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Treatment technologies for low and intermediate level waste from nuclear applications

Final report of a co-ordinated research programme
1991–1996

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FOREWORD

Radioactive waste is generated from the production of nuclear energy and from the use of radioactive materials in industrial applications, research and medicine. The safe management of radioactive waste from nuclear applications in developing countries which do not have the background of managing nuclear fuel cycle wastes is essential for the further development of the peaceful applications of nuclear energy. Despite the general low level of radioactivity involved, there are many significant hazards that could arise as a result of inadequate management.

The waste management programmes and activities in many developing Member States have been reviewed through a Waste Management Advisory Programme (WAMAP) implemented by the IAEA in 1987-1995. One of the WAMAP objectives was to assist in practical development and implementation of safe and efficient waste treatment methods. WAMAP has identified common problems in the treatment of radioactive waste and revealed that the treatment solutions adopted by developed Member States for a relatively small number of well characterized, large volume waste streams are too complex or expensive and may not be directly applicable for a variety of waste streams generally arising from nuclear applications. In this context the IAEA has initiated a co-ordinated research programme on treatment technologies for institutional wastes covering the most important recurring problems in developing Member States. The programme was intended to cover the research and development required for reliable waste treatment operations, including the likely variations in institutional waste inputs using simple low cost processes.

This co-ordinated research programme was initiated in 1991 and brought together 14 participants from 13 countries. The results of the studies were discussed at three research co-ordination meetings. This report summarizes the salient features and results obtained during five year investigations and provides recommendations for future work in this area. The report has been prepared by V. Tsyplenkov of the Waste Technology Section in the Division of Nuclear Power and the Fuel Cycle, Project Officer of the CRP, and K. Simpson of the United Kingdom, as consultant to the IAEA.

EDITORIAL NOTE

CONTENTS

PAPERS PRESENTED AT THE FINAL RESEARCH CO-ORDINATION MEETING

1. INTRODUCTION

Radioactive waste is a by-product of nuclear power generation and also results in smaller quantity from nuclear applications such as the use of radioactive materials in industry, research and medicine. Many developing countries are accumulating wastes from nuclear applications in the absence of a national waste management strategy, and are seeking to develop appropriate and safe waste treatment and immobilization procedures for future waste disposal. Treatment technologies pursued by developed countries for a relatively small number of well characterized but large volume waste streams may be too complex or expensive for the more varied waste streams with a lower activity and volume generally arising from nuclear applications.

In this context the IAEA initiated a Co-ordinated Research Programme (CRP) on Treatment Technologies for Low and Intermediate Level Wastes Generated from Nuclear Applications. The programme was intended to cover research and development which could lead to reliable application of simple low cost processes to specific institutional waste arisings. Such processes should be compatible with formation of a stable waste form to retain long-lived radionuclides.

In total 13 Member States participated in the CRP. Bangladesh, Bulgaria, China, the Czech Republic, Egypt, Romania, Thailand and Turkey took part from the start in 1991, and Belarus, Chile, Philippines and the UK joined the CRP in 1993. Three research co-ordination meetings were held: in Bangkok, Thailand in April 1993, in Istanbul, Turkey in February 1994, and in Manila, Philippines in April 1996.

2. SCIENTIFIC BACKGROUND

Waste from nuclear applications contains a variety of radionuclides and arises in a variety of physical and chemical forms. In some instances the amount of activity and waste volume may both be very small, and in others a small amount of activity may be dispersed in a large volume. Half-lives may be very different: for example, the activity may be in the form of long lived plutonium isotopes, or may be relatively short lived, as with iodine isotopes used in medical applications. Treatment may therefore be needed to produce a waste product suitable for long term storage and disposal, or the treatment objective may be volume reduction to simplify handling pending activity decay.

The selection of treatment technologies for wastes from nuclear applications should ideally be based on the national requirements for waste categorization and disposal, discharge limits and clearance levels for release of wastes from nuclear regulatory control. Whilst some of the participating countries are able to link waste treatment procedures to allowable discharge levels or permitted leach rates from immobilized waste, several participating countries have not yet established such a framework. Nevertheless it is often the case that relatively small decontamination factors will be needed to permit discharge of aqueous wastes from nuclear applications, compared with the decontamination factors sought for nuclear fuel cycle waste streams.

Contaminated organic wastes, particularly in the form of putrescible animal carcasses possibly containing infectious agents, often require treatment on grounds of hygiene and chemical safety. Treatment processes are likely to be geared to these factors rather than activity control alone.

There is a large literature on treatment technologies for low and intermediate level wastes. For example, the IAEA has summarized the experience gained with chemical precipitation processes for use with aqueous waste [Chemical Precipitation Processes for the Treatment of Aqueous Radioactive Waste, Technical Reports Series No. 337, IAEA (1992)], and has more recently reported on advances in the treatment for liquid wastes, including organic wastes [Advances in Technologies for the Treatment of Low and Intermediate Level Radioactive Liquid Wastes, Technical Reports Series No. 370, IAEA (1994)] The status of technology for volume reduction and treatment of low and intermediate level solid radioactive waste has been reviewed in a report of the same title [Technical Reports Series No. 360, IAEA (1994)]. Information is also available on the immobilization of activity, for example that is contained in precipitation sludges, in cement [Improved Cement Solidification of Low and Intermediate Level Radioactive Wastes, Technical Reports Series No. 350, IAEA (1993)].

Many of the well established techniques are in principle capable of adaptation for use with locally available, naturally occurring materials. Detailed investigation to support the use of such materials is required, and this has been undertaken by several countries within the CRP.

In some cases the chemistry of aqueous waste streams from nuclear applications, such as pH and salt content exert a significant influence on the choice of a process for activity removal, leading to the need for process flexibility or the specific tailoring of treatment to a waste stream. Again investigations targeted at real waste streams are needed.

3. SCOPE AND OUTLINE OF THE CO-ORDINATED RESEARCH PROGRAMME

The IAEA particularly encouraged participation of countries which do not currently have nuclear power programmes, but which need to treat institutional radioactive wastes to protect human health and the environment from hazards associated with their radioactive content.

A primary objective of the Co-ordinated Research Programme on Treatment Technologies for Low and Intermediate Level Wastes Generated from Nuclear Applications was to promote the exchange of information on both the approaches taken by participating countries as well as on detailed technical studies.

As indicated above, it was expected, from the nature of such institutional wastes, that there would be a wide spread in the research objectives of participating countries. The objectives are summarized below, country by country, and are collated by topic in Tables I-III.

Bangladesh (M. Rahman)

- optimize conditions for caesium precipitation with ferrocyanide;
- characterize stored wastes;
- examine caesium removal from stored waste under optimum.

Belarus (G. Juravskij)

- study decomposition of solid organic wastes using high pressure steam.

Bulgaria (G. Gradev)

- optimize precipitation processes for decontamination of multinuclide aqueous waste streams;
- improve precipitation process by addition of selective sorbents;
- examine activity removal by locally available sorbents with and without modification;
- examine activity release from loaded sorbents;
- investigate conditioning of sludge and spent sorbents.

Chile (E. Andalaft)

- investigate advanced separation processes for treatment of aqueous waste streams;
- develop electrical techniques for strontium removal using inorganic membranes.

China P. R. (J. Zeng)

- investigate actinide removal from a specific waste stream by sorption on Chinese apatites,
- investigate cementation of sorbents sludge,
- characterize cement waste form against national criteria

China P. R. (S. Feng)

- conduct rapid ashing of putrescible radiobiological wastes,
- investigate cementation of resultant ash,
- study additives to improve cemented waste form characteristics

Czech Republic (J. Holub)

- use incineration for volume reduction of biological waste containing actinides,
- examine cement, bitumen, and mixed media for ash solidification,
- examine physical properties and leach behaviour of waste forms,
- make comparative cost estimates of solidification options

Egypt (N. Ghattas)

- examine efficiency and rate of wet oxidation by hydrogen peroxide of spent organic ion exchange resins and scintillation counter liquids,
- study immobilization of wastes after oxidation

Malaysia (S. H. Sakuma)

- improve coagulation/flocculation process for removal of Zn-65, Mo-99 and I-125 from aqueous waste,
- improve removal of I-125 by oxidation to iodate and adsorption on laterite soil

Philippines (E. Valdezco)

- investigate removal of radioiodine by sorption on volcanic ash,
- optimize removal of caesium by precipitation

Romania (G. Filoti)

- use Mossbauer spectroscopy to elucidate behaviour of iron in precipitation processes for radioactive decontamination and in cemented precipitates

Thailand (P. Yamkate)

- identify readily available sorbents for caesium and technetium,
- identify coagulants for solutions resulting from monazite extraction,
- examine detergent efficiency and identify a decontamination procedure for laundry effluents

Turkey (A. Kahraman)

- investigate optimum conditions for caesium removal by solid sorbents,
- investigate optimum conditions for caesium removal by co-precipitation of ferrocyanides,
- study uranium removal by inorganic sorbents,
- improve the sodium diuranate precipitation process for uranium removal,
- investigate hardening times for cementation of residual sludge

TABLE I CRP WORK BREAKDOWN DECONTAMINATION OF AQUEOUS WASTE STREAMS

Method	Cs	Sr	Co	U	Pu/Am	Th	I	Misc/ General
Precipitation	Bangladesh Bulgaria Turkey Philippines Thailand Malaysia	Bulgaria	Bulgaria	Turkey		Thailand	Malaysia	Malaysia Romania Thailand
Adsorption/ Ion exchange	Bulgaria Turkey Thailand	Bulgaria	Bulgaria	Turkey	China		Malaysia Philippines	Bulgaria Thailand Philippines UK
Combined techniques	Bulgaria Turkey Philippines	Bulgaria	Bulgaria	Turkey				
Electrical techniques		Chile						Chile

TABLE II CRP WORK BREAKDOWN ORGANIC WASTE TREATMENT

Method	Cs	Sr	Co	Pu/Am	Non-Active
Incineration				Czech Republic	
Ashing	China	China	China	China	
Wet oxidation					Egypt
Steam oxidation					Belarus

TABLE III CRP WORK BREAKDOWN WASTE IMMOBILIZATION

Method	Cs	Sr	Co	Pu/Am	Misc/ General
Cementation	Bangladesh, Bulgaria China Thailand Turkey	Bulgaria China	Bulgaria	China Czech Republic	Bulgaria Egypt
Bituminization				Czech Republic	
Mixed media				Czech Republic	

UK (K. Simpson)

- critically review selective absorbents in relation to properties other than selectivity;
- discuss the value of decontamination for free release.

The range of topics covered by participants is wide, but can be broadly broken down into three areas:

(a) decontamination of aqueous waste streams
(b) treatment of contaminated organic waste material
(c) immobilization of activity for interim storage and disposal.

Tables I-III show the breakdown of research programmes undertaken by participants in these three topics and indicate common areas of interest.

4. RESULTS AND DISCUSSION

This section gives only a brief discussion and overview of the work carried out by countries participating in this Coordinated Research Programme on Treatment Technologies for Low and Intermediate Level Wastes Generated from Nuclear Applications. The final reports of individual participants are reproduced in the Appendix, and should be consulted for more detail on work programmes and results.

The three Research Co-ordination Meetings were well attended and, through presentation of research progress reports and discussion, allowed participants to identify common concerns, to exchange results and to debate possible future lines of investigation.

4.1. DECONTAMINATION OF AQUEOUS WASTE STREAMS

Several investigators (Bulgaria, Malaysia, Thailand) found that well known, general precipitation techniques, often using iron hydroxides, could remove activity from the specific waste streams arising in their different countries. Mössbauer spectroscopy (Romania), which is a sensitive technique, was used to illustrate the complexity of iron oxidation state and coordination in precipitates formed using slightly different procedures. The importance, where possible, of ensuring a uniform input waste stream was emphasized by Thailand in connection with use of a single and most effective laundry detergent: essentially complete activity removal from the well characterized waste stream could then be achieved by use of selective precipitating agents.

For caesium removal by precipitation, selective reagents were needed and several investigators (Bangladesh, Bulgaria, Turkey) sought to optimize the use of the ferrocyanide precipitation technique by investigating pH, reagent ratios, and choice of ferrocyanide salt. There was a general agreement that pHs on the alkaline side of neutral, e.g. pH 9-10, are very suitable but that decontamination factors declined at high pH (12 and above). Nickel salts were preferred for precipitation of insoluble ferrocyanides, but a range of cation/anion ratios gave satisfactory decontamination factors (generally of a few hundred).

In Bulgaria indigenous clinoptilolites, a zeolite type of ion exchanger, were shown to have a high selectivity for caesium and silver, with distribution coefficients of order 10^4 mL/g. In the absence of potassium ions, native clinoptilolites were shown to remove strontium and cobalt very effectively. In Thailand also inexpensive inorganic ion exchange materials were found to have a useful removal capability for caesium.

In some instances (Bulgaria, Philippines, Turkey) investigators explored the use of combined precipitation and ion exchange processes, either as sequential operations (ion exchange/adsorption following precipitation) or with the absorber added at the same time as the precipitating agent. The use of such combined procedures may be required to adequately decontaminate multinuclide waste streams, but not all participants identified the target decontamination factors they needed to achieve to allow discharge of the decontaminated aqueous stream.

It was not always possible to compare directly the results obtained by the participants because of the different ways of reporting the degree of decontamination

For iodine isotopes used in medical applications which have relatively short half-lives that is, the activity removal or concentration can avoid the need for hospitals to retain large volumes of liquid pending decay Philippine volcanic ash was shown to have some sorption capacity for iodine In Malaysia a sorption process has been developed through to implementation using local laterite soils pre-packed in columns for direct use by waste generators The Malaysian study, as well as identifying suitable pH and soil mass/liquid volumes, showed that complete conversion of radioactive iodine to iodate gave reliable decontamination factors which were adequate to allow discharge of treated liquid

The removal of uranium from aqueous solution by precipitation as sodium diuranate is well known The residual uranium in solution is determined by the solubility product Addition of either barium sulphate or silica gel after precipitation of the diuranate was shown (Turkey) to reduce uranium concentrations to below the Maximum Permissible Concentration (PMC)in water In Thailand, it was found that a one stage precipitation process using mainly alum and barium chloride could give adequate decontamination factors (of up to 20) for Th and daughters from a waste stream from a monazite extraction laboratory One objective of Chinese work (Mr Zeng) was to investigate sufficient removal of Pu/Am from a waste stream to allow the effluent to pass to an existing Low Level Radwaste Treatment Plant A decontamination factor of about 10 was required Several Chinese apatites were assessed as potential sorbents and the best of these was carried forward into an examination of the effects of temperature, sorbent particle size, pH and sorbent/liquid ratio The necessary decontamination was achieved at close to the initial acid pH of 1-2 provided the wt% of sorbent, in relation to liquid mass, was >3 25 wt%

Results from the investigation of advanced techniques for activity concentration in aqueous waste streams were contributed by Chile Electrical power is used as the driving force to move activity in ionic form across inorganic membranes which separate the compartments in which activity increases and decreases Importance to minimize water transfer (electro-osmosis) and to control the pH value was demonstrated in this regard The concentrated aqueous solution is then decontaminated Several similar techniques are already in non-radioactive industrial use

The selection of treatment processes for waste streams arising from nuclear fuel cycle activities results from critical appraisal of numerous factors The need to reduce plant construction and operating costs, and to produce waste products and activity concentrations which match disposal acceptance or free release criteria, may not be so cogent with the waste arising from nuclear applications This is because the volumes of waste to be treated are generally small, and treatment is likely to be intermittent rather than in-line Nevertheless, there are potential benefits in considering a wide range of issues when moving from laboratory investigations to small plant scale and the U K contribution to the CRP touched on some of these For example, aqueous waste streams are usually decontaminated so that the water can be discharged Often several processes can meet this main objective The extent to which it is worth concentrating the retained activity, and the form in which it is retained is a different issue, but one which also needs consideration, since secondary operations involve occupational exposure and generate secondary as well as primary wastes

4 2 TREATMENT OF CONTAMINATED ORGANIC WASTE MATERIAL

Incineration is an attractive technique for handling putrescible organic materials A Czech Republic study investigated the possible use of an existing dual chamber, controlled air incineration facility to treat biological waste containing plutonium and americium An ash suitable for immobilization (see Section 4 3) was produced As well as experimental work, the safety of the incineration process for actinide bearing wastes, particularly in connection with airborne dust, was examined and found to be satisfactory

Treatment of animal carcasses containing trace amounts of radionuclides was investigated in a Chinese study (Mr Feng) Equipment was specially developed to carry out rapid ashing The process takes place two stages, with an initial charring stage conducted under nitrogen atmosphere preceding the oxidation or ashing stage It was found that activity, including caesium, was retained in the ash, provided that the ashing temperature was limited to < 450°C in order to avoid volatilisation. Although it was not found necessary to eliminate all carbon from the ash, because the ash is immobilized (see Section 4.3.), it is desirable to produce a non-adherent product to ease equipment maintenance.

Organic liquid wastes are amenable to various wet oxidation techniques, and the treatment of organic ion exchange resins and scintillation counter liquids by 30% hydrogen peroxide at 80°C was studied on a laboratory scale, in the absence of radioactivity, in the Egyptian contribution to the CRP. Degradation was followed by infrared spectroscopy, and the rate was enhanced by addition of a ferric ion catalyst at a level of about 0.01 wt%. The process was found to be highly efficient, giving good volume reduction in the case of organic resins and removing the fire hazard in the case of the scintillation counter liquids. The aqueous solutions resulting from the wet oxidation runs were immobilized directly, without any water removal (see Section 4.3.).

Preliminary studies of the possibility of using high pressure steam to break down a variety of solid organic wastes into gaseous and liquid fractions, separable from condensed steam, were reported by Belarus, but the distribution of active contamination between the product streams from the system has not been reported to the CRP.

4.3. IMMOBILIZATION OF ACTIVITY FOR INTERIM STORAGE AND DISPOSAL

Cementation of precipitates, sorbents, incinerator ash and digested organic liquids was considered as an attractive immobilization technique to many contributors to the CRP (Bulgaria, China, Czech Republic, Egypt, Thailand, Turkey). Compressive strengths in the general range 100-200 kg/cm^2 were readily achievable. (However attempts at direct cementation of scintillation counter liquids gave a very unsatisfactory product.)

One contributor (Czech Republic) performed a comparison between cementation and bituminization of the incineration ash: the bituminized product demonstrated a lower leach rate by a factor up to 10, but actinide leach rates from both media were very low. The loading of cement and bitumen with the incineration ash was examined in some detail. No large differences were found in overall conditioning and disposal costs between bitiminization and cementation processes.

In China, where national solid waste disposal acceptance criteria exist, the quality of the cemented product could be assessed against all of these criteria, and work was reported to optimize the loading of the cement.

However at this stage of research and development, some participants were more concerned with being able to produce an immobilized form that was likely to be satisfactory than with optimizing waste product loading. In several countries, the location of disposal sites, and solid waste acceptance criteria have not been fixed.

For some waste products such as incinerator ash, where the activity is not held by the accompanying solid and may be readily released on contact with water, it can be argued that immobilization is needed to produce a suitable waste form for interim storage and disposal. On the other hand in cases where activity is strongly held in the solid, it might be argued that drying and drumming would be adequate for some solid wastes of low activity, particularly as an interim measure. The main advantage of cementation in such cases could almost be seen as a means of removing water.

5. GENERAL CONCLUSIONS

Many participants showed by laboratory scale testing that well established precipitation and sorption techniques could be adapted to the decontamination of specific aqueous waste streams from nuclear applications, often using native materials as sorbents, and that improvements were possible to increase the decontamination factor.

In separate applications, incineration, ashing and wet oxidation of organic wastes have been shown to be very satisfactory for volume and hazard reduction. Unacceptable releases of activity in off-gases from incineration and ashing could be avoided and the ash produced was suitable for the immobilization with cement. Work on high pressure steam oxidation is at an earlier stage.

Immobilization of intermediate waste (e.g., sludge) arising from the treatment of wastes from nuclear applications has been shown to be feasible and some countries have been able to assess the waste form quality against national acceptance criteria.

In most instances, participants' work is at the laboratory scale to date, as is expected from a Co-ordinated Research Programme.

There is thus an opportunity to consider carefully the extent of decontamination needed and the amount of solid secondary waste to be produced. Immobilization is essentially an irreversible process, and represents a commitment to interim storage and final disposal.

6. RECOMMENDATIONS

All countries with radioactive wastes should establish solid radioactive waste acceptance criteria for disposal (at least preliminary ones) and set discharge activity or concentration limits and/or clearance levels for the waste to be beyond regulatory control.

In selecting a suitable waste treatment method for radioactive wastes from nuclear applications, the extent of treatment needed should be taken into account (this should ideally be done against national criteria). Also the amounts of primary and secondary waste generated by the different treatment options and the associated occupational dose exposures. In this way a treatment option with an overall benefit can be adopted.

More specifically, precipitation and sorbent addition processes involve subsequent separation of a solid phase from a liquid one, and probably the transfer of the solid phase for immobilization. Consideration might be given to the extent to which the amount of residual water affects the volume of the final waste forms, and hence influence the need for solid handling and dewatering.

To gain confidence, before commitment to treatment of institutional waste streams, consideration should be given to larger scale testing of some processes investigated on a laboratory scale only.

It is recognized that some wastes will require immobilization in monolithic form before final disposal. Immobilization is generally irreversible, and where the required product quality is not yet known, consideration should be given to the full characterization of waste forms produced in order to ensure the safety of their interim storage and further disposal.

ZETA POTENTIAL CONTROL IN DECONTAMINATION WITH INORGANIC MEMBRANES AND INORGANIC ADSORBENTS

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Abstact

The application of some advanced separation processes such as microfiltration and ultrafiltration, electroosmosis and electrodialysis for treating nuclear waste from different aqueous streams is under examination at the Chilean Commission for Nuclear Energy. The application of these techniques can be extended to regular industrial wastes when economically advisable. This report deals mainly with electrodialysis, electroosmosis and adsorption with inorganic materials. Special attention is paid to zeta potential control as a driving factor to electroosmosis. For radioactive contaminants that are present in the form of cations, anions, non-ionic solutions, colloids and suspended matter, appropriate combination of the processes may considerably increase the efficiency of processes used. As an example, colloids and suspended particles may be retained in porous ceramic membranes by nanofiltration, ultrafiltration or microfiltration depending on the particle size of the particles. The control of zeta potential by acting in the solid phase or else on the liquid phase has been studied; a mathematical model to predict electrodialysis data has been developed, and finally, the use of a home-made inorganic adsorbent illustrated. The effect of gamma irradiation on the membranes has also been studied. Properties such as salt retention, water flux and pore size diameter determined on both organic and inorganic membranes before and after irradiation indicate deterioration of the organic membrane.

1. INORGANIC MEMBRANES

Inorganic membranes are more stable in the presence of ionizing radiation making them particularly suitable for use for decontamination of radioactive waste. Inorganic membranes also show wider operational range of pH and temperature. Figure 1 shows the pore size distribution of an inorganic membrane MK-40. It can be seen how pore size increases after irradiation at 7.5 MRads. After irradiation, this and other organic membranes do not transfer ions so well as before irradiation. On the contrary, inorganic membrane BPS transfer ions just as well as before irradiation with the same dose.

1.1. MANUFACTURE AND CHARACTERIZATION OF INORGANIC MEMBRANES

The procedure to manufacture the support is illustrated in Fig. 2 and the procedure to manufacture the membranes, in Fig. 3. The manufacture of an inorganic membrane is based on two feed solutions that are placed at each side of a suitable support in order to react to form a precipitate with appropriate characteristics. For the membrane called BPS-20, the two solutions, called L (left - side) and R (right - side), are the following:

L: 0.1 M barium chloride;
R: 0.1 M sodium orthophosphate with 0.2 M sodium silicate.

For a membrane called BPS-11, two solutions are:

L: 0.1 M barium chloride with 0.1 M sodium silicate
R: 0.1 M sodium orthophosphate with 0.1 M sodium silicate.

Membranes are made by placing the defined feed solutions L and R at the corresponding side of the selected support and allowing the precipitate to form on both faces of the support previously fitted between two semi-cells. Fig. 4 shows the experimental arrangement of the cells and membranes. This arrangement is utilized both for manufacture of the membrane as well as for the electrodialysis runs. While manufacturing the membrane, no external field needs to be applied.

In order to optimize the fixation of the membrane precipitate on the support, chemical precipitation is followed by electro-precipitation using the same feed solutions and external voltage applied ca. 10 V for three hours, after which the both solutions and the voltage are reversed for the same period of time. With this procedure the film formed on the support has better properties, and the reproducibility of results is assured.

In order to obtain a good inorganic membrane first it is necessary to have a well characterized support. In the previous work it was determined that the average pore size diameter needs to be within the range 0.3 to 2.5 μ. Outside this range, the membranes produced do not exhibit good properties because when the diameter is smaller, the penetration of the precipitate is not adequate, and when the diameter is larger, the precipitate does not adhere well to the support.

In the present work, the porous ceramic supports were made of alpha-alumina, A-5 and A-14, clays and diatoms (AD, 85% clay and 15% diatoms). Table I shows the properties of powders used to prepare the supports, some properties of the supports and of the membranes.

1.2. ELECTRODIALYSIS

Electrodialysis has been used for decontamination of some ionic radioactive solutions. This process is based on electromigration of ions through a membrane that permits the passage of ions of positive or negative charge. Inorganic membranes are not specific ion exchangers, to a large extent their exchange properties depend on the pH of the solution; being anion exchangers at low pH and cation exchangers at high pH. Figure 5 illustrates the reactions taking place in the electrodialysis cell and at each electrode. The experimental runs were carried out using a solution of 500 or 1000 parts per million Sr^{2+} (in nitrate form) as electrolyte. This concentration was chosen for a practical purpose. Typical radioactive wastes would have much lower concentration, in the order of a few parts per million or a few parts per billion prior to being concentrated.

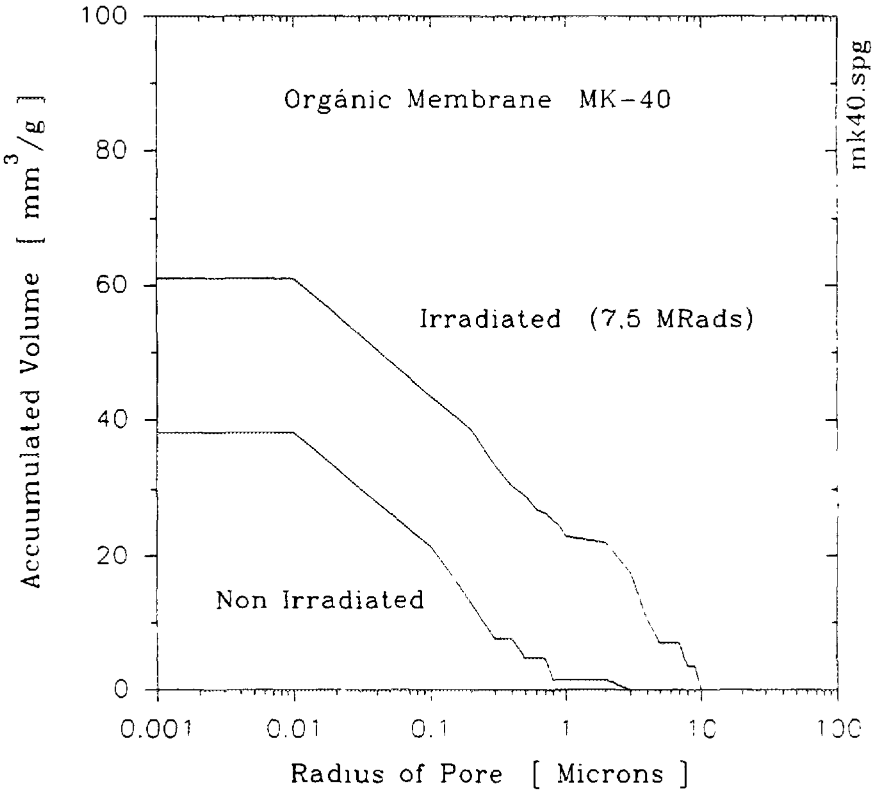


FIG. 1. Pore size distribution for an organic membrane MK-40 before and after irradiation at 7.5 MRads.

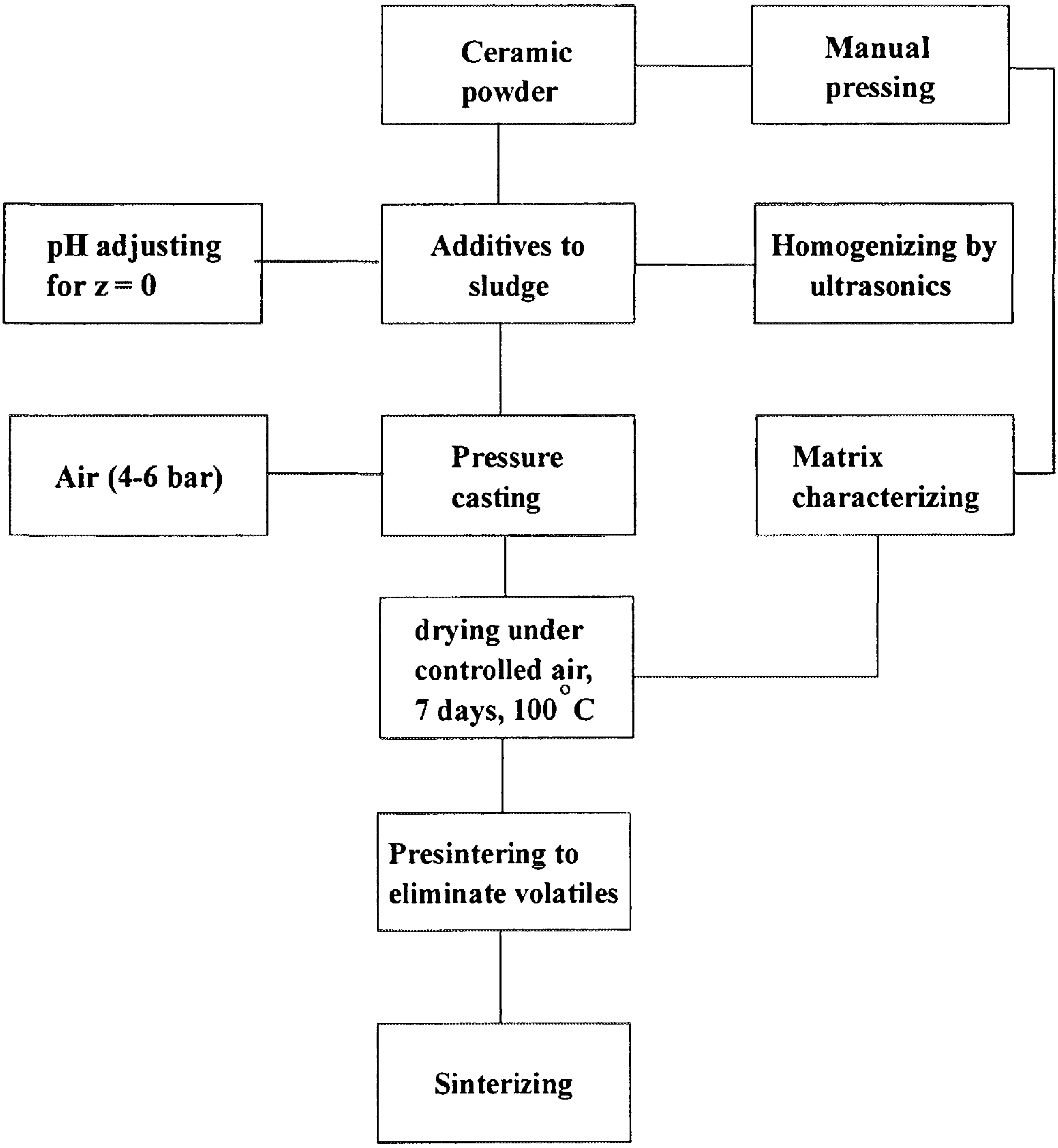


FIG. 2. Fabrication of a ceramic support.

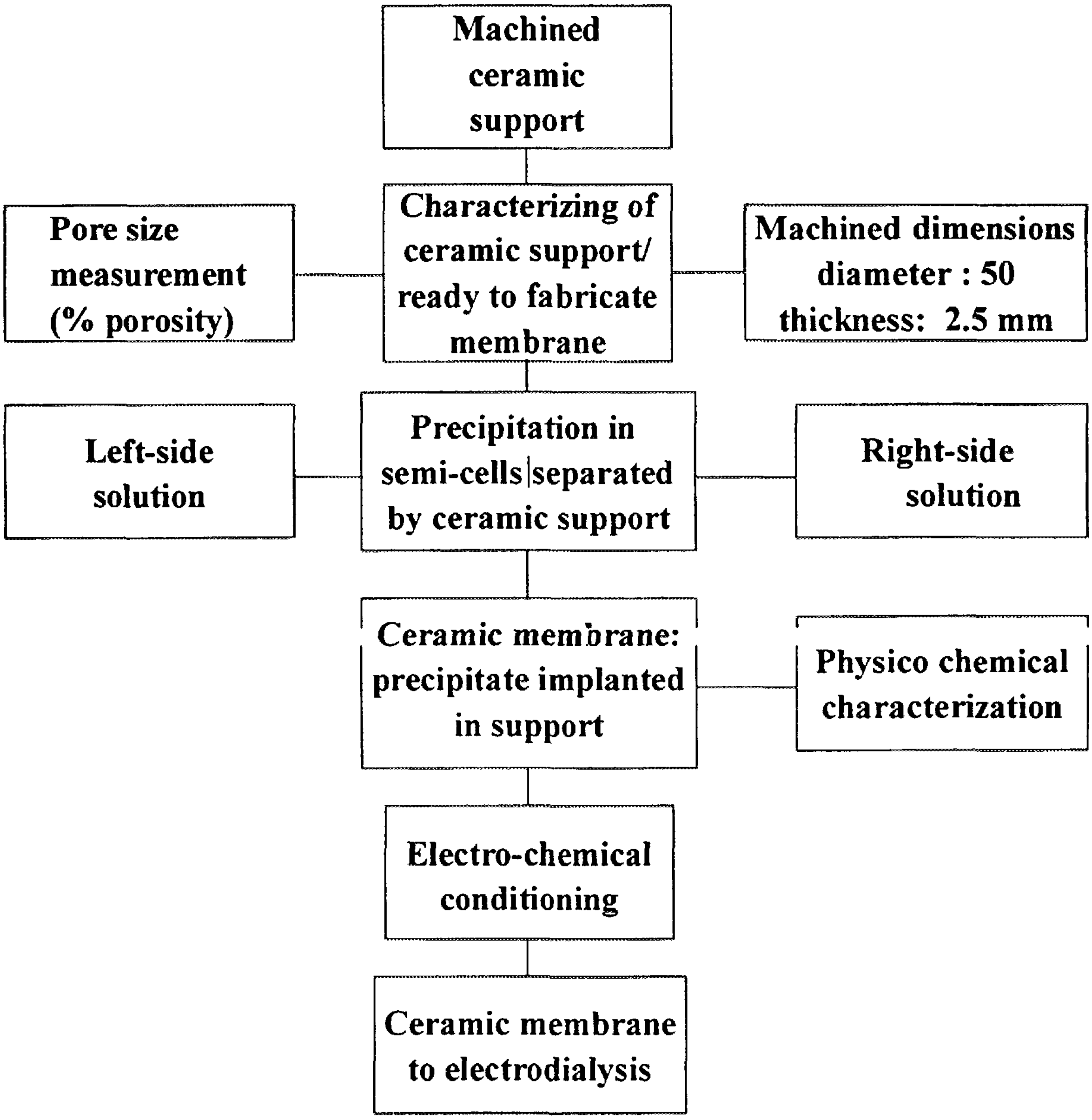
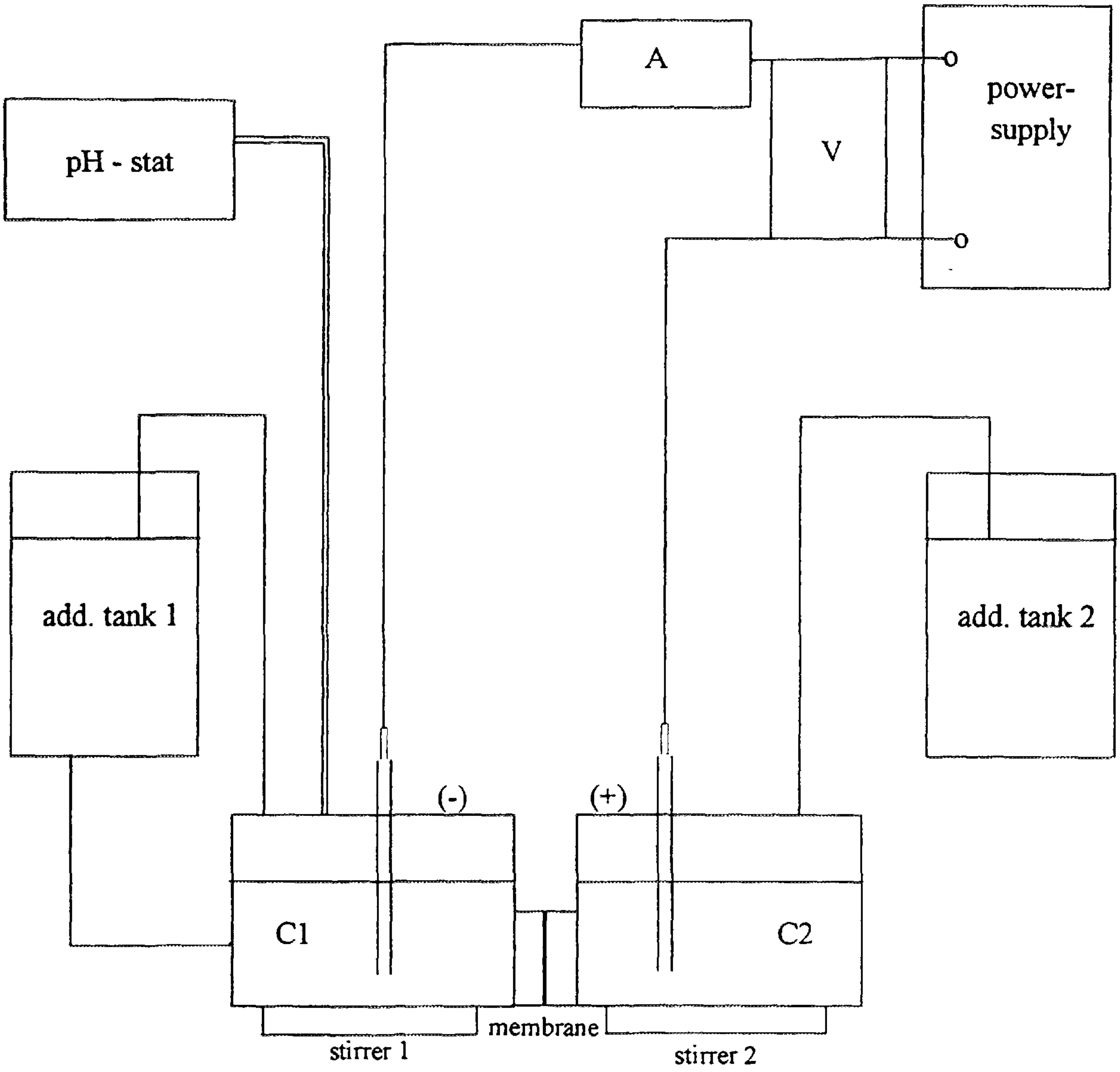


FIG. 3. Fabrication of an inorganic membrane.



A = ammeter
V = voltmeter
C1, C2 = cathode, anode semicell
add. tank 1, 2 = additional tanks
(-) = cathode
(+) = anode

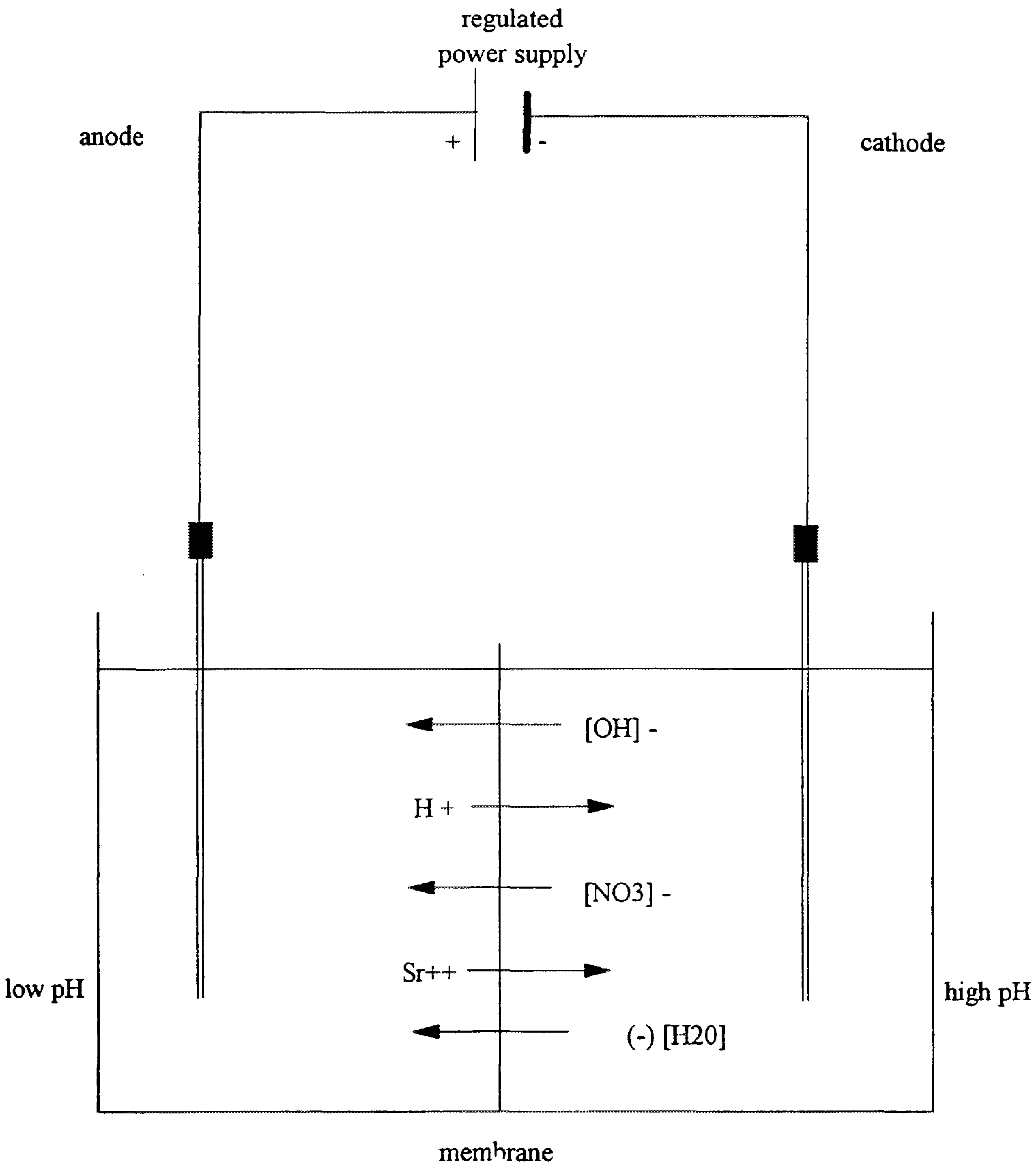
FIG. 4. Arrangement of the equipment for electrodialysis.

TABLE I. CHARACTERIZATION OF POWDERS, SUPPORTS AND CERAMIC MEMBRANES

Membrane	Al-14	Al-54	Al-56	AV	AD	Diatoms
1.Ingredients Alumina (%)	99.6	99.2	99.2	28.0	24.1	2
Silica (%)	0.08	0.02	0.02	50.8	57.9	98
Average grain size (μ)	2-5	6-10	6-10	0.1	1	12
Ligand	HMC	HMC	HMC	-	-	Natrosol
2.Conditions pH @ Z potential=0	7.8	7.5	7.5	-	-	-
Packing pressure (bar)	4	4	6	manual	manual	manual
Sintering temp.(°C)	1600	1600	1600	950	1000	1150
3.Support Average pore size (μ)	2.5	2.4	2.4	0.3	0.3	3
Porosity (%)	55	51	51	45	39	50
Permeability (*)	1000	1400	700	16	8	3200
Limit of compression (kg/cm^2)	620	89	338	715	530	36
4.Membrane BPS Average pore size (μ)	1.7	2.3	2.3	0.15	0.21	2.5
Porosity (%)	48	45	48	33	38	47
Permeability (*)	220	100	80	5	4	2400
Percentage of precipitate (**)	74	93	79	63	53	90

Key to symbols:

Al = Alumina
AV = Clay
AD = 85% clay, 15% diatoms
HMC = Hydroximethylcellulose
(*) = Permeability with respect to air in [cm^3/min· cm^2· bar]
(**) = Ratio of precipitate implanted in open pore volume in %.



cathode reaction: $2\ H^+ \quad + \quad 2e^- \quad \Longleftrightarrow \quad H_2(g)$

anode reaction: $2\ OH^- \quad \Longleftrightarrow \quad H_2O \quad + \quad 2e^-$

FIG. 5. Ions and water transfer in an electrodialysis cell.

1.3. ELECTROOSMOSIS

Inorganic membranes are made in a hydrophilic medium where two precipitating solutions are placed at each side of a thin support form, so as to have precipitation to occur inside the support material. Organic membranes are produced in a hydrophobic environment, and water cannot flow as freely as in the case of inorganic membranes. In fact, inorganic membranes show distinct behavior with water. Water flows through the membrane in large amounts during electrodialysis. Figure 6 shows the transfer of very large amounts of water for the membrane BPS supported on the paper Whatman-50. This water flows through by several mechanisms adding together their individual contributions towards the total water transfer; simple osmosis being the least important.

1.4. ZETA POTENTIAL CONTROL

The transfer of water from one semicell to another in electrodialysis may be an undesirable feature of inorganic membranes since it is energy consuming and also the flow of water may go in the wrong direction. An important objective of this investigation is to control the degree of electroosmosis taking place in electrodialysis. This study would seek to manipulate the conditions that determine the value of zeta potential of the membrane as the main governing factor to this phenomenon. Figure 7 shows the dependency of the Zeta Potential from pH. The maximum difference of 60 mV was found between pH 2 and 11.

1.4.1. Control in the solid phase

This part of the study is concerned with the support matrix inside which the membrane is formed and nested. Cellulose is the support material which shows very large electroosmotic ability. Using the ceramic support prepared by adjusting the zeta potential to value zero, shows important reduction of electroosmosis. Figure 8 shows a marked difference between a paper support and ceramic support, same as in Fig. 6, but this figure also shows the higher current consumption of the paper membrane due to water transport. Figure 9 shows that together with the lower power consumption the ceramic support can also be a better membrane than AD-3 and AD-2 for the transport of strontium.

1.4.2. Control in the liquid phase

The other part of this study is concerned with the liquid phase by controlling such properties as pH, current density, addition of specific ions. A marked reduction in electroosmosis is attained by controlling pH at constant current. The pH control is not easily achieved. Figure 10 shows how pH naturally takes extreme values as soon as the electric field is applied.

The main purpose of the present study is to review the results of the actions taken to gain control of the zeta potential as the main driving force for the total amount of water to be transferred by electroosmosis in electrodialysis with inorganic membranes.

In the earlier work we observed a similarity between the curve for the zeta potential and the volumes of water transferred over the same range of pH in the solution. The work reported here was originated by this observation. It was decided to fix pH at several values in the range 1 to 14, keeping the current at a constant value to eliminate its influence. As a greater current is passed at the same pH value, more water is transferred because more faradays charge is passed. Keeping the current constant, the influence only of pH on the electroosmotic effect would be demonstrated.

For the control of pH, either 1M HNO_3 or 1M KOH is added as required. The amounts added, even though very small, are considered in the volume calculations. In all these runs, barium phospho-silicate membrane (BPS-20) supported in Whatman paper type 50 was used.

Figures 11 and 12 summarize the results obtained. These figures are two different ways of showing the same data. Figure 11 shows that there is a trend to transfer less water at higher pH at each current density that was tested. Figure 12 shows a very high amount of water transferred per faraday. The results obtained are controversial because each faraday there appears to be transporting more than one g-mole (18 g of H_2O). There are numbers well in excess of one hundred moles per faraday.

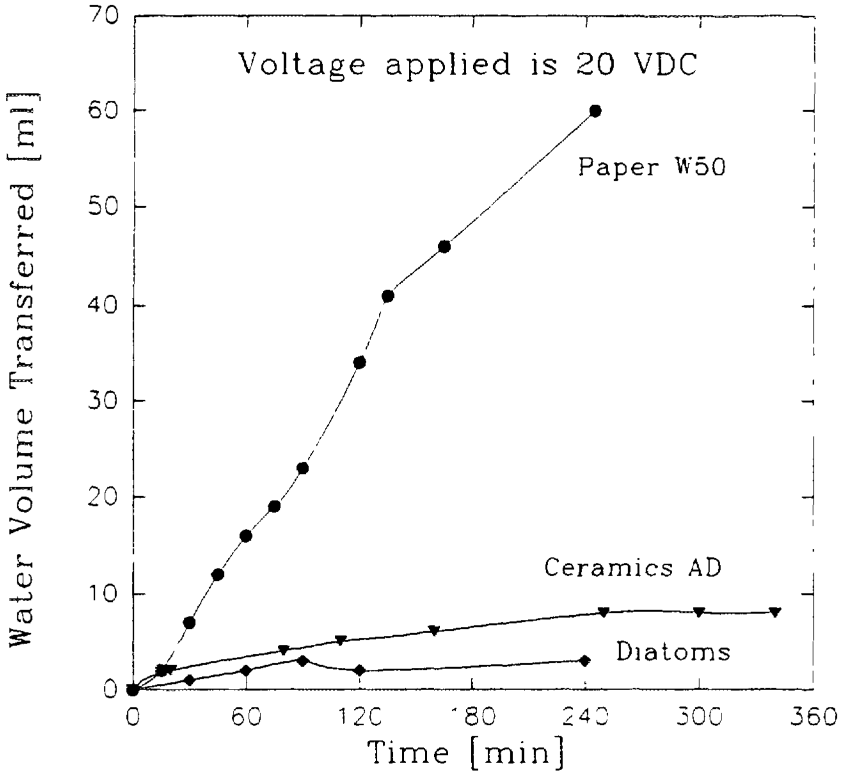


FIG. 6. Water volumes transferred by electroosmosis at 20V.

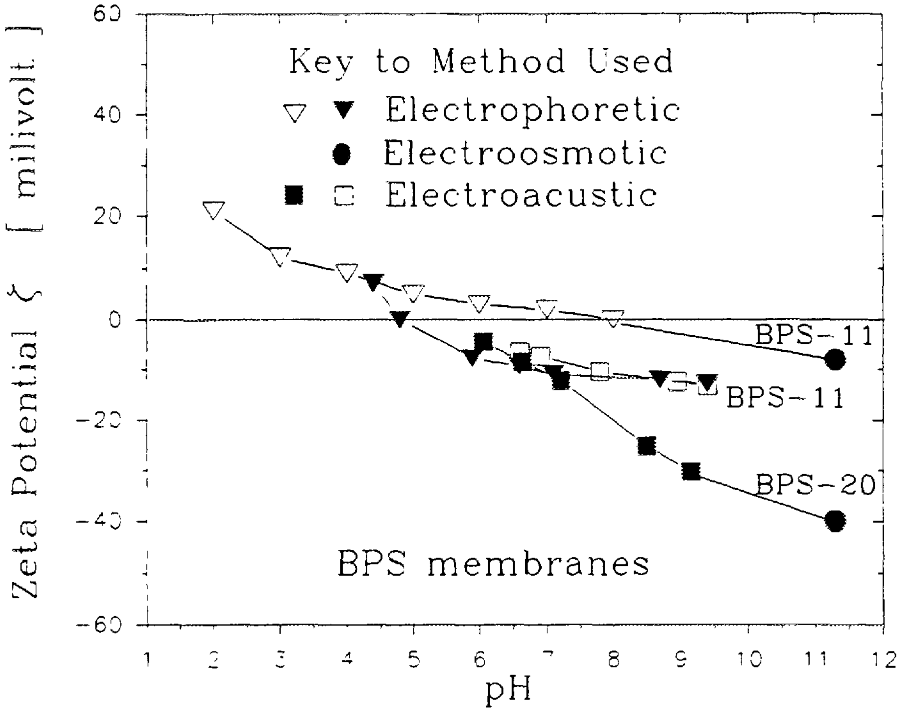


FIG. 7. Zeta potential for BPS membrane at pH2-7.

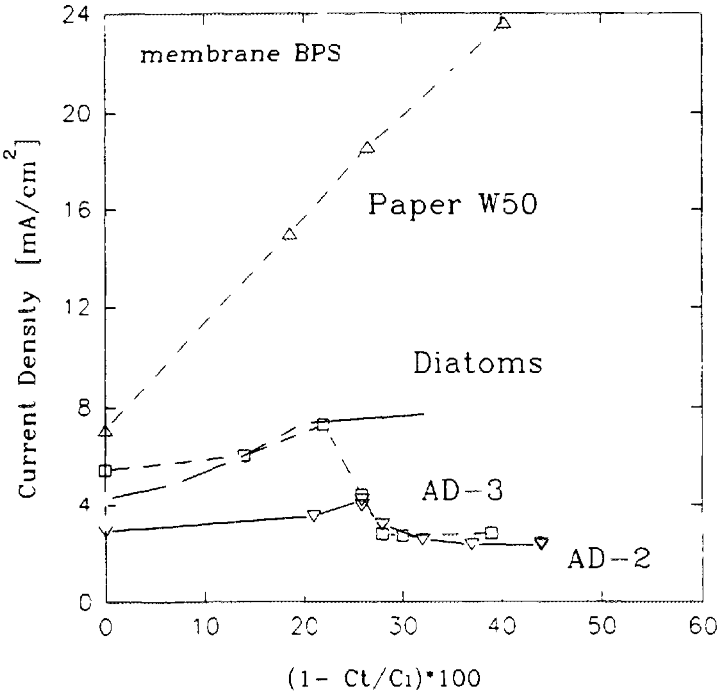


FIG. 8. Current density utilized to transfer ions with membrane BPS supported on several matrices

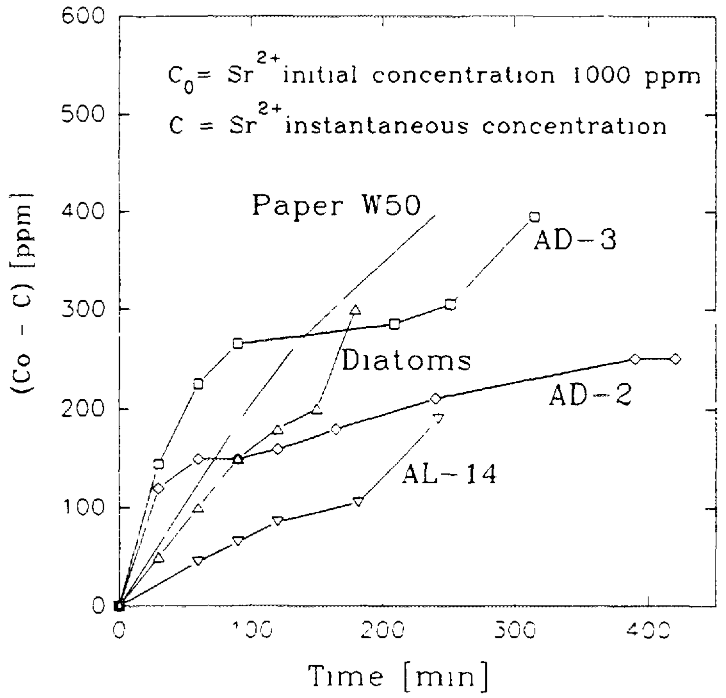


FIG. 9. Strontium transferred through membrane BPS supported by different matrices.

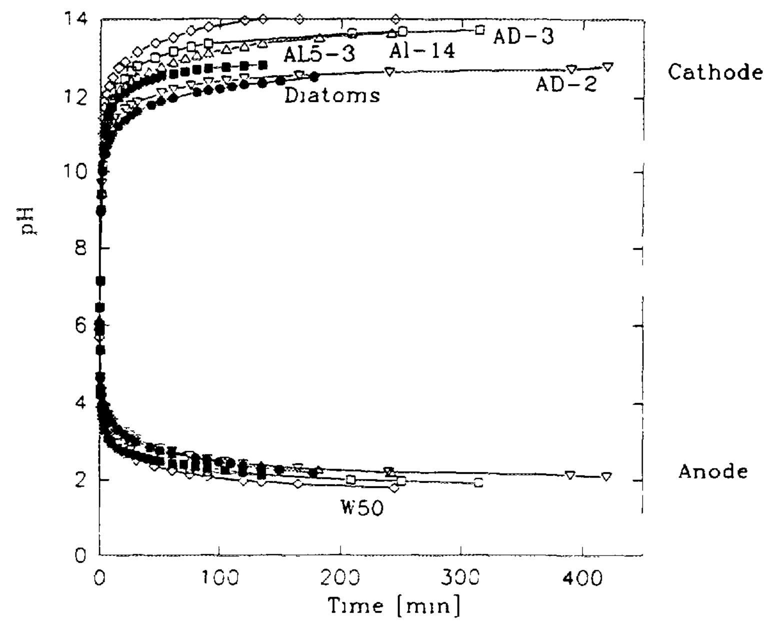


FIG. 10. Illustration of extreme separation of pH values for (high) cathode cell and (low) anode cell.

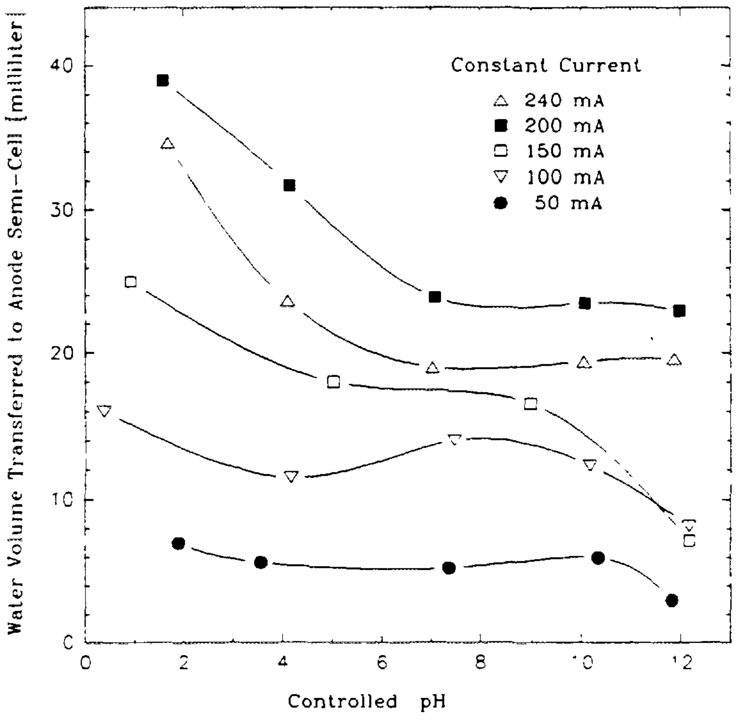


FIG. 11. Electroosmotic effect with an inorganic membrane BPS at constant currents of 50, 100, 150, 200 and 240 mA

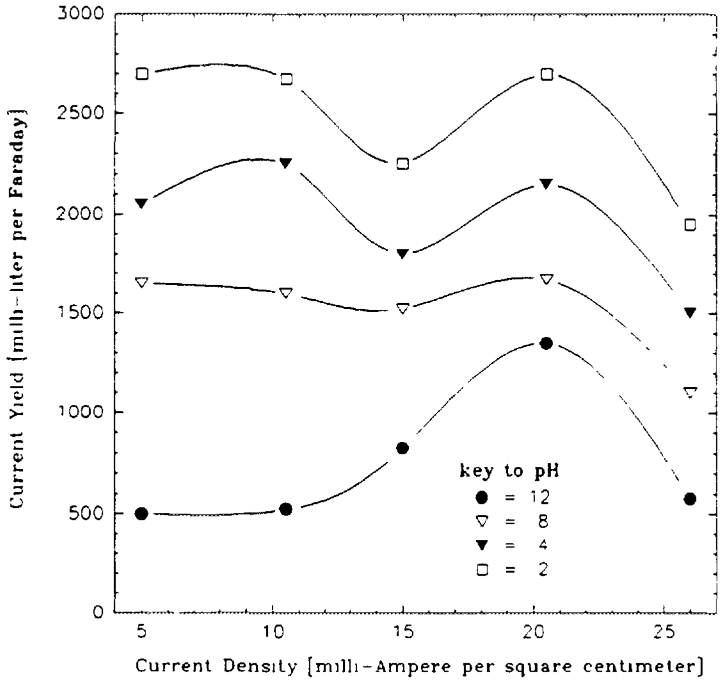


FIG. 12. Electroosmotic yield at different pH for the same current density.

2. MATHEMATICAL MODELING OF ELECTRODIALYSIS

The Nernst-Plank equation in the form presented by Goldman has been used to obtain the data needed to design a demonstration electrodialysis plant fitted with an inorganic porous membrane. The specific data needed in the model for each system are the membrane potential, the ionic mobility and the membrane thickness. This treatment falls in the realm of classical thermodynamics and is restricted to isothermal systems. Different treatment is advised to deal with organic membranes. Those can be treated as a series of barriers (corresponding loosely to the active centers). This treatment usually leads to an equation that requires data that are not available or too difficult or impossible to get. The resulting equations are too difficult to test experimentally.

The Nernst-Plank equation treats the flux J_j for ions j through the membrane in terms of the electrochemical potential. For ideal solutions, in a constant electric field inside the membrane, the equation known as the Goldman equation, is as follows:

$$J = -\frac{\alpha\mu RT(C_1 - C_n \exp\{\alpha\})}{d(1-\exp\{\alpha\})} \qquad \textbf{(1)}$$

where

μ is the ion mobility of species j,
d is the membrane thickness,
and α:

$$\alpha = \frac{zF\Delta\Psi}{RT} \qquad \textbf{(2)}$$

where

z	is the charge,
R	is the gas costant,
T	is the absolute temperature, and
$\Delta\Psi$	is the membrane potential.

From the theory of the absolute speed of reaction, a formula that is similar to Goldman equation can be obtained, if the factor $K_1 \Lambda^2 / d$ with the ionic permeability $\mu RT/d$ is identified:

$$J = -\frac{\alpha K_1 \Lambda^2 (C_1 - C_2 \exp\{\alpha\})}{d(1-\exp\{\alpha\})} \qquad \mathbf{(3)}$$

This equation can be used for the isothermal systems with negligible pressure effects, and with an equal mean distance between potential barriers, and also with constant electric field. Next, the relation between the flux and the instantaneous concentration can be considered as:

$$J = -\frac{V}{A} \cdot \frac{dC}{dt} \qquad \mathbf{(4)}$$

where

V	is the cell volume, and
A	is the membrane surface area.

Also, since the volumes on each side of the membrane are equal, the following relation for the anode and cathode concentrations can be obtained:

$$C_2 = 2C_0 - C_1 \qquad \mathbf{(5)}$$

where

C_o	is the initial concentration,
C_1	is the anode concentration, and
C_2	is the cathode concentration.

