rigid industrial effluent discharge standards increases. So the removal of the radium is an important step in uranium effluent process treatment because radium is a main radionuclide in uranium effluent. The discharge standards for effluents in the uranium industry to the environment in China are shown in Table 1.

Table I. The discharge standard of the liquid effluent from uranium industry

Element	U	Th	Ra^{226}	Pb	Hg	Cd	Cr	As	Cu	Zn	Mo	Ni	F	pH
Standard, mg/l	0.05	0.1	1.11 Bq/l	0.1	0.05	0.1	0.05	0.5	0.1	1.0	0.5	0.5	10	6.5-8.5

There are many methods that can be employed to remove radium from uranium mining and milling effluent. The normal methods used include: 1) barium chloride precipitation; 2) barite adsorption; and 3) pyrolusite removal of radium. In the barium precipitation process, good results for removal of radium can be obtained only when some sulphate ion exists in the effluent. The precipitated barium sulphate has poor deposition properties. So, large deposit cells are needed. Barite adsorption is one of the classical methods to remove radium, but there is no proper method to treat the adsorbed radium barite. Pyrolusite adsorption to remove radium is one of the economic methods to remove radium and the adsorbed pyrolusite can be recycled back to the leach process as an oxidizer. But different kinds of pyrolusite have significantly different adsorption properties. So, selection of an appropriate pyrolusite source is needed. In addition, activated sawdust, man-made zeolite, ion exchange resin and precipitation-air aeration-hydrated manganese hydroxide adsorption can be used to remove the radium from uranium effluent.

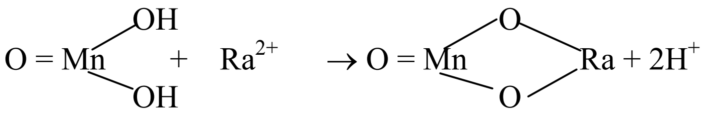
All uranium production countries have paid a lot attention to the treatment of uranium industrial liquid effluent. The discharge standard is very stringent. It is reported that there are about 26 countries with large and small scale of production capabilities for uranium. The discharge standards of liquid effluent have some little difference. In Canada, the maximum allowable level of ^{226}Ra is 0.37 Bq/l [1]. In China, the industrial discharge standard of ^{226}Ra in effluent is 1.1 Bq/l. The characteristics of uranium liquid effluents depend largely on the composition of the mined ore, local climate, hydrogeological regime, geographical location and most importantly the type of mining and processing techniques used to economically exploit the deposit.

The mechanism of precipitation-air aeration-hydrated manganese hydroxide adsorption takes advantage of the Mn^{2+} ion in uranium effluent to treat the effluent i.e. waste treatment is accomplished by the waste. Pyrolusite or manganese powder is used as oxidizer in most Chinese acidic leaching process uranium mills. So, uranium bearing effluent generally contains a great deal of Mn^{2+} ion. The processed tailing pulp is neutralized by lime milk to pH 7~8, then is discharged into a tailing pond. This effluent still contains radium, uranium, fluoride and manganese ions etc. Manganese ion content is about 100~200 mg/l. By further adjusting the effluent pH value, manganese ion reaction occurs as shown in equation (1) to form a hydroxide manganese deposit. This deposit is easily oxidized to form hydrated manganese hydroxide as shown by equation (2).

$$Mn^{2+} + 2OH^{-} = Mn(OH)_2 \qquad (1)$$

$$Mn(OH)_2 + \tfrac{1}{2}\,O2 = MnO(OH)_2 \qquad (2)$$

Previous research reports show that this hydrated manganese hydroxide has much better adsorption radium efficiency in alkaline medium than natural pyrolusite [2]. The adsorption mechanism for radium by hydrated manganese dioxide is shown in equation (3):



$$O=Mn(OH)_2 + Ra^{2+} \rightarrow O=Mn(O_2)Ra + 2H^{+} \qquad (3)$$

Under the experimental conditions, lime precipitation air-aeration formed hydrated manganese hydroxide complex sludge is stable. There is no obvious release of radium from the adsorbed hydrated manganese hydroxide complex sludge. Also, hydrated manganese hydroxide complex sludge has a very good re-adsorption ability to remove radium from uranium effluent. Real acidic radium bearing effluent samples were from the Lantan mill plant. The study was carried out on the lime precipitation and air aeration method to determine the process conditions and sludge stability. Certain achievements were made and some problems were found. The real effluent samples contain certain amount of aluminum, silica and magnesium ions, and the process efficiency for radium is not as good as reported by Cheng Shian [2]. It was found that when Al, Si, Mg contents are higher in liquid effluent, longer times are needed for clarification (about 7~8 days) or two steps are needed to process the effluent. First effluent pH is adjusted to 8 by lime milk, and Al, Si, and Mg are formed and removed. The second step is taking the supernatant liquid to pH 10.5~11, then air aeration for about 30 minutes to oxide $Mn(OH)_2$ deposit to form $MnO(OH)_2$ and remove radium by adsorption.

In the experiments, the adsorbed radium sludge was examined and analyzed regularly for six months. The results indicate that the adsorbed radium sludge is stable. Also, the lime precipitation air-aeration formed hydrated manganese hydroxide complex sludge has a very good re-adsorption ability for removal of radium from uranium effluent.

2. Experiments

(a) Instrument and equipment
  (i) Acidity metre pH s - 3c
  (ii) Air compressor Z - 0025/6
  (iii) Aeration cell
  (iv) 2000 ml cylinder
  (v) Adsorption column

(b) Chemicals

CaO	C.P (Chemical grade)
$MnSO_4$	A.R (Reagent grade)
Compressed air	
NaOH	A.R

(c) Air aeration operation

According to the processed effluent volume, 2000 ml cylinder or aeration cells are used for air aeration operation. Aeration strength is over 0.05l/cm^2 min.

(d) The composition of the effluent used in the experiments is shown in Table 2.

Table II. The composition of effluent

U	mg/l	5.8	F	mg/l	40
Th	mg/l	1.7	SO^{2}_{-4}	mg/l	1560
As	mg/l	1.0	Ca^{2+}	mg/l	300
Ra	Bq/l	31	Al^{3+}	mg/l	90
Cd	mg/l	<0.02	SiO_2	mg/l	80
Cr	mg/l	0.05	COD	mg/l	102
Mn	mg/l	41.0	pH		1.54

Because the manganese content in effluent is low, a quantity of manganese was added to guarantee the experiment ran smoothly.

3. Results and discussion

3.1. Experimental conditions on the formation of the hydrated manganese hydroxide sludge and simultaneous radium adsorption

3.1.1. Influence of pH on the adsorption of radium

As the pH increases in the lime precipitation and air aeration process, the residual radium content in the effluent decreases. When pH is adjusted to over 10.5, the radium content in effluent can be reduced from 31 Bq/l to 1.1 Bq/l. This result meets the required discharge standard. The results are shown in Figure 1.

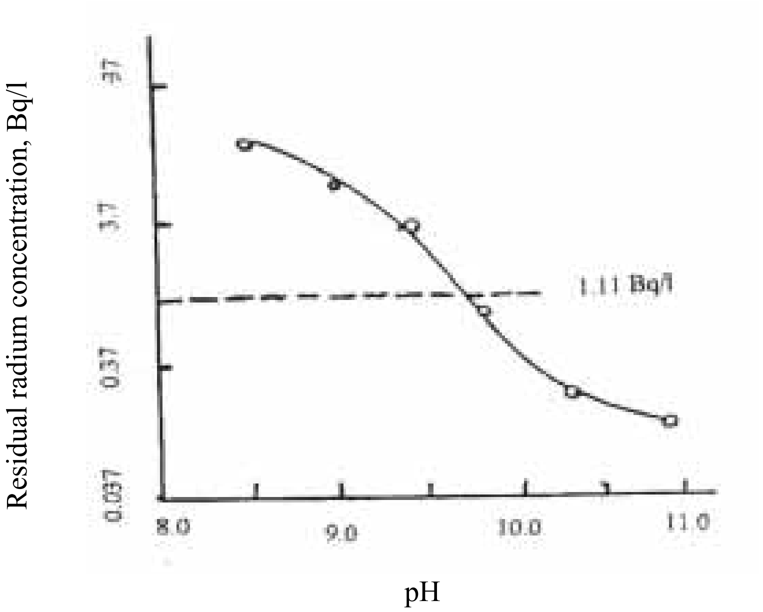
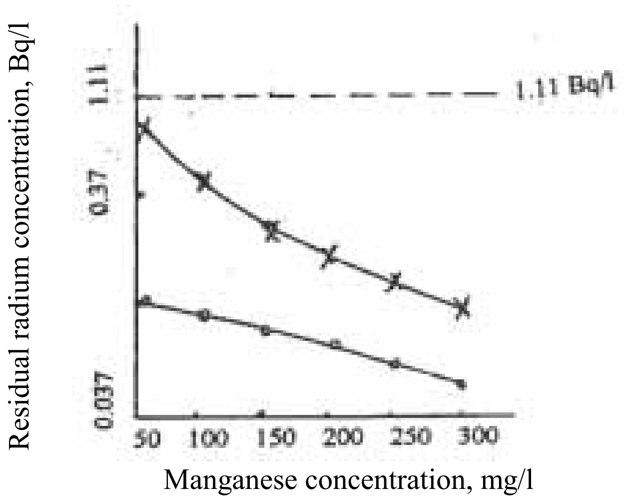


FIG.1. pH influence on the removal of radium in the precipitation process. Manganese content 150 mg/l. Air aeration time 30 minutes

3.1.2. Manganese content influence on the removal of radium

The effect of manganese content on the removal of radium is shown in Figure 2.

As shown by Figure 2, when manganese content in the effluent is increased, the residual radium content in effluent decreases. This is because the amount of hydrated manganese hydroxide formed increases with the amount of manganese present. Manganese content in the effluent should be increased with the increase in the original radium content of the effluent. When the original radium content in effluent is 3~40 Bq/l (typical) or 180 Bq/l (maximum), the manganese ions content in effluent must be over 100 mg/l or 200 mg/l respectively. In these cases, there are adequate amounts of manganese and the radium can be reduced as low as required. Good radium removal efficiency can be obtained with the increase of manganese ion in the effluent.



X-radium original content 33 Bq/l, o-radium original content 8 Bq/l, pH 11, aeration 30 minutes

FIG. 2. The influence of manganese content on the removal of radium.

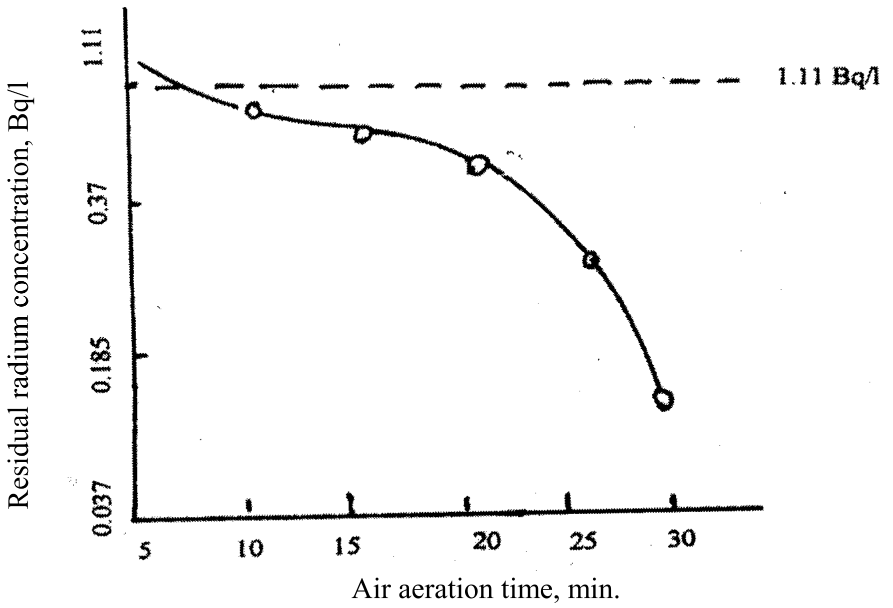
3.1.3. Aeration time

As the aeration time increases, the efficiency of radium removal is increased. This is because when other conditions are fixed, the longer aeration time provides enough oxygen from the air to oxidize the precipitated manganese hydroxide to form the large specific surface area of hydrated manganese hydroxide used to adsorb radium. That is, as aeration time increases, the production rate of hydrated manganese hydroxide is raised. For effluent containing radium between 3 and 40 Bq/l, manganese ion concentration of about 300 mg/l, with 30 minutes air aeration time can easily meet the required radium concentration. The result is shown in Figure 3.

3.1.4. Impurity elements of aluminum, silicon and magnesium effect on the removal of radium

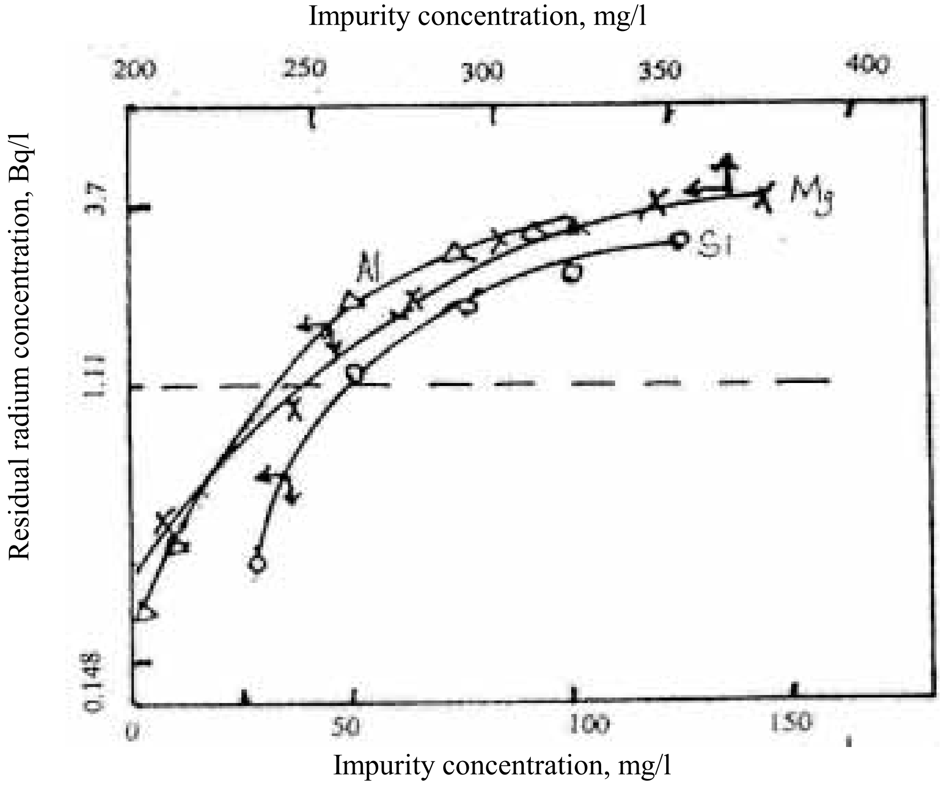
In uranium industrial effluent, there is always some amount of aluminum, silicon and magnesium. Their contents depend on the property of the ore and process technology. The aluminum, silicon and magnesium in effluent have a great influence on the lime precipitation-air aeration process to remove the radium from acidic uranium effluent. The result is shown in Figure 4.

Because the aluminum, silicon and magnesium contents in this effluent are relatively high, the results of removal of radium by lime precipitation-air aeration-hydrated manganese hydroxide adsorption are poor and cannot meet the requirements at these high impurity levels. The clarification needs 8~9 days. In this case, two steps are employed to treat this kind of effluent. First, effluent pH is adjusted to 8 to remove the aluminum, silicon and magnesium. Second, the clear solution is decanted and pH adjusted to 10.5~11 by lime milk, then, aerated by air. The removal result for impurities is shown in Table 3.



Manganese content 300 mg/l, pH 11, radium concentration 12 Bq/l

FIG. 3. Air aeration time influence on the removal of radium.



Manganese content 300 mg/l, pH 11, radium concentration 12 Bq/l.

FIG. 4. Impurity elements influence on the removal of radium.

Table III. Removal results for impurities elements

Elements	U mg/l	Ra Bq/l	Mn^{2+} mg/l	Al^{3+} mg/l	SiO_2 mg/l	Mg^{2+} mg/l	pH
Original effluent	5.8	31	300	90	80	91	1.54
Processed effluent	1.23	24	223	1.1	4.0	30	8

It can be seen from Table 3 that when the original effluent is adjusted to 8, aluminum, silicon are almost completely precipitated. And most of magnesium is deposited. The supernatant solution pH is then adjusted to 11.4. Air aeration takes 30 minutes. The uranium content in raffinate is reduced to below 0.05 mg/l, radium content is 0.2 Bq/l and other harmful elements can also meet required discharge standards.

3.1.5. Clarification time

In the lime precipitation-air aeration process to treat acidic uranium effluent, the longer the clarification time, the lower the radium in raffinate. Clarification time has relationship with original radium content and manganese ion content in effluent. When the content of aluminum, silicon and magnesium in effluent is low, 1~5 hours clarification time can meet requirements. If aluminum, silicon and magnesium content are higher in effluent, much longer time for clarification is needed for precipitation of the radium to required levels. Due to the aluminum, silicon and magnesium levels existing in effluent in the lime precipitation-air aeration process, some very fine particles or gel-type solution is formed, so longer time is needed to conglomerate large particles for settling.

3.2. Experiment on the stability of hydrated manganese hydroxide complex sludge adsorption

3.2.1. Re-dissolving experiment

(a) Taking one litre of effluent with radium content of 62 Bq/l, 300 mg/l manganese ion is added as $MnCl_2$ type salt. The effluent pH is adjusted to 11.1 by 10% w/w lime milk, then air aeration takes 30 minutes. After 40 minutes clarification time, U, Th, Ra and F etc., elements in the supernatant liquid are analyzed. Then this liquid continues to be contacted with the deposited sludge, being stirred periodically. Analysis of radium and other elements are carried out regularly to see if there is a redissolution problem. The results are shown in Table 4.

(b) Taking 1.6 litre of effluent with radium content of 62 Bq/l, 300 mg/l manganese is added as $MnSO_4$ type salt. The effluent pH is adjusted to 11.93 by 10% w/w lime milk, then air aeration takes 30 minutes. The deposit shows very dark brown. Measurement of radium etc., are taken regularly. The results are shown in Table 5.

(c) Re-dissolving the sludge by water: Taking 200g of lime precipitation-air aeration-hydrated manganese hydroxide sludge, 2000 ml tap water is added to re-dissolve radium in sludge. The contact ratio of solid to liquid is 1:10. The results are shown in Table 6.

Table IV. The re-dissolution results of radium from deposited sludge

	Ra Bq/l	U mg/l	Th mg/l	F Mg/l	pH
40 minute	8.5	< 0.05	<0.025	4.5	11.1
9 day	1.5				11.1
12 day	0.8				11.06
25 day	0.5				10.56
32 day	0.2				9.57
44 day	0.1				8.65
60 day	0.02				7.60
90 day	0.03				7.70
120 day	0.04				7.64
150 day	0.02				7.65
185 day	0.06	<0.05	<0.025	3.0	7.65

Table V. The re-dissolving results of radium from deposited sludge

	Ra Bq/l	U mg/l	Th mg/l	F mg/l	pH
1 day	4.5	< 0.05	<0.02	4.5	12.0
8 day	1.2				12.05
17 day	0.2				11.53
24 day	0.3				11.36
36 day	0.03				10.64
53 day	0.04				8.30
84 day	0.05				8.17
114 day	0.03				7.93
144 day	0.03				8.25
180 day	0.06	<0.05	<0.01	2.75	7.80

Table VI. The re-dissolving results of radium from deposited sludge by water

	Ra Bq/l	U mg/l	Th mg/l	F mg/l	pH
5 day	trace	< 0.05	<0.01	0.5	8.05
25 day	0.3				9.40
55 day	0.03				9.33
85 day	0.01				9.34
115 day	0.02				8.96
150 day	0.01	<0.05	<0.01	0.49	8.91

It can be seen from Tables 4, 5, and 6 that the radium adsorption on the sludge is stable. There is not much release of radium from the deposited sludge under the experimental conditions. This achievement is in agreement with the research results by I. Nirdosh et al [3,4], who reported that adsorption of radium on freshly precipitated hydrous oxides of Fe, Mn, Zr, and Ti were investigated at pH 1 and 10. Radium removal was found to be highly sensitive to the solution pH and all oxides effectively absorbed Ra at higher pH. However, significant radium adsorption was observed only on manganese dioxide. Desorption of Ra from the oxides was found to be difficult in alkaline solutions of EDTA.

The pH of the solution decreases with time. It becomes nearly neutral. This is because the effluent adsorbed CO_2 from air because the alkali solution contacted with air for a long time. This is a benefit for the lime precipitation-air aeration process. If the processed effluent by lime precipitation-air aeration is not directly discharged to the natural environment, the effluent does not need to be re-neutralized by sulphuric acid. This effluent can be stored in the tailings dam for some time and the pH can reach the neutral condition.

3.2.2. Re-leaching the radium from adsorbed hydrated manganese hydroxide

To further study the stability of the adsorbed radium hydrated manganese hydroxide, the re-leaching of radium from adsorbed hydrated manganese hydroxide is studied with carbonate and sulphate. The results are shown in Tables 7 and 8.

Table VII. Re-leaching of radium by sodium sulphate. Solid liquid ratio 1:5, leaching time 24 hours, intermittently stirring

SO_4^{2-}, concentration / ppm	200	500	1000	1500	2000
Ra, Bq/l in Leached liquor	0.5	0.4	0.4	0.3	0.3

Table VIII. Re-leaching of radium by ammonium carbonate. Solid liquid ratio 1:5, leaching time 24 hours, intermittently stirring

CO_3^{2-}, concentration ppm	200	500	1000	1500	2000
Ra, Bq/l in leached liquor	0.1	0.2	0.1	0.2	0.3

It can be seen from Tables 7 and 8 that the adsorbed radium hydrated manganese hydroxide is stable under the experiment conditions.

3.3. Re-adsorption of radium from uranium effluent by lime precipitation air-aeration formed hydrated manganese hydroxide complex sludge

In parts two and part three, the experiment shows that lime precipitation air-aeration formed hydrated manganese hydroxide complex sludge has the ability to remove radium from the uranium effluent and maintain the adsorbed radium. For the application of this technique in an industrial practice, a re-adsorption experiment on the radium by lime precipitation air-aeration formed hydrated manganese hydroxide complex sludge was done in this part and the normal uranium tailing sludge (with little manganese) was used as a reference.

3.3.1. Effect of effluent pH on the adsorption of radium by the hydrated manganese hydroxide complex

Two kinds of adsorbent are used: hydrated manganese hydroxide complex and the normal uranium tailing sludge. A 0.10-gram sample of each adsorbent is contacted with 100 ml of uranium effluent with variable pH for adsorption time of 24 hours. Then, separation was carried out and radium in the tailing effluent analyzed. The results are listed in Table 9.

Table IX. The effect of effluent pH on the adsorption of radium by the hydrated manganese hydroxide complex and normal uranium tailing sludge

Effluent pH	Adsorbent	Radium content in effluent	Radium in adsorbed liquor	Adsorbed liquor pH	Radium removal efficiency
1.45	hydrated manganese hydroxide complex	35 Bq/l	0.18 Bq/l	7.90	99.5%
	normal uranium tailing sludge		11 Bq/l	1.78	68.6%
7.0	hydrated manganese hydroxide complex	9.0 Bq/l	0.3 Bq/l	9.95	96.7%
	normal uranium tailing sludge		1.2 Bq/l	7.45	86.7%
9.42	hydrated manganese hydroxide complex	4.0 Bq/l	0.16 Bq/l	10.17	96%
	normal uranium tailing sludge		1.1 Bq/l	8.04	72.5%

3.3.2. Contact time influence on the radium adsorption

One gram of hydrated manganese hydroxide complex and normal uranium tailing sludge were respectively contacted with 100 ml, pH = 1.45, Ra = 35 Bq/l, U = 11.7 mg/l original effluent at different adsorption times to study the contact time influence on the radium adsorption process. The experimental results are shown in Tables 10 and 11.

Table X. Contact time influence on the radium adsorption by hydrated manganese hydroxide complex

No.	Contact time, minutes	Adsorbed effluent pH	U in adsorbed effluent, mg/l	Ra in adsorbed effluent, Bq/l	U removal efficiency	Ra removal efficiency
M1	5	2.56	11.7	25	—	28.57%
M2	10	2.95	11.2	20	4.3%	42.86%
M3	15	2.64	11.6	17	0.1%	51.43%
M4	30	2.58	11.4	19	2.5%	45.71%
M5	60	3.14	10.1	16	13.7%	54.29%
M6	120	5.24	0.9	1.6	92.3%	95.43%
M7	300	6.06	0.9	0.74	92.3%	97.89%

Table XI. Contact time influence on the radium adsorption by normal uranium tailing sludge

No.	Contact time, minutes	Adsorbed effluent pH	U in adsorbed effluent, mg/l	Ra in adsorbed effluent, Bq/l	U removal efficiency	Ra removal efficiency
W1	5	1.31	10.5	30	10.25%	14.28%
W2	10	1.30	10.8	35	7.69%	--
W3	15	1.29	10.3	34	11.96%	2.86%
W4	30	1.29	10.3	32	11.96%	8.57%
W5	60	1.29	10.3	33	11.96%	5.71%
W6	120	1.29	10.3	35	11.96%	--
W7	300	1.23	10.3	29	11.96%	17.14%

3.3.3. Influence of original effluent pH and contact time on radium adsorption by hydrated manganese hydroxide complex

pH value 1.45 uranium effluent was adjusted to 7.44 by sodium hydroxide. The uranium content in adjusted solution was below 1 mg/l, Ra content was 7.7 Bq/l. This solution (100 ml) was contacted with 1 gram hydrated manganese hydroxide complex at different contact times. The uranium content and radium content in adsorbed tailing effluent was analyzed to evaluate the effluent pH and contact time influence on radium adsorption. The results are shown in Table 12.

Table XII. The influence of original effluent pH and contact time on radium adsorption by hydrated manganese hydroxide complex

No.	Contact time, minutes	Adsorbed effluent pH	U in adsorbed effluent, mg/l	Ra in adsorbed effluent, Bq/l	Ra removal efficiency
M11	5	8.71	0.5	0.66	91.43%
M12	10	8.56	0.6	0.95	87.66%
M13	15	8.72	0.6	0.38	95.06%
M14	30	8.71	0.4	0.85	88.96%
M15	60	8.70	0.9	0.42	94.55%

3.3.4. Column adsorption experiment

Column diameter was 14.6 mm, 15 gram hydrated manganese hydroxide complex was compacted in this column. The packed column height was 120 mm, volume was 20 ml. Packed density was 0.75 g/cm^3. Inlet pH of the effluent was about 7, radium was about 9.0 Bq/l. Residence time was 30 minutes. The experiment took three months. The breakthrough point is defined as 1.11Bq/l. The column operation results are listed in Table 13.

In about three months of operation, 26000 ml of uranium effluent was processed with a discharge standard of radium of 1.11 Bq/l. About 22000 ml of the discharged uranium effluent had a radium content below 0.4 Bq/l. A total of 228 Bq radium was adsorbed by 15 gram hydrated manganese hydroxide complex sludge. The manganese content in the sludge was 5.6%. So, manganese content in 15 gram hydrated manganese hydroxide complex sludge is 0.84 gram. Thus, the process ability of manganese on radium adsorption is 271 Bq/g.

In general, as the experiments above show, pH has a great influence on the adsorption of radium by hydrated manganese hydroxide complex. The adsorption pH choice can be between 6.5 and 9. At this effluent pH, the adsorption residence time can be 5 minutes. Also, the hydrated manganese hydroxide complex shows good adsorption capacity for radium removal in uranium influent. The capacity at breakthrough point 1.11 Bq/l is 271 Bq/g manganese. The normal uranium tailing sludge has some radium adsorption capacity. But compared with the hydrated manganese hydroxide complex, this adsorption is small. Also, the radium in outlet effluent (the adsorbed effluent) is over the industrial discharge standards.

Table XIII. Column adsorption radium result by hydrated manganese hydroxide complex

No	Outlet volume, ml	pH of outlet effluent	Total volume, ml	BV number	Ra content in outlet effluent, Bq/l
1	50	8.53	50	2.5	0.19
2	50	8.56	100	5	0.09
3	50	8.53	150	7.5	0.08
4	69	8.30	333	16.65	0.06
5	68	8.44	469	23.45	0.04
6	51	8.43	679	33.95	0.15
7	50	8.21	830	41.5	0.15
8	50	8.13	982	49.1	0.10
9	50	8.17	1133	56.65	0.09
10	50	8.19	1233	61.65	0.12
11	50	8.13	1385	69.25	0.10
12	50	8.07	1537	76.85	0.12
13	50	7.0	1689	84.45	0.14
14	51	8.11	1842	92.1	0.16
15	50	8.19	2043	102.15	0.2
16	51	7.94	2247	112.35	0.08
17	51	8.04	2451	122.55	0.27
18	51	8.01	2655	132.75	0.15
19	50	8.09	2859	142.95	0.13
20	51	8.01	3012	150.6	0.18
21	51	7.97	3215	160.75	0.17
22	50	8.07	3417	170.85	0.15
23	75	7.90	3593	179.65	0.15
24	95	8.04	3688	184.4	0.16
25	50	7.91	3950	197.5	0.16
26	50	7.97	4150	207.5	0.14
27	50	8.03	4350	217.5	0.12
28	70	8.13	4616	230.8	0.14
29	50	8.10	4841	242.05	0.15
30	50	8.11	4991	249.55	0.15
31	60	7.76	5261	263	0.16
32	53	7.99	5524	276.2	0.17
33	55	7.99	5735	286.95	0.19
34	55	7.42	5998	299.9	0.17
35	54	7.90	6215	310.75	0.21
36	54	7.94	6429	321.45	0.16
37	57	7.96	6599	330	0.13
38	58	7.0	6862	343.1	0.16
39	53	7.92	7075	353.75	0.18
40	53	7.94	7286	364.3	0.16
41	55	7.93	7448	372.4	0.17
42	55	8.01	7553	377.65	0.18
43	54	7.90	8091	404.55	0.18
44	54	7.96	8461	423	0.2
45	54	7.90	8728	436.4	0.23
46	54	8.15	9155	457.75	0.21
47	54	7.98	9585	479.25	0.18
48	54	7.97	9905	495.25	0.19
49	54	7.82	10289	514.45	0.17
50	54	7.93	10659	532.95	0.18

No	Outlet volume, ml	pH of outlet effluent	Total volume, ml	BV number	Ra content in outlet effluent, Bq/l
51	52	7.86	10921	546	0.18
52	45	7.90	11228	561.4	0.19
53	53	7.53	11603	580.15	0.17
54	53	7.53	11976	598.8	0.18
55	53	7.35	12346	617.3	0.17
56	52	7.49	12612	630.6	0.18
57	53	7.45	12980	649	0.17
58	52	7.48	13347	667.35	0.20
59	52	7.46	13712	685.6	0.18
60	52	7.42	14076	703.8	0.18
61	52	7.50	14440	722	0.19
62	45	7.60	14680	734	0.19
63	44	8.43	15415	770.75	0.34
64	75	8.43	15835	791.75	0.31
65	45	7.67	16230	811.5	0.29
66	52	7.93	16947	847.35	0.32
67	155	7.82	17612	880.6	0.35
68	52	7.94	18329	916.45	0.38
69	51	7.92	19045	952.25	0.33
70	52	7.84	19757	987.85	0.34
71	51	7.86	20416	1020.8	0.37
72	51	7.82	21122	1065.1	0.40
73	50	7.84	21827	1091.35	0.40
74	150	7.86	22527	1126.35	0.43
75	52	6.65	23407	1170.35	0.52
76	55	6.52	24112	1205.6	0.81
77	77	6.42	24674	1233.7	1.06
78	70	6.53	24969	1248.45	0.88
79	70	7.00	25294	1264.7	1.08

3.4. Comparison with other methods

As the experiments above show, removal of radium from uranium effluent by air aeration hydrated manganese hydroxide adsorption is one way to treat uranium effluent. Its main advantage is to use the manganese ions in the effluent to treat the effluent, i.e. using the waste to treat the waste.

To further evaluate this method, comparative systems are employed as the reference. Under the Coordinated Research project (CRP) agreement with the Agency, the following work was done. They are: (i) neutralize effluent without aeration at pH 5, 8, and 11, in three tanks: duration 1 hour per tank; (ii) neutralize effluent with aeration at pH 5, 8, and 11, in three tanks: duration 1 hour per tank; (iii) neutralize effluent with barium chloride at pH 5, 8, and 11, in three tanks: duration 1 hour per tank.

The original effluent pH is 1.54, U = 11.8 mg/l, Ra = 32 Bq/l, SO_4^{2-} = 3.36 g/l, Mn^{2+}= 89.25 mg/l. The solution pH is adjusted by 10% lime cream. The test results are shown in Tables 14, 15, and 16 and Figures 5, 6, and 7.

Table XIV. Neutralize effluent without aeration at pH 5, 8, 11 by lime milk

pH Conditions	5	8	11
Stirring time, min	60	60	60
Classification time, h	4	4	4
U, mg/l, processed effluent	0.88	0.3	0.3
Removal efficiency rate, U	95.5%	97.5%	97.5%
Ra, Bq/l, processed effluent	24	10	8.6
Removal efficiency rate, Ra	25%	68.75%	73.13%

Table XV. Neutralize effluent with barium chloride at pH 5, 8, 11

pH Conditions	5	8	11
Stirring time, min	60	60	60
Classification time, h	20	20	20
Ra, Bq/l, processed effluent	2.1	1.4	0.81
Removal efficiency rate, Ra	93.44%	95.63%	97.47%

Table XVI. Neutralize effluent with aeration at pH 5, 8, 11

pH Conditions	5	8	11
Mn^{2+}, mg/l	300	300	300
Aeration time	60 min	60 min	60 min
Classification time, h	4	4	4
Ra, Bq/l, processed effluent	13 Bq/l	6.8 Bq/l	3.6 Bq/l
Removal efficiency rate, Ra	59.38%	78.75%	88.75%
Classification time, h	48	48	48
Ra, Bq/l, processed effluent	13 Bq/l	6.5 Bq/l	2.7 Bq/l
Removal efficiency rate, Ra	59.38%	79.68%	91.56%
Classification time,	7 days	7 days	7 days
Ra, Bq/l, processed effluent	13 Bq/l	5.3 Bq/l	1.0 Bq/l
Removal efficiency rate, Ra	59.38%	83.44%	96.87%
Classification time,	15 days	15 days	15 days
Ra, Bq/l, processed effluent	13 Bq/l	4.8 Bq/l	0.31 Bq/l
Removal efficiency rate, Ra	59.38%	85%	99.03%

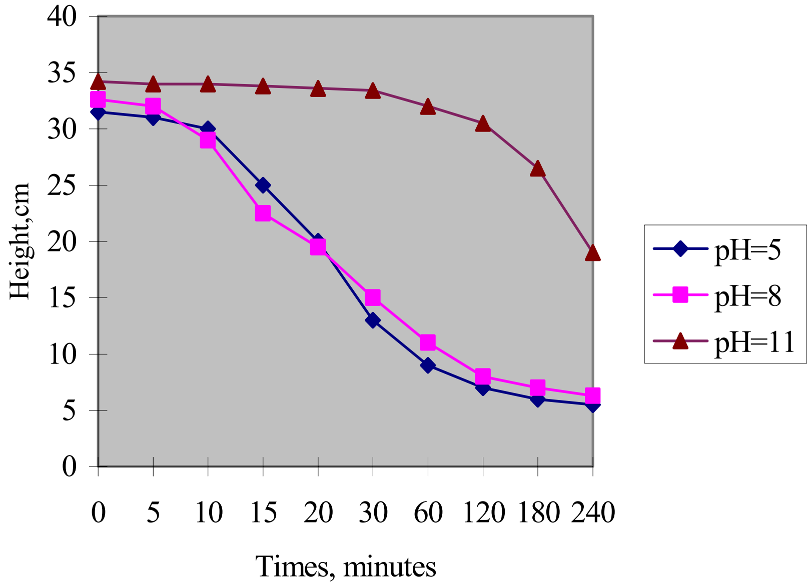


FIG. 5. The settling curve by alkali deposit.

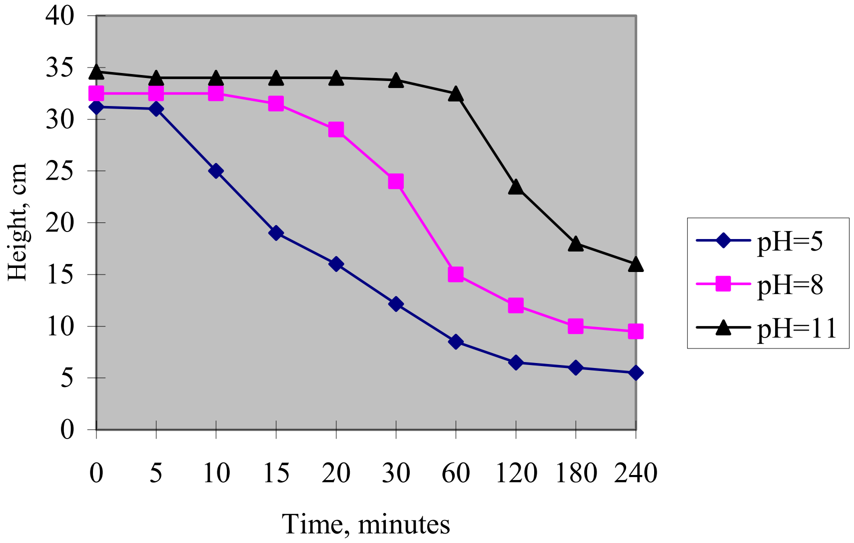


FIG. 6. The settling curve by barium chloride.

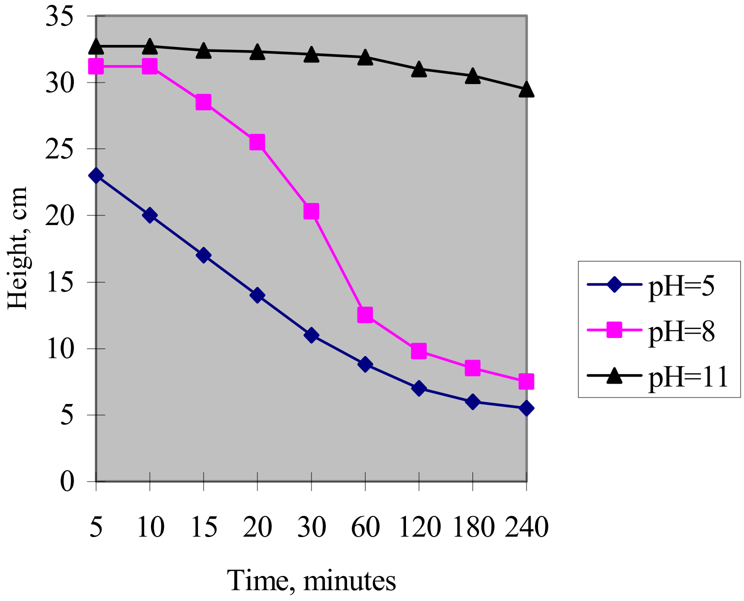


FIG. 7. The settling curve by air aeration hydrated manganese hydroxide.

Experiment results in Tables 14, 15 and 16 indicate that removal of radium from uranium effluent by air aeration hydrated manganese hydroxide adsorption can effectively remove radium from effluent. Under the experimental condition, the aerated effluent needs much long time for settling. As Table 16 shows, in seven days, the radium in the processed effluent can reach 1.0 Bq/l which meets the industrial discharge standard. In the real effluent, the higher concentration of aluminum, silicon and magnesium can greatly influence the removal efficiency (please see 3.1.4). Air aeration forms much smaller, stickier alkali particle of the hydrated manganese hydroxide, which needs long time for settling. Under the comparative tests, neutralizing by lime and barium chloride is effective too. The clarification time is shorter, but still needs 20 hours for settling. At all the experimental conditions, uranium in the effluent can be easily removed. It can be seen from Figures 5, 6 and 7, the higher the pH of the effluent, the longer the settling time. This is because under the experimental conditions of stirring and air aeration, an alkali gel solution is formed.

3.5. X-ray diffraction diagrams of hydrated manganese hydroxide, and two samples of conventional uranium tailing sludge, 1# and 2# are shown in Figures 8, 9 and 10. It is shown that the amorphous hydrated manganese hydroxide exists in the lime precipitation-air aeration sludge.

4. Conclusions

The advantage of lime precipitation-air aeration-hydrated manganese hydroxide adsorption to process uranium effluent is application of the waste ions in effluent to treat the effluent. This is beneficial for the environmental protection. And it is also an effective method to process the uranium effluent. The following points can be drawn from research and experiments:

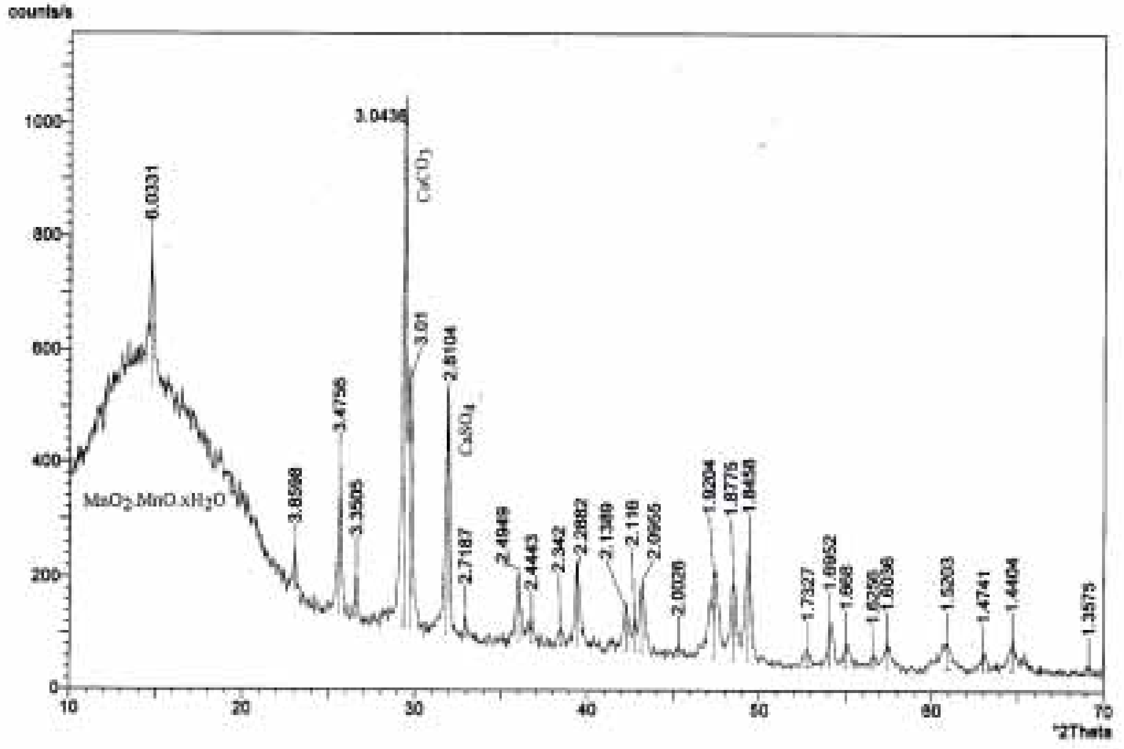


FIG. 8. X-ray diffraction diagram of hydrated manganese hydroxide, Mn Content: 5.6%.

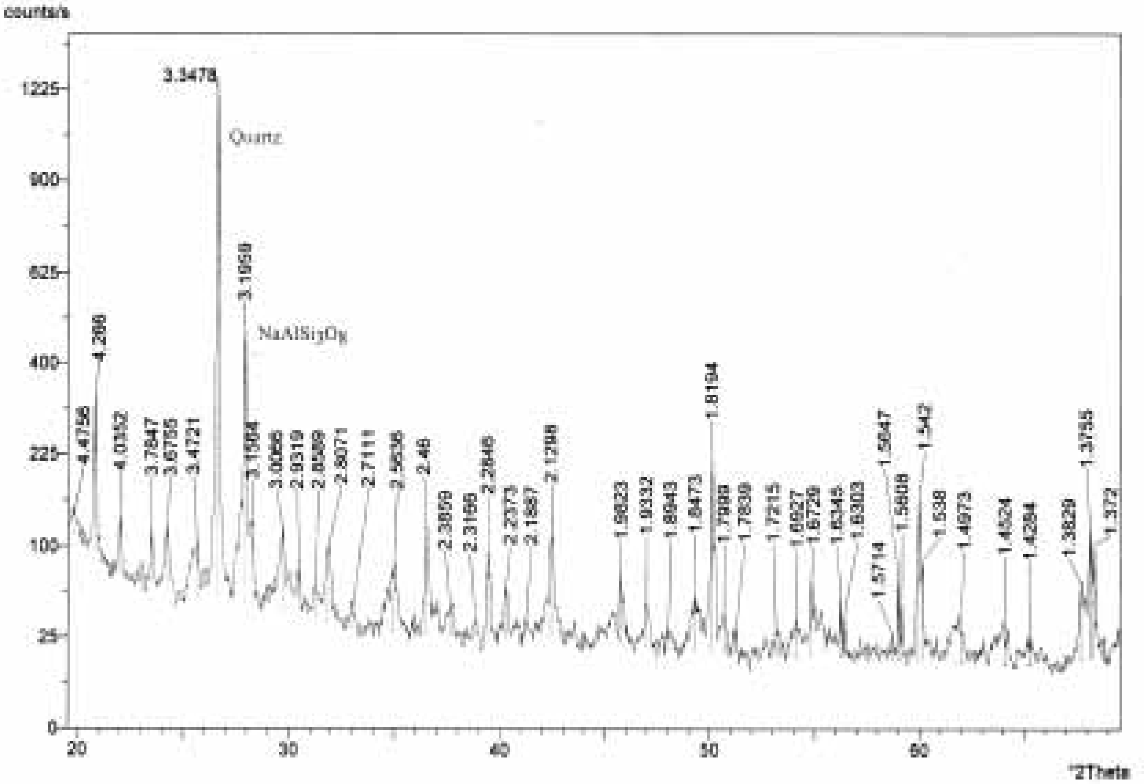


FIG. 9. X-ray diffraction diagram of conventional tailing sludge, 1#, Mn content: 0.38%.

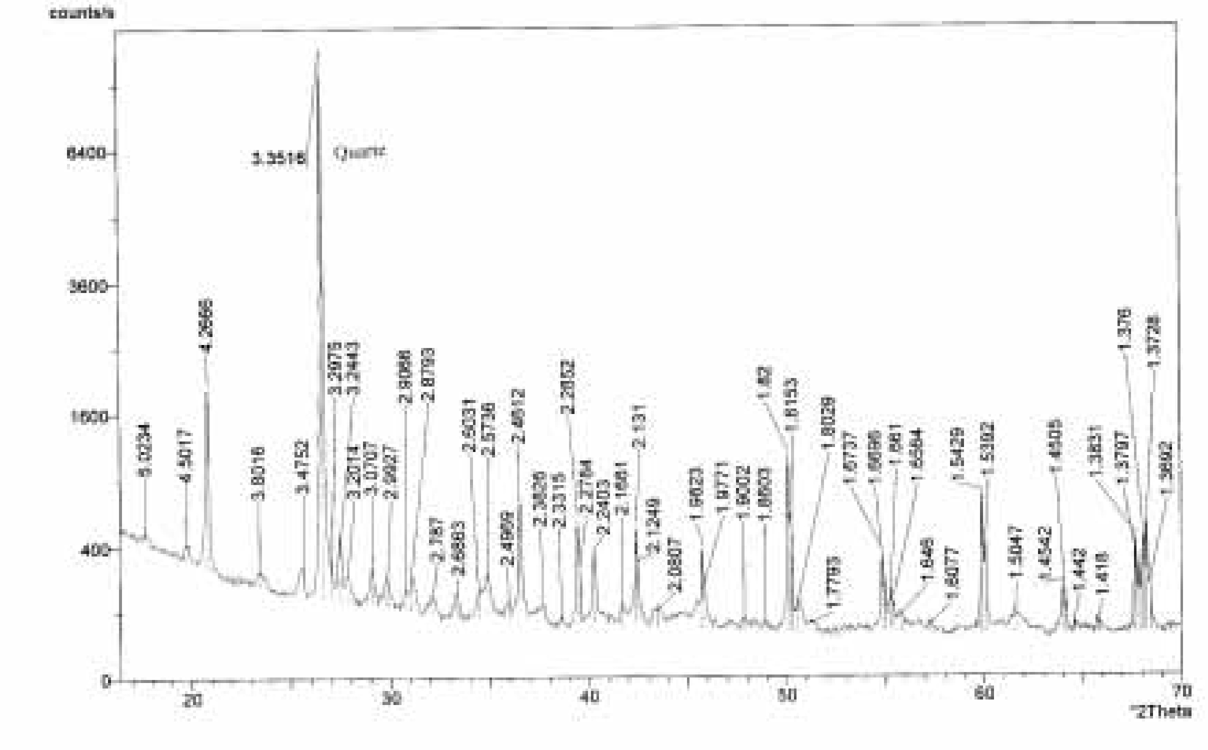


FIG. 10. X-ray diffraction diagram of conventional tailing sludge, 2#, Mn content: 0.4%.

1. The effluent pH of the air aeration to produce hydrated manganese hydroxide to adsorb radium and remove other harmful elements must be adjusted to about 11 by lime milk. Manganese ion concentration in effluent between 100–300 mg/l can meet the requirement to remove the radium. The contents of manganese depend on the amount of radium in original effluent and other impurities.
2. The longer the air aeration time, the better the result for radium removal because as aeration time increases, production rate of hydrated manganese hydroxide is raised. Normally 30 minutes of air aeration time can meet the requirement.
3. Impurity elements of aluminum, silicon, and magnesium have a great effect on the lime precipitation-air aeration-hydrated manganese hydroxide to process acidic uranium effluent. This is a big disadvantage. If higher contents of these elements exist in effluent, longer time for clarification is needed or two steps are required. First step to remove the impurity from the effluent by lime adjusting pH to 8, second step to remove radium by air aeration at pH about 11.
4. The longer clarification time benefits the effluent process. The clarification time is related to impurity levels in the effluent. For low concentrations of aluminum, silicon and magnesium in effluent, 1~5 hours can meet the requirement. For higher concentrations, the clarification time may be as long as 8–9 days.
5. Under the experimental conditions, the radium adsorption by hydrated manganese hydroxide sludge produced with lime precipitation-air aeration process is stable. There is no obvious release of radium from the sludge. If the processed alkaline effluent is stored in a tailings dam, there is no need to neutralize the effluent. It will be neutralized by adsorbing CO_2 from the air. This will save reagent cost.
6. pH has a great influence on the adsorption of radium by the hydrated manganese hydroxide complex. The adsorption pH choice can be between 6.5 and 9. At this effluent pH, the adsorption residence time can be 5 minutes. Also, the hydrated manganese

hydroxide complex shows good re-adsorption ability at radium removal in uranium effluent.

7. Compared with neutralizing effluent without aeration and the barium chloride process at pH 5,8, and 11, removal of radium from uranium effluent by air aeration hydrated manganese hydroxide adsorption can effectively remove radium from effluent. Of course, neutralizing by lime and barium chloride deposit is effective too. The higher the pH of the effluent, the longer the time for settling.

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Remediation options and the importance of water treatment at former uranium production sites in eastern Germany

G. Kiessig, R. Gatzweiler, A.T. Jakubick

WISMUT GmbH, Chemnitz,
Germany

Abstract. The WISMUT remediation project in the States of Saxony and Thuringia, Germany, comprises several mine and mill sites including large volumes of production residues. Due to the climate, the intensive land use and the regulatory conditions, the water path is most important in evaluating remediation options. Water treatment is an integral part of mine flooding, mine dump and tailings remediation and treatment costs represent a major portion of the overall costs of the project. Uncertainties in the estimations of quantities of mine and seepage waters, variations in quality from site to site and changing conditions in time demand a strategic approach to the selection and optimisation of water treatment methods. The paper describes options taken and experience gained including efforts to limit long-term treatment costs by developing and applying passive treatment systems and negotiating reasonable discharge limits.

1. Introduction

The remediation of the Wismut sites and objects is reached through a range of stabilization measures such as mine flooding, reshaping and covering of waste rock dumps, pit backfilling and in situ consolidation of the tailings ponds. The goal of these measures is not the complete stoppage of the release of all contaminants and dissolved salts but the reduction of the loading to fall within the natural assimilative capacity of the surrounding environment [1].

2. Sources of contaminated water at WISMUT

2.1. Discharge from flooded mines

Contaminated mine water discharge occurs or is expected at the sites of Poehla, Aue, Ronneburg, Koenigstein and Gittersee. The mine volumes range from 1 to 40 million m^3 and discharge rates can be as low as 20 m^3/h (Poehla) or as high as 1000 m^3/h (Aue).

Quality of mine waters is determined by solubility of the minerals in the ore body and by chemical changes due to oxidation of the exposed ore and wall rock. Furthermore, the mining method employed during production influences the mine water quality. A particular case is the Koenigstein mine where underground sulphuric acid in situ leaching was used for uranium extraction.

A more or less continuous decrease of the contaminant concentration is expected with time. The high contamination in the mine water discharge is likely to endure for 5 to 25 years depending on the specific site conditions.

2.2. Tailings ponds seepage

Because of the decision to follow a dry tailings remediation option, the supernatant water of the tailings ponds and the seepage from the tailings deposits have to be treated before discharge into the nearby streams.

Tailings pond waters arise at two sites:

Helmsdorf and Seelingstädt

The volumes of water being generated amount to 1 to 10 million m^3. The rate at Helmsdorf is approx. 250 m^3/h.

The water quality is determined by the technology used during processing of the ore.

The concentration of contaminants in the tailings pond water changes with time as the water is continuously diluted by precipitation, the portion of the supernatant water decreases and the portion of the pore water from the tailings deposit increases.

It is expected that the water discharge from the tailings ponds (both supernatant and pore water released during consolidation) will continue for 15 to 20 years.

2.3. Waste rock dump seepage

The seepage rates from the rock dumps are relatively small, typically amounting to 1 to 30 m^3/h. The water quality of the seepage is determined by the mineral content and solution processes in the waste rock, e.g. in case of the waste rock dumps in Aue the characteristic contaminants are U and As, in case of the Beerwalde waste rock dump at the Ronneburg site they are U, Mg and high sulphate and carbonates contents.

The time dependent decrease of the contaminant concentration in the seepage can range from several years (in case of the Luchsbachhalde waste rock dump at the Poehla site) to decades such as is likely to be expected for the Beerwalde dump.

3. Boundary conditions for remediation of the water pathway

3.1. Climatic conditions: precipitation

All sources of contaminated water within WISMUT are fed:

- by direct infiltration (tailings and waste rock dumps) or
- indirectly by combined infiltration and ground water inflow (mines).

The climatic conditions of the individual sites vary due to elevation (Ronneburg site 280 m NN, Poehla site 570 m NN) and geomorphology.

Regionally, average annual precipitations range from about 600 mm/a (Ronneburg site) to 800 mm/a (Aue site).

The evaluation of the hydrological influences on the object at individual Wismut sites must consider the available precipitation records over a time period of 50 to 100 years. Variations of the average on a site within this time period are substantial.

For the Ronneburg site e.g. the precipitation ranges from approximately 400 mm/a to 1000 mm/a.

3.2. Land use and population density

All WISMUT sources of contaminated water are situated in areas of high population density; Saxony has a population density of 247 persons per km^2 and Thuringia 154 persons per km^2. The land in the immediate vicinity of the sources is intensively used for agricultural purposes. Furthermore, the most extensive WISMUT tailings management facility, the Helmsdorf tailings pond is located directly above a small community, Oberrothenbach. The Oberrothenbach stream which feeds from the tailings pond runs across the community.

3.3. Regulatory framework

The mine waters and seepage from the WISMUT sites cannot be freely discharged into the close-by surface waters because of the radioactive components in the water (U and Ra) and chemical contaminants such as As, Fe, Mn which are usually above the regulated limits. Of regulatory concern are also other components common in the water of the Ronneburg remediation site such as Mg and Ca along with sulphides, chlorides and carbonates causing an excessive hardness of the water.

The treatment of the WISMUT waters is required by both radiation and water protection legislation. Not all waters arising in the course of remediation are considered as wastewater according to the water protection act. Because, there are no special regulations for remediation of uranium mines in Germany, the regulatory authorities base the permitted limits on comparison with other relevant industries. The aim hereby is to protect the overall aquatic population and to protect the drinking water supplies. Based on such considerations and availability of the technologies for achievement of the stipulated limits, the specifications needed for planning of the water treatment plants are formulated.

Unlike the water protection act, the radiation dose evaluations of a direct discharge have to be supplemented by considerations concerning potential long-term accumulation along with consideration of the indirect effects.

From the point of view of the boundary conditions, it is specifically sought to prevent the public from drinking the radioactively contaminated water, avoid accumulation of contaminants in weirs and sediments in the receiving streams or in flood plains.

Consideration is given to water consuming industries, such as water suppliers and paper mills. The radiation and health protection of the plant personnel is part of securing the reliable operation of the treatment plant.

The minimisation of the residues including immobilisation technology and safe storage of residues are demanded as well.

4. Economics of the water treatment

The economic evaluation at WISMUT considers total costs resulting from water treatment, i.e. the costs for the entire length of treatment are taken into account and the costs for residue immobilization and disposal are included.

Typical investment costs for the implemented and/or planned water treatment plants under the conditions of WISMUT are in the range from DM 15 to 30 million.

Operational costs experienced at the treatment plants vary from DM 1.75/m^3 in Aue to DM 8.32/m^3 in Helmsdorf. For the future plants at Ronneburg, Seelingstädt and Königstein the operational costs are expected to be in the range of 1.50 DM/m^3.

Costs of water treatment, including conditioning and disposal of residues are dominated by labour costs (for throughputs in the order of several cubic metres/hour) and by chemical costs for throughputs in excess of 200 m^3/h. Because neither the required personnel nor the dosage of the chemicals in the plant can be decreased below a threshold level, the expected continuous decrease of the contaminants in the mine water means that while the plant throughput remains constant, the costs for removal of a unit of contaminant will continuously increase. For small throughputs or low contaminant concentrations, labour costs, specific consumption of chemicals and energy costs can only be reduced to a threshold value. For example, in case of the Poehla plant which had to accommodate a drop in throughput from 80 to 17 m^3/h due to changes in the source, the specific costs of treatment increased from 4.40 to 8.32 DM/m^3.

Because the long-term trend in water quality development at the WISMUT sites is toward decreasing contamination loads, the operation of conventional water treatment technologies is likely to face a similar increase in specific costs.

Due to the long-term nature of treatment needs, water treatment costs are dominated by the post-remediation operation of the plant and associated residue management.

In the diagram below (Fig. 1), the time dependent development of the contamination load and selection of the appropriate treatment technology are shown in dependence from the regulatory limits. The diagram demonstrates that there is a considerable time span over which compliance with regulatory requirements would lead to economically inefficient water treatment if the conventional treatment plants were to remain in operation. The conclusion must be drawn that in the long term a technology switch from conventional to alternative treatment methods must be foreseen [1].

The significance of a well thought out approach to water treatment and timely adjustment to changing conditions becomes obvious from the fact that the portion of the water treatment costs in the overall WISMUT reclamation costs amounts to approx. 15% [2].

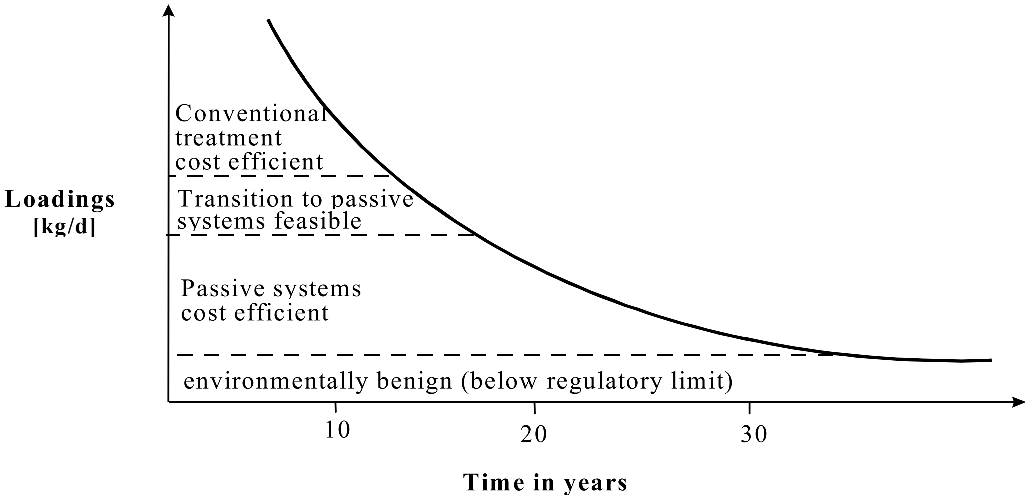


FIG. 1. Water treatment strategy as a function of contaminant loadings and time.

5. Development and selection of water treatment strategies

Under consideration of “Boundary Conditions for Remediation of the Water Pathway” an optimal solution is sought in regard to an appropriate capacity of the plant, capital investment, technology and operational costs.

The first question asked when considering water treatment is whether water treatment under site-specific conditions is justified, i. e. requirements and regulated limits from another site are not followed blindly but reconsidered whether reasonable at the new site.

In cases where water treatment is reasonable and site specifically justified, an optimised technological approach is sought for the contaminant concentrations in the discharge, while considering an adequate safety margin concerning fluctuations and future developments of the source.

The formal decision-making process uses risk assessment and multi-attribute analysis within a deterministic or probabilistic approach. During the strategy formulation and decision making process, a close contact is maintained with the regulating agencies to keep them informed and receive feedback.

The main role of the conventional water treatment in mining/rehabilitation operations is seen in treatment of effluents with peak contamination which are characteristic of the initial and early post-remediation stages. The hydrologic characteristics of the waters draining from the mining sites before and shortly after remedial action show residence times in the order of several days and wide fluctuations of the characteristics which must be met by the selected treatment technology. Because of the changes in quality and volume it is, however, essential to modify the plant operation based on the operational experience of the first year after commissioning of water treatment plants and follow-up with an optimization plan for long-term adjustments to these changes.

Besides requesting low treatment costs, therefore, the following specifications - which may vary from site to site - have to be incorporated at the plant design stage to allow later optimisation:

(a) The plant must be designed to accommodate large fluctuations of throughput and feed water quality

The assessment of the amount of water infiltrating into a mine is subject to major uncertainties at the beginning of and during the flooding process. The same applies to the predictions of quality of mine water and waste pile seepage. The stability of the treatment process relative to fluctuating conditions and flexibility to volume changes of the feed are a decisive criterion.

(b) Residue generation must be small

Residue minimisation follows from the need for cost and risk minimisation. On-site residue disposal must be ensured for the duration of the anticipated operation of the plant. Off-site disposal is not licensable in Germany and is an important cost factor everywhere. The decision-making strategy, therefore, includes besides the choice of the location of the plant, the availability of on site disposal possibilities for the residues.

(c) Possibility of switching to low maintenance and self-regulating systems should be considered

If a long-term need for water treatment is anticipated, e.g. for seepage from waste rock piles, preference is given to technologies that operate reliably with minimum input and control. This requirement stems from the previously described fact that at reduced loadings and flows, the operation of conventional treatment plants becomes uneconomic.

6. Water treatment plants of WISMUT

On all sites listed under “Sources of contaminated water at Wismut”, conventional water treatment plants are operated or presently planned. The treatment technology implemented at each site depends on the chemical composition of the contaminated discharges arising locally. In the following the technological solutions of water treatment used at the Helmsdorf and Aue sites are discussed.

The selected cases range from a complex treatment process at Helmsdorf, where due to the high carbonate and bicarbonate concentration a sophisticated treatment technology had to be implemented to the case of Aue, where the contaminant removal is achieved by relatively simple selective precipitation.

6.1. Water treatment at the Helmsdorf tailings pond

There were 74 million t of U ore processed at the Crossen plant between 1950 and 1989. Most of the tailings came to be deposited in the Helmsdorf tailings pond having a surface of 200 ha (480 acres) which makes it one of the largest Wismut tailings ponds.

At the time of closure the pond contained approximately 48.9 million t of radioactive tailings, approximately 6 million m^3 supernatant water and 22 million m^3 water in the pores of the tailings deposit. In addition, approximately 0.3 million m^3 per year of seepage is collected and returned into the tailings pond.

The Helmsdorf tailings pond water reflects the process water from the soda-alkaline extraction process employed at the Crossen plant. The typical chemical composition of the tailings water is shown in Tables 1 and 2.

Table I. Uranium-, radium- and arsenic load of the supernatant, pore and seepage waters of the Helmsdorf tailings pond (main components)

Components	Unit	Concentration			Discharge limit
		Supernatant water	Pore water	Seepage water	
U_{nat}	mg/l	8.0	2.0 – 30	10	0.5
Ra-226	mBq/l	400	500 – 2000	230	200
As	mg/l	55	< 6	2	0.3

Table II. Neutral salt load and pH of the supernatant and pore water of the Helmsdorf tailings pond (main components)

Components	Unit	Concentration	
		Supernatant water	Pore water
SO_4^{2-}	mg/l	4 300	1000 – 10 000
Cl^-	mg/l	1 300	100 – 2000
CO_3^{2-}	mg/l	1 500	< 2000
HCO_3^-	mg/l	1 900	300 – 4000
pH-	---	9.8	7.5 – 9.5

Based on a large scale laboratory investigation program more than 30 technological options for water treatment were considered and the selected water treatment process was verified in a pilot scale experiment.

The adopted technological process is presented in a simplified form in the schematic in Figure 2.

The concept involves the filtration of the contaminated water followed by removal of uranium on an ion exchange resin. For elution of the loaded ion exchange resin a NaCl solution is used. Subsequently, the uranium-loaded eluant is enriched in a follow-up membrane filtration step. In a final step the concentrate is immobilised, the main portion of the eluant from the permeate regained and reused.

The uranium free effluent after the ion exchange is treated in a precipitation step to remove the radium and arsenic content. The separation of the precipitate is achieved by flotation and dewatering of the precipitate by decantation.

The conditioning of the iron-arsenate sludges is achieved by unslaked fly ash and cement. The blending is in a continuously working high efficiency mixer which feeds the mix onto a slow moving conveyer belt and into a container truck. The filling of the container on the truck and transportation to the disposal site in a designated section of the tailings impoundment takes approximately 2 hours.

The conditioned residues are deposited on the tailings surface and covered by earth which is compacted. Each layer of residue is covered by a layer of soil before the next layer is placed, finally creating a dump which is laid out to fit into the planned final shape of the rehabilitated tailings pond.

The immobilisation of the uranium-loaded solution is done by mixing with cement and coal ash containing free lime. A fluid consistency mix is prepared in batches and transported by a slurry pump through a pipeline to small paddies prepared on the surface of the tailings deposit in a segment of the impoundment approximately 600 m from the treatment plant. The hardening of the mix takes place in the prepared paddies. Immediately upon hardening of the mix, a layer of gravel is placed to prevent suspension of dust from the surface of the immobilised waste product.

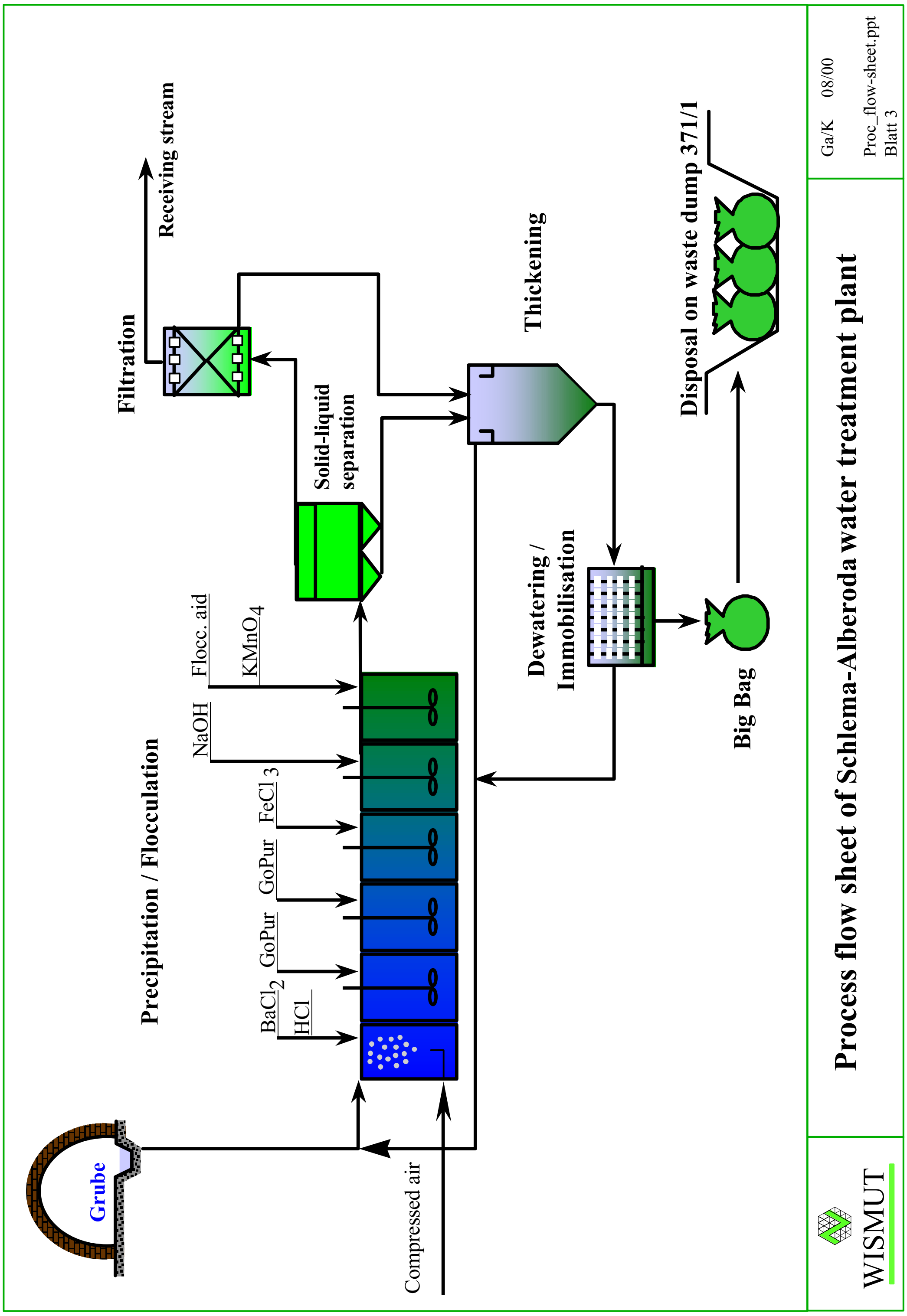


FIG. 2. Process flow sheet of Schlema-Alberoda water treatment plant.

The water treatment plant of Helmsdorf was commissioned in June 1995. Since then approximately 8 million m^3 of tailings pond water have been treated at Helmsdorf while maintaining the set regulatory limits (Table 1) at all times and discharging the treated water into the Zwickauer Mulde river in a controlled manner.

6.2. Treatment of the Schlema-Alberoda mine water

The flooding of the Schlema-Alberoda mine at the Aue site started in 1991.

Mine workings extend to a depth of approximately 1800 m. The floodable mine volume is in the order of ca. 37 million m^3. To date, about 90% of the mine voids are already flooded.

In the absence of flood control, flood waters are anticipated to flow out at the surface in about one year from now.

In order to minimise flood-related geomechanical impacts on mine stability and to implement and complete backfilling of near-surface mine workings, suspension of the flood process became necessary. As a consequence, a water treatment plant of 450 m^3/h was put on stream in 1998.

The current phase of the flooding process makes it clear that, depending on the rate of precipitation, the water infiltrating into the mine is in the order of between 500 and 1000 m^3/h. This volume is significantly higher than initial forecast indications. As a consequence, the currently available water treatment capacity is being increased to 1000 m^3/h by the construction of a second treatment line.

The contaminated mine water quality is indicated in Table 3. The values show that the mine water cannot be discharged without previous treatment.

Table III. Contaminant loading of the Schlema-Alberoda mine water (main components, average values in the 1st half of 2000) and the permitted discharge concentrations of the water treatment plant

Component	Unit	Concentration	Discharge value
U_{nat}	mg/l	7.2	0.5
Ra-226	mBq/l	3800	400
As	mg/l	2.0	0.3
Fe	mg/l	11.3	2.0
Mn	mg/l	5.9	2.0
SO_4	mg/l	2000	2500

The removal of the contaminants from the water is achieved by selective precipitation/flocculation.

The simplified process schematic of the plant is shown in Figure 3. The water in need of treatment passes through a treatment basin with several compartments.

WISMUT

Water treatment at rehabilitation sites of WISMUT GmbH

Process flow sheet water treatment at Helmsdorf site

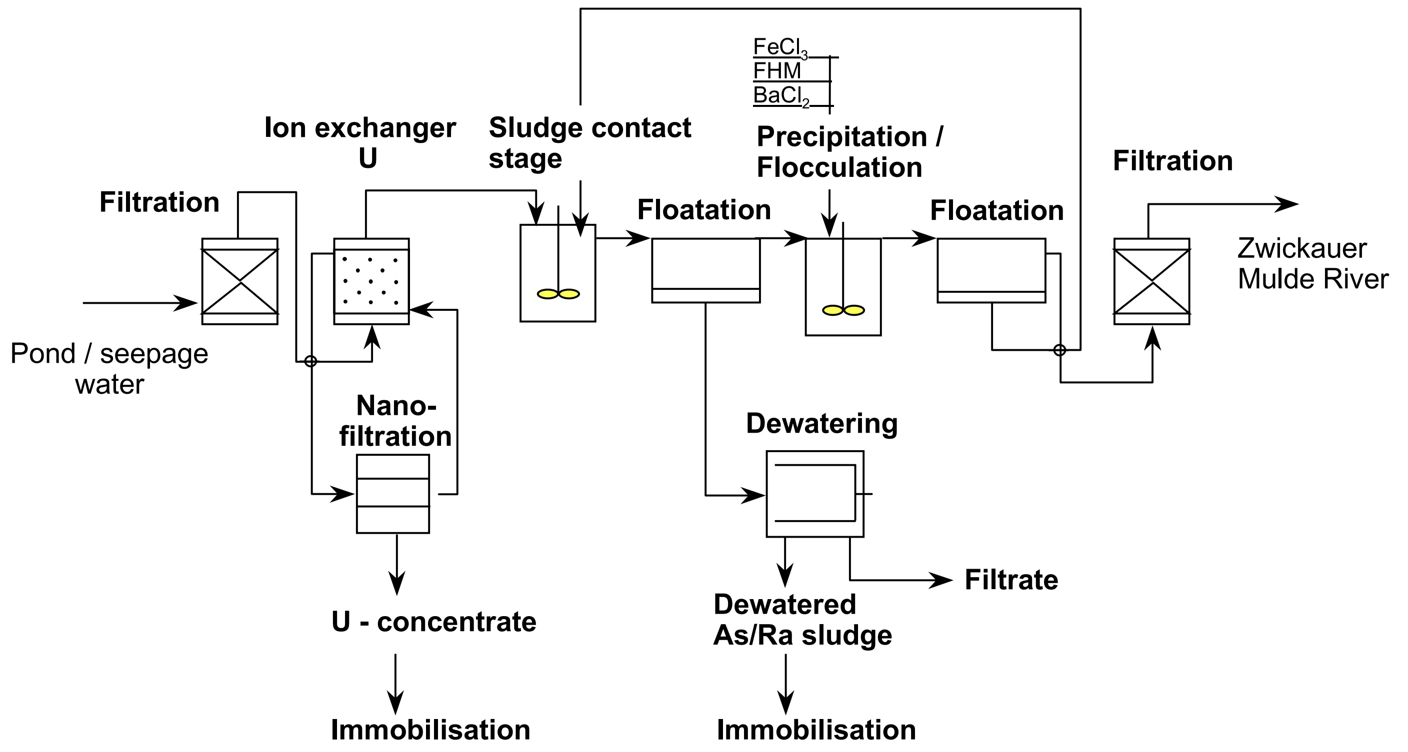


FIG. 3. *Water treatment at rehabilitation sites of WISMUT GmbH. Process flow sheet water treatment at Helmsdorf site.*

Uranium in the flood water occurs as a carbonate complex.

In the first chamber, HCl is added to adjust acidity to pH = 3.5 and air is injected. As a result, the carbonate complex is destroyed. Simultaneously, a $BaCl_2$ solution is added for Ra separation. The radium separates as a mixed $BaSO_4$ co-precipitate.

In the second and third chamber, uranium separation occurs at pH 5.8. By adding dissolved polymer (GoPur 3000), flocculation is affected and the uranium removed selectively.

In laboratory studies, maximum loading capacity of GoPur 3000 was 600 mg uranium per g of polymer applied.

In the following fourth chamber, an $FeCl_3$ solution is added thus affecting the precipitation of the iron hydroxides to which the ions of arsenic become attached.

In the fifth chamber, NaOH is applied to raise pH to 7.5. Simultaneously, a $KMnO_4$ solution is added for Mn separation.

By adding a flocculant, the particles present in the solution are aggregated to create macroflocculi which segregate by sedimentation. After a filtration stage the treated water is discharged into the stream.

The sludges are periodically removed from the settlement basin, pre-thickened and mechanically dewatered by a filter press. Specific sludge generation is about 115 g dry residue per cubic metre of treated water.

The dewatered slurry with a solid content of approximately 35% is mixed with cement to form mortar which is then cast into square blocks of about 1 m^3 for curing.

Once immobilised, the blocks are then disposed in an engineered section of a mine dump.

The water treatment concept in this case is relatively simple and no difficulties with process instrumentation and control have been encountered during operation.

The process and the plant proved to be capable of satisfying the regulatory requirements (Table 3) over a considerable range of throughput volumes and a wide range of fluctuations of the feed water quality.

7. Long-term solutions for water treatment

International experience with operating wetlands suggests that wetlands could reduce construction, monitoring and annual operating costs for water treatment by one order of magnitude, however, there are no reliable costs available on long-term maintenance. Even less hard data are available regarding handling and disposal of the loaded organic matter from the wetlands.

To decrease the long-term costs of water treatment, the feasibility of alternative technologies at the Wismut sites was evaluated. The potential uses of innovative cost efficient technologies were identified in:

- the replacement of conventional treatment plants which become inefficient due to the decrease of the contaminant load in the feed water, such as the mine waters;
- the treatment of low volume streams exhibiting an unchanged level of contamination over long periods of time such as in case of seepage from waste rock dumps and tailings ponds which would require a separate conventional treatment leading to high specific costs dominated by labour costs, as well as
- the in situ remediation of ground water contaminated by seepage from the waste rock dumps, tailings ponds or mine waters.

Following the success of alternative water treatment methods at numerous sites, it was decided to test the alternative methods for removal of radioactive and metallic contaminants from the discharges typical for the Wismut remediation programme.

The passive water treatment systems are presently in the stage of technology development and pilot scale field testing. The required developmental effort in this area was well represented by the large number of contributions at the WISMUT'97 Workshop on "Water Treatment and Residues Management - Conventional and Innovative Solutions" (1).

Using the international experience, Wismut in co-operation with external partners is testing the feasibility of the following passive-biological technologies for treatment of mine, ground and surface water:

- Constructed wetland,
- Reactive permeable walls,
- In-situ removal of contaminants by microorganisms.

The completed and ongoing lab scale and pilot scale tests are described below.

7.1. Pilot scale test of a passive/biological treatment of the Poehla-Tellerhäuser mine water in a constructed wetland

The Poehla site comprises the relatively small Poehla-Tellerhäuser mine which has a flooding capacity of 1 million m^3. In the course of 1995, contaminated flood water reached the level of natural overflow to the surface.

On average, flood water is in the order of 17 m^3/h.

Therefore, a conventional water treatment plant was commissioned in 1995 to separate U, Ra, As, Fe, and Mn from flood waters. This plant uses the same technology that is used for the treatment of flood waters from the Schlema-Alberoda mine (cf. Section 6.2).

Table 4 shows the development of relevant contaminant concentrations in the flood water from 1995 through 2000.

The requirement to treat the overflowing mine water (removal of radium and arsenic) is ongoing, and based on geochemical modelling, it is predicted to last approx. 20 years.

A closer look at the development of the water quality at the Poehla site indicates the need for a long-term optimisation strategy.

Table IV. Contaminant loading of the Poehla-Tellerhäuser mine water (main components, average values in the 2nd half of 1995 and in the 1st half of 2000) and the permitted discharge concentrations of the water treatment plant

Component	Unit	Concentration		Discharge value
		2nd half of 1995	1st half of 2000	
U_{nat}	mg/l	1.6	0.1	0.2
Ra-226	mBq/l	1 400	4 650	300
As	mg/l	0.9	2.3	0.1
Fe	mg/l	17	9.3	2.0
Mn	mg/l	3.7	0.7	2.0
SO_4	mg/l	140	5	200

In Summer 1998, the first constructed wetland of Wismut was put into experimental operation, treating a partial stream of the Poehla-Tellerhäuser mine water overflow. The lay-out of the constructed wetland is in Figure 4.

The constructed wetland was placed into a former retention basin. The basin was subdivided by concrete walls into five compartments creating the environment for the various reactions and various chemical/physical and biological efficiencies required at each stage. Since early 2000, an aeration cascade is in operation at the front end of the system.

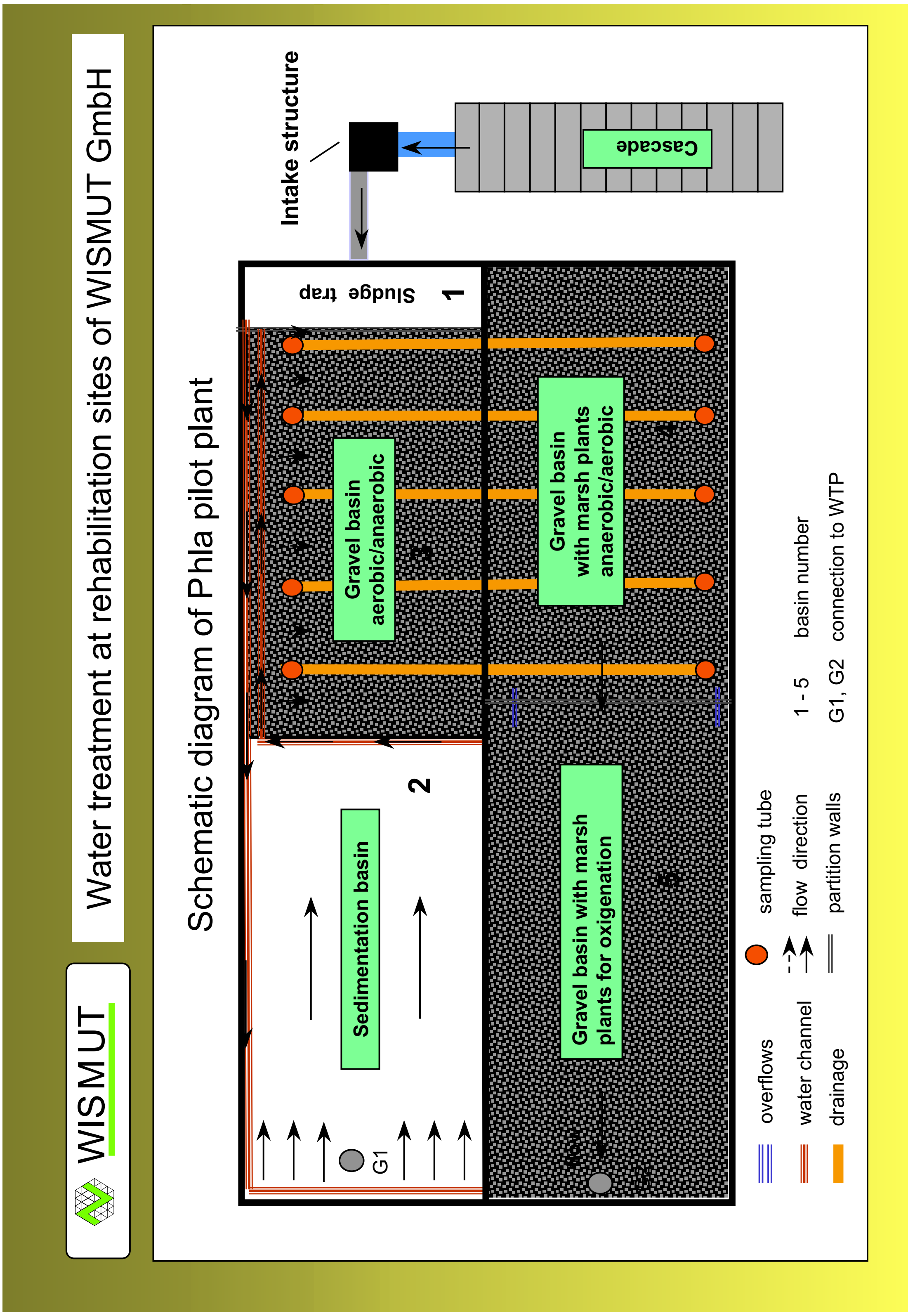
The water movement is achieved by an overall gradient across the system realised by the arrangement of overflows and base drainage between the compartments.

In the first compartment the oxidation of Fe(II) and the subsequent precipitation of iron hydroxide takes place followed by sedimentation of the precipitate. The iron precipitation is accompanied by adsorption of arsenic and radium.

Then the mine water passes through two compartments with gravel filters having different grading. The material serves both as filter and provides a surface for establishment of micro-organism populations. To promote the growth of autochthonous micro-organisms, nutrients were built into the compartments. The biomass can act either as a sorption agent for radium and uranium or as a catalyst for initiation of precipitation. Depending on the environmental conditions in the compartments, whether aerobic or anaerobic, other chemical reactions of contaminant separation become effective.

The last process step of the constructed wetland system is a finishing compartment. The compartment is filled with compost like matter and gravel on which helophytes are planted. The prime aim is to raise the oxygen content in the compartment. In addition, the plants and the microorganisms in the root zone of the helophytes remove the remaining contaminants.

The present throughput through the constructed wetland is 3.5 m^3/h.


Water treatment at rehabilitation sites of WISMUT GmbH

Schematic diagram of Phla pilot plant

FIG. 4. Water treatment at rehabilitation sites of WISMUT GmbH. Schematic diagram of Pöhla pilot plant.

The two years test period, demonstrated that the wetland can be successfully used for removal of the relevant contaminants at this site. Pilot wetland functioned dependably and showed a stable performance. The average removal rate in 1999 was:

Radium	approx.	73%
Iron	approx.	97%
Arsenic	approx.	83%

The overall goal is to identify the optimal operational conditions in the wetland so that the conventional treatment plant at the site can be phased out and replaced by a passive/biological treatment facility by 2002.

The commissioning of a pilot scale test of passive/biological treatment of neutral, sulphate rich seepage water from waste rock dumps at the Ronneburg site is also planned.

7.2. Application of permeable reactive walls for downstream treatment of the contaminated seepage from a tailings pond

A series of development projects to test the applicability of permeable reactive walls for ground water remediation were initiated and funded by the Federal Ministry of Technology. We are expecting that these projects will create the necessary conditions for the specific use of this technology for long-term treatment of contaminated water from the remediated tailings ponds.

The seepage from the tailings ponds is contaminated mainly by uranium, radium and arsenic. Presently, the captured seepage is treated by conventional methods jointly with the supernatant water from the tailings pond. The availability of this treatment method is limited to the period until the remediation of the tailings pond progresses to a stage where no more supernatant water is available. Beyond this stage, a pump and treat concept would be required to deal with the continuously escaping seepage water. In view of the high specific costs of the water treatment at the Helmsdorf site (approximately 8 DM/m^3 with the tendency to increase up to 20 DM/m^3 in the future) and of the enduring requirement to treat the seepage water (probably longer than 200 years) a cost efficient long term alternative to the Helmsdorf type of water treatment is needed for the diminished volume of the water stream in need of treatment.

A possible solution from the present day point of view is offered by use of permeable reactive walls.

The objectives of the various permeable reactive wall projects (carried out by Wismut and other relevant companies and institutions) are:

- the identification of suitable materials for the in situ removal of contaminants, such as sorption agents and suitable host materials;
- the optimisation of the removal efficiency and active lifetime of the reactive materials in laboratory and in column tests at the site of origin of the ground water;
- the modelling of the retention and transport processes in the reactive walls.

As a result of these studies, two products were developed which meet all the requirements related to the objective.

Product 1	Fine-grained heavy spar bonded in a matrix of expanded Geopolymer®,
Product 2	Product from expanding and linking of powdery titanium hydroxide with vinyl acetate adhesive.

The assembled products were crushed and sieved to produce a material with a hydraulic conductivity coefficient of > 10^{-4} m/s. These products have proven their long-term stability over a pH range from 4 to 10. Figure 5 illustrates the granularity and surface structure of the assembled materials.

FIG.5. Granulated heavy spar bonded in Geopolymer®

Results of column tests to determine the capability of products 1 and 2 compared to foamed zero valent iron for the selective separation of Uranium, Radium and Arsenic from original waters are shown in Table 5. Before breakthrough, the outlet concentrations were typically 10% of the feed. Feed concentrations were 10 mg U/l, 3 mg As/l, and 1500 mBq ^{226}Ra/l.

Table V. Column test results with regard to identification of appropriate reactive materials (extract)

Product	Contaminated groundwater Helmsdorf tailings pond		Mine water Pöhla-Tellerhäuser
	Uranium mg/kg	Arsenic mg/kg	Radium Bq/g
Foamed zero valent iron	4500	20 000	---
Product 1	---	---	85$^{1)}$
Product 2	3200	15 000	100$^{1)}$

$^{1)}$ after 350 days running

Based on the results of the tests, the specifications for the design of a prototype permeable, reactive wall for remediation of the ground water affected by uranium mining and processing will be developed.

7.3. In-situ ground water remediation by Autochthonous Micro-organisms

The US University of New Mexico was contracted by Wismut to test the applicability of microbiological treatment of contaminated ground water in situ. The tests are aimed at removal and fixation of uranium and other toxic metals directly in the ground.

The basic concept of the method is to initiate and enhance the microbiological processes underground by addition of nutrients which support the reduction of the dissolved uranium to form insoluble uraninite and affect the precipitation of dissolved toxic metals as metal sulphides.

The concept is in the stage of laboratory testing. An essential part of the tests is the demonstration that no remobilization of the fixed contaminants results when nutrients supply is suspended or environmental conditions change.

In follow-up to the laboratory tests, a concept for limited-scale field experiment will be developed.

The available results from both the permeable reactive material tests and tests of in situ use of autochthonous microbiological processes are very promising. We are optimistic that based on these advanced tests, it will be possible to develop cost efficient solutions for long term treatment of contaminated seepage from the remediated waste rock dumps and tailings ponds of Wismut.

8. Summary and Conclusions

Wismut is faced with evaluating technical and economic options for treating large volumes of contaminated water associated with tailings ponds, mine flooding and waste rock dumps. Each source of contaminated water presents unique problems demanding unique solutions. Thirty technological options were evaluated for treating tailings pond water, and those options finally selected were verified by pilot scale experiments. The resulting treatment scheme, which involves ion exchange treatment followed by immobilization of the resulting sludges has successfully treated 8 million m^3 of tailings water since commissioning of the plant in 1995. Treatment of mine waters is accomplished in a series of chambers that act in series to remove contaminants including uranium, radium, arsenic and manganese. Sludges from these chambers are immobilized and the resulting solids are disposed of in specially engineered mine dumps.

The need to employ longer-term water treatment technology has lead to evaluation of permeable reactive material and in situ use of autochthonous microbiological processes. Wismut is optimistic that based on these tests, it will be possible to develop cost effective solutions for long term treatment of contaminated seepage from remediated waste rock dumps and tailings ponds.

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Treatment of liquid effluents from uranium mines and mills during and after operation

M. Csövári, I. Benkovics, Zs. Berta, J. Éberfalvy, J. Csicsák, Zs. Lendvai

Mecsek Ore Environment Co.,
Pécs, Hungary

Abstract. Hungarian uranium mining and processing was terminated by the government decision at the end of 1997. The Hungarian government in 1997 adopted an overall remediation programme. One of the key tasks of this programme is the remediation of the two tailings ponds (TP) and ground water restoration in their surroundings, which is an important water catchment area. Calculations and estimations show that, a significant amount of different chemicals, mainly magnesium sulphate and sodium chloride, seeped into the ground water from the tailings ponds causing significant pollution of shallow and partly deeper ground water aquifers. As the aquifer is used partly (63%) for supplying with drinking water the town of Pécs, (165,000 inhabitants), appropriate measures have to be taken to protect the portable water. Environmental assessment led to the conclusion that one of the best solutions to protect the drinking water area is to cover the TP and remove the polluted shallow and regions of the near shallow groundwater, and to discharge it after treatment. In the first stage, the main task was to develop a water treatment process for the free water of the TP. This water can be characterised by high salinity (10-20 g/l TDS) and high radium-226 content (5-20 Bq/l) as well. The second step was to develop a pump and treat process for water to be removed from the surroundings of the TP with high salinity (10-18 g/l). Also it was important to make some prediction regarding the geochemical processes taking place when contaminated water passes through the soil. To develop appropriate water treatment processes physical and chemical methods have been investigated, but in the final decision a chemical process was proposed for both types of water. Also some data were obtained regarding the sorption behaviour of the soil beneath the TP. The developed water treatment processes are based on treatment with lime milk to reduce the total dissolved solids (TDS). Using this method it is expected that the TDS of removed ground water can be reduced to 5-7 g/l. For removal of radium from the free water of TP, the well-known barium chloride process was selected. As the radium concentration in ground water is very low, no special method is needed to decrease its concentration. The developed processes have been implemented and are being used by the company. Discharge limits for different components are as follows:

- U_{max} 2 mg/l
- Ra_{max} 1.1 Bq/l
- TDS_{max} 5.5 g/l

1. Development of a process for the treatment of the tailings ponds - Originating waters

1.1. Composition of the waters

In the mill operating period there was no direct water discharge because the mill and tailings ponds operated with closed water cycle. The historical data regarding the discharged process water onto the TP are presented in Figure 1. It can be seen that the TDS of process water varied over a wide range during the operating period reaching 35 g/l in the eighties but at the end of operation period it decreased to 7 g/l.

A portion of the process water remained in form of pore water in the deposited solid wastes, the residual formed the pond and of course a fraction of water left the tailings ponds. This fact is detected by the monitoring wells. The extent of the polluted area around the TP is shown in Figure 2.

The contaminated ground water has to be extracted to remediate the quality of water. The ground water extraction system consists of deep drainage and wells. The position of the drainage and wells are shown in Figure 3.

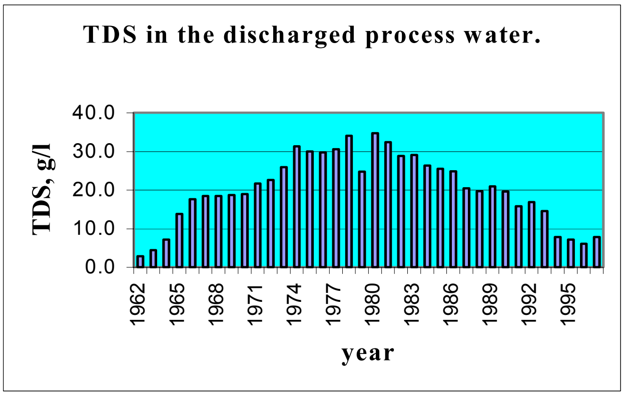

FIG. 1. TDS in the discharged process water.

It can be seen that the TDS in shallow ground water is much higher than the limit for drinking water (1 g/l). This fact has serious implications for the nearby drinking water aquifer (distance from the tailings ponds to the drinking water wells is 1 km), which is the main portable water source for town Pécs (with 165 thousand inhabitants). Because of the high contamination of groundwater, restoration measures must be undertaken. This means that contaminated groundwater must be removed from the area, to protect the drinking water aquifer.

After the termination of the mill operation, approximately 900 000 m^3 of pond water was in the two tailings ponds. Most of this water was in TP I, because this TP was used in the latest years. Prior to starting any remediation work on the TP, the pond water had to be discharged.

The composition of pond water, the seepage from dams and the contaminated groundwater are presented in the Table 1.

It can be seen that:

- The pond water has a high TDS and radium concentration but low uranium content;
- In the seepage from the dams, high TDS, low radium, but high uranium concentration is observed;
- Contaminated ground water is characterized by high TDS and low uranium and radium contents.

For the heavy metals, only the concentration of the manganese is substantial in pond water and seepage, but it is not detected in contaminated ground water. It is worth mentioning that the waters in question are not contaminated by arsenic.

Comparing the composition of pond water and the ground water, it can be seen that the ground water is less contaminated. It would appear that contaminants such as potassium, radium, manganese and uranium are sorbed by the soil particles directly or as a result of geochemical processes.

> *All three types of tailings ponds originating waters exceed the discharge limits for TDS. For pond water radium-226 is exceeded as well. Therefore all waters must be cleaned to reduce the TDS. Pond water additionally must be treated for removal of the radium.*

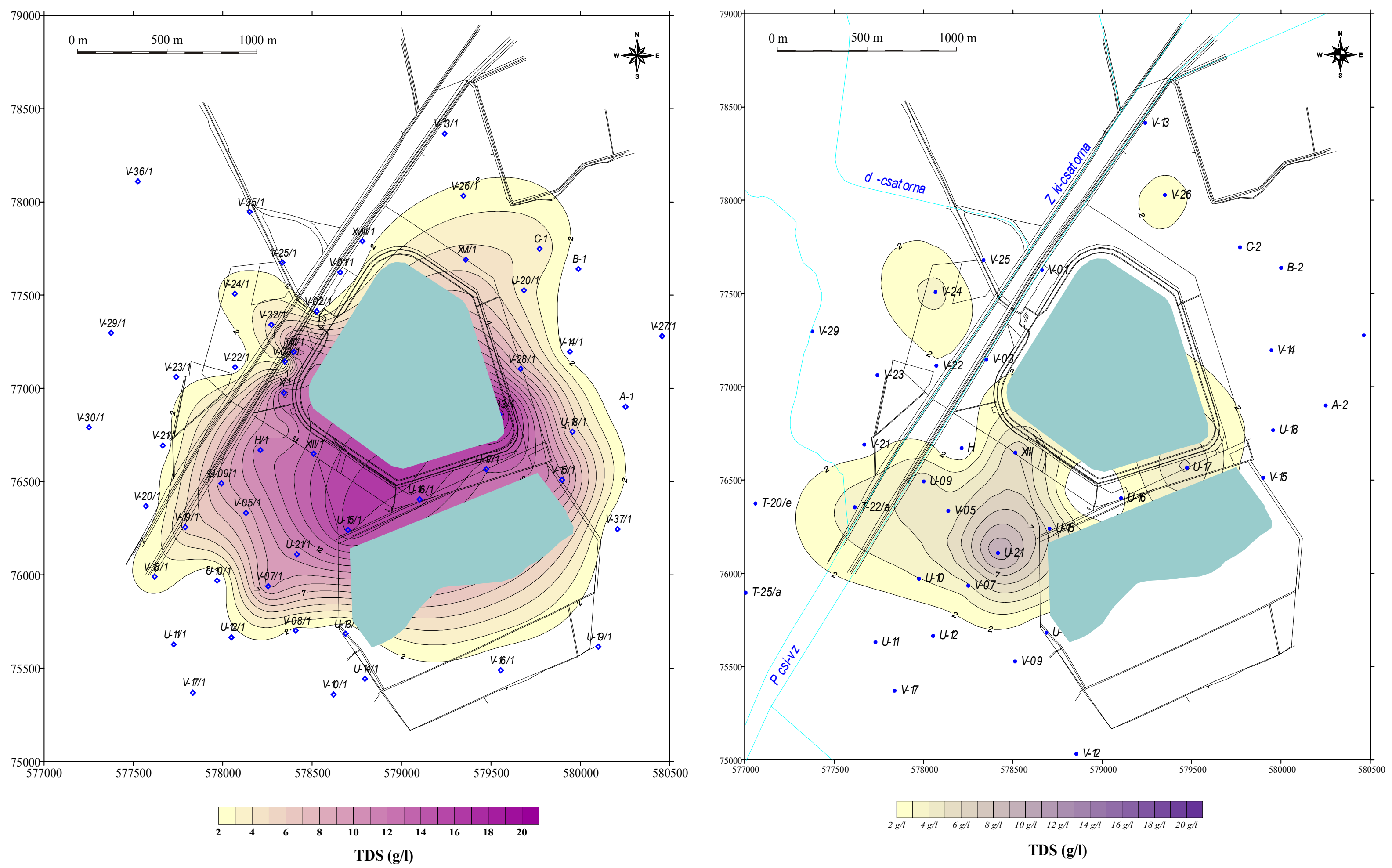

FIG. 2. Contamination around the tailing ponds.

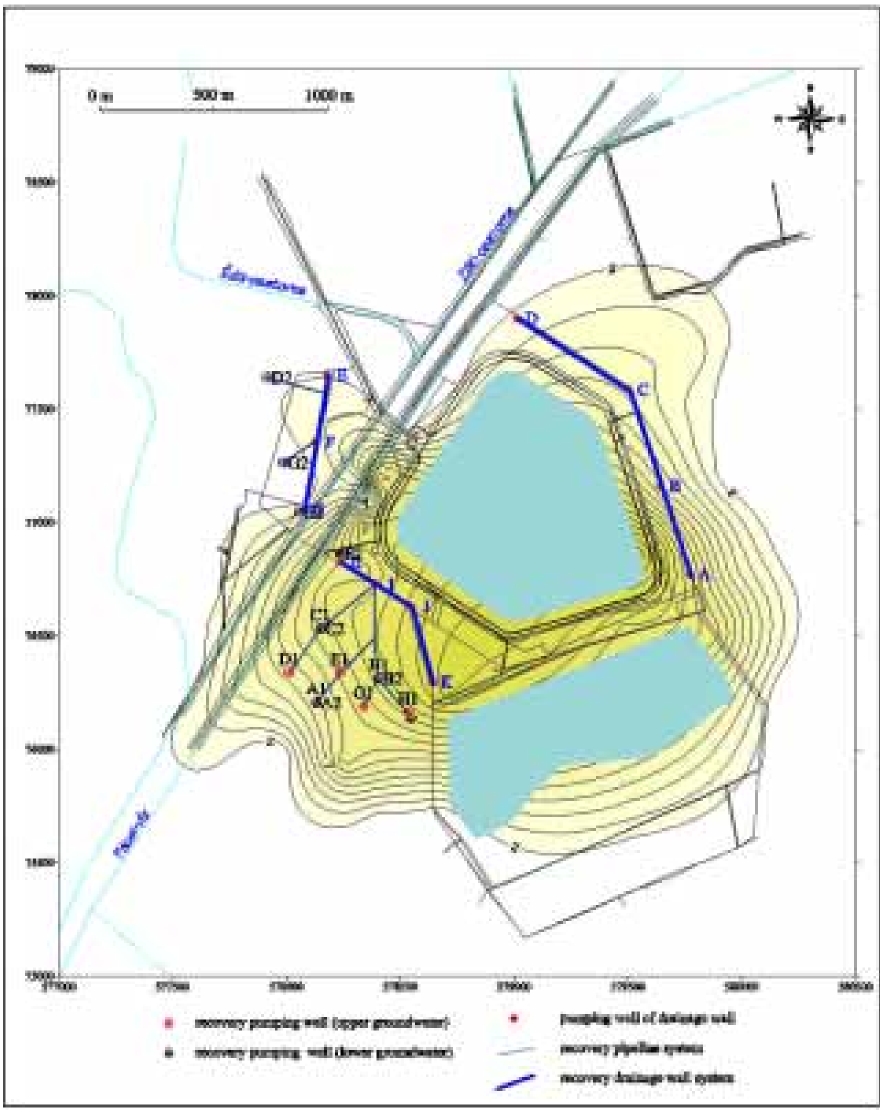

FIG. 3. Planned groundwater removal system.

1.2. Laboratory experiments

Water treatment is widely used in the mill process. The method chosen depends on the chemical composition of water to be treated. If the wastewater originates from an alkaline process, where the main pollutants are sodium sulphate or sodium bicarbonate, physical methods, such as evaporation, electro-dialysis and reverse osmosis can be used. In the case of acidic mill processes, the best method is the lime process and radium is removed by co-precipitation with barium sulphate. Of course in particular cases, special technical options are also used.

Though in general the lime process is well known, some research and development work was needed prior to building a water treatment plant or to integrating the process into an existing mill facility.

In our case, it seemed to be reasonable to carry out investigations relating to:

- the chemical process of the precipitation;
- the sedimentation and thickening process;
- the radium precipitation; and
- the solubility of the sludge from water treatment.

1.3. Chemical process

This investigation was aimed at determining the achievable composition of treated water during the lime process and the behaviour of the precipitate obtained in the process.

As the main part of magnesium is present in form of magnesium sulphate, the chemical process can be described as following:

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$$

A small portion of magnesium is present in form of magnesium chloride:

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$$

In the case of total precipitation of magnesium ions, soluble calcium chloride will be formed in the corresponding quantity. The bulk quantity of precipitate obtained will consist of magnesium hydroxide and gypsum.

It should be noted that the precipitation of gypsum is dependent on time and temperature, therefore in a real process system, the composition of the precipitate can be enriched in magnesium hydroxide. Because the process of the precipitation is extremely important from the operational point of view, this question was investigated in more detail.

1.3.1. Kinetics of the precipitation of magnesium hydroxide and gypsum

Batch experiments

In general terms, the kinetics of the precipitation of components present in water is important for designing the process. Because the main components in our case are magnesium hydroxide and calcium sulphate, the kinetic characteristics of the precipitation of these compounds was investigated.

The experiment was carried out as follows. 500 ml of seepage water from dams was neutralised with lime milk to pH ~10.7. After 30 min of mixing at 18ºC the mixture obtained was left in the reaction vessel without mixing, and in 0.5-hours time a sample was taken for assaying. Results of the measurements are presented in Figure 4.

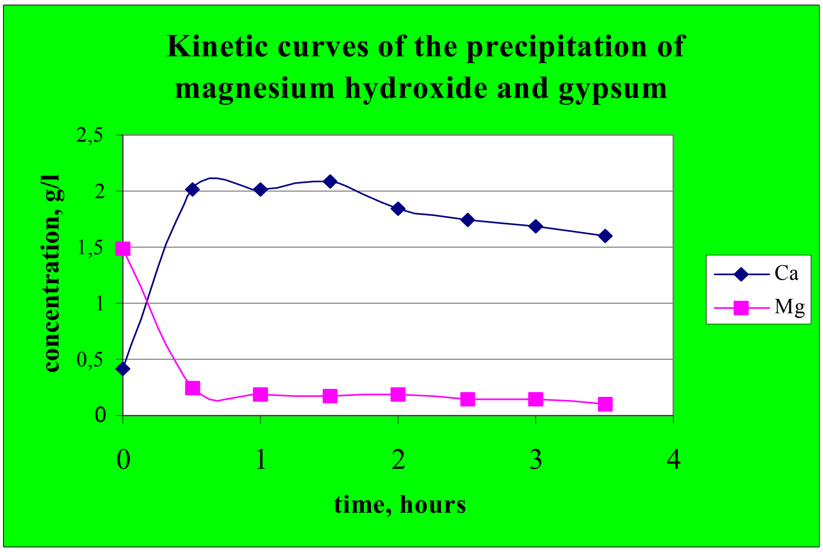

FIG. 4. Kinetic curves of the precipitation for magnesium and gypsum.

Table I. Composition of water to be treated

Type of water	Na	K	Ca	Mg	Cl	SO_4	CO_3
	mg/l						
Process water*	1100	180	550	2800	2400	12800	<10
Pond water	520	210	610	1520	2322	5632	<10
Seepage from the dams	560	133	485	2244	1489	9185	<10
Contaminated shallow ground water	741	<5	493	1608	1564	6668	<10

* average for mill operation period

Type of water	HCO_3	TDS	pH	Spec. cond.	U	Ra-226
	mg/l	g/l		microS/cm	mg/l	Bq/l
Process water*	<10	22000	7.2		**<0.5**	**5-20**
Pond water	49	14	7.2	14765	0.03	**5-20**
Seepage from the dams	159	17	7.2	12600	2-5	0.2-0.4
Contaminated shallow ground water	635	15	7.2	10550	0.01-0.04	<0.2

Type of water	Mn	NH_4	NO_3	NO_2	As
	mg/l				
Process water*	1200	<100	200		<1
Pond water	180	6	208	1.56	<1
Seepage from the dams	100	6	186	1.78	<1
Contaminated shallow ground water	0.36	n.d.	n.d.	n.d.	<0.1

It can be seen that the concentration of magnesium decreased very sharply to 0.1–0.2 g/l, but the concentration of calcium remained for the whole period of the experiment (3.5 hours) much higher (2-1.6 g/l) than the equilibrium concentration for calcium (0.7–0.8 g/l).

As it can be seen, the kinetics of the precipitation for the two main components is different. If the separation of magnesium and calcium is not required, this situation is unfavourable because a very long residence time is needed for the precipitation of gypsum (more than 4 hours).

Precipitation of the gypsum can be substantially accelerated by adding solid gypsum to the water, prior to or during the neutralisation, that is by gypsum recycle. The positive effect of the gypsum recycle is presented in Figure 5. Experimental data presented in Figure 5 show that using recycle, the precipitation rate of the gypsum is much quicker and the concentration of the calcium drops below 1 g/l in two hours.

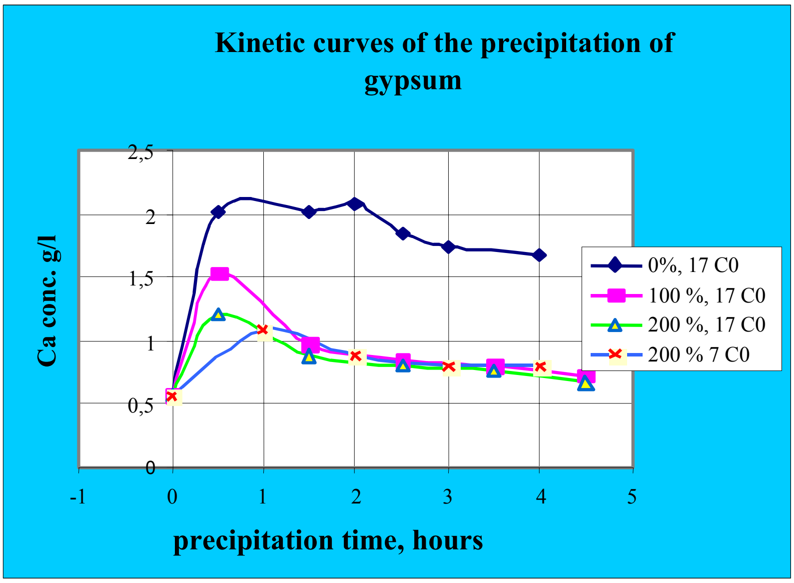

FIG. 5. Effect of the temperature and recycle for the precipitation of gypsum.

The experiments were carried out at temperatures of 17ºC and 7ºC. There was no difference between the data obtained at these two temperatures. Thus the gypsum can be precipitated much more rapidly if gypsum recycle is used. On the other hand if the separation of magnesium hydroxide and gypsum is required during the water treatment process, the recycle should be omitted.

Continuous laboratory experiment

Kinetic curves of the precipitation of gypsum were also determined in continuous laboratory experiments. The experimental set-up is shown in Figure 6.

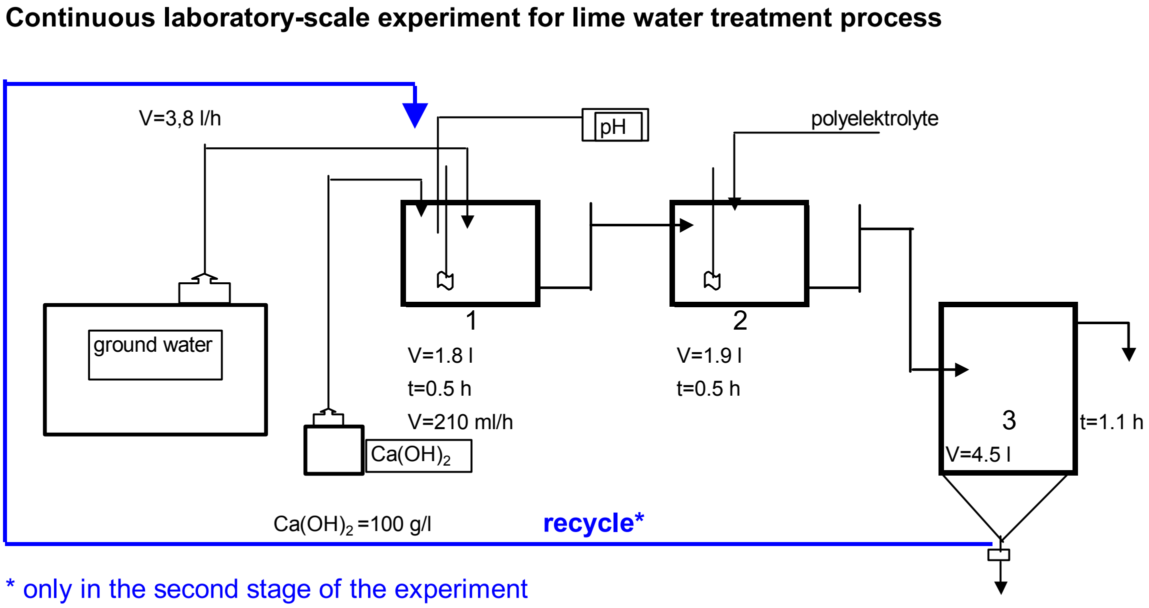

FIG. 6. The experimental set-up for continuous experiments.

The experiments using this rig aimed at proving the possibility of decreasing the TDS of the contaminated tailings ponds-originating water and undertaking more detailed investigation of the precipitation process.

Two sets of experiments were carried out, one without recycle and the other with the recycle of gypsum. The circuit operating time was the same for each experiment.

Results of the experiments are shown in Table 2. The experiment lasted 7 hours, but samples were also taken after 14 hours.

It can be seen that the calcium, in accordance with the results of batch experiments, precipitates much more effectively if recycle is used: without recycle about 1.5 g/l was measured while with recycle the concentration decreased up to 0.7g/l.

It can be seen that the TDS of the treated water can be reduced to 8.5 g/l without recycle, and with recycle to 6.5 g/l. The differences between the two data can be explained by the greater extent of precipitation of the calcium in the case of recycle.

Of course, in a real industrial process the precipitation of gypsum may differ from that obtained in a laboratory experiment, but the general conclusions will remain valid.

Table II. Results of continuous laboratory experiments

1. Without recycle

	1**			**2****			**3****			
time, h	**Ca**	**Mg**	**pH**	**Ca**	**Mg**	**pH**	**Ca**	**Mg**	**pH**	**TDS**
1	1.45	0.79	9.63	1.88	0.47	9.6	1.92	0.42	9.65	
2	2.12	0.28	9.62	1.88	0.31	9.68	2.27	0.17	9.86	9.25
3	1.9	0.1	10.23	1.87	0.24	10.23	1.53	0.28	9.44	8.15
4	1.75	0.15	10.45	1.85	0.18	10.25	1.38	0.25	9.8	
5	1.9	0.20	10.4	1.78	0.20	10.40	1.45	0.15	9.9	8.24
6	1.9	0.10	10.7	1.72	0.18	10.25	1.48	0.15	10.1	
7	1.9	0.18	10.65	1.85	0.10	10.05	1.54	0.14	10.1	8.35
After 14 h standing	1.45		9.82	1.47	0.14	9.82	1.37	0.12	9.8	7.13
Volume of the reactor	1.8 l			1.9 l			4.5 l			

2. With recycle (50-100 % for gypsum)

	1**			**2****			**3****			
time, h	**Ca**	**Mg**	**pH**	**Ca**	**Mg**	**pH**	**Ca**	**Mg**	**pH**	**TDS**
1	1.45	0.89	9.58	1.08	0.47	9.6	0.92	0.42	9.65	
2	1.32	0.25	10.52	0.88	0.31	9.68	0.72	0.17	9.86	7.25
3	1.2	0.18	10.23	0.97	0.24	10.23	0.85	0.28	9.44	
4	1.32	0.25	10.25	0.85	0.18	10.25	0.75	0.25	9.8	6.87
5	1.2	0.20	10.14	0.8	0.20	10.40	0.84	0.15	9.9	6.24
6	1.4	0.10	10.47	0.75	0.18	10.25	0.72	0.15	10.1	
7	1.2	0.18	10.65	0.75	0.10	10.05	0.86	0.14	10.1	6.05
After 14 h standing	0.85		10.21	0.77	0.24	9.92	0.74	0.19	9.7	6.13
Volume of the reactor	1.8 l			1.9 l			4.5 l			

** Number of the reactors

Composition of the contaminated ground water used in the experiments

Component	Concentration g/l
Ca	0.41
Mg	1.49
SO_4	6.84
Cl	1.42
pH	7.23
TDS	12.57

1.4. *Sedimentation and thickening process*

Sedimentation curves were determined by using 1.6-2.4 m long test tubes with diameter 24 mm.

Experimental work was initially directed at justifying the use of poly-electrolytes, to show the positive effect of the HDS-process used in some mills (Australia, Canada, Germany, etc.) on the density of the thickener underflow.

1.4.1. Effect of poly-electrolytes (PE)

It was found that a dosage of 5 ppm of PE is sufficient for sedimentation, which is illustrated in Figure 7. Without PE only 0.4 m/h sedimentation rate can be obtained, while using 5 ppm PE more than 1 m/h value can be reached in the first hour.

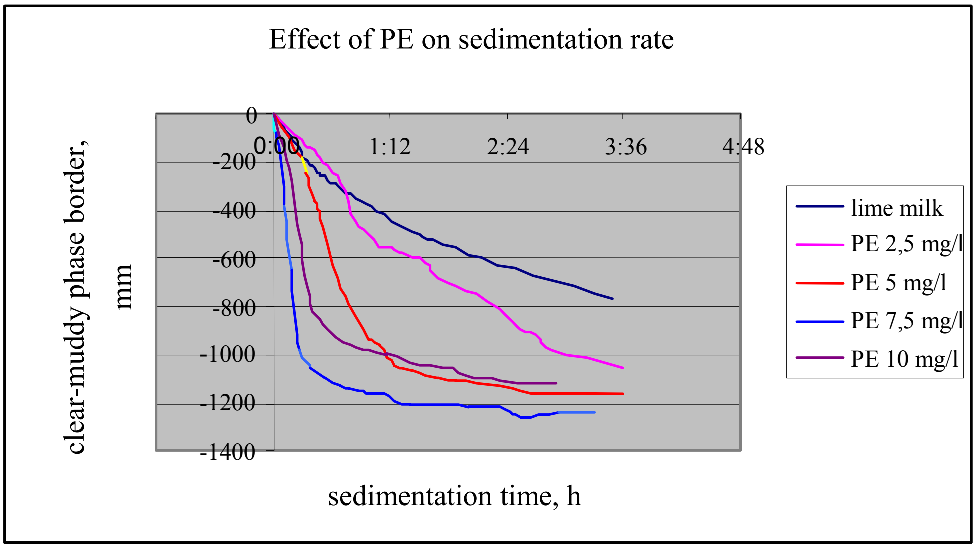

FIG. 7. Effect of the specific consumption of PE on the sedimentation rate.

On the basis of these results, it can be expected that the thickener can operate with at least a 1 m^3/m^2h specific loading.

In addition to the sedimentation rate, *the thickening* of the precipitate, i.e. the density obtained, is also a very important aspect of the operation.

In this respect one of the important questions is the influence of the recycle of the underflow on the thickener area. To answer this question laboratory batch experiments were carried in a glass tube (d=26 mm, H=170 cm), measuring different parameters. The sludge obtained in the previous experiment was added to the next portion of water and the sedimentation curve, etc. was determined again. In the experiments contaminated ground water was used.

The interface between the clear and sludge phases was observed and registered. The results of 4 subsequent experiments without PE are presented in Figure 8 and with recycle of the sludge in Figure 9 (R-means recycle in the figures).