If to equations (1) and (4) are equated, the resulting equation integrated, we will get, at a constant electric field:

$$C = \frac{C_0 \exp\left\{-\frac{\alpha A \mu RT (1+\exp\{\alpha\})}{Vd(1-\exp\{\alpha\})} \cdot t\right\} + 2C_0 \exp\{\alpha\}}{1+\exp\{\alpha\}} \qquad \mathbf{(6)}$$

This is the model equation sought. In order to test equation 6, values for the membrane potential $\Delta\Psi$, the ion mobility u, and the membrane thickness d (in order to calculate the ionic permeability, $\mu RT/d$) need to be known.

2.1. ION MOBILITY

Ion mobility, "μ", is the ion velocity under unit driving force, in this case, unit electric field. The ion mobility can be estimated from:

$$\mu = \frac{6.469 \cdot 10^{6} \cdot \lambda}{z} \tag{7}$$

where

λ is the electrolytic conductivity for the ion Sr^{2+}, its value is 59.4 $cm^2\Omega^{-1}g\text{-}eq^{-1}$ at 25 °C.

The ion mobility is then estimated at $1.92 \cdot 10^{15}$ $cm^2 s^{-1} J^{-1}$.

2.2. MEMBRANE THICKNESS

Membrane thickness can be estimated from:

$$d = \frac{4m}{\pi \rho D^2} \tag{8}$$

where

m is the mass of membrane,
π is 3.14159,
ρ is the density of membrane, and
D is the diameter of membrane.

The value obtained is $2.235 \cdot 10^{-2}$ cm.

2.3. MEMBRANE POTENTIAL

A membrane potential arises from the double layers formed on the membrane surface;or for porous membranes, inside pores. It can be measured in an arrangement such as :

solution 1 / membrane / solution 2

So that, the membrane potential $\Delta\Psi = \Psi_2 - \Psi_1$. This value was measured experimentally as 100 mV.

To obtain the numerical equation to be tested, the ionic permeability from the literature was estimated, the membrane thickness was calculated from the experimentally measured values. The other value needed, namely, the membrane potential was measured with standard electrodes each side of the membrane. The results are shown in Fig.13. The potential difference during about 60 minutes was measured, which is a time lapse of interest for the design. During this time the concentrations changed to 1.5 from the initial concentration. This value will be used to design the electrodialysis equipment. From the graph it can be seen that the potential difference remains almost constant at 100 mV. So this value was used. With all these values replaced in the equation, the following numerical equation can be finally obtained:

$$C = -0.96 \cdot C_0 \exp\left\{1.44 \cdot 10^{-3} \cdot \frac{A}{V} \cdot t\right\} + 1.96 \cdot C_0 \tag{9}$$

with t in seconds and C in parts per million.

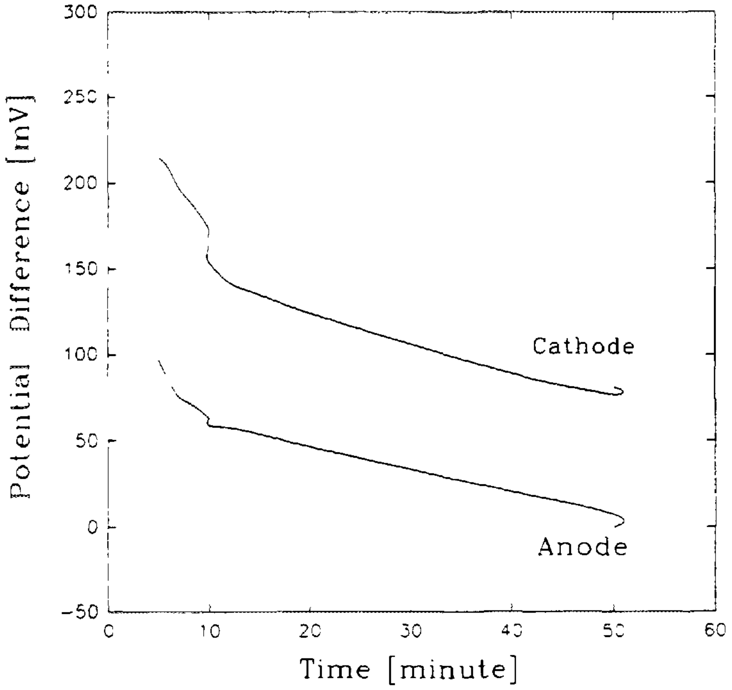


FIG. 13. Membrane potential for membrane BPS measured during the time lapse that will be used for testing the model equation and the design of the equipment.

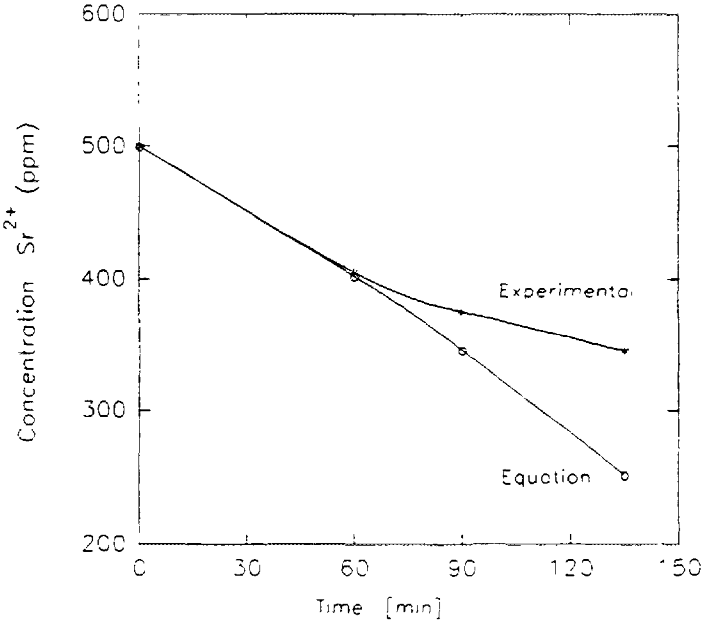


FIG. 14. Comparison of experiemental data with the data produced by the model equation for starting concentration of 500 ppm.

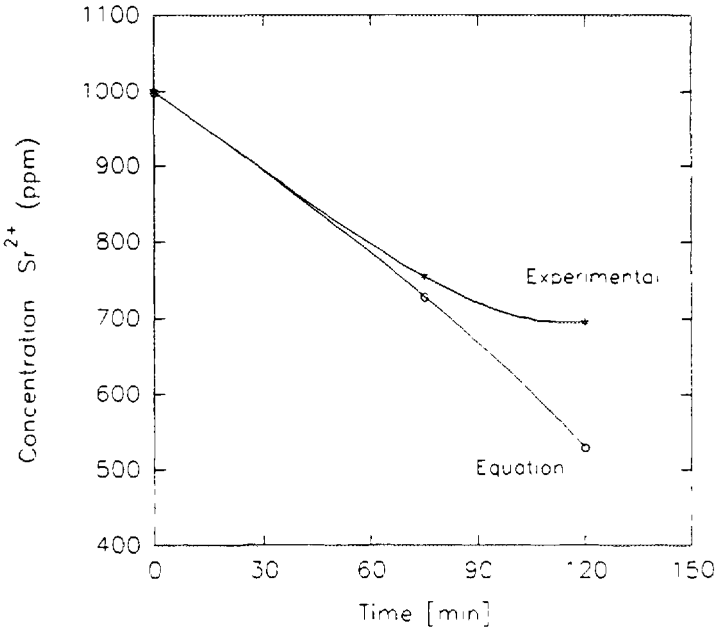


FIG. 15. Comparison of experimental data with the data produced by the model equation for starting concentration of 1000 ppm.

Figures 14 and 15 show the results of comparison of experimental data with the model equation. These two figures show that the model equation reproduces well the experimental data for up 60 minutes. This is enough time for design purposes.

3. THE USE OF INORGANIC ADSORBENTS

Homemade $MnO_2 \cdot SiO_2$ has been used to further decontaminate the final dilute effluent (permeate). Adsorbers may be of organic or inorganic nature. Organic materials known to be unstable at high levels of radiation, may be deformed at moderate temperatures and are not recommended for encapsulation in concrete. On the other hand, inorganic adsorbers are stable at high temperatures, may withstand higher levels of radiation and are more selective. Many inorganic materials have been tested, but here only one composite that is very easily manufactured and shows good results is described: $MnO_2 \cdot SiO_2$.Adsorber $MnO_2 \cdot SiO_2$ was prepared by reduction of $KMnO_4$ in the presence of sodium silicate at a basic pH.

Representative results for the stripping of electrodialysis permeates are shown in Table II, as decontamination factors and distribution coefficients. In the three cases shown, the decontamination factor was better than 98%.

A property to compare the performance of adsorbers is the distribution coefficient that is calculated as follows:

$$K_d = \frac{(c_i - c_f) \cdot V}{c_f \cdot W} \qquad \textbf{(10)}$$

TABLE II. DECONTAMINATION PERCENTAGE AND DISTRIBUTION COEFFICIENTS

Silica (%)	pH	Size (μ)	Decontamination	Distribution coefficients
10	5.8	less than 75	98.7 %	15500
17	10.9	between 250-420	98.2 %	11400
24	10.9	less than 75	98.5 %	13800

4. CONCLUSIONS

The use of inorganic materials, namely, inorganic membranes and inorganic adsorbents for treatment of radioactive waste is based on the fact that organic membranes have shown signs of deterioration when submitted to intense gamma radiation. So these inorganic materials should be preferred in the presence of high radiation fields. Inorganic materials are better from the standpoint of secondary waste to be immobilized for final disposal, and they also show a wider operational range with regard to pH and temperature.

These techniques have other advantages: they generate minimum amount of secondary waste, operate under mild conditions and have good process control variables. On the other hand, these techniques do not avoid some deficiencies. From one side, inorganic membranes do show a strong electroosmotic effect, in transferring large volumes of water to one electrode cell. This effect can be detrimental to the process. If the control of both the volume transferred and the direction of the electroosmotic flux is provided, this effect can be avoided and may be considered, as a desirable property. Recently it became known as electroosmotic dewatering.

4.1. ZETA POTENTIAL CONTROL

The results obtained confirmed the initial hypothesis as reported in the earlier work, that higher the pH, the lower the electroosmotic effect for the same current density. (It is of interest to study the number of moles of water transferred per faraday, in relation to the structure of water, for instance).

4.2. MATHEMATICAL MODEL

The electrodialysis model equation represents satisfactory the data for a reaction time up to 60 minutes.

4.3. INORGANIC ADSORBENT

The home-made inorganic adsorbent $MnO_2 \cdot SiO_2$ can effectively strip the electrodialysis tailings, leaving less than 1 ppm in the supernatant liquid.

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RADIOBIOLOGICAL WASTE TREATMENT-ASHING TREATMENT AND IMMOBILIZATION WITH CEMENT

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Abstract

This report describes the results of the study on the treatment of radioactive biological waste in the China Institute for Radiation Protection (CIRP). The possibility of radiobiological waste treatment was investigated by using a RAF-3 type rapid ashing apparatus together with the immobilization of the resulted ash. This rapid ashing apparatus, developed by CIRP, is usually used for pretreatment of samples prior to chemical analysis and physical measurements. The results show that it can ash 3 kg of animal carcasses a batch, the ashing time is 5-7 h and the ash content is less than 4 wt%. The ashing temperature not exceeding 450°C was used without any risk of high losses of radionuclides. The ash from the rapid ashing apparatus was demonstrated to be immobilized with ordinary silicate cement. The optimum cement/ash/water formulation of the cemented waste form was 35 ± 5 wt% cement, 29 ± 2 wt% water, and 36 ± 6 wt% ash. The performance of the waste form was in compliance with the technical requirements except for impact resistance. Mixing additives in immobilization formulations can improve the performance of the cemented ash waste form. The additives chosen were DH_{4A} flow promoter as a cement additive and vermiculite or zeolite as a supplement. The recommended formulation, i.e. a improved formulation of the cemented ash waste form is that additives DH_{4A} flow promoter and vermiculite (or zeolite) are added on the ground of optimum cement/ash/water formulation of the cemented waste form, the dosage of water, DH_{4A} and vermiculite (or zeolite) is 70 wt%, 0.5 wt% and ≤ 5 wt% of the cement dosage, respectively. The cemented ash waste forms obtained meet all the requirements for disposal.

1. INTRODUCTION

Radiobiological wastes are mainly produced from radioisotope applications in radiobiological tests and in radiation medicine. It is not possible to store these wastes for a long period because they are putrescible. They must be treated to become harmless. Generally, radioactive biological wastes are of very low activity. However, when high volume reduction factors are achieved by treatment, the ash residue will contain the considerable activity. From the standpoint of handling, transportation and disposal, immobilization of ash is necessary to reduce its potential dispersion. There is a variety of matrices that can be used for radioactive waste immobilization, hydraulic cement is most widely used for low level radioactive waste because of its low cost, shielding ability, and easy operation [1].

The RAF-3 type rapid ashing apparatus, developed in the China Institute for Radiation Protection for pretreatment of biological samples prior to chemical analysis and physical measurement [2]. Also, the apparatus can be used for treat a small amount of the radioactive biological wastes. To improve the performances of cemented waste form, additives were chosen and comparison of performances was made between cemented waste forms without and with additives.

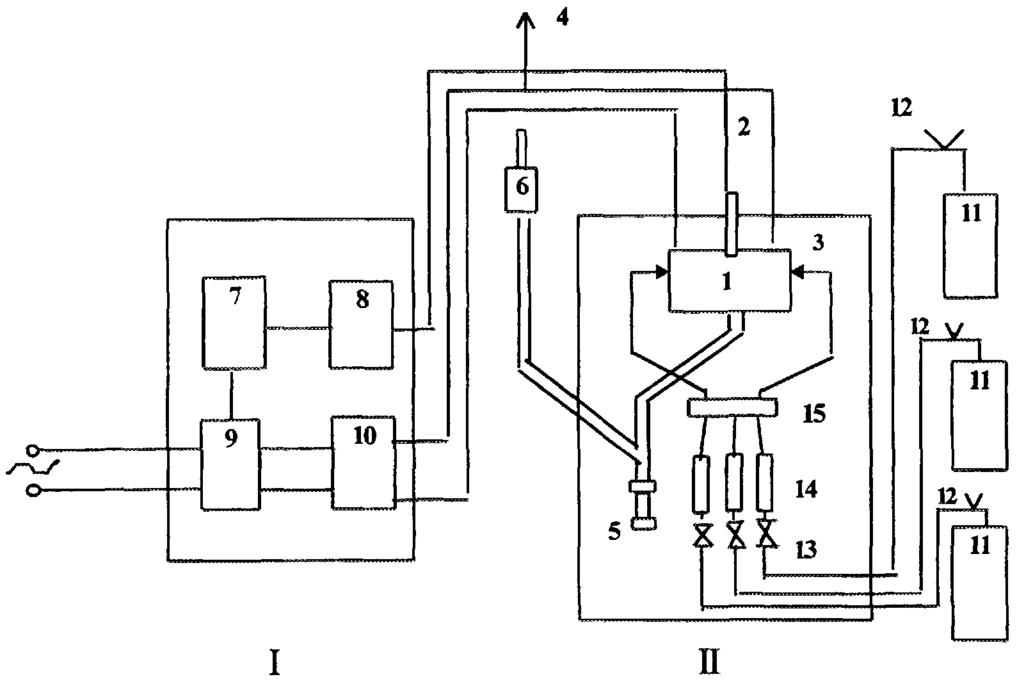
This report describes the feasibility study of biological wastes treatment using the rapid ashing apparatus and gives the results of an investigation of the immobilization of ash with cement and its additives.

2. TREATMENT BY ASHING

2.1. APPARATUS

2.1.1. Rapid ashing apparatus

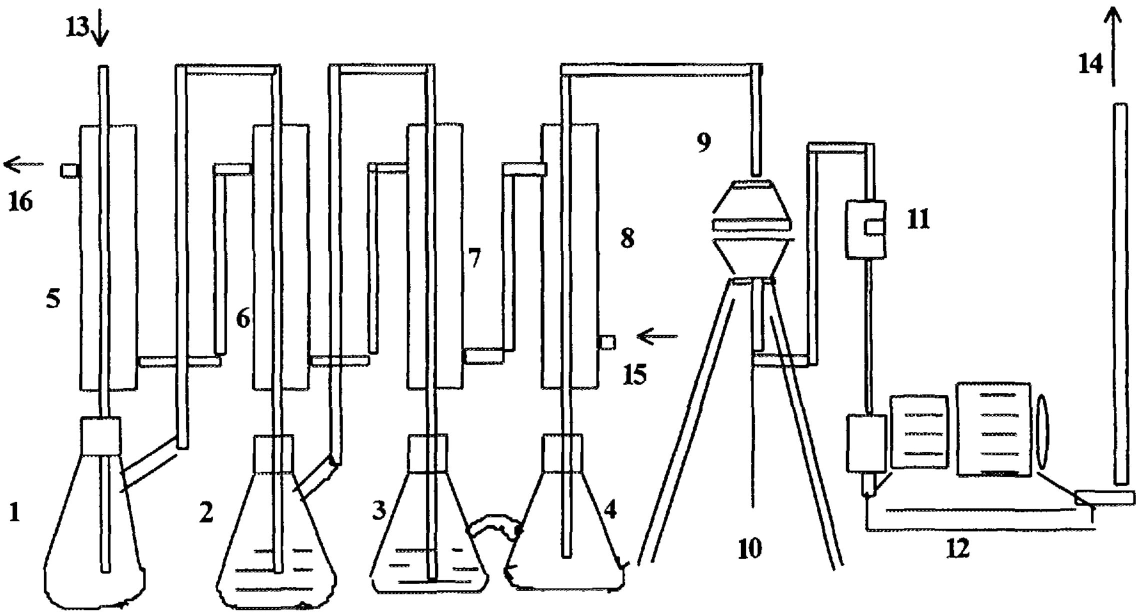
This apparatus consists of a rapid ashing furnace, an oxidation/reduction gases supply system and a temperature-programming cabinet. Figure 1 shows the schematic diagram of the apparatus.



I . Rapid ashing furnace **II . Temperature-programming cabinet**

1-chamber of furnace; 2- thermcouple; 3- inlet, 4- off-gases outlet; 5- waste liquid outlet; 6-observation window; 7- silicon controlled pressure regulator; 8- automatic programme controller; 9-silicon controlled rectifier; 10-transformer; 11- gas steel-bottle; 12- pressure-reducing valve; 13- needle valve; 14- flowmeter; 15-gase mixer

FIG. 1 Schematic diagram of the rapid ashing apparatus



1, 2, 3, 4–suction flask; 5, 6, 7, 8–condenser, 9- sampling head, 10- triangular prop stand, 11- flowmeter, 12-gas sampling pump, 13-off-gases inlet, 14-off-gases outlet, 15- water inlet, 16- water outlet

FIG. 2. Schematic of the aerosol sampling apparatus

2.1.2. Aerosol sampling apparatus

This apparatus mainly consists of a gas sampling pump (100 L/min.) and a sampling head (see Fig. 2). Because the off-gases are mainly O_2, NO_2, and a little water vapor and tar, four sets of suction flasks with condensers are positioned ahead, two of which contain 200 mL of 10 M NaOH solution, so that the gases harmful to the equipment can be eliminated before the off-gases pass through the sampling head.

2.2. ASHING PROCESS AND ACTIVITY DETERMINATION

2.2.1 Animal carcasses

Rats and rabbits were used in cold tests. Rats were used in radioactive tests. Before ashing, 1 mL of radioactive solution containing the radionuclides ^{134}Cs, ^{85}Sr, ^{60}Co, ^{65}Zn or ^{238}Pu as tracers were injected into each rat, then all the rats were killed.

2.2.2. Ashing process

The biological waste treatment undergoes two phases in the ashing furnace, i.e. a charring phase and an ashing phase. The charring of the biological waste is conducted under the inert gas N_2 atmosphere in order that safe and rapid charring could be carried out at a higher temperature. The ashing is conducted in an oxidizing atmosphere (O_2 and NO_2) in order to accelerate the oxidation/reduction process.

The ashing process is as follows:

When a stacked plate is pushed into the chamber of the furnace and power is on, the temperature in the furnace will be raised automatically. When the temperature reaches 150°C, the white steam and smoke can be observed through the observation window. This indicates that charring of biological wastes has begun. At this moment, the N_2 gas passage is opened. When the N_2 passage is closed, O_2 and NO_2 gases are allowed to enter the ashing furnace. The whole process usually takes 5-7 h depending on the waste type.

2.2.3. Measurement of γ-radionuclides

The crushed ash is dissolved in the 1:1 HCl solution, then γ-activity is measured by a well-type NaI (Tl) γ-scintillation counter. The filter paper is immersed in the 1:1 HCl solution and washed by distilled water. The activity in the filtered solution is measured with the same counter. The liquid from the exit and the NaOH adsorption solution are also counted.

2.2.4. Measurement of α-radionuclides

A fixed quantity of crushed ash is spread out in a measuring tray with anhydrous alcohol, then baked dry by an infrared lamp, and when flattened, it is measured by a FJ 2600 type α, β counter. The filter paper and the waste liquids are also baked in a measuring tray by an infrared lamp and measured with the same counter.

2.3. ASHING PARAMETERS

2.3.1. Selection of the ashing time

It is reported [3] that the ash content or the residual carbon content, which represents the extent of ashing, will be decreased with the increase of the ashing time. For rats, at the ashing temperature 400-500°C the satisfactory ashing can be accomplished in 5 h, at 350°C, 6 h of ashing is sufficient. For rabbits, it is sufficient to proceed wit ashing during 6-7 h. When the ashing time is more than 7 h, the residual carbon content of the ash can be reduced to minimum. However, for the purpose of waste disposal, it is not necessary to prolong the ashing time in order to obtain the ash without carbon.

TABLE I. ^{34}Cs, ^{85}Sr, ^{60}Co AND ^{65}Zn RECOVERY AFTER RATS ASHING

7 h of ashing time			^{134}Cs	^{85}Sr	^{60}Co	^{65}Zn
350°C	Ash	Injection amount (cpm)	2151	5765	1416	1186
		Measurement value (cpm)	2184	5739	1406	1187
		Recovery (%)	101 ± 6	99.5 ± 1	99.3 ± 1	100 ± 1
	Liquid wastes and aerosols		Undetected			
400°C	Ash	Injection amount (cpm)	2151	5765	1416	1186
		Measurement value (cpm)	2133	5611	1408	1182
		Recovery (%)	99.4 ± 1	97.3 ± 3	99.5 ± 1	99.7 ± 1
	Liquid wastes and aerosols		Undetected			
450°C	Ash	Injection amount (cpm)	2151	5765	1416	1186
		Measurement value (cpm)	2148	5795	1421	1172
		Recovery (%)	99.9 ± 2	100 ± 4	100 ± 1	98.9 ± 1
	Liquid wastes and aerosols		Undetected			

TABLE II. ^{238}Pu RECOVERY AFTER RATS ASHING

7 h of ashing time			^{238}Pu	Average
350°C	Ash	Injection amount (cpm)	269.2, 402.4	
		Measurement value (cpm)	374.4, 429.0	
		Recovery (%)	101.4, 104.4	103±2
	Liquid wastes and aerosols		Undetected	
400°C	Ash	Injection amount (cpm)	369.2, 438.4	
		Measurement value (cpm)	358.8, 418.4	
		Recovery (%)	97.2, 95.4	96.3±1.3
	Liquid wastes and aerosols		Undetected	
450°C	Ash	Injection amount (cpm)	438, 350, 561.5	
		Measurement value (cpm)	418, 342.8, 576,8	
		Recovery (%)	95.3, 97.9, 102.7	98.6±3.8
	Liquid wastes and aerosols		Undetected	

On the other hand, if the ashing time is too short, a higher residual carbon content will be obtained so that the stacked plate will be contaminated by black carbon, and it is difficult to clean. For example, at 350 or 450°C the ash content is <4 wt% for rabbits, while the residual carbon content in ash >45%, and the container wall is contaminated. Thus, the optimum ash time should be determined regarding both the ashing extent and contamination by black carbon of the container wall.

2.3.2. Selection of the ashing temperature

According to the experience in the biological sample pretreatment, the temperatures exceeding 550°C are usually not recommended because there were always the losses of radionuclides due to volatilization [4,5].

Thus, three safe temperatures have been selected: 350, 400, and 450°C. Table I and II give the recovery of radionuclides after ashing of the rats containing tracer radionuclides ^{134}Cs, ^{85}Sr, ^{60}Co, ^{65}Zn, and ^{238}Pu as well as the results of radioactive detection for aerosols and liquid wastes, respectively. The results show that complete recovery of the radionuclides can be achieved arrive at 100 % and no losses of the radionuclides were detected, I. e. the radionuclides contained in biological wastes remain in the ash.

3. ASH IMMOBILIZATION WITH CEMENT

3.1. CHARACTERIZATION OF THE ASH GENERATED FROM THE RAPID ASHING FURNACE

3.1.1. Particle-size distribution and volume density of the ash

There is a large amount of brittle bone-black in the ash generated from the rapid ashing furnace, so the particle-size distribution and volume density of the ash can be changed by stirring. The results of such changes are shown in Table III.

3.1.2. Water absorption capacity of the ash

The ash generated from the ashing furnace has a stronger absorption capacity for water. After 24 h of water immersion, the volume of the ash did not changed, but the water content in the ash reacted could attain to 48.2 wt% by filtering and 41.4 wt% by pumping. The water content was calculated as follows:

$$water=[(weight\ of\ wet\ ash-weight\ of\ dry\ ash)/weight\ of\ dry\ ash]x100\% \qquad \mathbf{(1)}$$

3.1.3. Adsorption and desorption of ^{134}Cs and ^{85}Sr on the ash

The adsorption distribution ratio (Kd, mL/g) for the adsorption equilibrium was calculated as follows:

$$Kd=C/C_0 \qquad \mathbf{(2)}$$

where

C is the activity in one gram of the ash, Bq/g, and
C_0 is the activity in one milliliter of solution, Bq/mL.

The desorption coefficient (Rd) can be calculated by the following equation:

$$Rd=(C_1/C) \times 100\% \qquad \mathbf{(3)}$$

where
C_1 is the activity in desorption liquid (Bq), and
C is the activity in one gram of ash before desorption, Bq.

The adsorption distribution ratio (Kd) and the desorption coefficient (Rd), for ^{134}Cs and ^{85}Sr are 0.89 mL/g, 82.6% and 128 mL/g, 21.8%, respectively.

3.2. CHOICE OF CEMENT TYPES

There are varieties of cement type, in which the ordinary silicate cement and blended cement are widely used for low and intermediate level radioactive waste immobilization. Recently, a lot of new type cement, such as alkali-activated slag cement, alumina cement, epoxy resin polymer-modified hydraulic cement, and improved Portland cement mortar with polyacrylates emulsion have been studied as immobilization matrices for waste solidification. The alkali-activated slag cement is a new cement product, which is made of 90% of a specific slag as a matrix, sodium silicate as a cohesion agent, and a little amount of silica cement [6]. Alumina cement, belonging to the expansion type cement, is a patented product of the China Institute of Building Materials. Two type of polymer cement mentioned above belong to the improved cement [7]. To obtain a good matrix suitable for immobilization of the ash, we compared their adsorption capacity for ^{85}Sr and ^{134}Cs and the performance of their solidified forms. The results are listed in Table IV.

TABLE III. PARTICLE-SIZE DISTRIBUTION AND VOLUME DENSITY OF ASH

Sieve size (mm)	Ash			Ash stirred one time			Grounded ash		
	Weight (g)	Content wt%	Density (g/cm$^{3)}$	Weight (g)	Content (wt%)	Density (g/cm^3)	Weight (g)	Content wt%	Density, g/cm^3
>10	102.3	26.2	0.18	29.6	7.7		0	0	
10-5	116.3	29.8	0.25	103.2	26.7		0	0	
5-3.2	14.6	3.7	0.28	16.0	4.1		0	0	
3.2-2	46.4	11.9	0.29	65.6	17.0		7.4	2.4	
2-1	29.0	7.4	0.34	56.8	14.7		41.5	13.2	0.53
1-0.5	20.0	5.1	0.38	41.6	10.8		53.8	17.2	
<0.5	61.3	15.7	0.40	73.2	19.0		210.8	67.2	0.62
Total	389.8	99.8	0.40	386.0	100	0.58 to 0.66	313.5	100	0.59
Density after two times stirring (g/cm^3)						0.75			

TABLE IV. CEMENT TYPES AND COMPARISON OF PERFORMANCE

No.	Cement type	Process parameter		Physical performance of the solidified form			Kd (mL/g)	
		W/C	Consistency (mm)	Compressive strength (MPa)	Porosity (%)	Density (g/cm^3)	^{85}Sr	^{134}Cs
1	Handan ordinary silicate cement	0.30	30	36.2	35.9	2.00	5.3	1.3
2	Datong ordinary silicate cement ^{1}	0.30	35	37.4	31.9	2.05	5.5	2.4
3	Datong ordinary silicate cement ^{2}	0.28	25	67.5		2.10		
4	Haining blended cement	0.30	35	26.6	35.4	2.05	7.2	6.3
5	Beijing alumina cement (I type)	0.30	28	30.2	52.3	2.05	23	2.9
6	Beijing alumina cement (II type)	0.35	28	33.8	41.7	1.99	14.5	3.2
7	Nanjing alkali-activated slag cement (1993)	0.30	50	46.2	48.2	1.69	996	110
8	Nanjing alkali-activated slag cement (1995)	0.32	45	71.2		2.02		
9	Epoxy resin-modified hydraulic cement	0.30	30	18.8	10.0	1.97	5.5	1.7
10	Improved Portland cement ^{3}	0.30	30	20.6	15.4	1.61	3.2	1.5

1. date of production: 1993; 2. date of production 1995; 3 improved with polyacrylates emulsion

From Table IV the following could be concluded:

(1) alkali-activated slag cement has the highest adsorption capacity for ^{85}Sr and ^{134}Cs, and its solidified form has the highest compressive strength: two type of polymer cement have the lowest adsorption capacity for ^{85}Sr and ^{134}Cs, and minimal porosity of their solidified forms;

(2) physical performance of both alumina cement solidified form and blended cement solidified forms are not better than that of the ordinary silicate cement solidified form;

(3) the same type of cement products but different place of production will make a difference in the performance of cement solidified forms.

Both alkali-activated slag cement and polymer cement are patented products, their sources are not wider than the ordinary silicate cement, and their price is higher. Thus, the ordinary silicate cement (Datong cement) was chosen as the immobilization matrix in our experiments.

3.3. IMMOBILIZATION WITH CEMENT

3.3.1. Specimen preparation

Certain amounts of cement, water, ash and additives were combined to provide the proper weight percentage compositions. After stirring for 3 minutes at a speed of approximately 137 rpm, the mixture was poured into the 4-5 cm diameter cylindrical glass container (beaker). Two samples were made for each formulation. After weighing, the specimen containers were covered to minimize the loss of water through evaporation and then set aside to cure for 28 days at ambient temperature. Daily checks were made for the presence of observable free standing water (bleeding water). The well cured specimens were taken out from the glass container (by breaking the beaker), the top and bottom surfaces of specimens were abraded with $0^{\#}$ coated abrasive to make its height-to-diameter ratio to be 1:1 - 1:1.1 [8].

3.3.2. Characterization methods

3.3.2.1. Compressive strength

Compressive strength of the formulation specimens was measured with Model NYJ-50 material test machine made in China. Compressive strength was calculated as follows:

$$P=0.01 \times (F/S) \qquad \textbf{(4)}$$

where

P is the compressive strength of the waste form (MPa),
F is the damage loading of the waste form (N), and
S is the cross section area of the waste form (cm^2).

3.3.2.2. Leachability

The National Standard of the People's Republic of China - GB 7023-86 "Long-term leach testing of solidified radioactive waste forms" was followed for the measurement of leachability. The leaching rate (LR) and the cumulative fraction leached (CFL) were defined as follows:

$$LR=(a_n/A_0) \times (1/t_n) \qquad \textbf{(5)}$$

$$CFL=(\sum a_n/A_0) \times (V/S) \qquad \textbf{(6)}$$

where

a_n	is the amount of the radionuclide leached in the n-th leaching interval (Bq),
A_0	is the initial amount of radionuclide in specimen (Bq),
V	is the volume of specimen (cm^3);
S	is the geometric surface area of the specimen immersed in leachant (cm^2),
t_n	is the time of the n-th leaching interval (d), and
$\sum a_n$	is the total amount of radionuclide leached out before the (n+1)th leaching interval (Bq).

3.3.2.3. Consistency and setting time

Consistency of cement mortars was measured by a falling cone consistometer. Needle penetration method was used to measure the setting time.

3.3.2.4. Thermal shock resistance

Thermal shock resistance of the specimens was measured by freeze-thaw cycle test. In the freeze-thaw cycle, the specimens were frozen for 4 h at -30°C and then set aside for 4 h at ambient temperature. After 25 cycles, the change in the compressive strength of the specimens was observed.

3.3.2.5. Water immersion

The specimens were immersed in water for 7 days at ambient temperature. Swelling of the specimens immersed was observed and their compressive strength was measured.

3.3.2.6. Impact resistance

Impact resistance of the specimens was expressed using the fall-down test results. After free falling down onto a concrete ground from a height of 9 m, the specimens should show no observable damage.

3.3.2.7. Fire resistance

Fire resistance of the specimens was determined by flame test, i.e. specimens were put on the flame of an alcohol blowtorch for 10 minutes. After the flame test, the specimens should exhibit no cracking.

3.3.2.8. Porosity

After 4 days of water immersion, the wet weight (G_W) and volume (V_W) of the specimens were measured, and then the specimens were dried during 2 days at 105°C. The dry weight of the specimens (G_d) was recorded. Porosity (HR) of the waste form can be calculated as follows:

$$HR=[(G_w-C_d)/V_w]\times 100\% \qquad \textbf{(7)}$$

3.3.2.9. Maximum central temperature during setting

A maximum central temperature during setting was measured under the adiabatic curing conditions for the cemented waste form. About 800 mL of cement-ash mortar stirred evenly was poured into a 1 L Dewar flask installed in a constant temperature bath. The variation of temperature was recorded. The bath water temperature was always kept close to the center temperature of waste block by manual control (normally, the temperature difference was not more than 2°C). The maximum center temperature and corresponding time were recorded.

3.3.3. Development of the cement/ash/water formulation

3.3.3.1. Requirements for the process and products

To successfully design a cement formulation for the immobilization of the ash, a number of process and product requirements have to be satisfied.

Process requirements:

(1) The product in a mixing stage must be fluid enough to ensure homogeneity. According to our test, the consistency of the cement-ash mortar should be in the range of 10-40 mm.
(2) No free water (bleed) should be observed on the surface after 24 h.
(3) Setting time of less than 1.5 days is desirable.

Product requirements: according to the National Standard of the People's Republic of China, the properties of the cemented waste forms should comply with the requirements listed in Table V.

TABLE V. CHARACTERISTICS REQUIREMENT FOR CEMENTED WASTE FORM

No.	Item	Characteristics requirement
1	Free standing water	No free standing water
2	Compressive strength	> 5 MPa
3	Leaching rate at the 42nd day	
	for ^{134}Cs	$\leq 1 \times 10^{-2}$ cm/d
	for ^{85}Sr	$\leq 1 \times 10^{-3}$ cm/d
4	Water immersion	No swelling, no cracking
5	Impact resistance	Falling down freely on concrete ground from a height of 9 m, no obvious damage
6	Freeze/thaw cycle test	Compressive strength > 5 × 0.85 MPa
7	Flame resistance	No cracking

3.3.3.2. Cement/ash/water formulation and ternary diagram

Water-to-cement ratio is an important parameter in the formulation design [9,10]. When the ash is solidified, a portion of the water is absorbed by the ash and thus water is not directly available for hydration of cement. A ratio of the weight (W) of the total water included in the formulation to the cement (C) can be expressed by the following equation:

$$W/C=(W_{abs}/C)+(W_{hyd}/C) \qquad \textbf{(8)}$$

where

W_{abs} is the weight percentage of the water absorbed within the ash, and
W_{hyd} is the weight percentage of the water used for hydration of cement.

TABLE VI CEMENT/ASH/WATER FORMULATION DESIGN TABLE

Q(%)	30				35				40				45			
n	W (%)	a (%)	W/C	a/C	W (%)	a (%)	W/C	a/C	W (%)	a (%)	W/C	a/C	W (%)	a (%)	W/C	a/C
0.10	14.5	55.4	0.48	1.85	15.5	49.5	0.44	1.41	16.4	43.6	0.41	1.09	17.3	37.7	0.38	0.84
0.20	19.2	50.8	0.64	1.69	19.6	45.4	0.56	1.30	20.0	40.0	0.50	1.00	20.4	34.6	0.45	0.77
0.30	23.0	47.0	0.77	1.57	23.0	42.0	0.66	1.20	23.0	37.0	0.58	0.93	23.0	32.0	0.51	0.71
0.40	26.4	43.6	0.88	1.45	26.1	38.9	0.75	1.11	25.7	34.3	0.64	0.86	25.4	29.6	0.56	0.66
0.45	27.9	42.1	0.93	1.40	27.4	37.6	0.78	1.07	26.9	33.1	0.67	0.83	26.4	28.6	0.59	0.64
0.50	29.2	40.7	0.98	1.36	28.7	36.3	0.82	1.04	28.0	32.0	0.70	0.80	27.3	27.7	0.61	0.62
0.55	30.6	39.4	1.02	1.31	29.8	35.2	0.85	1.01	29.0	31.0	0.73	0.78	28.2	26.8	0.63	0.60
0.60	31.9	38.1	1.06	1.27	30.9	34.1	0.88	0.97	30.0	30.0	0.75	0.75	29.1	25.9	0.65	0.58
0.65	33.0	37.0	1.10	1.23	32.0	33.0	0.91	0.94	30.9	29.1	0.77	0.73	29.8	25.2	0.66	0.56
0.70	34.1	35.9	1.14	1.20	32.9	32.1	0.94	0.92	31.8	28.1	0.80	0.70	30.6	24.4	0.68	0.54
0.80	36.1	33.9	1.20	1.13	34.7	30.3	0.99	0.87	33.3	26.7	0.83	0.67	31.9	23.1	0.71	0.51
0.9	37.9	32.1	1.26	1.07	36.3	28.7	1.04	0.82	34.7	25.3	0.87	0.63	33.2	21.8	0.74	0.43

TABLE VII RESULTS OF CEMENT/ASH/WATER FORMULATION TESTS

No	Composition (wt%)			W/C	a/C	Consistency of cement mortar (mm)	Compressive strength (MPa)
	Cement	Water	Ash				
1	30	26.5	43.5	0.88	1.45	very dry (not pourable)	
2	30	28	42	0.93	1.40	15	6.9
3	30	30.5	39.5	1.02	1.32	25	6.6
4	30	32	38	1.07	1.27	25	6.6
5	30	33	37	1.10	1.23	very thin (containing bleeding water)	
6	35	21	44	0.60	1.26	very dry (non pourable)	
7	35	24.5	40.5	0.70	1.16	8	8.9
8	35	26	39	0.74	1.11	10	6.4
9	35	27.5	37.5	0.79	1.07	20	9.1
10	35	29	36	0.83	1.03	26	7.7
11	35	31.5	33.5	0.90	0.96	30	9.8
12	35	35	30	1.00	0.86	very thin (containing bleeding water)	
13	40	20	40	0.50	1.00	very dry (non pourable)	
14	40	24	36	0.60	0.90	26	17.6
15	40	27.5	32.5	0.69	0.81	37	15.6
16	40	30	30	0.75	0.75	48	6.0
17	40	32	28	0.80	0.70	very thin (containing bleeding water)	
18	45	23	32	0.51	0.71	very dry (non pourable)	
19	45	27	28	0.60	0.62	51	12.2
20	44.7	27.4	27.9	0.62	0.62	--	7.1
21	45	31.5	23.5	0.70	0.52	55	13.0
22	45	36	19	0.80	0.42	very thin (containing bleeding water)	

The weight of water absorbed within ash is related to the weight of ash by

$$W_{abs}=n \times a \tag{9}$$

where

a is the weight percentage of the ash, and
n is the ratio of the weight percentage of the water absorbed within the ash.

Thus, equation (8) gives

$$W/C=(W_{hyd}/C)+(n \times a) \tag{10}$$

For the Datong OP cement, the ratio of water-cement is 0.26-0.34. As a matter of convenience, the W_{hyd}/C is considered as 0.3. In addition, we have

$$a+C+W=100\% \tag{11}$$

The following relation can be derived from (10) and (11):

$$W=[100 \ x \ n-(n-0.3) \times C]/(1+n) \tag{12}$$

According to equations (11) and (12), the formulations as highlighted in Table VI could be designed. On the basis of the formulations presented in Table VI, comparison of the formulations has been conducted. The results of formulation test are shown in Table VII. The results show that different formulations lead to a wide range of specimen consistency, from very dry (not pourable) to thin, and the formulations which will meet the process requirements (Section 3.3.3.1) fall in the range framed in a rough outline. Thus we can obtain a ternary compositional phase diagram of the cemented waste forms. Figure 3 is a compositional phase

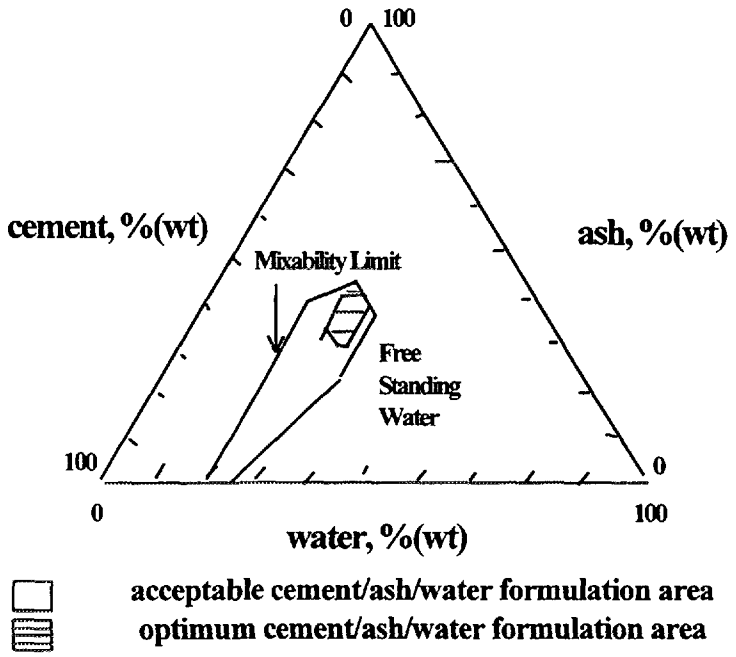


FIG. 3 Ternary compositional phase diagram for immobilization of ash with cement

diagram illustrating the region of formulation acceptable for the ash immobilization with cement. Constituents are expressed as weight percentage of cement, ash, and water. Formulations that contain the minimum water necessary to form a homogeneous mixable mortar fall on the line labeled “mixability limit”. None of these specimens exhibited free-standing water after 24 h cure time, but the formulations in the region of acceptable properties did not contain those for which the observable free standing water after 24 h was absorbed or combined into the waste form within one or two weeks.

The formulations that are on the boundaries of the envelope may not provide good reproducibility. It is necessary, therefore, to keep away from these boundaries as far as possible. A reasonable formulation should have good workability, which has to consider the fluidity of a cement-ash mortar, setting time, and high waste loading [11].

From the results shown in Table VI, when cement content is 30 wt%, 35 wt% or 40 wt%, the ash-to-cement ratio (a/C) is in the range of 1.40-1.27, 1.11-0.94 or 0.93-0.7, respectively. The water-to-cement ratio (W/C) shall be in the range of 0.93-1.06, 0.75-0.91 or 0.58-0.80, respectively.

Thus, the average values for a/C and W/C ratios are 1.05 and 0.82, respectively. The median formulation is 35 wt% of cement, 29 wt% of water and 36 wt% of ash. The variations of the process parameters are ±5 wt% of cement, ±2 wt% of water and ±6 wt% of ash. The optimum cement/ash/water formulations thus fall in the range of acceptable formulations, which is represented by the shaded area.

3.3.3.3. Characterization of the median formulation specimen

The specimens were prepared with the median of the optimum cement/ash/water formulation, that is 35 wt% of cement, 29 wt% of water and 36 wt% of the ash. The characteristics of the specimen are listed in Table VIII. The results show that the performance of the waste forms is in compliance with the technical requirements except for impact resistance.

TABLE VIII. PERFORMANCE MEASUREMENT RESULTS FOR THE MEDIAN FORMULATION SPECIMEN

No.	Item		Results
1	Cement-ash mortar consistency (mm)		25
2	Free standing water (%)		no
3	Setting time (h)		36
4	Maximum center temperature (°C)		65.5
5	Volume density (g/cm^3)		1.78
6	Compressive strength (MPa)		7.7
7	Compressive strength (after a week of water immersion) (MPa)		8.4
8	Compressive strength (after freeze/thaw test) (MPa)		8.3
9	Compressive strength (after flame test) (MPa)		7.9
10	Integrity after fall-down test		cracking
11	Total porosity (%)		47
12	Leachability at the 42nd day	^{134}Cs : LR (cm/d)	2.5×10^{-4}
		CFL (cm)	2.1×10^{-1}
		^{85}Sr : LR (cm/d)	9.0×10^{-4}
		CFL (cm)	4.4×10^{-2}
13	Appearance	Homogeneous, dense and free standing solid	

TABLE IX. COMPARISON OF CEMENT ADDITIVES EFFECT

No.	Additives	Mixture ratio		Mortar consistency (mm)	Solidified form compressive strength (MPa)	Others
		Additive/ cement	Water/ cement			
0	None	0	0.3	30	36.2	Guide sample
1	U type expansion additive	0.05	0.3	30	31.5	Raise anti-permeability
2	DH$_{4B}$ flow promoter	0.005	0.28	40		Reduce water dosage, setting time is 2-4 days
3	DH$_{4A}$ flow promoter	0.005 0.005	0.27 0.28	34 45	53.5 42.8	Reduce water dosage, setting time is 1-2 days
4	K$_w$ setting moderator	0.15	0.28	40	35.1	Big dosage of additive, setting time is 1-2 days
5	K$_w$ supper setting moderator	0.08	0.28	40	32.0	Bigger dosage of additives, setting time: 2-3 days
6	Rosin soap setting moderator	0.005	0.28	35		No obvious effect of reducing water dosage and moderated setting
7	Calcium lignosulfonate	0.002 0.005	0.26 0.26	40 50	38.6	Setting time is 3-4 days No setting
8	JRC-2 additive	0.005	0.26	45	38.9	Reduce water dosage Moderated setting
9	Vulcanizing agent	0.005	0.28	45	36.0	Reduce water dosage Moderated setting
10	S-F additive	0.005	0.28	40	35.0	Setting accelerator Reducing water dosage
11	MN additive	0.005	0.28	40	38.0	Setting promoter Reducing water dosage
12	Calcium saccharide	0.005	0.28	35		No setting

3.3.4. Investigation of the cement/ash/water/additives formulation

3.3.4.1. Selection of additives

Additives were used in order to improve the performance of the cemented waste forms. The additives were of two categories: one of which was cement additive, such as a setting promoter and setting moderator, and others were supplements such as vermiculite, zeolite and sodium silicate.

Such cement additives as sulfonate or naphthene, used to adjust the performance of cement and take an effect of a surface active agent, its dosage generally comprises 0.2-0.5% of the cement dosage in cement immobilization [12]. There is a variety of cement additives commercially available. 12 types of cement additives were tested in our experiment to compare their effect. The results are listed in Table IX.

TABLE X. EFFECT OF SUPPLEMENTS ON COMPRESSIVE STRENGTH OF SOLIDIFIED FORMS

No.	Supplement	Mixture ratio			Mortar	Solidified form
		Water/ cement	Supplement / cement	DH_{4A}/ cement	Consistency (mm)	Compressive strength (MPa)
0 *	None	0.28	0	0.005	45	42.8
1	Carbon fibre	0.283	0.01	0.005	45	51.9
2		0.289	0.03	0.005	40	36.3
3		0.285	0.05	0.005	13	29.2
4	Vermiculite	0.283	0.01	0.005	38	59.7
5		0.289	0.03	0.005	35	51.4
6		0.285	0.05	0.005	36	36.4
7	Zeolite	0.283	0.01	0.005	38	53.7
8		0.289	0.03	0.005	35	46.3
9		0.285	0.05	0.005	40	38.2
10	Microsilica	0.283	0.01	0.005	37	49.8
11		0.289	0.03	0.005	35	50.1
12		0.285	0.05	0.005	34	63.4
13	Sodium silicate	0.28	0.03	0.005	30	67.5
14	Sand	0.30	0.5	0.005	40	49.2

* as a guide sample

TABLE XI. ^{85}Sr AND ^{134}Cs ADSORPTION CAPACITY OF 5 TYPES OF SUPPLEMENT

Supplement	Specifications	Adsorption distribution ratio (Kd value) (mL/g)	
		^{85}Sr	^{134}Cs
Carbon fibre		20.8	16.2
Vermiculite	< 1 mm	232.8	3252
Zeolite	< 1 mm	45.8	4507
Microsilica	< sieve No. 80	11.5	0.5
Sand	< 1 mm	0.3	552

The results show that all the cement additives but S-F additive, MN additive and calcium lignosulfonate take an effect of reducing water dosage and moderated setting. Of which, DH_{4A} flow promoter has a stronger capacity of reducing water dosage, suitable effect of moderated setting, stable product performance and moderate price. Other additives, such as a U type expansion additive, can reduce porosity of a solidified form, but compressive strength of the solidified form will be reduced. K_w setting moderator and K_w super setting moderator, having dosage greater than other additives, will not lead to increase of compressive strength of the solidified forms. DH_{4B} flow promoter makes the setting time of mortar longer than 1.5 days. Thus, DH_{4A} flow promoter was chosen in the following tests as a cement additive.

Carbon fibre, vermiculite, zeolite, microsilica, sand and sodium silicate were tested separately. From Table X, it follows that all supplements used have the possibility of improving compressive strength of the solidified forms subject to correct dosage. For carbon fibre, the greater the carbon fibre/cement ratio, the lower compressive strength of the solidified forms. For microsilica, the greater the microsilica/cement ratio, the higher compressive strength of the solidified forms. For vermiculite and zeolite, compressive strength of the solidified form drops if the supplement/cement ratio is greater than 0.03.

TABLE XII. COMPARISON OF COMPRESSIVE STRENGTH OF CEMENTED ASH WASTE FORMS FROM VARIETIES OF FORMULATION

No	Mixture ratio					Consistency	Compressive strength
	W/C	Ash content (%)	DH_{4A}/C	Supplement	Supplement / C	(mm)	(MPa)
1	0.8	35		(no)		41	10.3
2	0.7	35	0.005			45	16.5
3	0.8	40	0.005			32	22.2
4	1.0	45	0.005			28	14.1
5	0.75	35	0.005	sable	0.1	36	10.4
6	0.7	35	0.005	sodium silicate	0.01	45	17.6
7	0.7	35	0.005		0.027	47	17.5
8	0.7	35	0.005		0.059	45	21.7
9	0.7	35	0.005		0.070	46	15.5
10	0.7	35	0.005		0.087	45	19.6
11	0.7	35	0.005	vermiculite	0.01	43	25.7
12	0.7	35	0.005		0.03	41	28.5
13	0.7	35	0.005		0.05	38	24.9
14	0.7	35	0.005		0.07	33	18.8
15	0.7	35	0.005		0.09	33	13.6
16	0.7	35	0.005	zeolite	0.01	39	14.4
17	0.7	35	0.005		0.03	39	21.4
18	0.7	35	0.005		0.05	36	27.6
19	0.7	35	0.005	carbon fibre	0.01	37	21.1
20	0.7	35	0.005		0.03	30	23.5
21	0.7	35	0.005		0.05	30	23.0

An adsorption test for ^{134}Cs and ^{85}Sr with 5 types of supplement has been done (see Table XI). The test results show that vermiculite and zeolite have stronger adsorption capacity for ^{134}Cs and ^{85}Sr than other supplements. Thus, vermiculite and zeolite were chosen as supplements.

3.3.4.2. Effect of additives on the cemented waste form performance

Table XII provides comparison of the cemented waste forms obtained from a variety of the cement/ash/water/additives formulations. From Table XII, we can see that the cement additive DH_{4A} increases flowability of the cement mortar raise, and improves compressive strength of the cemented waste forms. Both vermiculite and zeolite are good supplements since they can increase compressive strength of the cemented ash waste form. However their dosage must be less than 5 wt% of the cement dosage, otherwise compressive strength of the waste form will be lower. Thus, a recommended formulation of cemented ash waste form is that below 35 wt% of the ash content, the quantity of water, DH_{4A} and vermiculite (or zeolite) should be 70 wt%, 0.5 wt% and $\leq$ 5 wt% of the cement dosage, respectively.

3.4. PERFORMANCE APPRAISAL OF THE IMPROVED CEMENTED ASH WASTE FORM

To appraise completely the improved cemented ash waste form, their properties were determined and compared with that of the cemented ash waste form without additives or only having cement additive DH_{4A}.

TABLE XIII . COMPARISON OF PROPERTIES BETWEEN CEMENTED ASH WASTE FORMS WITH AND WITHOUT ADDITIVES UNDER RECOMMEND FORMULATION

No.		D1	D2	D3	DF	DZ	D
Mixture ratio	Water/cement	0.805	0.875	1.0	0.7	0.7	0.8
	Ash content (%)	35	40	45	35	35	35
	DH$_{4A}$/cement	0.005	0.005	0.005	0.005	0.005	0
	Supplements Supplement/cement	0	0	0	vermiculite 0.027	zeolite 0.027	0
Mortar consistency (mm)		55	45	36	51	45	25
Free standing water		no	no	no	no	no	no
Volume density (g/cm^3)		1.86	1.83	1.82	1.90	1.90	1.78
Compressive strength (MPa)		14.8	15.8	10.3	22.2	18.3	7.7
Compressive strength (after a week of water immersion) (MPa)		14.4	17.3	13.0	17.8	23.3	8.4
Compressive strength (after freeze/thaw test) (MPa)		14.0	17.2	12.2	17.5	18.3	8.3
Integrity after drop test		good	good		good	good	cracking
Leachability at the 42nd day							
LR (cm/d)	^{134}Cs	5.0E-4	5.4E-4	3.1E-4	6 7E-4	3.9E-4	3.7E-4
	^{85}Sr	9.1E-4	9.2E-4	1.0E-3	6.6E-4	6.2E-4	8.0E-4
CFL (cm)	^{134}Cs	4.7E-1	4.8E-1	4.6E-1	1.9E-1	1.0E-1	2.5E-1
	^{85}Sr	6.1E-2	6.2E-2	7.2E-2	4.5E-2	4.2E-2	4.2E-2

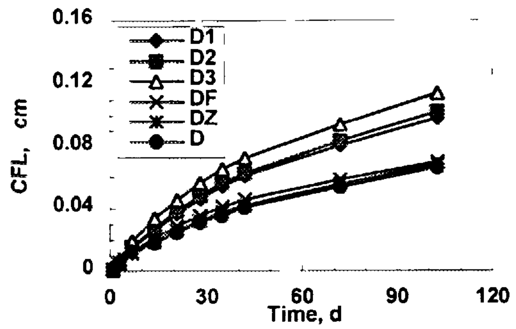


Fig. 4 CFL of ^{85}Sr from Various Cemented Waste Forms

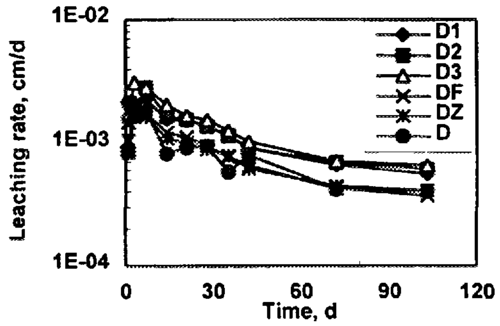


Fig. 5 LR of ^{85}Sr from Various Cemented Waste Forms

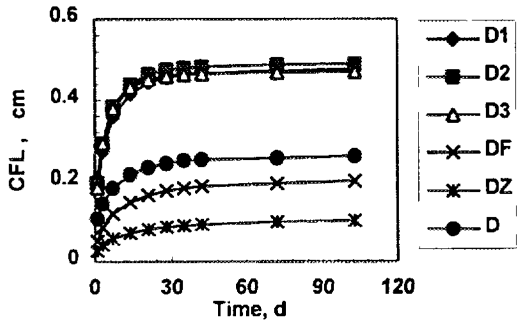


Fig. 6 CFL of ^{134}Cs from Various Cemented Waste Forms

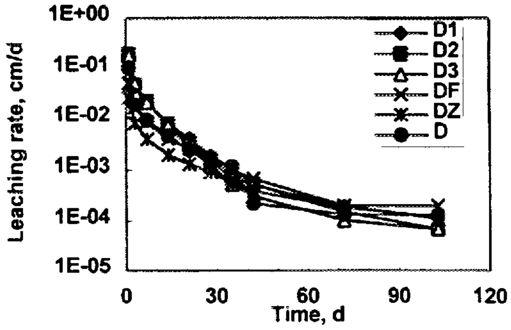


Fig. 7 LR of ^{134}Cs from Various Cemented Waste Forms

The results of the specimen measurements are listed in Table XIII. The variation of leaching rate and cumulative fraction of ^{134}Cs and ^{85}Sr with time are shown in Figs. 4, 5, 6 and 7, respectively.

The results show that compressive strength of the cemented waste form with cement additive DH_{4A} is higher than that without any additives by a factor of about 2 and their impact resistance is improved. However, their leachability is slightly lower. When both cement additive DH_{4A} and supplement vermiculite (or zeolite) are added, not only compressive strength of the waste form raises 2-3 times, but also leachability of the waste form, especially for ^{134}Cs, shows good improvement. After free falling down onto a concrete ground from height of 9 m, the specimens exhibited no cracking.

4. CONCLUSIONS

(1) The rapid ashing apparatus was used for biological waste treatment. Technical conditions for common biological sample ashing were adopted in the process including rapid charring, rapid ashing, and low ashing.

(2) The apparatus can ash 3 kg of animal carcasses in a batch. The ashing temperature was chosen within the range of 350-450°C. The ashing time is 5-7 h. The ash content is <4 wt%.

(3) The residual ash is loose and easy to dissolve. The residual carbon content in the ash is very low and it does not contaminate the container wall. If the ashing temperatures does not exceed 450°C, there is no risk of high losses of radionuclides.

(4) The ash is a type of light waste material which is liable to disperse. According to the radioactive waste disposal requirements, ash waste must be immobilized with a matrix to form a free standing solid. In-drum mixing was an effective and reliable treatment method for ash immobilization with cement.

(5) The optimal cement/ash/water formulation of the cemented waste form is 35 ± 5 wt% cement, 29±2 wt% water, and 36±6 wt% ash. The performance of the waste form was in compliance with the technical requirements except for the impact resistance.

(6) Mixing additives in immobilization formulations can improve the performances of cemented ash waste form. The additives were of two categories, one is a cement additive and other is a supplement. DH_{4A} flow promoter which has stronger capacity of reduced water dosage, suitable effect of moderated setting, stable product performance and moderate price was chosen as a cement additive. Vermiculite or zeolite which have stronger adsorption capacity for ^{134}Cs and ^{85}Sr were chosen as supplements.

(7) Compressive strength of the cemented waste forms with only cement additive DH_{4A} was larger than that without any additives by a factor of about 2 and their impact resistance was improved, but leachability was slightly lower. Adding both cement additive DH_{4A} and supplement vermiculite (or zeolite) in the formulation, not only compressive strength increased in 2-3 times, but also leachability especially for ^{134}Cs has a good improvement. And the drop test, the specimens of the waste forms did not reveal any cracking.

(8) The recommended formulation, i.e. a improved formulation of the cemented ash waste form is that additives DH_{4A} flow promoter and vermiculite (or zeolite) are added on the ground of optimum cement/ash/water formulation of the cemented waste form, the quantities of water, DH_{4A} and vermiculite (or zeolite) are 70 wt%, 0.5 wt% and ≤ 5 wt% of the cement dosage, respectively.

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MÖSSBAUER CHARACTERIZATION OF THE IRON SPECIES FROM THE RADIOACTIVE WASTE PROCESSING PRODUCTS

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Abstract

As part of the programme carried out in Romania in connection with the management of non-fuel cycle radioactive wastes, an experimental study has been performed on the low level aqueous waste (LLAW) processing products using mainly an "in situ" ^{57}Fe Mossbauer spectroscopy characterization method The study was focused on the LLAW treatment products obtained by chemical precipitation and on the conditioning of the products obtained by cementation

Starting from a series of Mossbauer spectra obtained on precipitates prepared in various experimental condition it was shown that the composition and structure of the final products strongly depend on the process parameters i e reagent composition and their concentration, the order and rate of the chemical addition, the ageing time, the presence of the coagulation promoters, etc Sometimes important effects were evidenced even at minor changes of the process parameters

The Mossbauer and other structural measurements on the cemented matrices resulted from the above mentioned precipitates or from other simulated LLAW concentrates have been also performed

1. INTRODUCTION

The precipitation of insoluble compounds is one of the oldest and most used process for the treatment of low level aqueous wastes while cementation is the most used process for the final conditioning of the sludge The precipitation can be performed either in a single step or by combined chemical treatment which mainly includes as radioactive carriers iron oxo-hydroxides, iron phosphate, calcium phosphate and copper ferrocyanide The contaminants together with other non-radioactive components are removed from LLAW during precipitation by different mechanisms such as coprecipitation, the isomorphous precipitation, scavenging by the particulate which is present, formed or added in the system, the sorption on precipitate by ion exchange, chemisorption or physical adsorption

All these processes are directly dependent on the precipitate properties and its structure, which are connected with the initial system composition and the precipitation procedure i e reagent concentration, rate and order of the addition chemicals, mixing rate, time and ageing conditions, etc In the case of cementation, the chemical nature and proportion of the precipitation products affect both the hydrolysis of the initial cement components and the reactions of metastable hydration constituents as well as the mechanical strength and the chemical resistance of the hardened cement system

Generally, the study of the precipitation products and their behaviour during the cementation and long term disposal is extremely difficult because of their complexity (phase composition and structure) and the lack of the non-destructive analytical methods By chance, iron is commonly present in nearly all systems and following naturally ^{57}Fe isotope by Mossbauer Spectroscopy (MS) is possible to valuable information about the composition, structure and coordination of the iron containing species

This work was carried out in order to establish the performance level and the limits of the MS use for the study of LLAW processing products Deeper knowledge of the implied mechanisms and of the structure and properties of the products could lead to the improvement of the LLAW processing and characterization of the final waste

2. MÖSSBAUER SPECTROSCOPY

MS is based on the resonant recoilless absorption-emission processes of gamma rays. The most used isotope is ^{57}Fe. The Mössbauer effect appears when the isotope is bonded in lattice. The *recoilless fraction* (f) of the events is given by:

$$f=\exp(-k_\gamma^2\langle x^2\rangle) \quad (1)$$

where

k_γ is the magnitude of the gamma wave vector, and

$\langle x^2 \rangle$ is the mean squared displacement of the atoms in the lattice, due to the lattice vibrations.