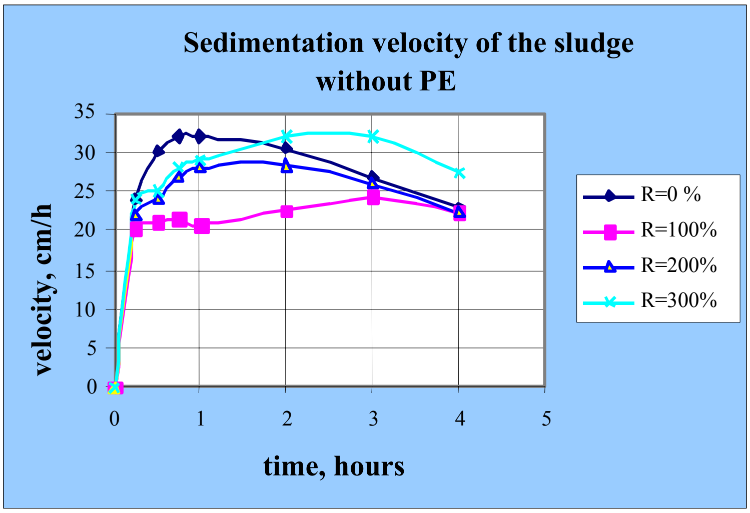

FIG. 8. Sedimentation without PE using recycle.

It can be seen that the recycle, even if it reaches 300%, has only a small effect on the sedimentation rate, which remain low (< 40 cm/h) in the absence of PE. It can also be seen that if PE is used, the recycle decreases sedimentation rate only a little, even at 300% sludge recycle, the sedimentation is still more than 1 m/h for first period of the sedimentation.

The solid content of the sludge after each step is presented in Figure 10. It can be seen that the solid content of the sludge is about 70 g/l without recycle, but it can reach almost 300 g/l if 400% recycle is used. Therefore it can be expected that the HDS-process will produce underflow with a high density in the case of groundwater treatment.

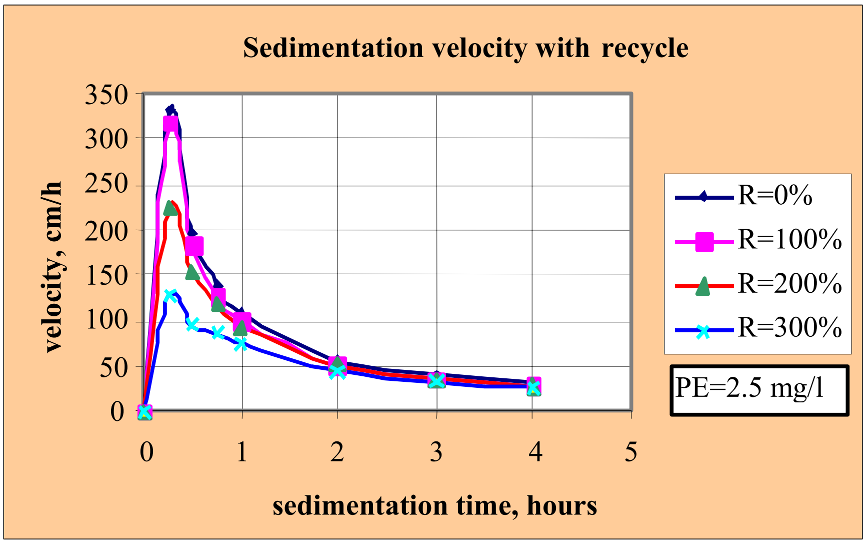

FIG. 9. Sedimentation with PE using recycle.

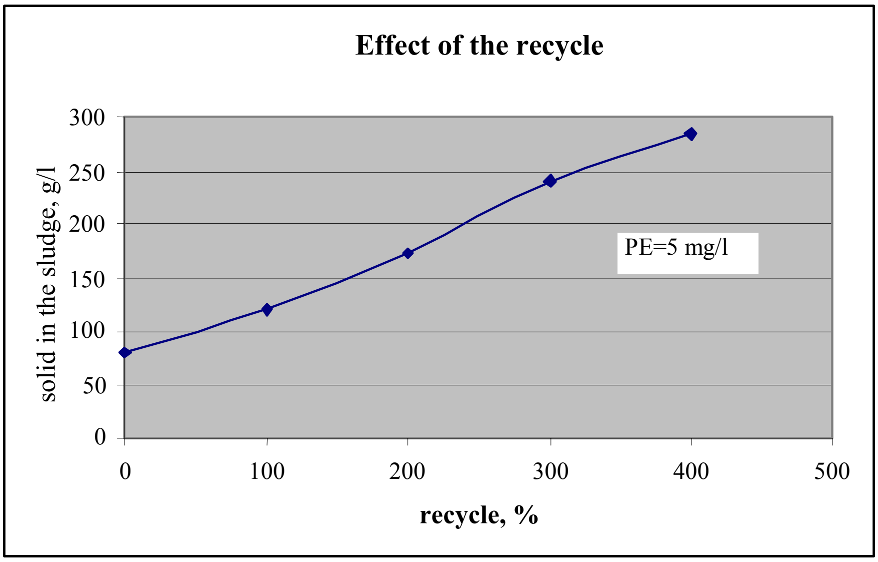

FIG. 10. Effect of the recycle on the solid content of the sludge

1.5. Radium removal

Laboratory experiments

As mentioned earlier, the radium-226 concentration exceeds the discharge limit only in the pond water, from which it must be removed prior to discharge into the receiving waters. Principally the task can be accomplished either by precipitation with barium chloride – this method is used worldwide, or by an ion-exchange process, for which a special ion-exchange resin has been developed by Dow Chemical Co. The results obtained confirmed the high efficiency of the resin: the resin can remove radium from some ten thousand volumes of pond water: nevertheless because of the regeneration problems, the conventional barium chloride process was still selected for the industrial process.

In spite of having information from the literature that radium can be easily removed from water by the barium chloride process, laboratory, pilot-scale and industrial- scale experiment were undertaken. For laboratory experiments, a rig similar to that presented in Figure 5 was used.

It was found that the radium concentration decreased from the original 25 Bq/l (radium concentration in pond water usually varied between 5–25 Bq/l) to less than 0.5 Bq/l.

The TDS of treated pond water decreased to 6.5 g/l. It is worth mentioning that without recycle the treated (and even filtered) water was over saturated for gypsum, which later partly precipitates and can be separated.

Pilot-scale experiment

As the removal of radium was a question of utmost importance, a pilot-scale experiment was carried out in the mill. For this a special system was installed using appropriate mill equipment. The set-up comprised a pumping system, mixing tanks, thickener (with diameter 6 m).

The experiments had three phases: in the first phase only lime milk was used without PE, in the second phase lime milk with PE (10 mg/l). In these two phases radium concentration also decreased, but it was still several Bq/l. A substantial reduction of the radium concentration was obtained only in the third phase when barium chloride was added to the water. In this case the radium concentration of the treated water decreased to less than 0.5 Bq/l. The experiment lasted some days.

The experimental data are presented in Figure 11. The radium concentration is presented for the feed (tailings pond water) and for the thickener overflow.

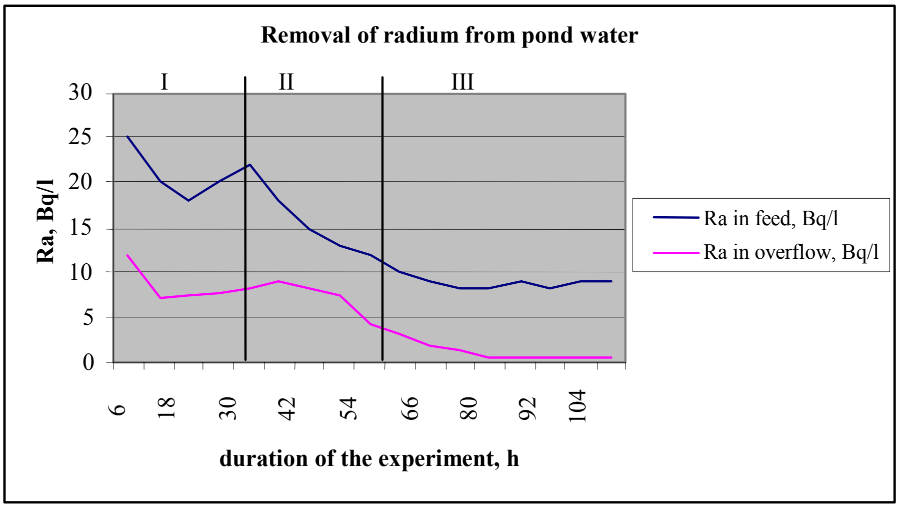

FIG. 11. Result of the pilot-scale experiment on radium removal.

To verify that radium can be precipitated in a plant situation, an additional experiment was carried out in the mill mixing tank designated for the planned mill water treatment circuit. The experimental set-up is shown in Figure 12.

The pond water was continuously fed and mixed in the first tank, with volume of 12 m^3, from which the water passed into the second tank and then into the thickener. Barium chloride (15 mg/l) and lime milk was added continuously in the first mixing tank. Water leaving the tanks was analysed for radium, the results are presented in Figure 13 for the first 10 hours of the experiment. It can be seen that in the real industrial mixing tank, the radium can be effectively precipitated by barium chloride.

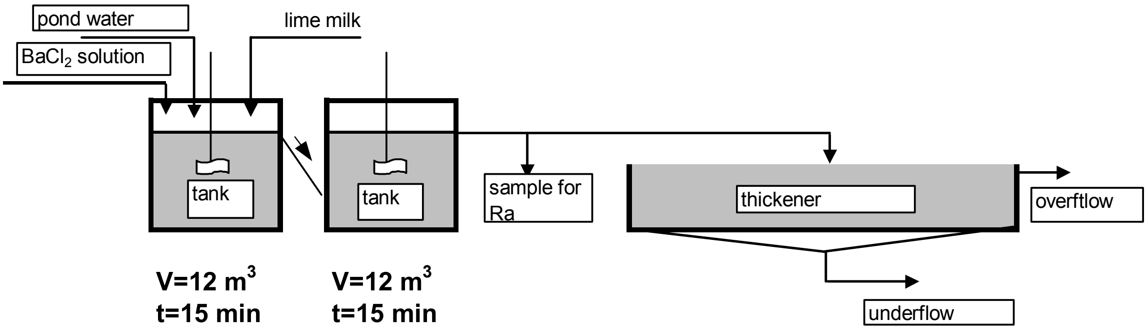

FIG. 12. Industrial set-up for the investigation of the precipitation of radium.

1.6. Composition and solubility of the sludge from water treatment

The sludge from water treatment requires a site for disposal. A very suitable location is the tailings ponds, if the sludge originates from the pond water treatment. For treatment of groundwater, another waste-deposit area can also be considered. In any case, it is important to have data regarding the solubility of the precipitate obtained from water treatment process. For this reason the solubility and composition of the sludge was investigated.

For the investigation, contaminated groundwater was treated with lime milk and the precipitate obtained was filtered. The filter cake contained 45% of solid, 55% of pore water. 25 g of cake was placed in a column and distilled water was fed on the top of the column. The seepage from the column was collected and analysed. Data obtained are presented in Table 3. It can be seen that in the seepage the calcium concentration remain at the level of the solubility of gypsum, while the magnesium concentration drops to about 20 mg/l. The sulphate concentration is 2 g/l.

The heavy metal content of the dried sludge obtained from pond water is presented in Table 4.

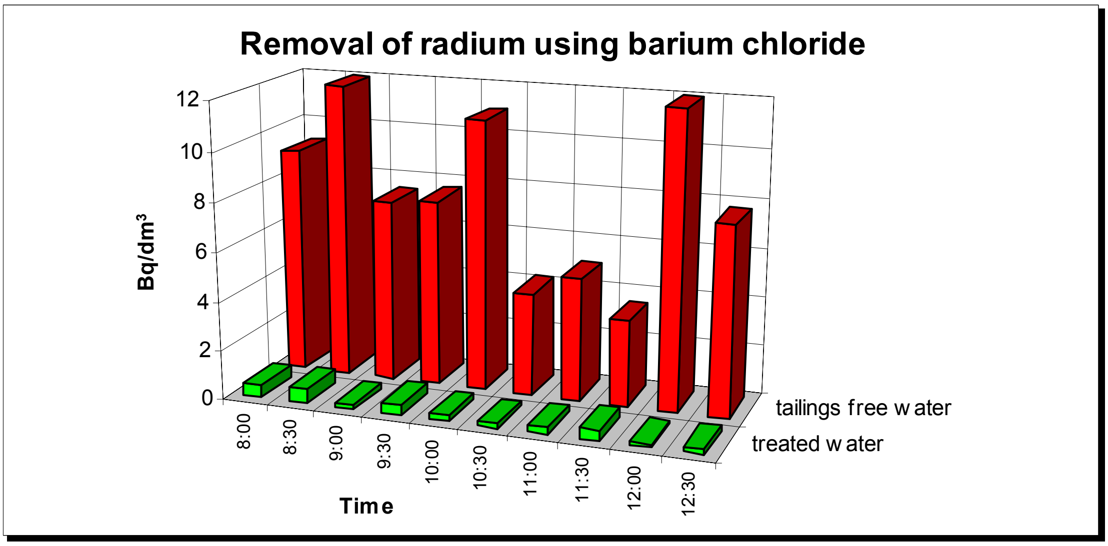

FIG. 13. Results of the industrial-scale experiment on the precipitation of radium.

It can be seen that the precipitate contains only manganese at substantial level (>2%), which originates from the pyrolusite used in the mill process. Barium content is due to the barium chloride used in the process.

If the sludge originates from the groundwater, the content of the heavy metals are all low. Even manganese remains well below 0.01%. The radioactivity is also low: 200-300 Bq/kg of dry precipitate. Calcium is of 20-16% (in form of gypsum) and magnesium 13-18% (in form of hydroxide).

Table III. Solubility of the sludge – composition of drainage solution

Date	V	Spec. conductivity	Ca	Mg	SO4
	ml	microS/cm	g/l	g/l	g/l
05.04.2000	7.5	6810	0.56	0.34	2.78
10.04.	2.5	not measured	0.56	0.437	
09.05.	3.0	not measured	0.56	0.218	
07. 06.	15	2312	0.64	0.097	
12. 07.	21	2167	0.56	0.048	
09. 08.	15	2214	0.56	0.029	
11. 09.	11	2225	0.59	0.032	2.22
25. 09.	12	1600	0.56	0.024	1.66
16. 10.	16	2013	0.56	0.019	

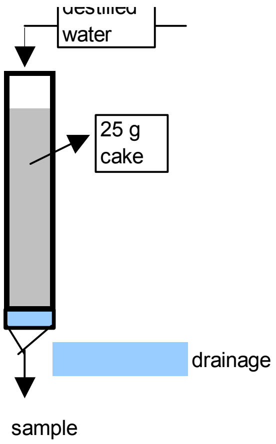

Table IV. Heavy metal content of the sludge

Component	**Cr**	**Mn**	**V**	**As**	**Co**	**Mo**	**Se**
Concentration, %	< 0.0004	> 2.935	< 0.0002	< 0.0004	0.0802	< 0.0004	0.0141
Component	**Ag**	**Sn**	**Sb**	**Tl**	**Ba**	**Pb**	**Cd**
Concentration, %	0.0023	0.0014	0.0027	0.0014	0.11	< 0.0012	< 0.0001
Component	**Cu**	**Ni**	**Zn**				
Concentration, %	0.0385	0.0035	< 0.0004				

1.7. General flow-sheet of the water treatment

On the bases of the presented data and other considerations, flow sheets were recommended for two periods of water treatment.

FIG. 14. Dried out tailings pond (TP I, August 2000).

For treatment of the pond water, the mill equipment was adapted. In this case radium was removed and the TDS of water was decreased to the planned level (Ra<0.5 Bq/l, TDS 5-7 g/l). All of the pond water was treated and after mixing with treated mine water was discharged. On the photos (Fig. 14) it can be seen that this even the deepest part of the tailings ponds became dry after discharge of the pond water.

As the mill must be demolished, a new plant for water treatment is needed for the processing of the 0.7–1 million m^3 per year of contaminated groundwater.

For the new water treatment plant the following key steps were recommended:

- Precipitation of magnesium with lime at pH=10.5;
- Sedimentation using PE;
- Recycle of a portion of the underflow of the thickener;
- Filtration of the underflow to obtain a sludge with water content appro. 50%;
- A retention basin to allow more time for precipitation of the gypsum;
- Provision for radium removal if the need arises during the rehabilitation works.

The overall flowsheet of the proposed water treatment process is presented in Figure 15.

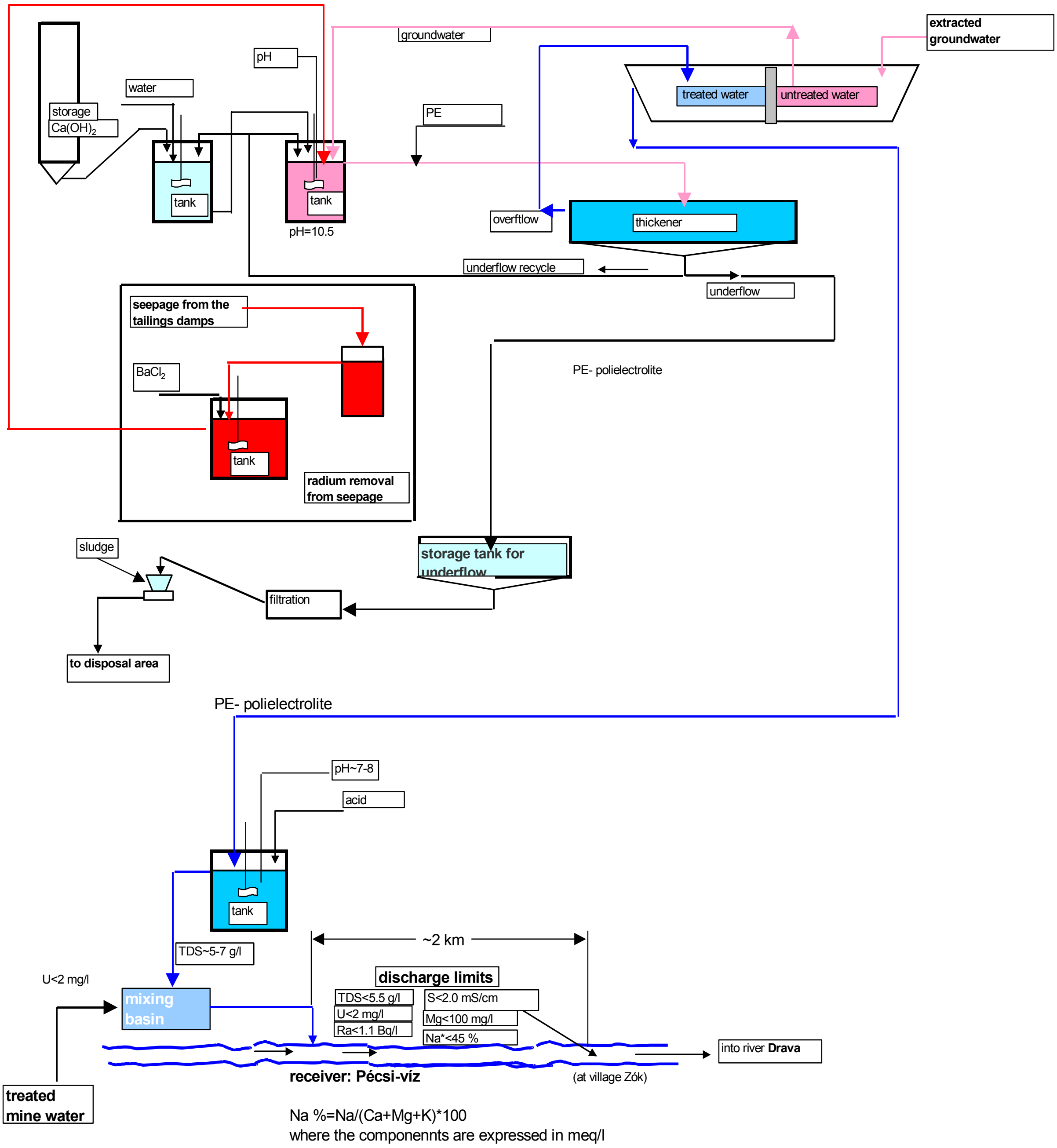

FIG. 15. Flowsheet for water treatment.

Taking into account the above mentioned recommendations, a new water treatment plant was planned by ENVIROTECH Ltd (Hungary) and constructed.

Main parts of the planned and constructed plants are:

- Preparing lime milk from calcium hydroxide;
- Chemical reactor for precipitation of magnesium;
- Chemical reactor for precipitation of radium;
- Thickener for possible use in the HDS process;
- A retention basin for more efficient precipitation of gypsum;
- Reactor for pH adjustment; and
- Filter press for decreasing the water content of the sludge.

Some pictures of the new water treatment station are presented in Figure 16.

Chemical reactor with lime container

Thickener (d=18 m)

Collecting tank for the underflow

Sludge from the water treatment

Basins for extracted groundwater and treated water

FIG. 16. Pictures of a new water treatment plant.

2. Passive methods of water treatment

In Section 1, results of investigations related to the natural attenuation of contaminants and the possibility of using zero valent iron (ZVI) are presented.

2.1. Ion-exchange properties of soil

Contaminated water contacts the soil underlying and surrounding the TP. It is of practical interest to have information regarding the geochemical processes taking place when contaminated water seeps through the soil layers.

It is known that soil has sorption capacity. The capacity depends on different properties. The first is composition of the soil. Clay-containing and organic- rich soil have greater exchange capacity for inorganic ions than sandy soil.

The sorption behaviour of the soil is important in relation to the self-restoration process for groundwater. The issue is whether the process of sorption of magnesium ions by soil (and desorption of calcium with magnesium) can take place when contaminated water (containing magnesium ions) is moving through soil, according the following equation:

$$MgSO_4 + \text{Ca-soil} = \text{Mg-soil} + CaSO_4$$

If the above exchange occurs the TDS of water must decrease because the $CaSO_4$ should precipitate from the saturated moving ground water and as a result the contamination of the groundwater, can be reduced to some extent. In other situations the ion-exchange process can occur between other ions. Whatever the circumstances, the composition of water will be changed as a result of the sorption-desorption processes.

As this form of restoration may be important when overall strategies are considered for groundwater, it is important to have additional knowledge about the natural sorption-desorption process of different ions originating from the TP.

Comparing the composition of discharged mill process water (see Part I) and the ground water to be extracted, it can see that the soil must have absorbed potassium, because this cation is not detected in the ground water. Because the main cations present in the contaminated water are magnesium, calcium and sodium, these ions are most interesting from the point of view of the sorption capacity of the soil.

Appropriate experiments have been started. Two sample sets from drilling through TPII (NY, K) and one sample set obtained from drilling nearby to the TPI were investigated. It is also planned to investigate other samples, obtained from drilling wells for removing of contaminated water. But this work cannot be carried out in the next months because the drillings are not yet finished. The first aim of the investigation is to determine the ion exchange capacity of the soil.

The experimental method developed on the basis of the literature consist of washing the sample with distilled water, drying it at 105°C and then carrying out the desorption of the ions by using batch method. Calcium and magnesium are desorbed with potassium chloride solution (10 g of dry soil + 50 ml 1 mol/l potassium chloride solution (treating solution)) by stirring, then the solution is analysed for calcium and magnesium by titrimetry.

Samples investigated up to now are listed in the following Table (Table V).

Sorption capacity of the soil beneath the tailings for calcium and magnesium (under the

Depth (from the surface of tailings)	Ca						Mg						total Ca+Mg capacity		Ca/Mg	
m	mg/l*		mg		meq/100 g		mg/l*		mg		meq/100 g		meq/100 g		meq/meq	
Sample	Ny	K	Ny	K	Ny	K	Ny	K	Ny	K	Ny	K	Ny	K	Ny	K
10		**1880**		**94**		**47,00**		**121**		**6,05**		**4,98**	**0,00**	51,98		9,4
11	1840	1880	92	94	46	47,00	121	121	6,1	6,05	4,98	4,98	51,0	52,0	9,2	9,4
12	400	1880	20	94	10	47,00	102	121	5,1	6,05	4,19	4,98	14,2	52,0	2,4	9,4
12,5		360		18		9,00		145		7,25		5,96		15,0		1,5
13	320	360	16	18	8	9,00	48	145	2,4	7,25	1,97	5,96	10,0	15,0	4,1	1,5
14	320	360	16	18	8	9,00	48	121	2,4	6,05	1,97	4,98	10,0	14,0	4,1	1,8
15	300	400	15	20	7,5	10,00	60	72	3,0	3,6	2,47	2,96	10,0	13,0	3,0	3,4
16	440	240	22	12	11	6,00	121	121	6,1	6,05	4,98	4,98	16,0	11,0	2,2	1,2
17	400	200	20	10	10	5,00	170	170	8,5	8,5	6,99	6,99	17,0	12,0	1,4	0,7
18	360	240	18	12	9	6,00	145	218	7,3	10,9	5,96	8,96	15,0	15,0	1,5	0,7
19	280	240	14	12	7	6,00	145	243	7,3	12,15	5,96	9,99	13,0	16,0	1,2	0,6
20	240	320	12	16	6	8,00	170	243	8,5	12,15	6,99	9,99	13,0	18,0	0,9	0,8

🟨 soil may be directly contaminated with tailings

Sorption capacity of the soil layers for calcium and magnesium
(100 m west from the TPI)

Depth from the surface	Ca			Mg			total Ca+Mg capacity	Ca/Mg
m	mg/l*	mg	meq/ 100 g	mg/l*	mg	meq/ 100 g	meq/ 100 g	meq/ meq
0	**1168**	**58,4**	**29,2**	**456**	**22,8**	**18,75**	**47,95**	1,56
0.5	784	**39,2**	19,6	524	26,2	21,55	41,1	0,9
1	336	**16,8**	8,4	243	12,2	9,99	18,4	0,8
2	272	**13,6**	6,8	174	8,7	7,15	14,0	1,0
3	448	**22,4**	11,2	145	7,3	5,96	17,2	1,9
4	368	**18,4**	9,2	165	8,3	6,78	16,0	1,4
5	224	**11,2**	5,6	116	5,8	4,77	10,4	1,2
6	224	**11,2**	5,6	155	7,8	6,37	12,0	0,9
7	224	**11,2**	5,6	136	6,8	5,59	11,2	1,0

*in potassium chloride solution

It can be seen that the soil has a small exchange capacity for magnesium and calcium (some meq/100 g[1]). The capacity of the soil for these cations is not very high but nevertheless it is measurable.

In the case of the samples from the subsoil of the TPII, the total capacity for calcium and magnesium is around 15 meq/100 g. The ratio of Ca/Mg varies between 1.5–0.7. In the case of soil from near of TPI, the ratio is approximately 1. To make a final assessment of the role of the soil on self-restoration process more data are needed. These investigations are continuing.

2.2. Removal of uranium from contaminated water by reactive barriers

Reactive barriers are often used for in situ remediation of contaminated ground water. There are many publications regarding the behaviour of these barriers. This techniques has proved to be very effective in the case of uranium and heavy metals such as arsenic, molybdenum etc. This type of remediation technique has also been investigated and used by our company. A brief summary is given below.

The work on reactive barriers covered first the lime-based reactive walls. Over the last few years of the IAEA project, the investigations were broadened, and now in addition to lime, zero valent iron is also included in the research programme.

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[1] Generally this unit is used in the soil chemistry.

2.3. *Lime-based reactive barrier*

On starting the remediation works, it became clear that the relocation of many millions of tons of heap leaching wastes will result in considerable elevation of the uranium concentration in the seepage from the relocated wastes. For this reason, our investigations commenced in the early nineties.

The investigations were carried out on laboratory scale. 400-650 kg of heap leaching wastes was placed in appropriate barrels. One barrel was for a control without a barrier, while the other had a lime barrier. The basic set-up for the investigations is shown in Figure 17.

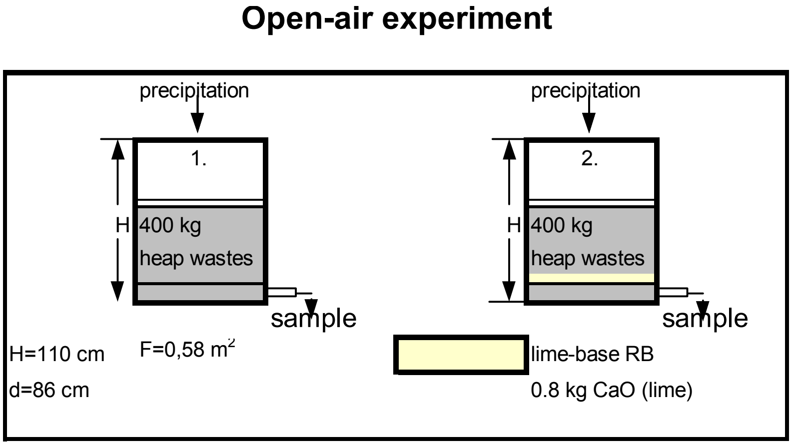


FIG. 17. Laboratory experiment on reactive barrier.

During the whole period of experiments the barrels were in open-air condition. In one barrel 0.8 kg of burnt lime was mixed with 4 kg of wastes. After placing in every barrel the heap-leached waste, the barrels were placed on the yard of the laboratory. Rainwater percolated through the waste and was collected in the vessel over a time period depending on the flow. The collected sample was analysed for different components: uranium, pH, specific conductivity, TDS, etc. Some of the experiments have lasted three years.

The experiment in question started in 1997 and ended in October 2000. Through this period almost 1 m^3 of rainwater passed through both barrels. In Figure 18, the uranium attenuation and pH in the seepage are presented.

It can be seen that the uranium concentration in the seepage from the barrel without a lime barrier was for the whole period higher than that with lime barrier. The difference is very significant.

The attenuation effect of the lime barrier is very high in the first period just after relocation of the wastes. Uranium concentration in this period reached 40-60 mg/l without a lime barrier, but decreased to less than 1 mg/l with a barrier.

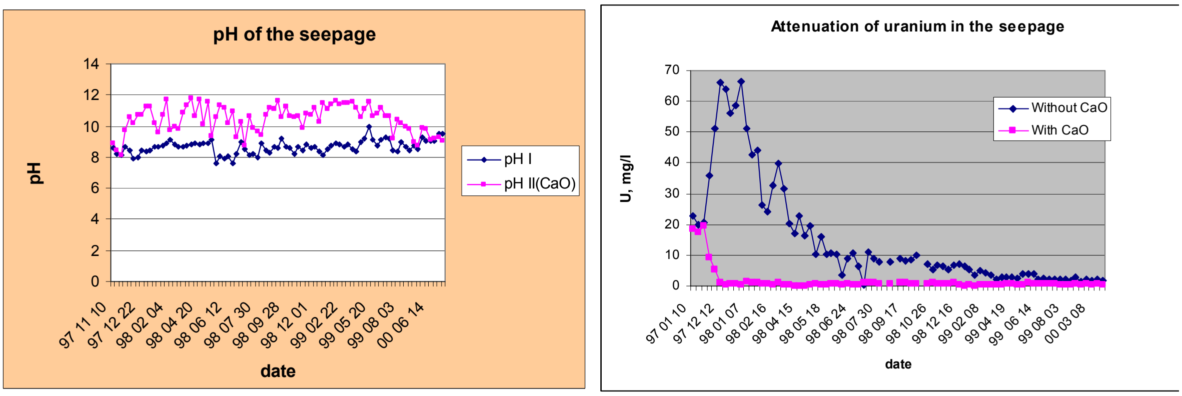


FIG. 18. Effect of the lime-based barrier.

The pH of the seepage water was a little higher, this is a small disadvantage of the process but an elevated pH tends to normalize in natural circumstances.

Preparation of the lime-based barriers

Pilot-scale experimental pile

Collection of seepage from the sectors of the pile

FIG. 19. Pilot-scale experiment on reactive barrier.

As very good results were obtained regarding the attenuation of uranium with a lime reactive barrier, an in situ experiment was carried out on waste rock pile NIII, where the wastes from heap leaching were to be relocated. The total surface of the experimental area was 2000 m^2. The area was divided into a control area and the area with barriers. This later area was further divided into smaller parts on which different lime quantities were used (from 3 to 15 kg/m^2) and a pile was built (A = 9*28 m^2, h = 2.3 m). The building of the barrier is presented in Figure 19.

The field experiment also proved that the lime-based barrier attenuates the uranium concentration in the seepage. From the area without a lime barrier, the uranium concentration in the seepage was around 20 mg/l, while from a number of sections, where the different lime additions were used, the uranium in seepage was only 1–5 mg/l.

On the basis of the experiments building of a lime barrier, using 1.2 kg/t of lime was recommended. The technology of the construction of the barrier is very simple: burned lime is spread on the surface of waste, in a layer a few cm thick, it is then mixed in place with some waste to prepare a layer about 10–20 cm thick. The relocated wastes are dumped on this layer. After reaching about 5 m, a new barrier is constructed.

Using this method the uranium content of seepage was substantially reduced.

2.4. Zero valent iron-based reactive barrier

It is known that the zero valent iron (ZVI) can be used for attenuation of uranium in ground water if it is used as barrier. ZVI also reduces the concentration of other heavy metals and is therefore a very effective reagent for in situ remediation. Though at this moment the company has no problem with uranium contamination of groundwater, some problems are foreseen on the waste rock pile and even on the dumps of TP from which uranium is dissolved in some extent. For these reasons, the possibility of reducing the uranium in ground water is interesting for the company.

For the moment some preliminary experiments have been carried out. In one set of experiments contaminated groundwater from the surroundings of waste rock pile N III were used (water from monitoring well). On this site elevated uranium concentration is observed in monitoring wells (U = 0.5 mg/l).

In other sets of experiments seepage water from TPI was used (U = 2-5 mg/l). In these experiments special iron (from USA used in reactive barriers) and iron pieces (with high specific surface) obtained as a by-product were used. In addition to batch experiments, column tests were also carried out. Results of these experiments are summarised in Tables 6 and 7.

It can be seen that the uranium concentration in the outlet is much less that of the feed water, thus the iron-composed bed is effective in decreasing the uranium content of water seeping through the bed. This was the case for both water samples (for sample from TP and that of from monitoring well).

It is worth mentioning, that the uranium attenuation in the case of seepage from TP is less than that for groundwater. This difference in performance needs further investigation. One explanation may be that the seepage water needs a greater residence time in the barrier. An indication for such an effect is that when the experiment was interrupted for some days, the uranium concentration decreased to less than 10 micro g/l. Nevertheless the effect of residence time should be further investigated.

3. Conclusions

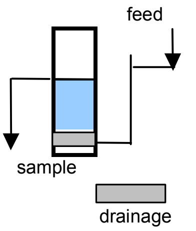
Experimentation was undertaken to develop the best means to protect groundwater from seepage from uranium mill tailings ponds. Both physical and chemical systems were evaluated and field-tested to determine the best system to treat both standing water in the tailings ponds and contaminated water in soil and aquifers beneath the ponds. Chemical treatment has been selected for both water sources. Based on information obtained in pilot scale experimentation, an interim water treatment plant was constructed in the uranium mill to treat the free standing water in the tailings pond. In addition, as part of the groundwater restoration work, a new water treatment has been planned and built.

Contaminated water seeping from abandoned heap leach piles is a potential source of contamination of underlying aquifers. A pilot scale experiment was conducted to evaluate the effectiveness of lime-based reactive barriers to control and neutralize water seeping from relocated heap leach piles. This experiment demonstrated that a lime-based reactive filter constructed beneath relocated material effectively reduced uranium content in seepage waters and these barriers will be utilized in the heap leach pile relocation programme.

Table VI. 1 Effect of ZVI. Contaminated groundwater from waste rock pile N III (from monitoring well:H/1)

1 Effect of ZVI. Contaminated groundwater from waste rock pile N III (from monitoring well:H/1)

Sample number	Volume	Volume, cummulative	time period	volume rate	linear rate	U	pH
	ml	ml	s	cm^3/s	cm/s	µg/l	
Contaminated ground water sample from well:H/1						**332**	**7.3**
201A	103	103	18900	5,45E-03	3,01E-04	50	
			69000				
202A	109	212	16500	6,61E-03	3,65E-04	14	
			154000				
203A	112	324	19200	5,83E-03	3,22E-04	<10	
			153000				
204A	110	434	21780	5,05E-03	2,79E-04	<10	
			66780				
205A	74	508	20640	3,59E-03	1,98E-04	<10	
			65520				
206A	58	566	11640	4,98E-03	2,75E-04	<10	
			248400				
207A	111	677	18780	5,91E-03	3,27E-04	24	
			67200				
208A	92	769	22260	4,13E-03	2,28E-04	<10	
			64080				
209A	33	802	13980	2,36E-03	1,30E-04	<10	7.92
Average in the 1st stage			**1051660**	**7,63E-04**	**4,21E-05**		
Long standstil			**591120**				
210A	110	912	23280	4,73E-03	2,61E-04	<10	7.89
			63900				
211A	149	1061	20400	7,30E-03	4,04E-04	<10	8.00
			57600				
212A	52	1113	15300	3,40E-03	1,88E-04	<10	8.24
			244800				
213A	104	1217	22200	4,68E-03	2,59E-04	<10	7.85
			55980				
214A	109	1326	24360	4,47E-03	2,47E-04	14	7.90
			62580				
215A	40	1366	19560	2,04E-03	1,13E-04	<10	8.30
			66240				
216A	86	1452	19140	4,49E-03	2,48E-04	<10	8.09
			68400				
217A	53	1505	14400	3,68E-03	2,03E-04	<10	8.37
Average in the 2nd stage			**778140**	**1,93E-03**	**1,07E-04**		

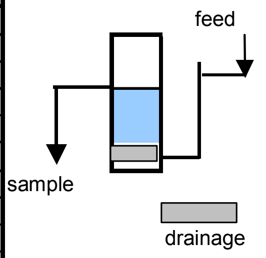


h= 55 mm
d= 24 mm
V= 99.55 cm^3
Fe 11.6 g

Table VII. 2 Effect of ZVI. Seepage water from TP I.

2 Effect of ZVI. Seepage water from TP I

Sample number	Volume	Volume, cummulative	time period	volume rate	linear rate	U	pH
	ml	ml	s	cm^3/s	cm/s	µg/l	
Seepage water sample from TP I						2860	7.6
201B	107	107	18900	5,66E-03	3,13E-04	540	
Standstil			69000				
202B	102	209	16500	1,27E-02	7,00E-04	970	
Standstil			154000				
203B	116	325	19200	1,69E-02	9,35E-04	850	
Standstil			153000				
204B	111	436	21780	2,00E-02	1,11E-03	870	
Standstil			66780				
205B	67	503	20640	2,44E-02	1,35E-03	580	
Standstil			65520				
206B	54	557	11640	4,79E-02	2,64E-03	530	
Standstil			248400				
207B	99	656	18780	3,49E-02	1,93E-03	110	7.95
Standstil			67200				
208B	78	734	22260	3,30E-02	1,82E-03	520	8.14
Standstil			64080				
209B	38	772	13980	5,52E-02	3,05E-03		7.92
Average in the 1st stage			**1051660**	**7,34E-04**	**4,06E-05**		
Extended period of no flow			**591120**				
210B	106	878	23280	3,77E-02	2,08E-03	11	7.89
Standstil			63900				
211B	123	1001	20400	4,91E-02	2,71E-03	60	7.95
Standstil			57600				
212B	57	1058	15300	6,92E-02	3,82E-03	460	8.16
Standstil			**244800**				
213B	105	1163	22200	5,24E-02	2,89E-03	32	8.09
Standstil			55980				
214B	103	1266	24360	5,20E-02	2,87E-03	460	8.11
Standstil			62580				
215B	31	1297	19560	6,63E-02	3,66E-03	515	8.14
Standstil			66240				
216B	65	1362	19140	7,12E-02	3,93E-03	185	8.18
Standstil			68400				
217B	51	1413	14400	9,81E-02	5,42E-03	485	8.21



h= 55 mm
d= 24 mm
V= 99.55 cm^3
Fe 11.6 g

▨ after long contact time in the column
new seepage water sample (U=2430 µg/l) from beginning of 210B

Biogenic treatment of uranium mill effluents

A.K. Mathur, V.K. Murthy

Atomic Minerals Directorate for Exploration & Research,
Department of Atomic Energy, Begumpet, Hyderabad, India

Abstract. It is necessary to treat mine/mill effluents before discharging to the environment as per the regulatory requirements. Effluents from a uranium mill normally contain ^{226}Ra as a pollutant, which needs treatment. Normally wastewater treatment consists of lime addition to increase the pH to 10 which precipitates most contaminants except ^{226}Ra. The current chemical treatment of ^{226}Ra is by co-precipitation as barium-radium-sulphate by addition of barium chloride. There is a considerable concern about the long-term stability of barium-radium sludge due to re-dissolution of radium when contacted with fresh water. Adsorption can be another metal specific physio-chemical process. The most recent development in environment biotechnology is the use of microbe based bio-sorbants for the recovery of toxic metals from industrial effluent. A fungal species of ***Pencillium chrysogenum*** has been found to be a ^{226}Ra specific biosorbent. It has been observed that up to 96% of ^{226}Ra values can be adsorbed by chemically treated biomass of ***Pencillium chrysogenum*** from effluent containing ^{226}Ra in the range of 400-2000 Bq m^{-3}. Biomass in the form of granules can be used in columns, like resins, to remove ^{226}Ra values. It is proposed that this process can replace or substitute the present barium chloride treatment of mill effluents.

1. Introduction

Environmental awareness and regulatory requirements necessitate adequate and economical processes to treat effluents from uranium extraction plants before release to the environment. The effluents from the mill or the dilute solutions from mining operations are aqueous solutions of inorganic and organic components, which are often toxic even though present in low concentrations (ppb or ppm). The wastes arising from the extraction of uranium from ores, consist of process waste water, mine water and overflow and seepage from active and inactive tailings areas. These constitute a particular class of low-level waste in which the radioactivity is naturally occurring and long-lived. Following uranium removal, the ^{238}U daughter ^{226}Ra with a half-life of 1620 years is the main pollutant of environmental concern. In India, the permissible concentration of ^{226}Ra for discharge to the environment is 400 Bq m^{-3}.

One large scale method for the treatment of mining and milling waste water consists of lime addition to increase the pH to 10. This chemical treatment precipitates most contaminants except ^{226}Ra, the latter persists at high activities. One current treatment for ^{226}Ra is co-precipitation as barium-radium sulphate by addition of $BaCl_2$ to sulphate rich effluents. However, as with most co-precipitation methods, settling ponds are required with residence times of several weeks. Effluents from these ponds often result in substantial release of ^{226}Ra to surface watercourses. There is considerable concern about the long-term stability of the barium-radium sulphate sludge since re-dissolution of the radium will take place if fresh water contacts the sludge [2].

One of the physio–chemical processes that can be used very effectively for sequestering low levels of contaminants from aqueous solutions is adsorption and this can be very metal specific. The most recent development in environmental biotechnology is the use of microbe-based biosorbents for the removal and recovery of toxic metals from industrial effluents. Biosorption can be an alternative to conventional waste treatment methods. A radium adsorption system could replace the present $BaCl_2$ treatment of tailings wastewater. After screening different types of microbes, ***Pencillium chrysogenum*** has been found to be the best ^{226}Ra specific biosorbent.

2. Materials and methods

2.1. Uranium extraction process (pug cure leaching)

A high grade sandstone ore from Domiasiat area, Meghalaya State, India, of 0.24% U_3O_8 grade was taken for uranium leaching studies. About 100 kg of ore was sampled and crushed to -35# (425 µm) size. About 10 kg of the sample was taken at a time for leaching. The ore was pugged with 8N sulphuric acid at 90% pulp density and cured at 70ºC using 2.5 kg MnO_2 for 2 hours. The leaching of the pugged mass was carried out in rubber lined pachuca at 50% pulp density and at 50ºC for 4 hours. 45 kg H_2SO_4/t was used for leaching. The pulp was filtered and washed with water, to remove uranium completely, in a filter press. The leach liquor obtained analysed:U_3O_8 - 1740 mg/l; Fe - 1870 mg/l; Mn - 317 mg/l; Pb - 1.04 mg/l; Cd - 0.73 mg/l; V - 19.2 mg/l; $SO4^{2-}$ - 15.5 g/l; TDS - 24 g/l; ^{226}Ra - 3056 Bq m^{-3}.

Ion exchange

A two column resin ion exchange technique was adopted for the recovery of uranium. Anionic complexes of uranium ($UO_2(SO_4)_3^{4-}$) were selectively adsorbed by the resin INDION 103 from leach liquor. Sodium chloride was used for reversing the exchange reaction for eluting the purified uranium solution. The barren liquor was collected separately. The barren solution analysed: U_3O_8 - ~20 mg/l; Fe - 1869 mg/l; Mn - 306 mg/l; Pb - 1.0 mg/l; Cd - 0.75 mg/l; V - 15 mg/l; $SO4^{2-}$ - 15.5 g/l; TDS - 24 g/l; ^{226}Ra - 3050 Bq m^{-3}.

This acid barren solution was neutralised to pH 10.0 using lime solution. The neutral barren solution analysed.

Fe - <10 mg/l; Mn - <1.0 mg/l; Pb - 1.0 mg/l; V - 0.5 mg/l; $SO4^{2-}$ - 2.5 g/l;
TDS - 12.4 g/l; ^{226}Ra - varied between 400 to 825 Bq m^{-3}.

This barren solution was taken for further biosorption studies for recovering ^{226}Ra values.

2.2. Screening of micro organisms suitable for ^{226}Ra adsorption

The following bacterial and fungal cultures were procured from the National Culture Collection Center of National Chemical Laboratory, Pune, India and were tested for their ^{226}Ra adsorption ability.

1. Rhizopus arrhazius NCIM 877
2. Penicillium chrysogenum NCIM 722
3. Streptomyces albus NCIM 2413
4. Saccharomyces cerevisiae NCIM 2812
5. Bacillus subtilis NCIM 2063
6. Bacillus pumilus NCIM 2327
7. Bacillus circulans NCIM 2107
8. Pseudomonas aeuroginosa NCIM 2036

Nutrient media used for culturing in laboratory : For fungal cultures

a) *PDA (Potato Dextrose Broth)*

200 g of peeled potatoes in one liter of water, steam for 30 minutes. Decant the extract and make up to one liter. Add 25 grams of dextrose. Sterilise at 15 lbs, for 20 minutes, in an autoclave.

b) *For yeast and streptomyces*

Malt extract	0.3%
Glucose	1.0%
Yeast extract	0.3%
Peptone	0.5%
Distilled water	1000 ml
pH	6.8

c) *Nutrient Broth (for bacteria)*

Beef extract	1.0%
Sodium chloride	0.5%
Peptone	1.0%
Distilled water	1000 ml
pH	7.0 to 7.2

d) *Nutrient medium for culturing Pencillium chrysogenum in batch fermenter (Bulk biomass production)*

Sucrose	40 g
Lactose	10 g
Malt extract	10 g
Beef extract	10 g
Peptone	10 g
KH_2PO_4	3 g
$MgSO_4\ 7H_2O$	0.25 g
$CaCl_2\ 2H_2O$	0.05 g
$MnSO_4\ 4H_2O$	0.02 g
$FeSO_4\ 7H_2O$	0.025 g
$ZnSO_4\ 7H_2O$	0.02 g
$CuSO_4\ 5H_2O$	0.005 g
Distilled water	1000 ml
pH	5.2

2.3. Preparation of acrylamide treated biomass

The biomass is initially washed thoroughly with hot water to remove any media components. It is dried at 80ºC for 24 hours. 1 gram biomass is taken in 10 ml water and mixed with 1.3 gram acrylamide, 0.68 mg bis. acrylamide and 1 ml 5% N-N-Tetra methyl ethylene diamine (TEMED) and 1 ml of 2.5% ammonium persulphate. This is mixed very well and left at room temperature for one hour and dried at 100ºC for one hour or taken for homogenisation and further use for making biomass granules.

2.4. Estimation of ^{226}Ra by Emanometry Principle (Ragavayya et al, 1980)

^{226}Ra is estimated by allowing buildup of its daughter ^{222}Rn for a known period and collecting the radon gas in a scintillation cell and counting the same, after equilibration with radon daughters, for alpha activity.

Radon sampling

Specially designed bubblers are used for collecting radon buildup from the effluents (Normally 7-10 days). After 7 days an evacuated scintillation cell is connected to bubbler through a hypodermic needle. Due to vacuum in the cell, air is sucked in through the solution, which carries the radon into the cell.

Counting and calculation

In about 200 minutes, the short lived radon daughters reach equilibrium with radon in the scintillation cell. The alpha counts are taken after this time. The scintillation cell is inserted in ^{222}Rn counting system. The counts are taken for 500 seconds. From the counts obtained, the radon activity transferred from the bubbler to the scintillation cell is calculated and the radium content of the solution in the bubbler is obtained by using an appropriate ingrowth factor which is a function of the ingrowth period and the decay constant of ^{222}Rn.

$$^{226}\text{Ra content in solution (Bq/L)} = \frac{C \times 1.883 \times 10^{-3} \times 0.037}{Ee^{-\lambda t}(1-e^{-\lambda t})\,(1-e^{-\lambda\theta})}$$

Where

C	is the gross counts obtained
E	is the efficiency of the scintillation cell (average 74%)
t	is the counting time delay (200 minutes)
T	is the counting duration (fixed 500 seconds)
λ	is the decay constant of radon (1.258×10^{-4} minutes^{-1})
θ	is the radon build up period (7-10 days)

2.5. Making of uniform sized biomass granules at a larger scale

(i) Bulk biomass of *Pencillium chrysogenum* was produced in a 15 litre fermenter using the above mentioned nutrient medium (S.No.iv) keeping the air flow at 4 m^3/min. and agitator shaft speed at 400 rev/min. for 35 hours. The biomass was washed, filtered and the cake stored at 0ºC.

(ii) 100 g of dry biomass was homogenised thoroughly in a blender for 30 minutes. 100 ml of this homogenised mass in water was taken and mixed with 50 g acrylamide and 100 ml 5% N-N- tetra methyl ethylene diamide (TEMED). After thoroughly mixing 10 ml of 2.5% ammonium persulphate was added and kept for one hour for polymerisation. Then the slurry was mixed with 10 g sodium alginate.

The slurry was ejected through a 1 mm nozzle using a peristaltic pump into 0.2 M $CaCl_2$ solution which was kept in stirring condition using a magnetic stirrer. Uniformly sized spherical granules of encapsulated biomass were formed having a gel based matrix, which has a biosorptive capacity for ^{226}Ra adsorption (Table 1).

Table I. Composition of the actual raw effluent obtained from uranium mill at Jaduguda Bihar, India (in mg/l)

Na : 295	K : 34	Ca : 348	Mg : 41	Mn : 30
Cu : 27	Al : 0.34	Fe(T) : 0.30	Ni : 0.3	Co: < 0.04
Pb : < 0.02	Cd : < 0.01	Zn : 0.011	Mo : 0.25	V : Nil
U : 0.43	TDS : 4340	NO_3^{2-} : 39	PO_4^{2-} : < 2	$S04^{2-}$: 2000
$CO_3^{2-} : Nil$	^{226}Ra : 1170 Bq m^{-3}			

2.6. *Test Results*

2.6.1. Shake flask tests

To screen microorganisms for ^{226}Ra biosorption, 200 ml of neutral barren liquor was mixed with a dry pellet of biomass and kept for shaking. After 2 hours, the contents were centrifuged and the liquor analysed for ^{226}Ra values. Results are shown in Table 2.

Table II. Results of shake flask tests to screen microorganisms for ^{226}Ra biosorption*

Microorganism	**Dry wt. of biomass (grams)**	**Contact time (hours)**	**^{226}Ra adsorption %**
Rhizopus arrhazius	25	2	23
Saccharomyces cerevisiae	0.5	2	2
Streptomyces albus	8.5	2	44
Penicillium chrysogenum	2	2	68
Aspergillus fumigatus	2	2	58

* Bacterial species of *Bacillus subtilus, Bacillus pumilus, Bacillus circulans* and *Psumdomonas aeuroginosa* did not show any ^{226}Ra adsorption.

^{226}Ra Biosorption tests with Pencillium chrysogenum

Based on initial screening tests ***Pencillium chrysogenum*** was selected for detailed work. A batch equilibration method was used to determine the sorption of ^{226}Ra by biomass of ***Pencillium chrysogenum***. A set of 250 ml Erlenmeyer Flasks containing 100 ml effluent were used. Tables 3, 4, 5, 6 and 7 show the effect of chemical treatment, biomass weight variation, contact time and pH variation on the uptake of ^{226}Ra values.

Table III. Volume of effluent - 100 ml, contact time - 2 hours and pH - 7.0

Nature of Biomass *Pencillium chrysogenum*	**^{226}Ra end values (Bq m^{-3})**	**^{226}Ra Biosorption %**
Native	194	50
Acrylamide treated	45	88
Formaldehyde urea treated	114	71
Control	387	---

Table IV. Biomass - weight variation, volume of effluent - 100 ml, contact time - 2 hours and pH 7.0.

Treated biomass (g)	^{226}Ra end values (Bq m^{-3})	^{226}Ra Biosorption %
0.5	310	22
1.0	228	42
2.0	51	87
3.0	47	88
4.0	44	89
Control	393	---

Table V. Contact time variation, volume of effluent: 100 ml, pH - 7.0 and biomass wt. - 2 g

Contact time hours	^{226}Ra end values (Bq m^{-3})	^{226}Ra biosorption %
0.5	320	20
1.0	140	65
2.0	52	87
3.0	52	87
4.0	52	87
Control	400	---

Table VI. ^{226}Ra adsorption at pH 4.0; volume of effluent - 100 ml, contact time - 2 hours, dry weight of biomass - 2 g and pH - 4.0 (adjusted with dilute acid)

Nature of Biomass	^{226}Ra end values (Bq m^{-3})	^{226}Ra biosorption %
Native	176	53
Acrylamide treated	166	56
Control	373	---

Table VII. Biosorption of ^{226}Ra in high concentration effluent; volume of effluent - 100 ml, pH - 7.0, dry WT of biomass - 2 g & contact time - 2 hours

	Initial ^{226}Ra conc. (Bq m^{-3})	Final ^{226}Ra conc. (Bq m^{-3})	^{226}Ra Biosorption %
1	1324	63.6	96
2	2644	166	93.7

2.6.2. Continuous loading of effluent on "Biomass" granules packed in glass columns

Five liter of the actual mill effluent was passed through 240 ml of Biomass granules packed in four columns (60 ml × 4 Bv) in series. Each batch of 1 l of the effluent was collected to determine ^{226}Ra adsorption results. Tables 8 (Shake flask test) and 9 (Column test) show the results.

Table VIII. Biosorption of ^{226}Ra by biomass granules from actual mill effluent

Volume of effluent	100 ml
pH	7.0
Wt. of biomass granules	2 g
Contact time	2 hours
Initial conc. of ^{226}Ra in effluent	1170 Bq m^{-3}
End concentrate of effluent	55 Bq m^{-3}
% biosorption	95

Table IX. Continuous loading of actual mill effluent in biomass granules packed columns

Volume of actual mill effluent	5000 ml
pH of effluent	7.0
Volume of biomass granules (in four glass columns)	240 ml
Rate of flow	2 ml/min
Retention time	18 minutes
Initial ^{226}Ra content of the effluent	1170 Bq m^{-3}

Sample No.	Batches	Vol. of liquor withdrawn batch wise (ml)	^{226}Ra end values (Bq m^{-3})	^{226}Ra biosorption %
1	B-1	1000	103	91
2	B-2	1000	178	85
3	B-3	1000	86	93
4	B-4	1000	46	96
5	B-5	1000	46	96

3. Conclusions

- Initial laboratory screening tests showed that ***Pencillium chrysogenum*** is a selective fungus for ^{226}Ra biosorption.
- Biosorption of ^{226}Ra by the native biomass was of the order of 50-68%. This could be enhanced up to 88% by chemically treating the biomass with acrylamide.
- The adsorption is pH dependent and maximum at neutral pH.
- A maximum of two hour contact time is required for the complete biosorption in shake flask tests.
- It is possible to make biomass granules at a larger scale in the form of gel based matrix which has high biosorptive capacity for radium.
- Tests on continuous loading of the actual raw mill effluent in biomass packed columns gave 96% of ^{226}Ra biosorption, which has a possible commercial application after scale up studies.
- This process could replace or substitute the present $BaCl_2$ treatment of effluent. Such an adsorption system would treat tailings pond effluent, which would pass through a system of adsorption beds in columns consisting of biomass granules. Schematic representation of the process is given in Figure 1.

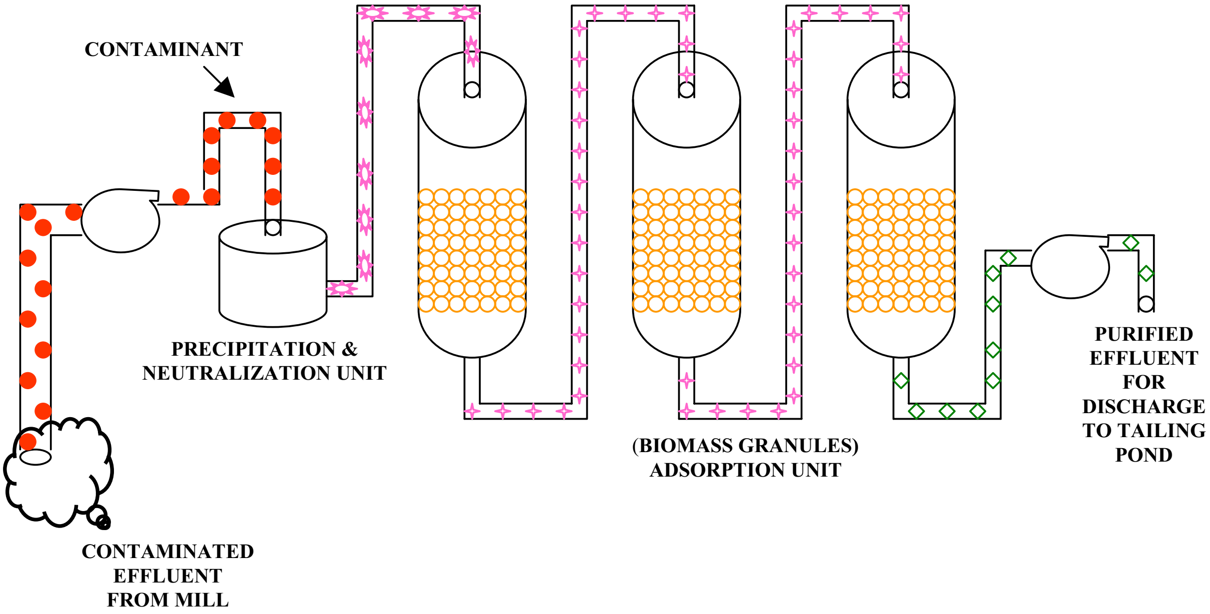


FIG. 1. Schematic representation of biosorption of Radium-226 technology.

ACKNOWLEDGEMENTS

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Radiochemical characterization of groundwater in Kazakhstan uranium province, prediction of influence of uranium ISL well fields on groundwater and environment

B.R. Berikbolov, P.G. Kayukov, L.S. Vyatchennikova, I.A. Shishkov, Yu.V. Popov

Joint-Stock Company “Volkovgeologia”,
Almaty, Kazakhstan

Abstract. Shu-Sarysu and Sredne-Syrdar’ya depressions are very large uranium provinces. Cretaceous and Paleogene permeable sediments of these provinces host uranium deposits in an important aquifer. Therefore an important task is an assessment of natural radioactivity levels in groundwater and the radioactivity and chemical influences of in situ leaching on these aquifers. Such an assessment will indicate whether some measures should be taken to purify contaminated water and prevent further contamination. This report makes an assessment of the radioactivity levels in groundwater in the Suzak region (a part of Shu-Sarysu uranium province). Investigations have shown that there is some potential for restoration due to natural processes. Shu-Sarysu and Sredne-Syrdar’ya depressions are known to contain the bulk of uranium reserves of Kazakhstan. Important features of these uranium provinces are their aquifers of fresh to somewhat brackish water. These reserves are a significant source of water supply for the regions contiguous to the Karatau mountain range (Fig. 1). Ecological investigations in this area are concerned with study of the interaction between radioactive orebodies and the natural increased radioactive plumes in groundwater, and the influence of uranium production on the environment. This paper presents results of geological and ecological investigations initiated by the Chief Geologist of Geological Group№ 5 of JSC “Volkovgeologia”, C.B. Aubakirov, several years ago and continued by Ecological Group№ 39 of JSC “Volkovgeologia”. Special investigations have been performed by specialists of the Central Scientific Research Laboratory of JSC “Volkovgeologia” under the framework of IAEA Contract № 9116 with the International Atomic Energy Agency (Technical Officer J.-P. Nicolet).

1. Determination of the natural radioactivity and composition of groundwater to develop measures for clean up in a uranium ore region

The first part of investigation was performed in the Suzak region including both uranium deposits and fresh aquifers.