Information about the iron atom, its surrounding, valence, spin and magnetic state can be obtained via the hyper fine interactions between nucleus and extranuclear fields (electric field gradient, internal magnetic field, electronic charge distribution). Such information is obtained from the energetical Mössbauer parameters: isomer shift (IS), quadruple splitting (QS), and hyper fine magnetic field (HF). Information about lattice vibrations, site populations, vacancies, defects, bulk or surface coordination of the atoms could be obtained from the relative area, experimental line width and the dependence of the Debye-Waller factor on temperature.

The Mössbauer investigations are performed on well or purely crystallized compounds, amorphous or glasses containing Mössbauer atoms, frozen solutions, metallic, covalent or coordination compounds processed in various forms: mono-crystals, polycrystalline powders, fine particles, thin layers, etc. Mössbauer measurements versus temperature are necessary in order to put in evidence magnetic transitions in various materials (including superparamagnetic transitions) or crystallographic transitions. The presence of at least one iron compounds in the precipitates of the low and intermediate level liquid wastes makes the Mössbauer spectroscopy one very useful tool for the investigations of the processes appeared in the radioactive waste treatment.

3. OBJECTIVES OF THE STUDIES

The main research directions, strongly connected to the stipulated objectives were:

- Study of iron chemical species in the precipitates obtained during the treatment of LLAW using iron compounds. Study of the influence of the precipitation procedure on the precipitate behaviour and decontamination factor.

- Mössbauer methodology and the characterization of iron species from radioactive waste processing products conditioned by cementation:

The following section was divided in five subsections:

4.1. Study of the iron precipitates obtained during the LLAW treatment.
4.2. The anion influence on the hydrated oxides formed by Fe^{3+} and Fe^{2+} precipitation.
4.3. The structural modifications in the iron hydrated oxides induced by foreign cation.
4.4. Precipitation processes with alternative or simultaneous presence of bivalent and trivalent iron ions
4.5. The influence of the precipitation procedures on the decontamination factor.

The purpose of Section 5 is to apply MS for the characterization of the iron components in the cement matrix obtained by the radioactive waste conditioning. The study was roughly divided in three parts:

5.1. Dry and hydrated cements
5.2. Precipitates simulating the precipitation process sludge cemented in the cement matrix
5.3. The influence of the cemented organic complexants on the hydration process

The greatest part of the above mentioned studies implied especially the Mössbauer spectroscopy. A ^{57}Co(Rh) radioactive source and a constant acceleration spectrometer were used. The Mössbauer investigations were performed at room temperature (RT), at 80K, and even at 4.2K. Some complementary data were obtained by X-ray diffraction and electron microscopy measurements.

Study of iron chemical species in the precipitates obtained during the treatment of LLAW using iron compounds. The influence of the precipitation procedure on the precipitate behaviour and decontamination factor.

4. STUDY OF THE IRON CHEMICAL SPECIES OBTAINED DURING CHEMICAL PRECIPITATION

4.1. STUDY OF THE IRON PRECIPITATES OBTAINED DURING THE LLAW TREATMENT

(a) pure iron oxo-hydroxide starting from Fe^{2+} and Fe^{3+} salts and sodium and calcium hydroxide
(b) calcium phosphate + copper ferrocyanide
(c) iron hydroxide + copper ferrocyanide
(d) iron hydroxide + calcium phosphate
(e) iron hydroxide + calcium phosphate + copper ferrocyanide

From the beginning it must be emphasized that the iron products obtained by fast neutralization, as in radioactive waste treatment, have quite different structures compared with iron oxides and hydroxides prepared by slow addition of the reactants when intermediate forms may be precipitated and redissolved during a long process. Generally they are poorly crystallized or even amorphous compounds.

The final precipitates obtained in (a)-(e) laboratory processing are dependent on three main factors: (i) initial iron compound, (ii) hydroxide used for precipitation, (iii) order of the reagent addition. As for the role of the polyacrylamide (PAM), it is known, as one promoting the particle agglomeration. The three above mentioned factors influences type, phase ratio and particle size in the final products.

(A) The iron hydroxide precipitation systems

The study of this system is nevertheless the most important, being the starting point in the subsequent studies on the double and triple co-precipitation systems. Iron hydroxide has been prepared from ferric chloride or ferrous sulphate (as the Fe^{3+} and respectively Fe^{2+} ions source) and from sodium or calcium hydroxide as neutralization reagent [1, 2]. Generally, the Mössbauer spectra obtained on such samples consist of broad quadruple and magnetically split patterns, with relative area depending on the (i)-(iii) factors.

The Mössbauer line broadness suggests an overlap of various contributions of uneqivalent iron positions, relaxation processes or multiphase composition. Nevertheless the best fit of the Mössbauer spectra could be obtained only using a complex algorithm, based on the distribution of the hyper fine parameters. To avoid such complications, an usual fitting procedure based on the model of the finite number of iron representative position were used. Owing the superposition of the above mentioned effects, many difficulties arise from the correct assignation of the Mössbauer patterns. Sometimes the hyper fine field values cannot label a given magnetic phase while the central doublet pattern can arise both from a real paramagnetic phase or from a superparamagnetic one. A certain lack of precision is induced also in the determination of the iron phase relative content. All these difficulties require a complementary method of analysis and correspondingly the X-ray measurements were used. Because of poorly crystallized precipitates, a part of the iron compounds exhibit very low and broad signals in the diffraction picture. So only a strong correlation of both methods can lead to an adequate interpretation of the specific mechanism.

TABLE I. MÖSSBAUER PARAMETERS ON SOME IRON HYDROXIDE PRECIPITATES MEASURED AT 295K

Syst	Samp	Precipitate Procedure	Subs.	H (T)	QS (mm/s)	IS (mm/s)	A (%)
a	71	900 mL H_2O + 1.5 g $Ca(OH)_2$+4.5 mL $FeCl_3$ + 0.2 ml PAM , pH10.5 ÷ 11	1	-	0.70	0.30	100
a	94	800 mL H_2O + 1.5 g $Ca(OH)_2$+ 20 mL $FeSO_4$ + 0.2 mL PAM , pH7.5÷8	1	-	0.66	0.33	100
a	3	900 mL H_2O + 2 mL $FeCl_3$ +NaOH, up to pH7	1	48.8	-0.31	0.30	8
			2	47.2	-0.32	0.36	42
			3	-	0.64	0.39	50
a	93	800 mL H_2O + 5 mL $FeSO_4$+5 mL NaOH, pH8÷8.5	1	48.4	-0.07	0.24	30
			2	45.0	-0.07	0.50	44
			3	-	0.55	0.36	26

TABLE II. MÖSSBAUER PARAMETERS ON SOME IRON HYDROXIDE PRECIPITATES MEASURED AT 80K

Syst	Samp	Precipitate procedure	Subs	H (T)	QS (mm/s)	IS (mm/s)	A (%)
a	71	900 mL H_2O + 1.5 g $Ca(OH)_2$+4.5 mL $FeCl_3$ + 0.2 mL PAM, pH10.5 ÷ 11	1	-	0.93	0.39	34
			2	-	0.55	0.39	66
a	94	800 mL H_2O + 1.5 g $Ca(OH)_2$+20 mL $FeSO_4$ + 0.2 mL PAM, pH7.5÷8	1	50.8	0.08	0.43	14
			2	48.3	0.06	0.47	15
			3	45.8	-0.09	0.45	19
			4	42.7	-0.05	0.45	18
			5	36.6	-0.26	0.33	11
			6	-	0.59	0.42	22
a	3	900 mL H_2O + 2 mL $FeCl_3$ +NaOH up to pH7	1	52.6	-0.17	0.49	73
			2	51.1	-0.18	0.46	27
a	93	800 mL H_2O + 5 mL $FeSO_4$+5 mL NaOH pH8÷8.5	1	53 6	0.04	0.48	14
			2	51.6	0.06	0.52	13
			3	51.4	0.05	0.30	24
			4	48.9	-0.12	0.48	12
			5	44.6	-0.18	0.51	14
			6	-	0.54	0.45	23

The mean hyper fine field value of the RT Mössbauer spectra are around 48.0 T for samples obtained from $FeCl_3$ and around 46.0 T for samples obtained from $FeSO_4$. The 80K Mössbauer spectra involve hyper fine field values of around 52.0 T and respectively 50.0 T. The quadruple split value of the central pattern (paramagnetic doublet) is between 0.50 and 0.90 mm/s for all samples and temperatures. In Table I and II the Mössbauer parameters of four representative samples measured at RT and 80K are shown.

TABLE III. 295K MÖSSBAUER PARAMETERS OF SOME DOUBLE AND TRIPLE PRECIPITATES

Syst	Samp	Precipitate procedure	Subs.	H (T)	QS (mm/s)	IS (mm/s)	A(%)
d	8B	900 mL H_2O + 5 mL $CaCl_2$+ 10 mL Na_3PO_4+ 7 mL NaOH+2 mL $FeCl_3$, pH8÷8.5	1 2	-	0.94 0.53	0.32 0.31	54 46
d	9	900 mL H_2O + 5 mL $CaCl_2$ +10 mL Na_3PO_4 + 2 mL $FeCl_3$+7 mL NaOH, pH8-8.5	1 2	-	1.01 0.61	0.27 0.26	26 74
d	76	900 mL H_2O + 4.5 mL $FeCl_3$ + 1.5 g Can + 3 g Na_3PO_4, pH8÷8.5	1 2	-	1.07 0.65	0.33 0.32	14 86
d	77	4.5 mL $FeCl_3$ + 3 g Na_3PO_4+ 900 mL H_2O + 1.5g $Ca(OH)_2$, pH8	1 2	-	1.00 0.58	0.31 0.31	26 74
e	100	800 mL H_2O + 20 mL $FeSO_4$+ 1.5g $Ca(OH)_2$/100 + 10 mL $CuSO_4$+5 mL $Fe(CN)_6$ + 10 mL Na_3PO_4, pH8÷8.5	1 2 3	-	1.07 0.62 -	0.32 0.36 -0.8	16 80 4
e	95	900 mL H_2O + 5 mL $FeSO_4$+ 5 ml NaOH + 5 mL $CuSO_4$+5 mL $K_4[Fe(CN)_6]$ +5 mL $CaCl_2$+10 mL Na_3PO_4, pH7	1 2 3	-	0.91 0.50 -	0.29 0.34 -0.05	56 33 11
e	40	900 mL H_2O + 2 mL $FeCl_3$ + 9 mL NaOH + 5 mL $CaCl_2$ + 10 mL Na_3PO_4+ 5 mL $CuSO_4$ + 5 mL $K_4[Fe(CN)_6]$, pH8	1 2 3	-	1.15 0.64 -	0.33 0.36 -0.11	33 64 3
e	38	900 mL H_2O + 2 mL $FeCl_3$ + 5 ml $CaCl_2$ + 10 mL Na_3PO_4 + 9 mL NaOH + 5 mL $Fe(CN)_6$ + 5 mL $CuSO_4$, pH8.5 ÷9	1 2 3	-	0.98 0.59 -	0.32 0.35 -0.09	41 53 6

Corroborating the preparation conditions with the above mentioned parameters, the magnetic pattern in $FeSO_4$ based precipitates, could be due to defected magnetite (Fe_3O_4), γ-Fe_2O_3, δ-FeOOH or β-FeOOH, whereas for the $FeCl_3$-base precipitates to α-Fe_2O_3, γ-Fe_2O_3 or δ-FeOOH [3]. The superparamagnetic part (smaller size particles) of the mentioned compounds together with some other paramagnetic phases can also contribute to the central doublet. At 80K, a lower superparamagnetic phase concentration is expected. Comparing Table I with Table II, it can be seen the $FeSO_4$ based precipitates (sample 94) contain more than 20% of paramagnetic phase at 80K, compared with the insignificant percentage in the $FeCl_3$-base precipitates.

Different samples from every considered system were measured by XRD The results infer for all $FeSO_4$ base samples the presence of Mossbauer δ-FeOOH in agreement with the Mossbauer results No direct evidence for Fe_3O_4 was found In the sample 94 the presence of Mossbauer β-FeOOH was pointed out, in agreement with the Mossbauer results On the other side, an amorphous phase was observed for the $FeCl_3$-base systems and in some other samples the δ-FeOOH was at presence too

Once again, considering the preparation conditions and the Mossbauer results, or γ-Fe_2O_3 could be most probably assigned to the X-ray observed disorder phase Accordingly, function of the preparation condition the $FeCl_3$-base precipitates seems to contain δ-FeOOH, α or γ-Fe_2O_3 or a possible mixture between these phases The precipitate granulation seems to be lower for $FeCl_3$ -base samples than for $FeSO_4$ ones, and also for $Ca(OH)_2$ as neutralization reagent than for Na(OH) ones The order reagent addition influence the precipitate granulation too

(B) Double and triple precipitates

The results obtained on the copper ferrocyanide precipitate in the multi-component system show that the initial iron containing compound is generally not influenced by the formation of other compounds, the Mossbauer parameters being almost the same as in pure compound So, a deep analysis becomes necessary only on systems (d) and (e)

The RT Mossbauer results for four significant samples from (d) and (e) systems are presented in Table III The considered results are valid both for bi- and tri-components systems, but the final precipitate are influenced by the addition of the time of Na_3PO_4 or $FeCl_3$ The RT Mossbauer spectra corresponding to systems (d) were fitted with only two doublets, one of these assigned to the superparamagnetic hydrated phase (Q_S= 0 70 mm/s) and the second one to a very defect iron phosphate (Q_S= 1 1 mm/s)

The XRD data show the presence of only β-Ca-pyrophosphate (not visible in ^{57}Fe MS) The lack of any form of iron phosphate from XRD spectrum seems to be consistent with very poor crystallinity of this precipitate, in agreement with the Mossbauer results

The evolution of the iron phosphate phase content from the RT Mossbauer spectra, opposite to the evolution of the active calcium phosphate one, depends on the intermediary reaction components [2,4] If the formation of the unstable iron phosphate is favoured, the trend is to transform it into calcium phosphate

For the most complex system (e), the RT Mossbauer spectra were fitted with two doublets (corresponding to the previous analyzed iron phases iron oxo-hydroxide and iron phosphate) and a singlet with Mossbauer parameters specific to ferrocyanide No definite signal assigned to ferrocyanide was evidenced in the XRD picture Connecting with the M S results, this behaviour suggest a poorly crystallized ferrocyanide

4 2 THE ANION INFLUENCE ON THE HYDRATED OXIDES FORMED BY Fe^{3+} AND Fe^{2+} PRECIPITATION

Since other iron salts such as Fe_2(SO)3, $Fe(NO_3)_3$ and $FeCl_2$ could be iron ion suppliers, it was considered of interest to extend the study to the anions corresponding to these salts and to compare then with the precipitates prepared from $FeCl_3$ and $FeSO_4$ In all cases the neutralizing reagent was NaOH For each system, many samples were prepared following various precipitation runs [5] The sequence of the addition, reagent dilution, pH and ageing time was modified

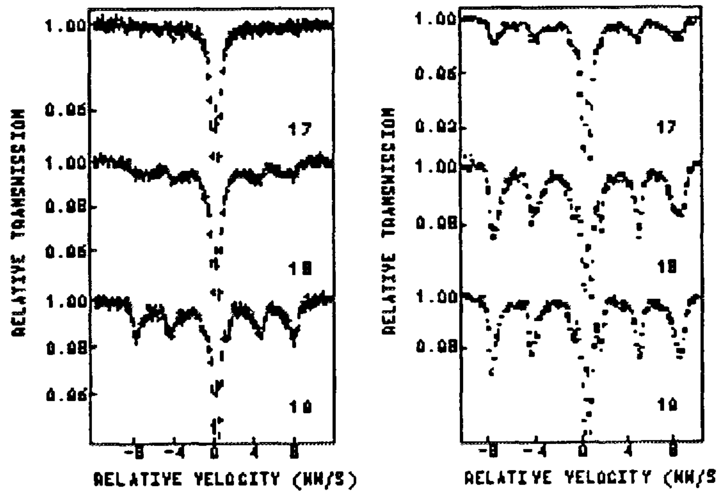
When the hydrated oxides are obtained by Fe^{3+} precipitation, particles with larger size and well crystallized structure are formed if the pH increases from acid to basic during the preparation, namely if NaOH is added over the iron salt The amorphous fraction is more important in the $Fe_2(_{SO})_3$ and $Fe(NO_3)_3$ -base series than in the $FeCl_3$ one

Opposite behaviour is evidenced in the hydrated oxides obtained by Fe^{2+} precipitation where well crystallized particles with higher size are obtained if the iron salts are added over NaOH. Generally, the crystallinity degree and the particles sizes is more reduced for the iron oxo-hydroxides obtained by Fe^{3+} ions precipitation than for Fe^{2+} one.

4.3. STRUCTURAL MODIFICATIONS IN IRON HYDRATED OXIDES INDUCED BY FOREIGN CATION

A large number of bi- and trivalent cations are present in the radioactive waste treatment precipitation system. The most important radionuclides of interest for chemical precipitation treatment are such cations as: Sr^{2+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cs^{+}. The influence of such cations on the ability of the iron hydroxide precipitate to decontaminate the radioactive waste was investigated. Many samples containing Mg^{2+}, Ba^{2+}, Cu^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Al^{3+}, Cr^{3+}, Ti^{3+} as foreign cations were prepared by various precipitation procedure simulating the contaminants removing mechanisms: co-precipitation, precipitation in the presence of foreign cations and foreign cations adsorbtion [6]. As previously mentioned, also in the presence of foreign cations, the Mössbauer results put in evidence phases with lower dimensionality of the particles in the ferric chlorate-base samples as compared with the iron sulphate ones.

The Mössbauer spectra of the iron sulphate-base samples show both magnetic and quadrupole patterns, for specific preparation conditions. Function of the foreign cation type, the magnetic contribution is different both in 295K and 80K spectra. Whereas the 295K Mössbauer spectra obtained on samples containing Ca^{2+} and especially Ba^{2+} present magnetic pattern (see Fig. 1), the Mössbauer spectra obtained on Mg^{2+} and Zn^{2+} containing samples are practically paramagnetic. These results could be explained by the compatibility between the radius of iron ion and the foreign cation. That foreign cation having almost the same radius with the iron ion can easy substitute the iron ion, changing the magnetic interaction in the final compound. The probability that calcium and especially, barium ions (with larger ionic radius) to substitute iron is very low, the final precipitate keeping almost the same magnetic properties like in the absence of the foreign cation. For the Ca^{2+} case, the substitution process seems to be influenced by the preparation conditions (see Fig. 1), the co-precipitation procedure leading to the highest substitution degree and/or to the lowest particles size.



RT

80K

FIG. 1. Mössbauer spectra of the iron sulphate base samples containing Ca^{2+} as foreign cation.

Due to the formation of the particles with reduced dimensionality in the $FeCl_3$ -base samples all the Mössbauer spectra (even at 80K) are magnetically unsplitted either for 3+ and 2+ foreign cations. In these situations only the doublet line width gives us useful information about the structural influence induced by the foreign cations: (i) in the presence of foreign cations, the lowest size of particles is obtained by the co-precipitation procedure, (ii) the Fe^{3+} substitution degree by a foreign cation is also more enhanced for cations with radius closer to the iron one, i.e. considering the precipitation in the presence of foreign cation procedure.

4.4. PRECIPITATION PROCESSES WITH ALTERNATIVE OR SIMULTANEOUS PRESENCE OF BIVALENT AND TRIVALENT IRON IONS

A set of samples (Nos. 130-139) have been prepared in condition of Fe^{2+} and Fe^{3+} co-precipitation or $Fe(OH)_3$ precipitation followed by the addition of Fe^{2+} over colloid or precipitation of $Fe(OH)_2$ and the addition of Fe^{3+} over the colloid. The Mössbauer data at 295K showed poorly crystallized (very fine particles) compounds, presenting broad absorption lines, while at low temperature (4.2K) the Mössbauer spectra put in evidence mainly two magnetic sextets with narrow lines. The XRD measurements confirmed the existence of the magnetite (Fe_3O_4) as a poorly crystallized compound and traced of maghemite (γ-Fe_2O_3) both with spinal structure. A deeper analysis of the existing data suggested the formation of a spinal solid solution of magnetite and maghemite with different ratios of Fe^{2+}, Fe^{3+}, and cation vacancies.

The following Table IV is referred to the iron octahedral occupancy in the spinal structure for samples with the initial precipitation of trivalent iron (Nos. 132-135) and respectively bivalent iron (Nos. 136-139). In this particular case of fine particles of a spinal solid solution, the highest number of the octahedral iron was obtained for the addition of $FeCl_3$ over the diluted NaOH (sample 134) and, respectively for the addition of NaOH over the diluted $FeSO_4$ (sample 136).

TABLE IV THE OCTAHEDRAL OCCUPANCY FOR SOME SAMPLES PREPARED WITH Fe^{2+} AND Fe^{3+} AS IRON

Sample	Procedure	Octahedral iron
132	($FeCl_3$/500mL+NaOH conc.)+ $FeSO_4$	64.5
133	(NaOH conc. +$FeCl_3$/500mL)+$FeSO_4$	68.9
134	(NaOH/500mL+$FeCl_3$)+$FeSO_4$	77.2
135	($FeCl_3$+NaOH/500mL)+$FeSO_4$	62.1
136	($FeSO_4$/500mL+NaOH)+$FeCl_3$	70.6
137	(NaOH conc.+$FeSO_4$/500mL) +$FeCl_3$	61.0
138	(NaOH/500mL+$FeSO_4$)+$FeCl_3$	61.6
139	($FeSO_4$+NaOH/500mL) + $FeCl_3$	59.4

4.5. THE PREPARATION CONDITIONS AND THEIR INFLUENCES ON THE DECONTAMINATION FACTOR

The use of ferric chloride, sodium phosphate and ferrocyanide as main reactants for the co-precipitation process treatment of LLAW, leads to the formation of ferric oxo-hydroxides, iron and calcium phosphates and copper ferrocyanide. The structure and composition of the individual species are strongly dependent on the precipitation procedure. As a function of a reagent addition order, the chain of the intermediate reactions changed and the individual insoluble products initially formed can alter the further reactions because the inner part of a particle (or agglomerate) is excluded from the subsequent reactions.

The "brutal" precipitation affects both the composition and the structure of precipitates and very small particles are obtained. The simultaneous use of ferric and ferrous salts improve the decontamination factor and the precipitate settling by the magnetite formation. From the decontamination factor point of view seems to be important when or how the magnetite precipitation proceeds.

TABLE V. DECONTAMINATION FACTOR DEPENDENCE ON THE PRECIPITATION PROCEDURE

No.	Precipitation procedure	DF(γ)	DF(β)
1.	Waste + ferric chloride + sodium phosphate + ferrocyanide + copper sulphate + PAM (final pH7.57)	23	36
2.	Waste + sodium phosphate + sodium hydroxide (pH9.44) + ferric chloride (pH9.08) + ferrocyanide + copper sulphate + PAM (final pH9.02)	35	60
3.	As (2) + ferrous sulphate (final pH8.57)	60	96
4.	Waste + ferrocyanide + copper sulphate + sodium phosphate + ferric chloride (pH7.56) + sodium hydroxide (pH9.12) + ferrous sulphate + PAM (final pH8.77)	75	124
5.	Waste + sodium hydroxide (pH=9.45) + (ferric chloride + ferrous sulphate) + PAM (final pH7.88)	114	90
6.	Waste + (ferric chloride + ferrous sulphate)(pH2.84) + sodium hydroxide (pH8.76) + PAM	86	139
7.	As (5) + sodium phosphate (final pH8.80)	99	164
8.	Sodium phosphate + sodium hydroxide + (waste + ferric chloride) + ferrous sulphate + PAM (final pH8.92)	265	290
9.	Sodium phosphate + sodium hydroxide + waste + ferrocyanide + copper sulphate + (ferric chloride + ferrous sulphate) + PAM (final pH8.76)	355	260
10.	Sodium phosphate + sodium hydroxide + (waste + ferrocyanide + copper sulphate + ferric chloride) + ferrous sulphate + PAM (final pH8.99)	560	375

Based on MS results presented above, some precipitation procedures were tested on simulated and real LLAW. The most significant results, obtained with real waste, are shown in the Table V, to prove the dependence of decontamination factors (DF(γ) and DF(β)) on the precipitation procedure.

5. CHARACTERIZATION OF IRON SPECIES IN CEMENTED RADIOACTIVE WASTE FORMS

Cementation has been the first and still remains the most widely used conditioning process for low and intermediate level radioactive waste [7]. There is a limited knowledge of the chemical reactions and of the products formed during the mixture of cement with solid or liquid waste and additional water. When cement is mixed with water, its hydrolysis constituents undergo a series of chemical coagulation and precipitation successive reactions. Hydrolysis and continuous reactions of the metastable hydration products are significantly influenced by the chemical nature and the proportion of the radioactive products conditioned by cementation. The main radioactive waste types conditioned by cementation are: precipitation sludge, evaporation concentrates, incineration ash and ion exchangers.

The purpose of this section is to describe the results of the Mössbauer methodology for characterization of the iron components in the cemented waste form.

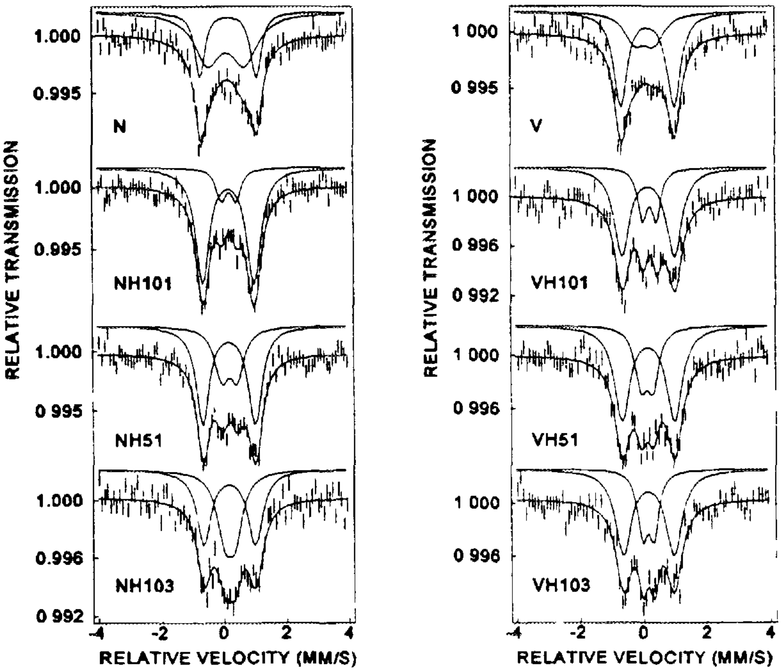


FIG.2. Mössbauer spectra of some N and V-type cements at 295K For low water/cement ratious, the central doublet area increases with the watter content

5.1. DRY AND HYDRATED CEMENT

Two series of samples were prepared starting from two Portland cement batches -N and V (N label the fresh cements and V label the six month preserved cements), the cement/water ratio varying from 10:1 to 1:1 as follows:

NH (or VH): **101** - 10 g cement + 1 mL distilled water; **51** - 5 g cement + 1 mL distilled water; 103: 10 g cement + 3 mL distilled water; **52** - 5 g cement + 2 mL distilled water; **105** - 10 g cement + 5 mL distilled water; **53** - 5 g cement + 3 mL distilled water; **107** - 10 g cement + 7 mL distilled water; **54** - 5 g cement + 4 mL distilled water; **109** - 10 g cement + 9 mL distilled water; **55** - 5 g cement + 5 mL distilled water.

All Mössbauer spectra obtained on both hydrated and dry cements were generally fitted with two doublets assigned to Fe^{3+} in two unequivalent positions [8, 9]. In the case of hydrated samples, quadrupole splitting of the central doublet present smaller values than in the N-type cement sample. The hyper fine parameters of two characteristic positions remain almost constant (QS=1.7 mm/s, IS=0.2 mm/s and QS=0.4 mm/s, IS=0.2 mm/s) but the relative area of the central doublet increases vs. the water content (see Figs.2, 3). This result could be explained by the water penetration near the oxygen neighbours around Fe^{3+} positions, the formed water bridges increasing the Fe-O distances and consequently decreasing the QS values.

The evident increase of the relative area of the central doublet at 80K compared with the RT measurements arises from the higher Debye-Waller factor of the hydrated phase owing to the water penetration and bridges formation. Consequently, for all temperatures, the central doublet percentage area seems to be a good evaluation for the cement hydration degree [10] At 295K the content of the central part in the N-batch become stationary (50% around R=0.35) where R =water/cement ratio, in agreement with the corresponding measurements of the cement hardness. The increase in the central part proportion due to hydration is almost 40% for cements N while for cement V it is only 30%, showing a lower hydration for the V-batch, again in agreement with the cement hardness measurements.

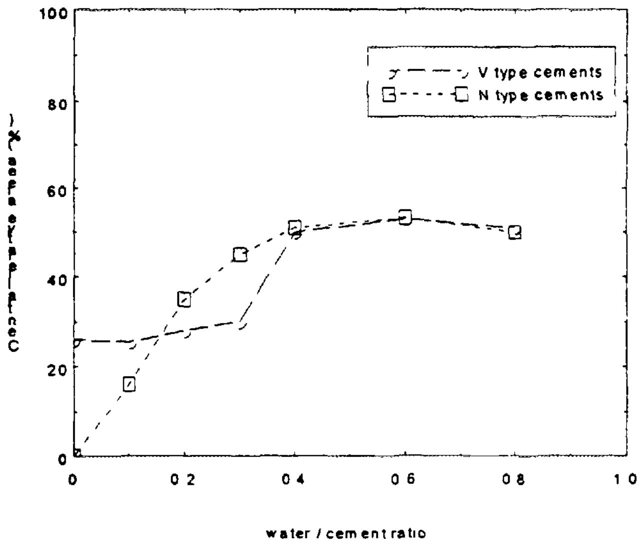


FIG..3. The central area evolution vs. The water/cement ratio (R) at 295K The saturation is attained around R=0.35.

5.2. SIMULATED PRECIPITATION PROCESS OF THE SLUDGE CONDITIONED IN THE CEMENT MATRIX

Preparation containing wet iron hydroxide or iron phosphate precipitates, according to conditioning procedure have been performed. The samples of iron hydroxides were prepared as follows: **Fe 1** - 20 mL $FeCl_3$(40%) in 1 L water were neutralized with 52.5 mL NaOH(20%), final pH6.2 ; **Fe 2** - 20 mL $FeCl_3$ were neutralized with 55 mL NaOH diluted in 1 L water, final pH7.4; **Fe 3** - 50 mL NaOH + 20 mL $FeCl_3$ diluted 1 L water , final pH7.1; **Fe 4** - 20 mL $FeCl_3$ /1 L water + 32 g Na_3PO_4 , final pH6.0

The conditioned samples of precipitates were:

nFeN(V) 52.5 - 5 g cement = 2.5g wet precipitate
55 - 5 g cement + 5 g wet precipitate , where n = 1,2,3,4

As could be seen from Table V, in the investigated samples only two positions have been used for the 295K spectra fitting. Both the iron containing precipitate and the hydrated iron from cement contribute to the second position (the central doublet in the Mössbauer spectra). The main problem: whether the iron precipitate is well embedded or not in a cement matrix, could be solved based on the results from TableVI in conjunction with the hypothesis of the maximum hydration degree of our samples.

A_1 - the area corresponding to the external doublet (equal in the above conditions with the area corresponding to the central part in the hydrated cement, see Fig.3) , A_2 - the area corresponding to iron from the embedded precipitate in sample **FeN52.5** and $A_2^{'}$ - the area corresponding to iron from the embedded precipitate in sample **FeN55**.

Considering the relative areas ratios (R for samples **FeN52.5** and R' for sample **FeN55**), it can be written:

$$\frac{A_1}{A_1+A_2}=R \qquad (2)$$

$$\frac{A_1}{A^1+A_2^{'}}=R' \qquad (3)$$

On the other hand, having in mind the significance of A_2' and A_2, these can be expressed as:

$$A_2 = Knf(T) \quad \text{and} \quad A_2' = Kn'f'(T) \qquad (4)$$

where

k	is a proportionality constant,
n	is the number of iron ions, and
f	is the Debye - Waller factor for the embedded precipitate in sample FeN52.5 and n' and f' in sample FeN55. In the above conditions n' = 2n .

From (2) , (3) and (4) the f'(T)/f(T) ratio is obtained :

$$\frac{f'(T)}{f(T)} = \frac{1}{2}\,\frac{R}{1-R}\,\frac{1-R'}{R'} \qquad (5)$$

Using (5) and the experimental values (Table V) for R and R', the following values for the f'(T)/f(T) ratio are obtained: 1.40 for 1FeN samples, 1.07 for 2FeN samples, 3.32 for 3FeN samples, 1.02 for 4FeN samples.

The better the precipitate is embedded, the higher the ratio is. So, the best embedded precipitate is one prepared with diluted $FeCl_3$ added to concentrated NaOH (3FeN), the cementation process implying one part cement and one part wet precipitate. The iron phosphate is not subjected to the embedding process.

TABLE VI. THE ROOM TEMPERATURE MÖSSBAUER PARAMETERS OF THE CONDITIONED SAMPLES

No.	Sample	Position	QS (mm/s)	IS (mm/s)	W (mm/s)	Conc. (%)
1	1FeN-52.5	1	1.56	0.16	0.71	32.2
		2	0.50	0.22	0.71	67.8
2	2FeN-52.5	1	1.61	0.18	0.61	30.6
		2	0.48	0.22	0.61	69.4
3	3FeN-52.5	1	1.63	0.17	0.58	23.8
		2	0.60	0.23	0.58	76.2
4	NP-52.5	1	1.79	0.11	0.34	17.9
		2	0.69	0.16	0.70	82.1
5	1FeN-55	1	1.32	0.29	0.57	19.3
		2	0.50	0.26	0.57	80.7
6	2FeN-55	1	1.27	0.30	0.53	21.0
		2	0.55	0.27	0.53	79.0
7	3FeN-55	1	1.61	0.16	0.62	6.8
		2	0.53	0.25	0.62	93.2
8	NP-55	1	1.70	0.20	0.64	10.6
		2	0.50	0.21	0.64	89.4

5.3. INFLUENCE OF OTHER VARIOUS COMPONENTS ON THE IRON DISTRIBUTION IN CEMENT

The samples with complexing agents (oxalic, citric, tartric acids, amonium oxalate and natrium citrate) were prepared using Portland cement and a solution of organic acid (or salt) in the ratio cement/water of 0.4. Either 1 or 3% wt solution was used . Fresh samples were kept 21 days in welded plastic bags before measuring. The Mössbauer spectra obtained both at 80K and 295K put in evidence two unequivalent positions of trivalent iron, reflected by two quadruple doublets. The RT Mössbauer parameters of all the analyzed samples are shown in TableVII.

The Mössbauer energetical parameters: quadruple splitting (QS) and isomer shifts (IS) show almost the same local configuration of iron in either 1% or 3% samples at 295K. The change of the relative concentration of the two sites function of the initial proportion (1% or 3%) is a good hint for the influence of the additional organic components on the hydration process implying iron atoms. The internal doublet area can be considered as a measure of the cement hydration degree. It should be noted that A_3 and A_1 is the internal doublet relative area for samples with 3%, respectively, and 1% initial proportion of solutions and K is their ratio. Depending on the K values (K<1 or K>1), the organic additional components could be considered as promoters or inhibitors of the hydration degree. The K values obtained from 295K spectra (Table VI) are: 1.07 for amonium oxalate, 1.77 for oxalic acid, 0.74 for citric acid, 1.01 for natrium citrate, 0.33 for tartric acid.

Accordingly, the citric and tartric acids can be considered as inhibitors of the conditioning process, the amonium oxalate and natrium citrate rather as neutrals while the oxalic acid as a good promoter. Therefore the undesirable presence could be avoided by their removal in the initial stages of the treatment procedure.

TABLE VII. THE ROOM TEMPERATURE MÖSSBAUER PARAMETERS OF THE SAMPLES WITH COMPLEXING AGENTS

No .	Sample	T (^{0}K)	Position	Q.S. (mm/s)	I.S. (mm/s)	W (mm/s)	Conc. (%)
1	Amonium oxalate-1%	295	1	1.6	0.2	0.7	64.2
			2	0.4	0.2	0.4	35.8
2	Amonium oxalate-3%	295	1	1.6	0.2	0.7	61.4
			2	0.5	0.2	0.5	38.6
4	Oxalic acid-1%	295	1	1.7	0.2	0.6	56.9
			2	0.5	0.2	0.5	43.1
5	Oxalic acid-3%	295	1	1.8	0.2	0.3	28.1
			2	0.6	0.2	0.7	71.9
7	Citric acid-1%	295	1	1.7	0.2	0.7	66.1
			2	0.5	0.1	0.7	33.9
8	Citric acid-3%	295	1	1.7	0.1	0.6	75.8
			2	0.7	0.1	0.9	24.2
10	Natrium citrate-1%	295	1	1.7	0.2	0.7	58.5
			2	0.5	0.2	0.6	41.5
11	Natrium citrate-3%	295	1	1.6	0.2	0.6	59.3
			2	0.4	0.2	0.6	40.7
14	Tartric acid-1%	295	1	1.7	0.2	0.5	68.3
			2	0.6	0.3	0.5	31.7
15	Tartric acid-3%	295	1	1.7	0.2	0.6	87.2
			2	0.5	0.1	0.4	12.8

6. CONCLUSIONS

The most important outcomings of the study are presented below:

Two original evaluations of the embedding process and respectively the hydration promotion in cements using only the Mössbauer data have been proposed.

Measurements down to 4.2K have to be performed in all cases of multiphase and very fine particles systems because the procedure of Mössbauer measurements at two fixed temperature 80K and 295K were not completely satisfactory.

Beside the usual absorption Mössbauer spectroscopy, the necessity of other structural correlated measurements (XRD and electron microscopy) was revealed.

The special preparations using enriched (85%) ^{57}Fe allowed us on the intimate mechanisms appearing in the waste conditioning by cementation.

Among the Mössbauer methodological approaches there are two non-destructive ones: use of the back scattered conversion electrons (CEMS) or scattered gamma radiation. Both are time consuming experiments but could be successfully used in the case of intact sample preservation.

The sensitivity of the Mössbauer energetical parameters (internal field, quadruple splitting and isomer shift) on the particle size and shape is one of the important gains during our research.

The simulation of LLAW precipitation and immobilization was successful and the Mössbauer spectroscopy proved to be a very sensitive investigation method.

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NEW TECHNOLOGY FOR THE TREATMENT OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE ORGANIC WASTE FROM NUCLEAR APPLICATIONS

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Abstract

A potentially attractive technique has been used for the oxidative degradation of combustible organic wastes using hydrogen peroxide as oxidant. Oxidative degradation process is simple, reliable and operates under mild conditions of temperature and pressure Infrared spectroscopy was used as a non-destructive tool to follow the degradation process. The results obtained show that the proposed process is highly efficient in transforming cation exchange resins from solid to liquid phase with a good reduction factor (up to 1250) and high conversion percentage (up to 98.46%). Oxidative degradation of a spent liquid scintillator was carried out before immobilization in cement matrix to avoid its negative retarding effect on the hydration of cement materials and to reduce the potential fire risk of the organic scintillator.

1. INTRODUCTION

A Research and Development Programme has been initiated in the institute to provide a simplified and effective method for the chemical decomposition of liquid and solid organic waste (e.g. liquid scintillators and ion-exchange resins) [1-3] originating from applications of radionuclides as tracers and from the Inshas research reactor. The goal is to avoid technical problems encountered in processes used for similar purposes (e.g. incineration, pyrolysis, acid digestion). The main objectives of the present research programme are to provide a safe and simple system that operates under mild conditions of temperature and pressure and to reduce the costs of construction operation and maintenance.

Modern technologies for the treatment and conditioning of solid radioactive wastes have been reviewed [4]. To overcome the drawbacks of a dry process and acid digestion, a new technique for the treatment of organic wastes has been suggested in USA patents [5,6]. Similar processes have also been proposed for the treatment of spent ion-exchange resins [7]. Methods for the decomposition of radioactive organic waste using hydrogen peroxide as an oxidizing agent and in the presence of a catalyst have also been developed [8-11]. Efficient elimination of organic liquids by wet air oxidation [12] and a generalized kinetic model for wet oxidation of organic compounds [13] are presented in the literature. Recently a catalytic wet oxidation process has been widely applied for treatment of different organic wastes [14-15] and for the selective oxidation of hydrocarbons [16] and non-water soluble polymers [17].

The present study focused on the chemical decomposition of cation exchange resins and spent liquid scintillator solution. Factors affecting the efficiency and rate of the oxidative degradation process were systematically studied on laboratory scale. Immobilization of organic wastes either directly or after their treatment was also studied.

2. MATERIALS AND METHODS

The system used in oxidative degradation of organic wastes in aqueous medium using hydrogen peroxide as oxidant consists of a three necked one litre flask, a metric pump, a magnetic stirrer and a heating manteel supplied with a contact thermometer The schematic diagram for the apparatus used is shown in Fig.1.

The waste materials studied were either solid organic resins (A) or spent liquid scintillators (B).

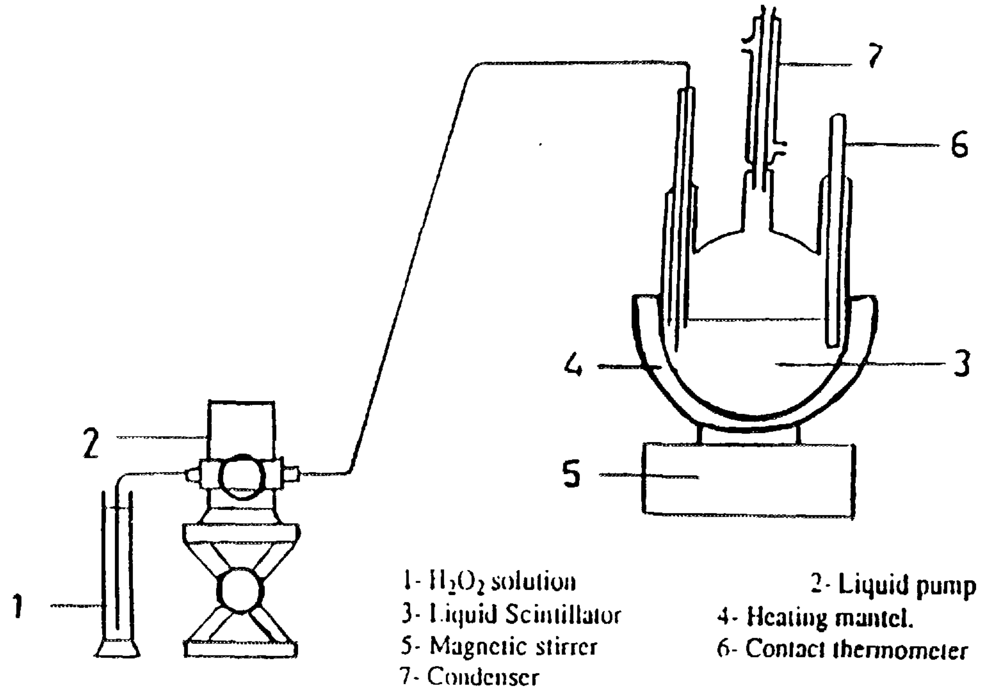


FIG. 1. Schematic diagram for oxidative degradation of the organic liquid scintillator.

(A) Spent Ion Exchange Resins:

The bead cationic exchanger used is an acidic resin in H-form that has sulphuric acid as functional group. The molecular formula for basic unit of this cationite is assumed to be $C_8H_7SO_3H$. The water content of the cation resin used was calculated by determination of the weight loss upon drying the resin in an oven at 105°C [18] for nine hours. The elemental analysis and water content of the resin are represented in Table I.

TABLE I. WATER CONTENT AND ELEMENTAL ANALYSIS OF CATION EXCHANGE RESINS.

Water content	C (%)	H (%)	N (%)
45.25	51.8	5.2	0.8

The bead ion exchange resin was ground for five hours using a ball mill grinder and the resulted powder was sieved for thirty minutes. The different fractions of the sieved resins are represented in Table II.

TABLE II. THE WEIGHT OF DIFFERENT FRACTIONS RESULTED FROM GROUND AND SIEVED CATION EXCHANGE RESIN

Fraction grain size (mm)	Weight of fraction (g)
> 0.250	353.69
0.250-0.125	300.60
0.125-0.063	120.05
<0.063	75.09

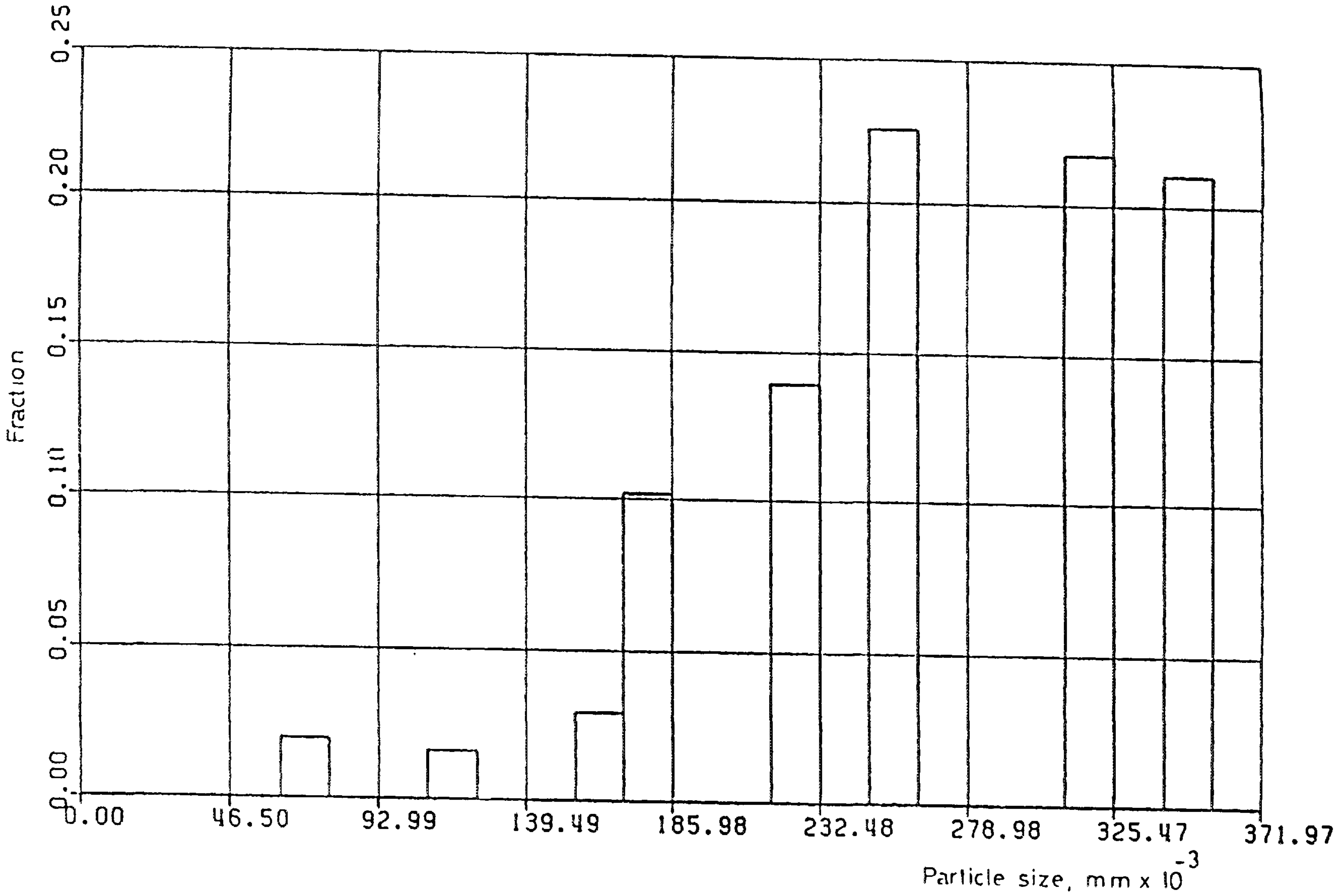


FIG. 2. Fraction distribution of cation-exchange resins after grinding and sieving. (grain size : 0.125 -0.250 mm).

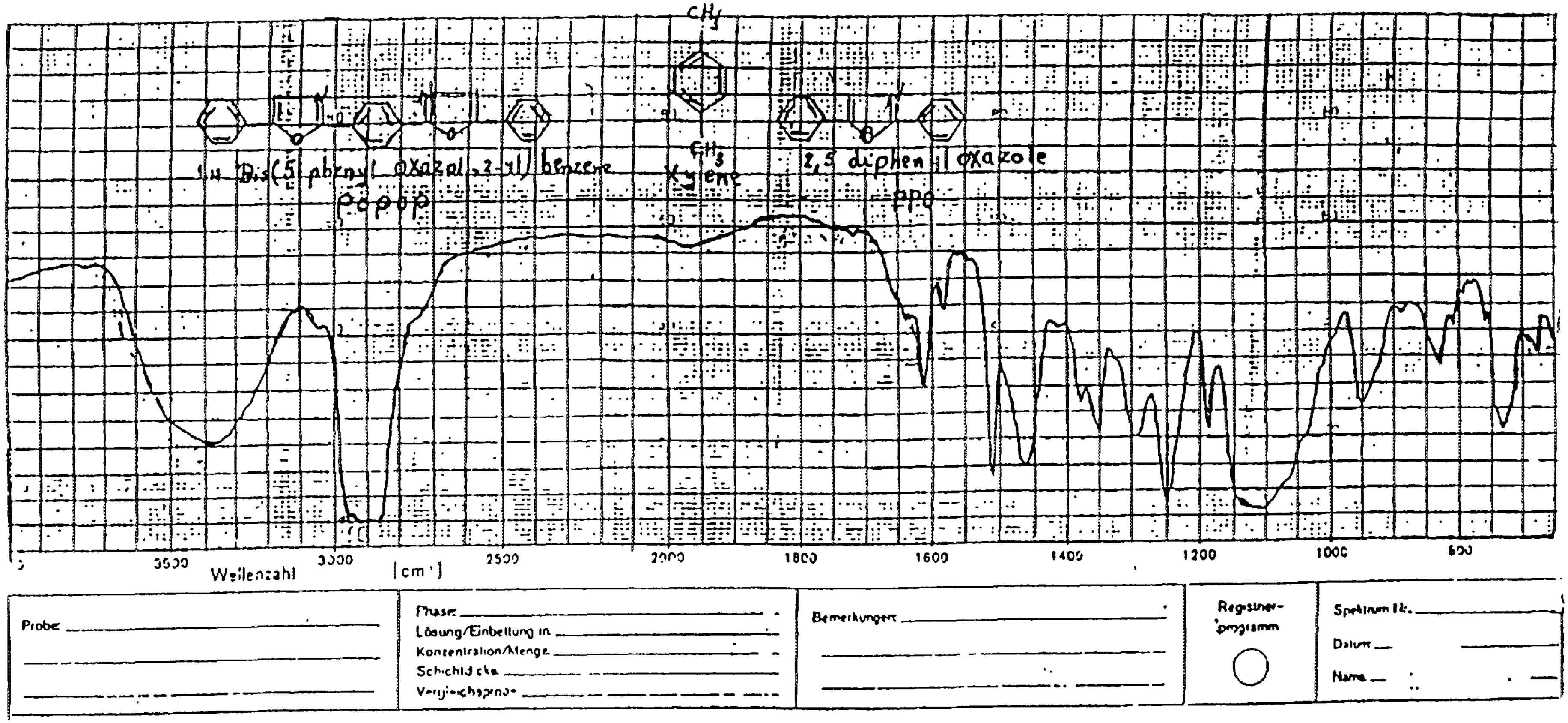


FIG. 3. Infrared spectrum of the organic liquid scintillator.

The fraction of grain size 0.125 - 0.250 mm was used in oxidation experiments. The fraction distribution of different particle size, within the chosen portion was shown in Fig. 2.

The desired amount of hydrogen peroxide was added totally to a predetermined weight of the waste and the temperature of the mixture was then gradually raised to the boiling point of the solution and refluxed for the required time. At the end of the reaction, the solution mixture was filtered and the carbon content in the liquid phase, weight of solid residue and its carbon content were determined.

The data obtained in oxidative degradation processes were represented in a different manner namely as oxidation rate, weight reduction percentage, weight reduction factor, conversion percentage and conversion factor to facilitate their comparison with previously given data in the literature.

$$Oxidation\ rate = \frac{added\ resin(g)}{reaction\ time(\mathrm{min})}$$

$$Weight\ reduction\ percantage = \frac{added\ resin\ \in\ g - weight\ of\ solid\ residue\ \in\ g}{added\ resin\ \in\ g}$$

$$Weight\ reduction\ factor = \frac{100}{100 - weight\ reduction\ percent}$$

$$Conversion\ factor = \frac{100}{100 - conversion\ factor}$$

$$Conversion\ percantage = \frac{added\ carbon - remaining\ carbon}{added\ carbon} \times 100$$

(B) Spent Liquid Scintillator

Monophase 40 liquid scintillator contains xylene as a solvent and supplied by Packard was used in the present study to simulate the waste. The infrared spectrum of this scintillator is shown in Fig. 3.

2.1. TREATMENT OF LIQUID SCINTILLATOR BEFORE CEMENTATION

The organic scintillator was introduced into the digesting flask with a predetermined weight of ferric sulphate [$Fe_2(SO_4)_3$] (100mg/L) as a catalyst. The mixture was heated up to ~ 80°C and hydrogen peroxide (30%) was added with a constant rate below the solution surface. More details concerning the wet oxidation process are given in previous publications [1,2]. Different ratios of hydrogen peroxide to organic scintillator were used. After the addition of hydrogen peroxide was stopped, the mixture was heated for one hour more to ensure complete destruction of the residual hydrogen peroxide. Samples of the reaction products were subjected to infrared analysis. The solutions resulting from the oxidation process were immobilized in cement materials as previously described in Section 1 and the compressive strength for the final solidified blocks were measured.

2.2. DIRECT IMMOBILIZATION OF A SPENT SCINTILLATOR IN CEMENT

An untreated liquid scintillator was thoroughly mixed with cement/water mixture. The homogeneous cement/scintillator mixture was poured in closed molds and left to solidify in a humid atmosphere. Free standing cylindrical blocks were obtained after 28 days. At the end of curing time the compressive strength for 3 to 5 blocks with average diameter 3.12+0.01 cm and average height 3.3+0.1 cm, was determined using an Instron Universal Testing Instrument Model 1178 (ASTM-D-695). The mechanical properties of the final solid blocks containing different amounts of the scintillator, keeping the percentage of water of hydration constant (35% by weight of cement), were studied systematically. On the other hand experiments demonstrating the effect of increasing the amount of scintillator at the expense of water of hydration, on the compressive strength of the incorporated blocks were also performed.

2.3. CEMENT MATERIALS

The cement used for immobilization process in the present work was the Ordinary Portland Cement (OPC). The raw materials are ground, sieved and a mesh size < 0.5 mm was chosen for specimens preparation. The average chemical analysis of the cement type used is given in Table III.

TABLE III. CHEMICAL COMPOSITION OF THE CEMENT

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	Insoluble residue (%)
19.84	4.74	4.00	61.01	2.50	0.60	2.42	0.95

- Loss on ignition = 3.5 %

3. RESULTS AND DISCUSSIONS

(A) Spent Ion Exchange Resins:

To evaluate the different parameters affecting the oxidative degradation of cation exchange resins, batch experiments were carried out. Infrared spectroscopy was used as a direct non-destructive method for recording changes in the structure of cation - exchange resins degraded batchwise by hydrogen peroxide in an aqueous medium at nearly 100°C.

The spectrum of undegraded cation-exchange resins is represented in Fig. 4. The broad intense band at 3460 cm^{-1} is attributed to the O-H stretching characteristics of the intrinsic water contained in the solid resins. It can also be seen that the stretching and deformation frequencies of C-H appears at 2920 cm^{-1} and 2850 cm^{-1} close to the characteristics of polystyrene [16] (Fig. 4). The band at 1630 cm^{-1} indicates -O-H deformation in water, the strong band at 1600 cm^{-1} was assigned to -C=C- stretching vibration of phenyl ring while that at 1450 cm^{-1} -C-H- deformation. The bands at 1180, 1130, 1040 and 1010 cm^{-1} arose from symmetric and asymmetric stretching vibration of -S-H- of the active sulphonic group attached to the polymer moeiity of the resin. Strong band at 840 cm^{-1} indicates a 1,4 di-substituted benzene ring while that at 775 cm^{-1} may be attributed to mono-substituted benzene ring. The stretching vibration assigned to the -C-S linkage occurred at 675 cm^{-1}. The infrared spectrum obtained for the untreated cation-exchange resin under consideration matches quite well with those spectra previously given for similar resin [19], and for cross-linked styrene benzene polymer [20].

The spectra of degraded cation-exchange resins samples which resulted from batch experiments using different resin: hydrogen peroxide ratios are shown in Fig. 5(a-d). The effect of oxidation using hydrogen peroxide on the formation or disappearance of functional groups was followed by comparing the spectra obtained for the degraded resin with that of undegraded one. The assignments of bands for untreated resin and its degradation products are given in Table IV.

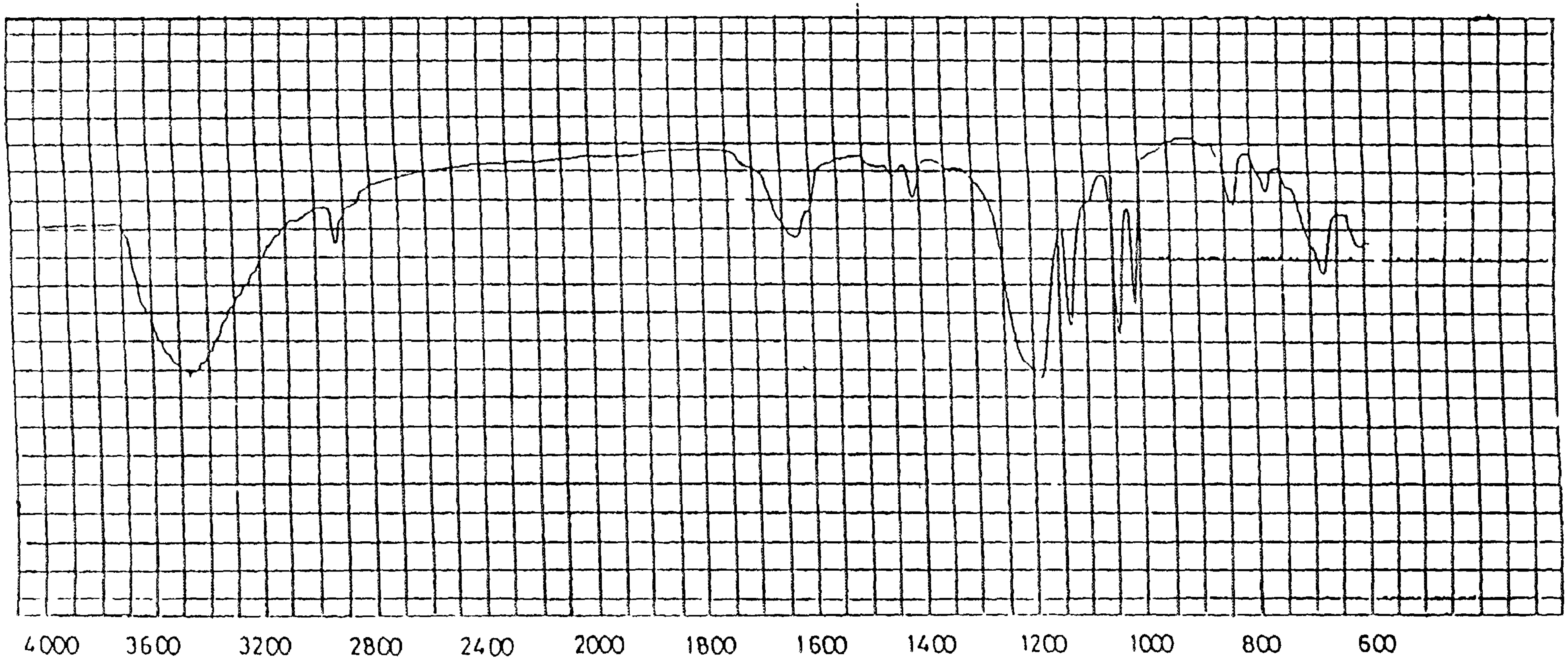


FIG 4. Infrared spectrum of the solid cation-exchange resins

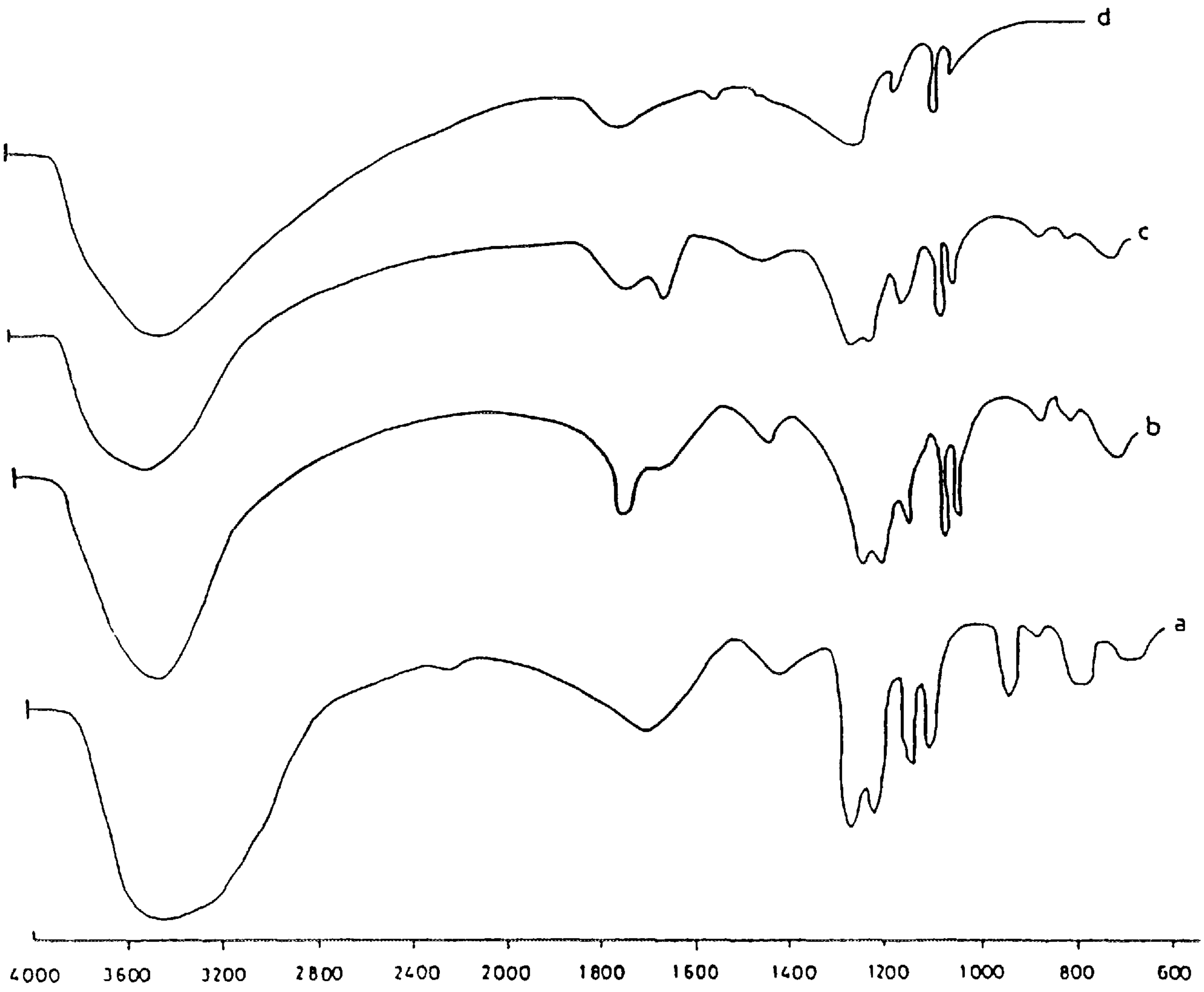


FIG 5 Oxidative degradation of the cation-exchange resins in aqueous medi a(Batch experiment) Infrared spectra of the degraded cation resins in the increasing amount of hydrogen peroxide a) 1 1, b) 1 2, c) 1 3 and d) 1 4 (g resins mL H_2O_2

The gradual disappearance of the 2920 cm^{-1} and 2850 cm^{-1} in Fig 5(c,d) may indicate the loss of function group -C-H stretching frequency (characteristic to polystyrene) by increasing the oxidizing agent (hydrogen peroxide resin ratio) On the other hand a band in the vicinity of 1700 cm^{-1} start to propagate in Fig 5-a corresponding to -C=O group Band near 1200 cm^{-1} which is characteristic to peroxide group was also detected These observations may also indicate the formation of intermediate oxidation products with carbonyl group and peroxide group As the decomposition process proceeds the intermediate oxidation products are expected to be converted finally to carbon dioxide and water [21] (Fig 5(d)) Although, at the end of the reaction, a considerable amount of sulfonic groups were still detected in the reaction medium [bands at 1120, 1040 and 1005 cm^{-1} (Fig 5,d)], yet the band characteristic to the attachment of this sulfonic group to the organic part of resin disappeared due to the oxidative degradation process (absence of band at 675 cm^{-1} of -C-S group) (Fig 5,d) The above results also illustrate the disappearance of the bands characteristic for both cross -linking and aromatic ring peculiarity, (absence of 1450 cm^{-1}, 840 cm^{-1} and 770 cm^{-1} bands) (Fig 4 d)

The mechanism of oxidative degradation of organic resin materials in aqueous medium differs according to the stability of the resins towards the oxidizing agent used (hydrogen peroxide) For cation - exchangers, generally a weak link exists at the tertiary carbon adjacent to benzene ring of the styrene moiety of the polymer Due to the weakness of this link, it is believed that, oxygen and other oxidizing agents tend to form hydroperoxide, subsequently, tend to split the carbon chain to form lower molecular weight degradation products accompanied by a gradual decrease in the degree of cross - linking results in a gradual increase in the volume of the resins and softening of it to a near gelatinous materials and finally dissolution of resins [11]

TABLE IV OXIDATIVE DEGRADATION OF CATION EXCHANGE RESINS IN AQUEOUS MEDIUM (BATCH WISE EXPERIMENTS) (The assignments of infrared bands in cm^{-1} for untreated and degraded resin)

	Resins H_2O_2				
Untreated	1 1 wt/vol	1 2 wt/vol	1 3 wt/vol	1 4 wt/vol	Band characteristic
3460	3500	3500-3400	3500-3460	3500-3440	O-H Stretch
2920	2930	2920	--	--	C-H Stretch in
2850	2850	--	--	--	ion exchange
--	1720-1700	1720-1700	1720-1690	--	polyester
1630	1640	1620	1630	1650-1620	O=C stretch
1600	--	--	--	--	O-H Deform (H_20)
1450	1450	--	--	--	C=C phenyl gp
1410	1410	1400	1400	--	C-H deform
--	1220	1210	1200	1200	Cross-linking
1180	1180	1170	--	--	Peroxide
1130	1130	1120	1120	1120	
1040	1040	1030	1040	1040	
1010	1010	1005	1005	1005	
840	830	830	830	--	$-SO_3$ group
770	770	760	760	--	
675	670	670	--	--	
					aromatic phenyl
					C - S bond

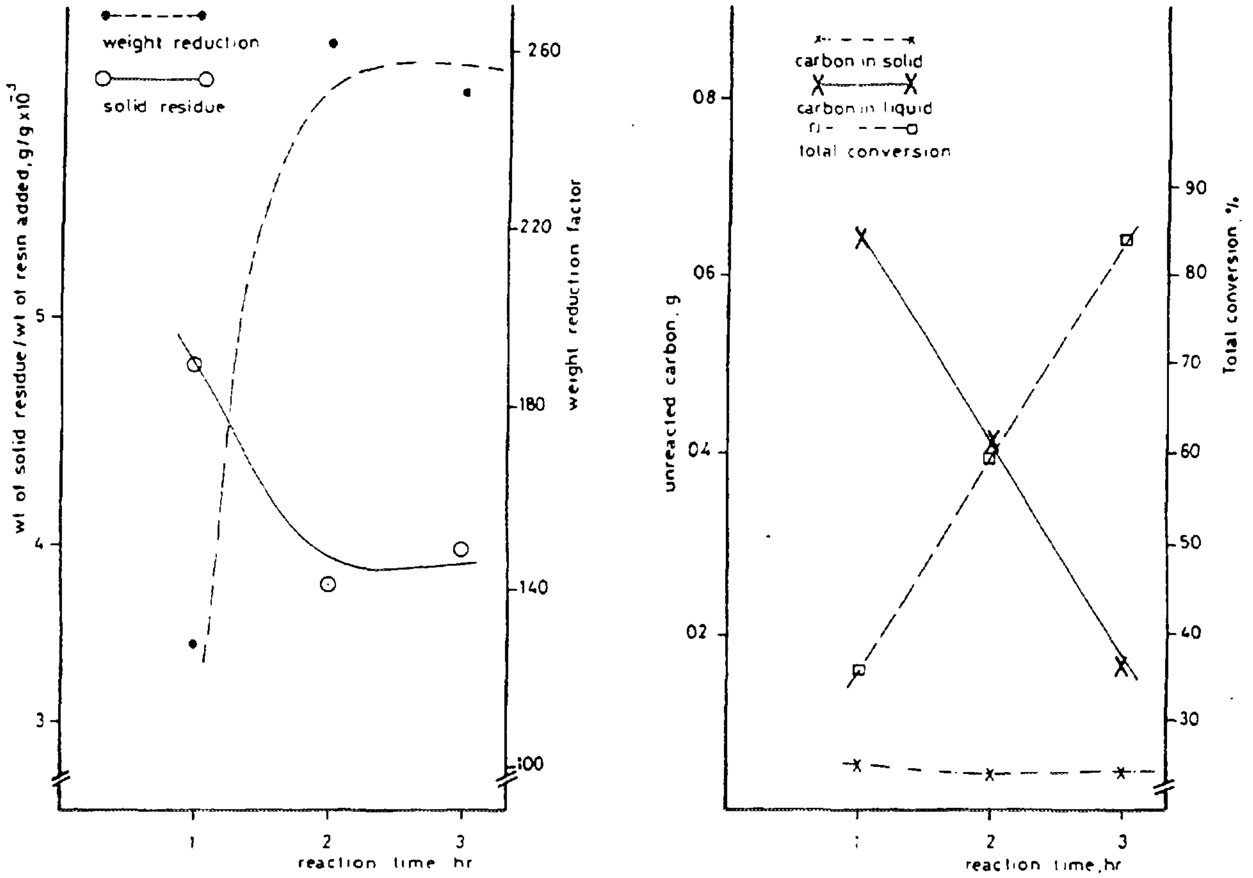
The above experimental data obtained prove the oxidative degradation effect of hydrogen peroxide and illustrate the above speculated mode of reaction However, the exact determination of the intermediate oxidation products needs to be confirmed by further experimental work and analytical tests The present work aims mainly at optimizing the process of oxidative degradation and achieving the highest possible volume and weight reduction of the spent resins

Preliminary batch experiments were conducted to optimize the time required for the oxidative degradation, resin / H_20_2 ratio and the concentration of catalyst used

Increasing the time of reaction, from one to three hours, the weight of solid residue and its carbon content were decreased, Table V It was clear from the data obtained that increasing the reaction time favors the oxidative degradation process, as expected, which in turn was reflected in the calculated weight reduction factor and conversion (based on the carbon on solid residue) (Table V, Fig 6 a) Heating the cation - exchange resin with hydrogen peroxide results in its degradation to low molecular weight organic compounds soluble in the liquid medium which stand for a relatively high carbon content in the solution compared with that in solid phase (Table V, Fig 6,b) As the process of oxidation proceeds, the soluble organic carbon was oxidized to carbon dioxide and water, as a result, its concentration in the liquid phase was gradually reduced

TABLE V. OXIDATIVE DEGRADATION OF CATION - EXCHANGE RESIN IN AQUEOUS MEDIUM (BATCH EXPERIMENTS). EFFECT OF REACTION TIME IN OXIDATION PROCESS.

Reaction time h	H_2O_2 consumption		Oxidation rate		Solid residue				Unreacted carbon									Total conver. factor
	mL /g	mL/g carbon	g carbon/min	g resin/ min	Weight		Weight reduction		In solid			In liquid			Total			
					g	g/g resin × 10^{-3}	%	Factor	wt g	g/g C ×10^{-3}	conver * %	wt g	g/g C	conver * %	wt g	g/g C	conver * %	
1	8	15 44	0.432	0 833	0.239	4.78	99 52	208	0 136	5.246	99 48	16 84	0 636	36 39	16 63	0 642	35.82	1.56
2	8	15 44	0.216	0.417	0.191	3.82	99.62	263	0 106	4 092	99.59	10.48	0.405	59.55	10.59	0.409	59.14	2.45
3	8	15 44	0.144	0.278	0.199	3 98	99 60	250	0 115	4 439	99.56	4.08	0.158	84 25	4.195	0.162	83 81	6.18



a) The variation of weight of solid residue and weight reduction factor as a function of reaction time.

b) The variation of weight of unreacted carbon in solid and liquid residues as well as of total conversion percentage as a function of reaction time

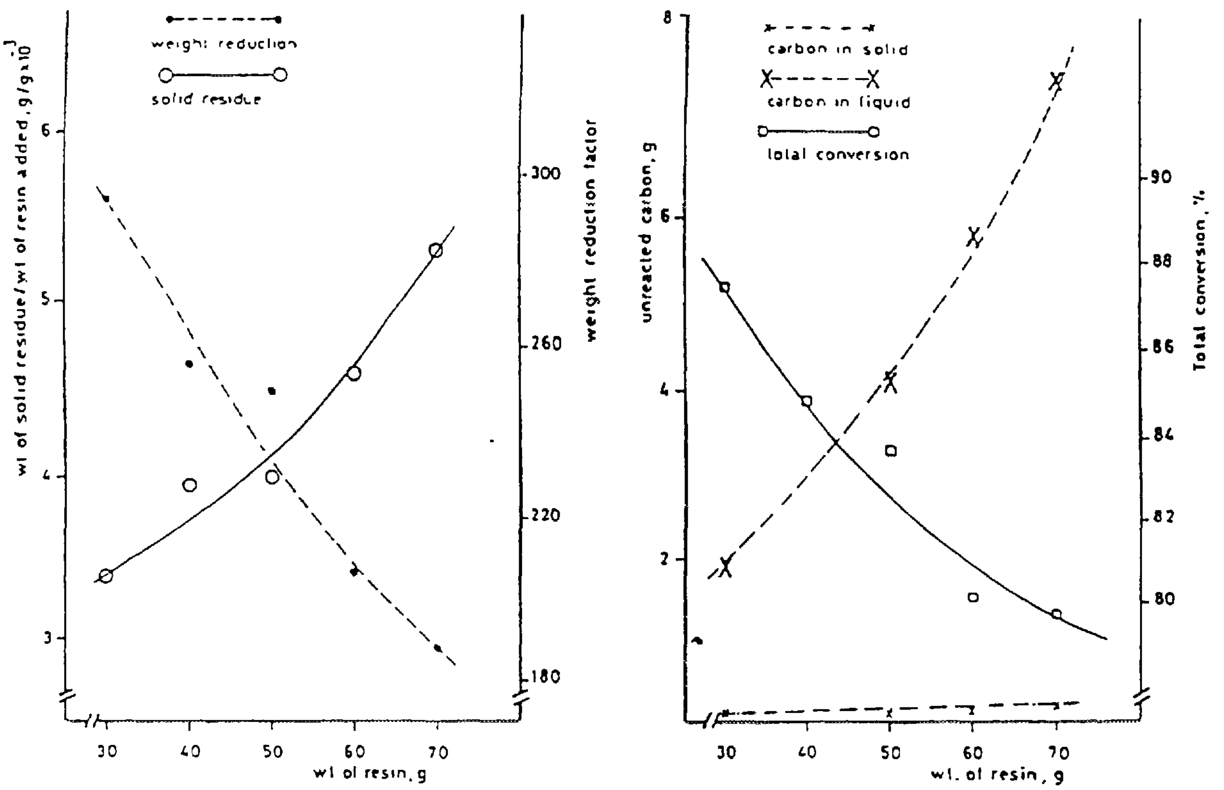
FIG. 6. Oxidative degradation of the cation-exchange resin in aqueous media (Batch experiment).

This also affects the total conversion percentage which increased from 35.8% to 83.6% by increasing the time of oxidative degradation from one to three hours. The relatively high carbon contents in the liquid phase results in decreasing the total conversion compared with the conversion percentage calculated based on carbon content of the solid residue.

Different weights of cation - exchange resins were used to optimize the hydrogen peroxide: resin ratio the data obtained are represented in Table VI and shown in Fig. 7. Both conversion (based on carbon in solid phase) and weight reduction percentage were always higher than 99.4% even when using a relatively low hydrogen peroxide resin ratio (less than 6 mL hydrogen peroxide per gram cation-exchange resin). As previously stated the degradation of cation - exchanger proceeds through the formation of soluble organic compounds, carbon dioxide, water and insoluble ashes, therefore, increasing the weight of resins added to a given volume of hydrogen peroxide increased the total unreacted carbon and consequently lower the total conversion percent. (Table VI). Increasing the weight of cation exchange resins from 30 to 70 g for a constant volume of hydrogen peroxide (400 mL) was accompanied with remarkable increase in carbon content in the liquid phase compared with that in solid residue. Although relatively smaller amounts of hydrogen peroxide were required to decompose the cation exchanger yet, for complete oxidation, of organic carbon soluble in the medium more hydrogen peroxide was needed.

TABLE VI OXIDATIVE DEGRADATION OF CATION - EXCHANGE RESIN IN AQUEOUS MEDIUM (BATCH EXPERIMENTS) EFFECT OF WEIGHT OF CATION RESIN IN OXIDATION PROCESS

Resin added		H_2O_2 consumption		Solid residue				Unreacted carbon									Total conver factor
g resin	g carbon	mL/g resin	mL/g carbon	Weight		Weight reduction		In solid			In liquid			Total			
				%	g/g resin × 10^3	%	Factor	wt g	g/g C ×10^3	conver * %	wt g	g/g C	conver * %	wt g	g/g C	conver * %	
30	15 54	13 33	25 74	0 1004	3 35	99 67	270	0 0559	3 60	99 64	1 88	0 1210	87 90	1 9359	0 1246	87 54	8 02
40	20 72	10 00	19 31	0 1578	3 95	99 61	256	0 0882	4 26	99 57	3 02	0 1450	85 42	3 1082	0 1500	85 00	6 67
50	25 90	8 00	15 44	0 1990	3 98	99 60	250	0 1150	4 44	99 56	4 08	0 1575	84 25	4 1950	0 1620	83 80	6 17
60	31 08	6 67	12 87	0 2780	4 63	99 54	217	0 1555	5 00	99 50	5 80	0 1866	81 34	5 9555	0 1916	80 84	5 22
70	36 26	5 71	11 03	0 3702	5 29	99 47	189	0 2118	5 84	99 42	7 16	0 1975	80 25	7 3788	0 2035	79 65	4 91



a) The variation of weight of solid residue and weight reduction factor as a function of resin added

b) The variation of weight of unreacted carbon in solid and in liquid residues as well as of total conversion percentage as a function of weight of resin added

FIG 7. Oxidative degradation of the cation-exchange resin in aqueous media (Batch experiment).

Decomposition process of hydrogen peroxide into water and molecular oxygen proceeds according to the following equation

$$2H_2O_2 \rightarrow 2H_2O + O_2 + 46 \ kcal$$

Although in principle such decomposition could be obtained by a thermal method, yet a number of substances are also very active decomposing catalysts particularly the oxide of various heavy metals. The oxidizing action of hydrogen peroxide is considerably enhanced by the presence of these metal oxide catalysts. Earlier investigations of catalysis by iron have been concerned with both ferric and ferrous salts. Iron in various forms is a very active catalyst in decomposition process of hydrogen peroxide [22]. The equation explaining the catalytic decomposition of hydrogen peroxide brought about by ferric and ferrous iron is given in Refs [22-24].

The effect of catalyst concentration on oxidative degradation of cation-exchange resins by hydrogen peroxide was studied and the data are represented in Tables VII and shown in Fig. 8. Although the oxidative degradation of cation - exchange resin in aqueous medium proceeds in absence of catalyst at the temperature around 100°C, yet, its presence in small amount increased the weight reduction and conversion percentages (based on carbon content in solid residue). Increasing the ferrous iron concentration increased the concentration of molecular oxygen which enhances the oxidation process and affects positively the total conversion percentage (Table VII, Fig. 8).

TABLE VII OXIDATIVE DEGRADATION OF CATION - EXCHANGE RESIN IN AQUEOUS MEDIUM (BATCH EXPERIMENTS) EFFECT OF CATALYST CONCENTRATION ON THE OXIDATION PROCESS

Catalyst concentr g/L	Solid residue				Unreacted carbon								
					In solid			In liquid			Total		
	g resin	g/g resin × 10^3	%	Factor	wt g	g/g carbon C ×10^3	conver %	wt g	g/g carbon ×10^2	conver %	wt g	g/g carbon C ×10^3	conver %
0	0 0710	2 3666	99 76	417	0 04200	2 702	99 73	2 060	13 256	86 740	2 1020	13 526	86 47
0 081	0 0837	2 7900	99 72	357	0 04500	2 896	99 70	1 253	8 063	91 940	1 2900	8 353	91 65
0 161	0 0323	1 0766	99 89	909	0 01710	1 100	99 89	1 045	6 725	93 280	1 0621	6 835	93 17
0 242	0 0494	1 6466	99 84	625	0 02500	1 609	99 94	0 886	5 701	94 300	0 9110	5 862	94 14
0 363	0 0320	1 0666	99 89	909	0 01640	1 055	99 90	0 486	3 127	96 870	0 5024	3 233	96 77
0 403	0 0238	0 7933	99 92	1250	0 01335	0 859	99 91	0 242	1 557	98 440	0 2554	1 643	98 46
0 806	0 0255	0 8500	99 92	1250	0 01325	0 853	99 92	0 235	1 512	98 490	0 2483	1 598	98 40

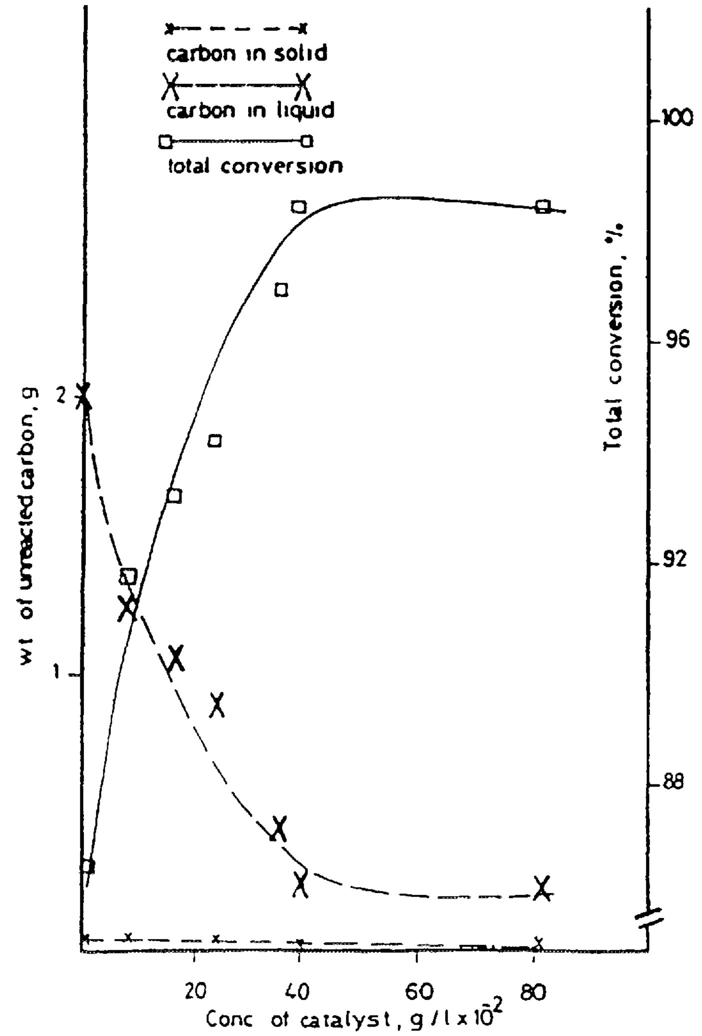


FIG 8 Oxidative degradation of the cation-exchange resins in aqueous media

(B) Spent Liquid Scintillator

3 1 TREATMENT BEFORE IMMOBILIZATION

To overcome the retarding effect of liquid scintillator on the hydration of cement matrix and to avoid the fire risk of the immobilized waste forms due to its organic nature, wet oxidation [1,2] of the organic liquid scintillator was carried out The main purpose of the oxidative degradation process is to decompose the organic materials converting them to a safe form easily handled and solidified

The liquid scintillator used as a counting tool, generally consists of two organic fluorescing compounds referred to the primary and secondary fluors These fluors are dissolved in an organic solvent such as toluene, xylene or dioxane [25]

To follow the oxidation of liquid scintillator in hydrogen peroxide at ~ 80°C, infrared spectroscopy was used as a direct and non-destructive method for recording the changes in the structure of the scintillator degraded The spectrum of non-degraded liquid scintillator was shown in Fig 3 The broad intense band at 3360 cm^{1} may be attributed to -N-H symmetrical and asymmetrical stretching vibration characteristic to the

TABLE VIII. OXIDATIVE DEGRADATION OF ORGANIC LIQUID SCINTILLATOR THE ASSIGNMENT OF INFRARED BANDS IN cm^{-1} OF UNTREATED AND TREATED SCINTILLATOR.

Untreated scintillator	Treated scintillator Scintillator: H_2O_2 Vol/Vol					Band characteristics
	1:1	1:2	1:3	1:4	1:5	
-	3400	3400	3400	3400	3400	-O-H stretch (H_2O)
3360	-	-	-	-	-	-H-N asymmetrical and symmetrical stretch, vibration
3040 2930	- -	- -	- -	- -	- -	C-H and methyl stretch in aromating ring
-						-N-H and adsorption tail indicates ammonium salts. The board strong band at 3400 cm^{-1} resulting from superimposed O-H and NH_3 stretching bonds.
-	2100	2390	2400	2400	-	-N-H stretching
-	1650	1650	1650	1650	1650	-C=O stretch and -O-H deformation
1610	-	-	-	-	-	-C=O stretch vibration oh phenyl group
1580 1510	- -	- -	- -	- -	- -	These bands result from interaction between -N-H & C-H bond vibration.
1460	-	-	-	-	-	C=N stretching band
1350	-	-	-	-	-	C-H aromatic deformation
1250	-	-	-	-	-	Absorption vibration due to C-O & C-N
-	1230	-	-	-	-	Peroxide group
1190	-	-	-	-	-	C-O-C stretch vibration & branching on the carbon atoms adjacent to 6 ring leads to splitting of -C-O-C
950	-	-	-	-	-	-C-N bond stretch vibration
830-740	830	815	830	830	-	-C-H out of plane bending absorption pattern of the aromatic and hetero-aromatic rings

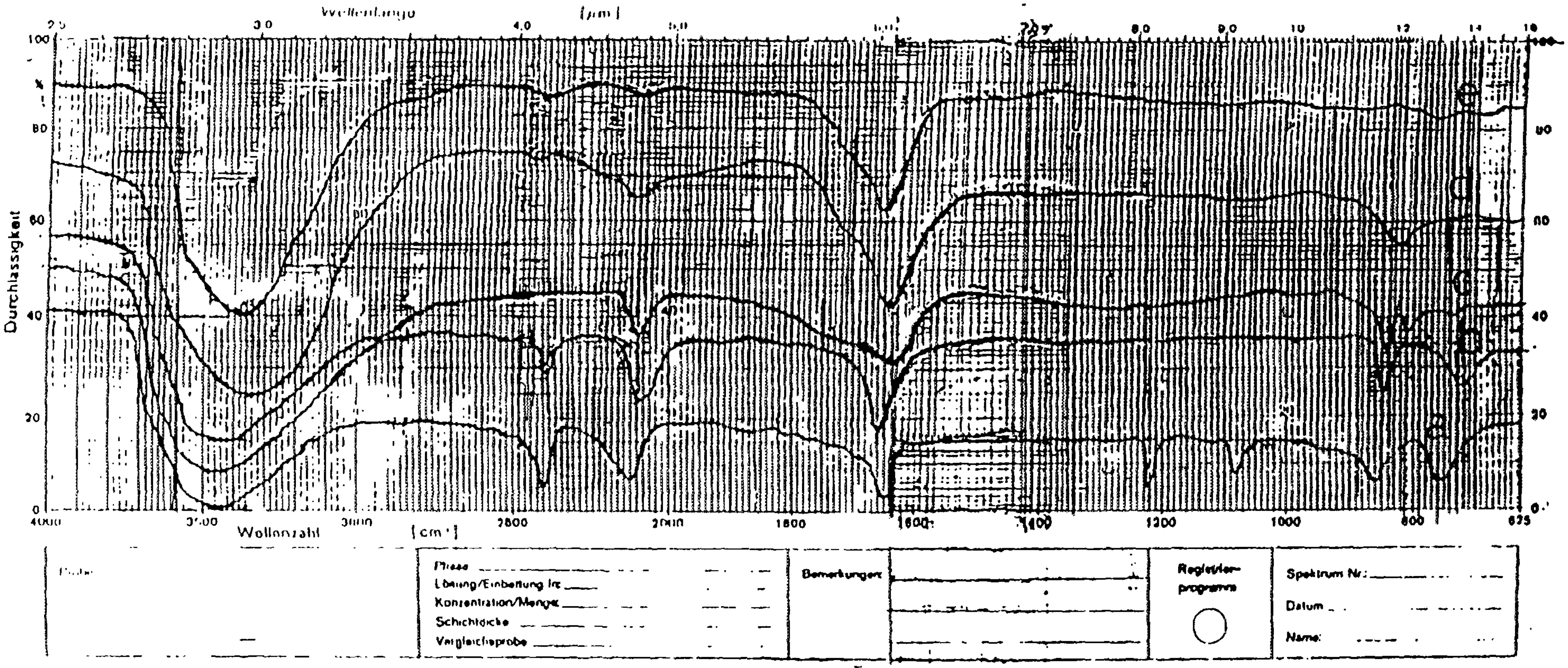


FIG. 9. Infrared spectra of the degraded liquid scintillator in increasing percentage of hydrogen peroxide. a) 1:1 b) 1:2 c) 1:3 d) 1:4 e) 1:5.

POPOP and PPO (two flours components in the scintillator) It can also be seen that the stretching and deformation frequencies of -C-H aromatics and methyl group of xylene appear at 3040 cm^{-1}, 2930 cm^{1} and 1350 cm^{1} The band at 1610 cm^{-1} indicates -C = C- stretching vibration of phenyl ring while that at 1580 cm^{1} and 1510 cm^{1} result from the interaction between -N-H and -C-H- bond vibration The band at 1460 cm^{1} and 950 cm^{-1} indicate -C = N- stretching vibration respectively On the other hand vibration absorption due to -C-O- and -C-N- appears at 1250 cm^{-1} The band at 1190 cm^{-1} and, 1150 cm^{-1} seem to be attributed to -C-O-C- stretching vibration and the branching on the carbon atoms adjacent to 6 ring leads to splitting of -C-O-C bands (Fig 3) Bands at 830 cm^{-1}, 810 cm^{-1}, 790 cm^{-1}, 760 cm^{-1} and 735 cm^{1} indicate -C-H out of plane bending absorption pattern of the aromatic and hetero - aromatic rings in both PPO, POPOP and xylene of the cocktail mixture (Fig 3)

The spectra of degraded liquid scintillator samples from experiments using different scintillator hydrogen peroxide ratios were shown in Fig 9(a-e) The effect of oxidation process on the formation or disappearance of functional groups was followed by comparing the obtained spectra of the treated scintillator with that of untreated one (Fig 3) The assignments of bands for organic liquid scintillator and the resulting degradation products are given in Table VIII

The broad intense band at 3400 cm^{-1}, (Fig 9(a-e)), in the spectra of degraded scintillator may be attributed to O-H of H_2O stretching vibration originating from H_2O_2 used The absence of bands at 3360, 1580, 1510, 1460, 1250, and 950 cm^{1}, may indicate the loss of -N-H, N-H & -C-H interaction, -C = N stretching and -C-N frequency, (characteristics to hetero-aromatic properties of PPO and POPOP ingredients) by addition of the oxidizing agent The disappearance of bands characteristics for aromatics and hetero-aromatics illustrate the destruction of the organic nature by adding H_2O_2, i e absence of bands 3040, 2930, 1610, 1340, 1190, 1150 , 850 and 735 cm^{1}) It is clear from Fig 9(a-e) that an absorption tail at 2400 cm^{1} start to appear which corresponding to N-H characteristic to ammonium salt result during the oxidation process The boarding of the strong band at 3400 cm-1 may also result from superimposed of O-H, (H2O) and -NH stretching bands (See Fig 9(a-e)) This observation may indicate the formation of ammonium salt due to the oxidation of oxazoles of the two scintillator fluors The band appears at 2100 cm^{-1} may be attributed to -N-H stretching of ammonium salt By increasing the addition of the oxidizing agent (H_2O_2) band in the vicinity of 1650 cm^{1} corresponding to -C =O group significantly appeared Fig 9(a-e) Band near 1230 cm^{1} which is characteristic to peroxide group was also detected in Fig 9(a) and disappear through further oxidation in the presence of higher amount of H_2O_2, Fig 9(b-e) These observations may indicate the formation of intermediate oxidation products with carbonyl and peroxide groups which by further oxidation are converted to carbon dioxide and water

The data obtained so far indicate that the oxidative degradation of spent liquid scintillator, using hydrogen peroxide results in aqueous secondary waste solution which is more suitable for subsequent immobilization compared with the original organic waste

TABLE IX COMPRESSIVE STRENGTH OF THE SOLIDIFIED FINAL WASTE-CEMENT FORMS CONTAINING DEGRADED AND UNDEGRADED ORGANIC LIQUID SCINTILLATOR

Immobilized waste (1)	Compressive strength (kg/cm^2)
Distilled water	263
Degraded liquid scintillator (A)(2)	268
Degraded liquid scintillator (B) (3)	249
Non-degraded liquid scintillator	3 8

(1) Immobilized waste cement ratio usually kept constant at 1 2 81 by weight

(2) Degraded scintillator (A) obtained from the oxidation of scintillator in 30% H_2O_2 with the ratio scintillator H_2O_2 = 1 4

(3) Degraded scintillator (B) obtained from the oxidation of scintillator in 30 % H_2O_2 with the ratio scintillator H_2O_2 = 1 2

Two laboratory oxidative degradation experiments were performed using solutions having different scintillator/hydrogen peroxide ratios, namely (1:2 & 1:4). The aim was to study the suitability of the resulting products for further immobilization in cement matrix. The obtained degraded solutions were mixed with cement powder at constant percentage (35 wt%) and compressive strength measurements were carried out for the final solidified blocks. The obtained values were compared with those values of solid blocks containing untreated liquid scintillator and pure water as mixing solutions. The results are represented in Table IX and no significant difference in the strength values was observed for the cement blocks incorporating the two degraded solution compared with the same percentage of pure water only. Solid cement blocks incorporating the same percent of untreated scintillator show very poor mechanical integrity unacceptable for subsequent transportation, storage and disposal processes [26]. However additional research work to optimize both treatment and immobilization process is needed.

3.2. DIRECT IMMOBILIZATION OF THE LIQUID SCINTILLATOR

The incorporation of radioactive waste into cement is the most widely used technique for its practical, technological and economical advantages [27]. Mechanical properties are important factors to be taken into consideration in evaluating the final solidified products [28]. It is worth mentioning that certain minimum values of mechanical properties are required for safe handling of the conditioned waste form during transportation and final disposal processes [26].

TABLE X. EFFECT OF LIQUID SCINTILLATOR PERCENTAGE ON THE COMPRESSIVE STRENGTH OF THE SOLIDIFIED FINAL WASTE FORMS

Liquid scintillator (%, by weight of cement)	Compressive strength (kg/cm^2)
0	263
5	216
10	183
15	135
20	113
25	99

- The water of hydration was kept constant (35%) in all experiments.

The results represented in Table X indicate the effect of increasing the percentage of organic liquid scintillator, directly immobilized into cement, on the compressive strength of the final solidified products. The data obtained show that increasing the organic liquid scintillator percentage, keeping the water of hydration percentage constant (35 % by weight of cement), decreased sharply the compressive strength values. The reaction of Portland cement with water leads to hydration of its compounds, setting hardening and develop strength in the set cement. Therefore, some relation exists between the amount of hydration, porosity and the compressive strength values [29]. The reduction in compressive strength values, Table X, with increasing liquid scintillator seems to be due to the formation of surface protecting layers surrounding the cement particles which delayed the hydration process [30].

This was further illustrated by increasing the liquid scintillator, at the expense of the water of hydration on the mixing solution, which results in drop in the compressive strength of the final solid blocks. Table XI. Increasing the scintillator percentage in the mixing solution from 0% to 20% results in a decrease in the compressive strength values of the final waste from 263 to 210 kg/cm^2. Moreover increasing the scintillator percentage to 80% and reducing the water of hydration to 20% in the mixing solution leads to great deterioration in the mechanical integrity of the cement blocks. On the other hand using liquid scintillator only as mixing material results in a highly fragile blocks having very low compressive strength values. (~ 3.8 kg/cm^2).

TABLE XI EFFECT OF LIQUID SCINTILLATOR/WATER RATIO ON THE COMPRESSIVE STRENGTH OF THE SOLIDIFIED WASTE FORMS

Mixing solution Liquid scintillator/water ratio	Compressive strength (kg/cm^2)
Zero 100	263
20 80	210
40 60	171
60 40	109
80 20	28
100 Zero	3 8

1 The mixing solution/cement ratio was kept constant at 1 2 81
2 The liquid scintillator was increased on the expense of water of hydration

The presence of organic liquid scintillator affects negatively the cementation process and consequently the properties of the final solidified waste form The data obtained reveal the need for special treatment of the liquid scintillator before immobilization in cement matrix to improve the properties of the final waste products

4. CONCLUSION

From the data obtained so far it could be concluded that oxidative degradation process using hydrogen peroxide is simple, reliable method that shows a highly acceptable efficiency in transforming cation-exchange resins from solid to liquid phase with a good weight reduction factor and high conversion percentage The proposed simple process operates at mild conditions compared with other processes operating under drastic corrosive conditions, relatively high temperature and complicated off-gas treatment system

In addition, wet oxidative degradation of spent contaminated liquid scintillator, using hydrogen peroxide improves highly the properties of the solidified final waste forms to comply with the requirement needed for the transport and disposal of final waste products

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DEVELOPMENT OF METHODS FOR TREATMENT AND CONDITIONING OF BIOLOGICAL RADIOACTIVE WASTE IN THE CZECH REPUBLIC

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Abstract

Incineration of biological radioactive waste was performed in a facility manufactured in the Czech Republic for combustion of burnable, radioactive and non-radioactive residues. The equipment has shown an adequate capability for combustion of biological waste. Basic technical parameters of the incinerator SP-603 can guarantee combustion of majority of wastes from different radionuclide users in the country. To ensure proper further handling with the resulting ash, three conditioning options were studied, the bituminization process, incorporation into cement, and embedding of ash into a mixture of bituminous and cementitious materials. Mechanical properties of the conditioned ash were in good compliance with those published elsewhere. Bituminized ash exhibits lowest leachibility, followed by the ash conditioned by means of the mixed process. Potential abnormal operation conditions were evaluated and their consequences assessed. The evaluation encompassed sensitivity analysis of the consequences potentially affecting the operating staff, nearby population and the environment. Cost estimate was carried out using a national approach for the calculation. From the results it can be seen that there are no large differences between the conditioning and disposal of wastes resulting from different conditioning processes.

1. INTRODUCTION

The former Institute for Research, Production and Application of Radioisotopes, presently named NYCOM, started to participate to the IAEA Co-ordinated Research Programme in 1991. Five Progress Reports were submitted to the Agency describing the work carried out during the period October 1991-April 1996 [1-5]. In addition, the results obtained were reported at the three IAEA Research Co-ordination Meetings on Treatment Technologies for Low and Intermediate Level Wastes Generated from Nuclear Applications, held in Bangkok, Thailand, May 1993 [6], Istanbul, Turkey, January 1995 [7], and Quezon City, Philippines, April 1996 [8].

2. VOLUMES OF WASTE FROM RADIONUCLIDE APPLICATIONS

After an appropriate segregation and separation of waste containing short lived radionuclides, the annual volume of waste was ranged in the period of 1977-1995 within 65 and 120 m^3. As a rule, these wastes are emplaced into steel drums of 200 liters; one part (compressible waste) is baled, and the content mixed with cement grout for solidification to minimize the mobility of the contained radionuclides. The total waste inventory is shipped to the repository for final disposal.

Typical composition of solid waste from medical applications was the following [9]:

(a) 55% of combustible materials, subdivided into:
  plastic fragments 25%
  paper and cloth 25%
  miscellaneous wastes (carcasses etc.) 5%
(b) 35% of hard materials (glass, metallic components, coating or lining fragments)
(c) 10% of waste resulting from smaller operational incidents: contaminated concrete, wood, etc.

As mentioned earlier, the annual amount of combustible waste represents one half of the total, i.e. 30-75 m^3. Among this waste, several waste streams suitable for incineration can be identified. Their characteristics are shown in Table I.

TABLE I. CHARACTERISTICS OF WASTE STREAMS SUITABLE FOR COMBUSTION

Waste stream	Nuclide	Activity (Bq)	Waste volume (m^{3})	c (Bq/g)
Biological research waste	^{3}H	6.0x10^{11}	3.0	2.0x10^{5}
Biological research waste	^{3}H ^{14}C ^{45}Ca	2.0x10^{11} 7.5x10^{10} 8.0x10^{8}	5.5	3.6x10^{4} 1.4x10^{4} 1.5x10^{2}
Hospital waste	^{3}H ^{14}C	3.5x10^{11} 5.0x10^{11}	12.0	2.9x10^{4} 4.2x10^{4}
Research waste	^{60}Co	1.3x10^{10}	2.2	5.9x10^{3}
Research waste	^{90}Sr	8.0x10^{9}	0.5	1.6x10^{4}
Biological research waste	^{239}Pu ^{241}Am	5.0x10^{8} 2.2x10^{8}	0.3 0.2	1.6x10^{3} 1.1x10^{3}

3. THE INCINERATION FACILITY

The incinerator SP-603 manufactured by the Uranium Mines Western Bohemia (KP CSUP) has been selected as the most suitable facility from the economic point of view. The unit is a dual chambered with controlled air incineration. The facility (see Fig.1) is composed of:

(a) a furnace with a combustion chamber including gas burners and piping.
(b) a fly ash removal system.
(c) a ventilation system.
(d) connecting piping.
(e) an automated control panel.

In general, the facility is suited for burning of solid waste with heating values ranging from 4,000 to 15,500 kJ/kg. The fraction of high heating value waste such as plastics, rubber must not exceed 10% of the overall waste feed.

The furnace consists of a steel furnace shell with a refractory lining designed for sufficient strength and resistance at the expected operation temperatures of 1200°C.The combustion chamber is provided with connections for pressure and temperature measurements and other instrumentation. The off-gas is passed into the afterburner chamber to ensure a complete burnout and cooled in a cooling chamber where after mixing with cooling air it attains a temperature of 300-350°C. The design of the afterburner chamber ensures sufficient temperature, turbulence and residence time to accomplish complete off-gas burning.

The furnace is equipped with two automated gas burners for waste ignition in the start-up phase as well as for auxiliary firing during operation to maintain the desired operating temperature. They are controlled by an automatic control unit.

Removal of ash is done by gravity. The ash is removed mechanically from the bottom of the facility by means of collection and storage hoppers. Fly ash removal is entrained throughout the incineration system by means of an air filter and a cyclone separator which is used also as a spark arrestor. The system is provided with ash discharge equipment, i.e. an attached hopper, located in the lower part of the separator.

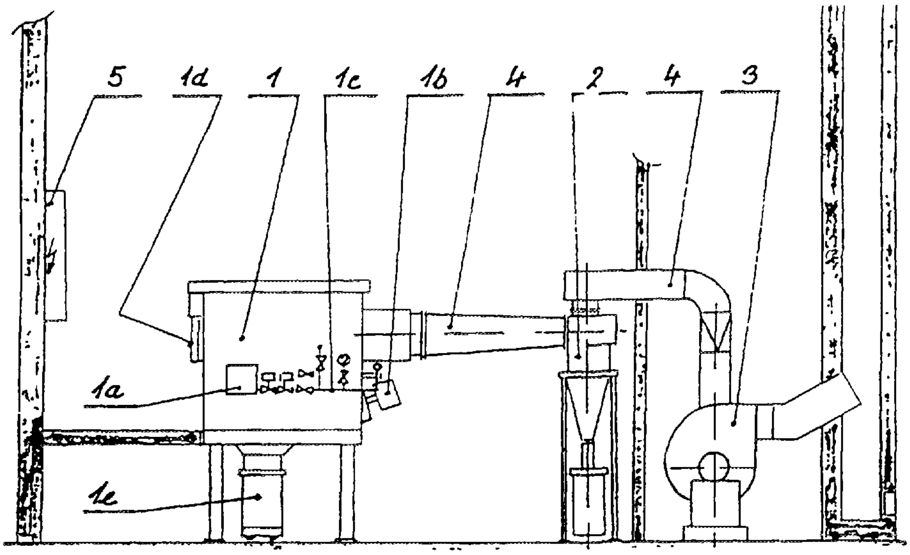

FIG.1. Incineration Facility SP-603
(1-Furnace Area, 1ab-Burners, 1c-Gas Connecting Tube, 1d-Waste In, 1e-Ash Bins, 2-Flying Ash Separator including air filter, 3-Ventilation, 4-Main Connecting Tube, 5-Control Panel)

TABLE II. BASIC TECHNICAL PARAMETERS OF THE INCINERATOR SP 603

Nominal capacity of the incinerator (kg/h)	60
Waste feed (kg)	10
Gas calorific value (MJ/m^3)	34.3
Gas overpressure (Pa)	1700
Gas power input (m^3/h)	21
Installed heat input (kW)	160
Heat consumption (MJ)	576
Specific heat consumption (MJ/kg)	7.6
Off-gas cooling temperature (°C)	300-350
Total electric input (kW)	12

The ventilation system consists of a radial, high-pressure ventilator which ensures the adequate underpressure in the combustion chamber, combustion and cooling air supplies, and transportation of off-gas to the stack. The design of the ventilation system enables its reliable operation under temperatures up to 300°C. The connecting piping provides for linking the individual components of the overall incineration system, including its connection with the stack. It consists of antivibrating components intended to prevent transfer of vibrations throughout the system.

The control panel includes sensors, control switches and position indicators for components and valves, and other process instrumentation necessary to ensure safe and reliable operation The instrumentation provides for reading and recording of parameters and automatically signals the need for corrective action The causes for the shutdown are annunciated and the control system requires that the deficiency is corrected before the operation is restarted

The following parameters are automatically measured

temperature in the combustion chamber,
pressure in the combustion chamber,
differential pressure across the filters

Basic technical parameters are summarized in Table II

After testing, the proposed incineration system SP-603 for non-radioactive effluent discharges and calculating the most severe scenarios, the application for a licence for combustion of radioactive biological wastes has been submitted to the competent regulatory authorities Based upon detailed studies of the test results, the following limits and conditions have been established for the proposed facility

(a) The radioactive wastes shall be segregated into categories consistent with the requirements of the proposed incineration scheme Burnable wastes shall include plastics, paper, pulp and contaminated animal carcasses
(b) Total annual amount of radioactive wastes to be incinerated in one single facility shall not exceed 3 m^3
(c) Weekly amounts shall not exceed 60 liters The waste shall be segregated into individual feeds prior to the shipment for incineration
(d) The waste activity shall be measured, for incineration only packages with surface exposure rates lower than 5 μGy/h may be received, activity of alpha-emitting nuclides shall not exceed 100 MBq in one feed
(e) The waste shall be contained in impermeable polyethylene packages
(f) Under the above conditions, the packaged material can be considered as waste which is in compliance with waste acceptance criteria for incineration

4. CONDITIONING OF THE ASH

The ash resulting from the operating incineration facility is collected in 200 L zinc-coated carbon steel drums Filling, drum capping and manipulation is accomplished in a work station designed for handling different types of institutional waste

Several laboratory and full-scale tests were carried out to check on a most suitable immobilization method Techniques studied were those already in operation at various Czech nuclear facilities The parameters observed were mechanical properties of the resulting product, its leachibility under simulated conditions, safety aspects of the incineration process and, last but not least, operational costs of the immobilization methods involved

In the studies performed, attention was paid to the two long lived transuranium radionuclides, ^{239}Pu and ^{241}Am, which are occasionally used in the biological studies carried out in some Czech research establishments Several samples of ash resulting from various incinerations were analyzed The results are presented in Table III For immobilization purposes, the ash was mixed with cement, bitumen, and a cement/bitumen mixture in different ratios as shown in Table IV

TABLE III. TYPICAL COMPOSITION OF THE ASH [10]

Component	Percentage range (%)
Loss by annealing	25.0 - 34.5
SiO_2	1.4 - 2.3
R_2O_3	18.5 - 24.8
P_2O_5	0.1 - 0.5
CaO	37.5 - 42.5
MgO	0.75 - 1.05
$Na_2O + K_2O$	2.1 -3.0
$S + SO_4^{2-}$	1.0 - 1.75
Cl^-	1.0 - 1.3

TABLE IV. MIXING RATIOS OF THE ASH AND THE IMMOBILIZING MATERICES

Sample No.	Mixing ratios		
	cem/ash	bit/ash	cem/bit/ash
111-113	1:1	1:1	1:1:1
121-123	1.5:1	1.5:1	1.5:1.5:1
131-133	1.25:1	1.25:1	1.25:1.25:1
141-143	0.75:1	0.75:1	0.75:0.75:1
211-213	1:1	1:1	1:1:1
221-223	1.5:1	1.5:1	1.5:1.5:1
231-233	1.25:1	1.25:1	1.25:1.25:1
241-243	0.75:1	0.75:1	0.75:0.75:1

5. PROPERTIES OF THE IMMOBILIZED ASH

After hardening of the product, the samples were subjected to the examination of some selected properties. These were density and porosity of the product, compressive and bending strengths in the case of cemented ashes, softening point and flame ignition temperature (by visual observation) in the case of ash incorporated into bitumens. The results are shown in Tables V-VII.

Leachibility of the immobilized ash was studied in view of its further disposal in a near surface repository of a rock cavity type, i.e. to the abandoned limestone mine Richard in the Northern Bohemia which is currently used for disposal of institutional waste [11]. Leach rates were determined by using two methods, static and dynamic ones [12]. The static method have undergone all samples whereas the dynamic method was applied to some selected samples containing the immobilized ash. Results of the static (batch) tests are shown in Figs. 2 and 3.

TABLE V. SELECTED PROPERTIES OF THE CEMENTED ASH

Sample No.	Compressive strength (MPa)	Bending strength (MPa)	Density (kg/dm^3)	Porosity (%)
111	21.2	1.95	2.05	4.9
121	26.8	1.96	2.22	4.6
131	24.7	1.84	2.14	4.2
141	15.4	1.72	1.71	2.9
211	29.6	1.65	2.20	3.1
221	23.7	1.69	2.38	3.6
231	20.8	1.82	2.15	4.4
241	13.0	1.68	1.80	2.8

TABLE VI. SELECTED PROPERTIES OF THE BITUMINIZED ASHES

Sample No.	Density (kg/dm^3)	Porosity (%)	Softening point (^{0}C)	Flame ign. temp. (^{0}C)
112	1.42	17.5	87	250
122	1.37	18.0	90	260
132	1.25	16.5	85.5	280
142	1.18	14.2	82	250
212	1.35	16.5	83	250
222	1.38	16.2	85	255
232	1.29	16.1	87	270
242	1.25	15.0	85	250

TABLE VII. SELECTED PROPERTIES OF THE ASHES INCORPORATED INTO CEMENT/BITUMEN MIXTURE

Sample No.	Density (kg/dm^3)	Porosity (%)	Sample No.	Density (kg/dm^3)	Porosity (%)
113	1.85	10.3	213	1.83	11.0
123	1.92	9.2	223	1.90	9.5
133	2.05	8.7	233	1.98	8.4
143	1.74	11.2	243	1.79	10.0

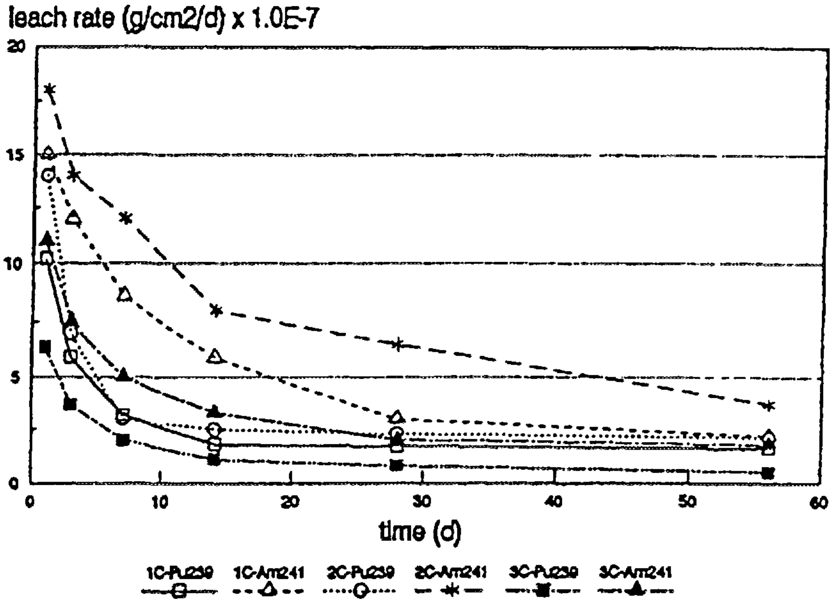

FIG.2 Leachibility of ^{239}Pu and ^{241}Am from cemented ashes

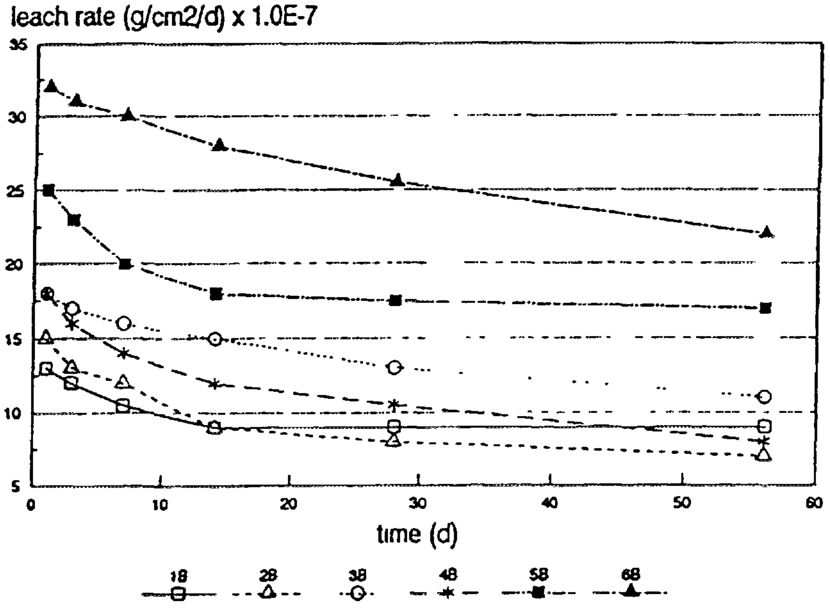

FIG.3. Leachibility of ^{239}Pu from bituminized ashes

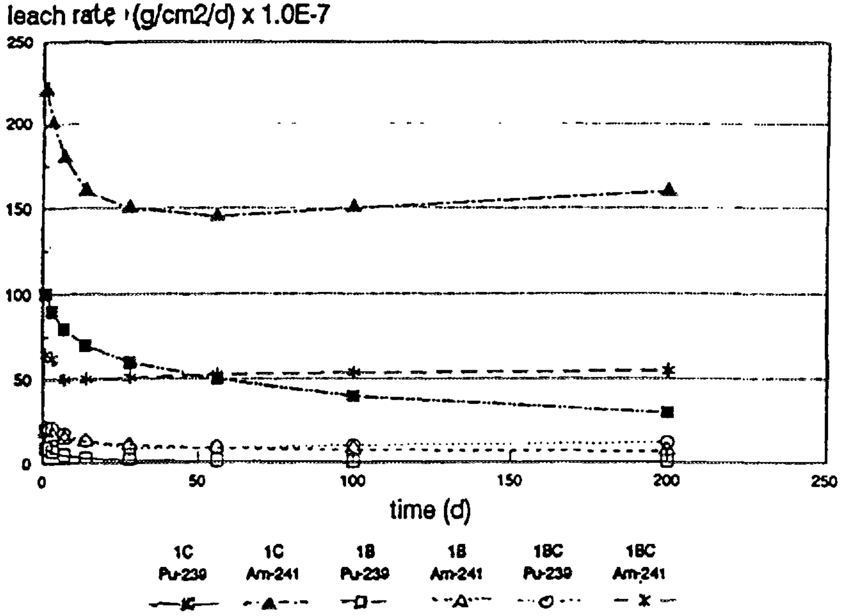

FIG. 4. Leaching of selected transuranics from immobilized ashes by means of a dynamic method

TABLE VIII. LEACH RATES OF ^{239}Pu AND ^{241}Am (in g/cm^2/d · 10^{-7}) FROM THE CONDITIONED ASH (DYNAMIC METHOD)

t (days)	Sample[a] nuclide					
	C: ^{239}Pu	C: ^{241}Am	B: ^{239}Pu	B: ^{241}Am	BC:^{239}Pu	BC:^{241}Am
7	105	170	16	20	30	51
14	82	165	10	18	25	46
21	69	160	7	18	20	45
28	55	151	5	17	16	40
35	45	145	3	17	14	37
49	40	127	2	18	11	36
70	39	112	2	16	8	37
84	38	105	2	17	6	37
98	35	100	2	16	7	35

a/ C...cementation, B...bituminization, BC...mixed process

Leach rates obtained under dynamic conditions consisted of continuous leaching of the sample with simulated groundwater of the composition shown in Ref [4] Similarly to our previous study, to obtain measurable leach rates, radionuclide concentration in the sample was increased by adding both transuranics to the ash in amounts approximately two orders higher than those originally contained in the product to be immobilized Results of the dynamic leaching tests are shown in Table VIII and in Fig 4

It can be clearly seen that the bituminized ash exhibits the lowest leachibility, followed by the ash conditioned by means of the mixed process Nevertheless, all the results obtained provide evidence that, in long term, continuous leaching by groundwater would result in very low contamination of the environment, giving rise only to negligible exposures of the population potentially using groundwater for drinking and/or agricultural purposes

It can be observed that the leachibility of both transuranic elements from all samples of the immobilized ash exhibits higher values at the very beginning, i e within few days from the start of the leaching process and, after approximately 10 days the leached quantities drop to a constant level The difference between the both radionuclides (higher leach rates obtained for ^{241}Am) could be caused by diverse chemical properties, namely solubility of both oxides present in the leached product

6. SAFETY ASSESSMENTS

In the calculation of exposures expected to result from the proposed incineration facility, parameter values were based on characteristics of the selected plant and on references available in the existing literature [13,14] Where the ranges of parameters were given, conservative values have been used

The procedure described in Ref [15] was used for calculation of doses due to atmospheric releases from the given incineration facility Possible exposure scenarios include

- exposure of the incinerator operator via inhalation of dust,
- release of gases to atmosphere via the stack, and subsequent exposure of the public from inhalation of the air

For the operator scenario, the equation may be written as follows

$$H=m \cdot t \cdot r \cdot c_d \cdot c_w \cdot DF \cdot (1-f_i) \cdot F \qquad (1)$$

where

H	is the dose to the operator from inhalation of dust,
m	is the mass reduction factor in the plant,
t	is duration of exposure of the operator,
r	is the breathing rate of the operator,
c_d	is the dust concentration in respirable particles,
c_w	is the concentration of radionuclide in the waste,
DF	is the dose conversion factor,
f_i	is the fraction of the total activity of radionuclide released through the stack, and
F	is the ratio of concentration in airborne dust to that in diluted ash

The general expression for doses which may be received by an individual as a result of releases to the atmosphere from the incinerator can be formulated as:

$$H = c_{air} \cdot r \cdot t \cdot DF \qquad (2)$$

and c_{air} is defined as follows:

$$c_{air} = X \cdot f_i \cdot R \cdot c_w \qquad (3)$$

where

X	is the average concentration of released material in air, and
R	is the average rate of waste incineration.

Other pathways such as external exposure, ingestion of contaminated foodstuffs or ash reuse have not been considered because of very low impacts expected.

In the incinerator operator scenario, the average airborne dust concentration of 10^{-3} g/m^3 has been assumed. Radionuclide fraction in the remaining ash represented 0.1 for ^{3}H and ^{14}C, whereas for other nuclides the value 0.9 was used. Mass relation factor 3 for incinerated waste was conservatively chosen [15].

The calculations issued from the following assumptions :

(a) According to the licence issued by the hygienical authority, the concentration of transuranic elements shall not exceed 100 MBq in one feed. The maximum amount did not reach the prescribed limit. In fact, the concentration in some feeds was lower than 10 MBq/feed.

(b) In our previous calculation [4] the ratio between the airborne dust concentration and the total concentration in the feed was taken at the level of 10^{-3}. For our sensitivity estimate a reasonably expected range 10^{-4} - $5\text{x}10^{-3}$ was used.

(c) Former it was assumed that the exposure duration in the case of loss of services may attain 30 minutes. Such conservative value is highly improbable and is not foreseen in the emergency instructions; several tens of seconds or minutes are more likely.

(d) Similarly, for public exposure calculation a conservative atmospheric dilution factor $5 \cdot 10^{-6}$ was used, as well as the most unfavourable Pasquill-Gifford atmospheric category , in which situation the duration of the contaminated cloud passage was 3 hours. However, such condition (less than 3d/y at the incinerator site) can never occur since the licence permits incineration under favourable dispersion condition only.

With the use of the most conservative input parameters, the dose calculations were performed and the results shown in Tables IX-XI.

TABLE IX. EXPOSURES OF THE OPERATOR AS RESULT OF ABNORMAL OPERATION CONDITIONS (LOSS OF SERVICES)

Radio-nuclide	Q(total) (Bq)	Q(air) (Bq)	c(air) (Bq/m^3)	Q(inh) (Bq)	H(i) (Sv)
^{239}Pu	$2.5\text{x}10^7$	$2.5\text{x}10^4$	$1.0\text{x}10^2$	$5.94\text{x}10^1$	$8.3\text{x}10^{-3}$
^{241}Am	$6.0\text{x}10^7$	$6.0\text{x}10^4$	$2.4\text{x}10^2$	$1.43\text{x}10^2$	$2.0\text{x}10^{-2}$

TABLE X. EXPOSURES OF AN INDIVIDUAL FROM THE GENERAL PUBLIC AS RESULT OF ABNORMAL OPERATION CONDITIONS (LOSS OF SERVICES)

Radio-nuclide	Q(total) (Bq)	Q(air) (Bq)	c(air) (Bq/m^3)	Q(inhaled) (Bq)	H(i) (Sv)
^{239}Pu	2.5x10^7	2.5x10^4	5.0x10^{-4}	1.8x10^{-3}	2.5x10^{-7}
^{241}Am	6.0x10^7	6.0x10^4	1.2x10^{-3}	4.3x10^{-3}	6.0x10^{-7}

In the tables above the symbols denote :

Q(total)- total radionuclide quantity in the waste feed;
Q(air)- total radionuclide quantity in the airborne dust;
c(air)- radionuclide concentration in the inhaled air;
Q(inhaled)- portion of radionuclide inhaled;
H(i)- effective dose equivalent by inhalation

TABLE XI. EXPOSURES OF THE OPERATOR AND OF AN INDIVIDUAL FROM THE GENERAL PUBLIC AS RESULT OF ABNORMAL OPERATION CONDITIONS (PRESSURE OR TEMPERATURE TRANSIENTS, FIRE)

Radio-nuclide	Q(total) (Bq)	c(air) (Bq/m^3)	c'(air) (Bq/m^3)	H(i,o) (Sv)	H(i,ind) (Sv)
^{239}Pu	2.5x10^7	1.25x10^5	6.25x10^{-2}	4.2x10^{-2}	3.15x10^{-5}
^{241}Aml	6.0x10^7	3.0x10^5	1.5x10^{-1}	1.0x10^{-2}	7.56x10^{-5}

In the Table XI the following abbreviations were used :

c(air)- radionuclide concentration inside the workplace;
c'(air)- radionuclide concentration outside the building;
H(i,o)- effective dose equivalent incurred by the operator through inhalation;
H(i,ind) -effective dose equivalent incurred by an individual from the general public by inhalation.

For the sensitivity analysis calculations, the same conversion factor per unit intake for both radionuclides was used (0.00014 Sv/Bq) [16] and a mean breathing rate of 0.00033 m^3/s applied. Doses potentially received by the operator and an individual of the general public are shown in Tables XII-XIV.