1.1. Radiogeochemical characteristics of Uyuck aquifer

One of the most explored ore horizons within the Kanzhugan and Moinkum uranium deposits is Uyuck water horizon (aquifer) of Lower Eocene. It extends ubiquitously from a depth of 170 m in Kanzhugan to a depth of 500 m in Moinkum. The thickness of the sandy part of the aquifer reaches 30–40 m. The Uyuck Aquifer is isolated from adjacent aquifers by clay – aleurite (silt) impermeable horizons with a thickness to 10–15 m. Ores are located along regional oxidation – reduction interfaces. The medium and fine sand fractions are characterized by medium rounded grains. Clay, silt, lignite and mud rolls are also present within the sandy part of the sequence of sediments (lenses). The length of the sediments is 200 m, the width to 22 m and the extension is one kilometer to tens of kilometers. The average grade of uranium is 0.05-0.07% in the ore sand. Uranium minerals are coffinite and pitchblende. Also the ore sand is characterized by the presence of certain chemical elements (Fe^{++}, S^{-2}, C_{org}, P_2O_5) which indicate their adsorption/precipitation characteristics. It is noted also that there is some decreasing content of feldspar and muscovite and increasing content of kaolin and sulfides in gray sand which is not the case for barren unoxidized and oxidized sand.

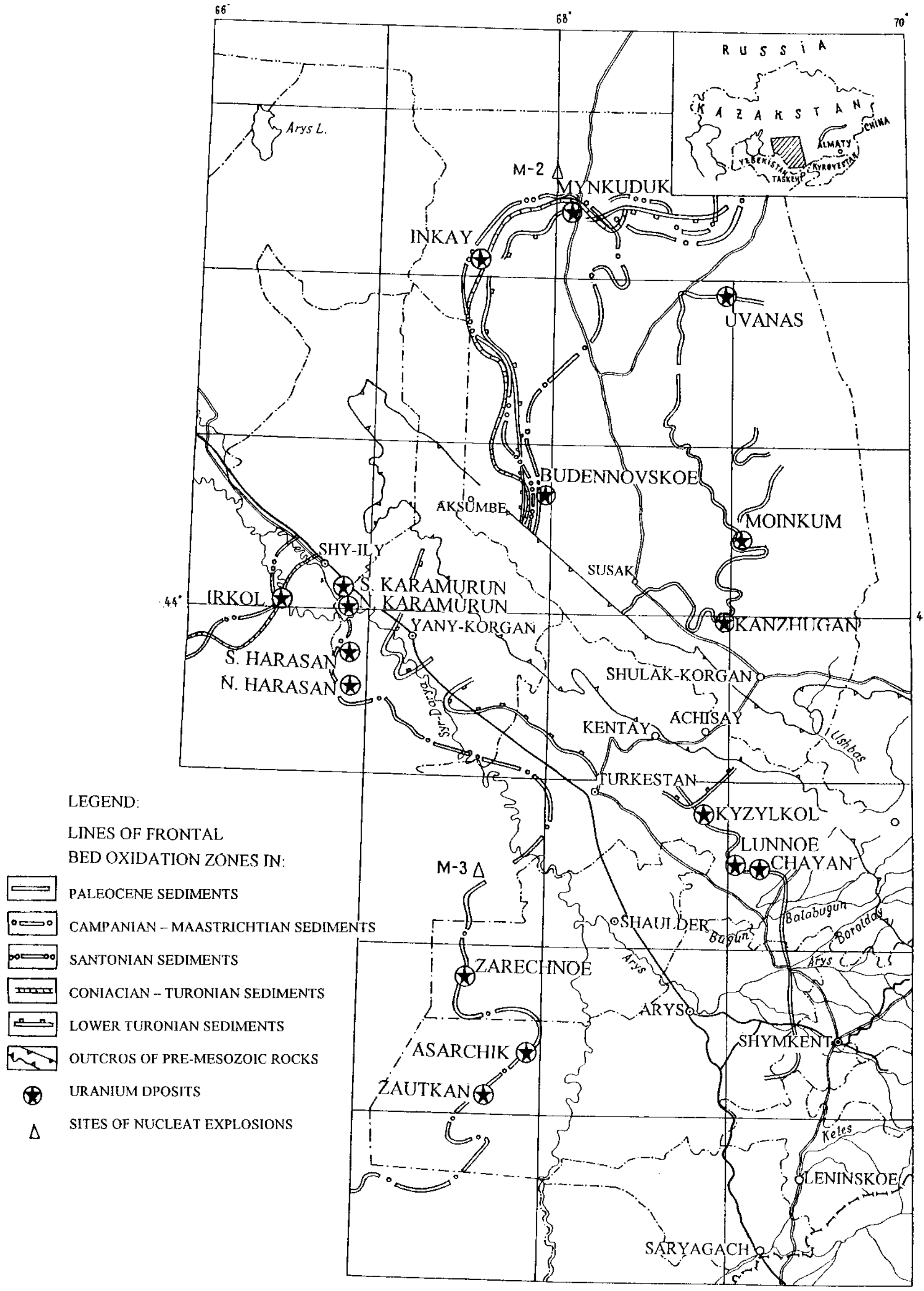

FIG. 1. Survey map of uranium ISL-provinces in Kazakhstan.

Comparison of geological, radiometric and radiochemical data performed on ecological – hydrochemical cross-sections through the Moinkum uranium deposit (Fig. 2) allows a separation into four geochemical zones in the direction from well No171в to well No 335г. The first zone located in the rear part of the deposit is characterized by an appearance signifying intensive oxidation processes. In aquifers of the zone, there is a significant amount of free oxygen that extensively oxidizes rocks in the zone. In the zone, both permeable and impermeable sediments with a thickness of the 5-10 m have been oxidized. Radioactivity of groundwater is very low in this part of the aquifers (wells No 171в, 304г, 156г), but sometimes the water can contain selenium.

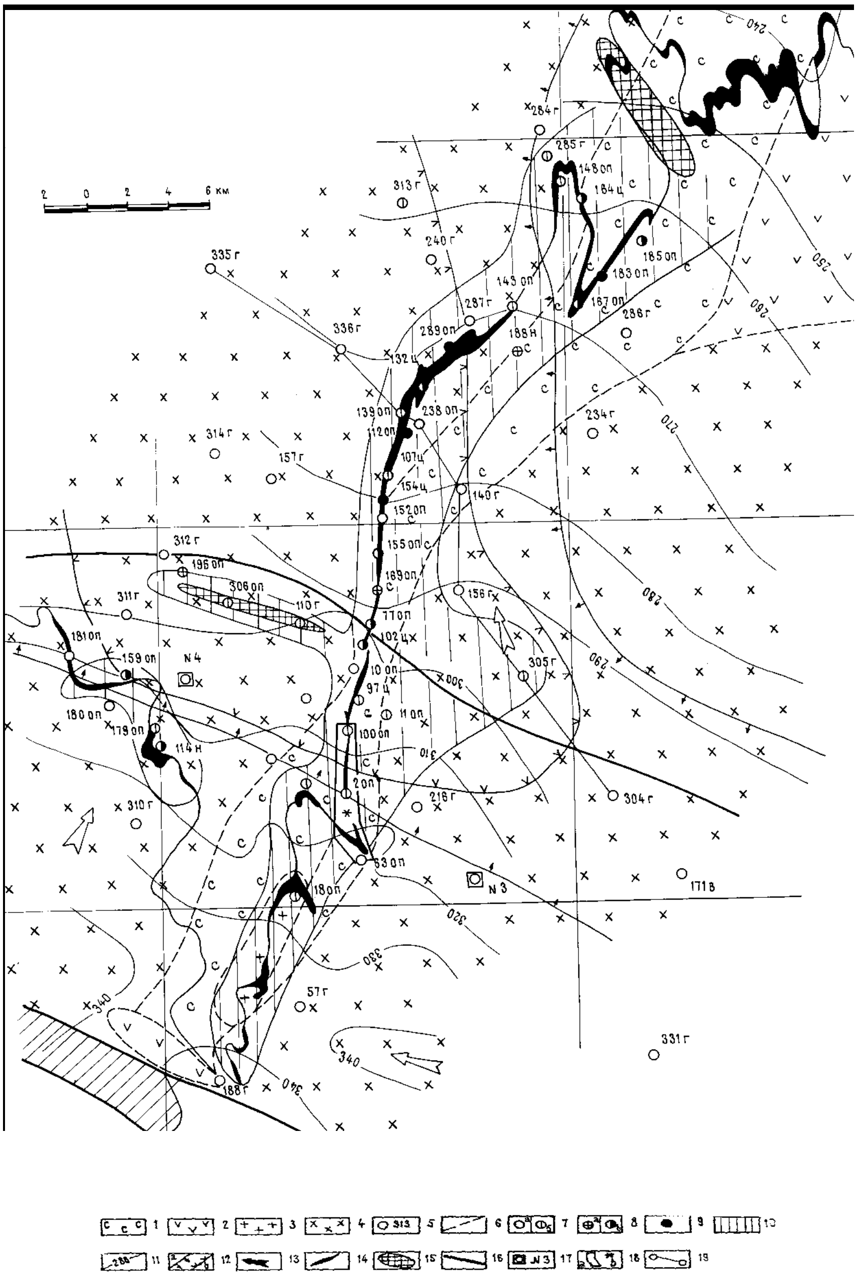

FIG. 2. Radiohydrogeochemical scheme of uyuck horizon ₽$_2$uk.
1-4) chemical composition of groundwater: 1) sulphate-carbonate sodium; 2) chloride – carbonate sodium; 3) chloride – sulphate sodium; 4) hydrocarbonate – chloride sodium; 5) hydrogeological well and its number; 6) a boundary of a groundwater spread of different chemical composition; 7-9) content of radium-226 in groundwater, multiple to the control level from NRB-96 (Standards of Radiation Safety): 7a - less 1, 7b – 1-3, 8a – 3-5, 8b – 5-10, 9 more 10; 10) a contour of projection of groundwater parts with content of Radium-226 more than the control level; 11) an absolute potentiometric level, m; 12) a projection of limits of artesian basin: a – in 1983 year, b – in 1989 year; 13) a main direction of groundwater flow; 14) uranium ore bodies (zalezhes); 15) a local uplift in Paleozoic basement; 16) a fault; 17) a water supply facility and its number; 18) an IS-leaching polygon: a – active production, b – experimental in past; 19) ecological-hydrochemical cross-section.

According to geological and geochemical features, the second zone shows only minor evidence of oxidation reactions. Here sandy rocks are fully oxidized, but clayey ones are only partly oxidized. Along the boundary between yellow and gray rocks, anomalous concentrations of uranium and selenium are noticeable, and groundwater is also characterized with high values of radionuclides (wells No 305г, 140г, and 238г). Groundwater in this zone does not meet drinking standards.

The third zone is the ore zone, with partial oxidation of permeable rocks where formation of orebodies take place, including enrichment of rhenium, selenium and other chemical elements. Groundwater in this zone is most enriched in radionuclides and can not be used as drinking water.

In the forth zone located down gradient from the orebodies, the rocks have the original color. Anomalous concentrations of uranium are not present in groundwater, but at times a high concentration of radium is observed 1-2 kilometers away from orebodies. Anomalous concentrations of Pb-210 are also found over a distance greater than 1-2 km (well No 336г). Groundwater of this zone cannot be used for water supply.

It should be considered that in the area, water from Uyuck is artesian that can lead to radioactive contamination of soil and ground around wells used without any control. Permeability coefficients of sand in the Uyuck Aquifer vary from 8 to 12 m/day. The measured velocity of groundwater flow is 10-15 m/year.

1.2. Determination of water quality

Hundreds of hydrogeological wells were drilled within ore fields before 1990 to assess regions suitable for mining using ISL. Solutions were analyzed to determine the following radionuclide concentrations, uranium, radium and radon in groundwater. During 1990-93, 70 special hydrogeological wells were constructed to assess the quality of groundwater in Uyuck Aquifer outside ore zones. Groundwater from these wells was also analyzed to determine radioisotopes such as Th-232, Th-230, Th-228, Ra-228, Po-210, Pb-210, and a wide range of other chemical elements.

In 1996-97 extensive hydrogeological data from “mined” Cretaceous-Paleogene aquifers (including Uyuck) were obtained to assess radionuclide levels of groundwater. Results of laboratory analyses were compared with permissible regulatory levels for radionuclides and chemical elements. As a result, it was shown that radioactivity is present in groundwater covering the zones of partial oxidation and unoxidized sands adjacent to the ore zone (Fig. 2).

On the whole, the data are in accordance with the established sequence of migration for elements in oxidised zones [6]. Both increased contents of radionuclides and V, Mo, Re are observed. However, only the concentration of selenium and radionuclides do not meet the water quality standards.

1.3. Extent of in situ leaching influence on groundwater quality

The oxidation processes of ISL intensify the naturally increased geochemical level of mineral zones. This was supported by a small ISL test performed on Ore Field 3u in the Kanzhugan Deposit in 1976 (Fig. 3).

Before the test, groundwater within contour of the ISL (area is 200 m^2) was characterized with values of pH = 6.7-7.2, Total Dissolved Solids (TDS) = 0.6 g/l and content of sulphate-ion

2.5 mg-equivalent/l. After the test, properties of groundwater within the contour changed: pH = 0.95-1.95, TDS = 15-20 g/l, content of sulphate-iron = 185 mg-equivalent/l. The concentrations of iron, aluminum, calcium and other chemical elements also increased significantly.

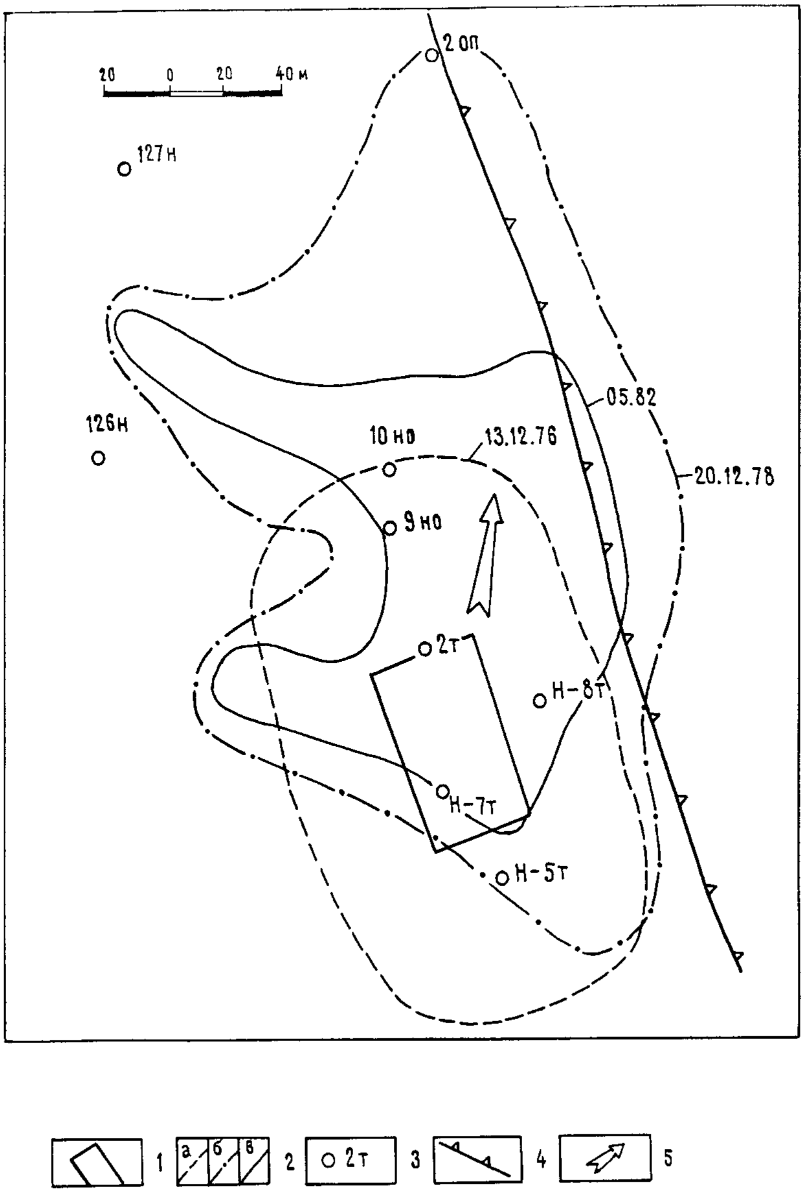

FIG. 3. The scheme of a spread of residual sulphate solution through an aquifer.
1) a contour of IS-leaching operation; 2) lines of pH = 7 at 13.12.76; 20.12.78 and 05.82; 3) a well and its number; 4) a front of a bed oxidation zone; 5) a main direction of groundwater flow.

After finishing the process of leaching, observations were made to monitor the spread and neutralization of residual solution inside and outside the affected contour. These were carried out from December 1976 to May 1982. The spread of polluted solution was located in the oxidized rocks (it is possible owing to conical depression caused by artesian hydrogeological well 2оп) within the area by the presence of radionuclides and selenium. It should be pointed out that the natural primary oxidized rocks have the ability to buffer sulphuric acid.

1.4. Determination of sorptive capacity of rocks

The sorptive capacity of possible cleaners of polluted groundwater – unoxidized sands sampled from Moinkum uranium deposit (sample 5) and zeolite from Sary-Ozek deposit (sample 6) located 140 kilometers from Almaty – were studied. The zeolite sample was especially prepared, first it was crushed, and then it was divided into fractions. Fractions from 0.25 mm to 2 mm were used in further investigations. Before subsequent experiments, both samples were analyzed to determine radionuclides (U, Th, Po-210, Pb-210, Ra-226, Ra-228, Th-228, K-40) and some other chemical elements: Se, Fe_{total}, S_{total}, and CO_2.

Experiments were performed in columns of ARSRICT (All-Russian Scientific Research Institute of Chemical Technology) at a fixed velocity of infiltration – 0.2-0.4 m/d. Residual solution from an ISL well field in the Kanzhugan Deposit was used as a typical lixiviant in these experiments. The solution had the following parameters: U = 14.4 mg/l, Fe^{3+} =781 mg/l, SO_4^{2-} = 9.8 g/l, Po-210 = 38.3 Bq/l, Pb-210 = 169 Bq/l, pH = 2.05 and Eh = -604 mV. Each sample was tested in several experiments: three for gray sand (5-1, 5-2, and 5-4) and two for zeolite (6-1 and 6-2).

Further methodology of these experiments is described in more detail in the next part of the paper. Here only results of these experiments are given. Concentration of chemical compounds in sand and zeolite before and after these experiments was used for calculations. Moreover analyses of these compounds were performed from four sections along a column with zeolite, this allowed careful calculation of sorptive coefficients and the observation of the distribution of chemical components along a column. Results of calculations for sorptive coefficients for the most restrictive radioactive elements are shown in Tables 1 and 2.

Table I. Sorption coefficients of sand and zeolite for polonium-210 and lead-210

Experiment/ sample numbers	Concentration in process solution, Bq/l		Volume of collected samples, l	L:S	pH	Concentration in collected samples, Bq/l		Sorption activity from solution, Bq		Sorption coefficients for sand, Bq/kg	
	Po-210	Pb-210				Po-210	Pb-210	Po-210	Pb-210	Po-210	Pb-210
				Sand							
5-2/10-1	<0.3[1]	<0.3[1]	0.674[1]	--	8.2	--	--				
5-2/10-2	38.25	169	0.616	0.4	8.0	<0.3	0.3	23.6	104.1		
5-2/10-3	38.25	169	0.917	1.0	4.0	<0.3	1.5	35.1	153.6		
5-2/10-4	38.25	169	0.485	1.33	2.5	<0.3	6.7	18.5	78.7		
Total			2.018					77.2	336.4	50.7	221.1
				Zeolite							
6-2/1	<0.3	<0.3	1.175[1]	-	7.8	<0.3	<0.3				
6-2/2	38.25	169	0.611	1.14	7.8	<0.3	<0.3	23.4	103.3		
6-2/3	38.25	169	0.307	1.72	4.2	<0.3	<0.3	11.7	51.9		
6-2/4	38.25	169	0.652	2.94	3.65	<0.3	<0.3	24.9	110.2		
6-2/5	38.25	169	0.415	3.71	3.62	<0.3	<0.3	15.9	70.1		
6-2/6	38.25	169	0,761	5.44	3.6	<0.3	<0.3	29.1	128.6		
Total			2.746					105.0	464.1	190.7	842.7

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[1] running water

Evaluation of the data was carried out by two approaches. Sorption coefficients were calculated for solution analyses (Table 1) and rock assays (Table 2).

These results of the experiments were used to calculate of volumes of gray sand and zeolite needed to clean groundwater containing high concentrations of radionuclides to the allowable limits. Zeolite can clean even process solution to this limit.

Table II. Data of sorption of radioisotopes polonium-210 and lead-210 in sand and zeolite

Experiment/ samples numbers	Weight of samples, g	Concentration of radionuclides before/after an experiment, Bq/kg		Sorption coefficients, Bq/kg	
		Po-210	Pb-210	Po-210	Pb-210
		Sand			
5-1 / 1	649.4	75.15 / 117	140.33 / 350	41.8	209.7
5-2 / 2	169.67	75.15 / 119	140.33 / 310	43.8	169.7
Medium value				42.8	189.7
		Zeolite*[2]			
6-2 / 1	102.39	10 / 530	25 / 4080	540	4055
6-2 / 2	95.58	10 / 86	25 / 115	76	90
6-2 / 3	158.96	10/25	25/25	--	--
6-2 / 4	193.65	10 / 25	25 / 25	--	--
Total on a column				123.2	769.6

The obtained results suggest the following conclusions:

— The higher radionuclide levels in groundwater in the Suzak region are due to uranium ores along the front of oxidation zones and these have become more reactive because of ISL. However this represents a small area compared with naturally polluted area.

— The impact ISL does not always lead to additional spatial contamination if the lixiviant solutions along the oxidation front or even on the side of oxidized rocks.

— Such natural substances as gray unoxidized uranium-free sand and zeolite can be used to clean groundwater containing higher values of radionuclides caused by natural or ISL processes. Zeolite is 10 times more effective than gray oreless sand.

2. Experimental-technological and mineralogical-petographic methods for assessment of the influence of ISL polygons on the environment

72% of Kazakhstan’s uranium reserves are suitable for in situ leaching (ISL). ISL has been used in Kazakhstan for more than 20 years and has substituted conventional mining methods. Undoubtedly using sulphuric acid allows for effective extraction of uranium from orebodies, up to 90%, but the acid also generates a great amount of chemical elements and compounds [7]. To demonstrate the feasibility of the ISL acid method, uranium producers carried out some large field experiments to demonstrate the concept of self-restoration. However the observed phenomena of self-restoration requires additional study. Our laboratory is carrying out investigations to enhance the accuracy of predicting the influence of ISL on the environment.

The methodology of these investigations is as follows:

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[2] Samples were selected by sections along a length of a column

- Laboratory tests to determine the sorptive-desorptive properties of sands from orebodies;
- Mineralogical-petrographic investigations of samples selected from the field and laboratory, and
- Periodical hydrogeological and geophysical monitoring of wells within and outside ISL fields.

The first two methods are being studied under the framework of IAEA project 9116, while the third method is being treated under the framework of Kazatomprom project "Assessment of influence of IS-leaching polygons on environment".

In both projects, samples of sands were selected from the Kanzhugan and Karamurun uranium deposits (Fig. 1), which are characterized by different geology and conditions for uranium leaching (Table 3).

Table III. Basic geological-hydrogeological parameters of North Karamurun and Kanzhugan

No	Parameters	North Karamurun	Kanzhugan
1.	Beginning of production	1979	1982
2.	Licensing area	12.96 sq. km	46.9 sq. km
3.	Depth of orebodies	525-530 m	240 m (₽ uk)[1] 285 m (₽ kn)[2]
4.	Average permeable thickness of ore horizon	40 m –K_2m	30 m (₽ uk) 30 m (₽ kn)
5.	Average orebody thickness	4.4 m	6.7 m
6.	Average uranium content	0.066%	0.038%
7.	Uranium minerals - accompanying elements	Pitchblende, coffinite Se	Pitchblende, coffinite --
8.	Carbonate content	0.5%	0.05-0.10% (₽ uk) 0.12-0.15% (₽ kn)
9.	Permeability coefficient	3-12 m/d	9.1 m/d (₽ uk) 7.1 m/d (₽ kn)
10.	Piezometric level of groundwater	- 3.2 - - 6.0 m	-127 - +25.8 m (₽ uk) - 51.7 -+30.6 m (₽ kn)
11.	Groundwater temperature	35-45°C	20-21°C (₽ uk) 23-25°C (₽ kn)
12.	Total dissolved solids (TDS)	0.5-0.9 g/l	0.5-0.7 g/l
13.	Velocity of groundwater flow	1-10 m/y	17.5 m/y (₽ uk) 14.0 m/y (₽ kn)
14.	Level of water table	0-5 m	12-17 m
15.	TDS in ground water	0.5-12.1 g/l	0.6-0.7 g/l
16.	Available confining bed		
	- upper orebody	300 m	0-20 m (₽ uk) 0-15 m (₽ kn)
	- lower orebody	3-20 m	0-15 m (₽ uk) m (₽ kn)

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[1] ₽-uk – Paleogene Uyuck horizon

[2] ₽-kn – Paleogene Kanzhugan horizon

2.1. Test methodology

2.1.1. Laboratory tests

Laboratory tests have been performed to determine sorptive-desorptive coefficients for gray and yellow sands selected from orebodies. These tests have been previously carried out using ARSRICT's (All-Russian Scientific Research Institute of Chemical Technology) columns at a flow rate 0.2-0.6 m/day. During this year researchers used the leaching column made by German firm Microwellen-Laboratorsystem ELMS ordered by IAEA under IAEA Project KAZ/3/002 "Modern technologies for uranium in-situ-leaching".

2.1.1.1. Determination of sorptive properties[3]

For the determination of sorptive properties of sands, leach solution is used from an ISL polygon where samples of sands are selected for filling the pipe. The solution was diluted 2, 4 and 8 times, and four tests were performed for each type of sand. Each test was performed in several stages. First running water was passed through the column to stabilize the hydrodynamic regime, then a non-sorptive indicator (solution of sodium chloride about 5 g/l) is passed. After achieving the initial value of the indicator concentration at the outlet of a column, leach solution is passed through the column. At the outlet, solution is sampled for:

- sorption indicators: Eh, pH and Cl^-;
- basic compounds: uranium, iron, aluminum and sulphate-ion.

These data allow calculation of hydrodynamic conditions and coefficients of permeability. Analytical results were used to determine the sorptive coefficients. After the tests, the content of columns are studied to determine particle size, petrographic and mineralogical characteristics.

It was evident that subsequent tests would require the following changes:

- The elimination of the use of sodium chloride as this solution is a source of cation exchange in mica; and lead to an error in the determination of the total retardation coefficients for chemical compounds in test samples;
- The replacement of the stabilizing (distilled) water by groundwater from the part of the test horizon located upstream of the sand sampling location. Properties of stabilizing liquid can differ from these of groundwater, and so final results on sorptive-desorptive properties will be affected by the properties of the stabilising solutions;
- Filtrates will also be analyzed to determine the content of silicic acid which is one of important components of sorptive-desorptive processes, and
- When using the ELMS leaching column, it should not be necessary to calculate the velocity of the filtrate as it is automatically controlled.

2.1.1.2. Oxidizing and recovery processing

To develop a methodology for determining the desorptive coefficients, uranium was leached from ore sand and then the sand was studied. In the first step, the sample was leached in 10 g/l sulphuric acid, and, in the second step, groundwater was used. Properties of the groundwater were similar to those of groundwater from ore sand. Before oxidizing, distilled water was passed through the column with the tested ore sand to stabilize the hydrodynamic conditions

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[3] These tests determine the retardation coefficients of chemical compounds in solutions flowing through sands.

(ISL groundwater will be used for this purpose in subsequent experiments). The present experiment was performed using the ELMS leaching column, provided with software to support the required pressure and flow in the column. This allowed the simulation of natural conditions for both ISL and post ISL processes.

2.1.2. Mineralogical–petrographic investigations

Size-by-size analyses and mineralogical-petrographic investigations were carried out on sand samples.

2.1.3. Hydrogeological and geophysical monitoring a pattern of observation wells within and outside ISL fields

Working regulations require a set of hydrogeological and geophysical observations on a specified set of wells within and outside ISL fields. These observations provide systematical control of injected and residual solutions within and outside contours of uranium extraction. They are performed 6 months. Hydrogeological control consists of sampling groundwater for pH, U, SO_4^{-2}, NO_3^- and basic chemical components analyses. Geophysical control consists of specifying conditions of different wells. In the current year, geophysical methods have been carried out to determine levels of groundwater (using current logging) and levels of electrical conductivity (using induction logging) to observe the extent of acidic reactions.

2.2. Outcomes of performed investigations

2.2.1. Laboratory tests

2.2.1.1. Determination of sorptive properties

The most complete tests have been performed for gray and yellow sands from the Kanzhugan uranium deposit using the method described in 2.1.1.1. When concentrations of initial solution and filtrate are known, sorptive coefficients are easily calculated. Results are shown in Table 4 and in Figure 4. The graphs show that the sorptive coefficients of sulphate-ion follow an exponential curve. They decrease with decreasing concentration of sulphate-ion in solution. During this year, similar investigations were carried out for three uranium deposits Kanzhugan, Karamurun and Uvanas under the framework of the project "Assessment of influence of IS-leaching polygons on environment". Sorptive properties were studied for the most permeable parts of the ore horizons that are likely to have the most impact on acquifers.

Table IV. Sorption coefficients calculated for SO_4, FE, AL, PB-210 in yellow and gray sand

Experiment number	Solution or dilution	Sulphate-ion		Iron		Aluminum		Lead-210	
		Initial concentration, mg/l	Sorption co-efficient, g/kg	Initial concentration, mg/l	Sorption co-efficient, g/kg	Initial concentration, mg/l	Sorption co-efficient, g/kg	Initial concentration, Bq/l	Sorption co-efficient, Bq/kg
Yellow sand									
7-1	Basic	9430	6.66	380	0.663	380	0.500	500	1100
7-2	1 : 1	4815	2.10	195	0.665	185	0.512	250	1050
7-3	1 : 2	3137	1.19	125	0.661	130	0.490	167	1010
7-4	1 : 7	1159	0.365	48	0.780	48	0.680	60	1060
Gray sand									
8-4	Basic	9400	14.33	320	4.92	295	3.73	40	5440
8-3	1 : 1	4720	5.74	160	4.72	146	3.64	200	4840
8-2	1 : 3	2370	0.74	80	4.37	75	3.41	100	5360
8-1	1 : 7	1150	0.35	39	4.52	38	3.62	48	5580

2.2.1.2. Oxidation and recovery processes

During ***the first stage*** of the experiment (Fig. 5), uranium is leached out of rocks with the first portion of the filtrate and reaches about 15% of total reserve at a liquid and solid ratio (L/S) of 0.2. The concentration of uranium is 110 mg/l and the concentration of sulphate-ion is up to 5g/l in filtrate. Then concentrations of uranium and sulphate-ion decrease to 0 when the ratio L/S is 0.5 after displacing 2-3 porous volumes. Other chemical compounds and elements such as iron, aluminum, and silicon oxide are not dissolved and are not present in the filtrate.

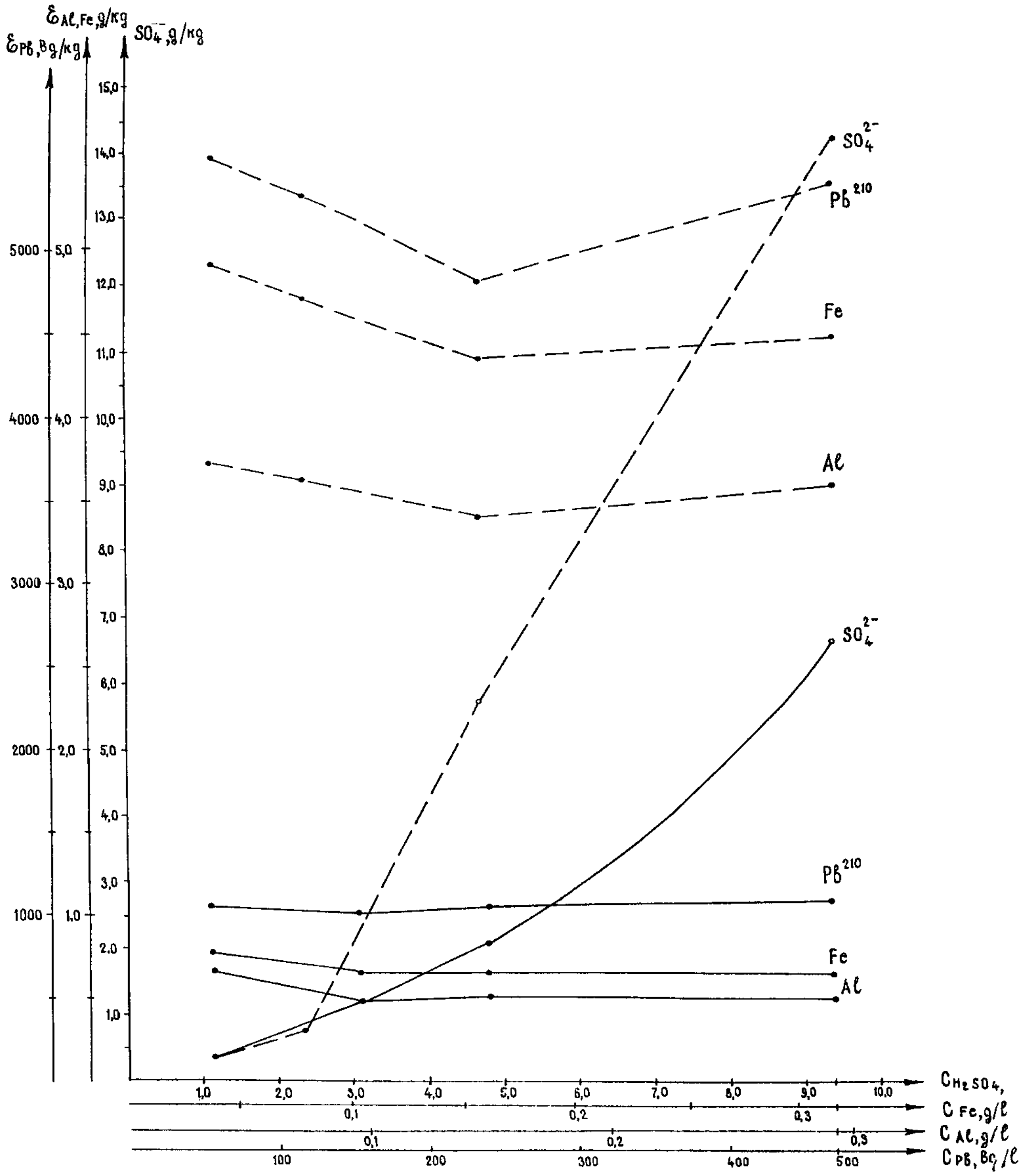


FIG. 4. Sorption capacity of yellow and gray sands for $S0_4^{-2}$, Al, Fe, Pb-210 depending on their content in solution.

LEGEND

_______________ *yellow oxidized sand;* ------------- *gray unoxidized sand.*

After achieving a L/S of 0.87 ratios and stabilizing the state of the infiltration, ***the second stage*** of the experiment (uranium extracted by sulphuric acid) is carried out at a 2 m/d flow velocity. This stage can be divided into 4 phases:

- Effect of “alkaline” leaching at L/S ratio 0.87-1.3;
- Active acidic leaching at L/S ratio 1.3-2.0;
- Bypassing acidic solution without noticeable extraction of essential and accessory components at L/S ratio 2.0-3.0 and
- Bypassing acidic solution with noticeable extraction of accessory components at L/S ratio 3.0-3.6.

During the first phase (a) pH decreases from 8.0 to 6.7 and uranium reaches 110 mg/l in filtrate, sulphate-ion increases up to 4 g/l from the reaction of sulphuric acid on rock, and Eh increases insignificantly from 190 mV to 210 mV. At this time the concentration of sulphuric acid is zero, and both iron and aluminum are absent in the filtrate. Other parameters such as Eh, pH, SO_4^{-2} reach a plateau as these parameters do not change during this phase. In this phase, 21% of the total amount of uranium is leached from the sample.

The second phase begins with an abrupt decrease of pH from 6.7 to 6.0 and Eh to 50-40 mV, this is caused by the passage of trivalent (up to 290 mg/l) and divalent (2 mg/l) iron into filtrate. Further decreases in pH and increases in Eh are accompanied by a simultaneous increase in concentration of uranium, Th-230, Pb-210, trivalent and divalent iron, aluminum and sulphate, and total acidity (Figures 5, 6, 7, 8), as well as generation of polysilicic acid ($xSiO_2*nH_2O$). At the same time, the pressure increases abruptly in the column indicating plugging from the generation of colloidal hydrous ferric and aluminum oxides and silicic acid. This leads to an increase of solution viscosity and a decrease in the infiltration coefficient. The blocking process continues to pH 2.0 and then all colloids are dissolved and the filtration coefficient increases and the pressure falls accordingly. At the L/S ratio 1.55, the concentration of uranium and all other elements reach maximum values in the filtrate (U–300 mg/l, Fe^{+3}–100 mg/l, SiO_2–350 mg/l, Al–700 mg/l, sulfation-iron–12 g/l, acidity–9 g/l, Eh–480 mV). Maximum values of aluminum and sulphate-ion appear at the L/S = 1.55, and the maximum concentrations of iron, thorium-230 and lead-210, accompanied by an increase in the concentration of silicic acid, appear a little later at (L/S = 1.6-1.7).

At L/S ratio 2.0, the process of active leaching ends, and *the third phase* starts. It corresponds to low steady values of all leached elements (U, Th, and Fe, except for Pb) and high steady values of Al, SiO_2, SO_4, and H_2SO_4. It indicates that the basic leaching process can be considered as complete when the L/S ratio reaches 2, although Pb-210 continues to wash out.

In *the fourth phase*, higher extractions of silicic acid and aluminum are noticed when the acidity reaches the initial solution concentration.

The third stage (–washout by natural groundwater–) begins at L/S ratio 3.6. Almost immediately the pH increases from 1.2 to 2.0 after displacement of one pore volume of sulphuric acid by groundwater (Fig. 6). The pH then increases gradually to 3.3. It is notable that values of sulphuric acidity and sulphate-ion decreases abruptly to safe level (from 10 g/l to 3.6 g/l. Just after washing out the first portions of pore solution with groundwater, the concentration of almost all elements in the filtrate almost reach groundwater levels. Silicic acid decreases from 350 mg/l to 150 mg/l and then remains steady at 100-120 mg/l for a long time. By comparison, the value of silicic acid is 18 mg/l in initial groundwater (Fig. 8).

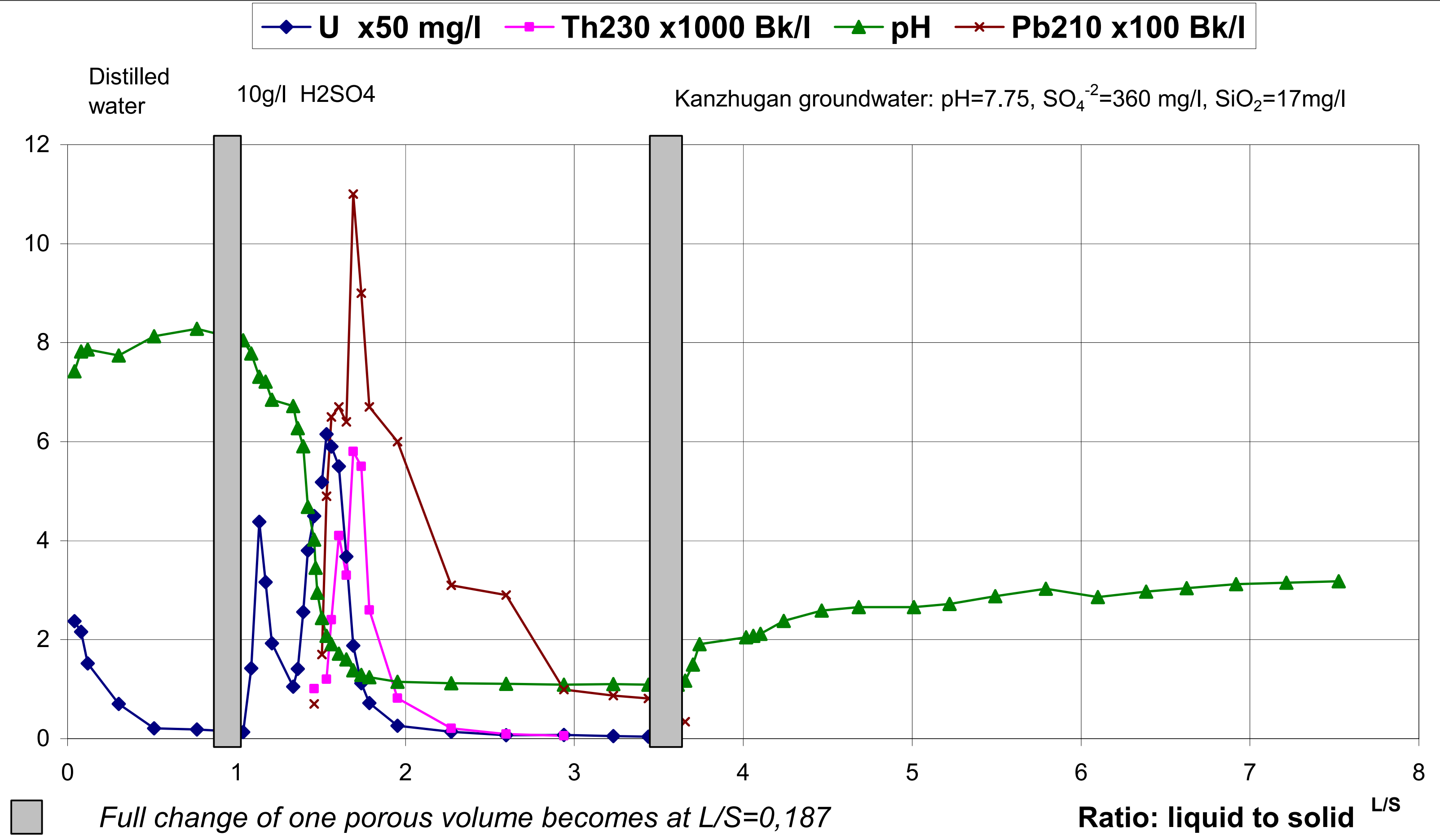


FIG 5. Change of pH, U, ^{230}Th, ^{210}Pb in process of uranium leaching and "recovery" of affected sand media.

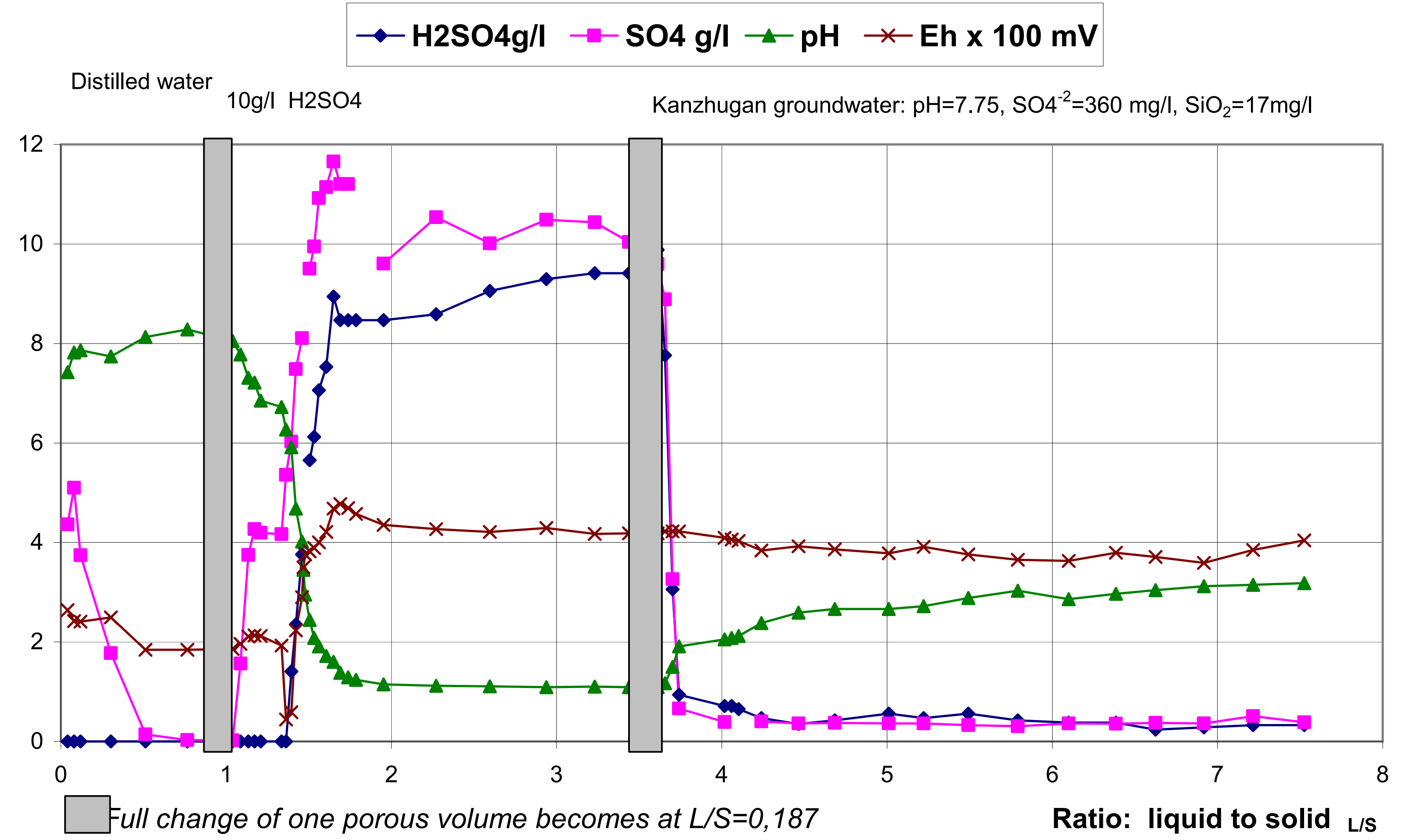


FIG. 6. Change of pH, Eh, H_2SO_4, SO_4^{-2} in process of uranium leaching and "recovery" of affected sand media.

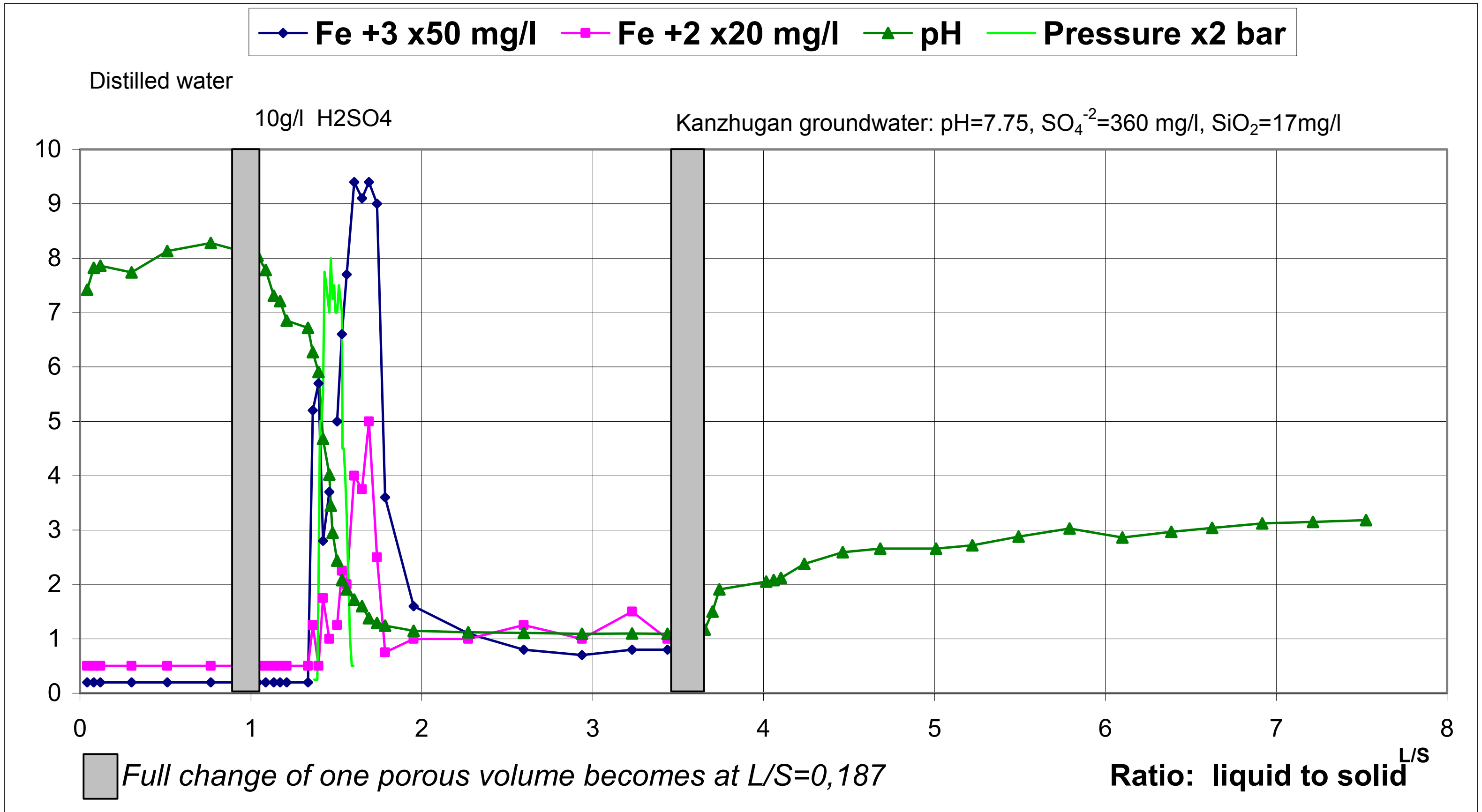


FIG. 7. Change of pH, Fe^{+3}, Fe^{+2}, pressure in process of uranium leaching and "recovery" of affected sand media.

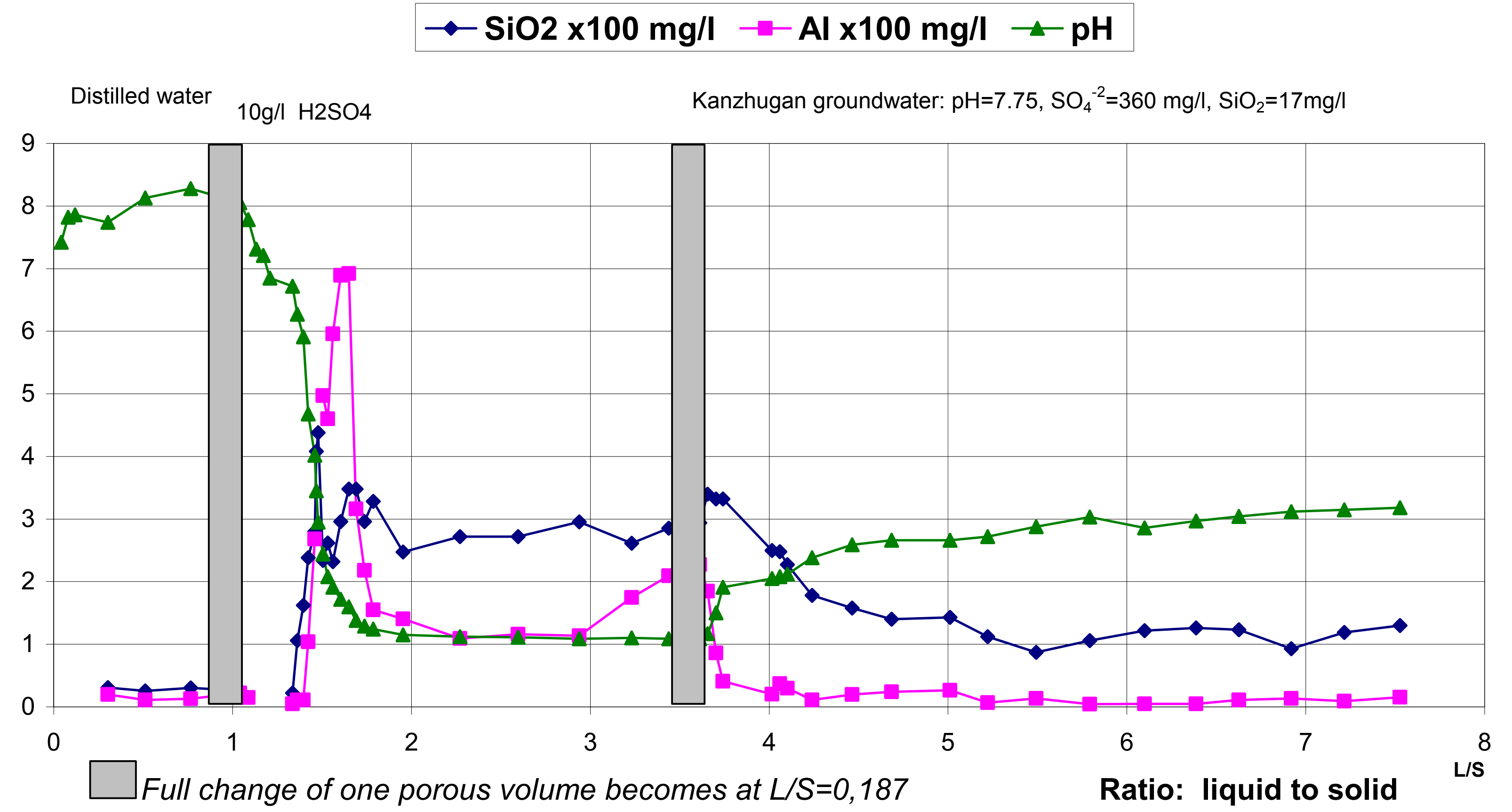


FIG. 8. Change of pH, SiO$_2$, Al in process of uranium leaching and "recovery" of affected sand media.

These results demonstrate that the reaction of the silicic core of the rock during the leaching process leads to a steady solubilisation of silicic acid under the influence of groundwater. It is likely that this does not allow the pH to return to the initial level as it remained at pH 3.0-3.1. This experiment should be continued to reach the initial pH and to obtain desorptive coefficients.

The experiments show that uranium extraction takes place in 3 stages. Using each stage in practice would allow the optimization of production processing by supplying the minimum necessary amount of sulphuric acid and thereby decreasing the negative impact on the environment. It should be recognized that forced passage of groundwater through affected sands with residual solution is not an effective method due to a peptization process. Although the concentrations of sulphuric acid and sulphate-ion decrease to a safe level, contaminants continue to enter the filtrate even after 20 pore volumes. Thus additional efforts are required to eliminate these elements.

Also, it can be expected that if the velocity of the filtrate in the experiment was near the real groundwater velocity of 0.005-0.06 m/d (for comparison, the experiment velocity was 0.24 m/d), recovery processes would not be needed, in so far as more stable fixing of new minerals would occur at the lower flow rate in the structure of porous space.

2.2.2. Results of mineralogical-petrographic investigations

2.2.2.1. Determination of sorptive properties

A comparison of the grain size distributions of initial and exposed sands shows very informative trends (Table 5, Fig. 9).

- A decreasing proportion of gravel and coarse fractions in gray sand and middle fractions of yellow sand.
- An increasing proportion of fine and silt fractions in gray sand and the fine fraction of yellow sand.
- Virtual absence of clay particles.

The following mineralogical-petrography features were observed in each granular fraction.

In the gravel and coarse sandy fractions, there a lot of aggregations of grains (up to 70%) in inequigranular sand with carbonaceous cement, especially in gray sand. The amount of quartz debris is 15–25%, and mud rolls are 10–12%. Moreover there is feldspar up to 10%, rock debris up to 5%, aggregations of *palygorskite and sepiolite* around 4% and rare plates of muscovite.

The decreasing amounts of gravel and coarse fractions of sand after treatment are explained by partial decomposition of cement. A new form of gypsum appears in a noticeable amount (up to 8%). The surface of calcite and ankerite is covered only partly with a thin friable incrustation of gypsum.

In addition, mud rolls are more porous, iron accumulates in a form of sulphate in new pores.

The medium sandy fraction consists of 69–71% quartz debris, 22–23% grains of feldspars and 5–8% aggregations with carbonaceous cement, rock debris, mud rolls, clastic plates of mica, aggregations of authigenic minerals of the palygorskite-sepiolite group.

FIG. 9. Changes of bulky weight of fraction according to initial weight.

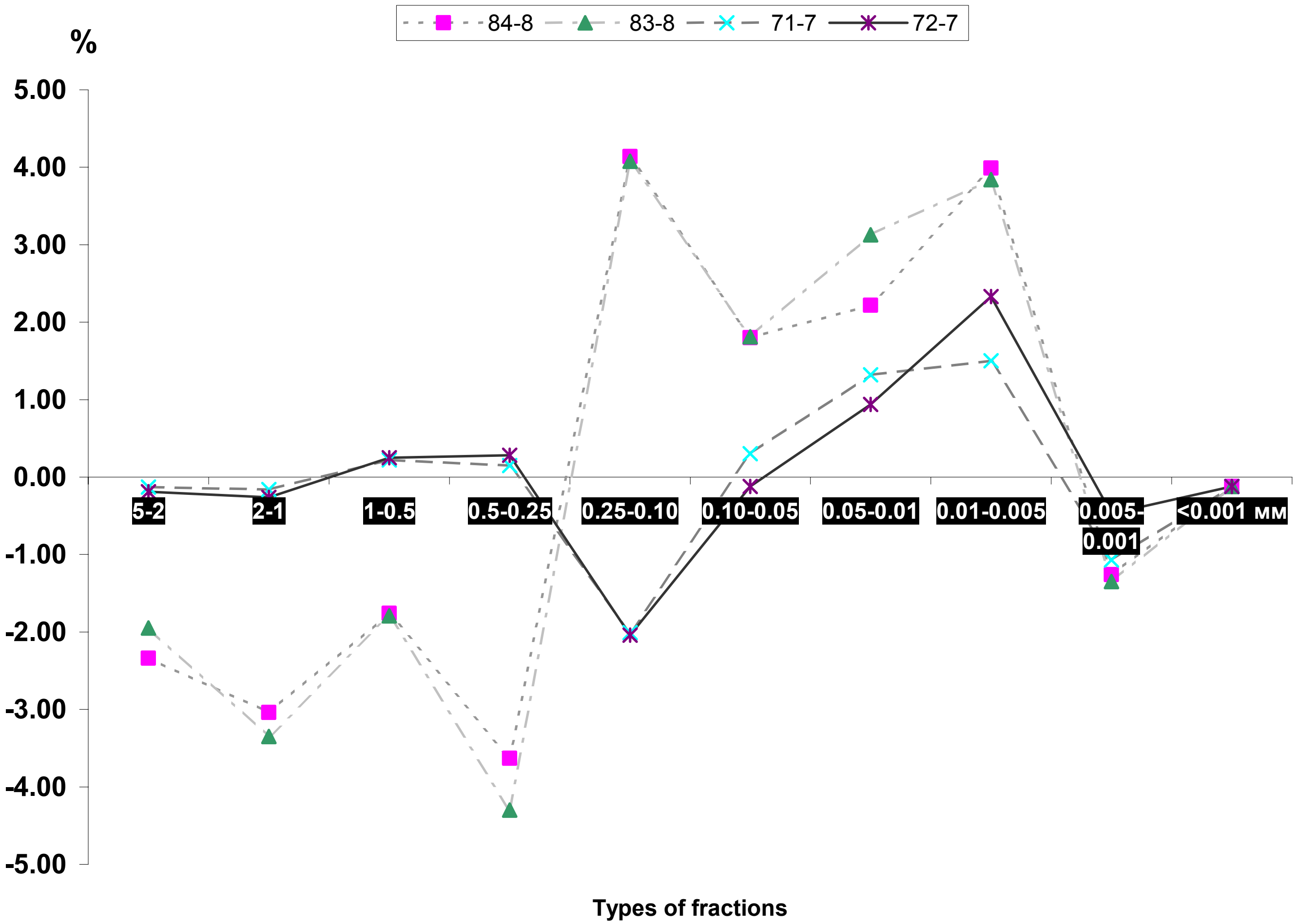


Table V. Grain size distribution of sample Nos. 8, 7, 84, 83, 71, 72

Grain size in distribution (% in fraction)																pH of washed water
Classes	Gravel			Sandy					Aleuriteous (Silt)			Clay			Grand total	
Fraction, mm	5-2	2-1	Total	1.0-0.5	0.5-0.25	0.25-0.1	0.1-0.05	Total	0.05-0.01	0.01-0.005	Total	0.005-0.001	<0.001	Total		
No of samples																
8[1]	2.89	4.56	7.45	3.02	38.60	39.83	4.41	85.86	2.30	2.57	4.87	1.70	0.12	1.82	100	7.84
84[2]	0.55	1.52	2.07	1.26	34.97	43.97	6.21	86.41	4.52	6.56	11.08	0.44	0.00	0.44	100	3.18
83[3]	0.94	1.21	2.15	1.23	34.30	43.91	6.22	85.66	5.43	6.41	11.84	0.35	0.00	0.35	100	4.27
7[4]	0.2	0.6	0.8	1.02	53.15	34.56	3.38	92.11	2.28	3.24	5.52	1.45	0.12	1.57	100	7.74
71[5]	0.07	0.44	0.51	1.24	53.30	32.55	3.68	90.77	3.60	4.74	8.34	0.38	0.00	0.38	100	3.24
72[6]	0.01	0.34	0.35	1.27	53.43	32.52	3.26	90.48	3.22	5.57	8.79	0.98	0.00	0.38	100	3.37

---

[1] Sample of gray sand before the sorption experiment

[2] Sample of gray sand after the sorption experiment with initial residual solution

[3] Sample of gray sand after the sorption experiment with residual solution diluted 1:1

[4] Sample of yellow sand before the sorption experiment

[5] Sample of yellow sand after the sorption experiment with initial residual solution

[6] Sample of yellow sand after the sorption experiment with residual solution diluted 1:1

Tuff debris has undergone a process of argillization associated with the development of gibsite observed as full pseudomorphs (Fig. 10). In some cases there are poikiloblastic structures of substitution of terrigenous grains of quartz by dickite (Fig. 11) and special opal. A film of clayey mineral (montmorillonite) develops on the etched surface of the grain then opal develops on this surface.