TABLE XII. INFLUENCE OF AIRBORNE DUST CONCENTRATION AND EXPOSURE DURATION ON THE DOSE (in Sv) RECEIVED BY THE OPERATOR FROM COMBUSTION OF 100 MBq (LOSS OF SERVICES)

t (min)	c_{air}/c_0					
	5x10^{-3}	2x10^{-3}	1x10^{-3}	5x10^{-4}	2x10^{-4}	1x10^{-4}
0.5	0.00154	0.00062	0.00031	0.00015	0.00006	0.00003
1.0	0.00308	0.00120	0.00060	0.00030	0.00012	0.00006
2.0	0.00616	0.00250	0.00120	0.00060	0.00024	0.00012
3.0	0.00924	0.00370	0.00185	0.00092	0.00037	0.00018
5.0	0.01540	0.00620	0.00310	0.00150	0.00060	0.00030

TABLE XIII. INFLUENCE OF AIRBORNE DUST CONCENTRATION AND EXPOSURE DURATION ON THE DOSE (in Sv) RECEIVED BY THE OPERATOR FROM COMBUSTION OF 25 MBq (LOSS OF SERVICES)

t (min)	c_{air}/c_0					
	5×10^{-3}	2×10^{-3}	1×10^{-3}	5×10^{-4}	2×10^{-4}	1×10^{-4}
0.5	0.00038	0.00015	0.00008	0.00004	0.00002	0.00001
1.0	0.00077	0.00030	0.00015	0.00007	0.00003	0.00002
2.0	0.00154	0.00062	0.00031	0.00015	0.00006	0.00003
3.0	0.00231	0.00092	0.00046	0.00023	0.00009	0.00004
5.0	0.00375	0.00130	0.00077	0.00037	0.00015	0.00007

TABLE XIV. INFLUENCE OF ATMOSPHERIC DISPERSION AND EXPOSURE DURATION ON THE DOSE (in mSv) RECEIVED BY AN INDIVIDUAL FROM GENERAL PUBLIC RESULTING FROM COMBUSTION OF 100 MBq OF TRANSURANICS (LOSS OF SERVICES)

t (min)	c_{air}/c_0				
	5×10^{-6}	1×10^{-6}	5×10^{-7}	2.5×10^{-7}	1×10^{-7}
30	0.0227	0.0045	0.0023	0.0011	0.0004
60	0.0454	0.0091	0.0045	0.0023	0.0009
90	0.0681	0.0136	0.0068	0.0034	0.0014
120	0.0908	0.0181	0.0091	0.0045	0.0018
180	0.1362	0.0272	0.0136	0.0068	0.0027

In any case the potentially incurred dose does not exceed limits for occupational exposure; in practice, occupational dose limits should be applied to all activities carried out by the operator, this means normal operation of the facility and its maintenance. Through the dosimetric survey over past several years it has been shown that the operators exposure did not attain some 10% of the limits.

As regards the public exposure, this should encompass all exposures other than occupational and medical ones. From the values given in Table XI it is evident that the potentially incurred dose resulting from incinerator abnormal operation condition is, in the worst case, ten times less than exposure due to natural sources of radiation.

7. DISPOSAL

The Richard repository was put into operation in 1964. A disused limestone mine, in which mining activities ceased in 1910, was adapted for acceptance of radioactive non-fuel cycle waste. It is still in operation and its capacity is sufficient for accommodation of all the expected waste arisings at least until the year 2005. The repository itself consists of a system of horizontal tunnels accessible directly from ground level at the bottom of a hill in which it is located. The waste in 200 L steel drums is emplaced into adjacent cavities each having volume of several hundreds of cubic metres. Full cavities will be sealed with a mixture of concrete and clay; another sealing is provided inside the cavities to prevent ingress of rain water to the waste. In addition, a drainage system composed of channels and pipes is available to drain rain water, which will eventually percolate through the surrounding rock, into the control sumps from where it could be passed to a river.

8. COST ESTIMATE OF THE ASH CONDITIONING PROCESSES

The cost estimate of the three conditioning processes is presented in Table XV. The values are given in Czech crowns (CzK) of 1996 (1 US$ is equal to 27.5 CzK). All costs are related to a process in which 100 kg of the ash from the incinerator were incorporated into the given matrix by ratio 1:1, packaged into a container, transported and disposed of in a national rock cavity type repository Richard in Northern Bohemia. The individual items of the cost estimate represent the material, energy, manpower, overheads, capital depreciations and investments. The container was a 200 L steel drum zinc-coated from both sides, produced by the Czech company MEVA. The fixing materials were: 350 Portland cement and bitumen emulsion 2ME20. Process steam for heating and evaporation of the bitumen emulsion was produced in the Institute's heating plant.

Manpower's cost was calculated from the actual salaries of the personnel of the waste treatment plant. Overheads represent 300% of the direct costs and include, e.g., the dosimetric survey, analytical laboratory, repair and maintenance of the building and equipment, administration, etc. Investments encompass earning (15%) and financial means used for research and development studies and for procurement of new equipment.

Annual capital depreciations represent 5% of the first costs in the case of a building (expected lifetime 20 years) and 12.5% in the case of equipment (expected useful lifetime 8 years). The cost estimate is supplemented by the transportation costs and disposal costs in the repository Richard, presently operated by NYCOM.

Table XV does not exhibit large differences between the conditioning and disposal costs of the waste resulting from different conditioning processes. Relatively high costs for disposal are mainly due to high maintenance expenditures for repository operation and for operating the environmental programme. Included is also refurbishment of older parts of the mine for future disposal activities.

TABLE XV. COST ESTIMATES OF DIFFERENT ASH CONDITIONING PROCESSES

Item		C[a]	B[a]	M[a]
Material	container	700	700	700
	cement	250	-	120
	bitumen	-	600	300
	water	20	-	10
Energy	electricity	30	20	20
	process steam	-	110	80
Manpower		400	400	400
Overheads		4140	5490	4860
Cap.depreciation	building	2000	2000	2000
	technology	380	900	640
Investments		1050	1050	1050
Transportation		600	600	600
Disposal		8400	8400	8400
Total		**17970**	**20270**	**19180**

[a]/ C...cementation, B...bituminization, M...mixed process

9. CONCLUSIONS

The studies have led to the following conclusions :

(A) The selected incineration facility has shown adequate capability for combustion of biological wastes. Basic technical parameters of the incinerator SP-603 can guarantee combustion of majority of wastes from different radionuclide users in the country. Nearly one half of combustible wastes generated in the country can be incinerated in the facility of the given type. This can result in some reduction of the available disposal capacity in the repository Richard.

(B) Inactive tests performed with the incinerator SP-603 have shown good compliance with limits for releases of particulates and off-gases, which have been established by national regulatory authorities.

(C) Mechanical properties of the conditioned ash are in good compliance with those published elsewhere. Highest densities, as well as compressive and bending strengths exhibit generally products with higher cement content. Similarly, in the case of bituminized ash, densities decrease with higher content of the ash in the final product. The same situation does not occur in the case of mixed products; the reason could be different process temperature or different hardening times.

(D) It could be seen that bituminized ash exhibits lowest leachibility, followed by the ash conditioned by means of the mixed process. Nevertheless, all results obtained give evidence that, in long term, continuous leaching by groundwater would result in very low contamination of the environment, giving rise only to negligible exposures of the population potentially using groundwater for drinking and/or agricultural purposes.

(E) A highly conservative approach was used in the preliminary safety analysis of the proposed incineration system. The obtained results of dose calculations have shown that, under normal operation conditions, operator's exposures to various radionuclides via inhalation are generally three orders below the limits internationally agreed. The same is valid for public exposures where the highest values obtained from the inhalation pathway represent only a few per cent of the value of 10 uSv/y which is reasonably regarded as trivial and forms the worldwide basis for exemptions from regulatory control.

(F) Abnormal operation conditions potentially occurring during the combustion process were assessed by means of a preliminary estimate. Despite most conservative input values used in the calculations, the exposures of the operating personnel will not exceed acceptable levels; as regards the exposures of the general public, those of the most exposed individual were several orders below the natural background.

(G) To assess the sensitivity of incurred doses towards the selected assumptions, several main parameters were evaluated and effects of variations within reasonable ranges calculated. In any case the potentially incurred dose does not exceed limits for occupational exposure. Through the dosimetric survey over past several years it has been shown that the operators exposure did not attain some 10% of the limits.

(H) As regards the public exposure, from the values given above it is evident that the potentially incurred dose resulting from incinerator abnormal operation condition is, in the worst case, ten times less than exposure due to natural sources of radiation.

(I) Cost estimate was carried out using a national approach for calculation. From the results it can be seen that there are no large differences between the conditioning and disposal of waste resulting from different conditioning processes. Relatively high costs for disposal are mainly due to high maintenance expenditures for repository operation and for operating the environmental programme. Included is also refurbishment of older parts of the mine for future disposal activities.

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DEVELOPMENT OF ECOLOGICALLY SAFE TECHNOLOGY FOR STEAM-THERMAL TREATMENT OF ORGANIC WASTES

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Abstract

The experience on mitigation of the consequences of the Chernobyl's nuclear power station accident proves that the treatment of large amounts of organic and mixed wastes containing radionuclides is a very urgent scientific and technical problem. In this connection a search for new ideas and development of highly efficient and ecologically safe technologies for treatment of organic radioactive wastes has been undertaken. This study is based on use of physico-mechanical properties of various organic materials (wood, rubber-containing composites, plastics, biomass) subjected to thermal decomposition in the overheated water steam medium. Under such conditions, there is a possibility, under relatively low temperatures (400 - 500°C), to realize thermal decomposition and considerably (in 8 - 50 times) to reduce the amount of wastes, to obtain the main concentration of radionuclides in the solid residue and to prevent releases of gaseous products containing radionuclides to the environment.

1. MODIFICATION OF THE LAB-SCALE FACILITY FOR CARRYING OUT THE STUDIES ON THE TREATMENT OF ORGANIC WASTE BY OVERHEATED STEAM

A special installation was manufactured to carry out our research on the treatment of organic waste by overheated steam. A general view of the installation is given in Fig.1. The installation is based on the steam generator EDA-22 1 (1), equipped with an automatic device to keep a required pressure of water steam and to guarantee its expenditure at 26 kg/h under pressure of 0.6 MPa.

Steam overheating is realized by an electric with steam generator 2, which is presented in the mounting state in Fig. 2. The overheating part consists of a pipe-line winded with an electrical heater. The power of the heater is regulated by a rheostat 2. The pipe-line itself with the heater is placed into the thermal insulating housing 3, filled in with the heat resistant material 4. The steam overheater allows to overheat the steam from 135°C to 500°C with the steam consumption up to 26 kg/h.

A thermochamber, where the steam treatment of waste is realized, is shown in Fig. 3. In the upper part of the housing a roof with the flange 3 and manometer 4 is mounted. In the lower part of the housing there is a grid 5 and a undergrid chamber 6. The feeding of wastes in the steam overheater is realized with a loading screw 7. Unloading of the solid residue is made by a delivery screw 8 into the container 9. The temperature in the housing is controlled by a thermometer 10.

A cooler, where gaseous products of thermal decomposition are condensed represents a heat exchanger with a tube bundle (see Fig. 4), which is composed of a housing 1, mounted on the supports 2. The tube bundle 3 where the steam-gaseous mixture is condensed, is built into the housing. In the upper part of the housing a lifting cover 4 is mounted and, when it is necessary, it may be taken off, to provide an access to the tube bundle.

The separation of waste decomposition products from water is realized in the separator (see Fig. 5). The separator is composed of a housing 1, valves 2, manometer 3, upper cover 4 and peephole 5.

This installation is operated as follows (see Fig. 1): highly saturated water steam from the steam generator 1 is fed into the steam overheater 2, where it is overheated up to T = 500°C. Then overheated steam is fed into the thermochamber 3, where the wastes are loaded using the loading screw. The inlet and outlet temperatures of the steam are controlled by the thermometers.

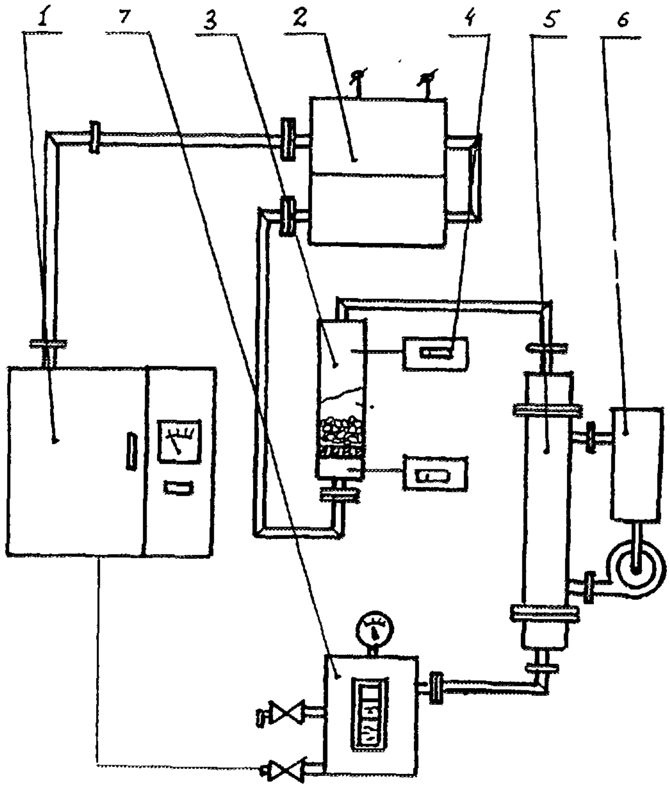

FIG. 1. The installation for the steam treatment of organic wastes (1- steam generator, 2- overheater, 3-thermochamber, 4- thermometer, 5-cooler, 6-tank for water, 7-separator).

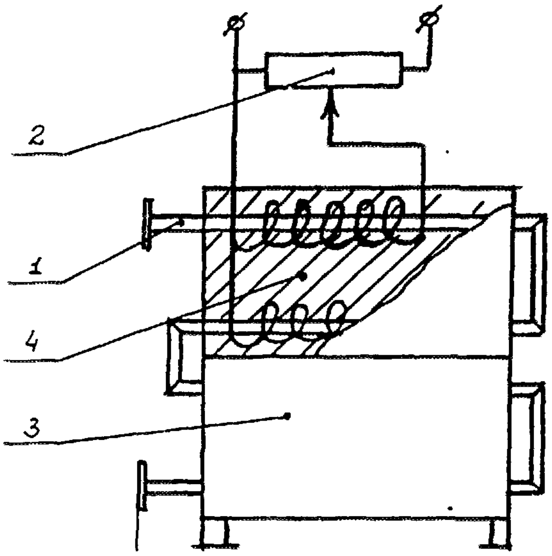

FIG.2. Steam overheater (1-pipeline, 2-rheostat, 3- vessel, 4-thermostable material).

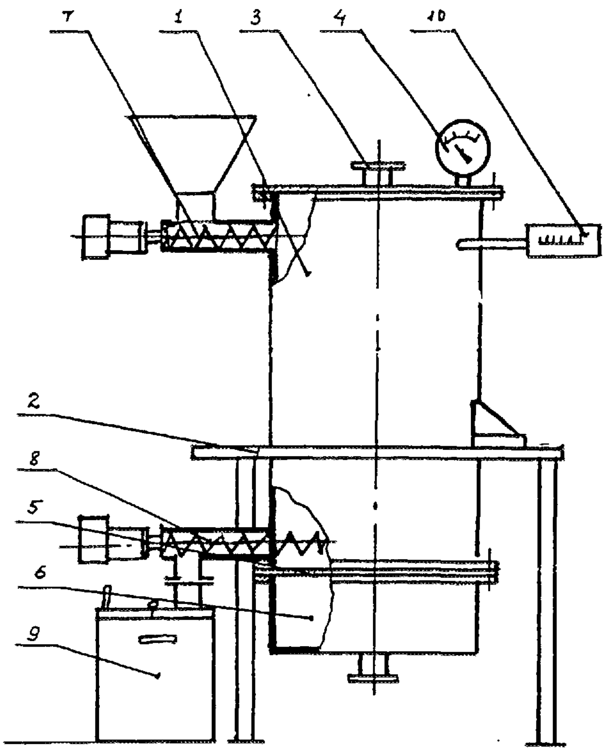

FIG. 3. Thermochamber (1- vessel, 2-supports, 3-flange, 4-manometer, 5-grid, 6-undergrid, 7-screw,8-delivery screw, 9-container, 10-thermometer)

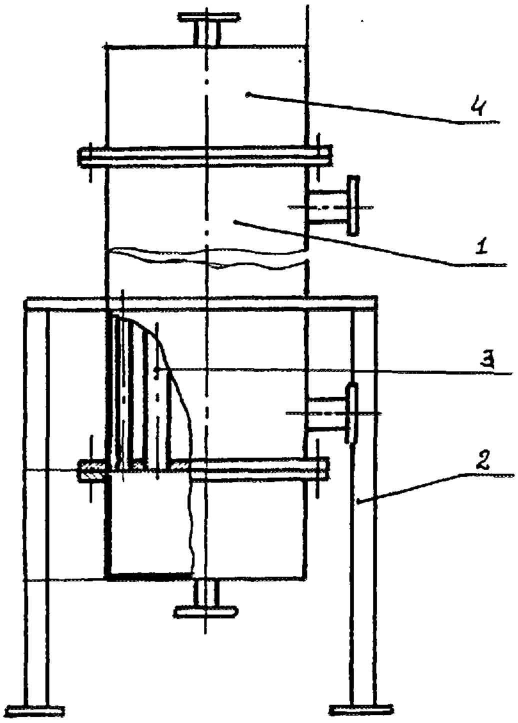

FIG.4. Cooler (1-vessel, 2-supports, 3-pipe bundle, 4-lid).

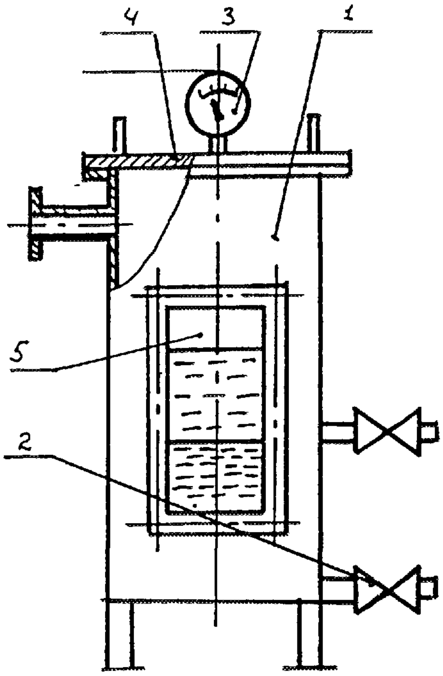

FIG. 5. Separator (1-vessel, valve, 3-manometer, 4-lid, 5-window).

The steam-gas mixture formed in the thermochamber goes through the pipe-line and comes to the heat exchanger 5, where it is cooled by water, feeding into the housing from the water's tank 6. The condensate is discharged into the separator 7. The solid products of thermal disintegration with a help of the delivery screw 8 are unloaded in the container 9. From the separator 7 the water comes back into the steam generator 1 and liquid hydrocarbons - into the store.

2. DEVELOPMENT OF THE METHODS FOR ANALYSIS OF THE RESIDUES

Particular methods for carrying out experiments for thermal processing by steam were developed. The temperature range of destruction (decomposition) of wastes depending of their kind (rubber, plastic, biomass) was detemined using derivatographic methods. Then temperature limits and values of endothermal and exothermal reactions for the waste treatment by overheaedt steam were determined. Using derivatograms, the amount of off-gases was found as well as time of the release. On the basis of data, obtained by derivatographic methods, the temperature tolerant intervals for treatment by steam were found in order to obtain the maximum amount of the solid residue and maximum concentration of radionuclides in it.

A composition of products of thermal destruction of wastes was analyzed by special methods. In the above-described installation the samples of organic wastes (rubber, plastic) were treated by the overheated water steam. The experiments show that the decomposition products consist of:

35 - 40 % of mass - liquid hydrocarbons
5 - 6 % - gaseous products
6 - 10 % - metal
53 - 45 % - solid residue

Liquid hydrocarbons are easily separated from the condensate and represent a liquor of dark-brown colour.

The main properties of the liquid hydrocarbons are shown in Table 1.

TABLE 1. THE MAIN PROPERTIES OF LIQUID HYDROCARBONS

No.	Properties	Value
1	Fraction composition - 10 % are destillated under temperature are destillated under temperature up to 250 C are destillated under temperature up to 360 C	 193°C 21% 76%
2	Viscosity under 50 C, -kinematic	 9.1 mm²/s
3	Temperature of solidification	+ 4°C
4	Ash content	none
5	Fraction of total mass for mechanic impurities	0.06 %
6	Density under 20°C	920 kg/m³
7	Low heat value	41300 kJ/kg

Gaseous products of destruction of rubber wastes are mainly composed of hydrocarbons and hydrogen. The solid residue is a substance of black colour. The density of the sample is 1780 kg/m³. The content of carbon is 89.5% , hydrogen -5,30%, sulphur - 1.07%, ash -5.2%. The heat of combustion of solid residue - 35.5 % MJ/kg. The treatment of solid residue was realized by catalytically burning within the range of temperature 300 - 360°C with the decreased amount of off-gases. The major part of radionuclides is concentrated in the ash which represents 5.2% of the solid residue. Thus the volume reduction of rubber wastes contaminated with radionuclides represents 36-4.

Polyethylene was used as example of polymer waste. Off-gases from the thermal destruction of polyethylene were collected after cooling and analyzed using chromatograph. The experiments were carried out in the temperature range 290-480°C.

Analysis of the experimental results shows that releases of the gases that were not condensated under the conventional conditions (P=1 MPa, T=273°K) are 20-41%. A condensated part of consists mainly of C_9-C_{20} with a boiling temperature of T=200-300°C. Paraffin hydrocarbons practically are not mixed with the condensate and can be easily separated. Analysis of the condensate has shown that it practically does not contain of hydrocarbons and because of that the condensate cannot be recycled for production of steam.

3. EXPERIMENTAL STUDIES ON DIFFERENT PROCESS PARAMETERS FOR THE TREATMENT OF RUBBER, POLYMERS AND BIOMASS

The experiments have been carried out as follows. Prior to the placement of a sample into the thermochamber it was heated to the required temperature which was selected in accordance to the objective of the experiment. The heated thermochamber then was loaded with the sample of biomass, rubber or polymers. The temperature of the cross-section of the sample, steam consumption and off-gases were registered during the experiment.

The steam-gas mixture coming out from the thermochamber was cooled down for separation of condensed and non-condensed gases. After the temperature has reached the given value the sample was unloaded from the chamber and cooled. The amount of the resulted condensate was measured.

The cooled sample was weighed and the amount of gaseous non-condensed products was determined as a difference of weights prior to and after thermal destruction taking into account the condensate amount.

The cooled sample was weighed and the amount of gaseous non-condensed products was determined as a difference of weights prior to and after thermal destruction taking into account the condensate amount.

It was found that the thermodestruction process of rubber waste starts at T=360°C and completed at T=500°C. For keeping such a temperature there is a need to have a certain amount of overheated steam in the chamber. This amount can be determined on the basis of the following considerations. There is a endothermal reaction during the destruction of rubber. In order to obtain the required temperature 360-500°C the rubber has to be heated to these temperatures (assuming the thermochamber has already been heated to this temperature). If the mass of rubber waste is M and its thermal capacity is C_r, then the amount of heat needed to heat the waste up to the temperature T is determined as:

$$Q_t = C_r \cdot M \cdot \Delta T \qquad \textbf{(1)}$$

Where $\Delta T = T - T_0$: T_0 is the ambient temperature.

Since the rubber waste is heated by overheated steam, the amount of the steam can be determined from Eq (1):

$$M_s = \frac{Q_t}{C_r \cdot \Delta T_{overh}} = \frac{C_t \cdot M \cdot \Delta T}{C_r (T_{st} - 100°C)} \qquad \textbf{(2)}$$

where

C_r is the specific isobar thermal capacity of the overheated steam; and

T_{st} is the temperature of the overheated steam.

For convenience Eq. (2) can be expressed through the mass entalpy of the overheated steam, i.e.:

$$M_{st} = \frac{C_r \cdot M \cdot \Delta T}{h_2 - h_1} \qquad \textbf{(3)}$$

Using Eq. (3) and also the table data for specific thermal capacity of the rubber waste and specific entalpy of the overheated steam the amount of steam needed to heat the waste up to 360-500°C. The specific entalpy volumes for overheated stem are given below in table. As follows from the table the specific entalpy equals at P=0.1013 MPa:

T (°C)	h (kJ/kg)
100	15.52
400	626.16
500	794.85

That means that for heating the rubber waste with overheated steam (with T=400°C) up to T=360°C the following amount of the overheated steam is needed:

$$M_{st} = \frac{1.38\ kJ/kg{\cdot}°C(360°C - 20°C) \cdot M_w}{(626.16 - 150.52)\ kJ/kg} \qquad \textbf{(4)}$$

$$M_{st}=\frac{1.38\ kJ/kg\cdot{}^{o}C(500^{o}C-20^{o}C)\cdot M_w}{(794.85-150.52)\ kJ/kg}=1.03\cdot M_w$$

i.e. $(M_{st}/M_w)\cdot 100\%=103$ wt%.

Thus from the above calculations follows that the maximum amount of overheated steam required for heating of M_w up to T=360-500°C is M_{st} = (1-1.03)·M_w, i.e. 100-103% of the mass of the waste to be treated.

At the temperature 360-500°C thermal destruction of the rubber waste occurs. The gases from the destruction together with water steam come to the cooler where condensation of steam and gaseous destruction products take place. Non-condensed gases may be directed to a steam generator for incineration.

The amount of the gas needed for providing energy to the thermodestruction process can be obtained as follows. Power needed for pyrolysis is determined by the energy needed for heating the waste from 20°C to 360°C, i.e.:

$$Q_r=C_r\cdot M\cdot\Delta T=1.38\ kJ/kg\cdot{}^{o}C\cdot 1000\ kg\ (360^{o}C-20^{o}C)=269.2\ MJ$$

The energy needed for production of steam:

$$Q_t=\frac{469.2\cdot 10^6\ J\cdot 2250\cdot 10^3\ J/kg}{2\cdot 10^3\ J/kg\cdot{}^{o}C\ (400^{oC}-100^{oC})}=1760\ MJ$$

Taking into account 10% of thermal losses for the thermotreatment the expenditure of energy will be:

$$Q_t=1.1\cdot 1760\ MJ=1936\ MJ$$

The amount of gas needed to burn 1 t of rubber waste will be:

$$M_g=\frac{1936\ MJ/kg}{38\ MJ/kg}=51\ kg$$

that represents 5.1% of the treated waste. The amount of off-gases produced by thermodestruction is 8%. That means that the amount of the gases is sufficient for providing energy for the thermal destruction. Condensed water and thermodestruction products are sent to a tank. The solid residue is removed to a collector. This solid residue contains up to 98% of stontium and caesium.

Parameters of the process used for destruction of polymer waste have been studied using polyethylene, polypropilene, and polystyrol. Stem heated the waste up to 400-500°C. By contacting with the steam the waste are heated and melted. The melted substance penetrates dispersed material (such as sand) forming a large specific surface for contacting with steam. Under heating the waste degraded and gases are produced. Gaseous products of destruction are mixed with the water steam and transferred into a cooler. Because of a different density of polymers, the upper layer consists of the polymer with a lower density. Owing to the separation of polymers and a gradient of the temperature, the thermodestruction process is intensified from the bottom to the top.

From literature it is known that during heating biomass is destructed: volatile materials are separated and the carbon-containing materials remain in a chamber. The process can be characterized as follows: the mass of wood decreased to 15-20% at 400°C, then further heating without oxygen access leads to insignificant (2-3%0 mass reduction. Above 400°C the amount of desublimated radionuclides increases that is resulted in the contamination of wood with gaseous products of decomposition and the need in high efficiency off-gas cleaning system. Taking into account the above the decomposition of wood should be done in the range of 250-400°C. Energy expenditures for the decomposition of biomass includes the energy required for heating from 20°C to 400°C, that is:

$$Q_h = C_p \cdot M \cdot \Delta T = 1.9\ kJ/kg \cdot K \cdot 1\ kg\ (400°C - 20°C) = 722\ kJ$$

The energy expenditure for production of gaseous decomposition products is:

$$Q_g = 2.6\ MJ/m^3 \cdot 1\ m^3 = 2600\ kJ$$

Taking into account 15% of thermal losses in the thermochamber the total energy expenditures will be:

$$Q_\Sigma = (722\ kJ + 2600\ kJ) \cdot 1.15 = 3820\ kJ/kg$$

This expenditure can be compensated by the heat released from catalytical incineration of the solid residues, that is 20-26 MJ/kg. Thus the useful amount of heat that can be obtained in this process will be

$$Q_{useful} = (26000\ kJ/kg) \cdot 0.20 - 3820\ kJ = 1380\ kJ$$

per kg of the contaminated biomass. The heat can be used for drying of wet biomass prior to decomposition.

The composition of the thermodestruction process is as follws: 40 wt% of carbon residue, 32 wt% of non-condensed gases (CO_2, CO,CH_4, H_2, C_2H_4) and 28 wt%of water. The condensate does not contain toxic substances and has no harmful effects on the environment.

4. CONCLUSIONS

The results obtained indicate that the process can be applyied to treatment of organic waste contaminated with radionuclides. Further research and development is needed for design and construction of a pilot scale plant.

DEVELOPMENT OF CARRIER USAGE FOR THE TREATMENT OF RADIOACTIVE EFFLUENT

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Abstract

Low level radioactive liquid wastes are produced in many nuclear applications.Their physico-chemical characteristics may vary considerably. Chemical precipitation is a convenient treatment method for the liquid streams of high salinity or solid content containing different radionuclide types. Generally, the concentrations of nuclides in liquid wastes are extremely low. For example, 1000 Bq of ^{137}Cs makes about $3 \cdot 10^{-10}$ g of caesium. Therefore conventional precipitation cannot be applied since the solubility product value is not exceeded. The carriers which are capable to adsorb the nuclides are used to achieve the nuclide removal. Stable isotopes of the nuclide are usually added as the carriers but any reagent which has similar chemical specifications with the nuclide can also be used as the carrier. Precipitation of these non-radioactive carriers ion together with the radionuclide is called co-precipitation. The operational steps of the chemical precipitation process should be established and applied in a treatment facility. Thus, the most suitable carrier for a particular nuclide and its usage conditions are required to be determined.

In this study, the carriers for removal of ^{137}Cs and uranium, their accurate amounts and usage conditions to achieve highest decontamination factors (DF) have been investigated. A number of such reagents as Al_2O_3, Fe_2O_3, MnO_2, TiO_2, CeO_2, SnO_2, bentonite, silica gel, silicon (powder), polystyrene (powder) were tested to find out the most suitable carrier for ^{137}Cs. Different pH and carrier concentrations were used. The highest DFs were obtained with bentonite and silica gel. Removal of caesium with ferro cyanides of Ni, Co, Cu, Fe was also investigated. The highest DFs were obtained with nickel ferro cyanide. Bentonite and silica gel were tested with nickel ferro cyanide to improve the removal of ^{137}Cs. Optimum pH and reactant concentrations were found. Uranium removal has been tested with TiO_2, SnO_2, Sb_2O_5, $BaSO_4$ and silica gel at different pH and sorber concentrations. The highest DFs were obtained with $BaSO_4$ and silica gel. The sodium diuranate precipitation (UO_2^{2+} +NaOH) process has been improved with $BaSO_4$ and silica gel. The optimal pH and reactant concentrations were identified.

Residual sludge volumes were evaluated for cementation purposes. The cement composite samples were prepared for each set of experiments and hardening times were measured.

1. INTRODUCTION

The objectives of liquid waste processing are to immobilize the radioactive elements and to reduce the volume to be stored. The solidified product must be non-dispensable, insoluble and with good mechanical and structural stability. Chemical precipitation is applied for the treatment of low level radioactive liquid wastes at Çekmece Waste Processing and Storage Facility (ÇWPSF). A comprehensive research programme on chemical precipitation was needed to specify the reliable operational procedures for each nuclide or nuclides group in the liquid waste stream. ^{137}Cs precipitation has been studied at different carrier concentrations in detail with a number of possible carriers. Optimum precipitation conditions and best carriers have been determined.

Uranium contaminated liquid waste is produced during the fuel preparation pilot plant operations at ÇNAEM. In normal operations, uranium is precipitated as much as possible at the fuel plant and the residual solution containing low concentration of uranium is delivered to the waste treatment plant. In some cases, the liquid containing uranium is taken from different steps of the fuel plant. Therefore, uranium content and chemical specifications of the liquid may change considerably. The objective of this study to remove by precipitation the uranium from the liquids.

2. THEORY

2.1. SCIENTIFIC BACKGROUND

Radioactive liquid waste contains radionuclides in their dissolved forms. By precipitation, they can be transformed to an insoluble (sparingly soluble) form. To form a sparingly soluble compound of the nuclide in liquid waste, a convenient partner ion must be added. The reaction may be written, simply

$$A^{+}+B^{-}\rightarrow AB\downarrow$$

Equilibrium constant K = [A+][B-]/[AB]
where [A] represents the concentration of A in the solution at equilibrium.

If AB is a sparingly soluble salt, the equilibrium shifts to the right hand side and very small amount of free ions of this salt can remain in the solution.

Solubility product, SP = K· [AB] = [A+][B-]

Precipitation cannot occur until the value of SP on the concentration product is exceeded. In addition, the solubility of a compound is influenced by the ionic strength of the medium, by the presence of common ions and by formation of complexes.

Decontamination factor (DF), is a means of describing the removal of radionuclides from the liquid. It is the ratio of initial activity to the remaining activity after the treatment of the liquid.

$$DF=\frac{initial\ activity\ concentration}{remaining\ activity\ concentration}$$

Chemical precipitation is applied for the treatment of low level radioactive liquid waste at many nuclear establishments. However, although the method seems to be easy and well developed, many difficulties which may cause poor results can occur. The main reason is that radioactive liquids usually contain radionuclides in extremely low concentrations, and therefore they cannot easily form an insoluble precipitate. General principles of chemical precipitation may no longer be valid for such low concentrations. Sometimes, a number of particles in these solutions is so low that the conditions of the mean statistical distribution according to the Maxwell-Boltzmann law may not be satisfied.

If the system involves at least 106 molecules, the fluctuations are negligible and the conditions of the mean statistical distribution are met. In this situation, it can be said that the system is reproducible.

^{137}Cs, $3\cdot10^{-12}$ g (or $2.3\text{x}10^{-14}$ mol) of ^{137}Cs has about 10 Bq of activity. That is about 10^{10} particles. Again, $8\cdot10^{-4}$ g of ^{238}U has about 10 Bq and it is about $2\cdot10^{18}$ particles.

Precipitation of caesium and uranium have been investigated in this study and the activities were always higher than 10 Bq for each experiment. Therefore all experiments were reproducible from a viewpoint of the mean statistical distribution. Because the radionuclide concentration is so low that radionuclides cannot form an insoluble precipitate with the pertinent oppositely charged ion, sorption of radionuclides on insoluble salts gains more importance than precipitation. Therefore, the use of a carrier is necessary.

The first type of adsorption called simple adsorption, consists of the formation of a deposit round the carrier. As soon as the carrier is completely covered, adsorption will stop. The second type, internal adsorption, consists of the deposition of a first coating, then the crystal will grow and adsorption can continue. In fact, the actual mechanism is very complicated as it involves several types of interaction with the ions in the solution.

It has been found that the precipitation of salts carries down certain radioelements contained in radioactive waste. This feature is exploited by addition of metal salts to the waste. Stable isotopes of the radionuclide in liquid waste are usually added as a carrier but any reagent which has similar chemical behaviour regarding the radionuclide can also be used as a carrier. Precipitation of this non-radioactive carrier ion together with the radionuclide is called co-precipitation. Adsorption of radionuclides on the surface of solids comprises a major part of co-precipitation. It is possible to precipitate the radionuclides at very low concentration by using adsorption. Solids which adsorb radionuclides can also be formed during chemical treatment.

2. DESCRIPTION OF RESEARCH

Removal of caesium and uranium from the liquid wastes have been investigated in this study. Both nuclides are somewhat problematic from a viewpoint of their special properties. Caesium is not easily precipitated, especially if the medium is not alkaline. Daughters of uranium contribute to the total radioactivity of the liquid waste. Additionally, some undesirable changes may occur in a strongly alkaline medium, e.g. the formation of radiocolloids.

2.1. BASIC RESEARCH EQUIPMENT

I - Canberra-85 gamma spectrometer with HP Germanium detector for ^{137}Cs analyses.
II- Delayed neutron counting system for uranium analyses.
III-A jar test equipment with 6 units for precipitation experiments.
IV- A membrane pump (2.4 m^3/h) for the suction of clean liquid.
V - Transparent PE containers (200 mL) as precipitation vessels.

2.2. PROCEDURE

(a) Six PE vessels are placed in jar test equipment. 150 mL of liquid waste is transferred to each vessel. Equipment is started to operate. pH is adjusted, if necessary.
(b) Chemicals and/or carriers are added.
(c) Rapid stirring is carried out for 2 minutes at 160 rpm, then mixing is continued at 120 rpm for 20 minutes.
(d) Vessels are left to settle for 24 hours.
(e) 100 mL of clear liquid (supernatant) is sucked from each vessel to another PE vessel and analyzed by gamma spectrometry in the case of the caesium experiments.
(f) 0.2 mL of supernatant is sucked with a pipette and prepared for delayed neutron counting system for uranium analysis.
(g) Residual sludge is collected, followed by cementation. A cement composite is prepared for each set of experiments and the hardening times of cement composites are measured.

2.3. TEST PROGRAMME

2.3.1. ^{137}Cs

A real liquid waste contaminated with ^{137}Cs has been used for the experiments. The activity of the liquid was arranged as 110 Bq/mL by dilution with water and this liquid was used as the stock solution for all caesium experiments. pH of this original solution was 6.5. The amount of activity decay was about 1 Bq for every 6 months and that was considered in the activity calculations.

The following studies have been done for ^{137}Cs:

(a) Al_2O_3, Fe_2O_3, MnO_2, TiO_2, CeO_2, SnO_2, bentonite, silica gel, silicon (powder), polystyrene (powder) were tested without adjusting pH and without adding any other compound.

(b) The experiments in (a) were repeated after adjusting pH to 9 with NaOH.

(c) Because bentonite and silica gel provided the highest DF in the experiments (a) and (b), they were tested at different pH values.

(d) Removal of caesium with the ferro cyanides of Ni, Co, Cu, Fe was examined. $K_4[Fe(CN)_6]$ solution was used to provide the ferro cyanide ion. $Ni(NO_3)_2$, $Co(NO_3)_2$, $CuSO_4$, $FeCl_3$ solutions were used for corresponding metal ions.

(e) Because the nickel ferro cyanide precipitation provided the highest DF in the experiments (d), bentonite and silica gel were tested with ferro cyanide precipitation to improve the removal of ^{137}Cs.

2.3.2. Uranium

Uranium is present in sea water due to the relatively high solubility of UO_2^{2+} ions in carbonate, sulfate, chloride and nitrate solutions. For example, the concentration of U in sea water varies between 0.5 to 5 mg/m^3, depending on the location.

Maximum permissible concentration (MPC) of ^{238}U has been given as $6 \cdot 10^{-6}$ Ci/m^3 which equals to 0.0179 g/L. MPC of natural uranium in water is nearly the same as ^{238}U. Therefore, MPC of ^{238}U has been taken as the discharge limit and this part of research was aimed at reducing the uranium concentration below 0.0179 g/L before the liquid is discharged.

The adsorption capacity of some promising oxides (TiO_2, SnO_2, Sb_2O_5), $BaSO_4$ and silica gel has been tested directly in uranyl solutions at different pH. After that, the well known $Na_2U_2O_7$ precipitation with NaOH has been improved by using silica gel and $BaSO_4$. Initial concentrations of uranium were adjusted to 0.064 g/L. Uranium analyses have been done by delayed neutron analysis.

The following tests have been carried out for uranium:

(a) TiO_2, SnO_2, Sb_2O_5, $BaSO_4$ and silica gel were tested without adjusting pH and without adding any other compound.

(b) Experiments in (a) were repeated at different pH values.

(c) The (UO_2^{2+} + NaOH) precipitation process was improved by the addition of $BaSO_4$ and silica gel.

3. RESULTS

3.1. ^{137}Cs

3.1.1. Possible carriers or sorbents

It has been found that Al_2O_3, Fe_2O_3, MnO_2, TiO_2, silicium (silicon powder) cannot be a carrier or a sorbent for ^{137}Cs. They were added to ^{137}Cs solution from 0.5 g/L to 2 g/L and mixed from 2 min to 2 h. Different pH values from 6.4 to 9.5 were tested but no sorptive capacity has been found for ^{137}Cs.

Polystyrene powder: Since it does not form a homogenous mixture with water, it was shaken with ^{137}Cs solution from 2 min to 2 h at pH ranging between 6.4 and 9.5. The liquid was sucked from the lower level (because the powder remained on the surface) and analyzed. No sorptive capacity has been found.

CeO_2, SnO_2: In the pH range from 6.4 to 8.5, no sorptive capacity has been found for ^{137}Cs. Values up to pH10 were investigated but very little sorption of ^{137}Cs was shown, and the best result did not exceed a DF of 1.2. Therefore, they have not been regarded as carriers or sorbents for ^{137}Cs.

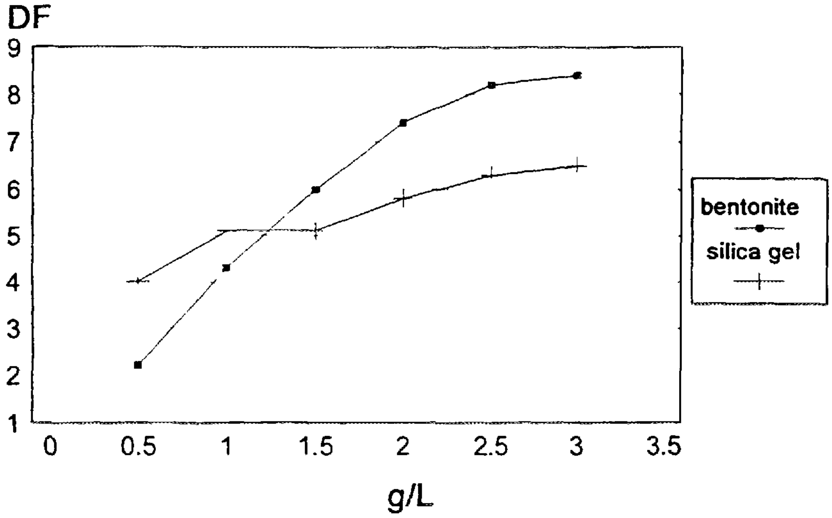

FIG 1 Removal of ^{137}Cs with bentonite and silica gel at pH = 8 5 - 10

Bentonite: It has been found that bentonite has some sorption capacity for ^{137}Cs at pH > 8, but no significant sorption has been found at the lower pH. The decontamination factors achieved were nearly the same between the pH interval from 8.5 to 10 (Fig.1).

Silica gel: Results have been found for silica gel were very close to the results of bentonite but lower DF values could be obtained than bentonite. Fig.1 shows the attained DF values against the amount of bentonite and silica gel used at pH8.5 - 10.

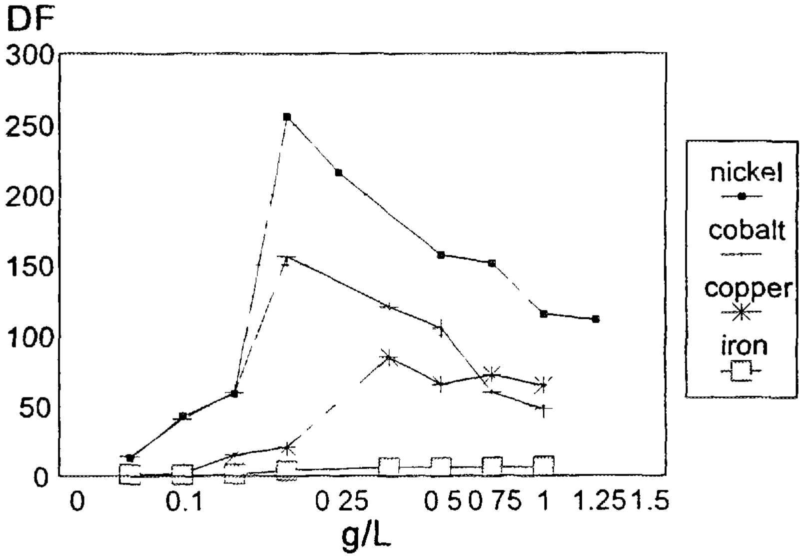

FIG. 2 Removal of ^{137}Cs with some metal ferro cyanides at pH = 8 and K_4 [Fe(CN)$_6$]= 0 5 g/L

3.1.2. Suitable concentrations of metals and cyanides

Different metal cyanides were used to remove caesium from the liquid. Cyanide concentrations were kept as $K_4[Fe(CN)_6]$ = 0.5 g/L for each experiment. Other metal concentrations (nickel, cobalt, copper and iron) were arranged from 0.05 to 1.25 g/L. pH was adjusted to 8 with NaOH solution. Figure 2 shows the attained DF values against different concentrations of metal ions.

The highest DFs (256 and 216) were reached when the nickel concentration was 0.2 and 0.25 g/L, respectively. Since the cyanide concentration was 0.5 g/L for each test as, it can be concluded that the theoretical amounts of nickel and cyanide provide the highest DF values (0.5 g of cyanide and 0.248 g of nickel are the stoichiometric amounts of nickel cyanide). Excess amounts of, whether cyanide or nickel, affect DF negatively. That effect was unimportant for the 3-5% excess of nickel but the same percent of excess cyanide affected the DF values significantly.

Similar results were obtained for cobalt cyanide. Again, the highest DFs were obtained with stoichiometric amounts and excess amounts of chemicals effected the DFs negatively.

Removal of caesium with copper cyanide was not very effective compared with the results for nickel and cobalt. DF was not significantly affected with the excess amount of chemicals.

DF values for $FeCl_3$ were very low because of the alkaline pH. Ferro cyanide was decomposed with alkalinity and $Fe(OH)_3$ was formed. It is known that iron hydroxide is not effective for the removal of caesium.

3.1.3. Suitable stoichiometric amounts of metals and cyanides

In this set of experiments, stoichiometric amounts of chemicals were increased proportionally and the question of which concentration gives the highest DF was examined. pH values were adjusted to 8. The cyanide concentration varied from 0.1 to 2 g/L and corresponding stoichiometric amounts of nickel, cobalt, copper concentrations and attained DF values are listed below.

$K_4[Fe(CN)_6]$	$Ni(NO_3)_2$		$Co(NO_3)_2$		$CuSO_4$	
g/L	g/L	DF	g/L	DF	g/L	DF
0.1	0.05	275	0.05	86	0.09	12
0.2	0.1	252	0.094	168	0.17	73
0.4	0.2	248	0.19	152	0.35	81
1	0.5	85	0.47	92	0.87	96
1.5	0.75	66	0.71	84	1.31	105
2	1	69	0.94	85	1.74	112

In contrast to expectations, the highest DF values were obtained at the lowest stoichiometric amounts of nickel and cyanide. But, the particles of the precipitate were not good enough to observe and settling time was much longer than the others (3-4 days). Therefore, the second lowest values of nickel can be taken as an optimum DF value. Figure 3 shows the results of this part of experiments.

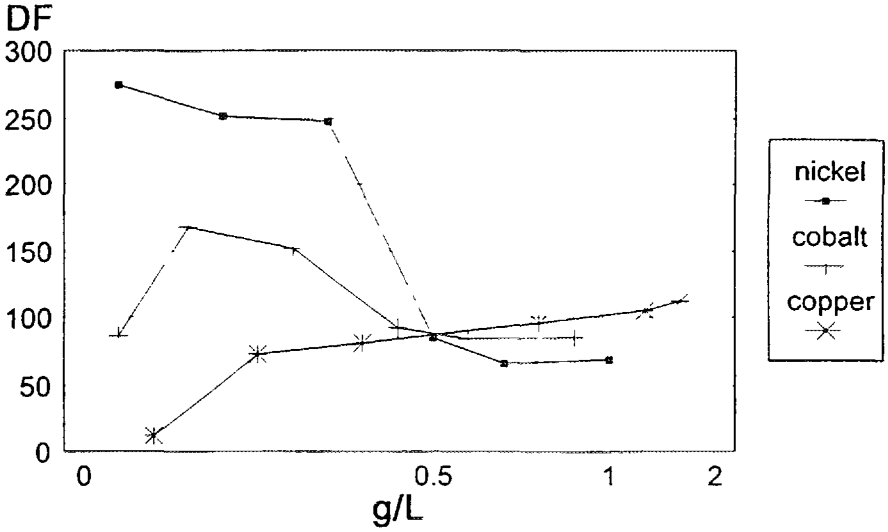

FIG 3 Removal of ^{137}Cs with stoichiometric amounts of some metal ions and $K_4[Fe(CN)_6]$, at pH=8

Like nickel, cobalt has been found also to give lower DF values with the increased amount of chemicals. But, DF values were nearly the same at the concentrations higher than 0.5 g/L. It has been found for copper that DF values have increased regularly by the increased stoichiometric concentrations.

3.1.4. Optimal pH

The most suitable concentrations of nickel, cobalt, copper and cyanide have been found as described in Section 3.1.3. These values were applied at different pH values to find out the most suitable pH for the removal of ^{137}Cs from the solution. Figure 4 shows the results.

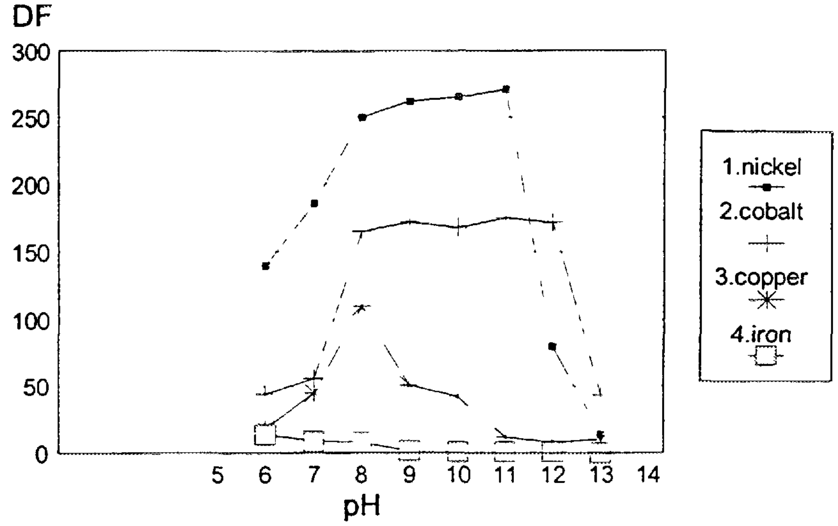

FIG. 4. DF - pH dependence of removal of ^{137}Cs with metal ferro cyanides.

1- 0.1 g/L nickel	+	*0.2 g/L cyanide*
2- 0.094 g/L cobalt	+	*0.2 g/L cyanide*
3- 1.5 g/L copper	+	*1.73 g/L cyanide*
4- 0.22 g/L iron	+	*0.5 g/L cyanide*

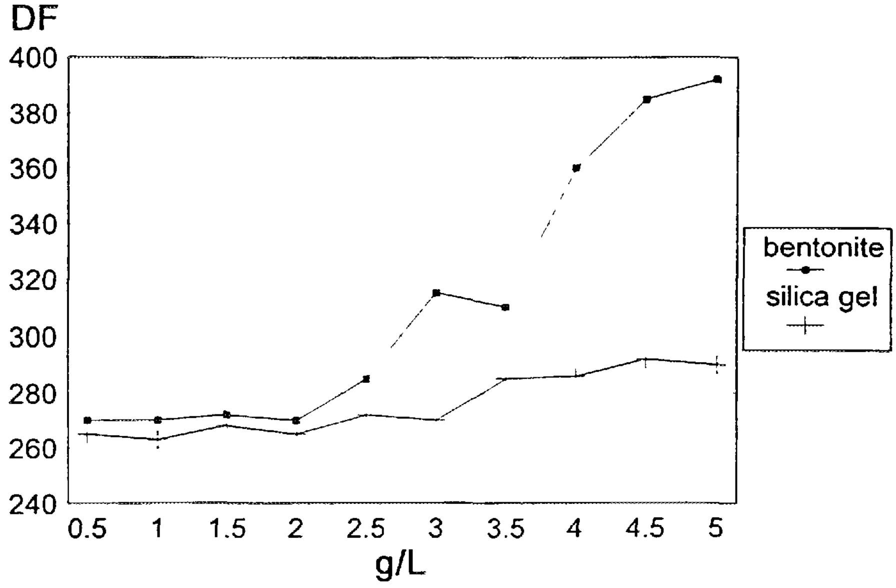

FIG. 5. Improved removal of ^{137}Cs with bentonite and silica gel. Nickel and cyanide concentrations are 0.1 and 0.2 g/L

For nickel the best pH level has been found as 11. It can be concluded that the best pH interval is between 9 and 11. For higher pH, DF decreased sharply, because of the formation of colloids. If there is not enough sensitivity during the adjustment of pH, it is better to keep the pH between 9.5 - 10. For cobalt and copper the most suitable pH was found to be between 8 - 12.

3.1.5. Improvement of nickel ferro cyanide precipitation

In the previous experiments, the best removal of ^{137}Cs has been obtained with 0.1 g/L nickel and 0.2 g/L cyanide at pH11. It has been determined that bentonite and silica gel were the best adsorbents among the compounds investigated. In this part of the research, bentonite and silica gel have been tested with nickel ferro cyanide precipitation. Figure 5 shows the results.

3.2. URANIUM

3.2.1. Possible carriers or sorbents for uranium

TiO_2, SnO_2 and Sb_2O_5: Those have been found not to be carriers or sorbents for uranium. They were added to uranium solution from 0.5 to 3.5 g/L and mixed from 2 min to 2 h. Different pH values from 5 to 10 were tested. No sorptive capacity has been found for uranium.

Silica gel and $BaSO_4$ have been found to have considerable sorption capacity for uranium.

3.2.2. Improvement of uranium removal with silica gel

In Fig. 6, improved uranium precipitation with silica gel is shown. Firstly, diuranate precipitation was applied with NaOH in uranyl nitrate solution containing 0.064 g/L uranium. After the formation of $Na_2U_2O_7$ flocs in the liquid, silica gel was added and mixed for 20 minutes. Uranium removal with this procedure is shown as curve "1" in Fig. 6.

After that, the procedure was repeated with the addition of silica gel before the formation of diuranate. Silica gel was added to uranyl nitrate solution and mixed for 20 minutes. Then, NaOH was added to raise the pH to 10. Mixing continued for 20 more minutes. Line "2" in Fig. 6 shows the results of this procedure.

Nearly the same DF values were obtained at higher pH while the lower pHs caused lower DFs. Therefore, pH dependence of the procedure was conceived such that the optimum pH value was around 10.

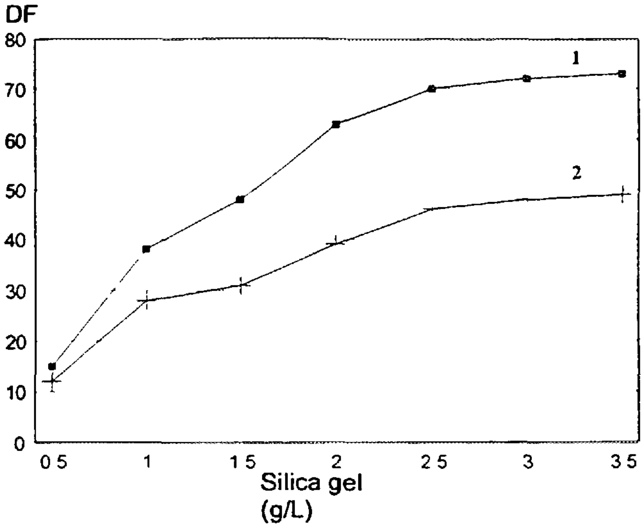

FIG. 6 Improvement of uranium removal with silica gel at pH=10.
1. silica gel addition after $Na_2U_2O_7$ formation
2 silica gel addition after $Na_2U_2O_7$ formation

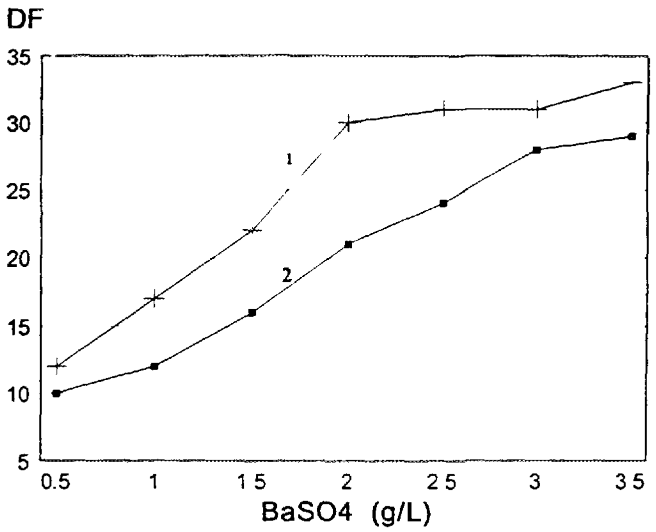

FIG. 7. Improvement of uranium removal with BaSO at pH=10.
1. $BaSO_4$ addition after Na_2U_2O- formation
2. $BaSO_4$ addition after $Na_2U_2O_7$ formation

3.2.3. Improvement of uranium removal with $BaSO_4$

The same procedures as described in Section 3.2.2. were applied using $BaSO_4$ instead of silica gel. Results are shown in Fig.7.

The dependence of uranium removal with $BaSO_4$ on pH was almost the same as reported in Section 3.2.2. pH10 can be assumed as the optimum alkalinity for the procedure. If the carriers are added before the diuranate precipitation, some part of uranium is sorbed by the carriers and residual uranium is precipitated with NaOH. If the diuranate precipitation is applied first, the residual uranium in the liquid is needed to be sorbed on the carriers. In both cases the precipitation sludge contains a mixture of $Na_2U_2O_7$ and carriers.

A comparison of the uranium removals with silica gel and $BaSO_4$ is shown in Fig.8. The optimum result for the uranium removal has been obtained with the addition of 2.5 g/L silica gel at pH10 after $Na_2U_2O_7$ precipitation.

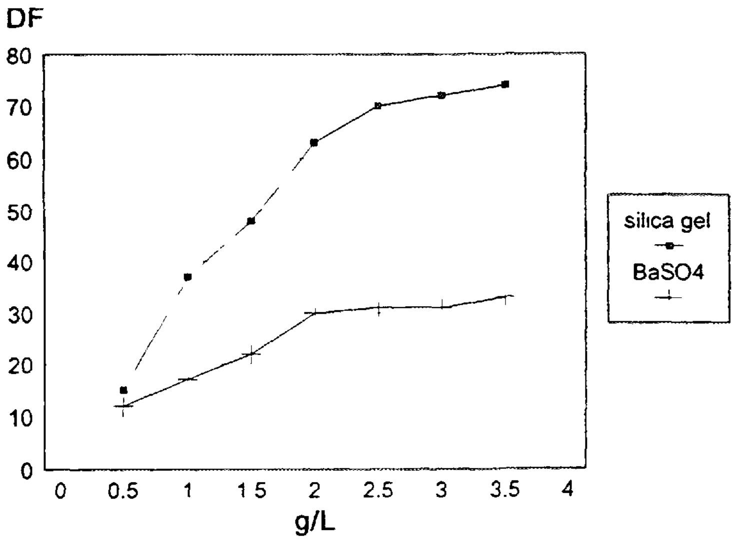

FIG. 8 Comparison of uranium removal with silica gel and $BaSO_4$ at pH=10 after $Na_2U_2O_7$ precipitation

3.3. CEMENT HARDENING TIME

The residual sludge from the experiments as described in Sections 3.1. and 3.2. has been cemented with ordinary Portland cement with a sludge/cement ratio of 0.5. Solid contents of the sludges were around 0.6-1.4 wt%. Cement-sludge composites were prepared after each set of experiments. A manually driven vicat needle device was used to follow solidification of the samples. Needling was carried out every 15 min and the time that the needle could not penetrate the last 1 mm from the upper surface was accepted as the final hardening time.

A great number of hardening data were obtained. Two sets have been selected and are plotted in Fig. 9. They were obtained from the composite samples of sludges giving the highest DF. The general trend is that the more the carrier amount used, the shorter the hardening time.

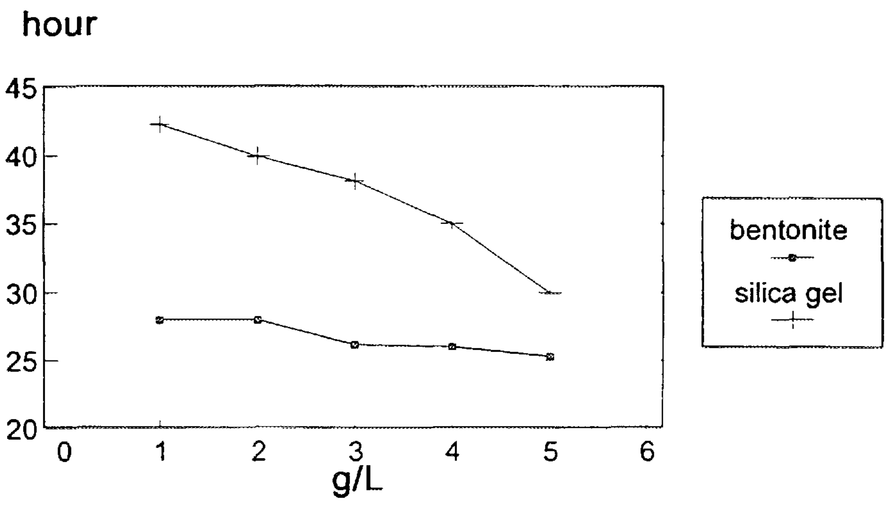

FIG. 9. Plot of hardening times from two selected sets of experiments.
1- 100 g cement + 50cm^3 sludge from ^{137}Cs precipitation (0.1 g/L Ni(NO$_3$)$_2$ + 0 2 g/L K$_4$[Fe(CN)$_6$] + pH=11 + bentonite)
2- 100 g cement + 50 cm^3 sludge from uranium precipitation (0 064 g/L uranium + NaOH, pH=10 + silica gel)

4. CONCLUSIONS

Metal ferrocyanides and some other carriers or sorbents have been studied in detail for precipitation of ^{137}Cs from low level liquid waste. Nickel ferro cyanide has been found to be the best compound to remove caesium. To obtain higher decontamination factors, bentonite and silica gel have been added to nickel ferrocyanide. The highest DF for ^{137}Cs has been obtained as 392 for 0.1 g/L of nickel nitrate + 0.2 g/L of potassium ferrocyanide +5 g/L of bentonite, at pH of 10.5 - 11. Greater amounts of bentonite have not been used because of the consideration of the volume of sludge. A sludge volume of less than 50 cm^3 for each litre of liquid waste has been sought. Metal cyanide precipitates have not been found as significant contributors to the sludge volumes. 5 g/L of bentonite or silica gel were the maximum amounts of sorbents for ^{137}Cs because the final sludge volume has tended to increase to be more than the target limit 50 cm^3/L of liquid if greater amounts of bentonite and silica gel were used. The 110 Bq/mL initial specific activity of ^{137}Cs could be decontaminated to 0.28 Bq/mL. 99.7% of ^{137}Cs in the liquid waste has been removed.

Uranium removal experiments were mainly carried out with $Na_2U_2O_7$ precipitation. In contrast to caesium, the theory and stoichiometric values for the diuranate application are known. Efficiency of the procedure decreases with the decreased concentrations. Therefore, the carriers, $BaSO_4$ and silica gel have been used in two different ways. If a part of the uranium in the liquid is sorbed on carriers as the first step, a very small part of residual uranium can be precipitated by normal precipitation process. But, if some part of uranium is precipitated for the first step, most of the residual uranium can be sorbed on silica gel or $BaSO_4$. Of course, that is completely dependent on the amount of carriers to be used. But, it has been found that the removal efficiency can be increased considerably by using the carriers after diuranate precipitation. Much higher DF values could be obtained by using larger amounts of carriers, but the residual sludge volume would become much larger too. This study was also aimed at producing the minimum amount of sludge. It has been concluded that, carriers are able to sorb uranium contained in solution in much lower concentrations than the concentrations which the normal precipitation can be applied. The highest DF (74) for uranium has been obtained for 3.5 g/L silica gel at pH10, after $Na_2U_2O_7$ precipitation. 0.064 g/L of uranium concentration could be removed down to 0.000865 g/L, that is 98.65% removal has been attained.

Hardening times of cement composites were around 8 to 48 hours. The sludge with bentonite or silica gel has been shown to lead to some shorter hardening times like 6 to 24 hours. These values can be accepted as normal hardening times and there is no need to use additional retarder or enhancer with cement-sludge composites.

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DEVELOPMENT OF IMPROVED RADIOACTIVE EFFLUENT TREATMENT TO REMOVE Zn-65, Mo-99 AND I-125 BY THE COAGULATION-FLOCCULATION PROCESS

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Abstract

Coagulation-flocculation treatment using aluminum sulphate, sodium carbonate, ferric chloride and coagulant aid was able to remove ^{65}Zn, ^{99}Mo and ^{125}I from an aqueous effluent. Chemicals' dosages into the samples were varied which contributed different decontamination factors. For ^{65}Zn removal, optimum pH value was 8 that provided the decontamination factor of 35. For ^{125}I, optimum pH value was 7 with the decontamination factor of 4.8. Treatment of the effluent containing ^{99}Mo at a laboratory scale was proved to be valid for the extrapolation to a plant scale. The pH range for optimum treatment was between 4.0 to 4.5.

1. INTRODUCTION

Treatment of effluents containing radioactive material can be conducted by using flocculation-coagulation process [1-4]. Main mechanisms for removing radionuclides in the process are: (1) Directly from coagulation and flocculation process, (2) Precipitation and co-precipitation, (3) Adsorption on the coagulant aid, (4) Ion-exchange and (5) Physical enmeshment by coagulant aid.

The treated effluents to be released to the environment must fulfill the conditions of the Environmental Act 1974 of Malaysia where the pH ranges between 5.5 to 9.0, COD < 50 $mg\cdot L^{-1}$, BOD < 20 $mg\cdot L^{-1}$ and suspended solid < 50 $mg\cdot L^{-1}$. For the release rate of 20 m^3 of radioactive liquid wastes per week, their activity must be less than 10^{-5} $\mu Ci\cdot mL^{-1}$ [5]. This limit is established for the liquid wastes contaminated with ^{90}Sr.

The aim of the study was to improve treatment of radioactive effluents to reduce the content ^{65}Zn, ^{99}Mo and ^{125}I as low as possible by the coagulation-flocculation process.

2. EXPERIMENTAL METHODS

For a given radioactive effluent, there were the interrelated optimum conditions for treatment. The conditions included pH, turbidity, chemical composition of the water, type of coagulant as well as physical factors such as temperature and mixing conditions. Jar test experiments were conducted using different dosages of chemicals for each treatment of the effluent sample containing radionuclides ^{65}Zn, ^{99}Mo and ^{125}I [1-4]. In the coagulation-flocculation process there was at least one pH range that provided the best results in the shortest time with a given chemical coagulant dosage. The volume of each sample test conducted was 1000 mL.

2.1. TREATMENT OF THE EFFLUENT CONTAINING ^{65}Zn

pH values of the effluents varied within the range 4.5-8.5. The adjustment was done by varying the soda ash dosage and maintaining the alum and coagulant aid dosages constant. A blank sample without ^{65}Zn radionuclide was also prepared which contains alum, soda ash and coagulant aid. A gas proportional counter (Canberra Model 2400) [6] was used to count the samples' activities for 20 minutes before and after treatment. In another experiment, an optimum alum dosage was determined at the optimum pH condition. Good estimation of the soda ash and alum dosages was used to maintain optimum pH condition.

2 2 TREATMENT OF THE EFFLUENTS CONTAINING ^{99}Mo AT LABORATORY AND PLANT SCALES

Both laboratory and plant scale experiments were conducted to treat the effluents containing ^{99}Mo The alum and coagulant aid dosages were maintained while the soda ash dosage was gradually increased The chemicals dosage used for each batch treatment for 1600 L effluents in the plant was calculated by ratio from 1 L effluent treatment on a laboratory scale The percentages of the radionuclide removed at different pH values at a laboratory scale and at a plant scale were compared to determine any large differences in removal of ^{99}Mo The proportional gas counter (Canberra Model 2400) was used to count the activity from each sample All samples' activities obtained from both treatment methods were corrected for decay before the treatment because of the short half-life of ^{99}Mo (2 75 days)

2 3 TREATMENT OF THE EFFLUENTS CONTAINING ^{125}I

Two jar test experiments were conducted each using different chemicals The experimental conditions for the two tests were similar The same dosages of alum (4 mL of 100 $g{\cdot}L^{-1}$ concentration) and coagulant aid Praestol (4 mL of 0 25 $g{\cdot}L^{-1}$ concentration were used in the first test The dosages of soda ash (100 $g{\cdot}L^{-1}$) were varied with an increment of 1 mL In the second test, the same dosages of ferric chloride (5 mL of 100 $g{\cdot}L^{-1}$ concentration) and Praestol (4 mL of 0 25 $g{\cdot}L^{-1}$ concentration were used The dosage of soda ash was varied according to pH requirements

2 4 FORMULAE

The following formulae are used in the calculation

$$A = A_0 \exp[(-0\ 693 \times t)/T] \tag{1}$$

where

A is the activity after time t (cpm),
A_o is the initial activity before treatment at t_o (cpm),
t is the time taken ($t-t_o$) (sec), and
T is the half-life (sec)

$$Sample\ activity = \frac{(A-B) \times 1000 \times 1}{E \times V \times Min \times 60} Bq/L \tag{2}$$

where

A is the average reading for sample,
B is the average reading for background,
E is the efficiency of the detector (34% for Canberra Model 2400),
V is the sample volume (mL),and
Min is the counting time (minutes)

$$Decontamination\ factor\ (DF) = \frac{Activity\ of\ the\ effluent\ before\ treatment\ (counts/sec)}{Activity\ of\ the\ effluent\ after\ treatment\ (counts/sec)} \tag{3}$$

$$Percentage\ radionuclide\ removed = \frac{Original\ activity - Final\ activity}{Original\ activity} \times 100 \tag{4}$$

$$Distribution\ coefficient = \frac{(initial\ activity) - (final\ activity)}{(final\ activity)} \times \frac{total\ volume\ of\ the\ solution\ used\ (mL)}{mass\ of\ the\ soil\ used\ (g)} \tag{5}$$

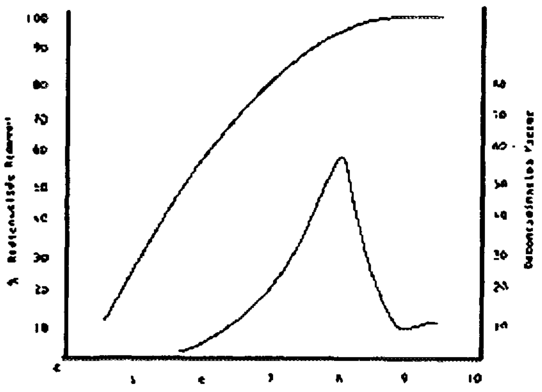

FIG. 1. % radionuclide removed against pH
Decontamination factor against pH

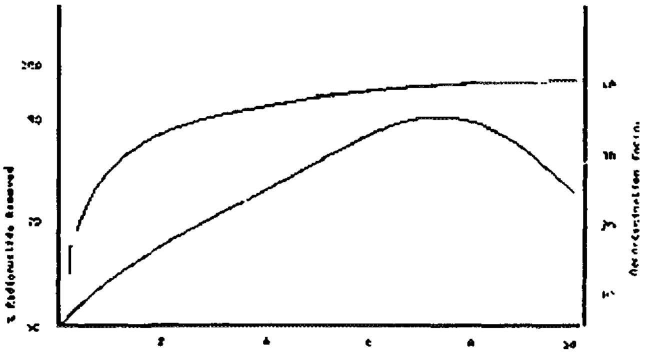

FIG. 2 % radionuclide removed and decontamination factor against alum (mL)

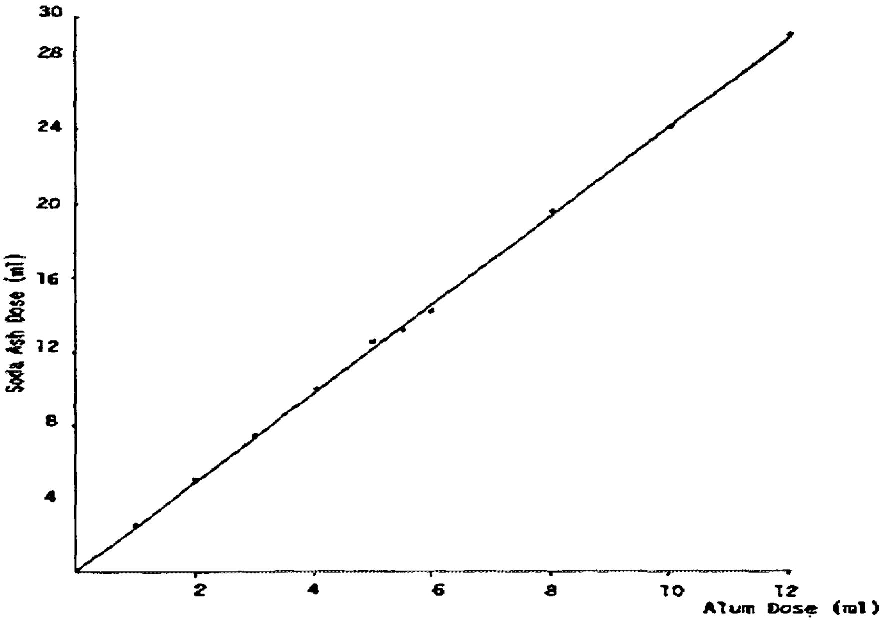

Fig. 3. Variations of alum and soda ash to maintain optimum pH8

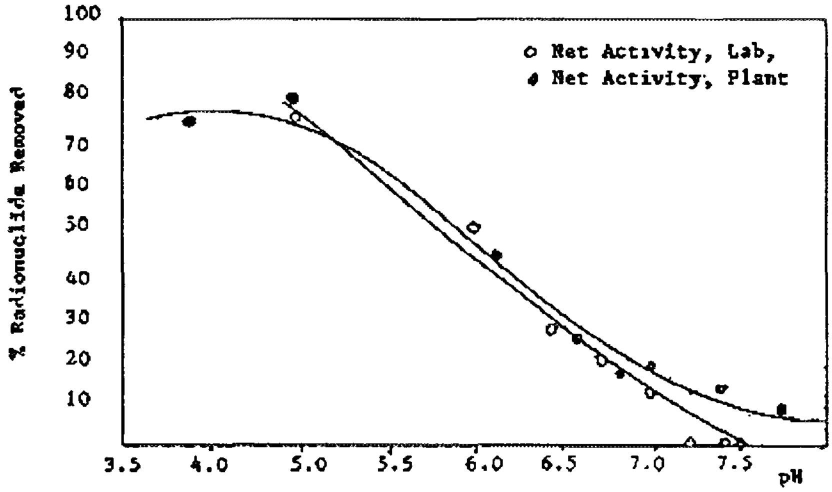

FIG. 4. Comparison of treatment in the laboratory and Low Waste Treatment Plant

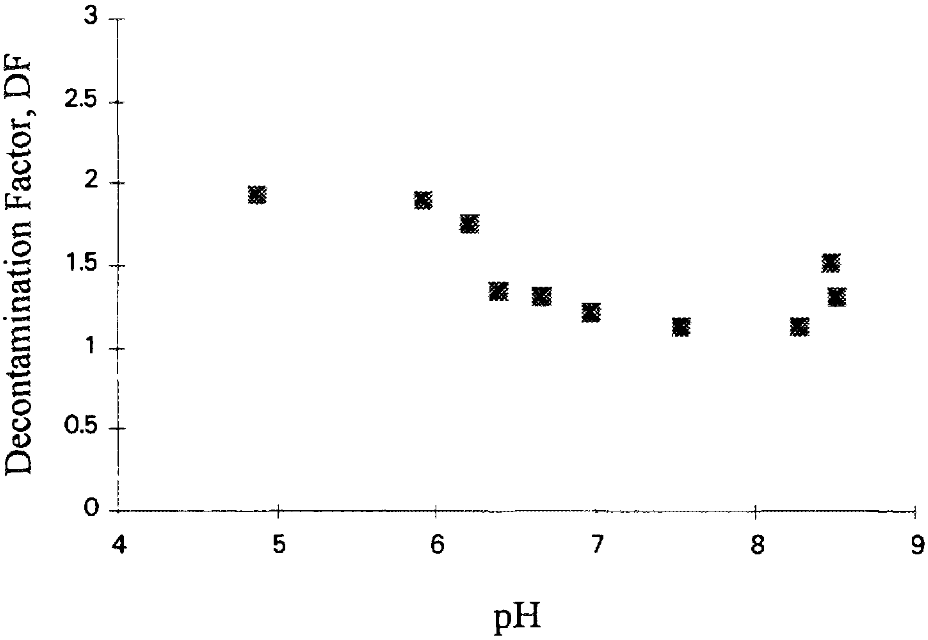

FIG. 5. Chemical treatment using alum as coagulant.

3. RESULTS AND DISCUSSIONS

Figure 1 shows that optimum pH value corresponds to the highest decontamination factor for removal of ^{65}Zn from the effluent. After pH8, the curve descends which shows there was a decrease in the percentage of the radionuclide removed. Experiments showed that alum and soda ash affected the size of particles produced. The particle size was reduced when reduced amounts of soda ash dosage were used. This produced lesser precipitation and caused smaller decontamination factor values. Increasing the amount of soda ash led to the increase of colloid particles produced.

Figure 2 shows the optimum alum dosage was 7 mL. The percentage of the radionuclide removed was nearly optimum at 95%. Major portions of the ^{65}Zn radionuclides were removed from the effluent. Figure 3 shows how the chemicals dosages of alum and soda ash were varied to maintain the optimum pH 8 condition. Figure 4 shows both plant and lab scales treatments for removal of ^{99}Mo. There are two curves

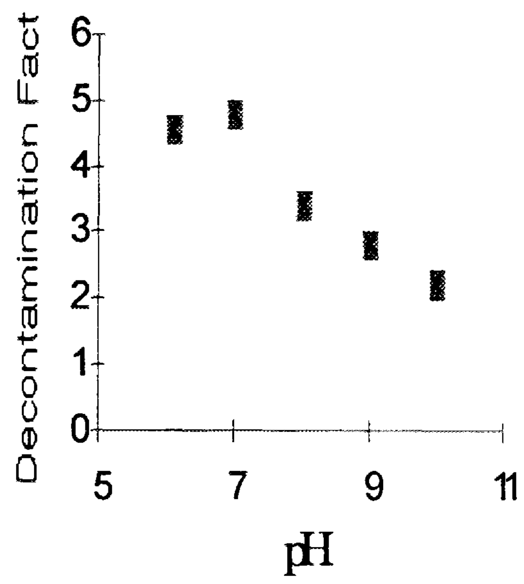

FIG. 6. Chemical treatment using ferric chloride as coagulant.

with little differences at different pH conditions. The jar test experiments at a laboratory scale were valid for the extrapolation to the plant scale treatment. Treatment of 1000 mL effluent on a laboratory scale, with similar conditions, methods and chemicals was scalable for the effluent treatment in the plant. The amount of the chemicals needed for the plant scale was calculated from the ratio obtained on the laboratory scale. The maximum pH range for removing about 80% of ^{99}Mo was between 4 and 4.5. Since the pH of the treated effluent was lower than the permissible discharge limit (i.e., pH6-9), pH adjustment was performed with the addition of soda ash.

Figure 5 shows the removal of ^{125}I using alum that produced the highest decontamination factor 2 with pH range 5.0 to 6.0. The value decreased between pH 6 to 8 and slightly increased again after pH8. Figure 6, between pH6 to pH7, the highest decontamination factor value determined was 5.0 using ferric chloride. The value decreased when the pH values increased.

4. CONCLUSION

From the experiments conducted, several conclusions can be made:

(1) The optimum pH for removing ^{65}Zn from the effluent is about 8;
(2) The optimum alum dosage for removing ^{65}Zn from the effluent is 7 mL;
(3) Extrapolation of the jar test results is scalable to the plant scale treatment;
(4) For the treatment of the effluent containing ^{99}Mo, the optimum pH is in the range of 4.0 to 4.5;
(5) For ^{125}I removal using alum, the highest decontamination factor value was 2 with pH range 5.0 to 6.0. However using ferric chloride, the highest decontamination factor value determined was 5.0, for pH between 6-7.

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DEVELOPMENT OF IMPROVED LIQUID RADIOACTIVE EFFLUENTS TREATMENT TECHNOLOGY BY PRECIPITATION AND ION EXCHANGE AND THE RELATED ANALYTICAL CONTROL SYSTEM

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Abstract

Chemical precipitation method for treatment of LLW and ILW by co-precipitation of caesium with nickel ferrocyanide was employed. High decontamination factors were observed in the pH range of 9 to~11. The percentage removals of ^{137}Cs from 37 kBq, 370 kB and 3.4 MBq per litre of simulated effluents were ~ 90%, 99.7% and 99.8% respectively. Liquid radioactive wastes generated from radioisotope production facilities of AERE, Savar were found to contain ^{134}Cs and ^{60}Co with the average activity levels of 13.23 kBq/L and 5.3 kBq/L, respectively. Test runs for removal of ^{134}Cs from the wastes varied from ~ 90% to 99%. The radioactive concentrates (sludges) were conditioned by cementation and safely stored in interim storage room.

1. INTRODUCTION

Low and intermediate level radioactive wastes are produced from diverse applications of radionuclides and radioactive materials in industry, medicine, agriculture and research and from operation and maintenance of research and power reactors, radioisotope production facilities, fuel processing/re-processing plants, etc. Many of the liquid wastes need treatment for safe management. Chemical precipitation processes are well established for the removal of radioactivity from LLW & ILW. These processes are suitable for the treatment of a large volume of liquid waste and may be employed to treat a wide variety of waste streams including large amounts of particulates and/or salts. This report aims at the development of low-cost and simple precipitation technology for the treatment of LLW and ILW.

2. DESCRIPTION OF RESEARCH

2.1. INVESTIGATION OF IDEAL PRECIPITATION CONDITIONS FOR CAESIUM

With a view to concentrating and separating the caesium radionuclides, ideal precipitation conditions based on precipitation of nickel ferrocyanide were investigated according to the following reaction:

$$\underset{\text{(aq)}}{K_4[Fe(CN)_6]} + \underset{\text{(aq)}}{NiSO_4} \rightleftharpoons \underset{\text{(ppt.)}}{\text{Ni-ferrocyanide}} + \underset{\text{(aq)}}{K_2SO_4}$$

The caesium in low concentration is likely to co-precipitate with the metal ferrocyanide under favourable pH condition.

2.1.1. Effect of pH

The precipitation was conducted at different pHs but at the Ni^{2+} to $[Fe(CN)_6]^{4-}$ mole ratio of 1.5:1 and using stable CsC1 as a carrier at a concentration of ~ 2x10 mole/L and ^{137}Cs (aq.soln.) as simulated effluent. Addition of chemicals was done under fast stirring condition. After 1 min. of thorough mixing, the speed was reduced and continued for ~ 5 min. The aqueous systems were allowed to settle for ~ 24 h, then the clear aqueous layers were taken by filtration and counted for residual Cs-137 by gamma spectrometry. The DFs were calculated from initial and final counts. Variation of DF as a function of pH is shown in Table I. The pH corresponding to the maximum DF is shown in Figure 1.

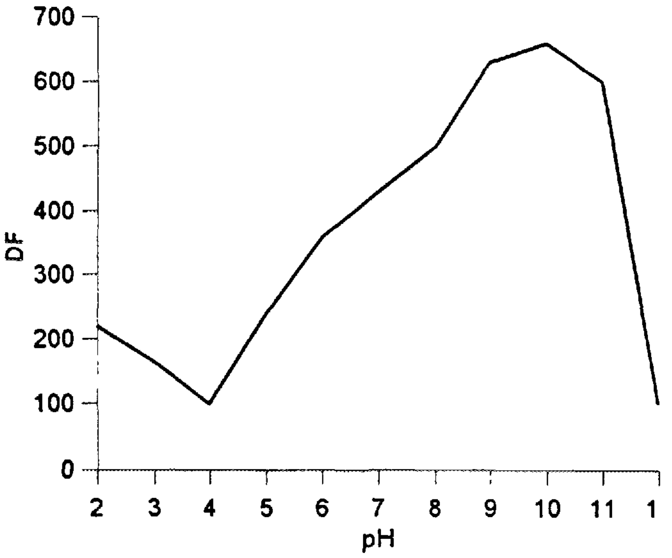

FIG.1. pH versus DF

TABLE I. VARIATION OFs DF AT DIFFERENT pHS (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	pH	Volume of $K_4[Fe(CH)_6]$ 0.5 Molar (mL)	Volume of $NiSO_4$, 0.75 Molar (mL)	DF
1	50	10	2	1	1	220
2	50	10	4	1	1	98
3	50	10	6	1	1	347
4	50	10	8	1	1	497
5	50	10	9	1	1	618
6	50	10	10	1	1	654
7	50	10	11	1	1	598
8	50	10	12	1	1	93

TABLE II. VARIATION OF DFs FOR DIFFERENT AMOUNTS OF $K_4[Fe(CN)_6]$ AT pH10 (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	Volume of $K_4[Fe(CH)_6]$ 0.5 Molar	Volume of $NiSO_4$, 0.75 Molar (mL)	DF
1	50	10	10 μL	1	60
2	50	10	50 μL	1	95
3	50	10	100 μL	1	140
4	10	10	500 μL	1	160
5	50	10	1 mL	1	280
6	50	10	2 mL1	1	275

TABLE III. VARIATION OF DFs FOR DIFFERENT AMOUNTS OF $NiSO_4$ AT pH10 (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	Volume of $K_4[Fe(CH)_6]$ 0.5 Molar (mL)	Volume of $NiSO_4$, 0.75 Molar (mL)	DF
1	50	10	1	10 µL	45
2	50	10	1	50 µL	80
3	50	10	1	100 µL	130
4	50	10	1	500 µL	180
5	50	10	1	1 mL	296
6	50	10	1	2 mL	293

TABLE IV. VARIATION OF DFs FOR DIFFERENT AMOUNTS OF CsCl AT pH10 (^{137}Cs activity of the simulated effluent - 3.7 kBq)

Exp. No.	Volume of simulated effluent (mL)	Volume of CsCl 10^{-3} Molar (mL)	Volume of $K_4[Fe(CH)_6]$ 0.5 Molar (mL)	Volume of $NiSO_4$, 0.75 Molar (mL)	DF
1	50	2	1	1	88
2	50	4	1	1	110
3	50	6	1	1	130
4	50	8	1	1	215
5	50	10	1	1	310
6	50	12	1	1	308

2.1.2. Effect of stoichiometric amounts of $K_4[Fe(CN)_6]$

The experiments were conducted as under 2.1.1. at pH10 but using different amounts of $K_4[Fe(CN)_6]$. The results are shown in Table II.

2.1.3. Effect of stoichiometric amounts of $NiSO_4$

The experiments were conducted as under 2.1.2. but using different amounts $NiSO_4$. The results are shown in Table III.

2.1.4. Effect of different amounts of the carrier (CsCl)

The experiments were conducted under optimum conditions as derived from the experiments 2.1.1. to 2.1.3, but using different amounts of the carrier (CsCl). The results are shown in Table IV.

2.2. OPTIMUM CONDITIONS

The results are summarized. The optimum conditions are shown in Table V.

TABLE V OPTIMUM CONDITIONS FOR TREATMENT OF THE SIMULATED EFFLUENTS

No	Parameter	Values
1	Volume of the simulated effluent	50 mL
2	Volume of stabile CsCl, 10^{3} Molar	10 mL
3	Volume of aq NaOH or acid, 1 Normal	as needed for pH adjustment
4	pH	10
5	Volume of $K_4[Fe(CH)_6]$, 0 5 Molar	1 mL
6	Volume of $NiSO_4$, 0 75 Molar	1 mL

TABLE VI RADIOMETRIC MEASUREMENTS ON THE REAL LIQUID RADIOACTIVE WASTES (on 31 05 94)

Waste ID	Date of interim storage	Volume of waste (L)	Container surface dose rate (μSv/h)	Specific activity (kBq/L)	
				Cs-134	Co-60
RW1	07 03 89	24	2 5	15 02	2 69
RW2	16 05 89	23	3 5	21 74	13 39
RW3	24 09 89	7	1 5	16 43	1 51
RW4	16 11 89	18	2 3	10 79	9 57
RW5	25 07 89	15	0 9	2 81	0 80
RW6	22 09 92	10	1 8	12 62	3 86

TABLE VII PHYSICO-CHEMICAL CHARACTERISTICS OF THE REAL LIQUID RADIOACTIVE WASTES

Waste ID	Physical appearance (colour, turbidity, etc)	Density (g/mL)	Dry extract	Fixed residue (g/L)	pH	Electrical conductivity (mS/cm)
RW1	Almost colourless, slightly turbid	1 03	96 1	85 1	10 43	67 7
RW2	Colourless to slightly yellowish, slightly turbid	1 04	89 2	88 3	10 98	58 5
RW3	Almost colourless, slightly turbid	1 05	105 3	90 8	10 24	75 4
RW4	Almost colourless, slightly turbid, dirty sediment	1 04	168 2	114 2	10 59	108 2
RW5	Brownish, turbid, dirty sediment	0 99	128 0	108 1	10 87	91 7
RW6	Almost colourless, turbid, dirty	1 01	118 2	96 5	10 67	45 3

2.3. CHARACTERIZATION OF LIQUID RADIOACTIVE WASTES

The selection of a chemical treatment process for liquid radioactive waste depends upon its radiological and physico-chemical properties and the quantity of arising waste. Therefore, in order to know the pertinent properties, the wastes generated from radioisotope production facilities of the Institute were studied as follows:

- surface dose rates (μSv/h) of liquid waste stored in plastic drums in the interim storage room were measured by a calibrated beta-gamma survey meter, Berthold LB-1200, Germany;
- the waste samples were analysed by gamma spectroscopy using HPGe detector (Vol:74 cc, resoln.:2.1 keV at 1332 keV for ^{60}Co), MCA (Canberra 40+ series 4096 channel) and the associated electronics;
- colour and turbidity of the wastes were ascertained by eye estimation as usual;
- a certain volume of the wastes was weighed to measure density;
- pHs of the wastes were measured by pH meter, Philips PW9432; electrical conductivities of the wastes were measured by digital conductivity meter, Philips PW9526;
- dry extract and fixed residue of the wastes were determined following standard procedures [2].

The results are shown in Tables VI and VII.

2.4. TEST RUNS WITH THE ^{134}Cs SEPARATION FROM THE LIQUID WASTES

The ^{134}Cs separation was conducted under optimum conditions (shown in Table V) as follows:

- the liquid wastes containing ^{134}Cs were used in the experiments (specific activity is shown in Table VI);
- twenty mL of the wastes were taken in 100 mL beaker, pH was adjusted accordingly;
- requisite amounts of carrier and precipitating agents, etc. were added and the volume adjusted to 100 mL;
- mixing was carried out at 160 rpm for ~2 min., subsequently at 120 rpm for 20 min;
- the system was allowed to stand for ~24 h;
- after the settling period, 50 mL of clear liquid layer was transferred to another 100 mL beaker and analyzed for ^{134}Cs by gamma spectrometry;
- DF was calculated from initial and final counts.

The results are shown in Table VIII.

TABLE VIII. REMOVAL OF ^{134}CS FROM THE REAL LIQUID RADIOACTIVE WASTES

Waste ID	Volume of waste (mL)	Final volume (mL)	% removal
RW!	20	100	98.26
RW2	20	100	99.11
RW3	20	100	90.98
RW4	20	100	94.25
RW5	20	100	96.17
RW6	20	100	98.13

TABLE IX. EFFECT OF ^{137}Cs ACTIVITY OF SIMULATED EFFLUENT ON % REMOVAL AT pH10

Exp. No.	Vol. of simulated effluent (mL)	^{137}Cs-activity (kBq)	Vol of CsCl 10-2 Mol (mL)	Vol of NaOH 1 Normal (pH adj.)	Vol of $K_4[Fe(CH)_6]$	Vol of $NiSO_4$ 0.75 Mol (ML)	Final volume	% removal of ^{137}Cs
1	500	18.5	10	5	10	10	606	89.9
2	500	186.0	10	4	10	10	564	99.7
3	500	1690.0	10	4	10	10	609	99.8

2.5. EFFECT OF ^{137}Cs OF SIMULATED EFFLUENT ON (%) REMOVAL AT pH10

The experiments were conducted at different concentration levels of ^{137}Cs of the simulated effluents. The results are shown in Table IX.

3. CALCULATIONS

The following equations were used :

$$Sp\ activity = \frac{(A-B)100}{EVT} Bq/L$$

where

A is the average counts for sample,
B is the average counts for background,
E is the efficiency of the detector,
V is the volume of sample (L), and
T is the time of counting (S)

B. Percentage removal of radionuclide

$$removal = \frac{original\ activity - final\ activity}{original\ activity} 100$$

C. Decontamination factor (DF)

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IMPROVED REMOVAL OF IODINE-125 FROM EFFLUENTS BY THE SOIL COLUMN METHOD USING LATERITE SOIL

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Abstract

The soil column experiments were conducted to treat the liquid wastes from hospitals containing ^{125}I. Three sorbent samples of laterite clay materials with different content of iron oxides (geothite, α-FeOOH) and hydroxides were used to sorb anionic iodate. Post-treatment of the liquid wastes with sodium hypochlorite (redox reagent) oxidized the iodide to the desirable iodate ion. pH after treatment ranges between 4.8 to 5.8 that is not very much different from the initial value pH4.5. The results show that 90 to 97% sorption of iodine with the decontamination factor between 10-32 could be obtained after the first two hours of experiments. The concentration has decreased from an initial value of 10 Bq·mL^{-1} to the concentration ranges 0.3 to 0.9 Bq·mL^{-1}. For the soil at pH between 4.5 to 6.0, positive charges predominated on the kaolinite, geothite and aluminum hydroxides. The negative ^{125}I anions were electrostatically held by the positive charges on the mineral components of the laterite clay materials. The treated effluents could be released to the environment safely after further dilution and decay. The storage period will decrease tremendously providing better management for the disposal of the wastes by generators. The batch experiments conducted using different sorbent masses of soils, show that there was a drop in sorption where the mass of soils falls below approximately between 0 to 0.25 g. The sorption remains constant with the soil mass above 0.25 g,. Another batch experiment using different concentration, shows that adsorption capacity of the laterite soil was 1.1 μCi/g. The adsorption is about 96% with a distribution coefficient of 1170. The experiments conducted show that anionic iodate in the liquid wastes can be removed by the laterite soil material and then the decontaminated effluent can be released to the environment. The column treatment method was more effective, easy to handle, and has low a capital and maintenance cost.

1. SCIENTIFIC BACKGROUND

Iodine-125 is routinely used in clinics, hospitals and research institutes for blood cell screening of hospital patients, blood donors and research. Table I shows the characteristics of the liquid wastes containing ^{125}I generated by different users in Malaysia since 1990. Most of the wastes were diluted with sodium hypochlorite by the users to eliminate any pathogens present in the effluent. The radionuclide has toxic properties and a half-life of 59.7 days [1]. Stable chemical forms of iodine exists as anions in solutions. Common anionic form of iodine such as iodate can be removed from the wastes by sorption other than ion exchange. Sorption mechanisms that possibly can occur are chemical reduction of the ions to a more easily immobilized form, or formation of insoluble species by incorporation into the crystal lattice of an insoluble matrix [2]. The prevailing valence state of the iodate ion would be (-1) during the treatment process. In groundwater, significant retention of the iodine by metal ions can be observed that are capable of forming strong cationic complexes or neutral compounds of low solubility or by chemisorption on soil minerals containing the same metals [3].

Many soils do not exhibit significant ion exchange absorption of iodine [4-5]. From literature [6] it is known that where the rocks and soil minerals containing copper, iron and lead sulfides were used, significant sorption of iodine occurred with high distribution coefficient values. The iodide and iodate ions are sorbed by those sulfides whose metal ions form an insoluble iodide or iodate. Table II shows the soil material samples in the presence of kaolinite, gibbsite and geothite with low net negative charge obtain low positive charges between 2 - 5 cmol/kg depending on the soil pH. Reference [3] states that anion exchange capacities of some common rocks and secondary minerals (clays) have comparatively high values Substitution of Fe(II) and Mg(II) by Fe(III) in the lattice lead to an increased net surface charge. Clay

TABLE I. CHARACTERISTICS OF AQUEOUS WASTES CONTAINING ^{125}I RADIOISOTOPE PRODUCED SINCE 1990

Source of wastes	Volume (m^3)	Concentration (kBq/L)
General hospital	6.80	57.00
Research institutes, clinics	2.00	22.00

TABLE II. CHARGE CHARACTERISTIC SHOWING COMPARATIVE LEVELS OF PERMANENT (CONSTANT), pH-DEPENDENT NEGATIVE AND POSITIVE CHARGES [7].

Colloid Type	Negative Charge			Positive
	Total (cmol/kg)	Constant (%)	Variable (%)	Charge, (cmol/kg)
Organic	200	10	90	0
Smectite	100	95	5	0
Vermiculite	150	95	5	0
Fine-Grained Micas	30	80	20	0
Chlorite	30	80	20	0
Kaolinite	8	5	95	2
Gibbsite (Al)	4	0	100	5
Geothite (Fe)	4	0	100	5

minerals exhibit some anion exchange properties due to the presence of hydroxy groups in the lattice. For soil with pH value between 4.0 and 6.5, the net overall charge for the soil is positive [7]. The formation of the positive charges enables the negative anion ^{125}I from liquid wastes to be attracted to the soil. The process lowered the aqueous effluent radioactivity.

1.1. CHOICE OF LATERITE SOIL

Laterite soil used in these experiments are commonly found in Malaysia. Laterite is a residual ferruginous material in the soil and frequently exists as lateritic pellets or nodules; locally it has developed into true laterite. The samples have different colors and composition contents of clay minerals. The minerals have pH dependent on the charge characteristics [7, 8]. The reddish brown and yellowish color of the laterite soil samples shows a high composition content of iron oxide. In the literature, it was reported that the soils have a texture and composition that is a matrix of finely granular gibbsite. It contains different proportions of limonite, hematite, chamosite, and kaolinite that form the actual ores [8].

The choice of the laterite soil samples is done accordingly to their acidity, high content of iron oxides and the presence of kaolinite clay minerals and aluminum hydroxides. The minerals have variable (pH - dependent) negative charges and exhibit modest positive charges at low pH values that can lead to effective effluent treatment. Specific adsorption of anions and cations by iron oxides at different pH equilibrium solution was reported in Ref. [9]. A literature review on the sorption of iodine radioisotopes by various minerals is also available in Ref. [9]

1.2. OBJECTIVE OF THE STUDY

The objective of this study was to investigate the performance of laterite soils by soil column techniques for the treatment of aqueous wastes containing ^{125}I. Iodine-125 in the form of iodide in the waste was oxidized to anionic iodate with sodium hypochlorite (redox reagent). The study has been accomplished by: (1) Determining a pH value suitable for optimum removal of the ^{125}I radioisotope, (2) Performing a paper chromatographic analysis to determine the iodine chemical species in the liquid wastes and after oxidation using redox reagent, (3) Separating and collecting the soluble effluent wastes containing iodate ions for treatment, (4) Preparating and conditioning the soil columns at the required experimental conditions, (5) Conducting three soil column experiments simultaneously with same experimental conditions, (6) Performing batch experiments to determine relative sorption using different masses of soil, and (7) Determining adsorption capacity of the laterite soil for iodate ion by the batch experiment.

2. EXPERIMENTAL METHOD

For the soil column experiments, aqueous wastes containing radioisotopes were obtained from the General Hospital at Kuala Lumpur. In batch experiments, ^{125}I as iodide radioactive solution was obtained from the supplier with concentration of 28 kBq·mL^{-1}. Counting was done by the Ortec gross beta/gamma detector and HPGe detector. Paper chromatographic analysis was performed prior to the actual experiments to determine the iodine chemical species in the liquid wastes and after oxidation using redox reagent. Three experiments were conducted to study the performance of the laterite soil sorption of the iodate ions.

2.1. DETERMINING OPTIMUM pH VALUE FOR REMOVAL OF ^{125}I

The batch experiment were conducted using kaolin clay minerals obtained from the Source Clay Minerals Repository, Geological Science Department, University of Missouri-Columbia. Ten stock solutions of 100 mL spiked with ^{125}I were prepared with pH between 3 and 9.0. Dilute sodium hydroxide or hydrochloric acid were used to adjust pH of the stock solution. The kaolin clay minerals were weighed precisely, giving the weight 1.0±0.001 g. Twenty mL of each stock solution were added into a 50 mL polycarbonate centrifuge tube and equilibrated for 14 days at room temperature. The tubes were centrifuged at 4000 rpm for one hour and the final pH values of the solutions were measured. Two mL of each solution were collected on a 0.2 μm disposable filter. It was then acidified by adding 10 μL of concentrated hydrochloric acid or nitric acid (6 M or 12 M) and then analyzed for gamma. The solid materials were removed from each tube by filtering through a 0.2 μm filter, then allowed to dry. The solid materials were transferred to counting tubes for gamma analysis.

2.2. SOIL COLUMN EXPERIMENTS

Iodide ions in the wastes were oxidized to anionic iodate with redox reagent sodium hypochlorite. The soluble aqueous wastes were separated by filtration through a 0.2 μm filter, collected, and then pH was adjusted to 4.5 for the treatment process. Three laterite soil samples were air dried, filtered by filters (size 0.250-0.350 μm) and then mixed with sand (0.250 μm) with ratio of 3:1. Sand was used to enable the column to be porous in order to allow the effluent to pass through the soil column. Each soil mixture was packed every 2 cm thick into a polyethylene tube (5.0 cm diameter, 12.0 cm height) and then compacted uniformly. The tube was filled up to 90 % full. The three laterite soil columns of the same dimensions were prepared by the same method. Prior to the actual experiment, preequilibrated distilled water of pH4.5 was run into the carefully saturated packed columns for 3 days. The conditioning of the soil column will enable to keep the soil at the required pH4.5 and provide a maximum contact between the solution and the soil.

For each column experiment, three liters of the wastes were used and poured into a holding container and allowed to pass through the saturated soil column at a constant rate for 2 days. The experiments were conducted simultaneously but using different apparatus. The treated effluents were collected at few hours intervals by using a fractional collector at the bottom of the column into ten mL test tubes. 5 mL treated samples were transferred to planchets for counting gross beta gamma by the detector. Three measurements were performed for each treated sample. Handling of treated samples was carefully performed to prevent contamination and to minimize an error.

2.3. SORPTION BY DIFFERENT SOIL MASSES

Batch experiments were conducted to determine relative sorption of the iodate ion by six different masses of two different soil types (A and B) ranging from 0.25 g to 2.00 g. 10 mL of iodate solution and respective soil mass were added into each 20 mL vial. All the vials were allowed to be equilibrated for 2 days after being shaken continuously at room temperature. After the equilibration period, all the vials were centrifuged and 6 mL of solution samples were collected and transferred into planchets for counting for gross beta/gamma. Solid sediments were removed from each vial by filtering through a 0.2 μm filter and then the sediments were allowed to dry. The solid sediments were transferred to planchets for gross beta/ gamma counting. All the solutions and the sediments were collected into counting planchets of the same geometry.

2.4. SORPTION OF IODATE IONS AT DIFFERENT CONCENTRATIONS

Another batch experiment was conducted using the concentrations of the solution in the range of 2.06×10^{-3}- 2.7×10^{-2} μCi. Into each 20 mL vial, the soil mass 0.11 g and 7 mL of the respective concentration solution was added. All the six vials were allowed to be equilibrated for 2 days at room temperature and then centrifuged. The solution samples of 3 mL were collected and transferred into planchets for counting for gross beta gamma. The solid sediments were removed from each vial by filtering through a 0.02 μm filter, allowed to dry, and then transferred to planchets for gross beta/gamma counting. All the solutions and the sediments were collected into counting planchets of the same geometry.

2.4. COUNTING PROCEDURES

All the samples were analyzed for gross beta/gamma. Prior to counting of samples, aliquots of a standard ^{125}I solutions were counted. Samples' activities (corrected for background) were calculated from the ^{125}I standard count rate and activity. The standard ^{125}I aliquots solutions were collected in planchets with the same geometry used for the samples counting. The solution samples were only analyzed before and after treatment. Counting was conducted on the same day to minimize error due to decay of the ^{125}I. Therefore, no correction for radioactive decay of the ^{125}I radionuclide was included. For each sample, three measurements were conducted. Estimation of errors was done for all the samples.

3. RESULTS AND DISCUSSION

The distribution coefficient was the highest for pH between 4.5-5 (See Fig. 1). This indicated that in that pH range, the ^{125}I activities were highest and lowest in the kaolin solid and effluent samples, respectively. There was optimum condition for the removal of the ^{125}I from the liquid wastes. Preequilibrated water at optimum pH4.5 was determined as suitable for soil column experiment.

Examination of the chemical species shows that the wastes obtained directly from the users contained iodide species. After the addition of redox reagents, iodate ions were present due to the oxidation of the iodide ions.

Figure 2 shows the treated effluent activity after treatment for 2 days by the three laterite soils. Effluent pH after the treatment ranges between 4.8 to 5.8 that is not very much different from the initial pH4.5. During the first two hours of experiments, the initial column volume of water presented in the soils had passed through. The treatment became more effective after 2 hours and slowly became constant after that period. The results show that the concentration has decreased from initial 10 Bq·mL^{-1} to the concentration range 0.3 to 0.9 Bq·mL^{-1}. Figures 3 and 4 show that 90 to 97% of radioiodine were sorbed with a decontamination factor between 10-32. Final pH between 4.8 to 5 of the treated effluent was not very much different from the initial value 4.5. The three laterite soils were able to decrease the radionuclide concentration to the levels permitting their release to the environment without long storage period. Laterite type C has demonstrated the best result for sorption processes with final pH5.8.

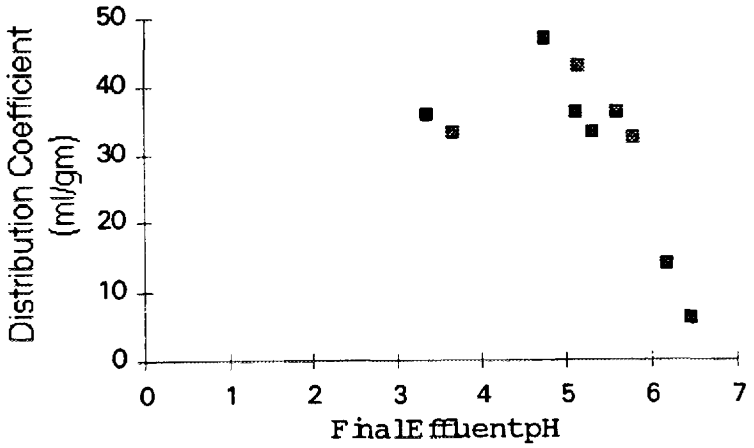
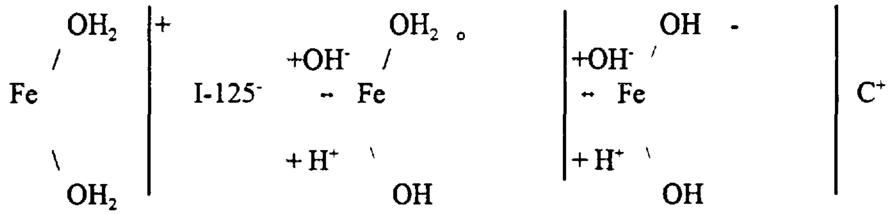


FIG. 1. Batch experiment after equilibration period.

Moderately acid soil between pH 4.0 to 6.5, exhibited net positive charges with the negative iodate ions electrostatically held by the positive charges on the mineral components of the laterite clay materials. It predominated on the kaolinite, goethite (ferrous oxide) and aluminum hydrous oxide that exhibited positive charges at the experimental pH4.5 condition. The reaction for ferrous oxides at the acidic condition can be explained as follows: Surface charge of ferrous oxide was created by an adsorption or desorption of H^+ or a desorption or adsorption of OH^-, respectively, in the potential determining layer consisting of the surface O, OH, and OH_2 groups. The results were comparable to the model proposed by Parks and de Bruyn [9].



$$\left|\mathrm{Fe}\begin{matrix}/\ \mathrm{OH_2}\\ \\ \backslash\ \mathrm{OH_2}\end{matrix}\right|^{+} \mathrm{I\text{-}125^-} \begin{matrix}+\mathrm{OH^-}\\ \text{--}\\ +\mathrm{H^+}\end{matrix}\ \mathrm{Fe}\begin{matrix}/\ \mathrm{OH_2}\\ \\ \backslash\ \mathrm{OH}\end{matrix}{}^{o}\ \left|\begin{matrix}+\mathrm{OH^-}\\ \text{--}\\ +\mathrm{H^+}\end{matrix}\ \mathrm{Fe}\begin{matrix}/\ \mathrm{OH}\\ \\ \backslash\ \mathrm{OH}\end{matrix}\right|^{-} \mathrm{C^+}$$

The pH-dependent charges ferrous oxide (positive surface charge) were balanced by an equivalent amount of ^{125}I anions that were electrostatically held in the outer diffuse electric double layer.

The reaction by the aluminum hydrous oxide in the laterite soil can be explained as follows: When the soils become acidic, H^+ ions are attached to the surface OH groups.

$>Al\_\_OH \quad + \quad H^+ \quad \text{--} \quad >Al\text{-}OH_2^+$
No charge (soil colloid) — (soil solution) — Positive charge (soil colloid)

Figures 5 and 6 show the percentage adsorption by soil A and B in the batch experiments using different sorbent masses of soils. There was a drop in the sorption on the soils as the soils mass falls below approximately between 0 to 0.25 g. For a soil mass above about 0.25 g and above, the percentage sorption slowly remains constant. Figures 7 and 8 show a distribution coefficient for the soil A and B depending on soil masses. The distribution coefficient values decreased as the soil mass is increased.

Figures 9 and 10 show the distribution coefficient and percentage adsorption using different concentrations of iodate. The distribution coefficient increases with the increase of the iodate concentration until it remains constant at 1.48 x 10^{-2} μCi. This also occurred where the percentage adsorption increased until it started to be constant about 96% at the 1.48 x 10^{-2} μCi of the iodate concentration. It was determined from the results that the adsorption capacity of the laterite soil was 1.1 μCi/g. The highest adsorption was about 96% with the distribution coefficient 1170.

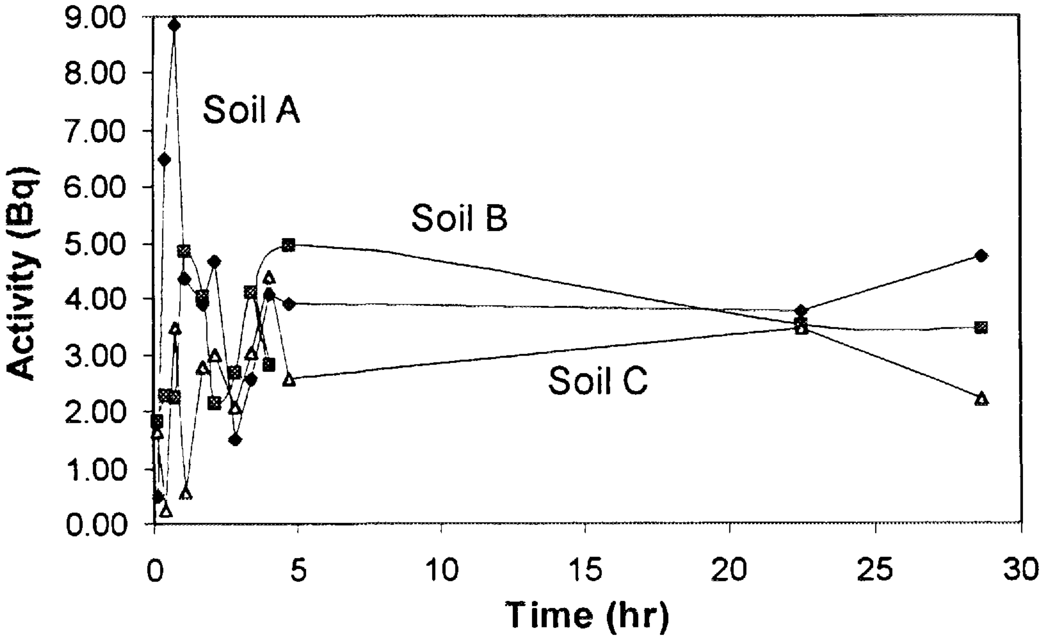


FIG. 2. Activity of effluents after treatment by three different soil.

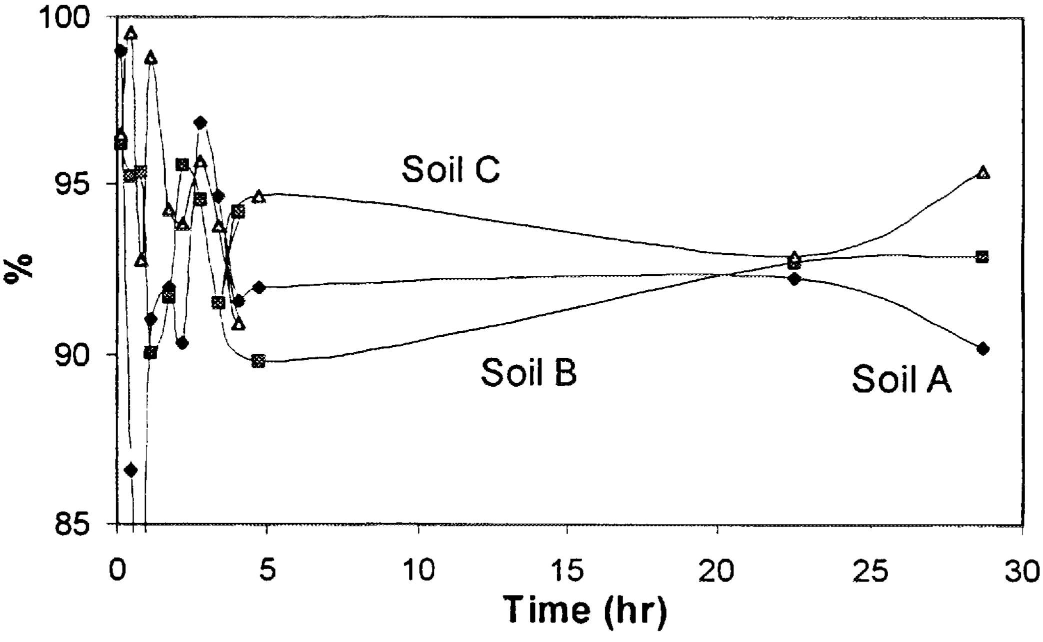


FIG. 3. Adsorption of I-125 by three different soil.

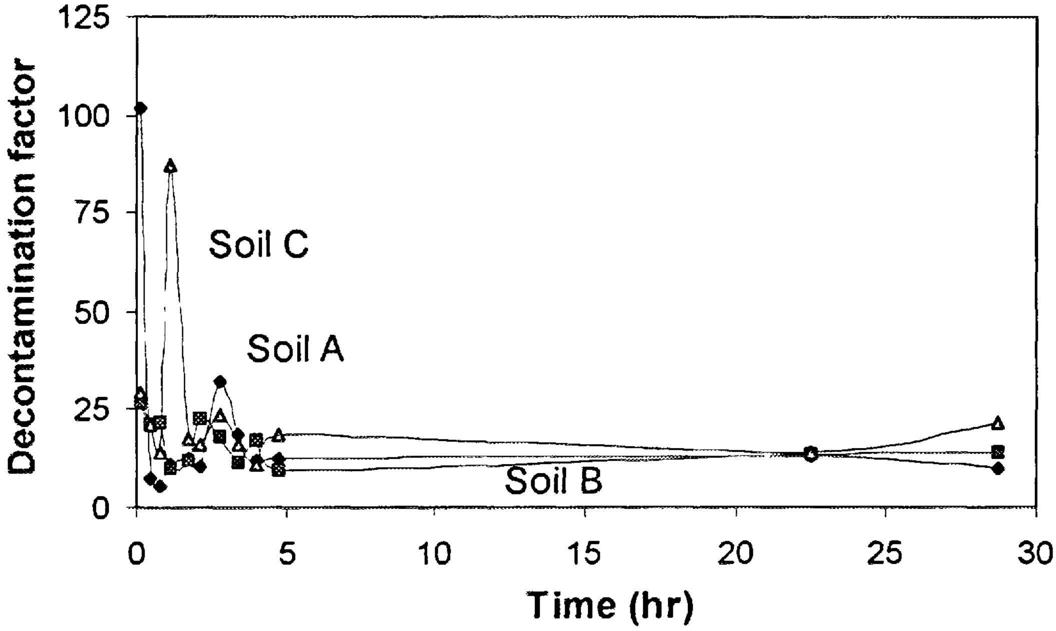


FIG. 4. Decontamination factors after treatment by three different soil.

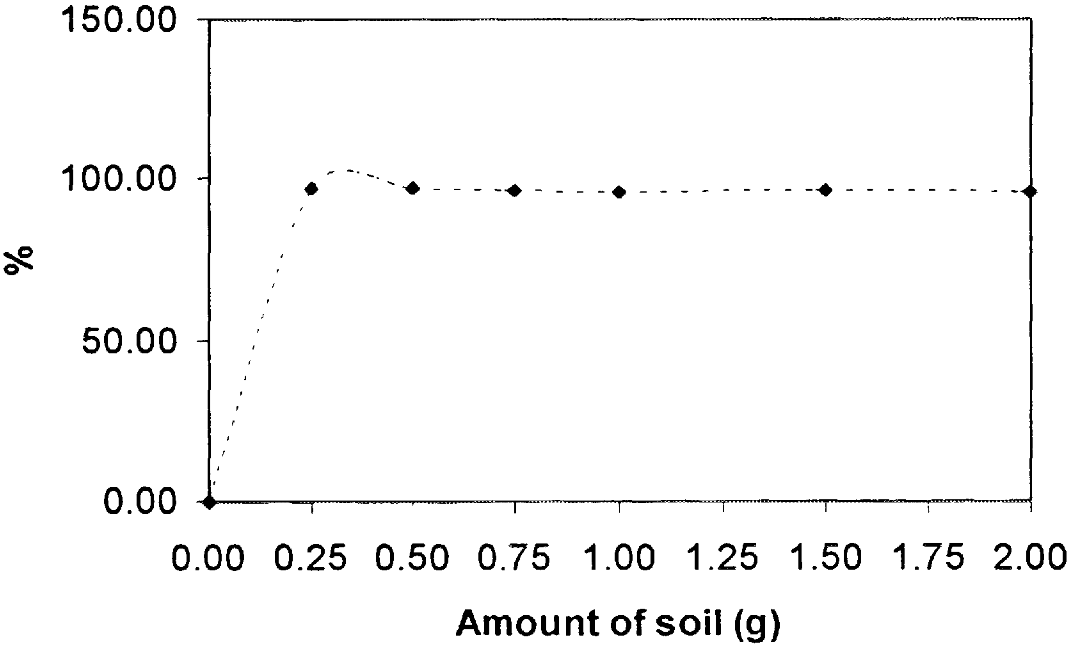


FIG. 5. Adsorption of I-125 by different masses of soil A.

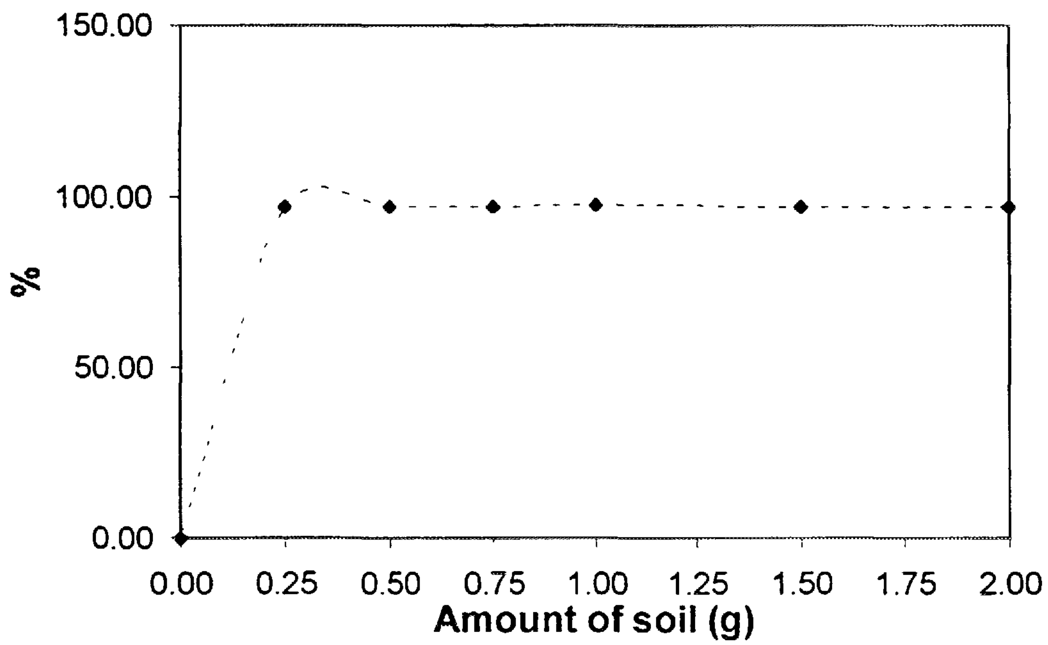


FIG. 6. Adsorption of I-125 by different masses of soil B.

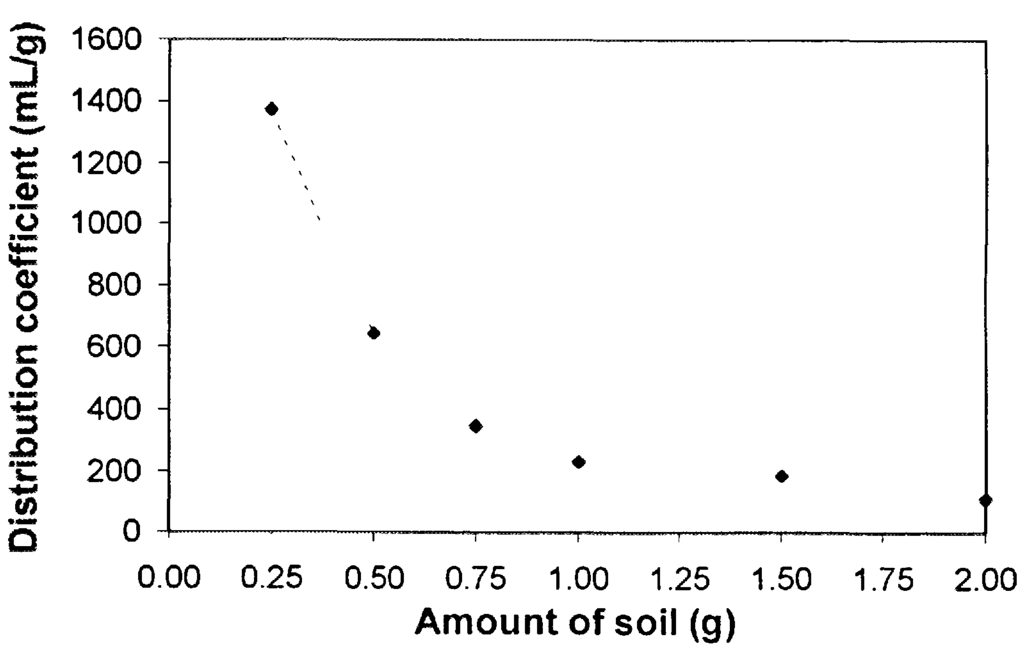


FIG 7. Distribution coefficients depending on the mass (soil A)

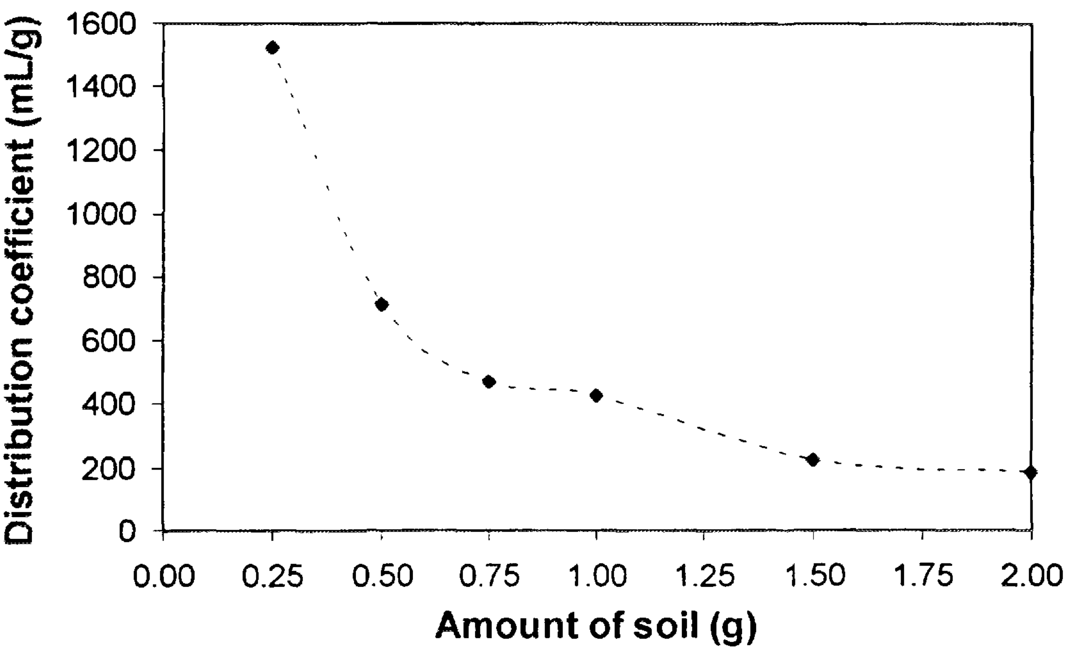


FIG. 8. Distribution coefficients depending on the mass (soil B).