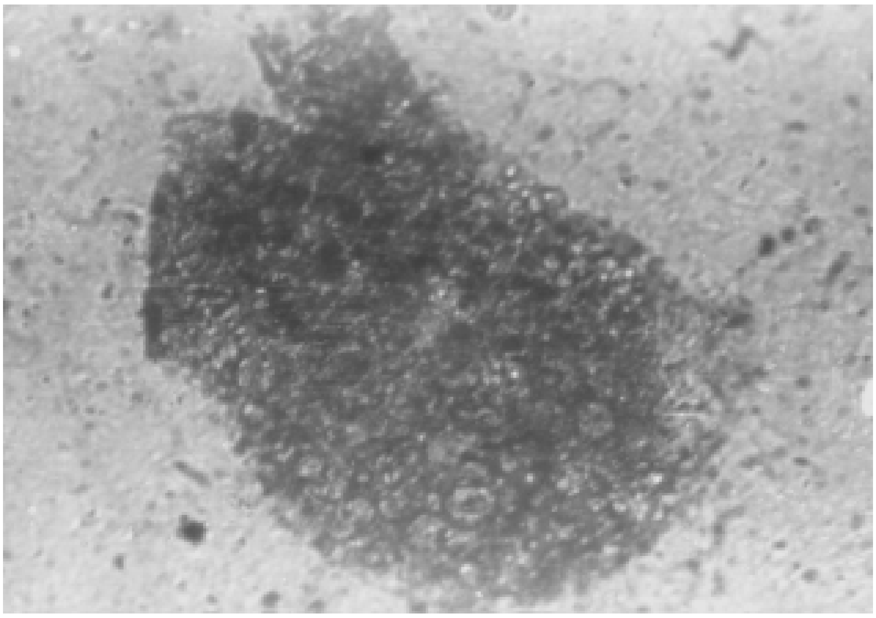


FIG. 10. Full pseudomorph of globular aggregations of gibbsite onto detrical (clastic) grain of vitrotuff with perlitic jointing. Immersion preparation, magnified 300x, parallel nicol prisms (P-).

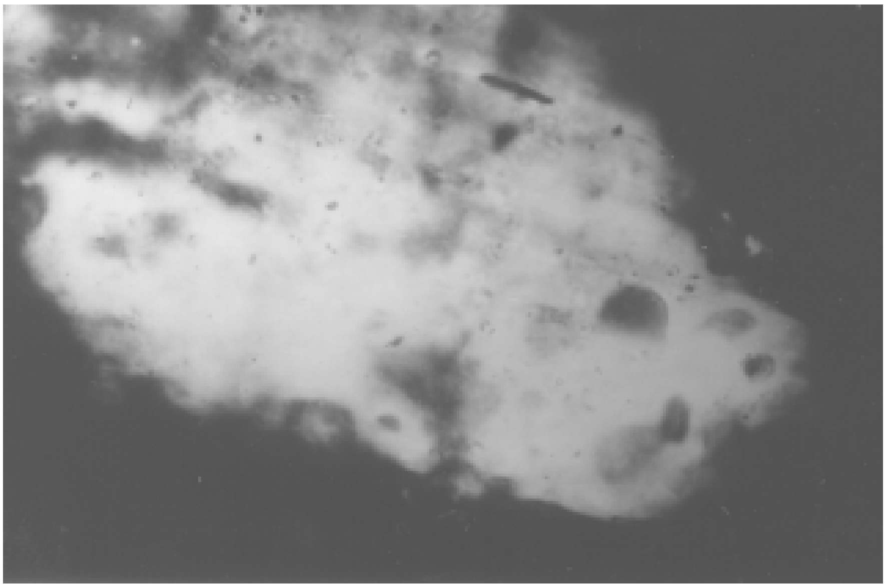
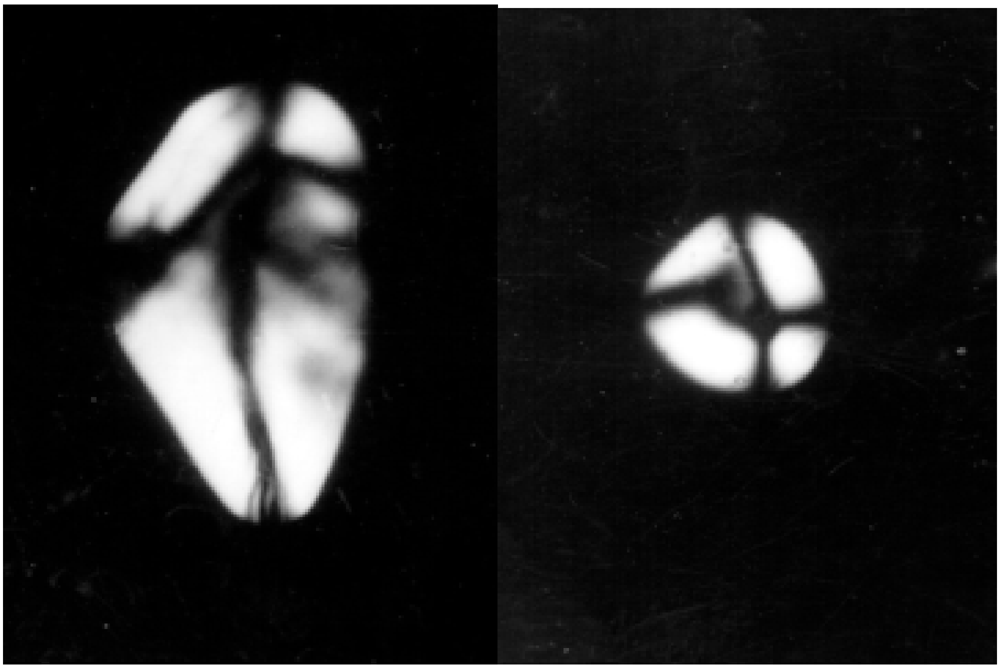


FIG. 11. Corrosive-limbate ("skirt" of montmorillonite) and poikiloblastic (oval separations of dickite – dark) structures of clastic grains of montmorillonite.

The fine fraction of sand class was very clean, containing only 4% of other minerals, including single plates of biotite, grains of ankerite and minerals of palygorskite-sepiolite group. The basic composition of the fraction is 50-55% clastic grains of quartz, 20-22% montmorillonite with small amount of glauconite and kaolinite. In this fraction there is an extensive list of authigenous minerals such as dickite, analcime, zeolites, group of palygorskite-sepiolite minerals, common potash, feldspar, albite, bituminous substances and several types of opal (shown in Figures 12, 13).



FIGS. 12, 13. Sample 8, sandy class. Spherical (0.027 mm) and ellipsoidal (0.06 mm) particles of opal-CT. Immersion preparation, magnified 670x, crossed nicol prisms (P+).

After treatment some alumen appears in the shape of small aggregations within montmorillonites. Soluble iron sulphate occurs in all structures of minerals, particularly, montmorillonites.

In the silty fractions, the content of montmorillonite increases to 60-70%, hydromica to 10%, and kaolinite to 3-5%, the quartz decreases to 5-10% and potash feldspar to 4-8%. There is also a considerable list of silty minerals from common opal to zeolites and bituminous substances.

During the experiment, two basic groups of silt minerals were generated. They consist of hydrous sulphates of calcium, magnesium, aluminum, iron and minerals of silica and aluminum. Examples of mineral changes are shown in Figures 14, 15, 16, and 17.

In clay fractions, the basic clay minerals are montmorillonite, hydromica and kaolinite. Frequently clay minerals are within the structure of feldspar and zeolites from which they were generated. After the sorption experiments, the compositions of the clay minerals changed significantly (Fig. 18).

In addition to investigations of solids before and after sorption experiments, *washed water* obtained after the wet sizing was also analysed. In wash water from gray sand that was not subject to sulphuric acid treatment, two mineral soluble forms of iron coquimbite ($Fe(SO4)_3 \cdot 9H_2O$) and melanterite ($FeSO4 \cdot 7H_2O$) were not found [Figs. 19, 20]. In the washed water of gray sand subjected to diluted sulphuric acid, Fe^{2+} is absent and Fe^{3+} is present in a small amount, up to 0.4 mg/l. In the washed water of gray sand subjected to strong acid, Fe++ is 3 mg/l and Fe+++ is 8 mg/l. These observations demonstrate that the investigations can assist in understanding the sorptive process occurring in the aquifer under natural and ISL conditions.

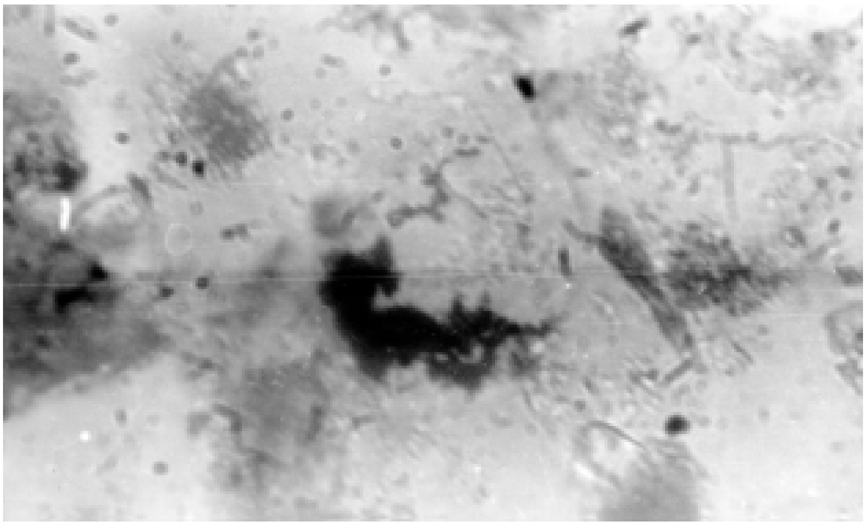


FIG. 14. Sample 83, clayey class. A structure of corrosive dilution of ore grains (iron sulfide?) with simultaneous growth of iron sulphate onto relic grains of sulfide. Immersion preparation, magnified 610x, parallel nicol prisms (P-).

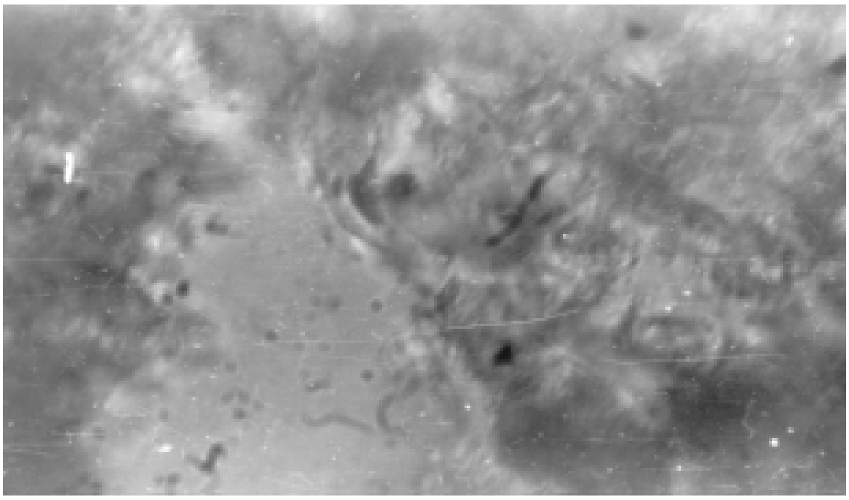


FIG. 15. Sample 71, a fraction of fine aleurite. Aggregations of alumen with microinclusions of aqueous phases (dark) in crystals.

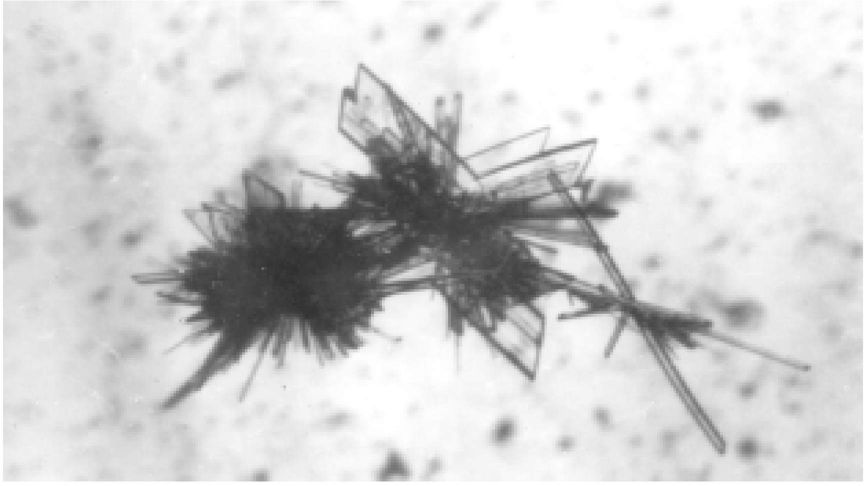


FIG. 16. Ontogenesis of single crystals of technogenous gypsum and its intergrowths. Spherical druses of thin needle-like gypsum, cruciform twins of tabular crystals, thin prismatic abruptly elongated crystals. Sample 84, magnified 100x, parallel nicol prisms (P-).

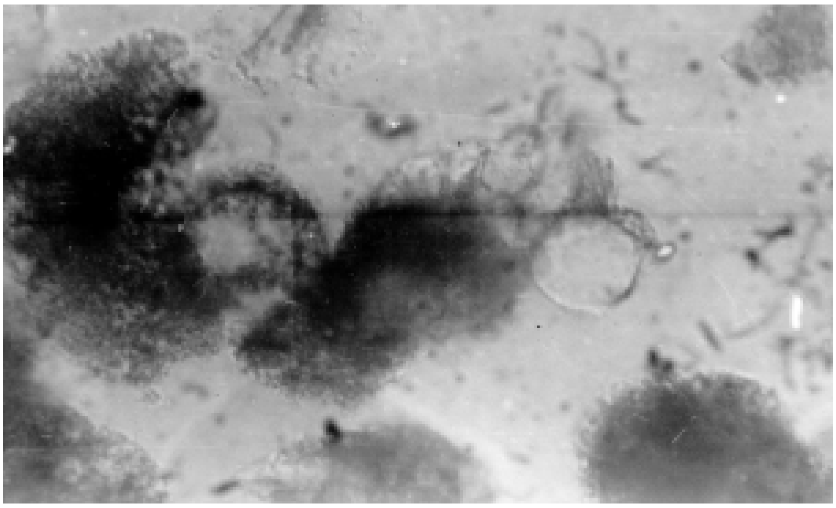


FIG. 17. Sample 83. A fraction of coarse aleurite. Globules of gibbsite (0.03 mm) are amongst montmorillonite aggregations (dark). Particles of montmorillonite are pseudomorphs onto zeolites with intensive corrosive structure.

Table VI gives the list of minerals in the sands before and after the treatment by acid.

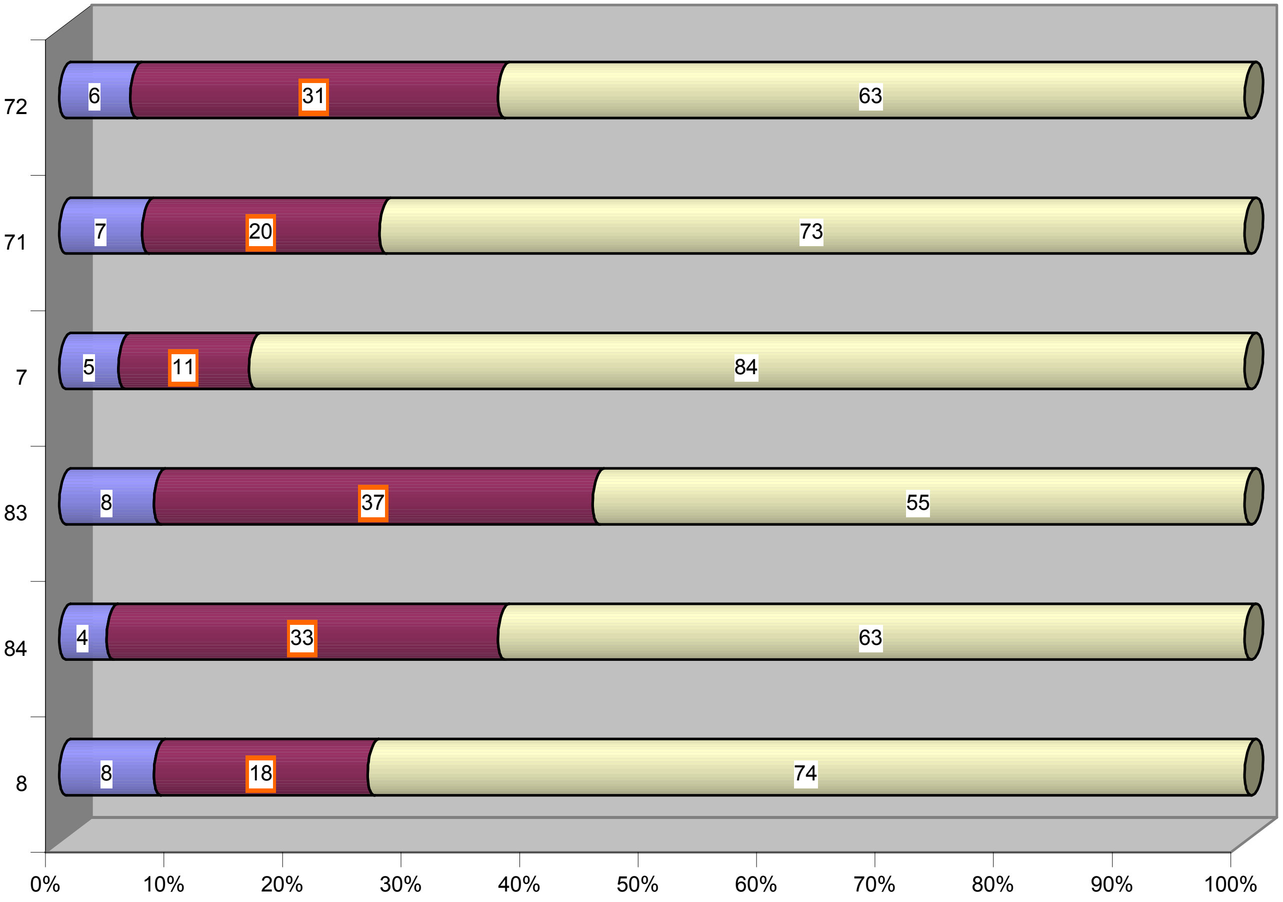
Table VI. Mineral identified in sands before and after treatment (experiment 1999)

Type of mineralization	Mineral composition					
	Basic		Secondary		Rare	
Naturally	Analcime	$NaAlSi_2O_6*H_2O$	Albite	$NaAlSi_3O_8$	Anglesite	$PbSO_4$
occurring	Ankerite	$Ca(Fe,Mn,Mg)(CO_3)_2$	Allophane	$Al_2O_3*SiO_2*nH_2O$	Crandallite	$CaAl_3(PO_4)_2(OH)_5*H_2O$
	Calcite	$CaCO_3$	Alumen	$KAl(SO_4)_2*12H_2O$	Cu sulphate	
	Chabasite	$CaAl_2Si_4O_{12}*6H_2O$	Bitominous		Dolomite	$CaMg(CO_3)_2$
	Common opal	SiO_2	substance		Jarosite	$KFe_3(SO4)_2(OH)_6$
	Desmine (Stilbite)	$NaCa_2Al_5Si_{13}O_{36}*14H_2O$	Carbonate-apatite	$Ca_5(PO_4CO_3)_3(OH,F)$	Mellite	$Al_2[C_6(CO\ O)_6]*18H_2O$
	Gibbsite	$Al(OH)_3$	Coquimbite	$Fe_2(SO_4)_3*9H_2O$	Mg-hydroscopic	
	Glauconite	$(K,Na)(Al,Fe^{3+},Mg)_2$	Dickite	$Al_2Si_2O_5(OH)_4$	mineral	
		$(Al,Si)_4O_{10}(OH)_2$	Ferriferous oxides		Siderite	$FeCO_3$
	Heulandite	$(Na,Ca)_{4\text{-}6}Al_6(Al,Si)_4$	and hydroxides		Sodalite (?)	$Na_4Al_3Si_3O_{12}Cl$
		$Si_{26}O_{72}*24H_2O$	Gypsum		Tuyamunite	$Ca(UO_2)_2(VO_4)_2*5\text{-}8H_2O$
	Montmorillonite-1	$R_{0,33}Al_2Si_4O_{10}(OH)_2*nH_2O$	Marcasite	$CaSO_4*2H_2O$	(calciocarnotite)	
	Montmorillonite-II	where R is one or some of	Mirabilite	FeS_2	Wairakite	$CaAl_2Si_4O_{12}*2H_2O$
		Na^+,K^+,Mg^{2+} and Ca^{2+}	Orthoclase	$Na_2SO_4*10H_2O$	Wavellite	$Al_3(PO_4)_2(OH)_3*5H_2O$
	Noble opal	SiO_2	Phosphates	$KAlSi_3O_8$		
	Opal-CT-I	SiO_2	Pyrite			
	Opal-CT-II		Se-mineral	FeS_2		
	Palygorskite	$(Mg,Al)_2Si_4O_{10}(OH)*4H_2O$	Uranium oxide			
	Quartz	SiO_2				
	Sepiolite	$Mg_4(Si_2O_5)_3(OH)_2*6H_2O$				
	Silicic alumogel					

Formed under ISL conditions	Basaluminite	$Al_4(SO_4)(OH)10*5H_2O$	Allophane*	$Al_2O_3*SiO_2*nH_2O$	Autunite	$Ca(UO_2)_2(PO_4)_2*10H_2O$
	Coquimbite*	$Fe_2(SO_4)_3*9H_2O$	Alunogen	$Al2(SO_4)_3*18H_2O$	Metatorbernite	$Cu(UO_2)_2(PO_4)_2*8H_2O$
	Ferriferous oxides and hydroxides*		Anglesite*	$PbSO_4$	Metatuyamunite	$Ca(UO_2)_2(VO_4)_2*35H_2O$
	Gibbsite*	$Al(OH)_3$	Jarosite*	$KFe_3(SO4)_2(OH)_6$	Wavellite	$Al_3(PO_4)_2(OH)_3*5H_2O$
	Gypsum*	$CaSO_4*2H_2O$			Zippeite	$(UO_2)_2(SO_4)(OH)_2*4H_2O$
	Kalinite	$KAl(SO_4)_2*11H_2O$				
	Melanterite	$FeSO_4*7H_2O$				
	Potassic alumen					
	Silicic alumogel Opal-CT	SiO_2				

Additional list of mineralization in sands (experiment 2000) (without separation):
Amarantite $FeSO_4(OH)*3H_2O$
Aragonite $CaCO_3$
Boehmite $AlO(OH)$
Carphosiderite *see* Hydronium jarosite
Epsomite $MgSO_4*7H_2O$
Goehtite α-$FeO(OH)$
Halite $NaCl$
Halotrichite $FeAl_2(SO_4)_4*22H_2O$
Hematite α-Fe_2O_3
Hydronium jarosite $(H_3O)Fe(SO_4)_2(OH)_6$
Limonite is a mixture of goethite, hematite, lepidocrocite and water
Metavoltine $(K,Na,Fe)_5Fe_3(SO_4)_6(OH)_2*9H_2O$
Roemerite $Fe^{2+}Fe_2^{3+}(SO_4)_4*14H_2O$
Sylvite KCl
Tachyhydrite $CaMg_2Cl_6*12H_2O$
Voltaite $K_2Fe_5^{2+}Fe_4^{3+}(SO_4)_{12}*18H_2O$

FIG. 18. Ratio of different types of clays in samples before and after the influence of residual technological solution.



	8	84	83	7	71	72
Montmorilonite	74	63	55	84	73	63
Hydromica	18	33	37	11	20	31
Kaolinite	8	4	8	5	7	6

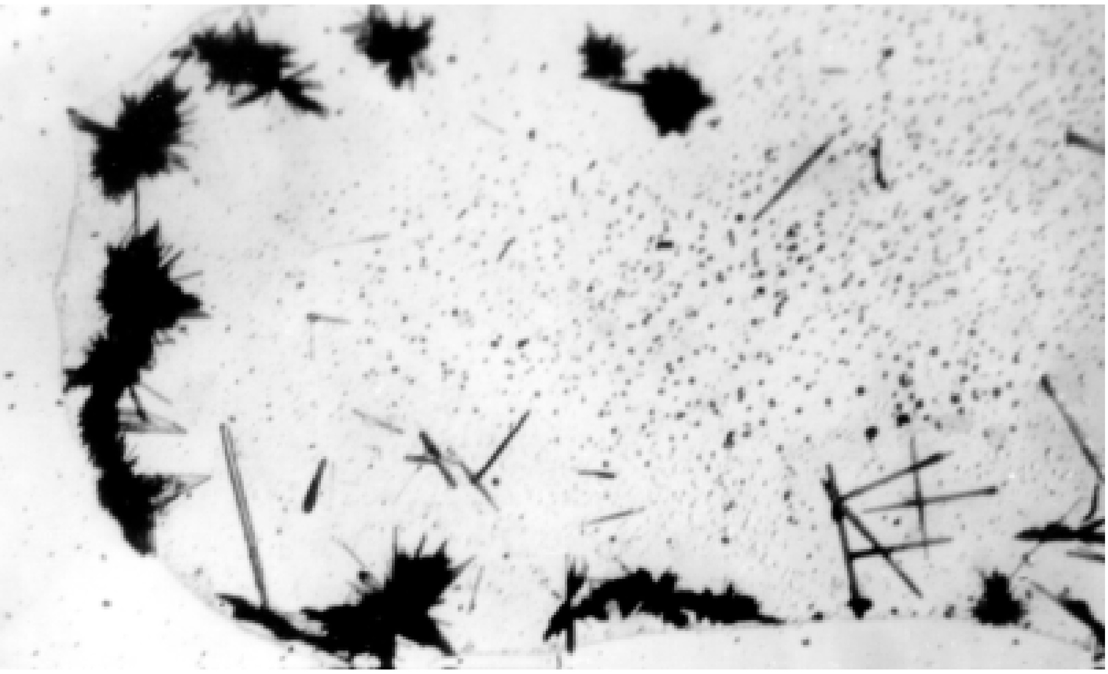


FIG.19. A preparation of washed water, sample 84. The character of distribution of soluble (90%) and dispersed (10%) (spots in the center) phases. The main mineral of the solution is needle-like gypsum and its spherical separations in the margin of the preparation. Magnified 25x, parallel nicol prisms (P-).

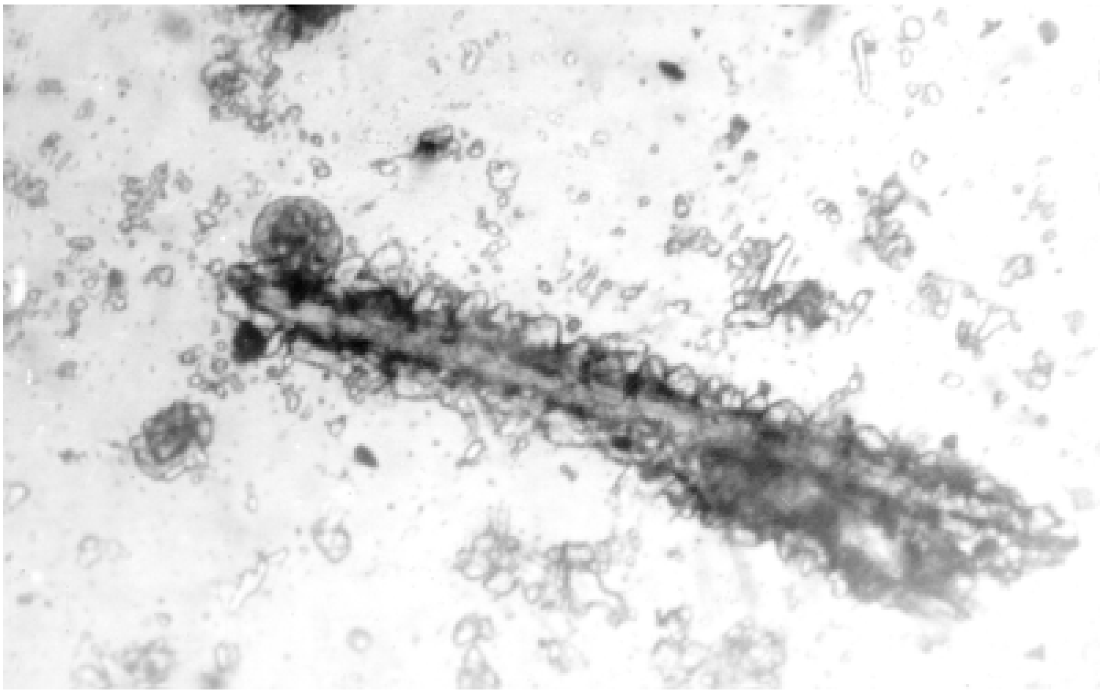


FIG. 20. A preparation of washed water, sample 84. A needle-like of gypsum, incrustate close-grained aggregation of melanterite. On the left is coaxial globule of gibbsite. Polydispersed structure and polycomponent composite of the margin of the preparation, small crystals of melanterite and needles of gypsum.

Many of naturally occurring minerals are sorptive. Basically the sorptive minerals are present as small particles. Physical-chemical properties of small particles (10-100 nm) essentially differ from those of much larger particles. Examination of high by-porous rock mineral assemblages under optical and electronic microscopes show that part of the samples has adsorption and ion exchange properties. The published data in Table 7 show some physical characteristics of some thin dispersed minerals.

Table VII. Characteristics of sorptive minerals

No	Name of minerals	Size of particles, μm	Average radius of pores, A°	Specific surface, m^2/g
1.	Quartz, SiO_2	0.00n-10n		
2.	Silicic gel Common opal Opal-CT Noble opal	0.0n-1n	8-40	560
3.	Allophane	0.0n-0.n	50	698
4.	Montmorillonite	0.0n-10n	7-12	
5.	Zeolite	0.0n-10n	3-9	

2.2.2.2. Oxidization and recovery processes

The first stage of the treatment with distilled water shows some soluble minerals and a small amount of dispersed-colloidal minerals. Among them, sulphates such as mirabilite, melanterite, epsomite, alumen, gypsum play a main role, and halides (halite, tachyhydrite, sylvite, carbonates of calcium, magnesium and iron (ankerite and aragonite), bicarbonates of calcium and magnesium, colloidal forms of aluminum silica gel, ferric hydrate and colloidal mineralization of uranium play a subordinate role. Distilled water is a weak oxidant, and can oxidise ferrous to ferric ion. Thus coquimbite and gypsum also appear in the filtrate. Insignificant but stable solubility of bicarbonates and carbonates leads to an increase in pH to 8.14. Changes in the aluminum silica gel were not observed.

After the treatment with distilled water the sample in the column was subjected to a *solution of sulphuric acid* (10%) and the *behavior of iron* was studied.

By decreasing the pH to 6.17, hydrolysis processes of iron hydroxide, in the form of crystalline goethite combined with gypsum (Figs. 21, 22), were observed, as well as divalent iron sulphate – melanterite. With a further decrease of pH, goethite is transformed to amorphous limonite, and melanterite transforms to coquimbite. At pH 2.5-1.3, soluble trivalent – divalent iron sulphate forms as voltaite (Fig. 23), then later to roemerite. The color of the filtrate changes from dark-green to brownish-brown. The appearance of roemerite is explained by lack of potassium in the leaching solution. There is also a notable amount of soluble divalent iron and aluminum sulphate – halotrichite – in combination with soluble divalent and trivalent iron sulphate. Simultaneous increases in the concentrations of Fe^{++} and Fe^{+++} are observed at pH 2.3-1.3 (Fig. 7).

Hydrolysis processes of freshly generated iron sulphates are completed by the formation of soluble basic sulphates. First carphosiderite (Fig. 24), then amarantite, and later metavoltine, appear in the filtrate.

The *behavior of aluminum* is complicated in the sulphuric acid leaching stage. The acid reacts with aluminum to form aluminum silicic gel in a highly dispersed form.

By reaction with sulphuric acid, aluminium hydroxide transforms partly into alumen and stays partly as the hydroxide. An increase in the Al^{3+} is observed at pH = 5.7 in the leach solution. At pH = 2.13 colloidal hydroxides of aluminum precipitate in a form of boehmite and a form of gibsite. Aluminum hydroxide shows high sorption capacity for uranium. At the same pH, a noticeable part of aluminum is also present as the sulphate (alumen and alunogen in Figures. 25, 26) and by decreasing to pH 1,3 halotrichite is observed.

FIG. 21. Goethite and gypsum are in a spot of filtrate at pH = 1.08; magnified 75x; parallel nicol prisms (P-).

FIG. 22. The same one, crossed nicol prisms (P+).

The form of silica is determined by the behaviour of collodial silica. The precipitation of colloidal silica is associated with gibbsite, and alumen by pH = 2.13, where it participates in processes of uranium mineralization sorption.

According to the literature, at pH = 1.9, the negative charge on surface of colloidal particles goes to positive change. At pH 1.6-1.3 chemical analysis show a maximum concentration of SiO_2 in the filtrate. The silica is present as sols, with aggregation of sols in close association with voltaite alomen and casphosiderate.

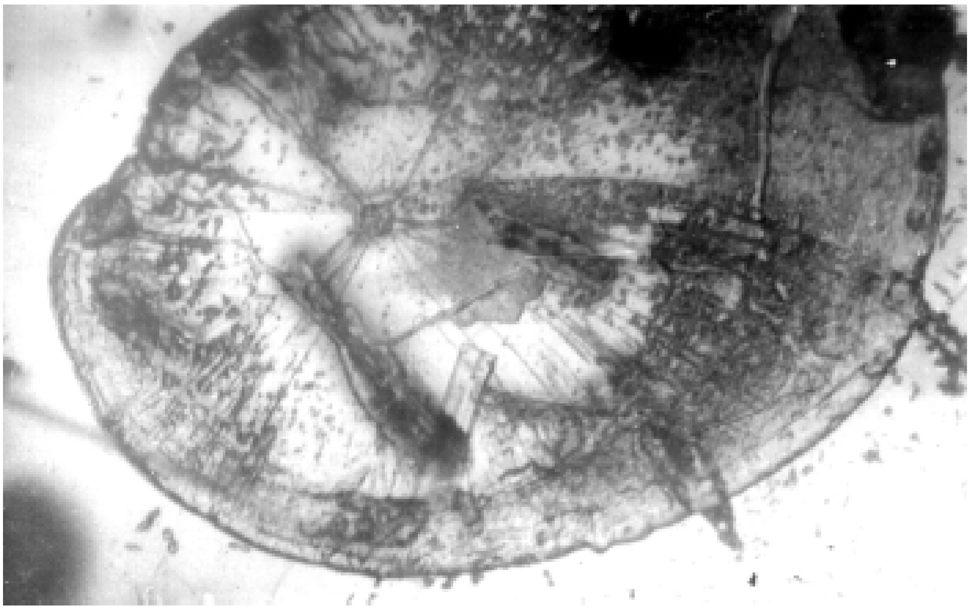


FIG. 23. A sphaero-crystal of voltaite, a spot of filtrate at pH = 1.08, magnified 70x; parallel nicol prisms.

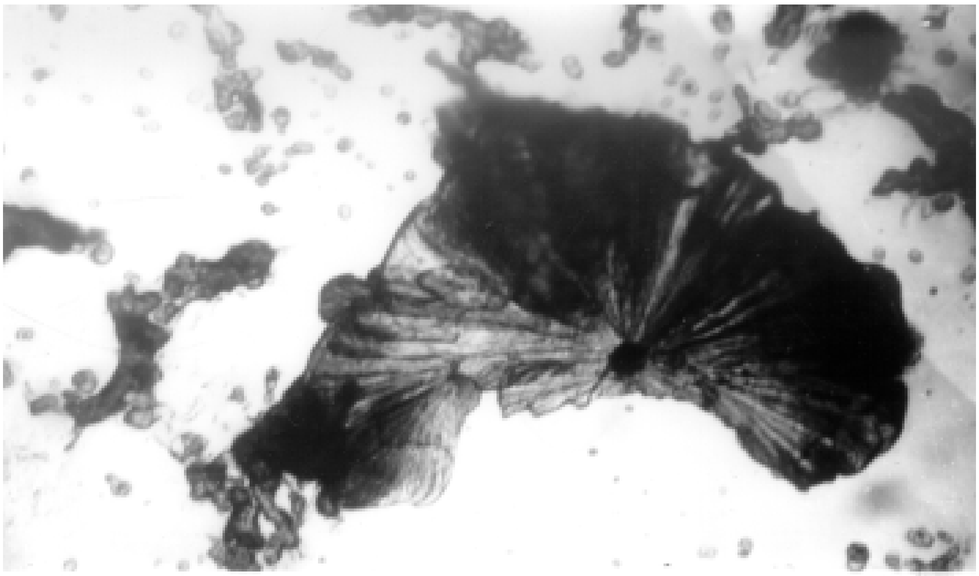


FIG. 24. Radial spines of carpho-siderite, a spot of filtrate at pH = 1.08, magnified 70x.

The third stage of the treatment recovery process start at pH = 1.09 with the passage of groundwater.

Behavior of iron in first the portions of filtrate indicates the presence of voltaite, with subsequent generation of metavoltine and halotrachite due to the sodium and potassium in the filtrate.

A great amount of coquimbite is observed in mineral composition of filtrate. It is possible that coquimbite is formed by two processes. Initially, coquimbite is the mineral formed in the sulphuric acid contact stage, later coquimbite is generated by oxidation of melanterite in groundwater.

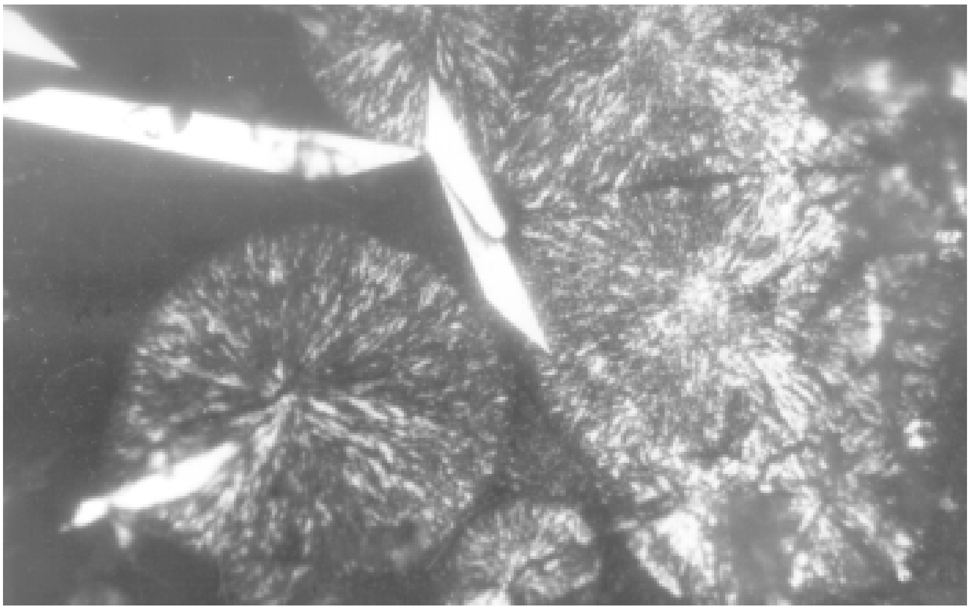


FIG. 25. A spherulite of spine crystals of alunogene, a spot of filtrate at pH = 2.13; magnified 75x; parallel nicol prisms (P-).

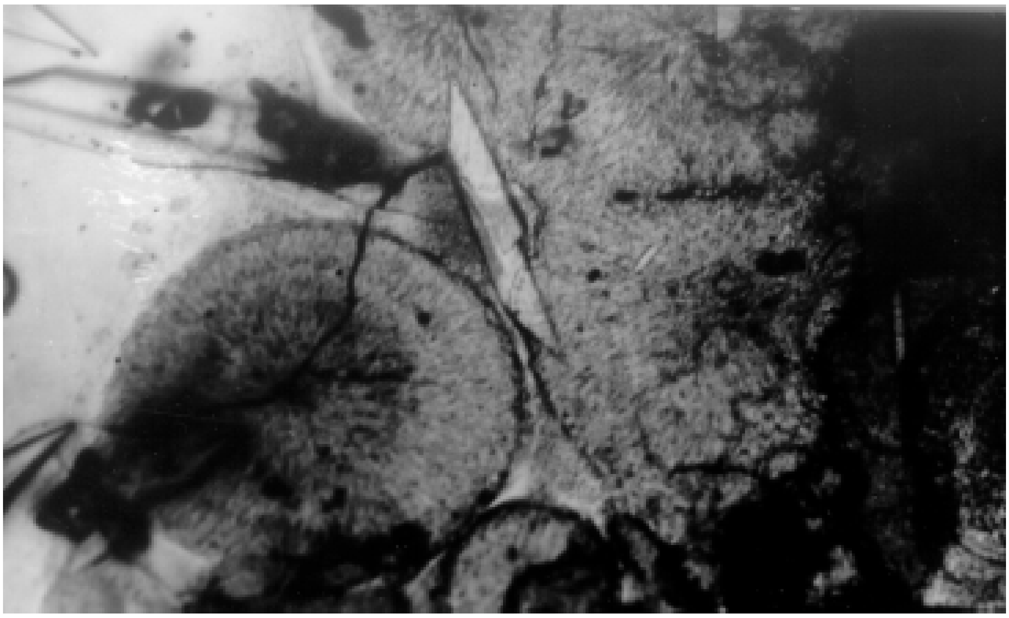


FIG. 26. The same one, crossed nicol prisms (P+).

Behaviour of aluminum in the third stage is characterized by its large concentration of the first groundwater washes out soluble aluminium sulphate (alunogen) in an appreciable quantity; then aluminum gel interacts with sulphate ion in the acidic media to generate alumen. Both factors sharply increased the total concentration of aluminum in filtrate to 220 mg/l.

Colloidal silica in groundwater at low pH generates a thin microglobular suspension. Globules of silica are anisotropic under the microscope but the most of the silica is isotropic. Optical observations indicate the presence of aggregations of halite, gypsum, alumen, coquimbite, melanterite and colloidal silica.

The mineralogical and petrographic observations clearly indicate the formation and changes of various minerals at different pH.

2.2.3. Results of hydrogeological and geophysical monitoring

It should be noted that hydrogeological and geophysical monitoring is highly effective during uranium production and it could also be effective for the control of some monitoring wells after decommissioning the well field. Data from induction logging wells in the Kanzhugan deposit show clearly the recovery of geophysical parameters to pre-operational levels in one year after the completion of active leaching. Hydrogeological data have not yet been evaluated.

2.3. Consideration of other parameters for prediction

In real geological situations, temperature should also be considered because permeability coefficients are higher in geological environments characterized by high temperature than in those with a lower temperature. Also variations in ore rocks significantly affect the production process and pollution paths. For example, South Karamurun ore aquifer is divided into several subaquifers in which filtration coefficients vary from 1 to 13 m/day.

Therefore, the effective velocity of underground streams must take into consideration hydraulic (pressure) gradient, open porosity and plugging effects.

2.4. Prediction of spreading contamination outside ISL-polygon

Sorption and filtration coefficients were used to assess the maximum spread of a polluted volume in the groundwater aquifer for gray and yellow sand. Assumptions were specific gravity of sediment is 2 g/cm^3, and effective porosity is 25%. Sorption coefficients for sulphate-ion were taken as average logarithmic values. For this reason, the calculated volumetric sorptive coefficient equals the sorptive coefficient of sand multiplied by 2. Results of calculations are shown in Table 8.

Table VIII. Maximum distance of spreading of 1 m^3 of contaminants for South Karamurun

Component	Concentration in residual solution	Concentration in contaminated rocks	Mass sorptive coefficient	Volumetric sorptive coefficient	Maximum distant of transfer, m
Gray sand					
SO_4^{-2}	9.43 kg/m^3	2.36 kg/m^3	2.24 kg/t	4.48 kg/m^3	0.53
Fe	0.32 kg/m^3	0.08 kg/m^3	4.5 kg/t	9.0 kg/m^3	0.009
Al	0.3 kg/m^3	0.075 kg/m^3	3.5 kg/t	7.0 kg/m^3	0.011
^{210}Pb	400 kBq/m^3	100 kBq/m^3	5000 kBq/t	10000 kBq/m^3	0.010
Yellow sand					
SO_4^{-2}	9.43 kg/m^3	2.36 kg/m^3	1.58 kg/t	3.16 kg/m^3	0.75
Fe	0.32 kg/m^3	0.08 kg/m^3	0.66 kg/t	1.32 kg/m^3	0.06
Al	0.3 kg/m^3	0.075 kg/m^3	0.55 kg/t	1.10 kg/m^3	0.07
^{210}Pb	400 kBq/m^3	100 kBq/m^3	1050 kBq/t	2100 kBq/m^3	0.05

Therefore the maximum distance that contamination can spread in the direction of underground flow is 0.95 m for conditions of S. Karamurun uranium deposit.

3. Conclusions

- Uranium orebodies possess high sorptive properties due to the availability of large quantities of sorptive minerals such as quartz, silicic gel, different opals, allophane, montmorillonite and zeolites.
- When the concentration of sulphuric acid is high, the sorptive minerals react more actively.
- The influence of sulphuric acid on environment during uranium production could be minimized by taking into account the three phases of uranium leaching.
- The prediction of the recovery of the environment affected by sulphuric acidic can be improved by determining sorptive-desorptive properties of rocks at real groundwater flow rates by taking into account changes in the rock types.

ACKNOWLEDGEMENT

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Geohydrological risks associated with abandoned uranium mines: The case of Cunha Baixa Mione (Central Portugal)

M.J. Matias, M.O. Neves

Laboratory of Mineralogy and Petrology, Technical University of Lisbon,
Lisbon, Portugal

Abstract. This paper addresses the hydrogeological risks associated with the now abandoned and most important Portuguese deposit, the Cunha Baixa uranium mine. The operation lasted from 1966 to 1993 and the ore was mined by open pit and underground methods. For low-grade ore heap leaching techniques were used. As this operation was located in farmlands the focus of research was the determination of the influence of the former mining activity on the quality of ground and surface water, identifying the contaminants and their diffusion. It was found that the observed contamination of water and soils is mainly due to acid drainage coming from the mine. Acid generation potential and acid neutralizing potential were carried out from rock samples of the open pit and the mine's surrounding. The role of the microorganisms (Thiobacillus) were also investigated in laboratory tests. The results of this study will form the basis for recommendations to reduce or eliminate the environmental impacts of the former mine.

1. Introduction

The uranium industry began in Portugal in 1907 when the radium-bearing ores were discovered in Urgeiriça. The Urgeiriça underground mine exploitation started in 1913 and continued, in spite of some virtual closures, until it was stopped, by the second world war, in 1939. The radium prospecting continued until 1944.

Several researchers have studied Portuguese uranium ore deposits [2], [4], [6], and [9].

Private companies introduced the prospecting of uranium deposits and after 1955 it was carried on by the Portuguese state company-Junta de Energia Nuclear (J.E.N.). Eleven ore deposits with more than 100t of U_3O_8 were defined from three hundred and seventy seven occurrences.

Uranium deposits are very common in the Iberian Peninsula throughout the Hercynian basement. Portuguese deposits occur in the tectonic Central Iberian Zone, which can be considered a uranium mining province, located in the centre of northern Portugal.

Small and large numbers of uranium ore deposits in this area are explained by the wide diversity of geological traps. In fact, there is a spatial connection between the Portuguese uranium ore deposits with the younger post-tectonic Hercynian granites. Concerning the location of the deposits, it is also possible to identify zones with predominant orientations (NNE-SSW, NE-SW, NNE-SSW and ENE-WSW, NNW-SSE). Mainly they are considered as belonging to the unconformity type, fact that has been connected with the several fault systems of the Hercynian and Alpine orogenies.

Concerning the morphology, the following types can be considered:

- hydrothermal veins that occur within Hercynian calc-alkaline granites and metamorphosed schists and greywackes, near the margins of the granites. Namely they are quartz veins, quartz breccia, milky quartz, smoked locally, with zoned overgrowths and stockworks,

- supergene impregnation along faults and sheared zones throughout quartz, aplite and pegmatite veins, and also the basement granitic and perigranitic zones and dolerite dykes,
- lacustrine deposits composed mainly by sandstones where uranium phosphates occurred.

It is difficult to distinguish between hypogene and supergene mineralization. The hypogene mineralogy is simple, comprising the uranium minerals, where pitchblende is the most abundant, and black uranium oxides and gummite. Sulphides minerals always exist, mainly pyrite and marcasite (they appear regularly), arsenopyrite, sphalerite, chalcopyrite and, galena. But this is usually accompanied by a complex assemblage of supergene uranium minerals, mainly phosphates (autunite, torbernite, uranocircite, sabugalite, saléeite, phosphuranylite, parsonite), sulphates (uranopilite, zippeite) and silicates (uranophane and beta-uranophane). Calcite and siderite are very rare. However secondary minerals predominate in most deposits and, in some of them, they are the only minerals present.

The primary uranium deposits were probably formed by the natural circulation of hydrothermal solutions related to Hercynian granite magmas and consequent infiltration along faults and sheared zones of meteoric waters. Later, Alpine tectonic reactivation of the ore structures promoted once more the infiltration and natural circulation of hydrothermal fluids, that remobilized and reprecipited minerals.

The mining methods used to exploit uranium deposits are based on underground works and open pit mining extraction. The processing of low-grade ores consists of acid leaching (generally using sulphuric acid) after ores have been reduced to small fragments by crushing.

At the present time uranium mining is finished, and a lot of old mines are abandoned. Large amounts of tailings, spoil piles contain toxic metals, mine galleries, open-pit mines, abandoned processing plants are some of the environmental impacts associated with the ceased mining activity.

2. The case of Cunha Baixa mine

The Cunha Baixa ore deposit is located in Beira Alta Portuguese province, 20km from Viseu. It lies in a place where the Hercynian granites are intrusive and involve a pelitic xenolith of the Ante-Ordovician Schist-Graywackean Complex.

The mineralised structures can be split in two types:

- vein type either within the Hercynian granite (a coarse grain porphyroid two-mica granite and a medium grain scarcely porphyroid two mica granite) or within the enclave of metamorphosed schists and graywackes,
- disseminated type, mainly, in the metamorphic rocks.

The vein structures were developed in fractures systems. The area is crossed by two conjugated fault systems with directions and inclinations of respectively N40°E and sub-vertical, and N70°W with dip 60°-65°N. When these faults cross different lithological units they undergo vertical refraction. The system is filled by brecciated quartz and sometimes with uranium mineralization. Autunite and torbernite predominate in the mineralization; phosphoranylite, gummites, black oxides and pitcheblende were found sometimes. In the same veins also occur metallic minerals such as the sulphides (pyrite and arsenopyrite) and manganese oxides.

The disseminated mineralization is also, generally, controlled by plans of foliation and joints.

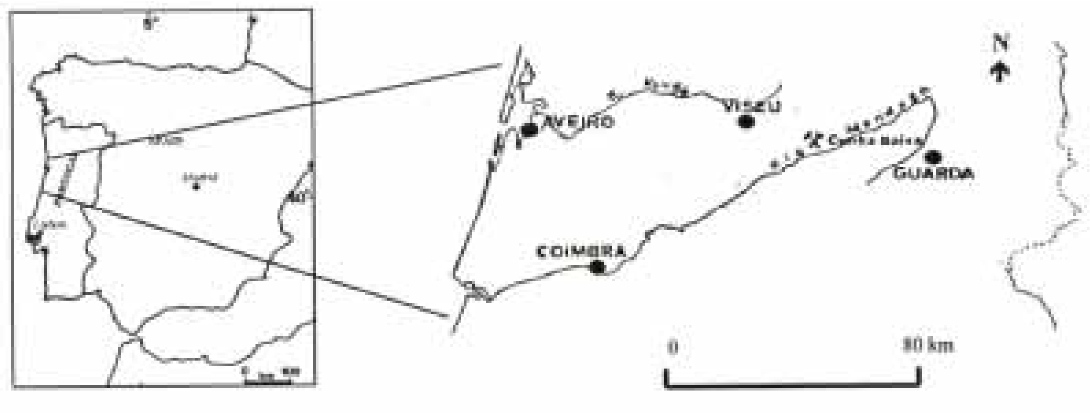


FIG.1. Localisation of Cunha Baixa region.

The Cunha Baixa ore deposit was one of the most important Portuguese uranium ore deposit with reserves of 1000t U_3O_8. The mining exploitation ran from 1966 to 1993. Deep veins were mined by underground works and, simultaneously, open pit mining was used for the upper disseminated type structures. The underground works reached 120 meters depth.

The extracted ore was controlled by radiometric assay and classified into three classes with different destination:
- the high grade ore — with higher radiometry, $U_3O_8 > 0.05\%$, that was then transported to the central Processing Plant in Urgeiriça, about 25km from Cunha Baixa ore deposit,
- a low grade ore — with $U_3O_8 \geq 0.02\%$, that was stockpiled regarding to their future processing by heap leaching,
- the class material with $U_3O_8 < 0.02\%$, that was stockpiled as waste.

Relatively large quantities of low-grade ore were produced and a heap leaching process was carried out from 1984 to 1993 to recover approximately 190 t U_3O_8. These quantities were extracted from about 46 0000 wet t of low-grade ore, with a mean of 0.045% U_3O_8 exploited both in Cunha Baixa and in the nearby Póvoa de Cervães mine.

The heap leaching process used the old pit mine to contain the ore. The second level drift, the main shaft and the ventilation shaft received leach liquor which was pumped upwards to the surface (Fig. 2).

The Project "Geohydrological risks associated with abandoned uranium mine: the case of Cunha Baixa mine (Central Portugal)" has the following goals:

- to determine if the quality of surface and ground water was affected, either by the mining activity, or by the mine closure,
- to identify the contaminants, their values and diffusion, and the changes with time,
- to find possible solutions to minimise the environmental problems that exist.

The study area covers about 6 square kilometres to the S-SW of the mine that is located on the western slope of a small hill. The study area stretches out to the riverside located around 1 km away.

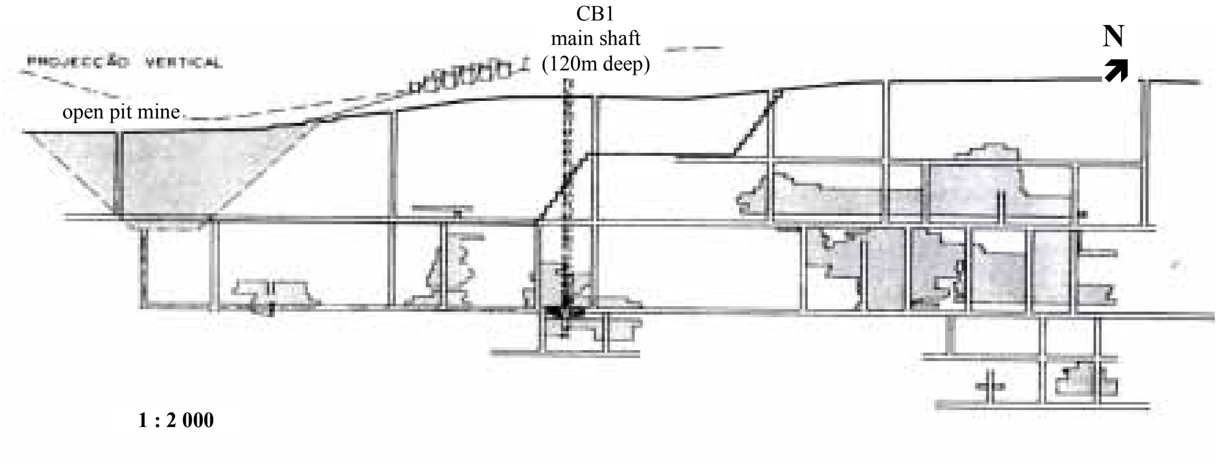


FIG. 2. Vertical section showing underground works and the open pit mining at Cunha Baixa,(Cordeiro Santo and others, 1983).

The village of Cunha Baixa is next to the mine. It is a rural area where the quality of water is important. The agriculture is performed on the flatland, while the high land is wild pine-clad.

The climate in the area is mild and characterised by an annual average temperature of 13°C, varying between 5 to 25°C. Annual precipitation reaches approximately 1100-1400mm of rain, the highest rainfall occurring during winter time (October to March).

The consequence of the close of the mining activity was the abandonment of the underground mining galleries, the open pit, waste rock dumps and the area where the heap leaching occurred.

In order to remediate the environmental damages related to the mining activity, ENU Company developed some actions, namely:

- the treatment of mine water , that is continuously pumped from the mine shaft since 1990. The pumped mine water is first neutralised with a mixture of calcite and portlandite, after that a barium chloride solution is added to precipitate the radium. Finally the water is discharged into a constructed sedimentation basin for solid deposition. This basin, with a capacity of 6000m^3, was constructed near the waste rock dump area. When the basin reached its maximum capacity, the overflow effluent was released in the waste rock dump area. However, after 1999, this effluent is drained into the open pit area rather than the waste rock dump area.
- the revegetation of the waste rock dumps in order to stabilize dump slopes and to minimise gullying and the visual impact.

2.1. Water quality studies

In order to evaluate the quality of surface and ground waters on the hydrological system in the surrounding area of the abandoned Cunha Baixa mine and to define polluted areas of different degrees of contamination we have carried out fieldwork campaigns.

The study began in 1995 and was planned in order to collect seasonal and periodical water samples. Fieldwork campaigns were performed at the end of September (end of summer) and at March (end of winter), representing consecutive dry and wet seasons. The first campaign was in September 1995.

Fourteen surface and twenty-eight ground water sampling sites were selected in the surrounding area of the abandoned Cunha Baixa uranium mine. The selection was made looking at parameters like population area, water used for agricultural land irrigation, topography and geological features.

In summer, because some of the watercourses are dry, it was only possible to collect surface water from a few sampling sites.

Ground water samples were collected from private wells at a depth of 1.5 m below water level.

The water samples were collected in acid-washed polyethylene bottles and transported on ice to the Urgeiriça laboratory (about 25km from the mine). They were filtered through a 0.45 μm Millipore membrane, after total alkalinity and dissolved oxygen (Winkler method) determination.

Water samples for cation analysis were acidified (pH< 2) with nitric acid. Filtered, unacidified samples were used for anion analysis. All the samples were stored at 4°C until analysed.