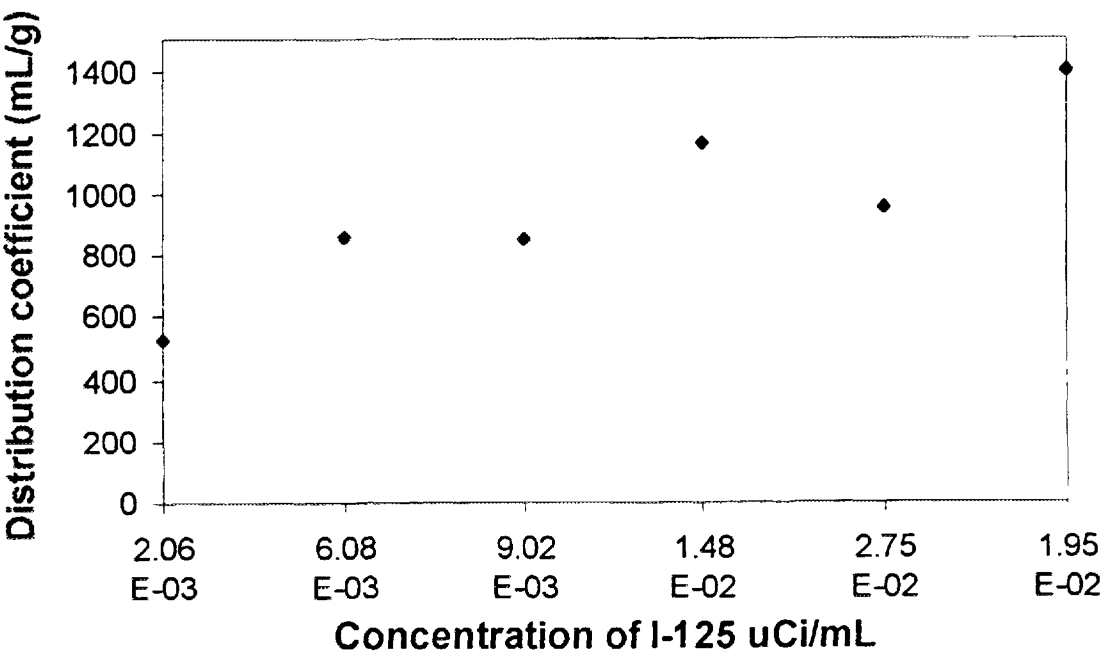


FIG. 9. Distribution coefficients depending on the concentrations of I-125

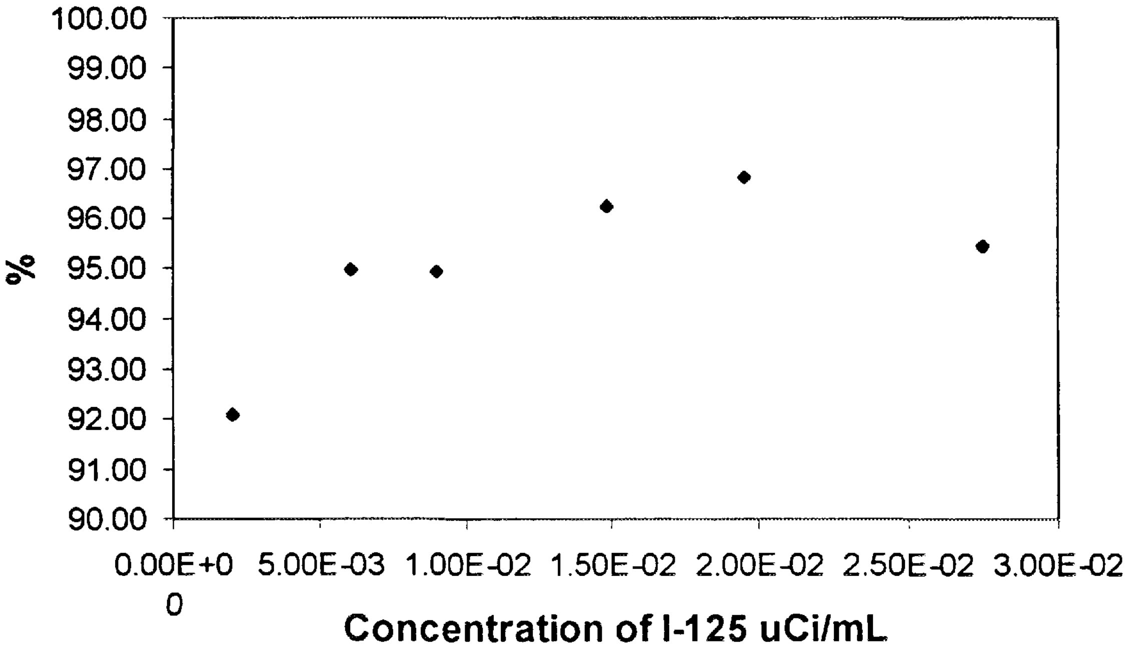


FIG. 10. Adsorption of I-125 depending on the concentration.

4. CONCLUSIONS

Several conclusions can be drawn from the study conducted:

1. Optimum pH for removal of ^{125}I was 4.5 which provided the highest distribution coefficient.
2. Results show that 90 to 97% sorption of radioiodine with a decontamination factor between 10-32 were obtained after the first two hours of experiments. The concentration has decreased from the initial 10 Bq·mL^{-1} to the concentration range 0.3 to 0.9 B Bq·mL^{-1}. Effluent pH after the treatment ranges between 4.8 to 5.8 that is not very much different from the initial value 4.5.
3. At the moderately acid soil condition with pH between 4.5 to 6.0, positive charges were predominated on the kaolinite, goethite and aluminum hydroxides present on the laterite soil clay. The negative ^{125}I anions were electrostatically held by the positive charges on the mineral components of the laterite clay materials. This is indicated by the high degree of sorption in the soil clays and soil minerals.
4. The batch experiments conducted using different masses of soils, show that sorption dropped when the mass of soils was in the range of 0 to 0.25 g. The sorption remains constant with the soil mass above 0.25 g.
5. Another batch experiment using different iodine concentration, shows that adsorption capacity of the laterite soil used is 1.1 μCi/g. The adsorption is about 96% with a distribution coefficient of 1170.
6. The experiments conducted show that anionic iodate in the liquid wastes can be removed by the laterite soil material. The treated effluents can be released to the environment much safer where it will undergo further dilution and decay. The storage period will be reduced tremendously providing better management for the waste generators.

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DECONTAMINATION FOR FREE RELEASE

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Abstract

Many countries are seekng to treat radioactive waste in ways which meet the local regulatory requirements, but yet are cost effective when all contributing factors are assessed In some countries there are increasing amounts of waste, arising from nuclear plant decommissioning, which are categorized as low level waste however with suitable treatment a large part of such wastes might become beyond regulatory control and be able to be released as non-radioactive The benefits and disadvantages of additional treatment before disposal need to be considered Several processes falling within the overall description of decontamination for free release have been developed and applied, and these are outlined In one instance the process seeks to take advantage of of techniques and equipment used for decontaminating water reactor circuits intermittently through reactor life

1. INTRODUCTION

As a background to a consideration of selective absorbers [1] for treatment of liquid waste streams, some information on waste categories was given It was pointed out that low level waste spans roughly a range of 10000 in activity between free release and intermediate level waste, and that the activity span covered by ILW, between LLW and HLW, is likely also to be several orders of magnitude The value of concentrating waste within a category may depend markedly on how disposal costs are weighted with regard to volume and activity and hence high selectivity is not always cost effective Selective activity removal from liquid wastes often provides an example of waste partitioning between categories, namely free release (water discharge) and ILW or LLW It may not be considered in this light because the option of avoiding the partitioning is not available due to large water volumes

Countries which have been operating reactors from the early days of nuclear power are now faced with plant decommissioning or replacement of major components such as steam generators Often there are large quantities of solid material in components peripheral to the reactor core region which at the end of their working life would be classed, most probably, as LLW and can be disposed of directly as such A recent example is the heat exchangers (boilers) from the prototype Winscale Advanced Gas Cooled Reactor (WAGR) in the UK which were lifted from the reactor building, and transported on public roads to the low level waste disposal facility at nearby Drigg However there is considerable interest in solid waste partitioning to produce a free release component This may be prompted by (i) bulk interim storage/surveillance requirements if a suitable disposal site is not immediately available (ii) cost of direct disposal (iii) resale value of materials The procedures are often referred to as decontamination for decommissioning (DfD) or sometimes as hard decontamination These titles point to the differing objectives of the regular decontaminations carried out on water reactor circuits of operating reactors and decontamination following withdrawal from operation DfD procedures may be chemical or mechanical, but the former are considered here A brief discussion is followed by specific examples

2. OBJECTIVES OF DECONTAMINATION FOR DECOMMISSIONING

The general overall objective of decontamination for decommissioning is to reduce decommissioning or waste treatment costs without significant increase in dose uptake by workers and public Achievement of free release status for the bulk of the material often produces the commercial driving force, particularly when the material has a significant scrap or resale value, and free release becomes the technical objective

TABLE I. SOME AVAILABLE DECONTAMINATION PROCESSES

Method	Comment
Alkaline Permanganate + Citrox	Concentrated chemical process 10% NaOH + 4% $KMnO_4$ + high organic concentration
Dilute Alkaline Permanganate	Preconditioning step (oxidizes Cr (III))
Acid Permanganate	Preconditioning step (oxidizes Cr (III))
CAN-DECON	Solution step - organic acids
CAN-DEREM	Solution step - organic acids (no oxalic)
LOMI	solution step - vanadous formate + picolinic acid

TABLE II. DIFFERENCES BETWEN IN-SERVICE DECONTAMINATION AND DfD

Objective	In-Service Dose Rate Reduction	DfD Free Release
Metal loss	To be avoided	Some required to achieve required DF
Oxide loss	Outer layer	All
Time	Constrained	Less important
Process cost	Higher cost can be economic	Probably only low cost economic
Process dose uptake	Trade-off	Must be low
Waste treatment of decontaminated solutions	Less important	Simple low volume required

TABLE III. EXAMPLES OF DECONTAMINATION FOR FREE RELEASE

Process	Allowed Release	Retention
Graphite incineration	C-14 + CO_2	Ash
Annealing	Segregate Tritium + Steel	--
Magnox dissolution	$Mg(HCO_3)_2$	Steel + IX Resin
Precipitation/IX	Water	Floc/IX
Chemical decontamination of steels	Steel	Removed Activity
Electropolishing	Metal	--
Mechanical decontamination	Metal	--

3. DEVELOPMENT TRENDS IN DECONTAMINATION FOR DECOMMISSIONING

It is interesting to recall that the need for intermittent circuit decontamination of Western design water reactors was not expected to be necessary and was not planned for. When recognized as necessary to alleviate dose uptake by workers, it represented an enormous challenge, even though the decontamination factors sought were not very great (generally 5-100). Simple decontamination techniques were either too aggressive or only partially successful in dissolving metal oxide. The time (outage), geometric (in situ), and benign (oxide only - no metal loss) requirements can now be met by several sophisticated multistage chemical, yet cost beneficial, decontamination processes (examples in Table I). Organic chelating agents such as citric acid or EDTA are often used to avoid metal oxide precipitation in reactor circuits during decontamination treatment and hence form part of the waste stream.

Decontamination for decommissioning is applied once a component is no longer required for service, removing constraints which apply to decontaminations on components to be returned to duty (Table II). Interest in simpler decontamination processes revived, partly because aggressive reagents were needed to remove surface metal as well as oxide to achieve the higher DFs, often > 1000, needed for free release, and partly to simplify the active waste management (e.g. avoid mixed wastes). One simple technique is the use of concentrated (0.05 to 50 Moles per litre) fluoroboric acid which attacks metals and oxides. This has been developed into the DECOHA technique, which has been used to clean pipework at Chernobyl [2,3]. Another technique uses the oxidizing power of cerium in the +4 oxidation state [4] but, for effective solution waste management, this needs to be coupled with a means of regenerating Ce(+4) from the Ce(+3) produced when metal and chromium oxide are taken into solution. Electrochemical regeneration has been investigated [5]. Ozone has been used in several one stage pilot decontaminations with cerium nitrate/nitric acid [6]. The cerium concentrations are typically of order 10mM and the $pH < 1$.

A middle road has also been sought whereby the effectiveness of decontamination necessary for free release could be achieved whilst retaining the major features (and hence experience and equipment) of the sub-system decontamination processes conducted during outages on operational reactors. Use of dilute solutions is attractive for activity removal and reagent regeneration by continuous (in-circuit) ion exchange. This work is described in more detail in Section 4.

Occasions will continue to arise where a process for decontamination for free release is tailored to a specific application. Some examples are given in Table III and include annealing (to remove tritium from steel) and incineration (graphite free released as carbon dioxide). A further example, which has been applied to Magnox debris from the fuel elements of the Magnox reactors which are cooled by carbon dioxide, is discussed in more detail in Section 4.

4. TWO EXAMPLES OF PROCESSES FOR DECONTAMINATION FOR FREE RELEASE

4.1. DISSOLUTION OF MAGNOX DEBRIS

The fuel elements of Magnox reactors are fitted with splitters or lugs, made of Magnox (mainly magnesium), which centre the fuel elements in the fuel channels which pass through the graphite moderator bricks. To increase the loading of fuel transport flasks, which take the elements for reprocessing at Sellafield, the splitters and lugs are removed at the power stations and held in storage vaults. Typical quantities accumulated at each site are approximately 100 tonnes occupying some 400-500 m^3 (uncompacted).

The Magnox material itself is only slightly active as a result of some surface contamination via the gaseous coolant and from activation of minor impurities in the Magnox, such as iron and cobalt. Nevertheless, it is classed as LLW as it is sometimes stored with small activated steel components, and would be suitable for shallow land burial. However, a plant has been constructed and is now in operation at Dungeness, a power station in Kent in the UK in which the Magnox is dissolved in carbonated water and the magnesium bicarbonate solution, at pH close to neutral, discharged to sea after filtration and monitoring [7, 8]. Provision is made for activity removal by ion exchange if necessary. Dissolution leaves behind any activated steel components.

The reaction is:

$$Mg + 2CO_2 \rightarrow Mg(HCO_3)_2 + H_2$$

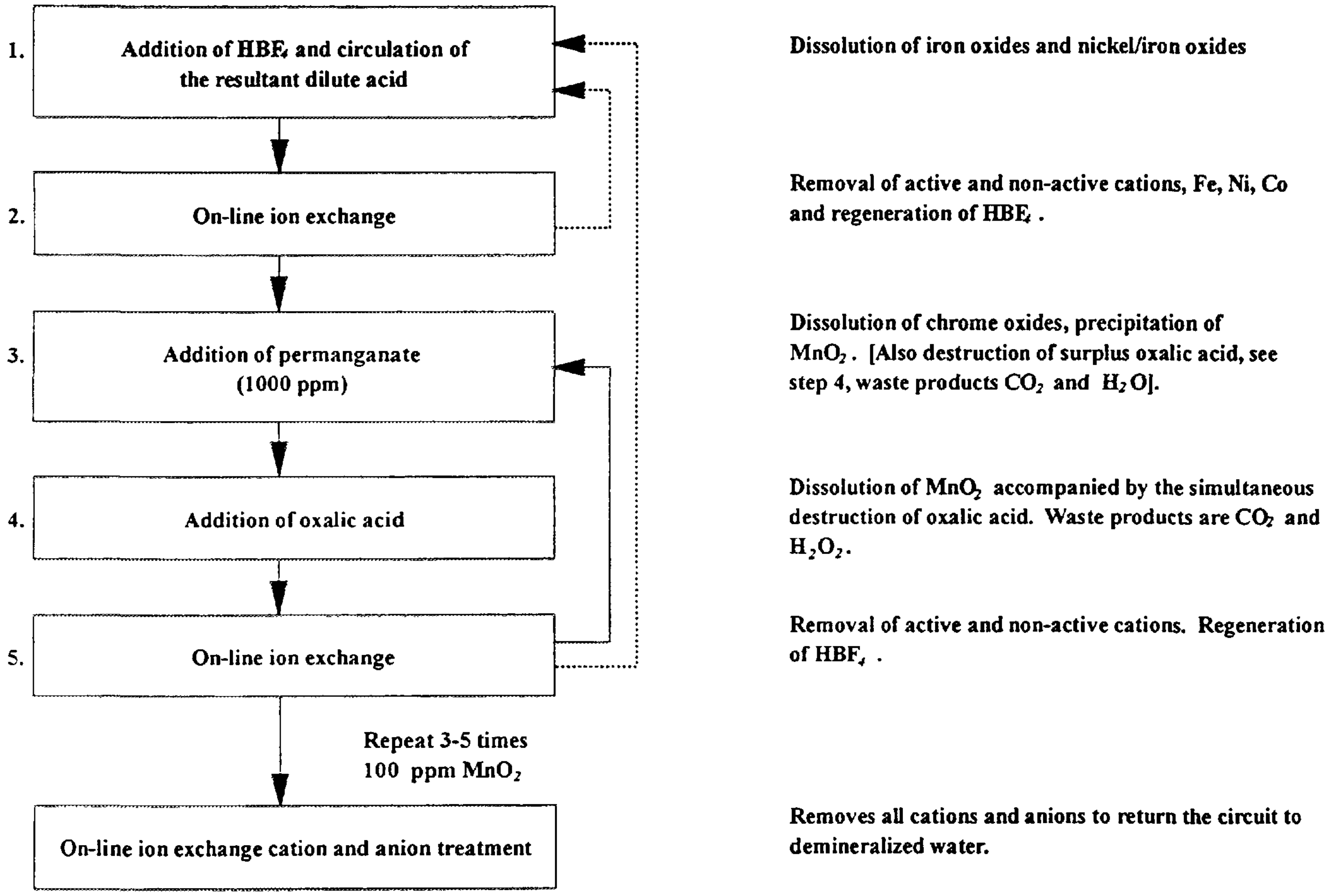
Corroded Magnox dissolves without evolution of hydrogen:

$$Mg(OH)_2 + 2CO_2 \rightarrow Mg(HCO_3)_2$$

Magnesium is of course a significant constituent of sea water at about 1300 ppm, and so the discharge is quite benign. The plant is designed to treat 75 kg of Magnox per day producing 45 m^3 of effluent per day containing 2 g per litre magnesium (as bicarbonate). It can thus be seen that the accumulated debris can be cleared in a few years. The volume reduction is obviously not as great as suggested simply by the insoluble fraction of the debris, and will depend on filter performance and ion exchange resin usage. Nevertheless, this process which essentially involves free release of the metal, is attractive and may be employed at other Magnox stations.

4.2. EPRI DfD PROCESS

The Electric Power Research Institute, EPRI, in the USA, has funded a research contract with Bradtec Ltd. To develop a decontamination process for decommissioning which could achieve the effectiveness necessary for free release, whilst retaining the major features of sub-system decontamination carried out on operational water reactors. The contamination is mostly likely to be in the form of oxides on Inconel and stainless steel.



All cycling between chemistries is performed in-situ without the need for draining and refilling. Final waste form is ion exchange.

FIG. 1. Schematic of Bradtec/EPRI DfD Process

The initial approach was to use a solution of fluoroboric acid which is very dilute (max. 10 nM) in comparison with the DECOHA technique. Whilst this proved satisfactory under certain conditions, such as cleaning an Inconel 600 sample taken from a PWR, chromium-containing oxides were resistant. It is the chromium-containing oxides which presented the major challenge in the development of satisfactory decontamination techniques for dose reduction to workers. In this case, the chromium (3+) is treated with an oxidizing agent to give chromium (6+) which is subsequently dissolved as a chromate.

Bradtec Ltd. [9] followed a similar approach for DfD, and ozone.was selected for trial first, specifically because it introduces no additional chemicals into the liquid waste stream. The improvement was not sufficient to dissolve all the oxide from an ex-reactor stainless steel sample, and hence potassium permanganate (initially at 1000 ppm) was substituted for ozone as the oxidizing agent. Potassium permanganate is widely used in theoxidation step of water reactor decontaminations and organic chelants added in excess to prevent precipitation of manganese dioxide and to increase the solubility of steel oxides. Such organic reagents are ideally not wanted in a liquid waste stream and the EPRI process, for which a patent is pending, involves adding oxalic acid stoichiometrically after action of the permanganate to dissolve the manganese dioxide. Excess oxalic acid is converted to carbon dioxide by the next addition of potassium permanganate and does not appear in the final waste product. With the permanganate sequence Dfs of 8000 in 24 hours were achieved on exreactor contaminated stainless steel samples. The whole process is outlined in Fig. 1 with more detail in Appendix 1. It can be seen that the fluoroboric acid is recycled, and that the ion exchange removes Mc (II) and the dissolved steel cations.

5. DISCUSSION AND CONCLUSION

As reactor components are replaced and some reactors reach the end of their working lives, interest in minimizing waste disposal costs remains strong. It is probably true to say that no country to-day has disposal facilities for all its radioactive waste, although some countries which plan direct disposal of fuel, such as Sweden, are making considerable progress. Other countries, such as the UK, only have sites for low level waste approved at present. The costs of waste disposal may therefore be unknown. The option of treating solid waste so that a large fraction can be classed as free release with only a small fraction retained as active waste for immediate or eventual disposal is attractive. Several processes are in operation. In the context of steel decontamination for decommissioning, work continues to simplify or optimize processes and hence make them attractive to reactor owners. This may be easier where there is familiarity with routine water reactor decontamination.

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APPENDIX 1

BRADTEC/EPRI PROCESS (CHEMISTRY)

Iron Oxide Dissolution

$Fe_2O_3 + 6H^+ + 6BF_4^- \rightarrow 2FE^{3+} + 6BF_4^- + 3H_2O$

Ion Exchange

$2FE^{3+} + 6BF_4^- + H^+$ -------Resin $\rightarrow$ Fe -------Resin + $6H^+BF_4^-$

Iron oxide dissolution continues throughout the process

Chrome Oxide Dissolution - (permanganate addition)
nett reaction

1. $Cr_2O_3 + 2MnO_4^- + H_2O \rightarrow 2HCrO_4^- - 2MnO_2$ (solid)

MnO2 Destruction - (addition of oxalic acid)

2. $MnO_2 + H_2C_2O_4 \rightarrow Mn^{2+} + 2CO_2 + H_2O$

Ion Exchange

$Mn^{2+} + H^+$ -------Resin $\rightarrow$ Mn -------Resin + $H^+BF_4^-$

Removal of Excess Oxalic Acid

3 $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Iron dissolution continues throughout the process Chrome dissolution is brought about by applying step 1-3 as many times as will continue to reduce the activity from the metal We expect this to be 3-5x permanganate at 100 ppm

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A CRITICAL REVIEW OF SELECTIVE ABSORBERS FOR RADIOACTIVE AND HAZARDOUS SPECIES

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Abstract

Selective removal of radioactive and hazardous species has been a fertile research area for several years. However, for commercial application sorbers need to possess satisfactory properties beyond selectivity and these are reviewed. The benefits of selectivity itself need to be set against the limits for liquid discharges and categorisation of solid wastes. Two examples are given to illustrate the aspects described.

Many current and potential applications of selective adsorbers are to process streams which were not designed for waste management, but consideration of this at the planning stage as now occurs in the nuclear industry can lead to economic benefit.

1. INTRODUCTION

Selective removal of radioactive and hazardous species has been a fertile research area for several years and has also provided a potential application for research from earlier years on complex formation which initially had only a curiosity value. In many instances, the nature of waste streams (liquid) or waste materials (solid) has been determined in advance of legislation now applying to discharge or disposal. These situations often present particularly challenging clean-up problems. Process development might be very different when waste requirements are incorporated at the design stage.

Selective absorbers for a particular element or species can be considered against several properties such as:

(i) distribution ratio or selectivity
(ii) reversibility
(iii) absorber stability (radiation, chemical)
(iv) absorber form
(v) cost and supply

However it is important first to consider some target levels which treated liquid and solid wastes must meet, so as to have a perspective on the extent of decontamination which may be required. Unfortunately, different countries define standards in rather different ways. To some extent this reflects the difficulty in defining a publicly acceptable or scientifically justifiable concentration. The sensitivity of measuring or monitoring devices is also pertinent.

This review begins with an initial brief discussion of some legislation, to give a feel for the extent of treatment which may be required. It then goes on to discuss in general terms, with some specific examples, absorber properties, as broken down above. Two examples are then given to illustrate some of the aspects described.

2. LEGISLATIVE BACKGROUND - RADIOACTIVITY

2.1. LIQUID DISCHARGES

Historically in the United Kingdom, major nuclear installations such as power stations, reprocessing facilities and prototype reactors were generally constructed on coastal sites where the sea offered a ready means of dilution of liquid discharges. Countries with less significant or no coastal boundaries that have developed nuclear power facilities, have often sited such facilities on rivers or lakes.

Again historically in the United Kingdom, radioactive liquid discharge limits were considered in relation to the critical group, those people whose lifestyle predisposed them to the largest exposure to discharged radioactivity by known pathways. This type of logical but narrow assessment allowed very substantial discharges from establishments such as Windscale in the 1970s. Gradually the focus for liquid discharge authorisations moved from what was considered necessary to what could be achieved. Concepts such as ALARP (As Low As Reasonably Practicable), ALARA (As Low As Reasonable Achievable) were favoured, parallelled by the perhaps slightly less onerous BATNEEC (Best Available Technology Not Entailing Excessive Cost) for non-radioactive waste applications. Some have questioned the real value of expenditure to meet or stay well below current authorisations compared with the benefits of direct expenditure on human and environmental problems.

2.2. SOLID WASTES

The regulations vary in different countries, and IAEA have recently issued a safety guide which discusses possible approaches to the classification of radioactive waste [1].

There is often a desire to define a level below which radioactive material need not be controlled, but this is not always achieved although several countries have exemption levels, and in some cases specific substances, unconnected with the nuclear industry may be exempt. The level exemption levels for nuclear waste are of the order of kBq/kg.

At the other end of the radioactive waste scale comes high level waste which is characterised primarily by its continued high heat generation. The vitrified fission products from reprocessing operations come into this category, but long stored thermal reactor fuel would probably not.

Solid wastes with intermediate characteristics are distinguished in some countries, e.g. USA, Spain, Italy, on the basis of half-life and in others simply on the basis of total activity, although a distinction is usually made between alpha and beta/gamma activity. In the UK, waste with <12 MBq/kg beta/gamma and <4 MBq/kg alpha is classified as low level waste, LLW, and waste with higher levels but not classified as heat generating is classified as intermediate level waste, ILW.

Thus very roughly LLW spans a factor of 10000 in activity between the exempt and ILW limits, and the activity span covered by ILW will also be several orders of magnitude. This perspective is important in considering the merits of selective absorbers.

3. ABSORBER SELECTIVITY OR DISTRIBUTION RATIO

There are different ways of expressing how effectively an absorber removes a desired nuclide, often depending on the process objective.

3.1. DISTRIBUTION RATIO

If it is simply required to remove activity from solution e.g. by contacting with a solid, the distribution ratio is often used. This is an experimentally measured quantity defined, for a solid sorber in contact with a solution containing species A, as

final concentration of A on sorber/final concentration of A in solution

Since the concentration of A on the sorber is measured as amount or activity per unit mass, and the concentration in solution by amount or activity per unit volume, the units of the distribution ratio are volume/mass, e.g. $m^3.kg^{-1}$. The distribution ratio as mentioned above is an experimentally measured quantity, and it may depend on the concentration of A and the solution properties (e.g. ionic strength), as well as on sorber surface to volume ratio.

This quantity is often used to describe sorption on natural materials.

3.2. SELECTIVITY

Under circumstances where it is desired to remove one, usually active, chemical species A in presence of another often chemically similar but inactive species B, a quantity called the selectivity is often used, defined as

(concn of A on sorber/concn of B on sorber)/(concn of A in solution/concn of B in solution)

This quantity is dimensionless.

For example, it is useful to describe the efficiency of removal of caesium in the presence of relatively large amounts of sodium, and strontium from large concentrations of calcium or magnesium, cobalt from iron.

3.3. DECONTAMINATION FACTOR

On some occasions, the term decontamination factor is used. This generally expresses the ratio of contamination level before treatment to that after treatment, and the quantity is dimensionless. It is a useful quantity when considering removal of activity from solids and in treating solutions e.g. by precipitation or flocculation.

3.4. DISCUSSION

The different ways of expressing the ability of sorbers to take activity out of solution, outlined above, do not lead to simple numerical generalisations, and can sometimes make literature comparisons difficult.

TABLE 1. EXAMPLES OF DISTRIBUTION RATIOS (R_D), SELECTIVITY (X) AND DECONTAMINATION FACTORS (DF).

Nuclide	Sorber	R_D (mL/g)	X	DF	Comment
Pu	Charcoal	150			
	Silico-titanates	>2000			
	Alumina	3000			
	Argillite	>10000			
Cs	Zeolite	10^5		40,000	
	Lewatit DN		100		
	Resorcinol - formaldehyde resin	3×10^4			in presence of sodium
	$K_2CoFe(CN)_6$				
	Silico-titanates		$>10^4$		100 ppm Cs^+ in 5 M Na^+
	MAG*SEPSM / clinoptilolite	>103		10	Application to milk Ref. 10
Sr	Synthetic Chabazite	4000			in 0.5 M $NaNO_3$
	" "	250			in 0.5 M Ca $(NO_3)_2$

This can be seen from examples given in Table I. It is obviously useful to assess both the decontamination factor and the selectivity desired in choosing a suitable sorber.

Thus to remove caesium from milk in the region around Chernobyl to give an activity below the intervention level of 370 Bq/L ^{137}Cs requires only a modest decontamination factor of about 10 (e.g.[2]), but a suitable process needs to leave the milk otherwise unchanged, i.e. without removal of other nutritionally important constituents and without addition of undesirable, though non-active, contaminants.

In other instances, the extent of decontamination required would lead to very inefficient use of sorber in a one stage process, thus prompting consideration of multistep processing. For this to be successful the initial sorption process or processes must be reversible, and this is discussed below. (Reversibility is also important if the cost of the sorber or its other attributes makes disposal undesirable - see later).

4. SORPTION REVERSIBILITY

The criteria for satisfactory sorption reversibility usually include relatively rapid kinetics to give reasonable cycle times, no degradation of sorber in the desorption cycle, no detrimental addition of chemicals to the process stream containing desorbed material.

Many natural absorbers, though having good sorption characteristics, are not amenable to straightforward reversion of the sorption process. This is well illustrated by inadvertently contaminated soils which hold activity strongly, resist activity dispersion by leaching, and now require decontamination as part of remediation programmes. Sorbed species may be recovered by treatment with strong chemicals, such as concentrated acids, but this often brings host materials into solution, complicating further processing, and preventing re-use of sorber.

To date the most suitable sorbers for regeneration and re-use are generally those which have been specially designed for this purpose and where the sorption process is well characterised. The few suitable natural materials include zeolites, such as clinoptilolite.

Ion exchange processes are often rapidly reversible, the desorption being achieved by exposure to a high concentration of a species which is probably less selectively sorbed. This method inevitably introduces an additional ion burden into the desorbed stream, which may or may not complicate further treatment.

The removal of activity by complex formation can, with careful design, sometimes be reversed semi-quantitatively, i.e. without the need to add a large excess of reagent, and also benignly, i.e. by simple pH changes or perhaps change in solution oxidation potential.

5. ABSORBER STABILITY

Satisfactory sorbers need to withstand the sorption process conditions, and consideration also needs to be given to behaviour during subsequent storage and processing for disposal.

5.1. SORBER STABILITY IN SORPTION PROCESS

Solutions from which it is desired to remove activity or trace elements may sometimes be strongly acid or fairly strongly alkaline. Aluminosilicates, which can be very effective for activity removal by ion exchange, are not stable indefinitely in alkaline solutions above about pH10.5. If such materials are to be used for caesium removal from alkaline solutions, the solution pH must be brought down beforehand, e.g. with carbon dioxide as used by British Nuclear Fuels Ltd in the SIXEP plant at Sellafield. Alternatively alkali-tolerant synthetic organic resins can be used to remove caesium from alkaline solutions, as practised by Nuclear Electric (See Section 8).

Sorbers with very high capacity and/or high selectivity may be subject to high radiation doses by dose accumulation if the sorber is recycled, potentially limiting extent of re-use. If the sorber is not reused, but stored with its retained activity pending final processing for disposal, some consideration needs to be given to any changes in suitability for consolidation or encapsulation However lifetime doses can be simulated fairly rapidly and this aspect of sorber stability checked

There may be some aspects of sorber stability which affect both storage and disposal safety issues One could mention combustion characteristics of organic resins which may be relevant to consideration of external hazards, and possible microbial degradation organic resins

6. ABSORBER FORM

To achieve efficient use of absorber and rapid processing it is desirable to have a large absorber surface area to solution volume, effectively good absorber mixing It is also necessary to separate the absorber readily and this tends to favour solid absorbers for use with solutions, although solvent extraction is a classic method and used in conventional reprocessing technology

A very common form of solid liquid interaction is that achieved by passing the liquid through a bed of the solid This achieves good use of absorber capacity, and is particularly convenient if the sorber is regenerated and reused, i e discharge of sorber is infrequent In such flow processes particle size is important to avoid high pressures/low flow rates Beds are however less suited to instances where the liquid to sorber volume ratio is very large, and to instances where the liquid is an intermediary for the transfer of activity from another solid such as soil Composite sorbers have been manufactured with specific properties Thus sorbers incorporating magnetic particles allow ready recovery of sorber after dispersion in a liquid [3] Another example of a composite sorber combines the selective advantages of inorganic sorbers with the controllable physical properties of synthetic resin particles [4] Examples of sorber form are given in Table II

TABLE 2 EXAMPLES OF DIFFERENT ADSORBER FORM TYPE

Natural Materials	Coal Clays Coconut Husks Shell
Inorganic	$K_2 Co Fe (CN)_6$ Silicotitanates Synthetic Zeolites
Organic Resins	Weak Acid Strong Acid Chelating
Composite	Organic/Inorganic Magnetic/Inorganic Magnetic/Organic

7. ABSORBER COST AND SUPPLY

The cost effectiveness of an absorber depends in large part on the difference between disposal costs before and after treatment, compared with the treatment cost

For example, there are cases where treatment results in 'free release' of a large volume of liquid or solid material, and a relatively small quantity of waste which requires protected disposal In other instances treatment produces little free release material, but alters or splits the waste classifications (As a gross example of this, fuel reprocessing produces a range of waste categories from irradiated fuel which, if disposed of directly, would probably fall in an intermediate category) The benefit of concentration of activity depends

Operations	
Option (1)	Option (2)
Box and bury	Soil washing
Recovery	**Recovery**
Packaging	**Processing**
Disposal of final volume	**Disposal of reduced final volume**

Capital costs
Operational costs
Waste costs
(Decommissioning)

Breakeven cost between approach (1) and (2) occurs when
Process Cost (2) = Disposal Cost (1) - Disposal Cost (2)
If the disposal costs are high or the difference in the final
disposal volumes is large then the processing option becomes economic

FIG 1 Outline cost benefit analysis

on disposal costs which are often not known Volume reduction, i e concentration, may be offset by the need for shielding or enhanced interim storage arrangements, e g cooling

An example of a simple cost benefit analysis is shown in Figure 1

In planning for processes which will operate over protracted timescales, manufacturing scale and security of supply of sorber material are factors which have to be addressed

8. CAESIUM REMOVAL FROM MAGNOX FUEL STORAGE PONDS

The history of removal of caesium from cooling pond water in which uranium metal fuel from the first generation of civil nuclear reactors in the UK illustrates several of the general points made above

The UK Magnox reactors have magnesium clad uranium metal fuel elements It was intended that after discharge the fuel elements would be stored briefly (100days) in cooling ponds on station sites to allow iodine and heat to decay prior to transport to Sellafield for reprocessing Station fuel ponds were originally not provided with caesium removal facilities since the expectation was that although magnesium was vulnerable to aqueous corrosion, clad penetration would be avoided by a short residence time

However a combination of factors resulted in fuel having to be held in station ponds for longer than intended, with the result that clad was locally penetrated by pitting corrosion exposing uranium metal which also corroded in water releasing caesium The corrosion of magnesium could be inhibited by making the pond water alkaline, but this complicated caesium activity removal, which was judged necessary to ensure that discharge limits could be met First the pH increase introduced a large sodium ion burden into the pond water, requiring an absorber which was highly selective for caesium, and second the absorber needed to tolerate the alkaline conditions This latter constraint essentially ruled out aluminosilicate sorbers which have an attractive selectivity for caesium over sodium Finally a phenol formaldehyde methylene sulphonic acid resin was adopted, sold as Lewatit DN

The Lewatit DN was to be used to exhaustion, and then disposed of. At the time sea dumping of radioactive waste was an annual event in several European countries. There was an activity limit, and the main other criterion was that the package would sink. Safety assessments assumed immediate release of all activity as soon as the package reached the sea floor. This was the 'dilute and disperse' approach. If sea dumping ceased, it was recognised that waste would have to be surface stored and then land disposed, and treatment options for the Lewatit resin were examined against what was described as the 'concentrate and contain' philosophy.

At exhaustion after passage of pond water, the active sites on the Lewatit DN were mainly occupied by sodium, since although the selectivity for caesium over sodium was a factor of 100, the sodium to caesium ratio in solution was several orders of magnitude higher than this. Resin regeneration and secondary sorption was attractive, but as discussed in Section 4, it was desirable to avoid the introduction of further competing cations in the regeneration step. Ammonium carbonate was therefore proposed as a regenerant [5] as there had already been some experience with this material [6] which can be removed from the regenerant solution by heating and recovered for re-use.

The activity of caesium on the resin at initial exhaustion may be roughly estimated assuming the resin capacity is 1 mequivalent per g, the selectivity for caesium is 100, the pond water has a sodium content of 5 mequ Na/litre and a caesium activity in the pond water of 50 kBq/L. This leads to an initial activity on the resin of 1 MBq/g of resin or 1 GBq/kg. Thus referring back to Section 2.2., on this estimate, the waste would be classified as intermediate level within the UK classification. A resin regeneration and second absorption using the same selectivity would increase the loading by a further factor of 100 to 100 GBq/kg, and a third to 10 TBq/kg. Even the last figure would probably still be ILW, and therefore the cost benefit of concentrating activity on the resin depends on how disposal costs for ILW will be weighted with regard to volume as against activity. Until the ground rules are clear, investment in volume reduction and activity concentration in this example is of doubtful value.

British Nuclear Fuels Ltd, BNFL, also need to remove caesium from pond water at the Sellafield site and they do this in the SIXEP plant. However they use a once through water flow at around pH11 in the pond complex, and bring the pH down to neutral by passing in carbon dioxide before caesium removal. This allows them to use a naturally occurring clay with high selectivity, good capacity, and long term stability (clinoptilolite) for caesium removal.

A further point can be mentioned. To further inhibit magnesium corrosion during transport of Magnox fuel from station sites to Sellafield, fluoride ion is added to the transport flask water to give a 1000 ppm concentration. When the procedure was first introduced by the electricity generators, potassium fluoride was used since this was much more soluble than sodium fluoride. However when BNFL introduced their caesium removal facility they required that sodium fluoride be used because the potassium adversely affected sorber usage, the sorber being less selective for caesium in the presence of potassium.

9. SELENIUM REMOVAL FOR WATER PURIFICATION

Although most of this review has been concerned with radioactive sorption, similar approaches are valuable in selecting materials and processes for removal of non-radioactive but hazardous species. As an illustration, water treatment for removal of selenium will be considered.

Oil refinery effluent plus drinking water project.

Some groundwaters potentially suitable as drinking water have selenium levels significantly higher than the WHO recommended limit of 0.010 μg/L (10ppb) such that DFs of 10^3 - 10^4 would be needed to achieve recommended levels. In another instance, oil refinery effluents in the San Francisco Bay area have an average concentration of 200 ppb, whereas new EPA guidelines will require levels of < 50 ppb, a relatively small DF.

Both situations have common features

(i) large volumes of water to be treated
(ii) very small amounts of material at very low concentration to be removed
(iii) maybe high anion concentrations present
(iv) economics dictate a rapid sorption process
(v) economics dictate sorber must be represented
(vi) a solid selenium product for recycling or protracted storage is advantageous

Selenium can exist in several oxidation states That most commonly occurring in natural aqueous systems open to the atmosphere is Se (iv) as the selenite anion SeO_3^{2} This is well known to sorb readily unlike Se (vi) as the selenate anion SeO_4^{2} Elemental selenium is insoluble in water Change in oxidation state thus offers, in principle, one means of removing sorbed selenium

Selenium removal as selenite has been investigated using readily available chemically stable, but non-specific, sorbents such as alumina [7] An alternative approach using highly selective functional resins has been developed [8] rapid collection of selenium (iv) by the use of bismuthiol II as a terfunctional reagent and a commonly used ion exchange resin has been demonstrated A proposal has also been made to adapt the reagents to the MAG*SEP^{SM} technology Selenium was separated at the elution stage as the red elemental form Oxidation of selenite to selenate as a means of desorption is another theoretical possibility The oxidation of selenite to selenate at a MnO_2 surface has, however, been shown to be rather slow [9] Thus the optimisation of selenium removal at low level from effluents and naturally occurring waters is still in progress

10. SUMMARY AND CONCLUSIONS

Many current and potential applications of selective absorbers are to process streams which were not designed for waste management When waste management is considered at the planning stage, or advantage is taken of previous experience, there can be considerable economic benefit Different applications produce different constraints on choice of sorber and the important sorber properties have been summarised Although to date in this review emphasis has been placed on radioactive species, the principles are also applicable to selective sorbtion of non-radioactive hazardous species Because of major progress in control of waste, particularly from modern nuclear reactors, it is probably in the hazardous waste area that the major challenges remain

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DEVELOPMENT OF A TECHNOLOGY AND A PILOT PLANT FOR TREATMENT OF SMALL VOLUMES OF LIQUID RADIOACTIVE WASTE

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Abstract

The development of technology for treatment of liquid radioactive waste is described. Waste arisings are estimated. Liquid wastes of concern are mainly low active wastes according to the Bulgarian legislation. The activity is determined by the presence of ^{134}Cs, ^{137}Cs, ^{60}Co, ^{90}Sr, ^{144}Ce, ^{65}Zc, ^{54}Mn, ^{110m}Ag. Different precipitation processes are compared. The mixed iron hydroxide - calcium phosphate precipitation is determined as suitable for decontamination of the liquid radioactive waste. Effective decontamination is achieved when precipitation is followed by ion exchange. Additional increase of the decontamination is possible when sorbents are added during the precipitation step. The sorption and desorption of radionuclides on zeolites are studied. Cement solidification and thermal treatment of zeolites are studied for immobilization of radioactive material from precipitation and ion exchange. Both methods produce stable waste forms suitable for containment of the radionuclides.

1. INTRODUCTION

The application of radionuclides in research institutions, hospitals and industry generates a range of aqueous waste streams needing treatment to reduce the quantities of radioactive contaminants to the levels which allow safe discharge of the decontaminated liquid to the environment and safe disposal of the concentrated radionuclides according to international requirements and national regulations.

The radioactive wastes from the nuclear applications in Bulgaria are collected by a special service unit in the Institute for Nuclear Research and Nuclear Energy. They are buried in a centralized shallow land disposal site located 30 km away from Sofia in the Lozen Mountain. The repository is in operation since 1964 and consists of:

- a concrete vault for low and intermediate level solid wastes, which comprises three separate cells with a total volume of 237 m^3;
- a concrete vault for biological wastes - a volume 80 m^3;
- four steel tanks for liquid radioactive wastes - a total volume 48 m^3;
- special apartment for spent gamma sources - a total volume 1 m^3;
- a concrete trench of seven separate units with a total volume 200 m^3.

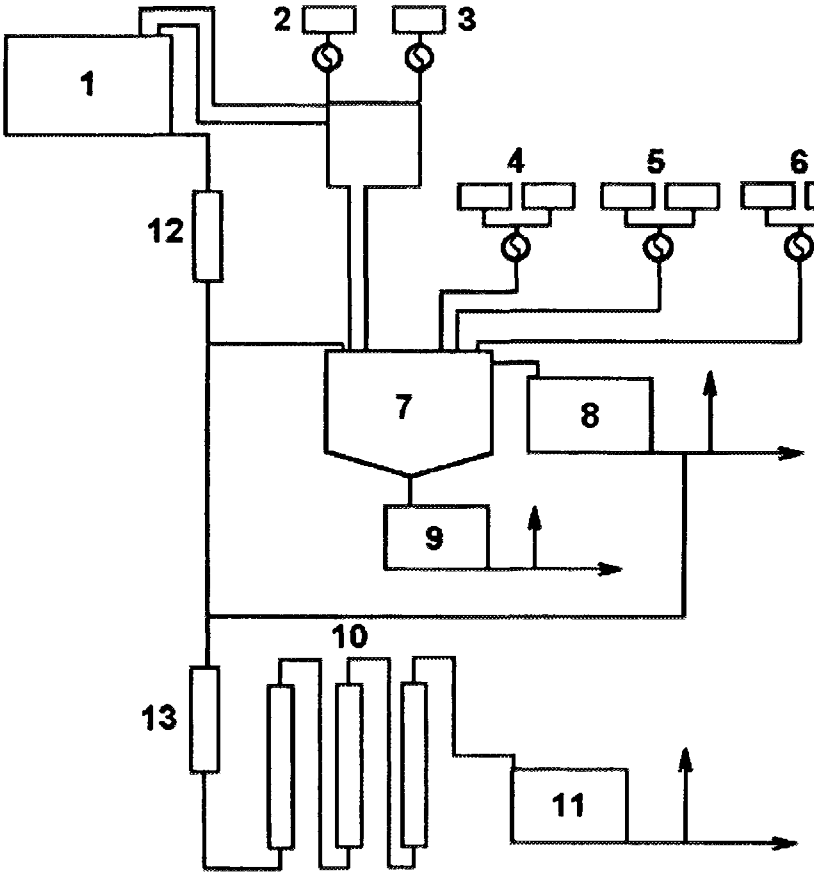
2. WASTE ARISINGS

The Bulgarian legislation [1] divides radioactive liquid waste into three categories according to their specific beta/gamma activity: low level waste - activity below $3.7 \cdot 10^5$ Bq/L, intermediate level waste, which has the activity from $3.7 \cdot 10^5$ to $3.7 \cdot 10^{10}$ Bq/L and high level waste with the activity higher than $3.7 \cdot 10^{10}$ Bq/L.

Radioactive liquid wastes are generated from medical diagnostic and treatment procedures, during production of radioisotopes, from scientific research and seldom in industry. Their specific activity depends upon the use of radioactive materials.

The radioactive liquids generated in hospitals and from biological research are low level waste They contain mainly short lived radionuclides ^{33}P, ^{35}S, ^{47}Ca, ^{51}Cr, ^{57}Co, ^{58}Co, ^{59}Fe, ^{67}Ga, ^{85}Sr, ^{90}Y, ^{99m}Te, ^{111}In, ^{125}I, ^{131}I, ^{133}Xe, ^{198}Au, ^{197}Hg, ^{203}Hg, and ^{201}Th After decay storage the producers discharge them to the environment

Radioactive wastes, which contain relatively long lived radionuclides as ^{60}Co, ^{134}Ce, ^{90}Sr, ^{144}Ce are mainly produced from scientific research. The waste producers send them to a repository either in a solidified form or as a radioactive liquid Less then 0 2 m^3 is the average annual quantity of the liquid waste received at the repository for treatment and disposal during its 25 years of operation [2] The activity is usually less then 3 7·10^5 Bq/L The wastes are low level according to the Bulgarian legislation



1 - Tank for radioactive liquid wastes
2, 3 - Vessels and metering pumps for chemical adjustment and pretreatment
4, 5, 6 - Vessels and metering pumps for chemicals used in precipitation
7 - Precipitator
8 - Decantate tank
9 - Sludge tank
10 - Ion exchange columns
11 - Decontaminated solution tank
12 - Filter
13 - Activated charcoal filter

FIG 1 Pilot plant for radioactive liquid waste treatment

Radioactive wastes, containing long lived radionuclides tritium and ^{14}C originate from biological research and labelling. They are received in a solid or solidified form. The waste containing radionuclides from uranium and thorium decay chains generated from uranium mining and milling are not received at the shallow land disposal site. According to Vassileva [3], a total volume of the liquid waste is about 130 m^3. They are low active according to the Bulgarian legislation. High level waste are not expected. The liquid waste from the decommissioning of a small research reactor IRT-2000 is expected to be a major contributor to the radioactive waste arisings during the forthcoming years.

The low level liquid wastes consist of two waste streams - dilute solutions, which contain the dissolved and finely divided contaminated material originating from a reactor vessel and a spent fuel storage pool, and solutions with a higher salt content from decontamination procedures. The activity of the former waste stream is determined from the fission and activated products such as^{134}Cs, ^{137}Cs, ^{60}Co, ^{65}Zn, ^{54}Mn, ^{110m}Ag. The main contributors are ^{137}Cs, ^{60}Co, ^{65}Zn. On the basis of the radionuclides, which are generated by neutron activation in the structural materials of nuclear reactors [4], the activity of the decontamination waste is expected to be governed mainly by the presence of ^{54}Mn, ^{60}Co, and ^{65}Zn.

3. PRINCIPLES OF THE LIQUID RADIOACTIVE WASTE TREATMENT

The Bulgarian legislation does not allow discharge of any radioactive liquids to the environment [1]. Radioactive liquid wastes have to be collected and treated in an appropriate way. The radioactive liquid waste management strategy, is as follows: collection and transport; decontamination; discharge of the decontaminated water; conditioning of wet wastes and disposal of the conditioned waste. After a careful consideration of the activity level, possible radionuclide content, chemical composition and available technologies, chemical treatment and ion exchange on natural inorganic sorbents are selected for decontamination of the radioactive liquids. Sludge and spent sorbents are disposed of in a solidified form.

A principle scheme of the pilot plant is given in Fig. 1. Radioactive liquid wastes are collected in a stainless steel tank 1, where chemical adjustment and pretreatment is performed. The radioactive wastes are pumped to the precipitator 7 for flocculation and precipitation. After settling of the sludge the clarified solution is pumped to decantate tank 8 and if the activity is below the limits, it is released to the environment. When the activity of the solution is above the limits, the solution passes through ion exchange columns. There are two filters in the pilot plant - a mechanical filter 12 and charcoal or kizelgur (13) to separate the detergents. The pilot plant is designed so that if radionuclides in the radioactive waste are in a form of ions the waste could be treated only by ion exchange. The radioactive sludge and spent sorbents are send to an in-drum cementation unit.

4. PRECIPITATION OF RADIONUCLIDES

In the chemical precipitation studies the following procedure is used: A given volume of the simulated radwaste solution (0.5, 1.0 or 2.0 l) is stirred for 5 min at a rate of 1500 revs/min and during this time precipitators are added and pH is adjusted. The solution is stirred for another 30 min at a rate of 240 revs/min. After a 30-40 min settling time, the clarified solution is filtered or centrifuged and analyzed. Gamma spectrometry, atomic absorption and emission spectrometry are used as analytical methods.

Different precipitation processes are studied. In order to compare them the experiments are carried out in such a way that about 100 mg of a coagulant is precipitated in 1 l of the solution with a composition similar to the diluted decommissioning waste. The solution contains cesium, strontium, cobalt and cerium in concentrations of 10^{-3} M. Hydroxide sludge is formed when the solution, which contains ferric/aluminum ions is alkalized. Calcium phosphate is formed by the interaction of soluble calcium salt (chloride, nitrate) and disodium phosphate, the hexacyanoferrates (II) - from transition metal nitrate and sodium hexacyanoferrate, sulphides precipitate after adding to the radioactive solution a transition/heavy metal ion nitrate solution and sodium sulphide. Manganese dioxide is produced from manganese nitrate and potassium

TABLE I. DECONTAMINATION COEFFICIENTS FOR DIFFERENT COAGULANTS

No.	Coagulant	Decontamination coefficient (%)			
		Cs	Sr	Co	Ce
1	Aluminum hydroxide	7.7	8.1	86.6	55.7
2	Calcium phosphate	15.4	33.4	99.4	99.3
3	Aluminium hydroxide + clinoptilolite	54.4	15.4	21.9	76.2
4	Calcium phosphate +clinoptilolite	54.9	44.3	100	97.8
5	Nickel hexacyanoferrate(II)	93.7			
6	Copper hexacyanoferrate(II)	99.1			
7	Cobalt hexacyanoferrate(II)	96.5			
8	Lead sulphide		99.95	94.4	
9	Copper sulphide			76.3	
10	Nickel sulphide			100	
11	Zinc sulphide			100	
12	Manganese dioxide		98.4	39.4	

TABLE II. DECONTAMINATION COEFFICIENTS FOR DIFFERENT COAGULANTS

No.	Coagulant	$C_{reagent}$ (mg.L^{-1})	Decontamination coefficient (%)				
			Sr	Co	Mn	Ce	Zr
1	Aluminum hydroxide	20	99.9	100	99.4	100	99.9
	pH9.0	30	99.4				
		50	99.7				
		100	99.9				
2	Ferric hydroxide	100	99.9	100	99.9	100	99.9
	pH9.0	200	99.9	100	99.9		
3	Calcium phosphate	50/120	74.2	100	99.9	98.8	99.9
	pH11.5	100/240	97.3	100	99.9	99.2	100
		100/600	99.4	100	99.9	99.6	100

permanganate. The results given in Table I show that caesium coprecipitates with hexacyanoferrates; for cobalt hydroxide, calcium phosphate and metal sulphide precipitation are effective; for cerium - calcium phosphate precipitation and for strontium - sulphide precipitation. The results confirm the available literature data [5, 6].

The addition of clinoptilolite during the hydroxide and calcium phosphate precipitation increases the efficiency for caesium and strontium removal, without affecting the precipitation of cobalt and cerium. After appropriate pH adjustment (pH9) from 98.9 to 100% removal of strontium, cobalt, manganese, cerium and zirconium is achieved by aluminum and ferric hydroxide precipitation. Rapid increasing of the concentration of the hydroxide sludge (2 and 5 times) doesn't lead to an increased separation of strontium, cobalt and manganese. The increasing of the amount of the calcium phosphate sludge increases the separation of radionuclides (Table II). Full decontamination of the solution is achieved when the excess of phosphate ions increases from 3 to 5 times.

TABLE III. DECONTAMINATION OF SIMULATED DILUTED DECOMMISSIONING WASTE IN ONE STAGE PRECIPITATION AND SORPTION PROCESS

No.	Process	pH Reagent	Decontamination coefficient (%)		
			Cs	Sr	Co
1	Hydroxide and calcium phosphate precipitation Ion exchange on clinoptilolite and vermiculite	pH9 Na_2CO_3	85.2	97.1	99.9
2	Hydroxide and calcium phosphate precipitation Ion exchange on clinoptilolite and vermiculite	pH9 Li_2CO_3	85.8	89.9	100
3	Hydroxide and calcium phosphate precipitation Sorption on MnO_2-modified clinoptilolite and Ni-hexacyanoferrate (II) modified clinoptilolite	pH9 Na_2CO_3	85.7	74.4	99.9
4	Hydroxide and calcium phosphate precipitation Sorption on MnO_2-modified clinoptilolite and Ni-hexacyanoferrate (II) modified clinoptilolite	pH9 Li_2CO_3	83.5	69.0	100
5	Hydroxide and calcium phosphate precipitation Sorption on Ni-hexacyanoferrate (II) modified amberlite	pH9 Li_2CO_3	57.0	50.5	100
6	Hydroxide and calcium phosphate precipitation Ion exchange on clinoptilolite in sodium form	pH9 Na_2CO_3	86.0	97.8	100

TABLE IV. DECONTAMINATION OF SIMULATED DILUTED DECOMMISSIONING WASTE IN TWO STAGE PRECIPITATION AND ION EXCHANGE PROCESS

No.	Process	Decontamination coefficient (%)			
		Cs	Sr	Co	Ce
1	Hydroxide precipitation Ion exchange on clinoptilolite	99.6	99.8	100	99.9
2	Hydroxide precipitation Ion exchange on vermiculite	98.4	84.2	100	100
3	Calcium phosphate precipitation Ion exchange on clinoptilolite	99.5	99.6	100	100
4	Calcium phosphate precipitation Ion exchange on vermiculite	80.7	89.1	100	100

TABLE V. DECONTAMINATION OF SIMULATED RADWASTE SOLUTION

No.	Process	Decontamination coefficient (%)			
		Cs	Sr	Co	Mn
1	Two stage process:				
	a. Hydroxide and phosphate precipitation, pH9.0	0	39.2	100	100
	b. Ion exchange on clinoptilolite in sodium form	99.4	97.5	-	-
2	Two stage process:				
	a. Hydroxide and phosphate precipitation, pH11.5	0	49.8	100	99.9
	b. Ion exchange on clinoptilolite in sodium form	99.5	99.5	-	-
3	One stage process: Hydroxide and phosphate precipitation, ion exchange on sodium clinoptilolite pH9.0	66.1	44.2	100	99.9

An attempt is made to increase the efficiency of the precipitation process by adding selective absorbers during the precipitation process in relatively high concentrations (1 $g{\cdot}L^{-1}$) and by using lithium carbonate as a pH-regulator, because it doesn't influence the sorption of radionuclides on the absorbers. The results (Table III) show that in the presence of clinoptilolite and vermiculite in a natural and sodium form, as well as in the presence of clinoptilolite modified with nickel hexacyanoferrate (II) form from 83.5 to 86.0% removal of cesium is achieved. In the presence of organic ion exchange resins modified with nickel hexacyanoferrate (II) only 57% of caesium is separated from the solution. The addition of clinoptilolite modified with manganese dioxide decreases the removal of strontium in comparison with precipitation in presence of clinoptilolite in natural and in sodium form.

We can compare the efficiency of the decontamination when the precipitation and sorption processes occur in one step (Table III) and precipitation followed by ion exchange (Table IV). It is seen that a separate application of the two processes leads to better decontamination of the solution.

Similar results are obtained for simulated radwaste solution with more complicated chemical composition: sodium chloride - 175 mg L^{-1}, sodium sulphate - 135 mg L^{-1}, manganese chloride - 355 mg L^{-1}, calcium nitrate - 130 mg L^{-1} and ferrichloride - 0.6 mg L^{-1}. It is seen that the coagulation and precipitation, even at low concentrations of the reagents-precipitators is sufficient for the full separation of cobalt and manganese, while for caesium and strontium the precipitation step must be followed by ion exchange on clinoptilolite.

TABLE VI. DECONTAMINATION OF SIMULATED RADWASTE SOLUTIONS

Process	Decontamination coefficient (%)					
	Cs	Sr	Co	Mn	Ce	Zr
Simulated solution No. 1						
Hydroxide, phosphate precipitation, Ion exchange on vermiculite and clinoptilolite, pH9 (Na_2CO_3)	66.6	66.0	100	99.3	100	99.9
Hydroxide, phosphate precipitation, Ion exchange on vermiculite and clinoptilolite, pH9 (Li_2CO_3)	84.4	72.5	100	99.9	99.9	99.9
Filtration	0	17.9	12.2	6.1	97.8	99.1
Hydroxide, phosphate precipitation at pH11.5	0	95.4	99.9	98.8	100	99.8
Ion exchange on clinoptilolite and vermiculite	94.4	99.2	100	99.9		100
Simulated solution No. 2						
Hydroxide, phosphate precipitation, Ion exchange on vermiculite and clinoptilolite, pH9 (Na_2CO_3)	71.8	51.3	50.1		99.8	99.7
Hydroxide, phosphate precipitation, Ion exchange on vermiculite and clinoptilolite, pH9 (Li_2CO_3)	75.6	51.7	52.8		100	99.7
Filtration	0	27.2	18.7		98.8	94.9
Hydroxide, phosphate precipitation at pH11.5	0	48.7	60.8		100	99.7
Ion exchange on clinoptilolite and vermiculite	98.7	81.7	57.7			99.8

The results from the treatment of the simulated radwaste solutions, which contain complex builders and detergents are given in Table V. Similar solutions are expected from decontamination procedures. Solution No. 1 contains: potassium permanganate - 250 mg· L^{-1}, sodium carbonate - 250 mg· L^{-11}, tartaric acid - 250 mg· L^{-1} and detergent - 1000 mg· L^{-1}. Solution No. 2 contains: potassium permanganate 250 mg/L, sodium carbonate - 250 mg· L^{-1}, tartaric acid - 250 mg· L^{-1}, citric acid - 250 mg· L^{-1}, boric acid - 10 000 mg· L^{-1} and detergent - 1000 mg· L^{-1}. Both solutions contain radionuclides of caesium, strontium, cobalt, manganese, cerium and zirconium. The solutions are treated by hydroxide/calcium phosphate precipitation and ion exchange on the natural inorganic sorbents clinoptilolite and vermiculite. Again one stage treatment process and separate performance of precipitation and ion exchange are compared. After precipitation the sludge and solution are separated by filtration through quartz filter. The results (Table VI) show that full separation of the hydrolysing elements (cerium and zirconium), which are in form of colloids in the solution, is achieved during the precipitation. For caesium, strontium, cobalt and manganese sufficient decontamination is achieved when the precipitation is followed by ion exchange on clinoptilolite and vermiculite. As it was expected, the decontamination coefficients for solution No. 2, which has more complicated composition, are lower.

The results show that the mixed iron hydroxide - calcium phosphate precipitation is suitable for decontamination of the liquid radioactive waste. Conclusion is drown that effective decontamination of the radioactive liquid wastes from nuclear applications can be achieved by precipitation followed by ion exchange. Additional increasing of the decontamination is possible when sorbents are added during the precipitation step.

5. SORPTION OF RADIONUCLIDES

5.1. SORPTION OF RADIONUCLIDES ON NATURAL SORBENTS

Zeolites are a class of alumosilicate minerals with unique ion exchange selectivities and a known resistance to radiation. These properties make them suitable for radioactive waste treatment and long term isolation of radionuclides from the environment. Natural clinoptilolite is a zeolite material with an ideal cell composition ($(Na_2K_2Ca)_3Al_6Si_{30}O_{72}\cdot 22H_2O$). The substitution of SiO_4 with AlO_4 tetrahedral creates a negative charge which is neutralized by exchangeable sodium, potassium, calcium and magnesium ions located in the cavities of the structure [7, 8].

Large zeolite deposits are located in the Rhodope Mountain in the south-east part of Bulgaria, which are in genetic connection with the first and second acidic paleogene volcanism [9]. The zeolitization is related to the alteration of vitric pyroclastic material under marine conditions. The clinoptilolite content reaches 82 - 85% [10, 11]. The zeolite rock contains also small amounts of other authogenic minerals - montmorilonite or celadonite, chlorate, adularia, cristobalite, etc., crystalloclasts - quartz, plagioclase, sanidine, biotite, etc., and lithoclasts. Mordenite rock contains 90% of mordenite and small amounts of celadonite, opal and chalcedony [11].

The comparison of the ion exchange properties of clinoptilolites from the six deposits and mordenite rock shows clinoptilolite from Beli Plast deposit as a most suitable sorbent for radionuclides under dynamic conditions and as an additive during the precipitation and confirms the previously obtained data [12-14]. Its favourable ion exchange properties are determined by the specific conditions of zeolitization and the higher content of easily exchangeable calcium and sodium ions.