All water samples were analysed for a set of physical and chemical parameters as follows:

— Temperature, pH, electrical conductivity (EC) and redox potential (Eh) were measured in situ;
— Total alkalinity and dissolved oxygen were measured a few hours after collection by titration;
— Total dissolved concentration of Na, K, Ca, Mg, Al, Fe, Mn, Cu, Pb, Zn, Ni, Cr, Cd and Co by Inductively Coupled Plasma (ICP), were performed at Aveiro University laboratory;
— Cl^-, NO_3^- and SO_4^{2-} concentration were measured by Ion Chromatography (IC);
— Si, F^- and P_{total} were measured by Colorimetric methods;
— Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) were obtained by filtration and evaporation of 500ml of water, respectively at 180°C and 105°C;
— Uranium analyses were performed at CIEMAT (Centro de Investigaciones Energéticas Medioambientales Y Tecnológicas, in Madrid) and Radium-226 activity at ENU l aboratory and CIEMAT.

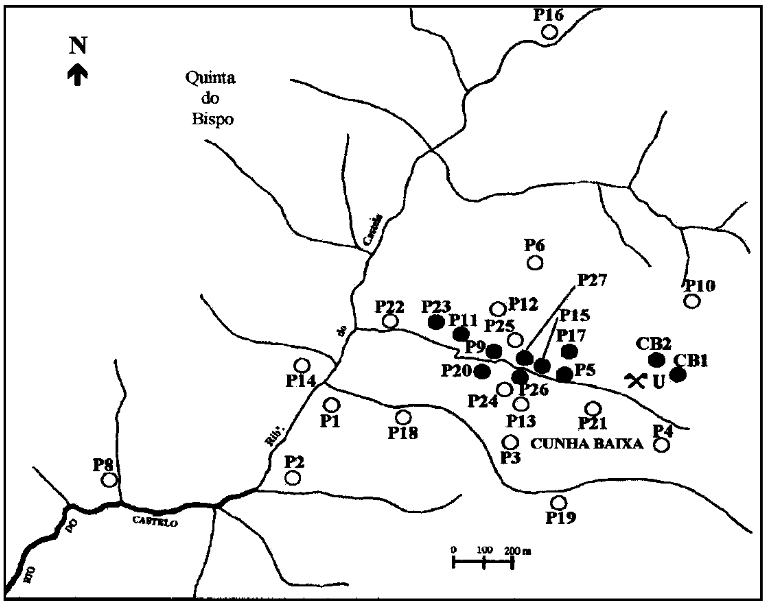


FIG. 3. Sampling ground water sites. • Contaminated water; o non-contaminated water.

2.1.1. Ground waters results

According to the physical and chemical composition (see appendix) it was possible to define according to quality criteria, two ground water groups (A-group and B-group).

- B-group represents waters that are not contaminated (Fig. 3: samples P1, P2, P3, P4, P6, P8, P10, P12, P13, P14, P16, P18, P19, P21, P22, P24 and P25) and so they present a quality enough for agricultural supply. Some of them could represent regional waters. They are typical soft waters with sodium, calcium chloride or bicarbonate components. In the neighbouring area mine the waters have increased hardness and contain more calcium and sulphate ions.
- The A-group represents contaminated waters (Fig. 3: samples P5, P9, P11, P15, P17, P20, P23, P26, P27, CB1 and CB2) which have calcium or magnesium sulphate composition. Generally, these waters present pH < 4.5–5.0, TDS >640 mg/l, electrical conductivity >1000 µS/cm, total hardness >120 mg/l $CaCO_3$, high sulphate (>575 mg/l), aluminium (>5 mg/l), calcium (>100 mg/l) manganese (>0.2 mg/l) and uranium (>250 µg/l) contents (Figs. 4, 5 and 6). The high calcium content is responsible for the high hardness, this characteristic being uncommon in waters from alkaline granite regions.

These waters are, according the Portuguese quality pattern (Table 1), not recommended for agricultural supply. The Maximum Recommended Values (MRV) for irrigation established for several parameters are exceeded. Both high conductivity and TDS value could provide soil salinisation. The high contents of calcium and sulphate ions can lead to the precipitation, by evaporation, of gypsum (at soil surface).

Table I. Portuguese quality pattern for irrigation and surface water
MRV (Maximum Recommended Value); MAV (Maximum Admissible Value)

Parameters		**Irrigation water**		**Surface water**
		MRV	**MAV**	**MAV**
PH		6.5-8.4	4.5-9.0	5.0-9.0
EC	µS/cm	1000	--	--
TDS	mg/l	640	--	--
TSS		60	--	--
Aluminium		5	20	--
Barium		1.0	--	--
Cadmium		0.01	0.05	0.01
Chlorine		70	--	250
Chromium		0.10	20	0.05
Cobalt		0.05	10	--
Copper		0.2	5	0.1
Fluorine		1	15	--
Iron		5	--	--
Lead		5	20	0.05
Manganese		0.20	10	--
Nickel		0.50	2	0.05
Nitrate		50	--	--
Sulphate		575	--	250
Zinc		2.0	10	0.5

– non-fixed value

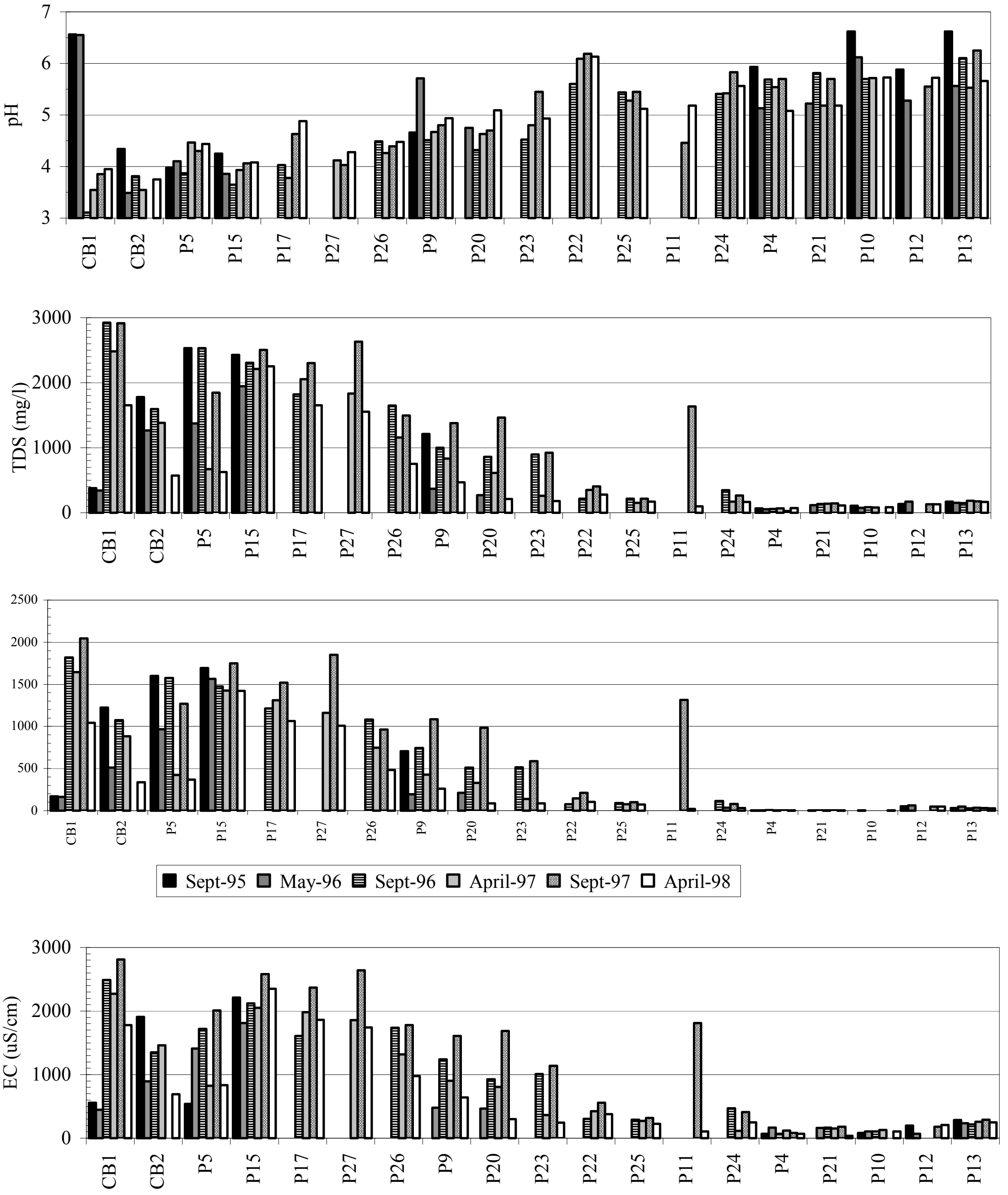


FIG. 4. pH, TDS, EC values and sulphate content in Cunha Baixa ground waters.

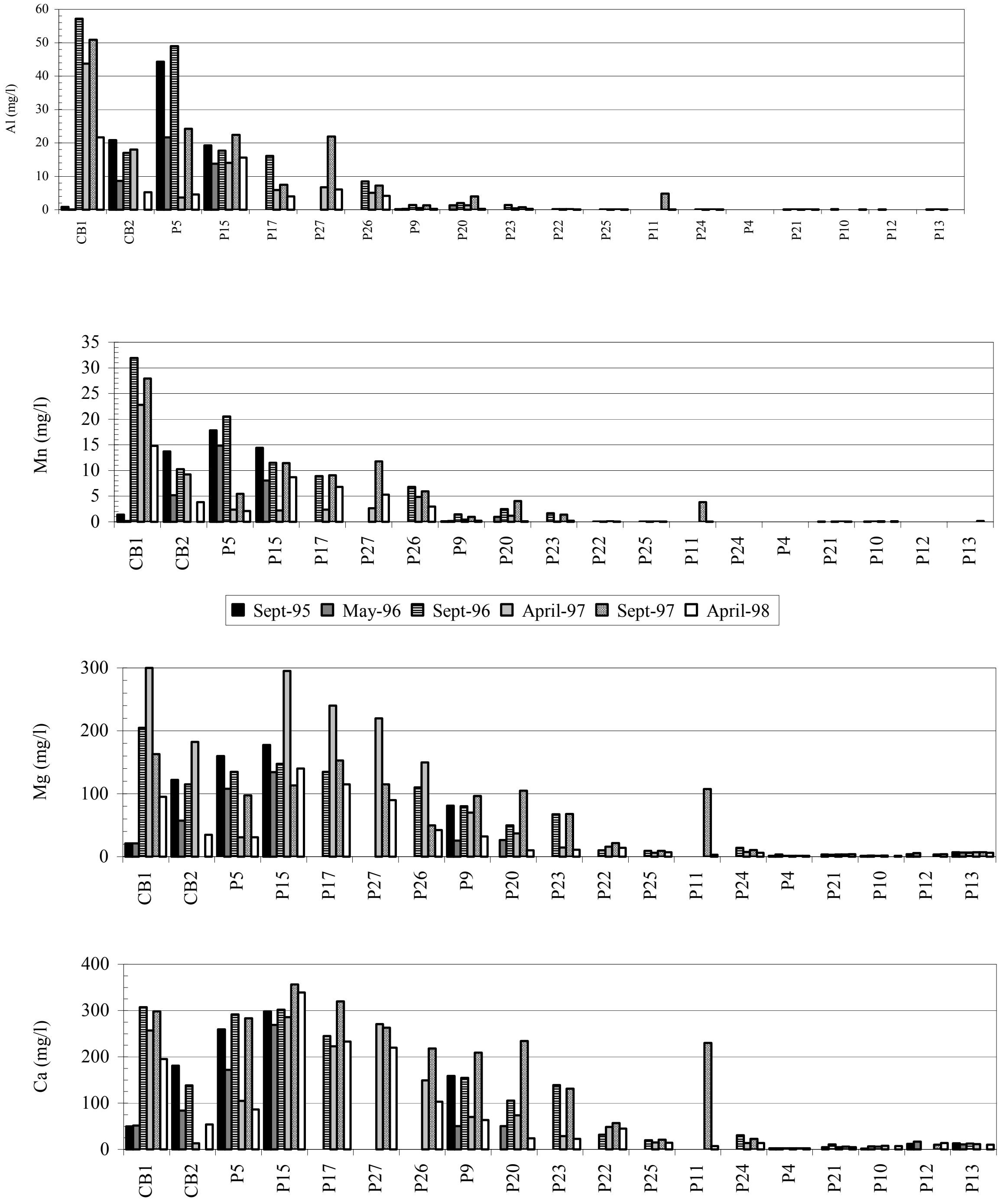


FIG. 5. Aluminium, calcium, magnesium and manganese content in Cunha Baixa ground waters.

The contents of aluminium and manganese ions are also important parameters to consider in irrigation waters, because they are phytotoxic elements. Sometimes the water from wells P5, P15, and P27 exceed the Maximum Admissible Value (MAV) (20 and 10 mg/l, respectively for Al and Mn). Mainly in dry season and in the wells that are located near the mine, the acid waters also contain high heavy and phytoxic metals contents (Ni, Zn and Co). But only in the case of Co are the values of concern (Fig. 6).

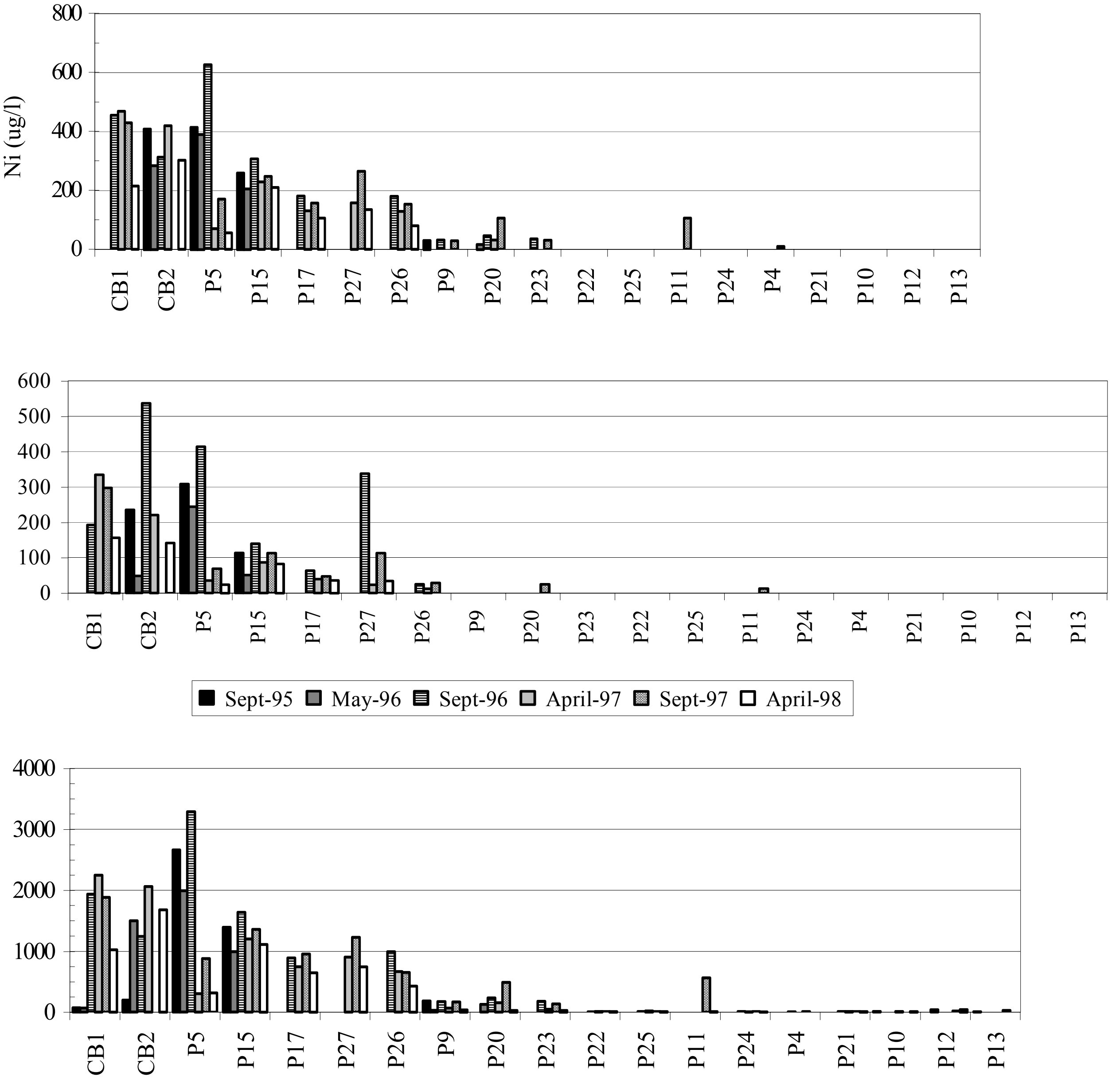


FIG. 6. Nickel, zinc and cobalt content in Cunha Baixa ground waters.

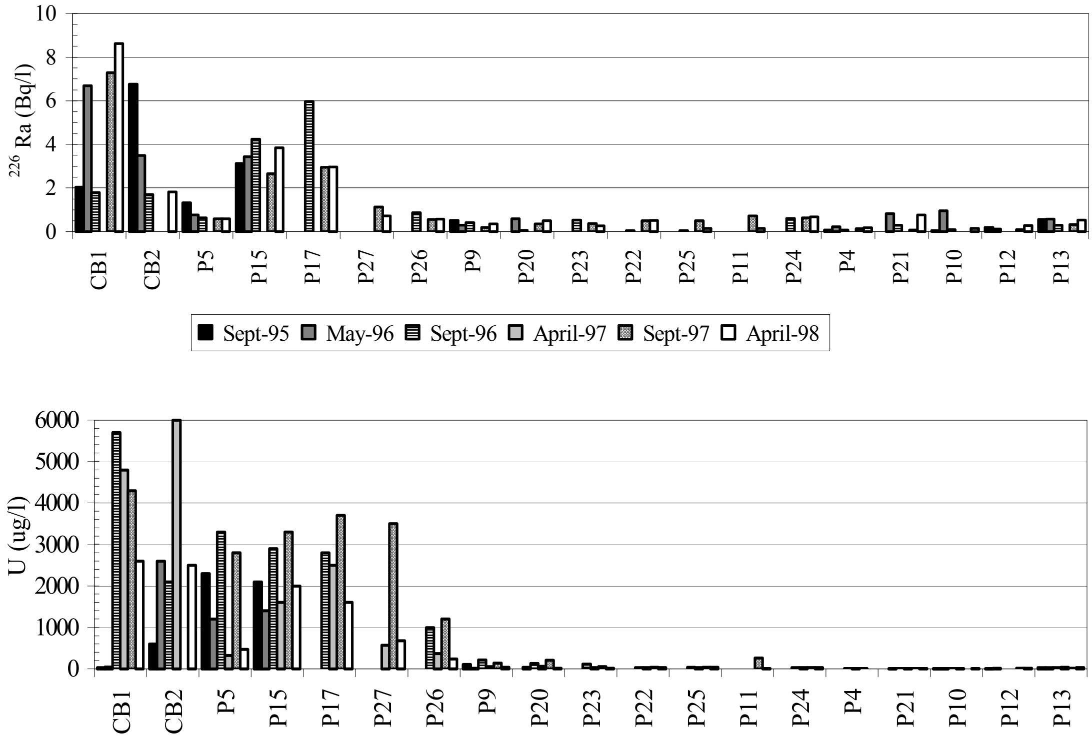


FIG. 7. Uranium content and ^{226}Ra activity in Cunha Baixa ground waters.

The uranium content, like other elements, varies with location and time. The greater uranium contents were registered in dry seasons (Fig. 7). In water P5, P15, P17, P26 and P27, the uranium ranged from 1 to 3.5 mg/l, while in the others sampling sites, the range was 0.2-1 mg/l. In the considered B-group waters, the uranium contents are much lower (< 30 µg/l) and the seasonal variation is not so wide as in the A-group. In these waters the mean of ^{226}Ra activity ranged between 0.05 and 1 Bq/l. Only in waters coming from P15 and P17 were the values exceeded (Fig. 7).

As in other countries, in Portugal there are no fixed uranium content and ^{226}Ra activity limits for irrigation water. However, in some sites, the uranium and radium contents could represent chemical or radiological risks to the soil and crops growing on it.

These waters (A-group) are in terms of physical and chemical composition, similar to the pumped shaft mine water (samples CB1 and CB2).

2.1.2. Surface waters results

The surface waters sampling is performed in the watercourse that drain the Cunha Baixa area, at the Castelo streamlet and Castelo river (Fig. 8). Water is also collected from the pond (L0 sample) that is formed on the open pit mine every wet season and from the treated water (BD sample) discharged from the decanting basin.

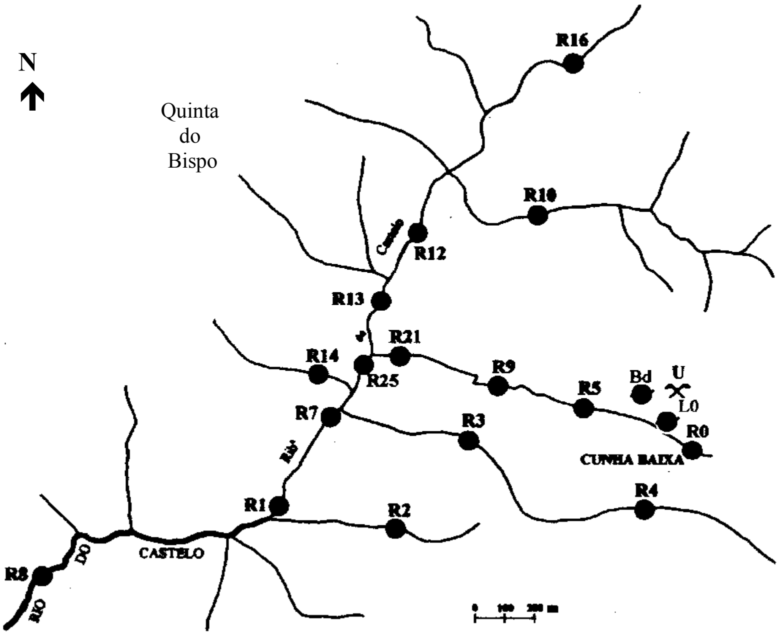


FIG. 8. Surface water sampling sites.

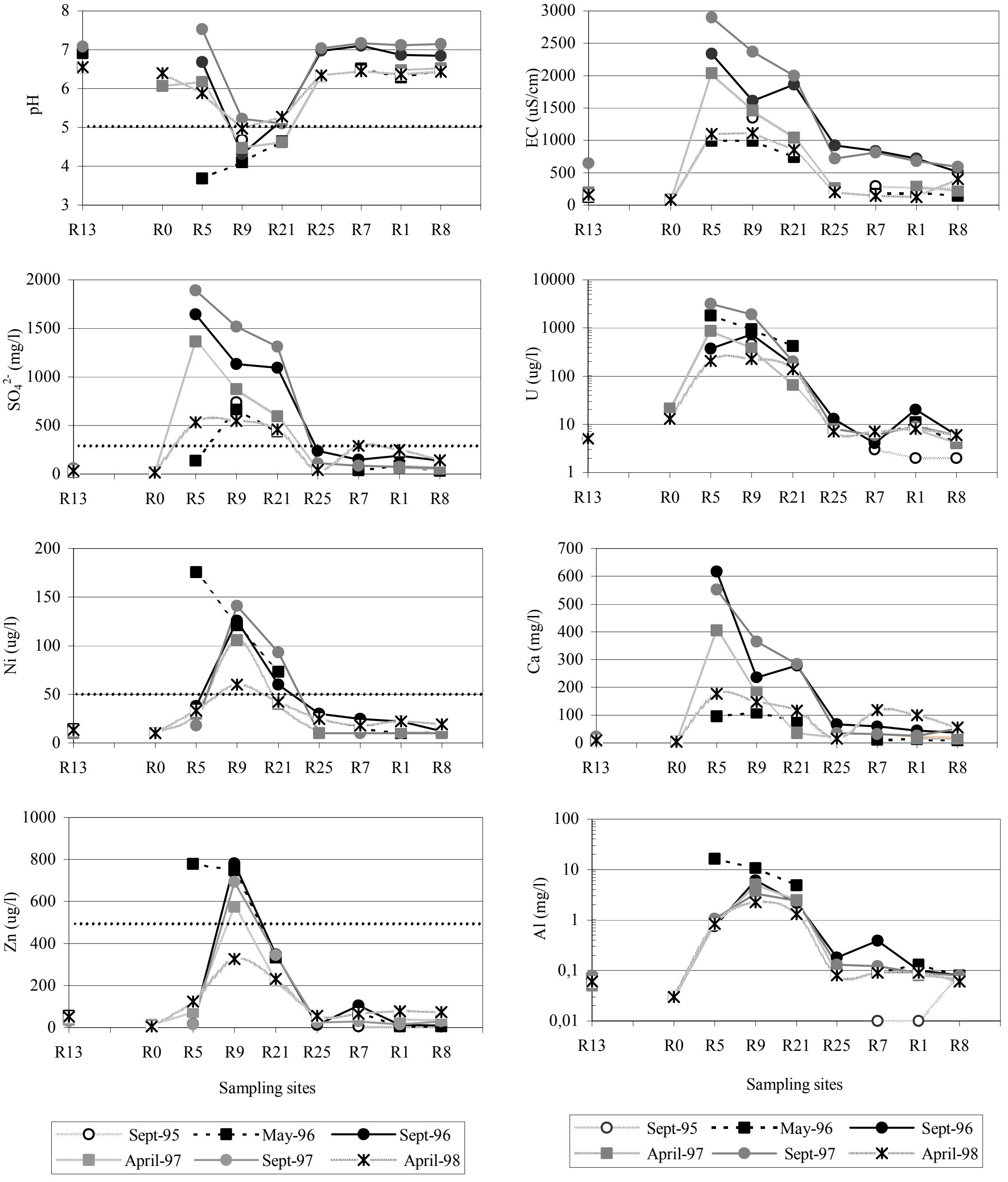
According to the physical and chemical composition (Appendix) it was possible to define three different water groups:

— The first group includes waters characterised by calcium sulphate composition with low pH (3.7-5.4), electrical conductivity between 467 and 1350 µS/cm, TDS >355mg/l, total hardness >190mg/l $CaCO_3$ and high ^{226}Ra content (Figs 8 and 9: samples R5, R9, R21). This waters were collected along of the watercourse that drains the old mine area and their ionic composition is directly influenced by the mining activity. This becomes clear when we compare the upstream (sample R0) and downstream water quality.

— The second group is characterised by sodium chloride or bicarbonate waters with pH (5.2 to 7), conductivity<180 µS/cm, TDS <140mg/l, total hardness <50mg/l $CaCO_3$ and low ^{226}Ra content (Fig. 8: samples R16, R10, R12, R13, R14, R4, R3 and R2). The composition of these waters shows no direct influence from the mining activity.

— The third group is characterised by waters with pH (6–7.2), electrical conductivity < 430 µS/cm, TDS <440mg/l, total hardness <195mg/l $CaCO_3$ and represents the mixture of waters from the polluted watercourse (first group) and Castelo stream waters (Figs 8, 9 and 10: samples R25, R7, R1 and R8). This group includes sodium sulphate type waters.

According to quality criteria for surface waters, the pollution do not show effects a long way from the mine. At a distance not greater than 1–1.5 km downstream, the contaminants from the mining activity decrease relatively quickly to typical regional concentrations (Figs 9 and 10). Among the parameters established by the Portuguese quality criteria for surface water only the pH value and sulphate, Ni and Zn contents had levels that normally exceed the fixed Maximum Admissible Value (MAV).



Maximum Admissible Value (MAV)

FIG. 9. Plots of pH, EC and sulphate, Ni. Zn, U, Ca and Al concentration in sampled surface waters.

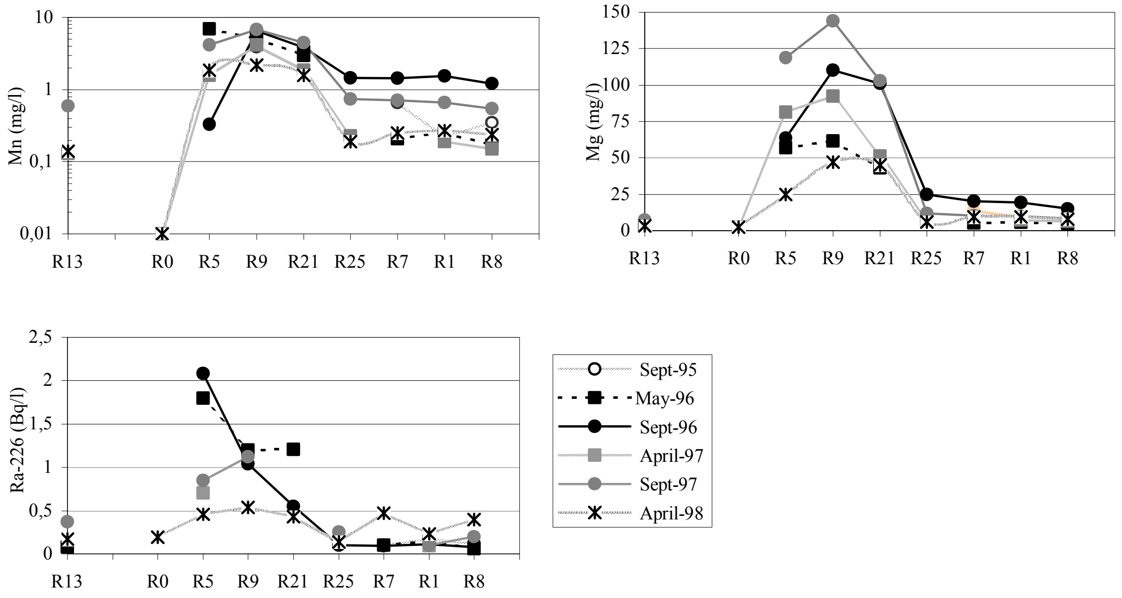


FIG. 10. Plots of Mn, Mg concentration and ^{226}Ra activity in sampled surface waters.

The water from the open pit pond (L0 sample) presents a physical and chemical composition very similar to the shaft mine waters. It is an acid water (pH< 4) with high values of electrical conductivity, TDS and ^{226}Ra (Fig. 11). The sulphate, nickel and zinc contents exceed the MAV for surface waters (250 mg/l, 50 µg/l and 500 µg/l, respectively).

The overflow effluent from the decanting basin (BD sample) after the neutralisation of the pumped water from the mine galleries is a water with pH > 8, but high electrical conductivity (> 1800 µS/cm). The chemical composition shows that the treatment with a mixture of calcite and portlandite and barium chloride solution is efficient to neutralise and remove dissolved Mn, Si, Al, Fe, Zn, Co, Ni, ^{226}Ra and U (Fig. 12). However after resting in the decanting basin, the water is released with relatively high dissolved Ca (475-650mg/l), F (3–7.5mg/l) and SO_4 (1100–2000mg/l).

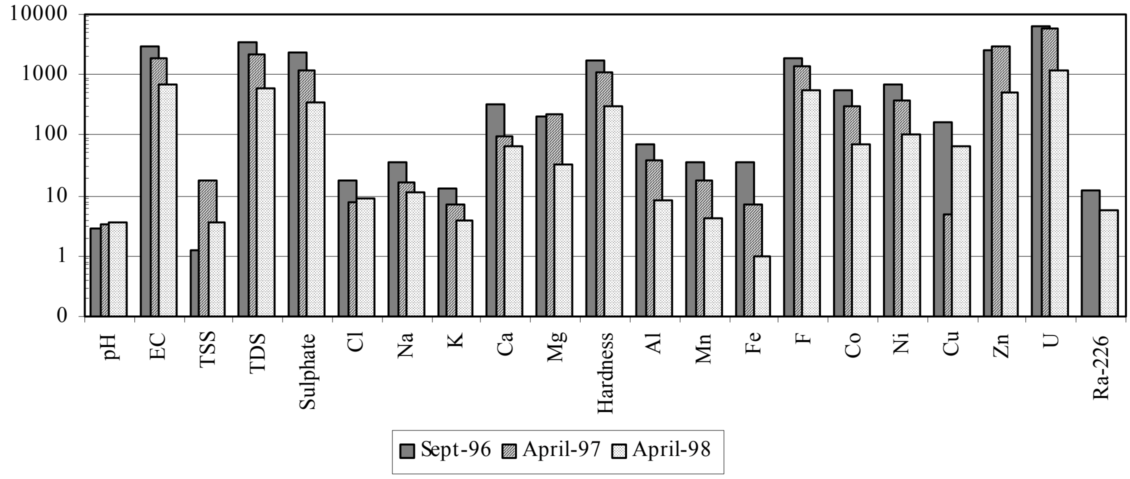


FIG. 11. Water quality in the open pit pond (L0 sample). Results express as: EC (µS/cm); TSS, TDS, sulphate, Cl, Na, K, Ca, Mg, Al, Mn and Fe (mg/l); hardness (mg CaCO3/l); F, Co, Ni, Cu, Zn and U (µg/l); Ra-226 (Bq/l).

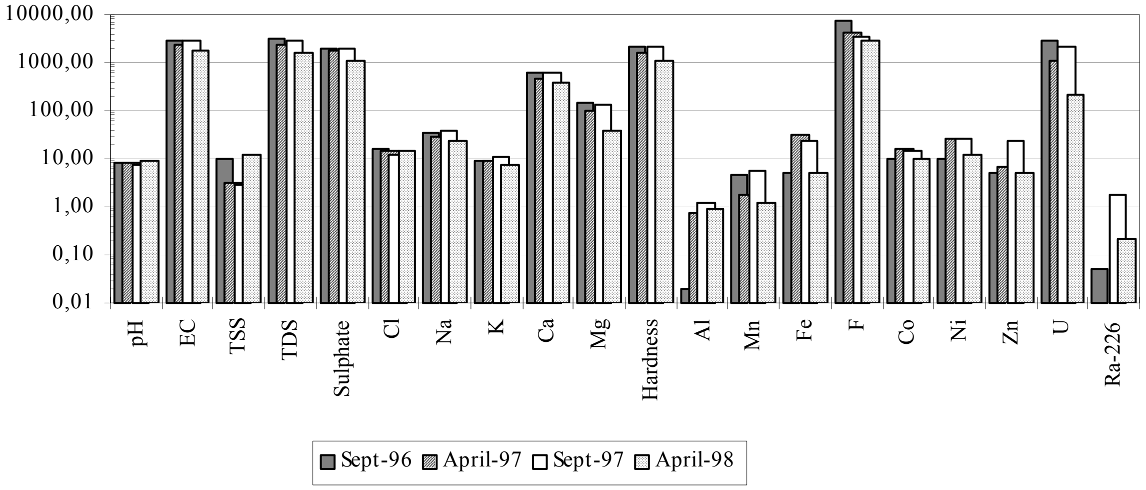


FIG. 12. Water quality of the overflow effluent from the decanting basin (BD sample). Results express as: EC (µS/cm); TSS, TDS, sulphate, Cl, Na, K, Ca, Mg, Al and Mn (mg/l); hardness (mg $CaCO_3$/l); Fe, F, Co, Ni, Cu, Zn and U (µg/l); Ra-226 (Bq/l).

In fact the neutralisation process is responsible for the high hardness presented by local surface and ground water.

2.2. Soil: its constituents and properties

In order to evaluate how the acid drainage contributes to the soil contamination, six soil samples were studied. Sampled soils (Fig. 13) were collected from tilled soils that were irrigated, mainly in summer time. Four sampled soils were irrigated by contaminated wells (5,15,17 and 27) and to other ones (2 and 24) with non-contaminated water. Composite soil samples were collected from the upper 30cm of the soil profile. Sampling was performed at the end of summer time.

Different soil parameters (chemical and mineralogical compositions, pH and texture) were analysed. These are the main properties conditioning the binding mechanisms of metals in soils. Processes such as precipitation-dissolution, and adsorption-desorption control the metals distribution between soil phase and soil solution, depending on the soil reaction.

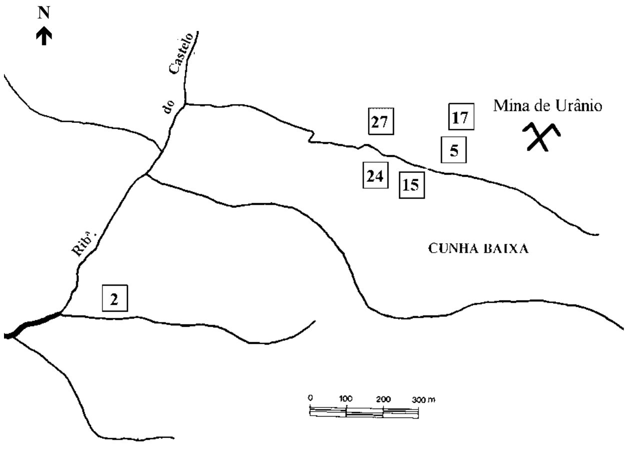


FIG. 13. Sampling soils sites.

The methodology used for the soils study is listed next:

- the physicochemical properties were determined as described by Page and others, 1982.
- the samples were dried at 40°C, passed through a 2mm sieve, then ground in an agate mortar and digested with a mixture 3:2:1 of HCl, HNO_3 and HF, followed by analysis of total concentration of the selected elements;
- the plant available Al and others elements were extracted, respectively with 1M KCl and 1N NH_4O acetate;
- the total and bioavailable element concentrations were determined by ICP and fluorimetry;
- the nitrogen and sulphur were determined by gaseous chromatography after ignition at 1800°C.

The studied soils belong mainly to the sandy loam class. Kaolinite is the main clay mineral present, but the clay fraction and the organic matter are present at a low content. The cation exchange capacity (CEC) is also low. Calcium is the dominant exchangeable cation, followed by Mg, K and Na (Tables 2, 3 and 4).

The soils 5, 15 and 17 contained 20 times greater concentration of uranium than the soils collected faraway from the mine site. The high uranium concentration represents a potential risk because vegetables easily absorb the soluble form of this element.

Animals may be contaminated directly through soil contact, or indirectly by ingestion of contaminated feeds.

The pH of the soil is the most important physical and chemical parameter affecting plant growth and also the behaviour of the other contaminants in soils. In the case of Cunha Baixa soils, only the contaminants Al, Mn and U in contaminated water used in irrigation may present potential risks to soil contamination. The pH of the soil affects the mobility and the bioavailability of these elements. This is the case of the soils 5, 15 and 17, with the $pH < 4$, where we can (Table 5) confirm larger bioavailability of those elements in the vicinity of the root system plant. In contrast, the soil 27 with pH 6.26, in spite of being also irrigated with contaminated water, presents lower bioavailability of the same elements.

Dissolved aluminium is regarded as a major cause of plant toxicity in soils, because an excess of this nutrient inhibits cell division in the meristems of root tips and therefore stops elongation. The roots remain bounded to the upper part of the soil and the plants become subject to drought.

Chlorosis, observed in several maize leaves grown in soils 5, 15 and 17, is one of characteristic symptoms of Mn toxicity on cereal crops.

Some maize plants (mature steam and leaves tissues) that grew in the soils 2, 5, 15, and 27 were analysed. The samples were washed with distilled water, dried in an oven at 40°C and ashed at 550-600°C. The ashes were dissolved in a mixture of HCl and HNO3. The selected elements content were determined by ICP. The results are given in Table 6.

All maize plants accumulated greater Al, Mn and U contents in their leaves than in stems. In the Cunha Baixa countryside, maize is used as animal feed and the corn is used to make bread.

Table II. Physical and chemical properties of the soil samples

Soil sample	**Size classification g/kg**				**Soil textural class**	**Color classification**	**Soil pH**
	Coarse sand 2<∅<0.2mm	**Fine sand 0.2<∅<0.02mm**	**Silt 0.02<∅<0.002mm**	**Clay ∅< 0.002mm**			
***2**	518	277	109	96	Sandy Loam	10YR 6/3	5.14
***24**	538	248	119	95	Sandy Loam	10YR 5/3	5.10
5	329	299	215	157	Loam	10YR 6/4	4.40
15	514	256	166	64	Sandy Loam	10YR 7/3	4.04
17	642	206	116	36	Loamy Sand	10YR 6/3	4.27
27	508	233	150	109	Sandy Loam	10YR 6/3	6.26

*** -** Soil irrigated with non-contaminated water.

Table III. Chemical properties of the soil samples

Soil sample	**Total Salinity mS/cm**	**Organic C g/Kg**	**CEC** **cmol_c/Kg**	**Exchangeable cations cmol_c/Kg**						**% Base Saturation**
				Ca	**Mg**	**K**	**Na**	**Mn**	**Al**	
***2**	0.287	7.7	2.36	1.48	0.33	0.20	0.02	0.02	0.101	86.9
***24**	2.500	20.3	4.68	4.72	0.97	0.65	0.08	0.02	0.011	100
5	2.560	19.0	6.38	4.89	1.67	0.51	0.08	0.27	0.280	100
15	10.480	13.4	3.83	10.95	6.87	0.29	0.71	0.12	0.406	92.5
17	3.090	16.0	4.14	2.33	0.92	0.43	0.05	0.10	0.343	100
27	2.570	12.3	4.21	6.74	1.96	0.24	0.11	0.03	0.007	100

Table IV. Clay minerals

Clay minerals	**Soil sample**					
	2	**24**	**5**	**15**	**17**	**27**
Kaolinite	❍	✧	●	●	❋	❋
Illite	❍	✧	❍	❋	❍	❍
Vermiculite	--	--	❋	❍	❍	✧
Mica –Vermiculite	--	--	✧	--	✧	--
Al-hydroxy Vermiculite	--	--	--	✧	✧	--

● Very common; ❋Common; ❍ Present; ✧ trace; -- Non-present

Table V. Total and bio-available element concentration (in brackets) in soil samples

		Soil sample					
		2	24	5	15	17	27
N	%	0.07	0.17	0.14	0.10	0.12	0.10
S	%	<0.05	<0.05	<0.05	0.28	<0.05	0.05
P	mg/Kg	182	285	447	319	488	199
K	g/Kg	34.30 (0.07)	32.95 (0.25)	33.80 (0.20)	34.30 (0.11)	37.45 (0.17)	33.75 (0.94)
Ca	g/Kg	2.47 (0.59)	3.63 (1.89)	2.78 (1.95)	4.42 (4.40)	3.37 (0.93)	3.12 (2.70)
Mg	g/Kg	1.89 (0.08)	2.32 (0.23)	4.03 (0.40)	3.45 (1.67)	1.99 (0.22)	2.44 (0.47)
Na	g/Kg (mg/Kg)	8.85 (4.60)	9.20 (18.40)	9.50 (18.40)	9.55 (163.2)	10.7 (1.15)	9.05 (25.28)
Al	g/Kg (mg/Kg)	70.00 (27.33)	68.50 (3.02)	90.00 (78.50)	74.50 (109.4	66.00 (92.45)	75.50 (2.02)
Cr	mg/Kg	10 (<0.2)	10.5 (<0.2)	30.5 (<0.2)	18 (<0.2)	7.5 (<0.2)	43.5 (<0.2)
Mn	mg/Kg	288 (11.0)	275 (11.0)	1238 (148.3)	281 (65.9)	287 (54.9)	278 (16.5)
Fe	g/Kg (mg/Kg)	12.45 (0.80)	12.25 (1.48)	21.00 (0.42)	15.10 (1.16)	10.55 (1.82)	13.30 (0.42)
Co	mg/Kg	5 (<0.2)	5 (<0.2)	12 (0.38)	5.5 (0.72)	5.5 (0.64)	5 (<0.2)
Ni	mg/Kg	5.5 (<0.2)	<5 (<0.2)	15 (0.72)	9.5 (1.08)	<5 (0.36)	22.5 (<0.2)
Cu	mg/Kg	20.5 (0.42)	31 (<0.2)	54.5 (1.28)	34.5 (0.84)	56 (0.36)	40.5 (<0.2)
Zn	mg/Kg	67.5 (<0.5)	78.5 (2.28)	127.5 (3.76)	90.5 (4.72)	71 (2.06)	90.5 (0.98)
Cd	mg/Kg	<2.5 (<0.1)	<2.5 (<0.1)	<2.5 (0.1)	<2.5 (0.14)	<2.5 (<0.1)	<2.5 (<0.1)
Pb	mg/Kg	38 (0.6)	35 (<0.5)	58 (0.62)	154 (1.4)	34 (<0.5)	51.5 (<0.5)
U	mg/Kg	9.8 (1.04)	27 (1.8)	362 (128)	225 (158)	302 (142)	56 (7.5)

Table VI. Mean Al, Mn and U concentration in mature stems (s) and leaf (l) tissues in maize

		M2		M5		M15		M17		M27	
		S	L	S	L	S	L	S	L	S	L
Al	mg/Kg	46	266	93	195	25	350	16	121	113	129
Mn	mg/Kg	7	29	51	124	47	370	13	65	16	45
U	µg/Kg	22	240	607	1636	271	770	88	620	320	480
U	mg/kg	0.4	4	9	35	2.5	6.8	1.3	8.7	7	13

(dm) - dry matter

In the case study, the contaminated irrigation water is acidic with a high heavy metals content**.** It is characterized by pH <4.5–5.0, TDS > 500 mg/l, electrical conductivity > 1000 µS/cm, total hardness > 180 mg/l $CaCO_3$, high sulphate (>575 ppm) and uranium (>1000 ppb) contents.

Contaminated water exists along the watercourse that drains the area next to the abandoned mine and next to the wells close to the mine. Pollutants increase with the proximity to the abandoned mine.

2.3. Determination of acid drainage generation

Determining why acid drainage persists in Cunha Baixa region in spite the lime neutralisation used for remediation was the goal of this work.

At first, it was considered that the acid drainage was the result of the groundwater flowing into the old under ground workings, rock fractures and faults. This ground water contains the remaining acid used in the past to extract uranium (from heap leaching low grade ore in the former open pit mine). This approach is not fully accepted, because acidity remains practically at the same level (no signs of depletion yet).

Secondly, it was considered that new acidity was been produced by oxidation of sulphide minerals. These sulphide minerals are present, although in small percentage and in a disseminated way, mainly in the schists neighbouring the ore deposit.

To validate this last hypothesis, some laboratory tests were performed, namely the Acid-Base Accounting (ABA), also known as the static prediction tests [5].

The rock samples submitted to these tests were collected from:

- the walls of the open pit mine (the schists A, E, B1, B2, C4 and granite D),
- the sediments (SdL0) laying in the bottom of the pit lake that forms every winter time (during the wet season),
- three drill cores performed in the open pit, drilled 20 – 35 meters deep, crossing the low grade ore materials that were, in the past, subject to the acid leaching,

Samples petrography description and chemical characterisation are presented in Tables 7 and 8. The rock samples were analysed by Flame Atomic Absorption Spectrometry (for Na, K, Ca, Mg and Mn), Colorimetric methods (for Si, Al, Fe, Ti and P), ICP (for Cd, Co, Cu, Ni, Pb and Zn), Fluorimetry (for U) and Gaseous Chromatography after ignition at 1800°C for S_{total} and C.

Table VII. Sample petrography description (by optical microscopy and x-ray diffraction techniques)

Sample	Description	Mode analysis (%)	
A	Pelitic schist with chlorites as the more important mica minerals. The feldspar is very altered to a clay mineral and sericite. Rock with macroscopic visible pyrite grains (Ø<0.1mmm).	Quartz	58.8
		Feldspar	14.0
		Muscovite	8.8
		Chlorite	17.1
		Biotite	0.1
		Tourmaline	0.1
		Apatite	0.3
		Pyrite	0.5
		Oxides	0.3
E	Pelitic schist with biotite breaking down to a chlorite, muscovite and sericite. Sericite is the result of breakdown of the muscovite and cordierite.	Quartz	40.6
		Feldspar	11.3
		Muscovite	4.6
		Chlorite	6.1
		Biotite	12.5
		Tourmaline	0.3
		Sericite	22.8
		Topaz	0.6
		Opaque (*)	0.05
B_1	Schist with muscovite as the main mica mineral, crossed by veins of quartz. Biotite is breaking down to a chlorite.	Quartz	44.0
		Feldspar	14.5
		Muscovite	23.0
		Chlorite	5.3
		Biotite	13.0
		Tourmaline	+
		Apatite	+
		Opaques (*)	0.6
B_2	Schist with chlorite as the principal mica mineral. It presents some heterogeneity by the presence of several small lens mainly of biotite and feldspar.	Quartz	51.4
		Feldspar	5.6
		Muscovite	3.5
		Chlorite	34.3
		Biotite	4.1
		Tourmaline	0.15
		Apatite	0.15
		Topaz	0.6
		Opaque (*)	0.5
C_4	Pelitic schist with muscovite biotite partially chloritized and cordierite also breaking down to a sericite. The contact between schist and a intrusive quartz dyke shows a development of biotite.	Quarto	37.6
		Feldspar	0.8
		Muscovite	20.1
		hlorite	0.5
		Biotite	20.5
		Tourmaline	0.3
		Sericite	14.5
		Cordierite	1.8
		Cristobalite?	3.3
		Opaque (*)	0.3
D	Coarse-grained granitic rock containing muscovite and biotite considerably altered in chlorite. The sodic plagioclase (1) and the microperthitic potassic feldspar (2) show significant alteration to clay minerals and sericite.	Quartz	33.8
		Feldspar (1)	22.1
		Feldspar(2)	26.0
		Muscovite	6.8
		Chlorite	9.1
		Sericite	1.5
		Apatite	0.15
		Opaques (*)	0.06
Sd L0	Silty and clayish material from the bottom of the open pit lake consisting of gypsum, quartz, muscovite, chlorite and clay minerals (halloysite, montmorillonite, kaolinite and illites).		
F1 **F2** **F3**	Core samples with granite and schist fragments and particles of quartz, micas, feldspars, clay minerals and others minerals of difficult identification.		

(*) - Sulphides, oxides and hydroxides

Table VIII. Chemical analysis of selected samples

		Samples						
		A	**E**	**B_1**	**B_2**	**C_4**	**D**	**Sd L.0**
SiO_2	%	69.44	56.18	64.43	60.00	63.05	67.89	52.25
Al_2O_3		13.92	21.61	17.63	20.48	18.89	15.59	24.46
Fe_{total}		6.05	7.85	6.12	7.10	6.16	3.70	6.22
MgO		2.32	2.74	2.16	2.57	2.07	0.75	1.04
CaO		0.50	0.55	0.53	0.44	0.23	0.62	0.47
Na_2O		1.38	1.48	1.85	1.65	1.21	3.24	1.16
K_2O		2.12	3.64	2.77	3.76	3.03	6.02	3.55
TiO_2		0.83	1.23	0.47	0.22	1.09	0.58	0.34
P_2O_5		0.25	0.28	0.25	0.18	0.19	0.45	0.26
MnO		0.04	0.07	0.07	0.06	0.04	0.04	0.06
S_{total}		0.12	0.23	0.03	0.01	0.02	< 0.01	0.33
C		< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	1.70
L.I.		2.35	3.40	2.80	3.50	3.39	1.36	10.27
Total		99.20	99.03	99.08	99.96	99.35	100.24	100.08
Cr	ppm	77	108	87	81	84	10	31
Co		18	20	18	16	20	8	9
Ni		33	36	41	37	23	5	17
Cu		60	575	21	24	35	16	60
Zn		84	268	230	156	168	246	241
Cd		< 5	< 5	< 5	< 5	< 5	< 5	< 5
Pb		18	13	18	29	32	31	64
U		70	16	12	136	127	55	432

L. I. – Loss of ignition

ABA tests rely on the assumptions that all sulphur present in the samples will oxidise to produce acid. This assumption could lead to an overestimation of the acid potential (AP) available in the sample. It was necessary to determine and distinguish the sulphide portion of the total sulphur and to correct the AP parameter. The following procedure was used (Laurence, 1990):

$$AP = \text{sulphide sulphur (\%)} \times 31.25$$

Sulphide sulphur content is calculated by subtracting the sulphate sulphur from the total sulphur amount.

This correction was done for the samples in which the sulphur from the sulphate could affect the AP value. The results are presented in Table 9.

Table IX. Acid-base accounting (ABA) test results

Sample	Paste pH	S (%)	AP***	NP***	NNP***	NPR
A	7.75	0.119* 0.114**	3.72 3.56	3.81	0.09 0.25	1.02 1.07
E	4.21	0.230* 0.189**	7.19 5.90	2.50	-4.69 -3.40	0.25 0.42
B_1	5.50	0.030	0.94	4.75	3.81	4.05
B_2	5.30	0.014	0.44	3.00	2.56	6.82
C_4	4.56	0.023	0.72	2.32	1.60	3.22
D	8.42	<0.01	<0.31	4.75	4.44	15.32
Sd L0	4.08	0.330* 0.233**	10.31 7.28	-2.94	-13.25 -10.22	0.28 0.40
F1	6.25	0.030	0.94	2.59	1.65	2.75
F2	4.97	0.030	0.94	2.97	2.03	3.15
F3	4.29	0.040	1.25	0.27	-0.98	0.22

* - Total sulphur; ** - Sulphide sulphur; *** - kg $CaCO_3$/t sample
AP - Acid Potential; **NP** - Neutralising Potential;
NNP - Net Neutralising Potential; **NPR** - Neutralisation Potential Ratio

The ABA test results (values of the net neutralization potential (NNP) and the ratio neutralization potential/acid potential (NPR)) indicate, in principle, that E, SdL0 and F3 samples are acid-generating materials. Concerning A, F1 and F2 samples, it is uncertain that they represent acid-generating materials.

Kinetic tests were performed in order to provide an assessment of the leachate quality and the dissolved metal flux, which could be expected from these materials with time. The Humidity Cell Test method [8] was chosen.

This test was conducted through repetitive 6 - 12 cycles (seven days each) of oxidation and leaching, by percolating distilled water. The effects of weathering were simulated in the humidity cells, where the crushed samples were placed.

The leachate recovered was analysed for a number of parameters including pH, redox potential, electrical conductivity, acidity and alkalinity (by titration), sulphate (by ion chromatography) and content of dissolved metals (by ICP and fluorimetry). The results are analysed and presented in Figs. 14 and 15.

Kinetic test results demonstrate that:

- materials are present with capacity to generate acid water as a consequence of sulphide oxidation;
- selected samples did not have a high capacity to develop acid drainage through time.

This is shown by the leachate from SdL0 sample, with pH< 4.5 and high conductivity and acidity. Sulphate and Al, Fe, Mn, Ni, Zn and U contents also presented high values. This sample did not have acid-neutralising capacity.

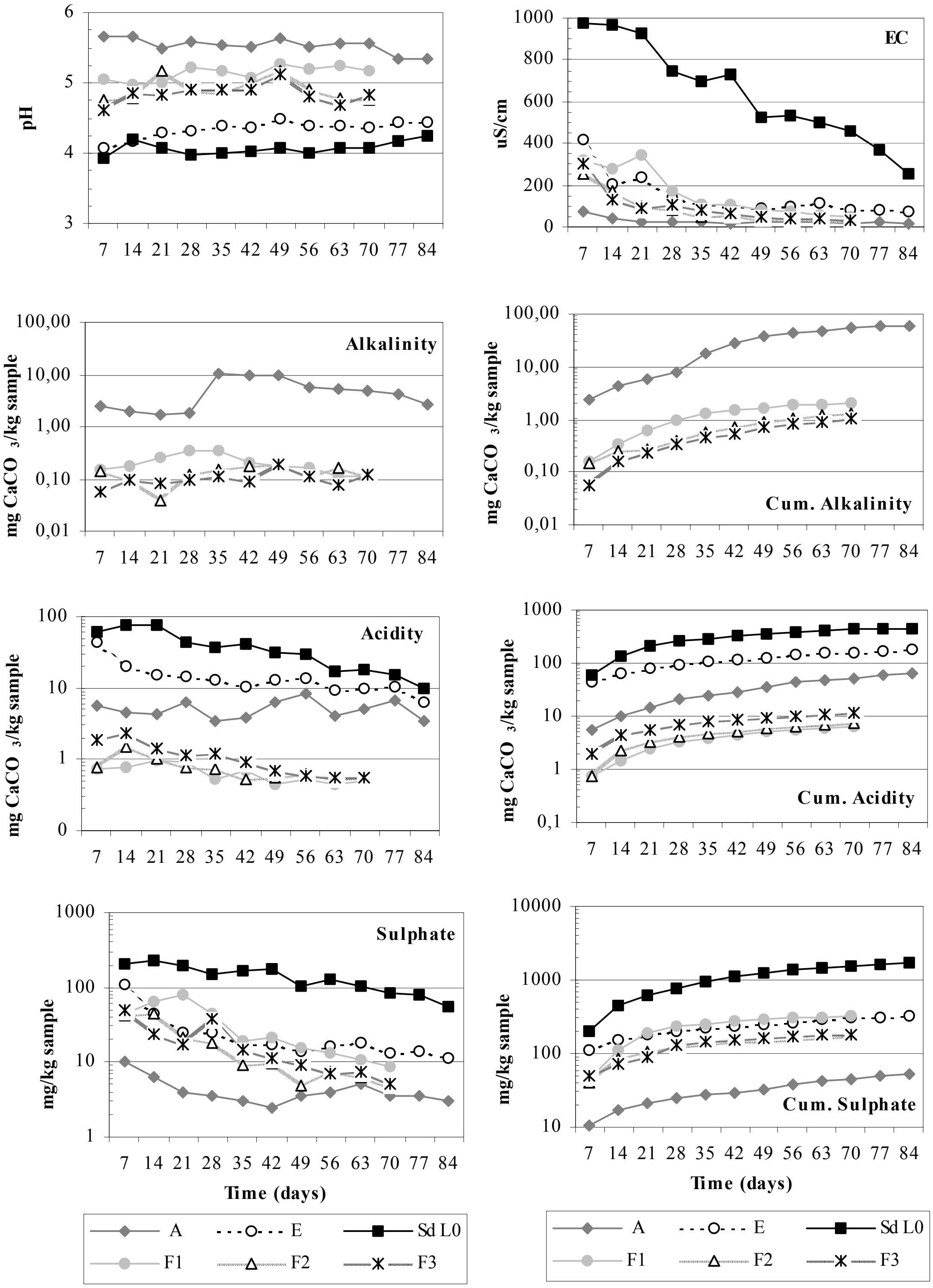


FIG. 14. Humidity cell test results.

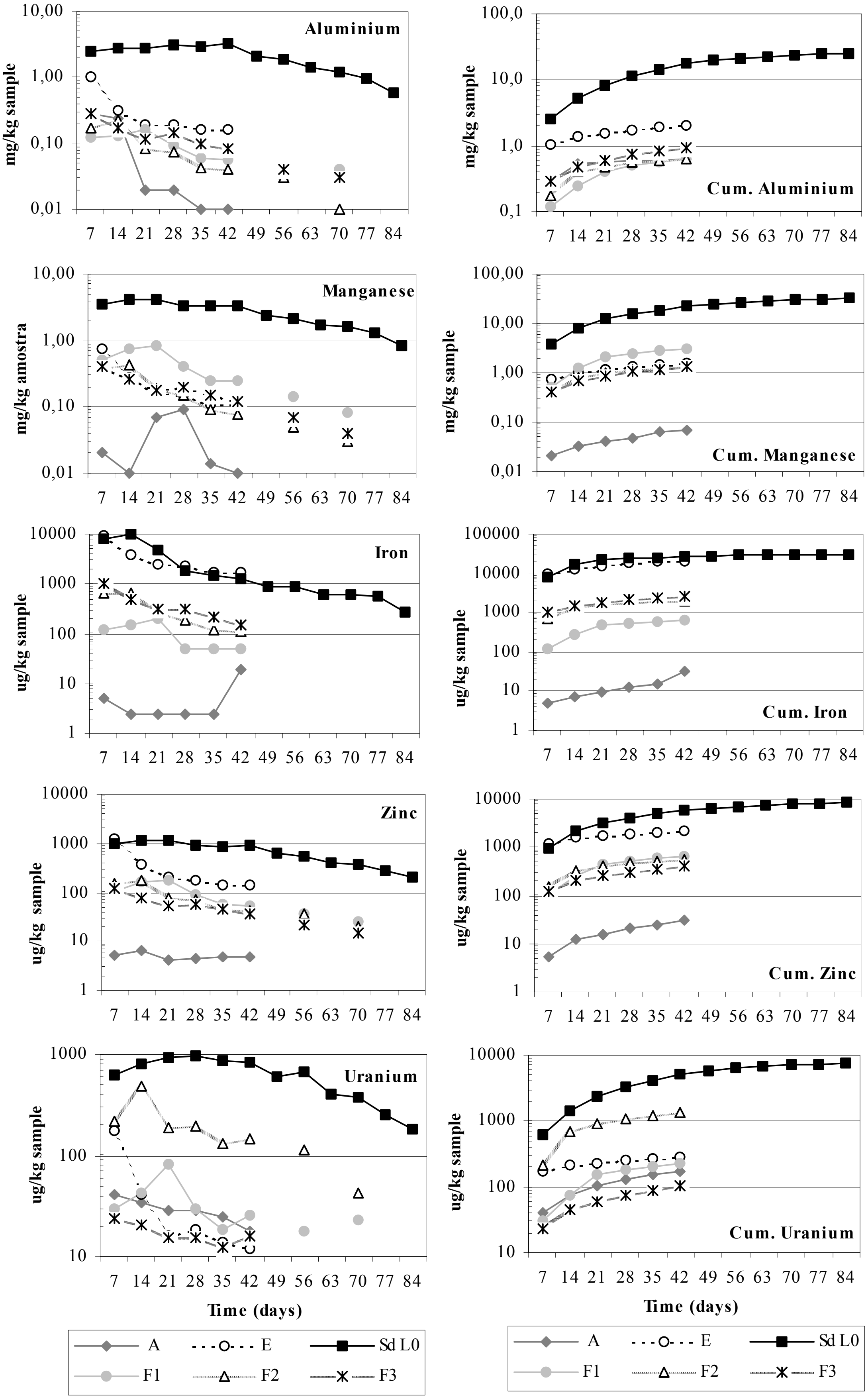


FIG. 15. Humidity cell test results.

The leachate from A sample, after the fifth-sixth cycle of oxidation / leaching showed an increase in acidity, sulphate and iron contents that could indicate sulphide oxidation process. However, the conductivity and acidity remains low until the end of the test and the sulphate contents decreased as the alkalinity. The greater acid-neutralising capacity from sample A could be explained by the presence of neutralising minerals such as chlorite. The other tested samples did not prove to have capacity to generate acidity.

However the existence of sulphide oxidation was confirmed by laboratory micro-organism tests. They were also performed on the mine water collected from the pit shaft, in order to detect the presence of the bacterium *Thiobacillus ferrooxidans* (Silverman and Lundgren, 1959). This bacterium has a remarkable action of direct oxidation of sulphides, such as pyrite. It is a powerful oxidant of these minerals, particularly once environment pH is below 3.5. These tests were positive. *Thiobacillus ferrooxidans* were detected in the mine water from the pit shaft.

3. Conclusions and alternative plan to the acid drainage problem

The study on the determination of risks associated with the Cunha Baixa abandoned uranium mine leads to the following conclusions:

- The main identified problem is the existence of acid drainage.
- Associated with the acid drainage, there is some contamination of the surface aquifer used as agricultural supply water mainly in dry season. According the Portuguese water quality requirements, the Maximum Recommended Values for several parameters are exceeded. It is clear that some dissolved pollutants are directly influenced by mining activities and drainage from the abandoned mine.
- The spread of pollutants seems to be confined to an area 1-1.5km downstream of the old mine.
- The contaminated water, when used to irrigate agricultural land, potentially affects directly or indirectly the quality and growth of crops, because:
  - Soluble contaminants are more easily assimilated by the plants, like plant nutrients.
  - Contaminated water can modify the bioavailability of the nutrients in the exchange complex of the soil**.**
- There are waste materials with capacity to generate acid water as a consequence of sulphide oxidation. Meanwhile we need also consider that the acid drainage could yet be the result of leaching of the remained acid used, in the past, to extract uranium.

  So, in order to mitigate the acid drainage problem, we think the most effective measure might be to minimize water flow in and around all the mine site area.

To implement this main measure, it will be necessary:

- To restore the landscape, using dump materials to fill the open pit mining area. Once relocated the material should be compacted (to restrict percolation of water and oxygen) and covered with a layer of impermeable material (clay).
- To collect the surface water to prevent its infiltration into the underground mine workings.
- A final cover with soil and revegetation with appropriate crops to stabilise slopes, minimise gulling and visual impact, and maximize evapo-transpiration of water percolating through the ground.

- To evaluate cessation of pumping water from the shaft mine because this operation induce oxygenation (provided its alternative discharge from the mine working area are well understood).
- To continue monitoring the water composition (both surface and ground water). This operation will indicate if it will be need to improve some other type of neutralisation process or to physically remove any ongoing pollutant source.

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APPENDIX

Ground and surface water data in September 1995

Ref	Date	T	pH	EC	Eh	DO	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Si	Al	Na	K	U	Fe	Co	Zn	Cu	Ni	Hard.	Ra^{226}
		° C		*uS/cm*	*mV*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*(*)*	*Bq/l*
P1	SEPT/95	14.2	6.45	157	200	3.8	50.6	118.6	16	5	23	23.5	< 50	207	7.7	3.8	0.08	8.5	n.d.	14.4	3.2	2	< 5	< 10	< 5	< 5	< 10	35	0.39
P2	SEPT/95	16.4	6.25	176	294	4.6	3.4	102.8	18	11	25	20.4	< 50	120	11.8	4.5	n.d.	4.7	n.d.	14.1	1.8	2	< 5	< 10	< 5	< 5	< 10	48	0.30
P3	SEPT/95	16.0	5.90	54	414	7.7	0.6	168.8	19	43	26	21.0	106	325	14.2	4.9	n.d.	8.0	n.d.	19.0	9.3	19	< 5	< 10	< 5	< 5	< 10	55	1.62
P4	SEPT/95	15.5	5.93	71	350	4.4	1.6	67.0	10	2	3	15.7	156	196	2.3	1.5	n.d.	10.2	n.d.	7.8	1.5	4	< 5	< 10	< 5	< 5	< 10	12	0.07
P5	SEPT/95	15.8	3.98	537	422	3.7	0.6	2533.2	27	21	1598	n.d.	92	1066	259.0	160.0	17.85	23.8	44.34	39.5	37.1	2300	78	308	2660	77	415	1304	1.32
P6	SEPT/95	15.2	6.83	395	316	6.0	4.0	248.6	18	47	48	85.2	128	241	43.6	6.1	n.d.	13.2	n.d.	22.3	4.0	11	< 5	< 10	< 5	< 5	< 10	134	0.17
P8	SEPT/95	17.1	6.54	230	365	5.7	1.6	141.6	17	29	18	42.5	< 50	217	22.8	3.6	0.01	9.3	0.06	14.8	2.2	2	12	< 10	< 5	< 5	< 10	72	0.05
P9	SEPT/95	17.2	4.66	n.a.	385	6.0	3.2	1213.4	14	22	706	n.d.	65	577	158.5	81.3	0.10	13.8	0.13	38.5	7.5	105	7	< 10	183	< 5	30	730	0.51
P10	SEPT/95	15.7	6.62	82	380	10.3	3.2	108.2	14	n.d.	1	18.3	73	150	1.9	1.2	n.d.	12.4	0.02	13.3	1.0	6	43	< 10	9	< 5	< 10	10	0.05
P12	SEPT/95	16.0	5.88	198	348	5.4	1.0	136.2	10	7	52	15.4	74	183	12.3	3.8	n.d.	10.9	n.d.	16.5	2.0	12	< 5	< 10	< 5	< 5	< 10	46	0.19
P13	SEPT/95	15.4	6.62	284	341	5.9	2.4	172.6	30	20	31	40.7	99	241	13.4	7.0	n.d.	3.7	0.04	20.5	12.0	23	15	< 10	8	< 5	< 10	62	0.55
P14	SEPT/95	16.5	6.18	55	335	6.7	3.0	55.6	9	1	5	10.7	< 50	161	2.3	1.2	0.01	8.6	0.02	7.2	0.8	4	18	< 10	27	< 5	< 10	11	0.07
P15	SEPT/95	17.2	4.25	2210	391	7.2	2.2	2429.6	17	13	1694	n.d.	55	1121	298.5	177.5	14.42	23.8	19.26	39.0	11.9	2100	49	113	1391	62	260	1475	3.11
P16	SEPT/95	15.7	5.94	160	335	3.9	n.d.	108.2	16	9	19	25.9	< 50	197	14.3	2.0	n.d.	4.9	0.07	13.0	3.9	4	< 5	< 10	< 5	< 5	< 10	44	0.06
P18	SEPT/95	15.4	6.02	37	402	5.2	11.0	125.8	16	11	20	21.3	< 50	153	9.1	4.1	n.d.	5.2	n.d.	15.4	3.4	2	< 5	< 10	< 5	< 5	< 10	40	0.12
P19	SEPT/95	17.7	6.62	74	238	10.5	2.4	49.6	9	6	3	14.8	< 50	170	2.5	1.6	n.d.	6.0	n.d.	8.1	1.2	1	< 5	< 10	< 5	< 5	< 10	13	0.07
CB1	SEPT/95	19.3	6.56	558	51	7.2	35.8	378.8	8	n.d.	172	111.9	280	892	50.0	21.0	1.43	11.7	0.79	19.0	14.2	30	14	< 10	70	9	< 10	211	2.03
CB2	SEPT/95	14.5	4.34	1909	-63	n.d.	17.8	1780.0	10	n.d.	1225	n.d.	< 50	1535	181.0	122.0	13.72	29.7	20.82	23.0	7.9	595	11939	235	198	19	409	953	6.76
R1	SEPT/95	17.1	6.35	260	312	5.1	2.8	200.8	24	4	84	25.0	< 50	270	22.8	9.4	0.22	6.7	n.d.	20.8	2.8	2	< 5	< 10	< 5	< 5	< 10	96	0.17
R2	SEPT/95	18.4	6.22	130	445	6.5	9.2	113.8	18	17	20	18.9	< 50	172	10.4	3.6	n.d.	6.2	n.d.	13.5	6.1	1	< 5	< 10	< 5	< 5	< 10	41	0.06
R4	SEPT/95	16.2	5.56	60	440	7.6	3.0	64.0	12	4	1	16.2	94	92	2.4	1.4	n.d.	9.3	n.d.	9.3	1.5	1	< 5	< 10	< 5	< 5	< 10	12	0.04
R7	SEPT/95	18.5	6.45	290	370	2.7	19.8	250.2	19	2	124	23.8	< 50	282	31.6	13.5	0.66	7.2	n.d.	19.5	2.5	3	< 5	< 10	< 5	< 5	< 5	134	0.10
R8	SEPT/95	19.1	6.42	260	388	2.6	4.6	192.2	24	3	69	38.1	290	331	20.2	8.1	0.35	6.9	0.08	21.1	3.8	2	< 5	< 10	< 5	< 5	< 10	84	0.12
R9	SEPT/95	18.2	4.69	1350	313	6.8	24.2	1272.0	22	26	735	n.d.	< 50	931	180.5	92.5	3.94	14.9	3.81	31.3	18.7	466	< 5	< 10	< 5	< 5	< 10	831	n.a.

Ref - sampling site;**(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

Ground and surface water data in May 1996

Ref	Date	T	pH	EC	Eh	DO	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Si	Al	Na	K	U	Fe	Co	Zn	Cu	Ni	Hard.	Ra^{226}
		° C		*uS/cm*	*mV*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*(*)*	*Bq/l*
P1	MAY/96	12.5	5.12	75	372	3.4	5.6	55.2	8	5	11	5.5	n.d.	62	3.5	1.7	n.d.	4.8	0.07	7.4	1.1	4	< 5	< 10	< 5	< 5	< 10	16	0.09
P2	MAY/96	10.4	6.13	162	312	4.6	6.0	92.0	23	21	30	18.3	n.d.	< 40	11.9	4.9	n.d.	5.7	0.00	10.0	1.5	3	< 5	< 10	< 5	< 5	< 10	50	0.19
P3	MAY/96	13.5	5.89	178	413	2.8	2.6	154.0	28	26	26	16.2	190	133	9.8	3.5	0.01	8.7	0.12	14.1	8.0	16	44	< 10	25	< 5	< 10	39	0.60
P4	MAY/96	13.4	5.13	164	418	3.8	2.0	56.2	13	1	5	12.0	100	88	2.6	3.5	n.d.	9.6	0.04	7.0	0.9	4	21	< 10	< 5	< 5	< 10	21	0.21
P5	MAY/96	13.1	4.10	1410	462	2.9	1.8	1374.5	36	20	965	n.d.	< 50	852	172.0	107.9	14.83	21.1	21.64	21.6	20.7	1200	102	244	1991	34	390	873	0.76
P6	MAY/96	13.6	7.08	294	255	5.2	0.8	272.2	15	20	59	118.9	56	402	54.0	13.3	n.d.	7.7	0.10	9.1	9.6	32	< 5	< 10	< 5	< 5	< 10	189	0.09
P8	MAY/96	11.7	6.00	176	331	4.5	0.6	116.6	23	28	26	18.3	n.d.	< 40	15.5	3.2	0.01	7.5	0.07	10.1	3.0	2	16	< 10	7	< 5	< 10	52	0.06
P9	MAY/96	13.0	5.71	477	409	5.5	1.6	369.4	13	20	195	10.8	< 50	283	50.3	25.8	0.17	10.2	0.23	18.9	4.7	18	31	< 10	28	< 5	< 10	231	0.30
P10	MAY/96	12.4	6.12	104	263	2.0	34.4	78.8	26	1	2	30.0	< 50	105	6.8	1.6	0.08	9.5	0.13	11.6	1.7	10	409	< 10	0	12	< 10	23	0.95
P12	MAY/96	14.0	5.28	70	309	4.9	0.6	172.2	13	16	64	11.6	< 50	89	17.0	5.5	0.01	9.1	0.06	18.5	23.7	17	5	< 10	33	< 5	< 10	65	0.12
P13	MAY/96	12.7	5.56	235	369	4.7	8.8	152.2	26	32	48	19.2	70	87	10.8	6.7	n.d.	5.1	0.06	19.8	10.6	24	28	< 10	0	< 5	< 10	55	0.57
P14	MAY/96	13.9	5.29	66	323	5.9	0.8	54.4	5	3	11	6.7	< 50	86	3.1	1.3	0.01	6.7	0.05	7.1	1.0	11	40	< 10	11	< 5	< 10	13	0.08
P15	MAY/96	12.9	3.86	1810	488	5.8	3.8	1944.0	22	n.d.	1563	n.d.	< 50	1014	268.9	134.3	8.07	19.4	13.79	31.7	7.2	1400	88	50	993	41	206	1223	3.42
P16	MAY/96	12.7	5.79	140	310	3.3	0.4	103.6	10	10	22	25.0	n.d.	160	15.1	2.0	n.d.	4.1	0.08	8.8	2.5	3	< 5	< 10	< 5	< 5	< 10	46	0.14
P18	MAY/96	13.5	5.57	118	348	5.8	2.2	81.8	12	8	20	11.0	n.d.	107	6.0	2.8	n.d.	4.7	0.00	11.3	2.1	5	< 5	< 10	< 5	< 5	< 10	26	0.01
P19	MAY/96	13.3	5.47	82	297	8.0	0.4	60.4	8	9	5	7.9	n.d.	86	2.8	1.6	n.d.	6.1	0.00	7.3	1.8	2	< 5	< 10	< 5	< 5	< 10	13	0.08
P20	MAY/96	14.6	4.75	466	397	3.8	1.2	271.5	28	25	212	n.d.	n.d.	248	50.6	26.3	0.97	9.1	1.30	16.6	8.8	32	37	< 10	125	12	17	235	0.59
P21	MAY/96	14.1	5.22	159	376	8.7	2.2	117.2	28	43	3	4.8	< 50	44	4.8	3.7	0.06	7.5	0.12	17.3	3.9	10	12	< 10	< 5	< 5	< 10	27	0.82
CB1	MAY/96	13.0	6.55	446	389	3.1	19.4	342.4	15	n.d.	163	38.4	< 50	570	51.5	21.1	0.18	10.7	0.07	14.0	8.1	43	234	< 10	65	< 5	< 10	215	6.68
CB2	MAY/96	11.9	3.49	895	520	9.1	6.2	1266.2	12	n.d.	510	n.d.	n.d.	562	84.1	57.2	5.19	21.3	8.60	11.1	3.7	2600	472	148	1498	132	285	445	3.48
R1	MAY/96	11.4	6.29	188	255	8.9	8.5	240.6	24	8	84	19.2	50	280	13.3	5.5	0.25	6.8	0.13	12.3	2.4	11	114	< 10	83	< 5	< 10	56	0.15
R2	MAY/96	12.9	6.34	96	266	8.7	0.8	75.6	10	4	13	18.3	< 50	120	6.3	2.3	n.d.	6.1	0.00	8.3	2.8	1	< 5	< 10	< 5	< 5	< 10	25	0.10
R3	MAY/96	13.1	6.50	112	300	8.4	2.4	69.5	14	6	18	19.8	n.d.	48	6.1	2.4	n.d.	5.4	0.01	10.1	3.9	1	38	< 10	< 5	< 5	< 10	25	0.13
R4	MAY/96	14.0	5.28	70	309	7.5	0.4	53.6	10	4	1	11.6	56	55	2.1	1.3	n.d.	8.4	0.00	8.5	1.4	2	< 5	< 10	< 5	< 5	< 10	11	0.05
R5	MAY/96	14.1	3.69	994	520	8.7	4.8	373.5	15	2	135	n.d.	n.d.	635	95.6	57.0	6.88	20.7	16.39	13.5	4.2	1800	1315	127	778	69	176	473	1.80
R7	MAY/96	12.3	6.51	177	272	8.7	8.8	109.0	12	6	39	21.9	142	190	10.2	5.0	0.21	5.8	0.09	12.8	2.3	5	105	< 10	74	< 5	14	46	0.10
R8	MAY/96	12.6	6.48	145	225	8.6	1.4	104.2	11	5	33	18.3	< 50	163	9.8	4.6	0.17	5.8	0.08	11.3	2.0	4	109	< 10	76	< 5	11	43	0.06
R9	MAY/96	13.7	4.11	998	469	8.6	6.4	653.0	23	8	663	n.d.	n.d.	891	109.4	61.7	5.08	17.5	10.71	18.7	9.0	942	657	77	749	40	121	527	1.20
R10	MAY/96	12.6	6.33	81	284	7.7	1.2	58.6	9	1	11	17.7	< 50	123	4.2	2.0	n.d.	5.9	0.00	9.6	1.4	1	< 5	< 10	< 5	< 5	< 10	19	0.04
R12	MAY/96	15.4	6.92	127	227	8.2	0.6	91.4	14	6	13	23.8	238	178	5.9	2.0	0.08	5.6	0.00	13.4	2.3	1	< 5	< 10	< 5	< 5	< 10	23	0.84
R13	MAY/96	15.1	6.91	127	273	8.6	5.4	89.0	14	6	23	22.6	235	193	8.1	3.3	0.16	5.8	0.07	13.9	2.1	2	< 5	< 10	56	< 5	14	34	0.08
R14	MAY/96	14.3	5.19	177	304	4.8	0.8	131.4	7	n.d.	64	6.1	< 50	246	9.0	4.4	0.14	8.7	0.23	17.8	0.2	1	82	< 10	7	< 5	< 10	41	0.79
R16	MAY/96	13.1	6.90	89	246	9.5	1.2	67.6	11	3	9	15.9	< 50	129	4.2	1.4	0.11	5.3	0.05	9.7	1.3	1	< 5	< 10	0	< 5	< 10	16	0.19
R21	MAY/96	16.2	4.64	745	385	7.4	4.0	537.6	15	n.d.	438	n.d.	< 50	333	80.1	43.0	2.96	13.2	4.86	16.4	6.6	415	164	39	1033	19	73	376	1.21

Ref - sampling site;**(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

Ground and surface water data in September 1996

Ref	Date	T	pH	EC	Eh	DO	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Si	Al	Na	K	U	Fe	Co	Zn	Cu	Ni	Hard.	Ra^{226}
		º C		*uS/cm*	*mV*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*(*)*	*Bq/l*
P3	SEPT/96	16.0	5.50	198	345	2.6	0.6	151.4	16	25	19	30.5	125	278	12.0	3.9	0.01	7.9	0.06	16.3	9.8	26	11	< 10	< 5	6	< 10	46	0.49
P4	SEPT/96	15.4	5.69	68	255	7.0	0.2	58.8	10	2	6	10.7	113	149	2.5	1.4	n.d.	9.6	< 0,02	7.8	1.3	6	7	< 10	6	< 5	< 10	12	0.07
P5	SEPT/96	16.5	3.87	1720	681	4.3	n.d.	2533.6	16	6	1574	n.d.	80	1588	291.5	135.0	20.50	21.0	49.00	29.0	16.3	3300	72	414	3288	< 5	626	1283	0.63
P6	SEPT/96	14.9	5.86	355	281	7.2	1.8	276.8	18	49	47	68.0	90	146	37.5	6.4	0.02	12.5	0.09	20.6	3.3	10	6	< 10	21	< 5	< 10	120	0.13
P8	SEPT/96	16.5	5.87	235	374	3.6	2.6	178.4	14	21	22	39.6	n.d.	251	22.1	3.8	0.02	8.8	0.06	12.9	3.0	4	< 5	< 10	< 5	< 5	< 10	71	0.11
P9	SEPT/96	17.4	4.51	1240	342	5.1	0.6	997.8	11	11	743	n.d.	53	616	154.5	80.0	1.45	13.3	1.40	33.0	6.4	215	14	< 10	173	< 5	32	715	0.41
P10	SEPT/96	16.0	5.70	104	219	3.4	5.4	84.6	14	1	1	28.7	89	124	6.0	1.3	0.03	11.7	0.04	12.0	1.2	9	63	< 10	< 5	< 5	< 10	20	0.10
P13	SEPT/96	15.1	6.10	218	241	5.6	18.6	150.8	23	15	29	41.8	119	182	12.4	6.7	0.02	4.2	0.05	21.8	11.3	30	52	< 10	< 5	< 5	< 10	58	0.29
P14	SEPT/96	16.5	5.69	62	232	5.0	3.4	51.0	7	1	5	13.4	n.d.	104	2.6	1.1	0.04	7.9	0.02	6.7	0.7	8	22	< 10	16	< 5	< 10	11	0.10
P15	SEPT/96	16.7	3.65	2120	420	6.2	3.0	2305.0	14	8	1473	n.d.	< 50	784	301.5	147.5	11.50	21.2	17.67	38.5	9.6	2900	23	139	1639	44	307	1359	4.24
P17	SEPT/96	20.7	4.03	1610	362	6.4	2.8	1821.0	11	11	1213	n.d.	60	687	245.0	135.0	8.90	22.1	16.10	39.0	8.2	2800	24	63	892	69	181	1167	5.97
P20	SEPT/96	18.9	4.32	925	312	3.0	0.4	861.6	21	22	510	n.d.	< 50	569	105.3	50.0	2.51	10.1	2.03	28.8	14.2	123	42	< 10	233	< 5	46	468	0.06
P21	SEPT/96	15.8	5.81	167	243	5.6	22.4	135.0	23	26	2	24.1	< 50	97	11.0	3.3	n.d.	7.3	0.07	18.0	3.8	6	40	< 10	11	< 5	< 10	41	0.29
P22	SEPT/96	16.3	5.60	303	104	6.4	2.8	215.6	16	41	77	24.4	< 50	416	32.0	10.0	0.05	8.8	0.14	11.6	1.8	25	10	< 10	7	< 5	< 10	121	0.05
P23	SEPT/96	16.9	4.52	1010	344	4.0	3.2	894.6	11	5	515	n.d.	< 50	427	139.0	67.5	1.69	10.9	1.41	28.3	5.1	119	26	< 10	176	< 5	35	624	0.53
P24	SEPT/96	16.0	5.41	469	249	5.5	0.4	346.8	28	33	114	28.0	60	215	30.3	14.3	0.02	7.2	0.08	34.3	16.8	27	< 5	< 10	9	< 5	< 10	134	0.60
P25	SEPT/96	16.4	5.44	291	276	5.7	n.d.	215.4	7	11	96	7.6	58	203	19.6	9.3	0.03	9.5	0.10	16.8	4.2	37	14	< 10	14	< 5	< 10	87	0.05
P26	SEPT/96	14.7	4.49	1736	312	5.8	4.4	1647.2	18	11	1082	n.d.	n.d.	865	256.0	110.0	6.83	15.1	8.45	33.5	35.6	1000	118	25	991	12	179	1091	0.86
CB1	SEPT/96	17.4	3.11	2490	407	n.d.	1.8	2925.2	16	1	1817	n.d.	n.d.	1351	307.0	205.0	31.90	46.1	57.17	36.0	10.5	5700	11897	338	1936	< 5	455	1609	1.79
CB2	SEPT/96	15.3	3.81	1350	5	n.d.	16.2	1595.0	14	1	1074	n.d.	n.d.	647	138.5	115.0	10.25	33.1	17.01	24.0	6.5	2100	12571	193	1238	< 5	313	819	1.69
L0	SEPT/96	18.8	2.92	2880	476	5.0	1.2	3344.6	18	1	2329	n.d.	n.d.	1813	334.0	212.5	34.50	53.7	69.34	36.3	12.9	6300	36640	537	2534	162	699	1707	12.21
BD	SEPT/96	17.8	8.20	2778	167	9.5	10.2	3238.0	16	n.d.	2017	81.1	n.d.	7510	645.0	150.0	4.82	0.8	0.02	36.3	9.2	2900	< 5	< 10	< 5	< 5	< 10	2226	0.05
R1	SEPT/96	14.4	6.88	718	111	2.0	1.2	470.8	51	1	190	129.2	585	451	45.1	19.5	1.54	7.5	0.10	54.5	8.2	20	193	< 10	13	< 5	22	193	0.11
R5	SEPT/96	19.3	6.68	2340	194	8.5	1.2	2811.4	16	n.d.	1644	25.0	n.d.	3524	618.0	63.5	0.33	3.8	0.74	36.8	10.0	372	31	14	17	20	38	1803	2.08
R7	SEPT/96	11.5	7.10	838	-200	n.d.	5.8	538.4	75	4	146	236.6	2925	318	59.3	20.0	1.44	7.2	0.39	60.0	11.5	4	11	< 10	105	21	25	230	0.09
R8	SEPT/96	14.7	6.84	517	122	2.4	4.4	394.4	47	n.d.	135	108.8	604	369	37.0	15.0	1.22	7.8	0.08	47.5	6.9	6	102	< 10	10	< 5	12	154	0.08
R9	SEPT/96	17.7	4.32	1610	420	7.5	0.2	1939.8	15	4	1132	n.d.	n.d.	640	236.0	110.0	6.52	15.9	6.05	35.3	18.5	736	6	24	782	< 5	126	1041	1.04
R21	SEPT/96	15.6	5.19	1866	270	7.4	0.2	2140.0	17	8	1097	3.4	n.d.	1105	278.0	101.3	3.89	9.5	2.17	34.3	10.8	175	20	10	349	< 5	60	1110	0.55
R25	SEPT/96	14.3	6.97	925	-148	0.0	3.0	684.6	66	76	237	185.9	2309	411	66.0	25.0	1.45	7.5	0.18	66.5	13.3	13	863	< 10	11	7	30	267	0.10

Ref - sampling site;**(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

Ground and surface water data in April 1997

Ref	Date	T	pH	EC	Eh	DO	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Si	Al	Na	K	U	Fe	Co	Zn	Cu	Ni	Hard.	Ra^{226}
		° C		uS/cm	mV	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	ug/l	ug/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	(*)	Bq/l
P3	APR/97	14.6	5.82	204	227	3.1	1.2	135.6	15	28	21	22.0	140	337	10.2	3.8	n.d.	8.7	0.07	16.0	9.8	20	19	< 10	10	< 5	< 10	41	n.a.
P4	APR/97	13.2	5.54	121	336	7.4	0.4	69.4	9	2	3	11.6	120	112	2.4	1.4	n.d.	9.4	< 0,02	7.5	1.3	9	9	< 10	< 5	7	< 10	12	n.a.
P5	APR/97	13.9	4.46	823	352	5.7	1.8	669.0	14	10	424	n.d.	< 50	323	104.8	31.0	2.35	9.1	3.63	17.5	6.8	330	23	35	303	10	70	389	n.a.
P6	APR/97	14.0	6.40	418	277	5.7	1.2	325.6	22	46	63	101.5	70	366	52.3	11.5	0.01	9.6	0.12	14.5	6.6	32	8	< 10	10	9	< 10	178	n.a.
P9	APR/97	13.8	4.67	905	333	5.6	n.d.	834.0	17	16	426	1.5	50	358	70.0	42.5	0.42	11.4	0.50	32.0	6.4	56	< 5	< 10	68	8	< 10	349	n.a.
P10	APR/97	12.5	5.72	130	282	2.7	8.6	82.8	15	1	1	146.3	< 50	104	7.8	1.7	0.10	8.6	0.04	11.8	1.4	12	62	< 10	9	8	< 10	26	n.a.
P13	APR/97	12.9	5.53	259	323	5.1	0.8	184.8	25	30	34	23.5	80	263	11.6	7.3	n.d.	5.1	0.05	20.0	11.3	39	< 5	< 10	< 5	< 5	< 10	59	n.a.
P15	APR/97	13.4	3.93	2050	189	6.1	3.8	2211.8	12	6	1424	n.d.	< 50	1097	285.5	295.0	2.22	18.9	14.06	34.0	8.3	1600	22	86	1197	37	229	1926	4.67
P17	APR/97	14.9	3.78	1980	387	5.5	2.0	2052.4	11	9	1311	n.d.	60	1077	255.0	285.0	2.37	22.4	17.82	37.0	8.2	2500	45	74	996	65	198	1808	n.a.
P20	APR/97	13.2	4.63	805	341	4.1	0.4	611.0	20	25	329	0.6	n.d.	311	73.8	37.0	1.19	8.4	1.30	21.5	11.1	65	8	< 10	155	8	31	336	n.a.
P21	APR/97	15.6	5.18	150	192	8.5	1.4	140.6	22	33	2	4.9	< 50	141	4.6	3.5	0.05	7.6	0.10	17.0	3.5	11	< 5	< 10	14	< 5	< 10	26	n.a.
P22	APR/97	14.7	6.09	425	279	5.6	0.6	351.8	15	22	145	39.6	n.d.	418	48.3	16.0	0.06	9.3	0.17	15.0	1.9	31	< 5	< 10	11	< 5	< 10	186	n.a.
P23	APR/97	14.6	4.80	365	323	3.9	n.d.	263.0	13	6	141	20.1	< 50	148	28.5	14.5	0.04	7.3	0.38	13.0	2.5	31	< 5	< 10	47	6	< 10	131	n.a.
P24	APR/97	13.1	5.42	254	117	5.7	0.2	173.4	20	31	35	17.1	< 50	190	13.5	7.5	0.01	5.6	0.07	18.5	7.7	29	< 5	< 10	7	< 5	< 10	65	n.a.
P25	APR/97	15.4	5.28	261	273	6.9	0.6	153.0	12	10	75	6.7	80	256	15.1	6.3	0.03	9.6	0.09	14.5	3.7	29	< 5	< 10	17	< 5	< 10	63	n.a.
P26	APR/97	13.7	4.27	1316	240	5.7	0.8	1155.6	18	15	749	n.d.	< 50	691	149.0	150.0	4.86	14.1	5.10	23.8	24.0	370	30	12	666	9	128	989	n.a.
P27	APR/97	14.0	4.11	1859	250	5.4	1.2	1833.4	12	2	1163	n.d.	n.d.	992	270.5	220.0	2.62	13.1	6.69	30.0	5.8	570	22	23	900	9	158	1580	n.a.
CB1	APR/97	16.6	3.54	2270	348	n.d.	3.0	2479.8	14	n.d.	1644	n.d.	100	1071	257.0	300.0	22.80	43.6	43.74	27.0	9.3	4800	13861	335	2243	< 5	468	1875	n.a.
CB2	APR/97	13.1	3.54	1460	503	6.8	n.d.	1384.8	13	n.d.	884	n.d.	< 50	746	13.3	182.5	9.21	38.5	18.04	22.0	12.9	6000	763	220	2061	163	419	784	n.a.
L0	APR/97	19.0	3.26	1930	432	7.7	17.4	2111.8	8	n.d.	1174	n.d.	n.d.	1390	98.0	215.0	17.85	35.3	37.20	16.0	7.2	5800	7217	309	2922	< 5	364	1129	n.a.
BD	APR/97	17.4	8.16	2360	223	9.2	3.2	2411.6	15	15	1715	36.6	n.d.	4065	458.0	100.0	1.78	1.9	0.76	27.5	9.3	1100	33	16	7	10	26	1554	1.27
R0	APR/97	14.5	6.06	89	249	n.a.	1.6	79.0	9	3	14	11.6	< 50	114	4.0	2.4	n.d.	7.3	0.03	8.5	0.7	21	22	< 10	11	12	< 10	20	n.a.
R1	APR/97	15.4	6.48	284	222	4.8	0.8	192.2	20	3	61	41.8	435	173	16.2	7.0	0.19	7.0	0.08	19.0	3.8	8	106	< 10	40	10	11	69	0.09
R5	APR/97	17.6	6.16	2040	313	8.5	6.4	2053.2	17	1	1361	22.9	n.d.	3809	405.0	81.3	1.56	3.4	0.82	25.5	8.2	870	15	16	74	9	30	1345	0.70
R8	APR/97	14.0	6.52	223	177	6.1	10.2	176.8	15	9	53	34.8	310	66	15.3	6.3	0.15	5.9	0.07	17.0	3.0	4	105	< 10	34	11	< 10	64	n.a.
R9	APR/97	13.2	4.48	1461	353	7.4	2.8	1364.0	19	13	876	n.d.	< 50	1127	182.5	92.5	4.16	13.5	5.01	27.0	14.3	375	18	18	573	7	106	836	n.a.
R13	APR/97	15.1	6.52	195	170	7.2	3.6	103.4	18	2	27	35.1	320	78	11.0	3.9	0.13	6.0	0.05	25.0	2.8	3	155	< 10	37	11	< 10	43	n.a.
R21	APR/97	15.7	4.62	1042	277	n.a.	2.8	913.8	16	11	597	n.d.	< 50	553	34.8	51.3	1.86	10.4	2.46	23.5	7.4	66	59	< 10	225	12	40	297	n.a.
R25	APR/97	14.7	6.32	259	1	7.1	1.8	167.2	14	3	57	32.0	260	108	18.3	7.0	0.23	5.9	0.09	16.5	3.0	8	108	< 10	51	12	< 10	74	n.a.

Ref - sampling site;**(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

Ground and surface water data in September 1997

Ref	Date	T	pH	EC	Eh	DO	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Si	Al	Na	K	U	Fe	Co	Zn	Cu	Ni	Hard.	Ra^{226}
		°C		*uS/cm*	*mV*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*(*)*	*Bq/l*
P4	SEPT/97	15.1	5.70	82	297	7.9	34.4	28.2	12	2	2	13.4	160	357	2.5	1.4	0.01	10.8	0.02	8.0	1.4	7	13	< 10	< 10	< 5	< 10	12	0.14
P5	SEPT/97	17.5	4.30	2010	359	6.3	2.0	1846.6	17	11	1270	n.d.	< 50	921	283.0	97.5	5.46	12.6	24.25	34.8	15.8	2800	49	69	880	35	170	1107	0.59
P9	SEPT/97	18.0	4.80	1607	222	4.6	0.6	1379.0	12	13	1085	2.4	60	840	209.0	96.3	0.96	13.9	1.33	42.7	10.0	135	8	< 10	165	< 5	29	918	0.19
P11	SEPT/97	18.2	4.46	1812	217	7.4	n.d.	1634.8	14	6	1314	n.d.	< 50	935	230.0	107.5	3.86	13.4	4.85	32.6	11.2	260	11	13	562	15	105	1016	0.72
P12	SEPT/97	16.2	5.55	182	284	4.7	1.8	132.8	11	5	48	14.3	80	49	10.3	3.5	0.01	11.3	0.04	15.8	1.9	16	< 5	< 10	19	< 5	< 10	40	0.09
P13	SEPT/97	15.7	6.25	291	34	3.6	46.4	177.4	28	26	30	39.6	100	180	12.9	7.2	0.18	5.3	0.03	21.1	11.2	22	1090	< 10	30	< 5	< 10	62	0.32
P15	SEPT/97	17.7	4.06	2580	379	6.3	0.6	2506.2	13	5	1749	n.d.	< 50	1218	356.0	113.0	11.45	21.6	22.42	41.9	11.4	3300	31	113	1360	54	247	1353	2.66
P17	SEPT/97	18.3	4.63	2370	350	3.8	2.0	2303.2	12	16	1521	n.d.	n.d.	1316	320.0	153.0	9.05	22.6	7.94	46.9	10.5	3700	23	47	955	62	156	1428	2.94
P20	SEPT/97	18.3	4.70	1687	274	3.6	1.6	1461.8	16	11	983	1.2	< 50	688	234.0	105.0	4.07	12.0	3.99	36.9	18.0	205	24	25	485	12	105	1016	0.35
P21	SEPT/97	16.8	5.70	180	259	8.5	0.6	142.8	27	36	2	9.5	n.d.	406	6.3	3.6	0.04	7.7	0.10	17.0	3.2	11	< 5	< 10	13	< 5	< 10	30	0.07
P22	SEPT/97	16.8	6.19	558	273	5.0	0.2	404.2	13	10	211	32.9	n.d.	677	56.8	21.6	0.12	10.9	0.19	18.4	2.4	35	9	< 10	12	< 5	< 10	231	0.50
P23	SEPT/97	17.1	5.45	1138	281	2.5	8.6	922.0	15	3	587	10.1	n.d.	893	131.0	67.7	1.41	11.0	0.75	27.9	11.6	52	53	< 10	134	< 5	30	605	0.37
P24	SEPT/97	16.3	5.83	410	295	5.3	1.4	265.0	32	38	79	29.9	70	90	22.7	10.7	0.01	7.2	0.07	27.7	13.5	31	< 5	< 10	14	< 5	< 10	101	0.63
P25	SEPT/97	16.7	5.45	316	287	5.9	n.d.	216.6	10	14	102	14.9	70	138	21.2	9.3	0.03	10.8	0.10	18.4	4.5	33	< 5	< 10	12	< 5	< 10	91	0.49
P26	SEPT/97	17.0	4.39	1777	389	4.0	4.0	1495.8	18	10	963	n.d.	< 50	850	218.0	50.0	5.96	13.8	7.21	31.8	26.5	1200	81	28	651	14	153	750	0.56
P27	SEPT/97	18.1	4.03	2640	358	6.8	1.0	2629.6	14	4	1849	n.d.	< 50	1239	363.0	115.0	11.75	20.5	21.93	41.3	11.8	3500	49	113	1230	47	264	1379	1.13
CB1	SEPT/97	16.6	3.85	2810	18	n.d.	3.0	2916.4	13	n.d.	2045	n.d.	< 50	1641	298.0	163.0	27.90	44.7	50.88	34.5	11.0	4300	49100	297	1880	< 5	429	1414	7.28
BD	SEPT/97	18.1	7.85	2920	169	8.8	3.0	2931.8	13	n.d.	2007	84.7	n.d.	3446	606.0	133.0	5.88	2.8	1.16	37.5	11.5	2100	24	14	23	< 5	27	2059	1.71
R1	SEPT/97	16.5	7.12	679	3	n.d.	5.2	335.6	34	99	74	187.8	2525	858	25.8	9.8	0.66	7.2	0.09	58.1	10.3	9	771	< 10	14	< 5	< 10	105	0.10
R5	SEPT/97	20.0	7.53	2900	267	8.5	1.4	2865.4	14	n.d.	1892	75.9	n.d.	4333	552.0	119.0	4.16	2.6	1.05	36.6	9.7	3200	9	< 10	30	< 5	< 10	1867	0.85
R7	SEPT/97	15.9	7.17	810	-156	n.d.	8.0	392.4	51	7	83	219.5	3265	511	31.0	10.4	0.72	7.3	0.12	72.1	12.6	6	1270	< 10	29	< 5	< 10	120	n.a.
R8	SEPT/97	16.3	7.15	593	96	0.8	8.6	291.2	87	86	63	167.3	2500	294	51.2	8.5	0.54	7.4	0.08	51.2	8.6	6	602	< 10	28	< 5	< 10	163	0.20
R9	SEPT/97	17.7	5.22	2370	319	7.3	20.8	2248.0	15	8	1517	6.1	n.d.	1606	365.0	144.0	6.76	13.1	3.35	37.8	16.8	1900	10	35	693	< 5	141	1503	1.12
R13	SEPT/97	15.7	7.08	649	-8	0.3	5.0	297.0	50	62	56	192.9	2320	419	21.5	7.3	0.60	6.8	0.08	56.4	10.6	5	808	< 10	30	< 5	< 10	84	0.37
R21	SEPT/97	17.5	5.11	2000	314	7.6	9.8	1804.8	24	14	1313	3.1	n.d.	1062	284.0	103.0	4.46	11.7	2.40	43.0	15.5	200	21	20	346	< 5	93	1132	n.a.
R25	SEPT/97	15.6	7.04	722	-0.2	n.d.	0.6	353.8	55	6	109	176.2	2215	843	34.2	11.7	0.74	7.2	0.13	58.2	10.3	8	669	< 10	24	< 5	< 10	133	0.25

Ref - sampling site;**(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

Ground and surface water data in April 1998

Ref	Date	T	pH	EC	Eh	DO	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Si	Al	Na	K	U	Fe	Co	Zn	Cu	Ni	Hard.	Ra^{226}
		°C		*uS/cm*	*mV*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*(*)*	*Bq/l*
P4	APR/98	12.7	5.08	69	281	7.8	78.8	73.2	11	1	3	11.6	104	50	2.5	1.4	0.01	9.2	0.02	8.2	1.1	4	< 5	< 10	< 5	< 5	< 10	12	0.17
P5	APR/98	12.5	4.44	832	307	6.4	0.6	626.6	17	17	370	n.d.	< 50	344	86.3	31.0	2.10	12.7	4.56	19.6	13.0	470	23	24	313	17	56	343	0.59
P9	APR/98	12.9	4.94	641	300	6.1	0.2	468.0	11	21	261	4.3	< 50	336	63.4	32.0	0.20	10.2	0.29	24.6	5.7	32	< 5	< 10	35	< 5	< 10	290	0.36
P10	APR/98	11.8	5.73	107	265	4.7	5.2	87.4	13	n.d.	2	39.9	< 50	82	7.3	1.5	0.09	11.4	0.05	11.8	1.2	7	616	< 10	10	< 5	< 10	25	0.16
P11	APR/98	13.3	5.18	107	316	5.2	0.8	97.8	9	10	20	7.9	< 50	116	7.3	3.3	0.04	13.4	0.08	7.7	1.2	12	< 5	< 10	11	< 5	< 10	32	0.15
P12	APR/98	14.1	5.72	208	242	5.4	n.d.	128.8	16	12	47	17.1	79	94	13.7	4.2	0.01	10.3	0.04	17.9	2.6	14	< 5	< 10	42	< 5	< 10	51	0.28
P13	APR/98	12.7	5.66	248	288	5.5	n.d.	167.2	22	26	27	23.8	82	157	10.4	6.0	0.01	5.4	0.03	19.7	11.0	24	< 5	< 10	< 5	< 5	< 10	51	0.52
P15	APR/98	13.5	4.08	2350	339	5.8	1.0	2252.2	12	3	1421	n.d.	< 50	1257	339.0	140.0	8.70	17.8	15.60	35.3	9.4	2000	17	83	1110	50	210	1422	3.85
P17	APR/98	13.3	4.88	1864	275	6.3	0.4	1655.4	11	11	1064	3.1	n.d.	1323	233.0	115.0	6.80	18.6	3.95	40.8	7.8	1600	15	36	648	52	106	1054	2.97
P20	APR/98	13.7	5.09	300	294	6.1	1.8	211.2	16	21	86	5.5	< 50	215	23.8	10.3	0.13	5.9	0.25	16.6	8.7	14	< 5	< 10	28	< 5	< 10	102	0.50
P21	APR/98	14.8	5.18	35	302	8.5	0.2	114.6	22	32	2	5.5	< 50	82	5.0	3.9	0.06	7.4	0.12	18.6	4.1	10	< 5	< 10	13	< 5	< 10	28	0.75
P22	APR/98	13.8	6.13	378	256	5.9	0.2	278.4	15	18	105	42.7	n.d.	254	45.0	14.3	0.06	9.5	0.10	13.7	1.8	24	< 5	< 10	9	< 5	< 10	171	0.51
P23	APR/98	12.8	4.93	245	304	5.2	0.4	178.0	11	11	87	3.4	< 50	205	22.5	10.9	0.23	7.0	0.28	12.2	2.4	20	< 5	< 10	31	< 5	< 10	101	0.27
P24	APR/98	13.0	5.56	248	297	5.2	0.6	166.8	24	30	32	20.1	< 50	187	13.5	6.2	0.01	5.8	0.05	18.6	7.5	25	< 5	< 10	7	< 5	< 10	59	0.68
P25	APR/98	13.6	5.12	226	319	7.6	0.6	172.6	8	10	73	6.7	< 50	91	14.3	7.1	0.03	9.8	0.08	13.9	3.7	39	< 5	< 10	14	< 5	< 10	65	0.15
P26	APR/98	13.1	4.48	977	353	4.0	0.2	752.4	15	12	485	n.d.	< 50	538	103.0	42.5	2.96	11.2	4.18	21.6	18.4	239	25	< 10	429	< 5	80	432	0.57
P27	APR/98	13.2	4.28	1740	377	5.5	0.8	1555.2	11	2	1008	n.d.	< 50	953	220.0	90.0	5.30	13.2	6.07	28.2	7.0	680	15	34	744	13	134	919	0.73
CB1	APR/98	14.9	3.95	1779	348	0.0	0.6	1653.0	13	n.d.	1042	n.d.	n.d.	1256	195.5	95.0	14.82	34.0	21.64	25.7	8.1	2600	21688	156	1020	80	215	879	8.62
CB2	APR/98	11.9	3.75	690	335	10.7	1.8	571.2	10	n.d.	339	n.d.	n.d.	360	54.0	35.0	3.86	23.4	5.19	12.5	4.1	2500	406	142	1678	118	302	279	1.82
L0	APR/98	14.0	3.72	714	418	9.5	3.6	601.6	9	n.d.	355	n.d.	n.d.	534	63.0	32.5	4.30	21.7	8.12	11.5	3.8	1200	960	69	509	65	101	291	5.86
BD	APR/98	12.9	8.85	1863	144	9.9	11.8	1693.2	15	n.d.	1143	36.0	n.d.	3014	375.0	40.0	1.26	5.9	0.88	24.8	7.8	222	< 5	< 10	< 5	< 5	12	1100	0.21
R0	APR/98	11.7	6.40	82	214	10.5	7.2	68.4	10	2	18	12.2	< 50	136	4.6	2.4	0.01	6.7	0.03	8.7	0.7	13	44	< 10	< 5	< 5	< 10	21	0.19
R1	APR/98	12.6	6.37	127	294	9.6	14.6	417.4	14	6	247	19.5	< 50	419	99.8	9.6	0.27	5.9	0.09	15.6	3.1	8	30	< 10	79	< 5	22	288	0.23
R5	APR/98	12.0	5.88	1101	227	10.2	9.0	904.2	14	4	531	6.1	n.d.	1153	177.0	25.0	1.86	8.7	0.84	18.3	5.3	205	479	< 10	124	< 5	33	544	0.46
R7	APR/98	13.3	6.45	145	288	9.2	7.8	514.8	14	5	291	21.9	< 50	479	118.0	9.6	0.25	5.9	0.09	16.0	3.1	7	29	< 10	66	< 5	18	334	0.47
R8	APR/98	13.1	6.43	400	272	9.9	3.4	269.4	13	9	142	18.9	< 50	371	55.2	7.8	0.24	6.0	0.06	14.0	2.8	6	45	< 10	73	< 5	19	170	0.40
R9	APR/98	13.1	4.97	1144	311	8.6	1.0	927.4	16	6	548	3.4	n.d.	664	146.5	47.0	2.20	9.8	2.24	23.2	10.3	228	15	< 10	327	< 5	60	559	0.54
R13	APR/98	13.6	6.55	157	214	9.9	3.8	107.4	13	6	32	23.2	108	244	9.7	3.3	0.14	6.0	0.06	12.8	2.4	5	93	< 10	50	< 5	13	38	0.17
R21	APR/98	13.9	5.28	854	286	9.1	2.8	768.4	14	7	459	3.7	n.d.	507	116.5	45.0	1.57	9.2	1.31	22.1	8.4	140	50	< 10	231	< 5	42	476	0.43
R25	APR/98	13.3	6.34	201	204	9.7	5.2	136.0	13	6	41	21.9	92	295	15.6	5.9	0.19	6.1	0.08	14.3	2.7	7	85	< 10	57	< 5	12	63	0.14

Ref - sampling site; **(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

Ground and surface water data in 1999-2000

Ref	Date	T	pH	EC	Eh	TSS	TDS	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	P	F	Ca	Mg	Mn	Al	Na	K	Ba	B	U	Fe	Co	Zn	Cu	Ni	Hard.
		° C		*uS/cm*	*mV*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*ug/l*	*ug/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	*mg/l*	mg/l	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*ug/l*	*(*)*
CB1	JULY/99	20.2	5.59	2830	336	33.0	2956.6	11	1	1938	n.d.	<50	1309	486.0	131.0	17.20	43.40	33.6	9.6	13	<10	3200	18700	235	1630	136	330	1751
P5	SEPT/99	18.1	4.34	1485	333	1.6	1253.0	38	33	781	n.d.	<50	1390	220.0	61.7	4.06	12.10	32.6	14.7	20	45	1100	24	58	624	32	119	803
P9	SEPT/99	19.5	4.51	1524	296	2.8	1291.8	10	13	870	n.d.	71	567	203.0	98.9	1.86	2.49	43.5	7.6	32	14	306	<10	<10	282	13	44	913
P11	SEPT/99	18.4	4.98	1265	294	8.0	1053.6	14	12	612	3.7	<50	1125	149.0	67.7	1.30	1.56	33.1	6.5	37	16	166	13	<10	252	16	39	650
P15	SEPT/99	20.0	4.03	2350	323	1.2	2336.6	3	7	1461	n.d.	55	1378	353.0	152.0	8.52	16.80	42.4	10.6	22	<10	2200	24	82	1030	63	191	1506
P17	SEPT/99	20.0	4.57	2270	307	2.8	2235.2	7	12	1445	n.d.	<50	799	333.0	149.0	7.87	8.45	41.4	10.0	27	<10	2300	28	43	841	70	137	1444
P20	SEPT/99	20.5	5.64	1034	250	42.8	788.0	29	27	451	18.7	<50	360	114.0	51.8	0.62	0.31	34.1	22.2	50	61	33	<10	<10	72	11	15	497
P27	SEPT/99	19.3	4.01	2420	358	1.8	2408.8	7	13	1629	n.d.	<50	1390	365.0	151.0	8.95	18.70	39.7	11.4	23	<10	2400	95	87	1100	59	210	1532
CB1	SEPT/99	20.1	3.66	2750	330	5.0	2849.0	10	1	1811	n.d.	<50	3561	445.0	133.0	16.70	43.00	34.3	9.4	11	<10	2600	12900	232	1700	117	323	1657
R9	SEPT/99	18.2	4.37	2020	314	0.6	1861.4	18	15	1180	n.d.	55	1085	285.0	123.0	5.83	8.18	37.9	19.1	35	28	883	20	35	883	14	161	1217
CB1	NOV/99	17.4	3.35	3000	438	2.0	2927.4	21	1	1807	n.d.	<50	3903									2700						
P5	SEPT/00	17.1	4.83	2100	271					1664	4.3																	
P9	SEPT/00	17.0	4.63	1364	227					906	2.6																	
P11	SEPT/00	17.4	4.59	1336	245					770	n.d.																	
P15	SEPT/00	16.4	4.06	2260	294					1662	n.d.																	
P17	SEPT/00	16.1	4.75	1873	278					1437	1.7																	
P20	SEPT/00	17.6	5.17	758	283					369	13.7																	
P26	SEPT/00	14.5	4.37	1857	329					1268	n.d.																	
P27	SEPT/00	16.2	4.05	2230	367					1558	n.d.																	
CB1	SEPT/00	16.0	3.94	2180	229						n.d.																	
R1	SEPT/00	15.1	7.05	703	164						258.4																	
R9	SEPT/00	16.5	4.35	1433	290						n.d.																	
R13	SEPT/00	17.1	7.07	709	138						272.9																	
R25	SEPT/00	16.4	6.92	698	193						268.7																	

Ref - sampling site;**(*)** express as mg $CaCO_3$/l; **n.a.** - not analysed; **n.d**. - not detected.

▨ - Values that exceed the Maximum Recommended Portuguese Quality Pattern for irrigation and surface water

TREATMENT OF LIQUID EFFLUENT FROM URANIUM ENTERPRISES IN UKRAINE

A. Molchanov, Y. Soroka, N. Isayeva

Ukrainian Ministry of Fuel and Energy,
Ukrainian Research and Design Institute for Industrial Technology,
Zhovty Vody, Ukraine

Abstract. Ukraine's uranium facilities are located in the central part of the country, in urbanized districts with a high population density, fertile black soils and intensively developed agriculture. Nearly 50 years of uranium mining and processing at these facilities have caused radioactive contamination of the environment. The most widespread source of contamination of the uranium sites has been liquid effluents. This paper is devoted to investigations of the magnitude of such contamination and measures to be taken for its mitigation. Proposed methods for treatment of liquid effluent, including treatment by natural mineral sorbents, treatment by natural biological systems, and treatment of aquifers by intercepting polluted water are described in this paper.

1. Introduction

The nuclear industry of Ukraine is represented by two large enterprises: Vostochny Mining and Milling Company (VostGOK) and Pridniprovsky Chemical Plant (PChZ). The headquarters of VostGOK are located in town of Zhovty Vody. PChZ is located in Dniprodzerzhinsk city in the Dnipropetrovsk region.

At present, VostGOK is mining uranium ores by underground methods in the Smolinsky and Ingulsky mines. Processing of the uranium ores to produce U_3O_8 is carried out at Zhovty Vody's Hydrometallurgical Plant. Uranium ore processing was also carried out at PChZ between 1947 and 1991. VostGOK also produced uranium using *in situ leaching* (ISL) technology until 1993.

Therefore, the main sources of contamination by liquid effluents at Ukrainian uranium enterprises include:

- liquid effluents produced by mills;
- mine waters from operational mines;
- residual solutions from former ISL sites.

2. Surface and groundwater contamination at tailing ponds sites

Two tailings sites (tailings "D" and tailings "Sch") have been chosen for research. These sites are characterized by two different situations: tailings at an operating mill ("Sch") and tailings at an inactive mill ("D"). The "Sch" tailings belong to VostGOK and are situated near the town of Zhovty Vody. The "D" tailings belong to PChZ and are situated in Dniprodzerzhinsk city.

2.1. Methods for reduction of surface and groundwater contamination at the "Sch" tailings site

2.1.1. General information

Wastes from the Zhovty Vody Hydrometallurgical Plant are stored in the "Sch" tailings impoundment, which is located 1.5 km south of the town within "Scherbakovskaya" gully. The "Sch" tailings pond covers a total area of 250 ha and is the largest uranium tailings impoundment in operation in Europe. The "Sch" tailings pond consist of two parts, the older of which was used from 1959 to 1980. Since 1980, it is used as a reserve pond. The newer section of the tailings pond has been in operation since 1979. Uranium wastes are discharged as subaqueous hydroflows. The tailings total activity is about 1.8 PBq.

The thickness of the tailings varies from zero to 19 m in the older section of tailings impoundment and from zero to 12 m in the newer section. Approximately 40 million tonnes of tailings have been discharged into the tailings impoundment. The permeability of the tailings deposits is inhomogeneous and anisotropic. Infiltration coefficients vary from $9 \cdot 10^{-2}$ to $1.1 \cdot 10^{-2}$ m/day (vertical) and from $7.5 \cdot 10^{-1}$ to $0.3 \cdot 10^{-1}$ m/day (horizontal).

Average radionuclide content in tailings material is as follows:

U-238 – 0.007% — 0.02%;
Ra-226 – 4140 — 8790 Bq/kg;
Pb-210 – 8628 — 14300 Bq/kg;
Po-210 – 7955 — 11936 Bq/kg;
K-40 – 440 — 1036 Bq/kg.
Rn-222 flux from dry beach surface is within the range 0.5 — 2.0 Bq/$m^2 \cdot s$.

The chemical and radiochemical composition of the tailings impoundment water are shown in Table I.

Table I. Chemical and radiochemical composition of tailings waters.

Component	**Concentration, mg/l**		
	Section		**Permissible concentration**
	New	**Old**	
Ca^{2+}	470	222	--
Mg^{2+}	1310	139	--
Na^{+}	580	230	--
K^{+}	36	5	--
HCO_3^{-}	--	181	--
Cl^{-}	176	123	350
SO_4^{-2}	6560	1291	500
NO_3^{-}	446	1.4	45
TDS	9820	2474	1000
Concentration, Bq/l			
U-238	2.2	--	10(2)[1]
Ra-226	8.1	--	1(2)[1]
Pb-210	0.8	--	0.5(2.8)[1]
Po-210	0.5	--	0.2(14.4)[1]

The tailings impoundment is underlain in ascending order by granite and gneiss with varying degrees of fracturing, eluvial weathering products of the granite and gneiss, Neogene clays and an early quaternary complex of loess and loams. Liners were laid during construction and operation of the tailings pond.

The tailings pond site hydrogeology has been altered by artificial factors. There were two aquifers underlying the tailings pond before its construction: the shallower aquifer was in Paleogene and Neogene sands, the deeper one is in the fracture zone of the granite and gneiss and their weathering surface.

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[1] In brackets - permissible concentration according to old USSR standard.

During the tailings pond operation an artificial aquifer was formed that is supplied with tailings water and discharges into the Zhovta River (Fig. 1). This artificial aquifer has a convex upward surface with the apex at the tailings pond surface. TDS of this aquifer's water near the tailings pond reach 5.8-9.8 g/l; a zone with TDS of more than 5 g/l extends towards the east and south-east of the impoundment, i.e. in the direction of greater water discharge. Slightly salty water (1-3 g/l) has been detected in the north-north-western (NNW), western and south-western (W and SW) parts of the site 0.7-1.5 km distance from the tailings pond.

Tailings impact boundaries were determined taking into account all available factors that have an influence on hydrochemical conditions, in particular considering the contents of sulphate-ions and nitrate-ions in groundwaters. The boundary of contamination extends 0.7 km eastwards reaching the Zhovta River. The southern boundary of contamination extends to a distance of 2.5 km. The western boundary is 1.6 km from the older section of the pond and 0.8 km from the newer section.

The data in Table I show that concentrations of the main long-lived natural radionuclides do not exceed "old" USSR standard values, except for Radium-226. It is important to note that sulphate, nitrate and TDS also exceed permissible concentrations.

The map and profile of groundwater contamination (Figs. 1 and 2) show sulphate and nitrate plumes drawn as isolines for sulphate concentrations (6000, 3000, and 500 g/l) and for nitrate concentrations of 200 and 45 mg/l. Figures 1 and 2 show that the greatest concentration of tailings seepage water moves in the aquifer flowing in crystalline rocks towards the south and south-east.

A forecast for changes in hydrochemical conditions in the area surrounding the "Sch" tailings pond was performed with the help of "Groundwater Flow Simulation" software (Russian-Swedish Joint Venture GEOSOFT- EASTLINK "GWG" Moscow). This forecast shows that significant changes should be expected in 10-15 years. During this period the boundary with a sulphate content of 3000 mg/l will have moved by 600-800 m and will be located 700-900 m away from the Zhovta River. Sulphate concentration values in the aquifer when approaching the river will exceed the accepted standard (500 mg/l) in 5-7 years and reach 520-580 mg/l. Table II gives the results of the forecast performed for the next 3, 6 and 15 years (2001, 2004 and 2013, respectively).

Two changes in current operations were considered in order to reduce groundwater contamination at the tailings pond site and to protect the Zhovta River. The first recommendation is to decrease the TDS of the tailings water at the expense of lower tailings neutralization at the processing plant. The second recommendation is to intercept the groundwater plume in the south-eastern direction by a system of drainage wells that return the contaminated water to the plant. The first approach will allow time to better forecast sulphate migration as well as to decrease contamination of groundwaters in the future. Applying the second approach will prevent contamination of the Zhovta River. There is evidence to suggest that it would be reasonable to apply both approaches either consecutively or simultaneously, depending on the river contamination level. The first approach was investigated in the laboratory, while the second approach was evaluated by computer modelling methods.

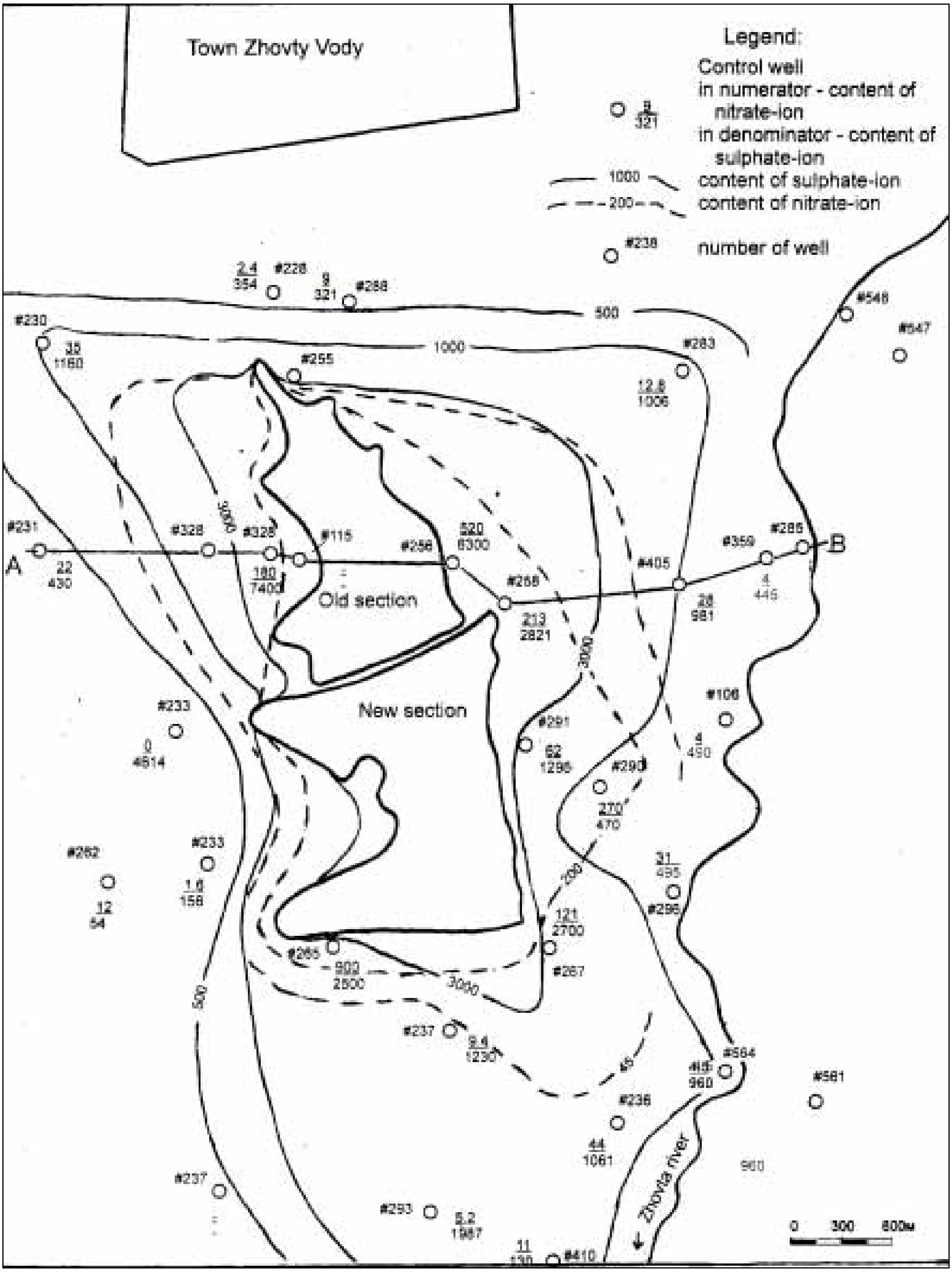


FIG. 1. Content of sulphate- and nitrate-ion in groundwater near "Sch" tailing ponds, mg/l (1997).

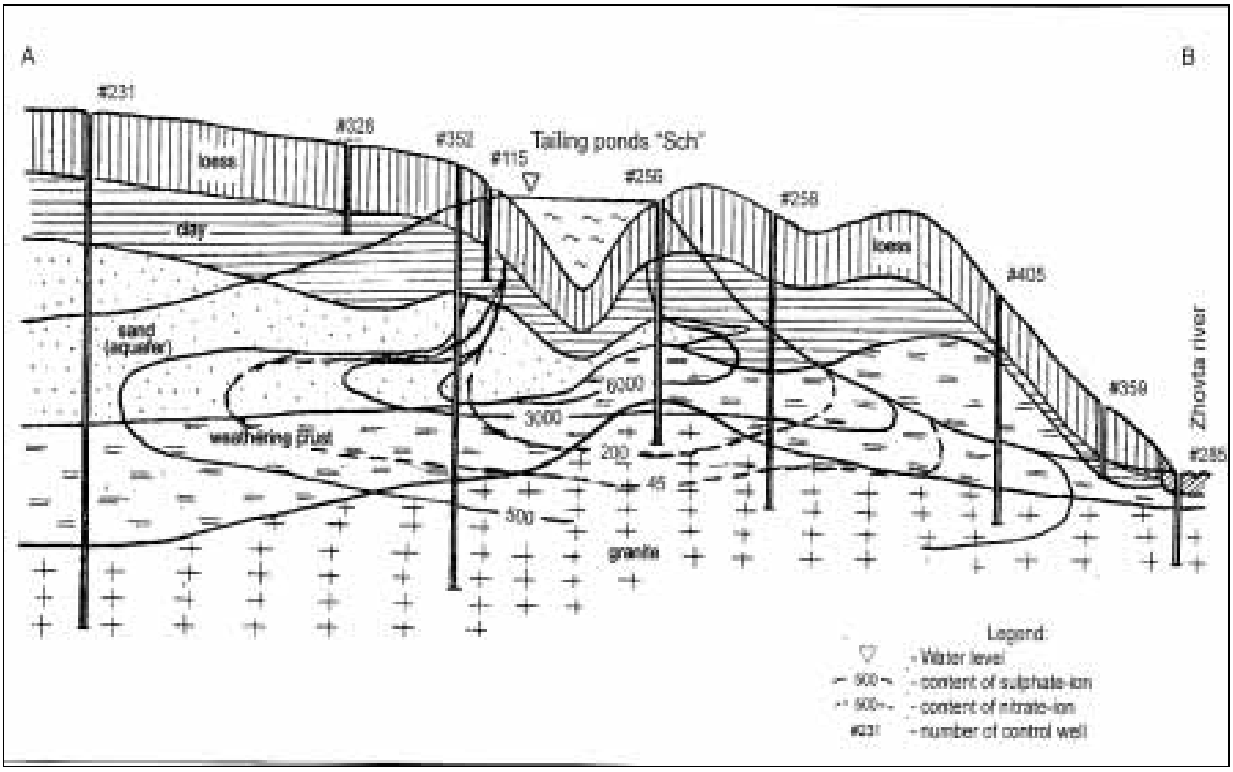


FIG. 2. Arched sketch hydrogeological profile.

Table II. Prognosis of sulphate concentrations (g/l) in groundwaters.

Distance from tailings pond, m	Years		
	2001	2004	2013
0	6.58	6.58	6.58
50	5.45	5.53	5.65
130	3.51	3.8	4.36
210	3.36	3.65	4.33
300	3.38	3.76	4.45
470	3.10	3.41	4.03
480	3.07	3.37	3.98
560	2.86	3.10	3.63
980	2.44	2.54	2.78
1410	2.23	2.32	2.5
1480	2.23	2.32	2.5
1690	2.03	2.15	2.33
2040	1.55	1.67	1.86
2210	1.22	1.36	1.59
2410	0.83	0.98	1.22
2620	0.59	0.70	0.91
2630	0.58	0.69	0.89

2.1.2. Laboratory research results

The data presented in Table III indicate that during pulp neutralization at a pH=7 almost all magnesium and sulphate-ions remain in solution. These are the components that make up most of the TDS of tailings waters. During experiments, samples of tailings water were treated with lime milk to a pH=10.5. Results of the experiments are shown in Table III.

Table III. Dependence of ionic concentrations on tailings water pH.

Component	Concentration, mg/l		
	pH = 7.4	**pH = 9.0**	**pH = 10.5**
Ca	470	450	450
Mg	1310	689	41
Na	580	510	510
K	36	30	25
Cl	176	170	170
SO_4	6560	2150	504
NO_3	446	380	317
TDS	9820	4300	2020
U	0.18	---	0.09
	Concentration, Bq/l		
Ra	8.1	---	6.2

This table shows that strong tailings treatment will considerably decrease the total TDS in both the tailings and infiltration waters. Some decrease of radionuclide concentration was observed, which is probably caused by $Mg(OH)_2$ co-precipitation and adsorption processes.

2.1.3. Modelling of contamination plume interception

One of the methods for decreasing contaminated groundwater volume was to intercept groundwater flow from the tailings pond towards the Zhovta River. This method envisages the construction of a linear drainage well system at a distance of 1 km from the tailings pond and 2 km from Zhovta River. It is assumed that pumping water from drainage wells will reduce the volume of contaminated water approximately by half and that the boundary of the sulphate plume will be moved away from Zhovta River.

This assumption was checked by computer modelling of hydrochemical and hydrogeological processes using the GEOWS software. The following tasks were carried out:

- Elaboration of undergroundwater flow conceptual model,
- Conceptual model allowing for numerical modelling,
- Model verification using routine observational data,
- Elaboration of groundwater contamination analytical model,
- Drainage well system parameter evaluation for localizing the contamination halo.

Conceptual hydrogeological model

The “Sch” tailings pond district covers the area between the Zhovta River and the Zelena River (Fig. 3). Its hydrology is divided into four layers:

- Surface water,
- Aeration zone,
- The first (from the surface) aquifer (calculated),
- Water confining layer.

The aquifer is assumed to be partly confined and partly free flow. Groundwater flow is directed from the tailings pond towards the surface water courses, which are natural boundary conditions. The thickness of the saturated zone varies within the area because it is influenced by the impact of infiltrating effluents: maximum thickness is under the pond; minimum thickness is near the pond’s boundary; the average thickness is about 30 meters. The tailings pond is approximated by a constant pressure contour.

Calculation of drainage well system working parameters

Input data included water intake parameters from the drainage well system:

- pumped water volume;
- two periods for pumping time were considered: 10 years and 20 years from start of the drainage system;
- wells should not be allowed to dry up during their operation time; and
- the contamination plume boundary should be moved closer to drainage zone.

The optimal parameters for the drainage system operation, according to the model are the following:

- total drainage rate 250 000 m^3/year;
- number of boreholes in the drainage system – 20 units;
- water level decrease in the drainage centre within 20 years – 20 m.

Conclusions

According to the modelling results (Fig. 3) it is evident that the simulated drainage well system would successfully reduce the contaminated groundwater volume threatening the Zhovta River.

2.2. Evaluation of "D" tailings influence on surface water and population

Tailings pond "D" is located along the right beach of the Dnipro River within the first flood-plain terrace (Fig. 4). Tailings pond "D" was utilized from 1954 to 1968. Wastes from treatment of uranium ores from Ukraine, Germany, Hungary, Czechoslovakia, Romania and Bulgaria were deposited in this tailings pond.

The area of the tailings is approximately 73 ha, the amount of wastes is about 22 million tonnes, and the total activity is about 1460 TBq. The tailings pile is covered with a 1 to 16 m-thick phosphogypsum layer. Phosphogypsum, which is itself a waste of the chemical industry, has a high moisture absorbing capability.

Within the tailings body an artificial aquifer was formed which is hydraulically connected to the natural aquifer in the alluvial sediments of the flood-plain (basin). There is no low-permeability rock layer under the tailings. Groundwater within the tailings area exceeds allowable concentrations of TDS, iron, ammonia, nitrate, and silicon.

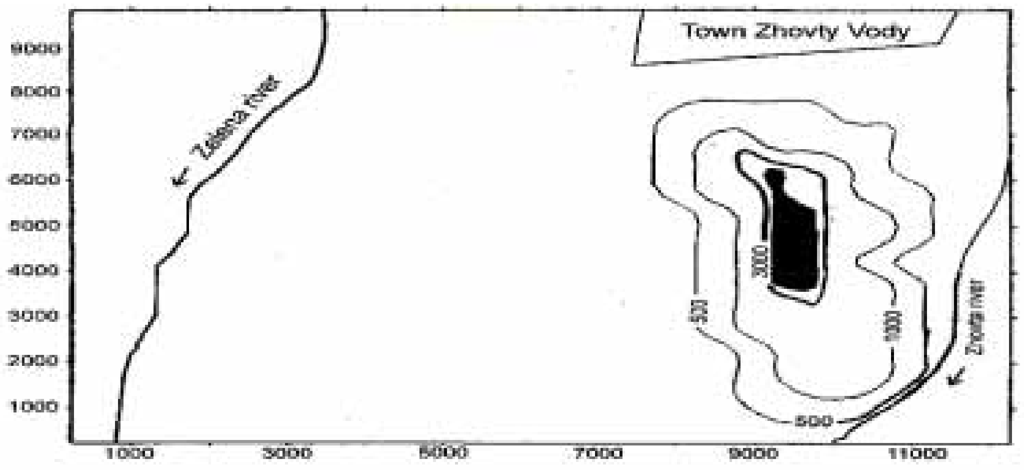
Radioactive contamination of both surface and groundwaters is still being studied. It is assumed that the plume of contaminated groundwater moves toward the Dnipro and Konoplianka Rivers.

For determining the influence of the "D" tailings pond on surface water and the nearby population, water samples from the Dnipro River and Konoplianka River have been sampled and analysed for natural radionuclide content. Figure 4 shows the water sampling sites. Results of analysis for the uranium content at these sites sampled in 2000 are presented in Table IV. Results of similar analyses for previous years are shown on Figure 5.

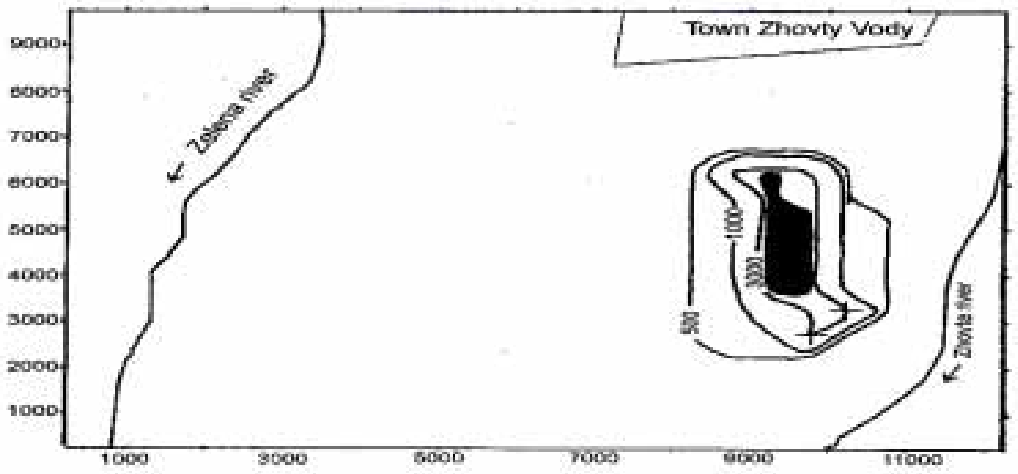
Table IV. Uranium concentrations in water of rivers Dnipro and Konoplianka, μg/l

Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8
2	1.6	4	16	6	8	18	22

Results of the uranium analyses show that there is a clear impact of "D" tailings effluents on the Dnipro and Konoplianka Rivers because near the tailings uranium concentrations in the water increase 2.5 - 8 times. More detailed analysis of water for natural radionuclides (NR) was performed for estimating the dose to the population. On the basis of these preliminary results and taking into account conservative assumptions about use of the river as a source for drinking water, initial estimates of individual and collective doses for reference population groups were calculated. Results of this calculation are shown in Tables V, VI and VII.



A - todays situation.



B - situation after 20 years of pumping.

FIG. 3. Schematic maps of groundwater contamination with sulphate near the tailings pond "Sch", (modelling results).

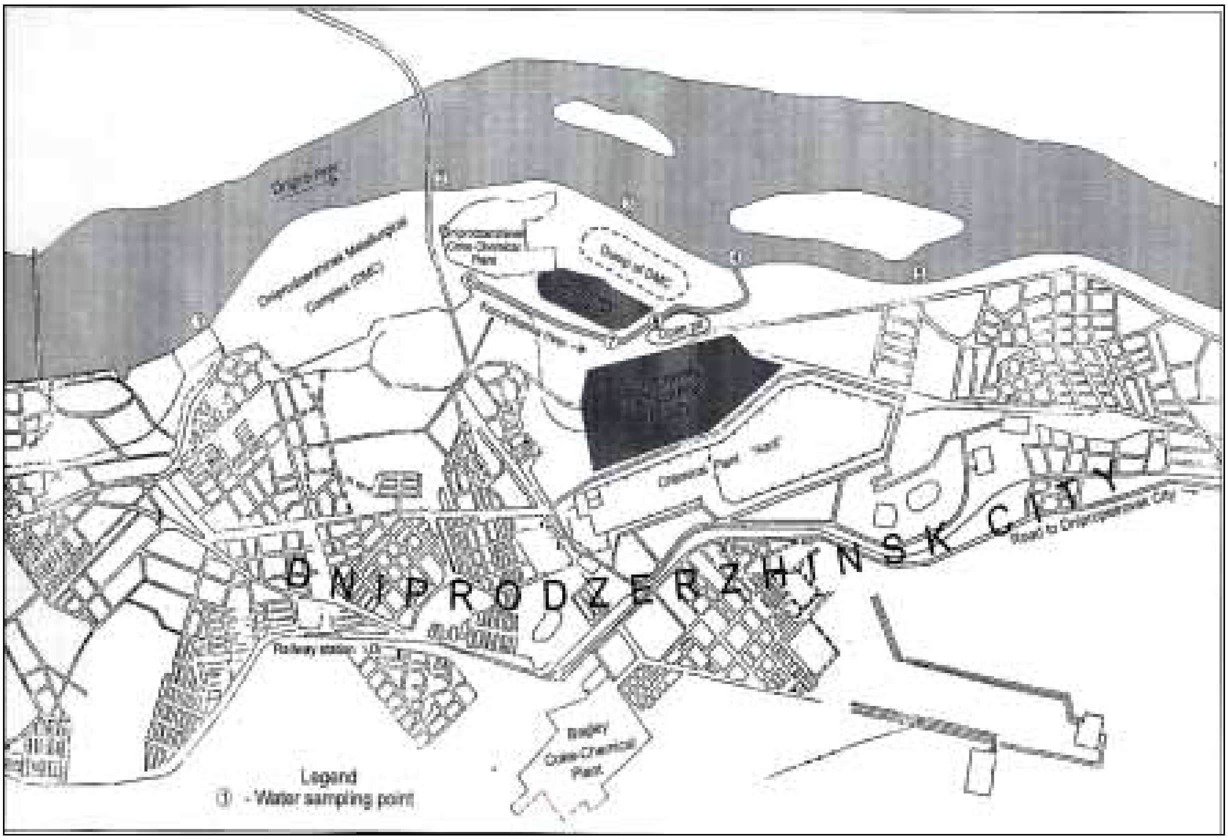


FIG. 4. Location of the PChZ industrial site.

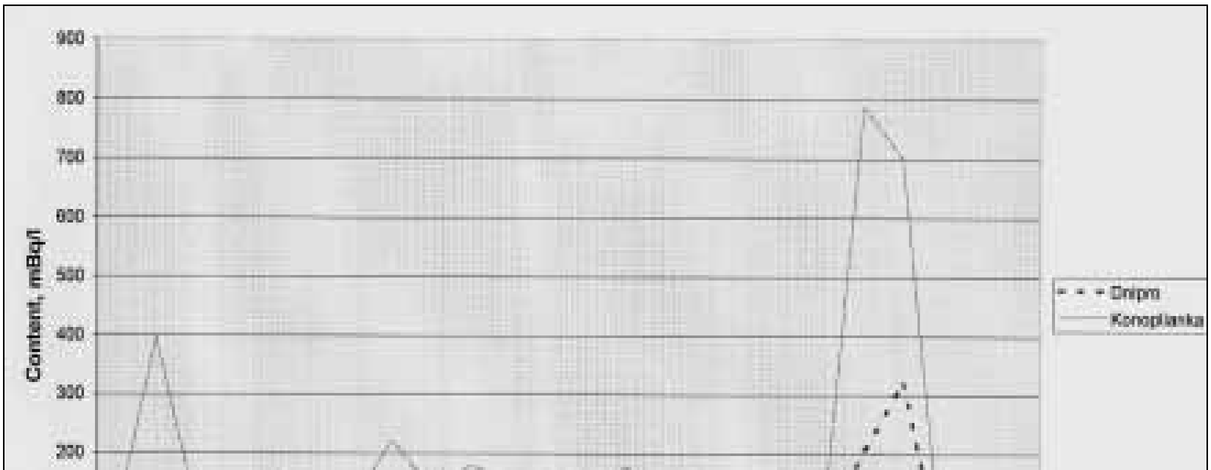


FIG. 5. Uranium content in Dnipro and Konoplianka river's water.

Table V. Initial data for calculation of dose on population via water pathway.

Radionuclides	Concentration of NR in surface water, mBq/l	
	Background	Dnipro river
^{238}U	15	146
^{234}U	15	146
^{230}Th	2	13
^{226}Ra	15	120
^{210}Pb	4	25
^{210}Po	1	8
^{235}U	0.8	7.5
^{231}Pa	0.8	7.5
^{227}Ra	0.8	7.5
^{232}Th	1.5	15
^{228}Ra	15	120
^{228}Th	1.5	15

Table VI. Individual effective doses on referent groups of population via water pathway.

Referent groups of population	Doses, mSv
3 month	1.0
1 year	0.237
5 year	0.205
10 year	0.298
15 year	0.523
Adult	0.125

Table VII. Collective effective doses on population of Dniprodzerzhinsk town via water pathway.

Referent groups of population	Volume of groups, ×1000 people	Doses, man•Sv/year
3 month	1.5	1.5
1 year	1.6	0.379
5 year	11.2	2.296
10 year	17.3	5.155
15 year	22.4	11.715
Adult	222.0	27.75
Total	276	48.795

The calculated values of individual doses vary from 0.125 mSv/year for adults up to 1.0 mSv/year for infants. The collective effective dose for the population is 48.8 man•Sv/year. Though preliminary, the results show the seriousness of the situation at the "D" tailings site and the necessity to take urgent measures to protect the nearby population.

3. Mine water treatment

Problems connected with mine water treatment in the uranium industry of Ukraine mainly concern two uranium mines: Ingulskaya and Smolino, which are located in the Kirovograd region.

Both mines currently use standard systems for mine water treatment (Fig. 6). After treatment, the mine waters are discharged into the surface water system. The effluent volume is:

- 2.4 million m^3/year at Ingulskaya mine,
- 2.8 million m^3/year at Smolino mine.

Until recently, mine water treatment at Smolino was only concerned with decreasing TDS of waters that are discharged into the surface water system. At the Ingulskaya mine (TDS =2-4 g/l) the mine water treatment system ensured the treatment for radionuclides, but did not decrease the TDS.

Currently the problem of mine water treatment has increased, because of the new standards for radiation safety approved in 1997 (HPSY-97) in the Ukraine. New safety standards impose stricter requirements on discharged water quality as well as considerably reduced maximum allowable concentrations of natural radionuclides in the water. In this connection, in the framework of the present project, we have begun researching ways of reducing radionuclides in mine water.

The research has been carried out in two directions. The first approach was to study parameters of passive biological treatment by a natural aquatic system. The other approach was to study mine water treatment with natural mineral sorbents.

3.1. Mine waters treatment by natural mineral sorbents

The purpose of the research was to determine opportunities for using local natural mineral sorbents for further lowering radionuclide content of mine water. One of the main conditions of this research was availability of sorbents near the active mine sites. As part of the research Ingulskaya mine water samples were analysed in laboratory experiments. Table VIII shows the water chemistry.

Table VIII. Chemical composition of Ingulskaya mine water

pH	Component concentration								
	Mg/l								Bq/l
	Na^++K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	TDS	U-238	Ra-226
7.4	350	251	52	360	659	278	1.8	0.5	1.5

Different kinds of clays of the Kirovograd region have been used as natural mineral sorbents. Dried and milled clays were added to mine water samples and mixed for 30 minutes. After sediments had settled, the water was decanted and the radionuclide content was determined.

One of the experiments used clay together with lime and polyacrylamide for better sedimentation and treatment of the solution. Measurement results are shown in Table IX.

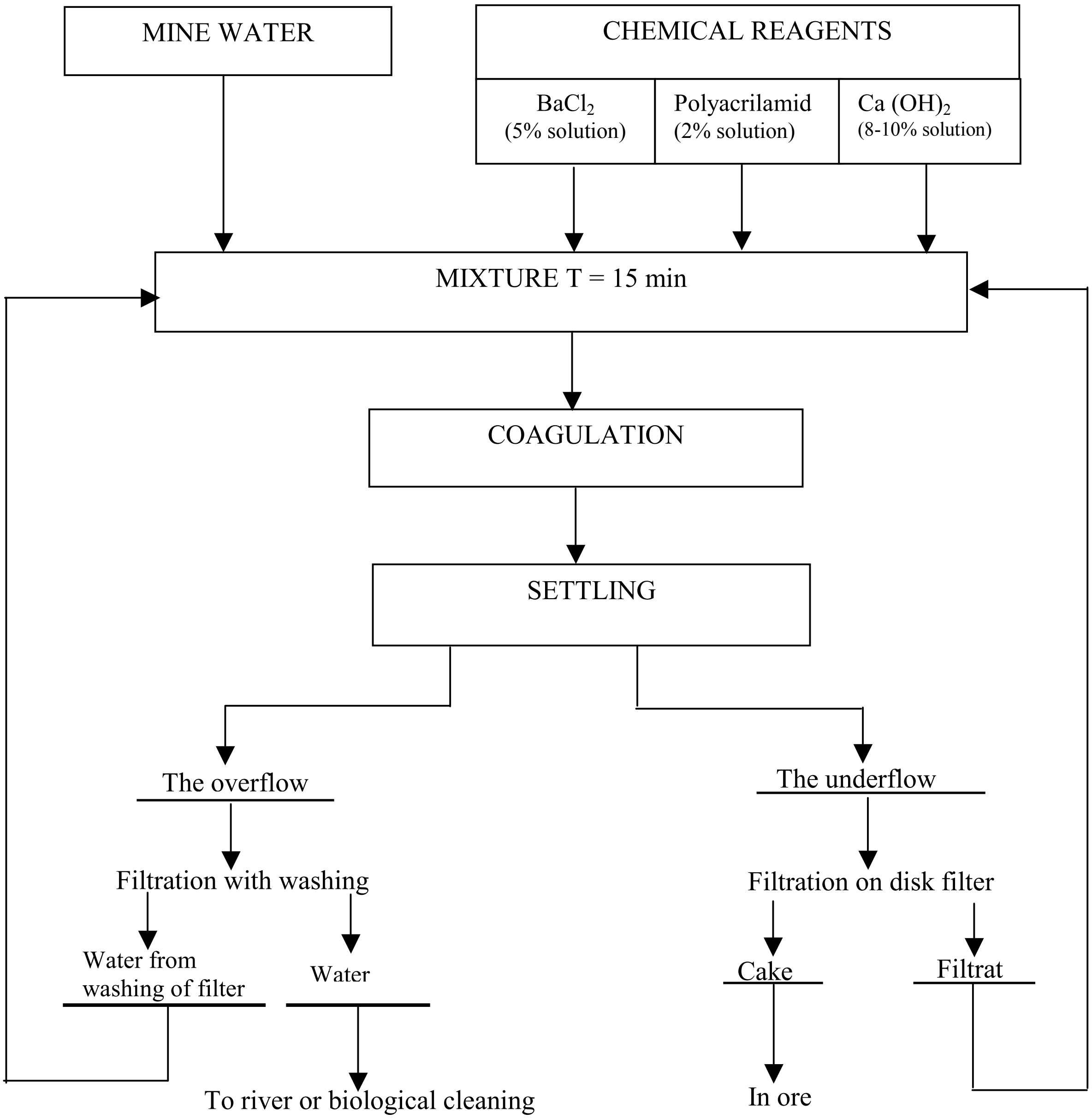


FIG. 6. Technological scheme of mine water treatment.

Table IX. Efficiency of mine waters treatment for radionuclides by natural mineral sorbents

Sorbent type	Radionuclides concentrations in mine water, Bq/l							
	Before treatment				After treatment			
	U-238	Ra-226	Pb-210	Po-210	U-238	Ra-226	Pb-210	Po-210
Montmorillonite clay	6.2	1.5	0.8	0.15	3.4	0.36	0.17	0.041
Kaolinite clay	6.2	1.5	0.8	0.15	4.3	0.62	0.29	0.065
Loam	7.4	1.4	0.68	0.13	5.2	0.8	0.37	0.078
Montmorillonite clay+$Ca(OH)_2$+ polyacrilamide	7.4	1.4	0.68	0.13	0.6	0.09	0.13	0.028

The data in Table IX show that the highest treatment efficiency, especially for Ra-226, is obtained when using montmorillonite, but considerable time is required for sedimentation of fine suspensions. Therefore, applying this clay together with both lime milk for improving treatment for U-238 and polyacrilamide for accelerating the flocculating process provided the best results for treatment of mine water. For this mixture, the efficiency for both U-238 and Ra-226 is around 92%.

The results obtained during the research suggest that natural sorbents may be successfully used in mine water treatment systems and moreover they could replace such reagents as barium chloride.

3.2. Study of parameters for passive biological treatment of mine water

The Kurnikov stream, into which Smolino mine water is discharged, was selected for this research (Fig. 7). The stream bed is divided by dams into ponds with cultivated marsh environments along the entire length of the stream bed (~2 km) up to where it flows into the Kilten River. At present, due to a shortage of stream water, the aquatic system is being supplemented with Smolino mine effluent. The total pond area is around 165 000 m^3 with one metre average depth. Mine water was discharged into pond I from 1974 to 1985, during which mine water treatment was not being carried out. Since 1985, after the mine water treatment facility was built, the water was discharged from the left streambed (Fig. 7).

Samples of mine water, as well as silt and reeds, were collected at points indicated in Figure 7. Both Uranium-238 and Radium-226 content in the samples were measured by gamma-spectrometry and radiochemical analysis. Measurement results, which are shown in Table X, show the following:

- The radionuclide concentrations decrease by a factor of 12 in mine waters due to passive biological treatment during the summer;
- Radionuclides mainly accumulated in the silt;
- Vegetation accumulated more Radium-226 (in terms of activity) than Uranium-238;
- Reed roots serve probably as physiological barriers for high uranium contents;
- Cumulative ratios for the "reed and silt" system are: for U-238, 0.027- 0.088, for Ra-226, 0.057 – 0.158;
- Half of the area of the total system has been the subject of study of reduction of radionuclides in mine effluents.

Measurements of the radionuclide content in the water of Kurnikov stream during the winter season have shown that concentration is reduced by a factor of 10 by passive biological treatment. Though less than the summer time value (12 times), the minimal seasonal difference shows the subordinate role of vegetation in the process of water treatment by passive biological treatment.

The sorption mechanisms for both uranium and radium conditioning forms in Kurnikov stream silt were studied. The correlation between water-soluble, exchanged, acid-soluble and firmly bound forms of radionuclides have been studied. Sequential extractions from dry samples were performed using distilled water, CH_3COONH_4 (1M), HCl (1M), and H_2O_2. The ratio of solid to liquid phase was 1:5, the interacting time of leached silt samples with the solution was 1 hour. The solutions obtained were analysed for both uranium and radium concentrations.

Table X. Radionuclide distributions in the system of passive biological treatment of Smolino mine waters.

# of point	Sampling place	Vegetation (reed)				Silt		Water	
		U-238, Bq/kg		Ra-226, Bq/kg		U-238, Bq/kg	Ra-226, Bq/kg	U-238, mg/l	Ra-226, Bq/kg
		Roots	Stems	Roots	Stems				
1.	Discharging mine waters after treatment into relief	1220	252	859	840	15130	14770	1.38	0.515
2.	Pond I, former effluent of mine N1 to 1985	780	189	1658	629	17700	16100	0.97	0.312
3.	Pond II, beginning	844	237	1873	754	16570	18324	0.82	0.23
4.	Pond II, end	356	340	161	538	4000	2207	0.69	0.112
5.	Pond III, control point	61	32	109	67	1245	910	0.49	0.087
6.	Pond before discharging into Kilten-river	---	---	---	---	272	353	0.11	0.042
7.	Kurnikov-stream above discharging point (background level)	48	16	66	23	72	44	0.059	0.024
8.	Kilten-river above point of the stream mouth (background level)	---	---	---	---	---	---	0.008	0.029

Results of these experiments show that the main forms of Ra-226 in the silt are the exchangeable and the acid-soluble form (80-94%). For U-238 the main forms are bound to organic matter and to oxides of both iron and aluminium (65-90%). Changes in water chemistry along the stream indicate some decrease of contamination level (Table XI).

Table XI. Chemical composition of Smolino site waters

	Water type	pH	Components, mg/l						
			Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	NO_2	TDS
1.	Discharge Smolino mine waters into relief (point 1)	8.2	84.4	38.3	65.0	251.6	6.5	3.5	780
2.	Kurnikov stream water in control (point 5)	7.3	76.6	42.1	56.6	158.6	2.7	0.2	685
3.	Kilten River water, 500 m above the stream mouth	7.1	43.5	40	53.5	45.9	0.281	0.054	564

Taking into account the data obtained and history of “dirty” mine water discharge from mine N1, an effort was made to assess the efficiency of the biological system for the total time of discharging of mine water.

The efficiency of mine water treatment by a biological system is determined by the accumulation of major radionuclides (uranium and radium) in the system. The accumulation was determined by balancing in- and outputs.

Taking into account the data on the biological system and effluent discharge parameters, both the uranium and radium activity balance have been calculated for the biological treatment system according to the formula:

$$A_1 + A_2 = A_p + A_s + A_w + A_r,$$

where A_1 - total activity of radionuclides being discharged without treatment for 10 years;
A_2 - total activity of radionuclide being discharged with treatment for 13 years;
A_p - radionuclide accumulation in vegetation;
A_s - radionuclide accumulation in silt;
A_w - radionuclide accumulation in water;
A_r - radionuclide removing from system.

Calculation results are shown in Table XII.

The Kilten River receives 14.5% of the total uranium activity, i.e. the effectiveness of mine water treatment by the biological system is 85.5%. As the calculation results show, Ra-226 entering the Kilten River is insignificant, i.e. almost all Ra is within the natural treatment system. The results obtained allow us to consider a passive biological treatment system using a constructed marsh land as being very effective for reducing radionuclide content in mine water.

Table XII. Uranium and radium activity balancing results

# of point	Water reservoir	Accumulation in vegetation A_p, Bq		Accumulation in silt A_s, Bq		Accumulation in water A_w, Bq		Removing from system A_r, Bq		Total, Bq	
		U	Ra	U	Ra	U	Ra	U	Ra	U	Ra
1.	Waste pond	$4.1 \cdot 10^6$	$4.7 \cdot 10^6$	$7.2 \cdot 10^{10}$	$7.1 \cdot 10^{10}$	$1.9 \cdot 10^8$	$6.28 \cdot 10^6$	---	---	---	---
2.	Pond I	$9.1 \cdot 10^6$	$2.1 \cdot 10^7$	$2.8 \cdot 10^{11}$	$2.5 \cdot 10^{11}$	$4.8 \cdot 10^8$	$1.25 \cdot 10^7$	---	---	---	---
3.	Pond II	$1.4 \cdot 10^7$	$1.5 \cdot 10^7$	$5.01 \cdot 10^{11}$	$1.09 \cdot 10^{11}$	$1.22 \cdot 10^9$	$2.8 \cdot 10^7$	---	---	---	---
4.	Pond III	$8.5 \cdot 10^7$	$8.5 \cdot 10^6$	$8.4 \cdot 10^{11}$	$1.9 \cdot 10^{10}$	$4.4 \cdot 10^8$	$5.8 \cdot 10^6$	---	---	---	---
5.	Kilten-river	---	---	---	---	---	----	$1.6 \cdot 10^{11}$	$2.3 \cdot 10^6$	---	---
	Total	$3.57 \cdot 10^7$	$4.9 \cdot 10^7$	$9.38 \cdot 10^{11}$	$4.49 \cdot 10^{11}$	$2.3 \cdot 10^9$	$5.25 \cdot 10^7$	$1.6 \cdot 10^{11}$	$2.3 \cdot 10^6$	$1.1 \cdot 10^{12}$	$4.5 \cdot 10^{11}$

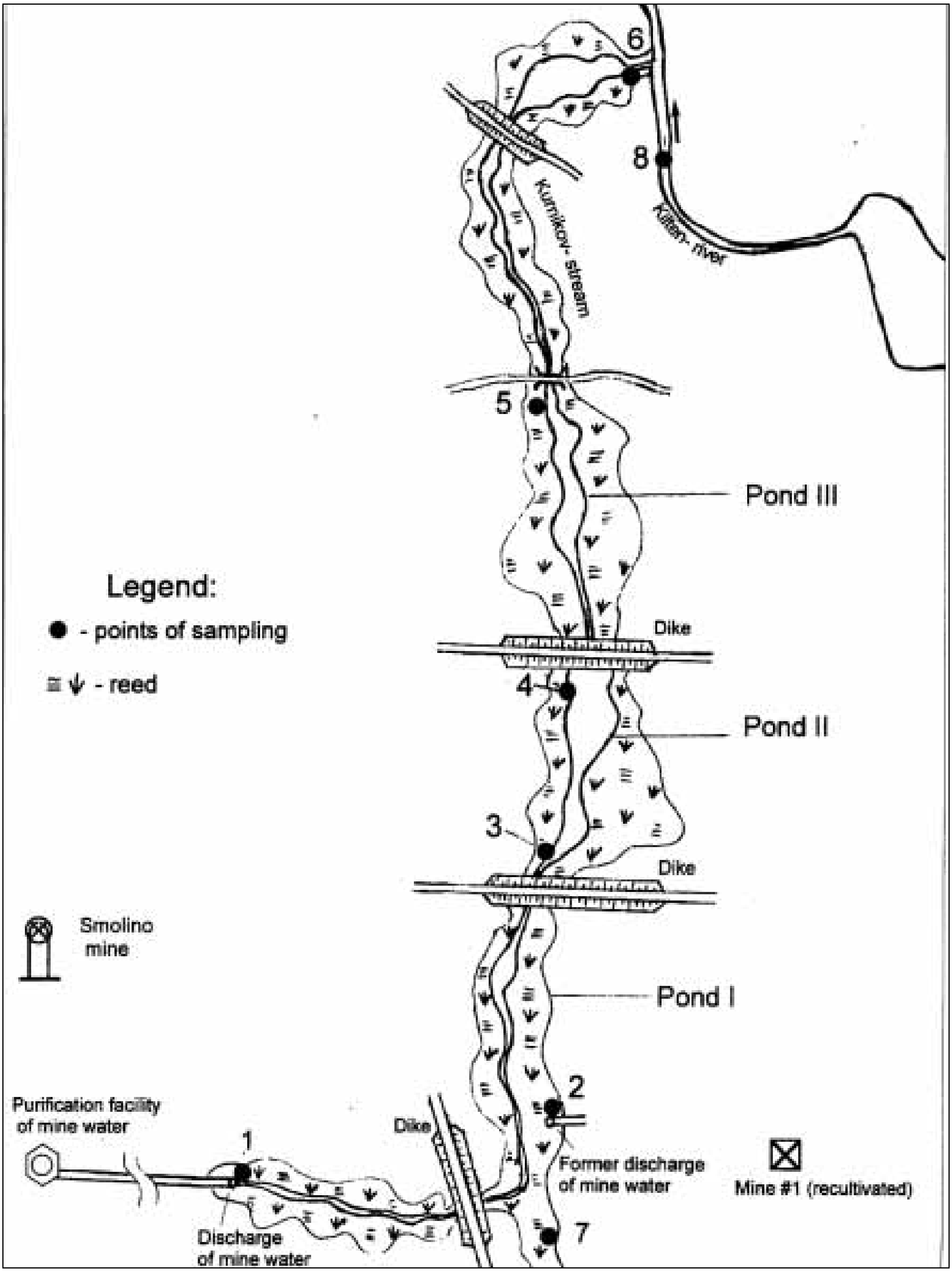


FIG. 7. Scheme of natural treatment of mine waters at the Smolino site.

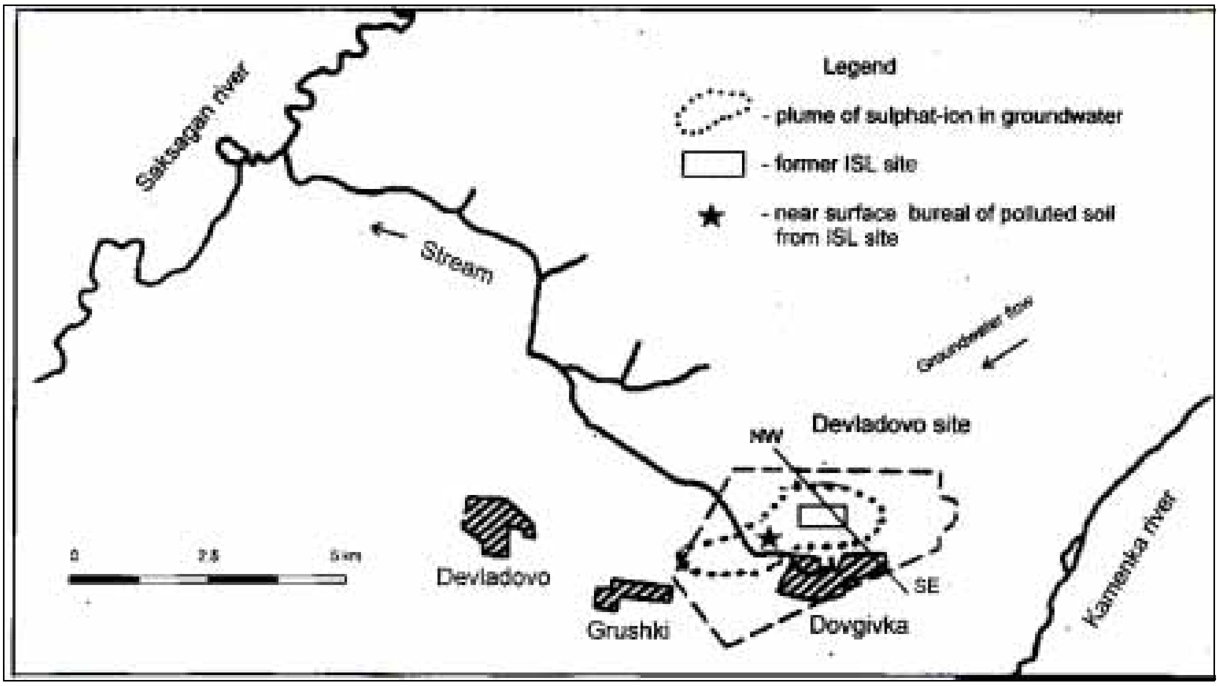


FIG. 8. Location of Devladovo site.

4. Residual solutions at former ISL sites

4.1. General information

In-situ leaching (ISL) of uranium was carried out in the Devladovo, Bratskoe and Safonovka deposits. After the exploitation of these deposits ended, all working solutions within the former orebodies were left in place. Their total volume (at all ISL sites) was about 14 million m^3. Thus the spreading and migration of the residual solutions in groundwater is a common problem for all the former ISL sites because aquifer restoration activities were not carried out after exploitation had ended.

The situation at the Devladovo site has been studied as part of this research work. The Devladovo site was the first site of ISL extraction of uranium in the former Soviet Union. The site was used for the testing and improvement of ISL technology. The Devladovo site is located in Dnipropetrovsk region (30 km to the south-east from Zhovty Vody) near the villages of Devladovo and Dovgivka (Fig. 8). The ISL methods were used on an industrial scale from 1966 to 1983. Sulphuric and nitric acid were used as the leach solution.

As a result of ISL mining, underground waters were contaminated to a depth of 80 m. In addition to the ISL operation, a near-surface burial site was constructed for contaminated soil removed during recultivation of the ISL sites. These wastes were disposed of in the flood plain of an intermittent stream and covered by a 0.5 m thick clay layer. Location of the burial place is shown on Figure 8 with a star.

Decision making on the restoration of the contaminated aquifer and on the near-surface burial site requires modelling of contaminant migration in the environment. Modelling result will determine what kind of restoration work is required and the effectiveness of that effort.

4.2 Site information

The Devladova ISL site is located between two rivers (Figure 8):

- Saxagan River to the west,
- Kamenka River to the east.

The Saxagan River represents the most significant drinking water resource in the region. At a regional scale the studied site is located on the edge of the Ukrainian crystalline shield, which is formed by Precambrian granites, migmatites and gneisses. The geology is complicated by a fault system that forms a block structure with a linear depression. A weathering layer was developed on top of the basement rocks. The sedimentary cover overlying the basement is formed by Paleogene and Quaternary sediments with a total thickness of up to 90 m. The geology, stratigraphy and geometry of the Devladovo uranium deposit are shown in Figure 9. Four aquifers can be distinguished in the Devladova area (see table below).

Aquifer	Geological index	Thickness	Functional description
Quaternary	Q	5.6 – 12.5	Loess, loam
Sarmat	N_1s	8.2 - 24.8	Sand
Buchaksky	P_2bc	19.2	Sand
Paleozoic	PZ-KZ	>51	Fractured and altered crystalline rocks

The Quaternary aquifer is unconfined: it supplies surface flow. The Sarmat, Buchaksky and Paleozoic aquifers are confined at least within the site limits.

4.3. Contamination problems

The Devladovo site includes two major sources of contamination: a near-surface burial site of wastes and the contaminated Buchaksky aquifer. The volume of residual solutions in the Buchaksky aquifer is estimated at 7 million m^3, and at 1 million m^3 in the near-surface burial site. The volume of contaminated soil in the near-surface burial site is around 40 000 m^3. The near-surface burial site contains residues from uranium ore processing, including dissolved radionuclides, sulphates and nitrates. The burial site does not have an impervious layer at the bottom. It lies directly on the Quaternary surface aquifer. Therefore, any seepage through the burial site due to infiltration may cause contamination of this unconfined aquifer. The area of the burial site is around 120 000 m^2 with a thickness of 0.42 m. The uranium concentration in water (C_{water}) is between 2 and 20 mg/l.

The Buchaksky aquifer (P_2bc) contains the highest levels of contamination. The maximum concentrations of uranium in water (C_{water}) of the Buchaksky horizon are between 20-40 mg/l. This aquifer is overlain by clays of the Kievsky layer (P_2kv). No significant vertical transfer occurs through this layer. However, this natural protection is not sufficient to confine the contamination. As shown on Figure 9 the Paleozoic (PZ-KZ) aquifer permits communication between the Buchaksky aquifer and the Sarmat aquifer (N_1s).

The main source of information for the following analyses is the "Database of chemical elements in water from boreholes and wells", created by the Ukrainian R&D Institute for Industrial Technology.

These data show that:

- Within the site limits there is no significant direct vertical exchange between the aquifers.
- Within the site limits the Kievsky horizon confines the Buchaksky aquifer, which contains the residual solutions.
- The Quaternary aquifer is contaminated through various activities (burial site, piping, etc.).
- At the surface, the stream acts as a conduit for the contamination.

Two contamination problems, therefore, have been identified:

- Contamination of the Quaternary aquifer by releases from the burial site;

- Contamination of the Paleozoic (PZ-KZ) and the Sarmat aquifers by the Buchaksky residual solution.

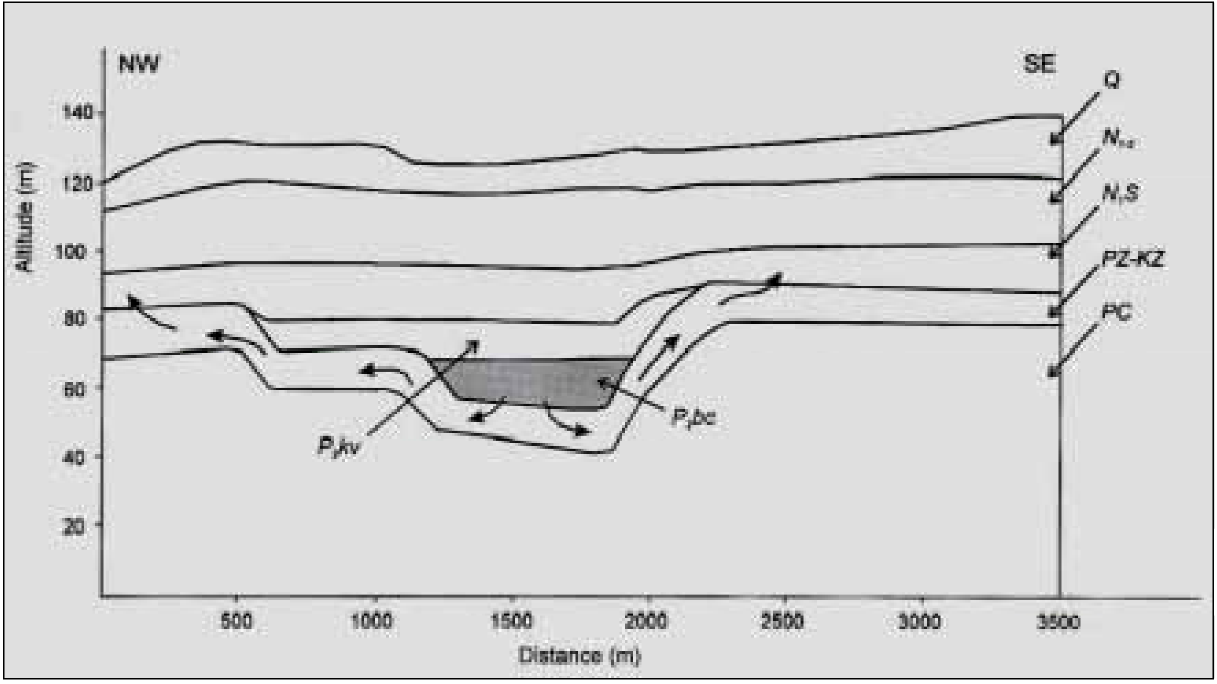


FIG. 9. Geological cross section of "Devladovo" Site in direction NW – SE.

In order to understand the behaviour of the contamination, the following section describes the results of contamination transport modelling through the groundwater pathway.

4.4. Modelling and prognosis of surface and groundwater contamination

4.4.1. Objectives of modelling

The objectives of the modelling are as follows:

- to quantify the current contamination, using available information, considering:
    - release of nuclides and toxic contaminants;
    - transport of contaminants through the groundwater pathway;
    - resulting exposure and dose to the population.
- to predict possible evolution of the current situation over the next 1000 years, according to the behaviour of the contaminants.

Modelling has been carried out for an area that is located between the Saxagan and Kamenka Rivers (Fig.8). The computer software tools "MODFLOW" "MT3D" and "MODPATH" (USA) were used for the modelling.

4.4.2. Quaternary aquifer modelling

The Quaternary aquifer is unconfined and supplies surface streams. Groundwater flow is mainly directed towards surface water streams, which represent natural boundary conditions.

An analytical model was used to predict advective-dispersive transport of a contaminant released continuously from a three dimensional source in a three dimensional medium.

The goal of the modelling was to predict the possible evolution of uranium concentration over a period of 1000 years, considering the Saxagan River as a target and the burial site as a source of contamination. These predictions were handled by using Monte-Carlo simulations. Taking into account the uncertainties involved in the model parameters, 1000 Monte-Carlo simulations have been performed.

As shown on Figure 10, if the acceptable limit of uranium concentration is 1.8 mg/1, 80% of the calculations show a concentration exceeding this limit.

4.4.3. Sarmat aquifer modelling

The Sarmat aquifer may be contaminated by transfer of pollutants from the Buchaksky aquifer as shown on Figure 9. In order to estimate the most probable uranium concentration taking into account the uncertainties involved in the model parameters, 1000 Monte-Carlo simulations have been conducted. The results of these simulations are shown in Figure 11. As shown in Figure 11, if the acceptable limit of uranium concentration is 1.8 mg/l about 6% of the calculations indicated a concentration exceeding this limit in 1000 years.

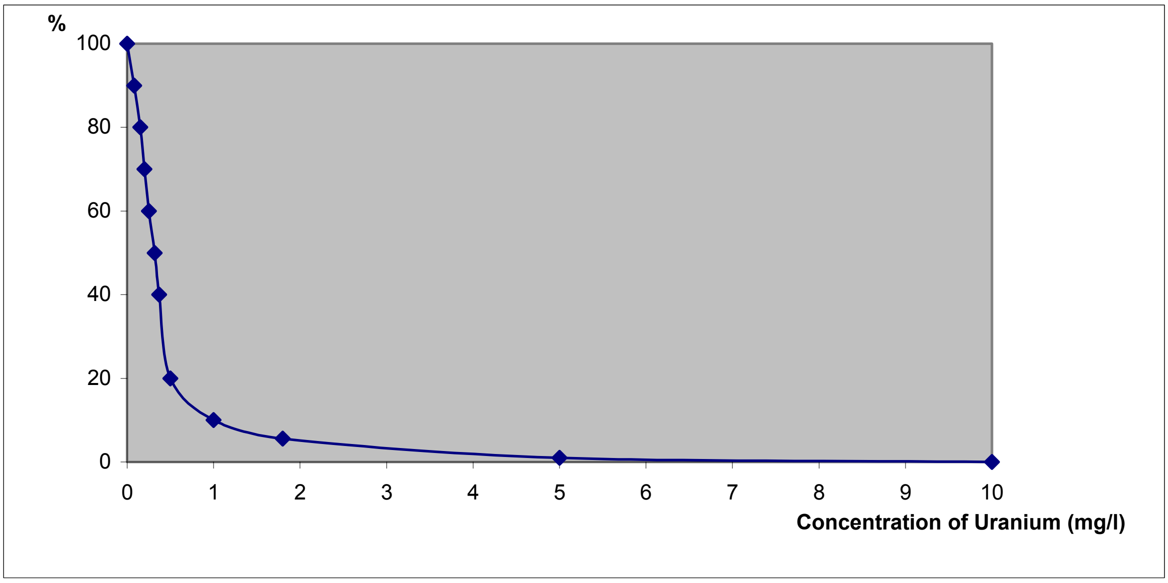


FIG. 10. Risk of exceeding an acceptable uranium concentration limit for the Quarternary horizon.

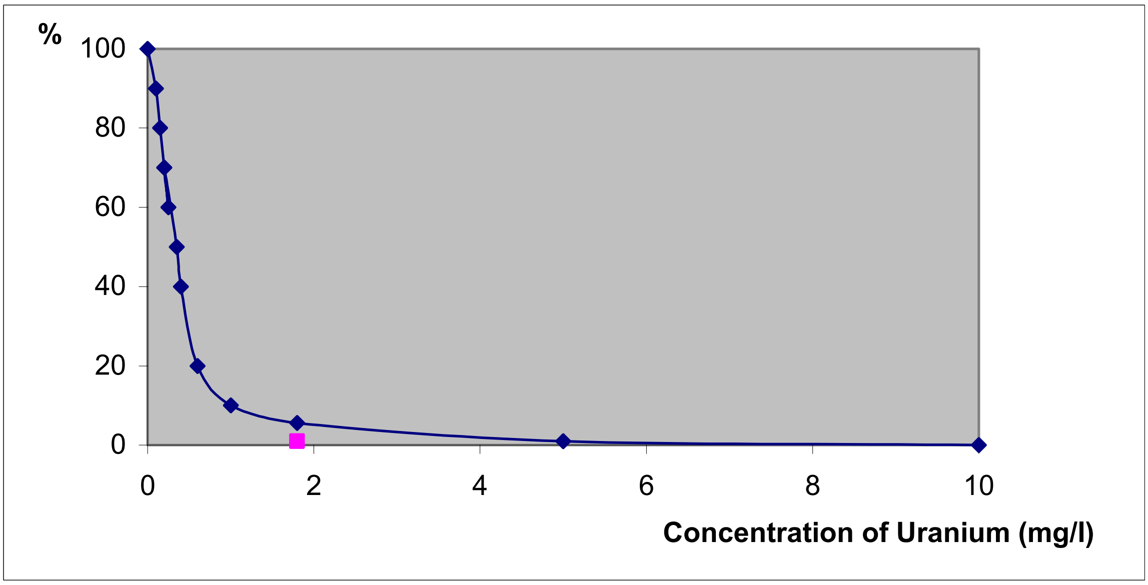


FIG. 11. Risk of exceeding an acceptable uranium concentration limit for the Sarmat horizon.

5. Conclusions and recommendations

The present work may be considered as a first step in a global data analysis of the Devladovo site. Extraction of uranium by the ISL process has considerably modified the physical and chemical properties of the main regional groundwater resource.

The simulation over 1000 years of contaminant release from the burrial site showed that there is a high probability that contaminants will reach the Saxagan River with concentrations exceeding the acceptable limits. This river is the main regional water resource.

The simulation over 1000 years of releases of residual solutions from the Buchaksky aquifer showed that there is a 6% probability that contaminants reaching the Sarmat aquifer will be greater than the acceptable limits.

Based on the study results, it is not necessary to implement urgent measures for groundwater restoration. However, monitoring systems are needed to obtain more detailed information about groundwater conditions and hydrogeological parameters to ensure more precise predictions.

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LIST OF PARTICIPANTS

Banik, J.	Mecsek Ore Environment Co., 19 Esztergar L. Street, 7633 Pécs, Hungary
Baudu-Picquet, I.	COGEMA, Service d'Etudes de Procedes et Analyses (SEPA) Laboratoire, B.P. No. 71, 87250 Bessines sur Gartempe, France
Benkovics, I.	Mecsek Ore Environment Co., 19 Esztergar L. Street, 7633 Pécs, Hungary
Csövari, M.	Mecsek Ore Environment Co., 19 Esztergar L. Street, 7633 Pécs, Hungary
Csicsak, J.	Mecsek Ore Environment Co., 19 Esztergar L. Street, 7633 Pécs, Hungary
Edwards, C.	CAMECO Corporation, 2121 11th Street West, Saskatoon, Saskatchewan S7M 1J3, Canada
Guler, H.	Turkish Atomic Energy Authority, Ankara Nuclear Research and Training Center, 06105 Saray-Ankara, Turkey
Hideg, J.	Mecsek Ore Environment Co., 19 Esztergar L. Street, 7633 Pécs, Hungary
Holden, P.	Australian Nuclear Science & Technology, Organization (ANSTO), Ore Processing Group, New Illawarra Rd, Private Mail Bag 1, Menai NSW 2234, Australia
Jarrell, J.	CAMECO Corporation, 2121 11th Street West, Saskatoon, Saskatchewan S7M 1J3, Canada
Kayukov, P.	Joint-Stock Company "Volkovgeologia", 168 Bogenbay Batyr Str., Almaty 480012, Kazakhstan
Kiessing, G.	WISMUT GmbH, Jagdschenkenstrasse 29, 09117 Chemnitz, Germany
Kunze, C.	WISMUT GmbH, Jagdschenkenstrasse 29, 09117 Chemnitz, Germany

Lendvai, Z.
Mecsek Ore Environment Co.,
19 Esztergar L. Street,
H-7633 Pécs, Hungary

Mathur, A.K.
Mineral Technology Laboratory,
Department of Atomic Energy, Atomic Minerals,
Directorate for AMD Complex,
Begumpet, Hyderabad – 500 016, India

Matias, M.J.
Laboratory of Mineralogy and Petrology,
Technical University of Lisbon,
Av. Rovisco Pais,
1049-001 Lisbon, Portugal

Molchanov, I.A.
Ukrainian Scientific Research and Design,
Institute of Industrial Technology,
37, Petrovsky Street,
Zhovty Vody, Dnipropetrovsk Region 322530,
Ukraine

Neves, O.
Laboratory of Mineralogy and Petrology,
Department of Mines,
Av. Rovisco Pais,
1096 Lisbon, Portugal

Ring, R.J.
Australian Nuclear Science & Technology,
Organization (ANSTO), Ore Processing Group,
New Illawarra Rd, Private Mail Bag 1,
Menai NSW 2234, Australia

Xu, J.
Chinese National Nuclear Corporation,
Bureau of Mining & Metallurgy,
P.O. Box 234, Beijing 101149, China

Zhang, J.
Chinese National Nuclear Corporation,
Beijing Research Institute of Chemical,
Engineering & Metallurgy,
P.O. Box 234, Beijing 101149, China