The ion exchange of radionuclides ^{137}Cs, ^{90}Sr, ^{60}Co, ^{65}Zn, ^{54}Mn, ^{110m}Ag and ^{144}Ce, which determine the activity of some liquid radioactive wastes from nuclear applications, on natural clinoptilolite from Beli Plast deposit is studied. Natural (untreated), sodium and ammonium exchanged forms are used. The exchanged forms are prepared under dynamic conditions by treating crushed zeolite, grain size 0.25 - 0.50 mm, with 1.0 N solutions of the corresponding nitrates up to full saturation of the sorbent. The batch ion exchange capacities for caesium, strontium, silver, cobalt, zinc, manganese and cerium are given in Table VII

TABLE VII. BATCH ION EXCHANGE CAPACITY OF NATURAL AND MODIFIED CLINOPTILOLITE

Sorbent form	Batch ion exchange capacity (meq.g^{-1})						
	Cs^+	Sr^{2+}	Ag^+	Co^{2+}	Zn^{2+}	Mn^{2+}	Ce^{3+}
Natural	1.34	1.14	1.01	0.22	0.34	0.23	0.16
Sodium	1.48	1.28	1.28	0.41	0.52	0.56	0.19
Ammonium	1.52	1.26	1.04	0.35	0.31	0.36	0.16
Calcium	1.24	1.20	1.08	0.20	-	0.27	-

TABLE VIII. DISTRIBUTION COEFFICIENTS FOR ^{134}Cs, ^{110m}Ag, ^{65}Zn, ^{54}Mn AND ^{60}Co ON CLINOPTILOLITE

Form of the clinoptilolite	^{134} Cs	^{110m}Ag	^{65}Zn	^{54}Mn	^{60}Co
Natural	$2.92.10^4$	$9.50.10^3$	$1.35.10^4$	$8.6.10^3$	$4.31.10^3$
Sodium	$4.04.10^4$	$2.23.10^4$	$3.90.10^4$	$3.86.10^4$	$1.20.10^4$
Ammonium	$3.72.10^4$	$2.24.10^4$	$3.55.10^4$	$3.0.10^4$	$7.75.10^3$
Hydrogene	$5.73.10^3$	$4.95.10^3$	$2.50.10^3$	$2.01.10^4$	$7.41.10^3$
Calcium	$2.02.10^4$	$8.50.10^3$	$2.00.10^4$	$7.61.10^3$	$3.69.10^3$
Potassium	$3.27.10^3$	$6.21.10^3$	$9.63.10^3$	$5.7.10^3$	$3.16.10^3$

(1g sorbent is equilibrated with 25 - 100 mL 0.1 N solution). In order to determine the selectivity of the sorbent ion exchange isotherms for different pair of ions are plotted and the thermodynamic constants and standard free energy of exchange are calculated. The results show a high selectivity for caesium, strontium and silver over sodium, calcium and magnesium, and a satisfactory selectivity for cobalt, zinc and manganese. The presence of potassium strongly influences the sorption of radionuclides.

The results confirm the previously obtained data [13,14]. They show that natural clinoptilolite has a high selectivity for big, slightly hydrated monovalent cations and is an attractive sorbent for decontamination of ^{137}Cs and ^{110m}Ag containing liquid radioactive wastes. In addition, particular clinoptilolite has a considerably good selectivity for ^{90}Sr and ^{60}Sr from the solutions with no or trace amounts of potassium.

The sorption of mixture of trace amounts radionuclides ^{134}Cs, ^{110m}Ag, ^{65}Zn, ^{54}Mn and ^{60}Co on different cationic forms of clinoptilolite from the simulated radioactive waste solution is compared in Table VIII. The sorbent and the solution are equilibrated for a period of seven months to be sure that the equilibrium is reached. The sorption isotherms are linear and the calculated distribution coefficients are given in Table VIII. It is seen that in low concentration region sodium form of clinoptilolite is selective sorbent for ^{134}Cs, ^{110m}Ag, ^{65}Zn, ^{54}Mn and ^{60}Co. The distribution coefficients vary from $2.50 \cdot 10^3$ to $4.04 \cdot 10^4$ mg$\cdot$ L^{-1}. At the increased inactive salt content the selectivity for radionuclides of bivalent ions ^{65}Zn, ^{54}Mn and ^{60}Co decreases. The distribution coefficients for ^{65}Zn on the natural, sodium and ammonium forms from the solutions with a total salt content $3 \cdot 10^2$ N are $3.6 \cdot 10^2$; $4.5 \cdot 10^2$ and $5.3 \cdot 10^2$ mg$\cdot$ L^{-1}. A great attention is paid to the desorption of radionuclides from loaded zeolites, because radioactive sorbens are temporary stored before conditioning.

The experimental procedure for loading the samples for the desorption studies is as follows: 2 g clinoptilolite, grain size 0.25 - 0.50 mm, are equilibrated with 500 mL of distilled water, which contains 1.10^{-5} N Cs$^+$, labeled with ^{134}Cs. After 1.5 months the solution is separated and analyzed. The average loading of the zeolite is $2.48 \cdot 10^{-3}$ meq.g^{-1}. The zeolite is washed with distilled water twice and 250 mL of different desorption solutions are added. The contact time for desorption studies is 4 - 5 moths.

The desorption of ^{134}Cs with different cations is studied: monovalent alkaline lithium, sodium and potassium plus ammonium ion, alkaline-earth magnesium, calcium, strontium and barium ions and polyvalent ions of aluminum and iron. The experiments are performed with 0.1 N solutions of the desorption cations. The results (Fig. 2) show that it is difficult to replace ^{134}Cs from the zeolite. Bivalent alkaline-earth magnesium, calcium and strontium, monovalent alkaline lithium and sodium desorb only small fraction (0.4 - 6.8%) of ^{134}Cs. Notable desorption is observed in the presence of barium (15.2%), ammonium (20%) and

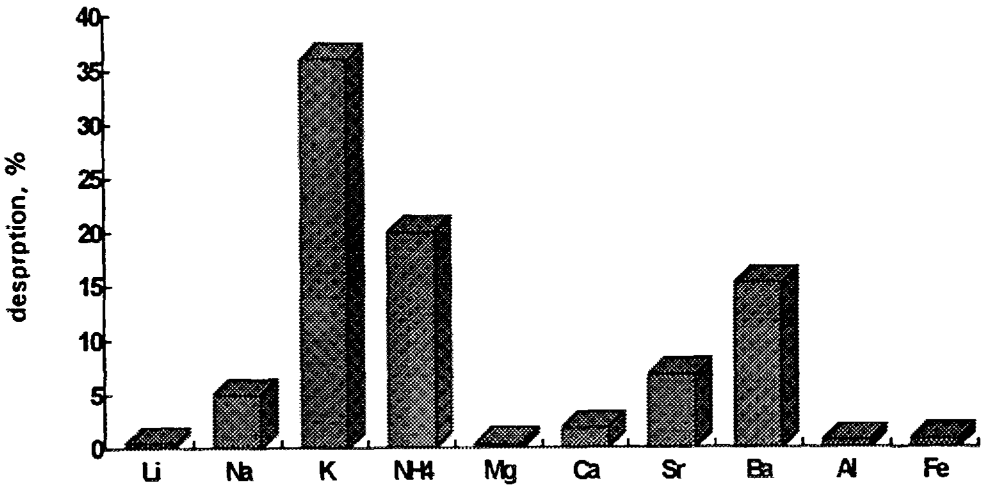
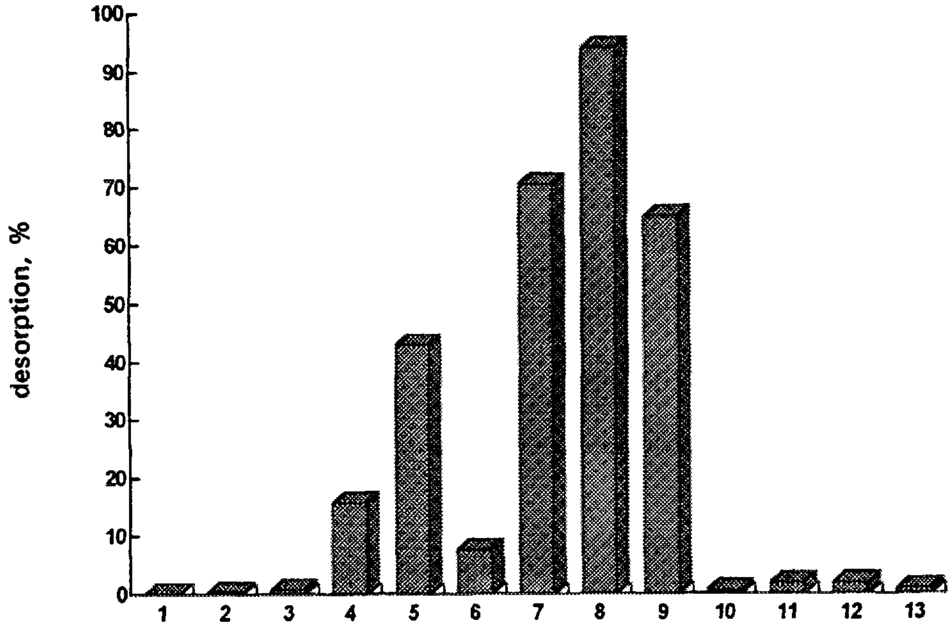


FIG. 2. Desorption of^{134}Cs with differentiations



1- distilled water
2- potable water
3 - river water
4 - sea water
5 - cement pore fluid
6 - $MgCl_2$ - brine

7 - NaCl - brine
8 - KCl - brine
9 - $CaCl_2$ - brine
10 - loess water
11 - 3.10^{-2} N $NaHCO_3$
12- 3.10^{-2} N NaCl
13 - 3.10^{-2} N $Ca(NO_3)_2$

FIG. 3 Desorption of^{134}Cs with different simulated environmental waters potassium (36%) solutions. The desorption of ^{134}Cs in the presence of polyvalent ions is negligible. According to the degree of ^{134}Cs desorption the desorption cations form the following sequences:

$$K^+ >> NH_4^+ > Ba^{2+} >> Sr^{2+} > Na^+ > Fe^{3+} \approx Al^{3+} \approx Li^+$$

The desorption of ^{134}Cs in different simulated environmental waters is studied: potable water, river and sea water, loess water - ground waters from a potentially suitable site for radioactive waste disposal, different brines ($MgCl_2$, NaCl, KCl and $CaCl_2$ brines) and simplified typical groundwaters, which are presented in a typical geological strata (3.10^{-2} N NaCl, 3.10^{-2} N $NaHCO_3$ and 3.10^{-2} N $CaCl_2$). The results (Fig. 3) show that significant releases of sorbed radiocaesium could be expected only in brines - almost all ^{134}Cs (95%) is released from the sorbent in saturated solution of KCl. The desorption of ^{134}Cs from loaded zeolite in simulated cement pore water is studied. The chemical composition of the solution is 0.4 N NaOH plus 0.3 N KOH. The results show significant desorption - about 43% of the loaded caesium is released in the solution. The desorption is lower than in NaCl, KCl and $CaCl_2$ brines.

The influence on the desorption of ^{134}Cs of complex builders (EDTA, tartaric, citric and oxalic acids) and detergents which could be leached from the solid waste form is studied. The experiments are performed with 0.1 N Na^+ solutions, which contain also 0.01 M of the corresponding complex builders, the concentration of the detergents is 100 and 250 $mg{\cdot}L^{-1}$. The results show a insignificant increase in the desorption of ^{134}Cs. The presence of complex builders (EDTA, tartaric, citric and oxalic acids) and detergents which could be leached from the solid waste form increases the desorption of ^{134}Cs. The replaced ^{134}Cs increases up to 9% only in high acid solutions. The influence of the type of the anionic constituent of the inorganic salt on the desorption of ^{134}Cs is studied. The experiments are performed with 0.1 N solutions of NaCl, $NaNO_3$, NaF, $NaHCO_3$, Na_2CO_3, Na_2SO_4 and $NaHPO_4$. It is seen that the type of the anion practically doesn't influence the desorption of caesium.

TABLE IX. INFLUENCE OF THE CONCENTRATION OF NATURALLY OCCURRING IONS ON THE DESORPTION OF ^{134}Cs

N	Degree of desorption (%)				
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
1.10^{-5}	0.14	0.20	0.10	0.15	0.16
5.10^{-5}	0.16	0.25	0.10	0.17	0.20
1.10^{-4}	0.17	0.30	0.11	0.25	0.29
5.10^{-4}	0.18	0.42	0.16	0.33	0.35
1.10^{-3}	0.19	0.53	0.21	0.35	0.45
5.10^{-3}	0.20	2.0	0.24	0.49	1.85
1.10^{-2}	0.20	5.11	0.31	0.72	4.90
5.10^{-2}	2.80	18.8	0.34	0.95	11.8
1.10^{-1}	5.00	36	0.46	1.80	15.2
0.5	16.8	78	1.30	3.50	25
1	27	90	2.16	5.80	-

The influence of pH on the desorption of ^{134}Cs is studied. The experiments are performed at pH3, pH4, pH5, pH6, pH8 and pH10. The results show that the change in pH of the solution does not influence the desorption of ^{134}Cs. In strongly acid solution (pH3) the desorption increases up to 9% as a result of the hydrated hydrogen ion competition for the exchangeable sites of the sorbent. The same is observed in 0.1 N solutions of HCl.

The influence on the desorption of ^{134}Cs of the concentration of naturally occurring sodium, potassium, magnesium, calcium and barium ions is studied. The experiments are performed in a wide concentration region - from 5.10^{-5} to 1 N solutions of the corresponding ions. Because of the solubility limit the highest barium concentration is 0.5 N. The results (Table IX) show that in the low concentration region (up to 1.10^{-2} N) the desorption of ^{134}Cs is insignificant. At concentrations higher than 5.10^{-2} N significant desorption is observed, particularly in the presence of potassium and barium ions. The desorption in the presence of magnesium and calcium is low in the studied concentration region.

The same experiments indicate significant release of ^{60}Co from loaded zeolites. It is concluded that the calcium variety of clinoptilolite is a suitable sorbent for decontamination of radioactive waste from caesium and its isolation from the human environment during disposal.

5.2. SORPTION OF ^{60}Co ON MODIFIED SORBENTS

In order to increase the removal efficiency of ^{60}Co of potassium containing solutions thin layer sulphide sorbents on the zeolite grains are prepared. They combine the high selectivity of sulphide sorbents for ^{60}Co - distribution coefficients up to 10^5 mg· L^{-1} are reported [15,16], and the mechanical stability of zeolites. The nickel, copper, zinc and lead exchanged forms of clinoptilolite are prepared at elevated temperature 70 - 80°C under dynamic conditions. After that 0.1 N solution of potassium sulphide passes through the column. Potassium replaces the heavy transition metal ion from the zeolite. Sulphide anions from the external solution and the replaced ions form thin metal sulphide films on the zeolite particles.

The dynamic capacity of the thin film metal sulphide sorbents is determined by passing 0.1 N solution of cobalt nitrate labelled with ^{60}Co till saturation (Table X). High capacity of copper and zinc sulphide is obtained. The influence of pH (1.0; 6.5 and 11.0) indicates that in a highly acid medium the competition of hydrogen ions is substantial. The higher values noted for the alkaline medium may be explained by the deposition of cobalt hydroxide.

The hindering effect of lithium, sodium, potassium and calcium ions on the sorption of cobalt gives the sequence:

$$K^+ > Na^+ \approx Ca^{2+} >> Li^+$$

The distribution coefficients for ^{60}Co from different simulated waste solutions (a total inactive salt concentration ranging from $1 \cdot 10^{-2}$ to $2 \cdot 10^{-3}$ N) range from $5 \cdot 10^2$ to $5 \cdot 10^3$ mg· L^{-1}. The highest values are obtained for clinoptilolite coated with cupric and nickel sulphides.

The desorption with 0.1 N solutions of sodium, potassium and calcium nitrates is studied (Table XI). The eluted activity of ^{60}Co is the highest for potassium solution (as much as 13% for 20 bed volumes); up to 10% for sodium; and 0.3 - 6.0% for calcium. The lowest results are obtained for nickel sulphide - about 1.2% for potassium nitrate. The desorption with sodium and calcium nitrates is negligible. Analogous results are obtained for ground water and sea water. These data show stable fixation of ^{60}Co in the crystal structure of sulphides.

TABLE X. DYNAMIC CAPACITY FOR COBALT OF SULPHIDE SORBENTS FORMED ON CLINOPTILOLITE GRAINS (FRACTION 1.0-0.50mm)

Sorbent	Capacity (meqv/g)	
	Total	Sulfide
Clinoptilolite with:		
1. Copper sulfide - 36 mg/g	0.12	3.31
2. Zinc sulfide - 37 mg/g	0.09	2.38
3. Lead sulfide - 180 mg/g	0.10	0.56

TABLE XI. DESORPTION OF ^{60}Co FROM SULFIDE SORBENTS FORMED ON CLINOPTILOLITE (FRACTION 1.0-0.50 mm)

Sorbent	Desorbed quantity (%)		
	Sodium nitrate	Potassium nitrate	Calcium nitrate
Clinoptilolite with:			
1. Nickel sulfide	0	1.17	0.31
2. Copper sulfide	6.90	13.38	3.23
3. Zinc sulfide	9.61	13.57	5.40
4. Lead sulfide	8.96	13.79	5.94

5.6. CONDITIONING OF THE SLUDGE AND SPENT SORBENTS

The radioactive sludge and spent sorbents, which are formed during the decontamination of liquid waste have to be incorporated in a solid matrix prior their disposal. Two methods of conditioning are studied: cement solidification and thermal treatment of zeolites.

In the cement solidification studies ordinary Portland cement, which is available on the market is used. The caesium loaded zeolite is prepared under dynamic conditions - 2200 - 2350 bed volumes simulated waste solution, which contains 10^{-5} N caesium, labelled with ^{134}Cs, passes through the sorbent. The total caesium content in the zeolite varies from 0.022 to 0.024 meq.g^{-1}. The precipitate sludge is prepared by mixed ferric hydroxide - calcium phosphate precipitation of the simulated waste solution, which contains ^{134}Cs and ^{60}Co. The cemented samples contain 5 wt% of sludge and from 10 to 40 wt% of spent sorbents. In some samples 5 wt% of vermiculate is added to absorb the excess water. The cemented samples meet the requirements. They are homogeneous, with a compressive strength after 28 days of curing higher than 25 MPa and sufficient water resistance. The leachability is studied according to the IAEA standard procedure [19]. Synthetic groundwater is used, which simulates the sulphate-hydrocarbonate-sodium-calcium type groundwater at Novi Han Repository. The leaching rates after 30 days of leaching are less than 1.10^{-5} g.cm^{-2}.d^{-1} for ^{134}Cs and less than 1.10^{-5}g.cm^{-2}.d^{-1} for ^{60}Co.

TABLE XII. LEACHING FROM SINTERED ZEOLITES (IAEA LEACH TEST PROCEDURE)

Sample	Loaded ion	$C_{\text{loaded ion}}$ (meq.g^{-1})	T (°C)	R (g.cm^{-2}.d^{-1})		
				distilled water	surface water	sea water
Cs^+ -zeolite	Cs^+	1.76	1100	2.9.10^{-7}	3.7.10^{-7}	1.3.10^{-6}
Cs^+ -zeolite	Cs^+	1.76	1200	1.3.10^{-7}	8.1.10^{-7}	6.6.10^{-7}
Sr^{2+} -zeolite	Sr^{2+}	0.97	1100	5.4.10^{-8}	7.1.10^{-8}	1.4.10^{-7}
Sr^{2+} -zeolite	Sr^{2+}	0.97	1200	1.5.10^{-8}	3.5.10^{-8}	1.7.10^{-7}
Cs^+-Sr^{2+} -zeolite	Cs^+	1.17	1100	1.8.10^{-7}	2.7.10^{-7}	1.1.10^{-6}
	Sr^{2+}	0.59		7.6.10^{-8}	9.9.10^{-8}	4.5.10^{-7}
Cs^+-Sr2$^+$ -zeolite	Cs^+	1.17	1200	8.2.10^{-8}	9.9.10^{-8}	3.2.10^{-6}
	Sr^{2+}	0.59		5.4.10^{-8}	6.2.10^{-8}	3.7.10^{-7}
Fe^{3+} -zeolite	Fe^{3+}	0.44	1200	1.0.10^{-8}	8.6.10^{-9}	1.1.10^{-8}
Co^{2+} -zeolite	Co^{2+}	0.34	1200	n.d.	n.d.	3.2.10^{-8}
Ni^{2+} -zeolite	Ni^{2+}	0.25	1200	3.5.10^{-8}	3.2.10^{-8}	7.9.10^{-8}
Cr^{3+} -zeolite	Cr^{3+}	0.31	1200	n.d.	n.d.	2.5.10^{-7}
Ag^+ -zeolite	Ag^+	0.90	1200	4.3.10^{-9}	6.5.10^{-9}	2.3.10^{-9}
mixed zeolite	Fe^{3+}	0.23	1200	4.3.10^{-8}	2.7.10^{-7}	4.2.10^{-8}
	Co^{2+}	0.03		n.d.	n.d.	2.4.10^{-7}
	Ni^{2+}	0.17		3.3.10^{-9}	6.8.10^{-8}	1.1.10^{-7}
	Cr^{3+}	0.12		n.d.	n.d.	n.d.
	Ag^+	0.40		2.6.10^{-9}	2.5.10^{-9}	2.5.10^{-9}

Clinoptilolite loaded with different ions is used for thermal treatment studies: caesium, strontium, cobalt, silver, nickel, iron and chromium exchanged form of clinoptilolite, mixed caesium-strontium zeolite and mixed silver-iron-cobalt-nickel-chromium zeolite. The loaded zeolites are prepared in columns by saturation with 0.1 - 0.5 N nitrate solutions of the corresponding ions. The calcination procedure is as follows: Loaded zeolites are washed with distilled water, dried at temperature of 105-110 °C for 2 hours and grinded. A weighted amount of the powder is wetted with water and the samples are moulded in special cylinders 15 mm high and 12 mm diameter. The samples are heated in furnace for 15 min at temperatures 1100 and 1200 °C. Rate of increasing the temperature is about 10 °C.min^{-1}. X-ray diffraction shows that under the above experimental conditions a glassy product has been produced, i.e. vitrification of zeolites occurs. Only for one sample - clinoptilolite loaded with 1.29 meq.g^{-1} caesium crystallization of $CsAlSi_5O_{12}$, which is caesium mordenite is observed.

Long term leaching rates are determined using the standard IAEA procedure [17]. The leachant is distilled water, sea water and simulated environmental water from the potential disposal site.The leaching rates are very low - about 10^{-8} - 10^{-9} g.cm^{-2}.d^{-1} after about one year of leaching (Table XII). The leaching rates in distilled and environmental water are comparable. The leaching rates in sea water are one order of magnitude higher.

The sintered zeolites are mechanically stable even after long-term immersion in boiling water. The after 30 days Soxhlet leach test the compressive strength is comparable to the initial samples. The results show that both methods - cement solidification and thermal treatment of zeolites produce stable waste forms suitable for isolation of the radionuclides loaded on the zeolites. Cement solidification is practical for economical reasons and will be used in the waste treatment plant.

7. CONCLUSIONS

A technology for treatment of the low level liquid waste from nuclear applications is developed, consistent with the variable chemical and radionuclide composition of the waste.

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TREATMENT OF LOW-LEVEL RADIOACTIVE WASTE USING VOLCANIC ASH

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Abstract

The effective application of volcanic ash, an indigenous adsorptive material abundant in the Mt Pinatubo area, in the removal of radioiodine from radioactive waste streams was demonstrated Factors such as availability, low cost and comparative retention capacity with respect to activated charcoal make volcanic ash an attractive alternative in the conditioning of radioactive waste containing radioiodine Chemical precipitation was employed in the treatment of low level aqueous waste containing ^{137}Cs It was shown that there exists an optimum concentration of ferric ion that promotes maximum precipitation of caesium It was further demonstrated that complete removal of caesium can be achieved with the addition of nickel hexacyanoferrate

I. INTRODUCTION

The Science Act of 1958 created the Philippine Atomic Energy Commission, presently known as the Philippine Nuclear Research Institute (PNRI) The PNRI is under the control and administration of the Department of Science and Technology (DOST) In general, the PNRI is tasked with the control of peaceful applications of atomic energy The Institute is therefore responsible for the regulation and safe use of all radioactive materials in the country This responsibility includes the management of radioactive wastes generated by users of radioactive materials in industry, medicine and research

The radioactive wastes produced by these users (i e , 92 medical and 100 industrial) are mainly spent sealed sources In addition however, liquid and solid wastes arise from the operation of the research reactor and various radioisotope applications in the Institute With the anticipated increase in nuclear applications resulting from the projected operation of the TRIGA-converted 3 MW research reactor, the total volume of radioactive wastes will increase to an estimated 300 m^3 after ten years

Before 1988, storage of unconditioned radioactive wastes was the only option available for radioactive waste management However, the PNRI proposed to develop an integrated facility for treatment, conditioning and storage of newly generated as well as accumulated radioactive wastes under the technical assistance programme of the IAEA

The PNRI is currently implementing an IAEA TC project on the upgrading of its low level radioactive waste management facility Technical assistance in the form of equipment supply, training and expert services were provided over a period of four years starting in 1991 Equipment totaling about US$ 206,690, 22 man-months of fellowship training costing about US$ 58,350 and expert services in the amount of US$ 26,720 were provided by the IAEA over a period of 4 years In addition to the expert services provided under the project, several missions including a WAMAP and an evaluation mission of the WAMAP were conducted in the last five years Most of the recommendations of these experts and WAMAP missions have either been implemented and/or are in various stages of implementation

The waste compactor provided by the IAEA had been commissioned and with the routine operation of the cementation facility, most of the solid compactable wastes have already been conditioned and stored in a newly constructed interim storage trench The most urgent task now is to remove radioactive waste stored in the old trench and segregate, treat, condition and transfer the wastes to the new trench In view of these important tasks, a research contract proposal was submitted to the IAEA particularly concerning the treatment of liquid wastes prior to conditioning.

Problems in the treatment of liquid waste have been highlighted in the Philippines especially those containing ^{14}C, tritium and radioiodine. The project aims to conduct studies of options for a cost-effective treatment of radioactive wastes containing radioiodine,^{14}C and tritium; to identify simple low cost processes required for reliable liquid waste treatment operations; to review current waste treatment technologies for possible adoption under local conditions using indigenous materials and to provide inputs in the design and construction of a radioactive waste treatment facility appropriate for the type and volume of wastes generated from nuclear applications.

Initially, treatment methodologies for liquid wastes containing radioiodine, ^{14}C and tritium were considered. With the commissioning of the chemical precipitation plant as part of an IAEA assisted Technical Cooperation project on the establishment of a waste management facility in the country and following the recommendations of the second Research Coordination Meeting in Istanbul, the project objectives were expanded to include the management of wastes contaminated with ^{137}Cs.

2. METHODOLOGY

2.1. ^{131}I, ^{14}C and ^{3}H- BEARING WASTES

An extensive literature study on current treatment technologies for radioactive liquid wastes containing radioiodine, tritium and ^{14}C was undertaken to identify those which can be adopted locally in conjunction with utilization of indigenous materials.

Experimental runs of selected treatment processes were conducted. Radioiodine adsorption using volcanic ash and activated carbon were conducted following the methodology and procedures outlined below.

Activated carbon (commercial grade, powdered) and volcanic ash from Mt. Pinatubo sampled at Porac, Pampanga around 20 km from the site of the volcano were used as adsorbent materials for radioiodine. 50 g (activated carbon) and 60 g of volcanic ash with different mesh size (32 mesh and 60 mesh) were weighed and soaked separately for 5 hours with continuous stirring in a liter of 10% w/w sodium hydroxide solution. The activated carbon and volcanic ash were then filtered off and washed thoroughly with water before drying in an oven at 80-100°C.

A glass column with a length of 34 cm and 1.25 cm in diameter was used in the experimental test runs. The dried pretreated activated carbon/volcanic ash was packed in a glass column with glass wool placed at the bottom and on top of the pretreated activated carbon/volcanic ash.

100 mL of synthetic waste spiked with ^{131}I was poured into the packed column of pretreated activated carbon/volcanic ash and the eluate was controlled at a rate of 10 mL per 10 minutes. One mL samples were taken from each eluate for G-M counting.

Similarly, treatment methods for ^{14}C and tritium were identified. Basically, the waste will be absorbed in sawdust and incinerated, provided however that the radioactive waste does not contain alpha-emitting radionuclides and the activity of other radionuclides is below 1×10^{-10} Bq/mL of waste. The ash which will contain both ^{14}C and ^{3}H which are long lived, will then be immobilized by cementation for interim storage. Wastes with activity beyond the set limits will be absorbed in sawdust, immobilized by cementation and stored in the interim storage facilities.

A locally fabricated incinerator is currently being installed and is expected to be fully operational in the middle of 1996. It is planned to use incineration for wastes containing ^{14}C and tritium subject to certain conditions.

Experimental runs will be conducted to validate theoretical computations in order to determine the maximum concentration limits for incineration of ^{14}C and ^{3}H wastes (i.e., 1.37 x 10 $^{-7}$ Bq/kg for combustible ^{14}C wastes and 3.66 x 10 $^{-6}$ Bq/kg for combustible ^{3}H wastes).

Further experimental runs will also be carried out for other treatment methods for specific radionuclides. It is also planned to chemically precipitate ^{14}C in aqueous waste by carbonate precipitation. The precipitate will then be conditioned by cementation. The supernatant liquid which is expected to be non-radioactive (following complete removal of ^{14}C as carbonate) will be neutralized prior to sewage disposal. The chemical precipitation plant is currently being installed. Cold runs will be conducted prior to the commissioning of the plant scheduled in the middle of this year.

2.2. WASTES CONTAMINATED WITH ^{137}Cs

Chemical precipitation was used in the treatment of low-level aqueous waste. Precipitation was achieved by using the ferric hydroxide process. Finely divided ion exchange material was added in order to maximize the decontamination of specific radionuclides.

The use of nickel hexacyanoferrate as a specific ion exchange material for caesium removal was investigated using the lowest possible concentration which would yield a high decontamination result. A small amount of polyelectrolyte was added to aid in the particle agglomeration of the precipitate so as to produce a floc that will ensure efficient separation. About 100 mL of actual aqueous waste known to contain ^{137}Cs radionuclide with an activity of about 170-180 Bq/mL was used in every experimental test.

Different concentrations of ferric ion in the form of ferric chloride were added at pH2 with vigorous stirring in every experimental test and neutralized to pH7 with either nitric acid or sodium hydroxide solution to determine the optimum concentration needed in the ferric hydroxide precipitation process.

After determining the optimum concentration of ferric ion needed in the solution, different concentrations of potassium ferrocyanide and nickel nitrate mixture at a ratio of 1:1 was added in every test specifically to determine the effective concentration of the mixture needed for the removal of ^{137}Cs radionuclide at a controlled low stirring rate. pH was maintained between 9 and 10 by the addition of small amounts of sodium hydroxide in order to provide good levels of caesium removal. An anionic polyelectrolyte was added at a low stirring rate after pH adjustment to produce a larger floc that will either settle or otherwise be removed by filtration. Experimental runs. at different values of pH in the precipitation of caesium were also conducted between pH 9 and 10.

3. RESULTS AND DISCUSSIONS

3.1. ^{131}I

The following data were obtained from experimental test runs.

EXPERIMENT 1

60 g pretreated volcanic ash (32 mesh)
volume of synthetic waste = 100 mL
initial count of synthetic waste = 22140 cpm
pH7-8

Residence time (minutes)	Eluate volume (mL)	Eluate (counts/min)	Adsorption (%)
10	10	18378	17
20	10	14398	35
30	10	10395	53
40	10	11390	49
50	10	8381	62
60	10	6394	71
70	10	6083	72 5
80	10	6578	70

EXPERIMENT II

60 g pretreated volcanic ash (60 M)
volume of synthetic waste = 100 mL
initial count synthetic waste =20910 cpm
pH9-12

Residence time (minutes)	Eluate volume (mL)	Eluate (counts/min)	Adsorption (%)
10	10	17029	18 6
20	10	20274	3 0
30	10	17676	15 5
40	10	15537	25 7
50	10	16136	22 8
60	10	16723	20.0
70	10	5968	71 5
80	10	23209	-

EXPERIMENT III

50 g pretreated powdered activated carbon
volume of synthetic waste = 100 mL
initial count synthetic waste = 12349 cpm
pH7-8

Residence time (minutes)	Eluate volume (mL)	Eluate (counts/min)	Adsorption (%)
7200	10	1981	84 0
7210	10	1550	87 4

NOTE The long residence time of synthetic waste in the pretreated activated carbon was due to the slow rate of penetration of the synthetic waste in the finely powdered pretreated activated carbon A coarser grain of the activated carbon will be used in the succeeding experiments

$$\%\ adsorption = \frac{initial\ counts - eluate\ counts}{initial\ counts} x100$$

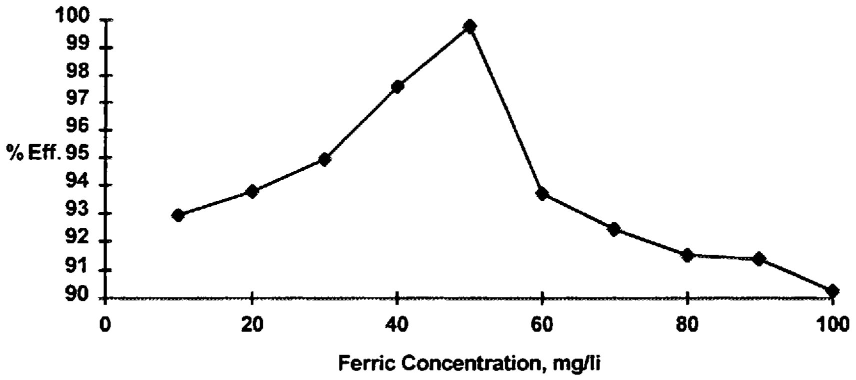

Figure 1
Ferric Concentration vs. Efficiency

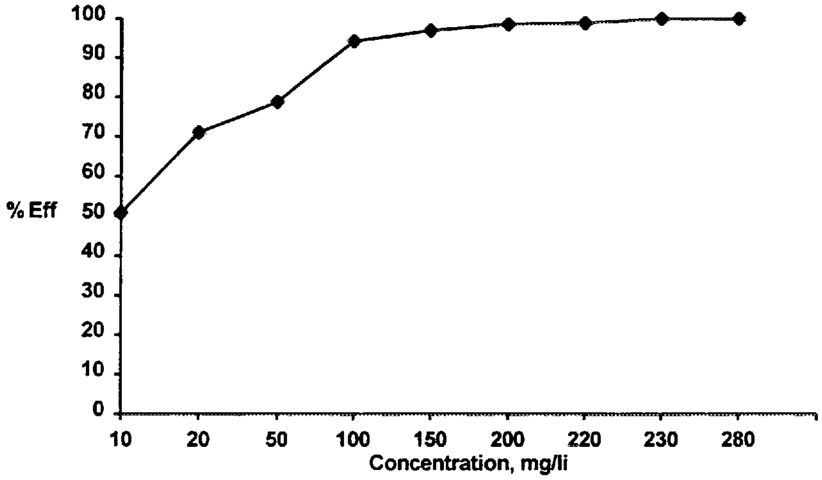

Figure 2
Hexacyanoferrate Concentration vs Efficiency

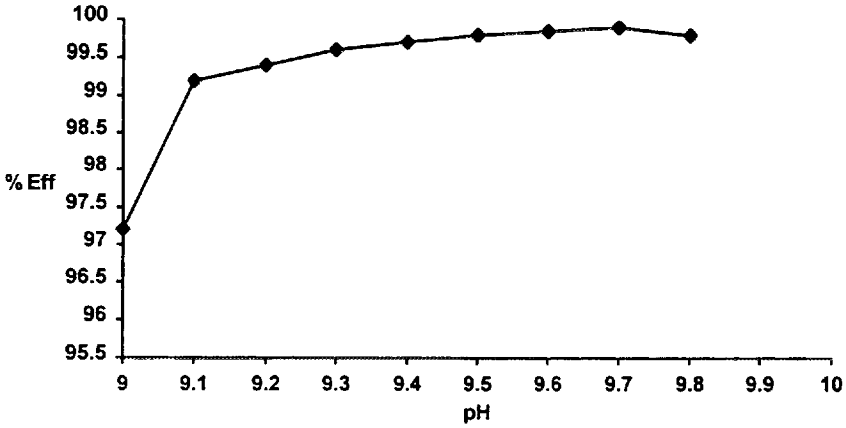

Figure 3
pH vs Efficiency

Results indicate that volcanic ash, which is an indigenous material can also be used to effectively adsorb radioiodine. Initial results showed a 65 - 70 % adsorption for volcanic ash and 80 - 85 % for the normally used activated carbon.

3.2. ^{137}Cs

Results are presented in Figures 1 - 3. As shown in Fig.1, there is indeed an optimum ferric ion concentration (50 mg/L) that promotes maximum precipitation. The degree of precipitation decreases significantly at higher concentrations of the oxidizing agent. There is a marked improvement in precipitation efficiency at hexacyanoferrate concentrations up to 100 mg/L (Fig. 2). Above this value, caesium removal increases only slightly up to a maximum value of 280 mg/L where 100% efficiency is achieved. Fig. 3 shows that a pH range of 9 to 10 does not have a significant effect on efficiency precipitation.

4. CONCLUSIONS

1. Effectively good retention (i.e., 65 - 70%) of radioiodine by volcanic ash has been demonstrated. This adsorptive capability is comparative with the 80 - 85% retention by activated carbon. Considering availability and cost factors, the results are encouraging for the use of the indigenous material in the conditioning of radioactive waste containing iodine.
2. The adsorptive properties for radioiodine of lahar - which has replaced the volcanic ash abounding in the Mt. Pinatubo area - need to be investigated further using the same parameters and conditions of earlier experiments with the original volcanic ash.
3. There exists an optimum concentration of ferric ion (i.e., 50 mg/L) that promotes maximum precipitation of caesium. A precipitation efficiency of 99.78 % was achieved in this case.
4. Precipitation of caesium is enhanced with the addition of nickel hexacyanoferrate. 100 % removal was achieved at a hexacyanoferrate concentration of 280 mg/L.
5. Maintaining pH of the solution between 9 and 10 does not have a significant effect on the efficiency of caesium precipitation.

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RESEARCH AND DEVELOPMENT ON TREATMENT OF LIQUID RADIOACTIVE WASTES IN THAILAND

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Abstract

The studies have been directed towards treatment technologies for low level waste. The simple physico-chemical method has been studied for applying to various kinds of waste streams such as reactor waste, isotope production waste and liquid waste from the hospitals. The characterization of inorganic ion exchangers including the effect of pH, equilibrium time, temperature and concentration of such exchangers were tested. The results revealed that the local simple brand-washed detergents, which are very cheap, can be succesfully used for decontamination instead of a more expensive imported decontaminating agent. It was also revealed that chemical precipitation can be successfully used forthe treatment of such wastes.

In considering an immobilization process for the treated waste, cementation was selected. The basic properties of the cemented waste forms have been investigated including leachability of the cemented sludge resulted from the chemical precipitation of the decontamination waste. The results revealed that the cemented inorganic ion exchangers and the sludge waste exhibit high compressive strength and low leach rates. The compressive strength of 118-207 kg/cm^2 and 15% and 20% waste loading was found to be optimum for the waste forms. A cumulative fraction leached rate from the cemented sludge was found to be about 30 x 10^{-3} cm/day at 30 day leaching time.

1. INTRODUCTION

The application of radionuclides in research, medicine, agriculture and industry in Thailand has been gradually increased since the introduction of the "Atom for Peace" programme in Thailand in 1962. A wide range of applications generates a variety of radioactive aqueous waste streams needed to be treated prior to release to the environment. The Office of Atomic Energy for Peace (OAEP) has been assigned to take the responsibility for the safe management of such radioactive wastes. All radioactive wastes generated by any user in Thailand are sent to the OAEP for treatment and subsequent storage and disposal. A survey of sources, types, volumes and characteristics of radioactive wastes arising in Thailand has been carried out. The information obtained from the survey was used for design of a new waste treatment plant to be in 1997. The data are summarized in Table I.

2. TREATMENT OF LOW-LEVEL RADIOACTIVE WASTE BY INORGANIC ION EXCHANGERS

The study was aimed at selecting inorganic ion exchangers that are inexpensive and suitable for conditioning and disposal. The experiments were conducted to determine the sorption characteristics of various inorganic ion exchangers. The sorption capacity of the ion exchangers were tested for ^{137}Cs and ^{99}Tc under various conditions including the effect of pH, equilibrium time, temperature and concentration (weight). Bentonite, kaolinite clay, sand and sandy soil were used as natural inorganic exchangers. Titanium dioxide, zeolite, antimony pentoxide and hydrated antimony pentoxide (HAP) were used as synthetic inorganic exchangers. Furthermore a basic study on the cementation immobilization process was conducted and basic properties of waste forms such as physical stability, compressive strength and leachablility were tested.

TABLE 1. DISTRIBUTION OF LIQUID WASTE STREAMS

Waste stream	%	Major radionuclides	Composition
Medical	32	^{67}Ga, ^{51}Cr, ^{99m}Tc, ^{131}I ^{201}Tl, ^{3}H, ^{14}C	Laboratory and decontamination wastes Pump oil, scintillators
Education/ research	43	^{32}P, ^{35}S, ^{51}Cr, ^{45}Ca, ^{99m}Tc, ^{131}I, ^{60}Co, ^{137}Cs	Liquids, hot cell experiments Serum blood
Reactor operations	20	Fission and activated corrosion products	Reactor coolant, storage pool water
Monazite extraction	5	U, Th and their daughter products	Extraction solvent, plant wastes

Total waste volume: aqueous solutions = 200 - 300 m^3, organic waste = 6 - 8 m^3 per year.

It was found that the sorption capacity of titanium dioxide, zeolite, bentonite, kaolinite, montmorillonite, sand, sandy-soil, hydrated antimony pentoxide (HAP) and antimony pentoxide for ^{137}Cs were 70, 99, 80, 98, 98, 86, 87, 85 and 98%, respectively. Optimum conditions for the sorption of ^{137}Cs on the exchangers are listed in the Table II.

TABLE II. THE OPTIMUM SORBTION CONDITIONS FOR ^{137}Cs

Exchangers	pH	Time (min)	Concentration (g/mL)	Temperature (^{0}C)
Titanium dioxide	3-6	20	3	25-50
Zeolite	1-13	5	0.3	25-50
Bentonite	1-13	20	1	25-50
Kaolinite	3-11	10	0.3	25-50
Montmorillonite	3-10	15	0.2	25-30
Sand	3-11	20	1	25-30
Sandy soil	3-11	20	1	25-30
HAP	1-7	30	1	25-30
Antimony peroxide	1-9	20	1	

* The volume of test solution is 30 mL each.

The sorption capacity for ^{99m}Tc on all but one of the inorganic ion-exchangers under investigation was very poor. Only the antimony pentoxide specimen has shown a good sorption capacity of about 80-90%. The optimum condition was found at pH1-9, the optimum time of 5 days and weight-ratio of 3 g to 30 mL of solution.

3. TREATMENT OF LOW LEVEL RADIOACTIVE WASTE BY CHEMICAL PRECIPITATION

3 1 CHEMICAL TREATMENT OF LIQUID WASTE FROM THE CHEMICAL EXTRACTION OF MONAZITE

The studies were performed to find the best condition for the treatment of a waste stream from the monazite extraction laboratory which contains a very low level of U/Th and their daughter products The parameters included the type and the concentration of the chemical coagulant, efficiency of treatment, pH, rate of sedimentation including the coagulant aids The results obtained as shown in Table III, disclosed that the aluminium and the barium chloride were main chemical coagulants for the treatment of monazite extraction process waste and could give a decontamination factor up to 20

TABLE III OPTIMUM CONDITIONS FOR THE CHEMICAL TREATMENT OF THE LIQUID WASTE STREAM FROM THE MONAZITE EXTRACTION PROCESS

Chemicals	Concentration (ppm)	pH		Removal (%)	DF
		before	after		
Alum	200	3 85	8 9	95 53	22 41
NaOH	600				
$BaCl_2$	700				
Orgatite	6				
Separan	10				
Alum	200	3 85	5 6	88 26	8 52
Na_2CO_3	800				
$BaCl_2$	700				
Orgatite	6				
Separan	12				
Alum	200	3 85	7 4	95 52	21 07
$Ca(OH)_2$	500				
$BaCl_2$	700				
Orgatite	8				
Separan	8				

3 2 CHEMICAL TREATMENT OF THE DECONTAMINATION AND LAUNDRY WASTE

In a radiation laboratory, it is necessary to clean the items contaminated with radionuclides every day This process creates low level liquid wastes of various types and quantities An attempt to minimize a number of types of the waste from such cleaning process has been made One of the actions were to encourage the radioisotope users to use only a few branded names of detergents and decontaminating agents To achieve such a goal, R&D for an appropriated detergent and decontaminating agent has been commenced.

3.2.1. Detergent efficiency in the radioactive material decontamination

Searching of the most suitable detergents was undertaken by counting the activity of the fixed-form contaminated radioactive tracers on 3 kinds of cloth which were cotton, calio and polyester, before and after being washed by the 24 locally available commercial detergents The washing efficiency of 24 detergents for radioactive decontamination of cotton, calio and polyester varied from 0-98 47% and can be summarized as follows

Hand-washed powder detergent	*cotton > calio > polyester*
Machine-washed powder detergent	*polyester > cotton > calio*
Hand and machine-washed liquid detergent	*calio > polyester > cotton*
Pre-washed stain remover	*calio > cotton > polyester*
Commercial decontaminating liquid	*cotton > calio > polyester*

3.2.2. Treatment of the waste from laundry and decontamination processes

A machine-washed liquid detergent was selected to be used as a detergent and a decontamination agent in a radiochemical laboratory. The composition of the detergent was as follows:

Detergent composition

Dodecycle benzene sulfonic acid sodium (DBS)	12.5%
Sodium tripolyphosphate	25.0%
Nitrilotriacetic acid	30.0%
Sodium sulphate, anhydrous	25.0%
Citric acid	6.25%
Carboxymethyl cellulose	1.25%

The waste from the washing and decontaminating processes carried out in the Office of Atomic Energy for Peace Laboratory were collected and characterized. Characteristics of the waste stream was as follows:

Characteristics of the waste water after the washing process

pH	7.21± 0.01	
Ca^{+2}	19.03±0.48	ppm
K^+	2.61±0.01	ppm
NO_3^-	3.77±0.4	ppm
Cl^-	25.0±1.30	ppm
PO_4^{-3}	> 10	ppm.
Temperature	24.83±0.04	°C
Conductivity	418.75±1.30	ms/cm
Total dissolved solid	281.75±0.83	ppm
Total hardness	86.25±0.83	ppm
Dissolved oxygen	2.28± 0.04	ppm
Activity		
gross alpha	$< 1.02 \times 10^{-5}$	Bq/L
gross beta	0.145±0.002	Bq/L

Coagulation-precipitation methods have been tested to find the best condition for the treatment of the waste stream. The results obtained are shown in Table IV.

TABLE IV. THE PRECIPITATION CHARACTERISTICS FOR THE WASHING WASTE

Precipitation method	Chemicals	pH	Radionuclide	%Removal
Phosphate coagulation	$Na_3PO_4.12H_2O$ $Ca(OH)_2$	10	^{90}Sr	93.3
Copper Ferrocyanide coagulation	$K_4Fe(CN)_6.5H_2O$ $CuSO_4.5H_2O$ Bentonite	5-6	^{134}Cs	100
Cobalt precipitation	$Fe(NO_3)_3$ $.9H_2O$ NaOH Diethyl dithio-sodium carbamate	10-11	^{60}Co	100

4. IMMOBILIZATION OF THE TREATED WASTES

Immobilization of radioactive waste is a step required to produce a waste form suitable for handling, transportation, storage and disposal. Immobilization processes involve conversion of waste to solid forms that reduce the potential for migration or dispersion of radionuclides from the waste. The cementation method was chosen for the studies on the immobilization of ion exchange materials as mentioned in Section 3.1 and the sludge from the washing process as mentioned in Section 3.2.

4.1. THE BASIC PROPERTIES OF THE CEMENTED WASTE FORMS

Physical and mechanical properties of the cemented waste form have been investigated. The results are given in Tables V and VI.

TABLE V. DENSITY OF THE CEMENTED ION-EXCHANGE MATERIALS

Ion exchange materials	Density (g/cm^3)
Titanium dioxide	0.7056
Zeolite	0.5967
Bentonite	0.7954
Kaolinite	0.9716
Sand	1.3667
HAP	0.8392
Antimony pentoxide	1.6579
Portland cement (without additive)	1.3581

(* Normal Portland cement was used in this study)

TABLE VI. OPTIMUM WEIGHT RATIO OF THE ION EXCHANGER AND THE SLUDGE TO CEMENT

Ion exchanger materials	Weight ratio	Compressive strength (kg/cm^2)
Titanium dioxide	45:55	128-148
Zeolite	25:75	188-207
Bentonite	19:81	118-138
Kaolinite	24:76	128-147
Sand	54:45	180-201
HAP	--	--
Antimony pentoxide	--	--
15% loading of sludge	*34:50*	*160-166*
20% loading of sludge	*32: 47*	*150-160*

4.2. LEACHABILITY

Leachability of the simulated waste forms was measured using the Brookhaven National Laboratory's Accelerated Leach Test Method. The leaching rate (LR) and the cumulative leached fraction (CLF) are defined as follows:

$$\text{Leach rate (LR)} = (A_t \times W_o)/(A_o \times S \times t)\ \text{g/cm}^2.\text{d}$$

where

W_o is the initial weight of the sample,
S is the surface area of the sample (cm^2), this experiment~83.8 cm^2,
A_o is the initial activities in the cemented sample,
A_t is the activity in the leachant removed in time (t), and
t is the leaching time (day).

Leach factor (LF) = $\sum a \cdot V/A_o \cdot S$ cm/t

where

V is the volume of the specimen (cm^3),
S is the surface area of the specimen (cm^2), and
$\sum a$ is the total amount of the radionuclide leached out in t leaching interval.

The results of the leaching test for 15% and 20% loaded sludge are shown in Table VII.

TABLE VII. LEACHABILITY OF THE CEMENTED WASTE FORMS

Leaching time(d)	CLF x 10^{-3} (cm/day) 15% loaded sludge at 25°C	CLF x 10^{-3} (cm/day) 15% loaded sludge at 50°C	CLF x 10^{-3} (cm/day) 20% loaded sludge 25°C	CLF x 10^{-3} (cm/day) 20% loaded sludge 50°C
0.08	3.13	8.97	3.14	17.54
0.2	8.77	17.55	8.77	21.04
1	11.22	21.05	11.23	23.42
3	14.21	25.47	14.22	25.46
7	15.67	27.91	15.67	27.91
10	16.27	28.78	16.27	28.78
14	16.73	29.56	16.73	29.56
21	17.10	30.15	17.10	30.17
30	17.37	3 0.61	17.37	3 0.61

5. CONCLUSION

The simple method has been studied for applying to many kind of waste streams such as reactor waste, isotope production waste and liquid waste from hospitals. It is concluded that the inorganic ion exchangers can be used for the treatment of the low-level liquid wastes. But for implementation on a larger scale, there is a need to consider how to control the optimum condition.

The results from the investigation on the efficiency of detergent in the radioactive decontamination revealed that the locally available hand and machined-washed detergents, which are very cheap, can be used as a decontaminating agent instead of the more expensive imported decontaminating agents. According to the results received, the OAEP will recommend the radioisotope laboratories to use the simple detergent for radioactive work, so that the waste stream from the waste generators will contain a similar composition of laundry waste. The treatment method for such a waste as indicated in the investigation revealed that chemical precipitation methods can be used successfully for treating of such a waste arising.

Considering the immobilizing process for treated waste, cementation method was selected. The basic properties of the cemented waste forms have been investigated as well the leachability of a particular type of sludge. The result revealed that cemented waste forms of inorganic ion exchangers and sludge from the chemical precipitation of decontamination waste exhibited a high compressive strength and a low leach rate.

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TREATMENT OF LIQUID WASTE CONTAINING ALPHA NUCLIDES BY ADSORPTION

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Abstract

In this paper, experimental investigations on the removal of actinides from a decontaminating waste stream by using adsorption technique following the cementation of a resultant absorbent sludge are described. One kind of apatites was selected as an actinide absorbent from a number of indigenous materials by batch equilibrium tests. The influence of contact time, temperature, particle size and pH variables on the adsorption of actinides is given. The removal of total alpha activity is higher than 97% by absorbent precipitation process when the absorbent addition percentage of the liquid waste is more than 3.25 wt%, making alpha-activity level of the primary waste stream below 3.7×10^3 Bq/L, which can meet the acceptance requirements of the Low Level Radwaste Treatment Plant. The studies on the cementation of the absorbent sludge included the selection of cements used for solidification, formulation and characterization of the selected cemented waste forms. The results obtained have shown that both 525 type Portland cement and 325 type Portland pozzolana cement were compatible with the absorbent sludge. The selected cemented waste forms meet the requirements of the Chinese National Standard (GB 14569.1-93): Characteristic Requirements for Solidified Waste of Low and Intermediate Level Radioactive Waste—Cement Solidified Waste.

1. INTRODUCTION

In the China Institute of Atomic Energy (CIAE), about 70 m^3 of liquid waste containing ^{239,240}Pu, ^{241}Am, etc. generated from cleaning a glove-box and other laboratory equipment have been stored in an A-01/2 stainless steel tank for about 20 years. The waste is not suitable for treatment in the Low Level Radwaste Treatment Plant (LLRTP) because its alpha-activity level exceeds 3.7×10^3 Bq/L, the acceptance limit of the LLRTP. This waste should be safely treated in coming years according to the schedule of the CIAE Waste Management Programme. A conceptual treatment process for this specific liquid waste was proposed, which includes: (1) The liquid waste will be pretreated by adsorption, making its alpha-activity levels below 3.7×10^3 Bq/L prior to transfer the waste to the LLRTP; (2)The absorbent sludge will be immobilized with cement. The purpose of the present study is to demonstrate the feasibility of the conceptual treatment process on a laboratory scale.

2. REMOVAL OF ACTINIDES FROM THE DECONTAMINATING WASTE

There are many approaches to the removal of actinides from radioactive liquid wastes. Treatment of alpha bearing wastes has been reviewed in IAEA Technical Reports Series No.287 in 1988 [1]. A study of treatment of plutonium- and americium-bearing waste, performed in our laboratory by Mr. Xianhua Fan et al. [2], have shown that P301 material, a kind of apatites, was suitable for treating these wastes because of their high affinity for Pu(Am). Rd value of Pu(Am) is in the range 10^3-10^4 mL/g at pH1-3. Owing to this reason the P301 material is considered as a prospective absorbent.

P301 absorbent was obtained from the Guizhou Kaiyang Phosphorus Mineral Prospecting Bureau. Seven kinds of phosphorus ore from different mining areas were collected for the present study. Two other kinds of phosphorus ore from Sichuan and Jiangsu province were also collected for comparison.

2.1. EXPERIMENTAL ARRANGEMENTS

2.1.1. Preparation of absorbing materials

At first, nine samples of phosphorus ore collected for the test were given their code number, and then crushed and sieved. The particles in the range of 30-60, 60-120 and 120-200 mesh were selected for the test.

2.1.2. Sampling and analysis of the liquid decontaminating waste

Sampling of the liquid decontaminating waste stored in a stainless steel tank was carried out by means of a suction pump system. The chemical composition of the liquid waste was analyzed using a weight method, titrimetry, chromatography of ions and ICP-AES method. The concentration of radionuclides was determined by HPGe gamma-spectroscopy for gamma-emitters, by radiochemical analysis for ^{90}Sr-^{90}Y, and by alpha-spectroscopy for alpha-emitters.

2.1.3.Determination of an adsorption ratio

The amount of 0.25 g of each granulated material (generally 60-120 mesh) was added to 5.0 mL of the liquid waste in a polyethylene vials (15 mL) or centrifuge tubes (10 mL). These samples were mixed either by electromagnetic stirring for 5 minutes, or by shaking. The contact time was 24 hours, phases separation was usually performed by high speed centrifugation at 18000 rpm for 30 minutes. The supernatant liquid was analyzed for gross alpha-activity, appropriate aliquots of each test solution were affixed to stainless steel planchets and measured by a low background alpha-measurement apparatus (Model FJ-332, made in China).

The adsorption ratio Rd (mL/g) was calculated from the following equation:

$$Rd=\frac{C_o-C_t}{C_t}\cdot\frac{V}{W} \qquad (1)$$

where

C_0 is the initial alpha-activity per mL of the liquid waste (cpm),
C_t is the alpha-activity per mL in the supernatant liquid after the contact time t (cpm),
V is the volume of liquid phase (mL), and
W is the weight of the absorbent used (g).

2.1.4. Experimental procedure for absorbent precipitation

Each 100 mL portion of the liquid waste was taken out into 150 mL Erlenmeyer flasks. pH value of samples was adjusted to 2.0 by the addition of 4 mol/L of NaOH solution. The samples were then heated to a desirable temperature on a constant temperature magnetic stirrer. Various amounts of absorbent were added into flasks. Phase mixing was carried out by magnetic stirring for 15 minutes. The flasks were made to stand overnight at a given temperature. The supernatant was then filtered through the 0.2 μm micropore filter film. The filter liquor was measured for gross alpha activity and pH. Percentage of the alpha activity removal was calculated.

2.2. RESULTS AND DISCUSSION

2.2.1. Characteristics of the liquid decontaminating waste

The chemical composition and radionuclide concentration of the liquid waste are listed in Table I and Table II, respectively. It can be seen that the composition of the liquid waste is rather complex, consisting of many non-radioactive components such as sodium nitrate and significant amounts of polyvalent metal ions, including hydrolyzable ions such as iron, aluminum and manganese. Fission products are primarily ^{90}Sr, ^{90}Y and ^{137}Cs, actinides are ^{241}Am and ^{239,240}Pu.

TABLE I. CHEMICAL COMPOSITION OF THE LIQUID WASTE

Constituent	Content (mg/L)	Constituent	Content (mg/L)
K	<15	F^-	6.3
Na	907	Cl^-	58
Al	88	PO_4^{3-}	<15
Ca	1000	NO_3^-	15600
Ce	<0.03	SO_4^{2-}	240
Cr	2.5	$C_2O_4^{2-}$	<50
Fe	580		
Mg	190	Acidity	0.119 (mol/L)
Mn	28	Specific density	1.03 (g/mL)
Ni	0.65	Total residue (dried at 180°C for 2 hours)	6700
Sr	1.0		
Ti	0.58		

TABLE II. RADIONUCLIDE CONCENTRATION OF THE LIQUID WASTE

Radionuclides	Concentration (Bq/L)	Analytical method
^{137}Cs	6.3×10^5	
^{155}Eu	8.9×10^3	
^{154}Eu	8.9×10^3	HPGe-Spectroscopy
^{60}Co	3.0×10^4	
^{90}Sr-^{90}Y	2.1×10^6	Radiochemical Analysis
^{241}Am	4.70×10^4	HPGe-Spectroscopy
$^{239+240}$Pu	4.33×10^4	α-Spectroscopy
^{241}Pu	1.30×10^4	

2.2.2. Selection of absorbent materials

The adsorption ratios of actinides for the liquid waste and nine kinds of phosphorus ores are shown in Table III. It can be seen that not all of phosphorus ores have a high adsorption capacity for actinides. Both collophane from Jiangsu and svanbergite from Sichuan are not comparable with apatite from kaiyang of Guizhou with regard to actinide adsorption. Of apatites only P301 and absorbent D sorb well when pH value of the liquid waste is adjusted to 2.0, adsorption ratios are 676 and 808, respectively. Absorbent D was used in the subsequent experiments. Its chemical composition is given in Table IV.

TABLE IV. CHEMICAL COMPOSITION OF THE ABSORBENT D

Constituent	Content (wt%)	Constituent	Content (wt%)
SiO_2	3.54	P_2O_5	31.48
Al_2O_3	1.16	CO_2	1.74
TFe_2O_3	2.32	F	2.05
CaO	50.98	Loss on ignition	3.51
MgO	0.30		

TABLE III. RESULTS OF THE DETERMINATION OF AN ADSORPTION RATIO

Material	Origin	Code name	Initial pH	Final pH	Rd (mL/g)
Apatite	Guizhou	P301	1.09	2.44	41
			2.00	5.61	676
		A	1.09	2.59	58
			2.00	5.05	90
		B	1.09	1.89	66
			2.00	3.58	109
		C	1.09	1.92	66
			2.00	3.53	197
		D	1.09	1.89	57
			2.00	3.49	808
		E	1.09	1.84	70
			2.00	3.38	280
		F	1.09	1.92	72
			2.00	3.82	159
Collophane	Jiangsu	G	1.09	---	---
			2.00	4.84	62
Svanbergite	Sichuan	H	1.09	1.28	6
			2.00	2.72	130

2.2.3. Influence of several variables on the adsorption ratio

The influence of temperature on the adsorption ratios is illustrated in Table V. These data show that Rd increases when the temperature of the liquid is increasing. When temperature reaches 38°C, Rd value of the order of 10^3 could be obtained. In the subsequent experiments the temperature was selected as 38°C.

TABLE V. INFLUENCE OF TEMPERATURE ON THE ADSORPTION RATIO
(particle size 60-120 mesh; initial pH2.0)

No.	Temperature (°C)	Rd (mL/g)
1	17	1.6×10^2
2	28	8.1×10^2
3	38	1.1×10^3

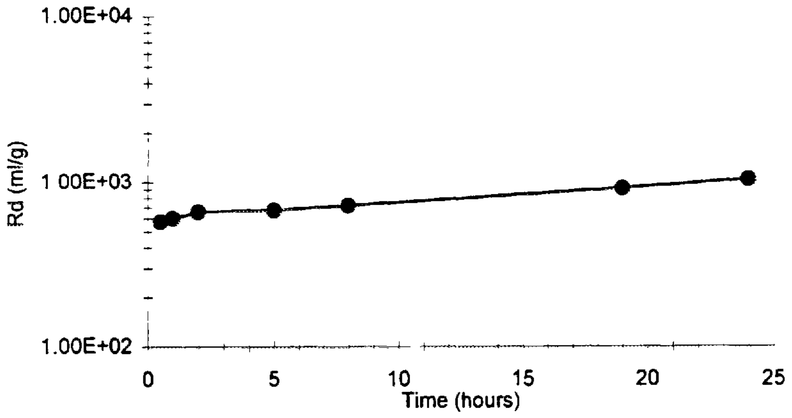


Fig.1 Rd of actinides as a function of contact time

Figure 1 illustrates Rd of actinides as a function of the contact time. It shows that Rd rises steeply initially and then gradually. However, equilibrium could not be reached before 24 hours. It indicates that sorption kinetics of the apatite absorbent behaves not very well. In the subsequent experiments the contact time of 24 hours was used.

TABLE VI. INFLUENCE OF A PARTICLE SIZE ON THE ADSORPTION RATIO (initial pH2.0)

No.	Range of particle size (mesh)	Rd (mL/g)
1	30 — 60	7.2×10^2
2	60 — 120	1.1×10^3
3	120 — 200	3.8×10^3

Table VI summarizes the results of the influence of a particle size on the adsorption ratio. It can be seen that Rd increases when a particle size is decreasing. This indicates that adsorption processes occur mainly on the surface of the absorbent. The larger specific surface is, the higher adsorption ratio is.

An influence of pH on the adsorption ratio can be studied as follows. Take out each 100 mL of the liquid waste into 150 mL Erlenmeyer flask, raise pH of the liquid to desirable pH by addition of 4 mol/L NaOH solution, stand the flask over night, and then filter the liquid through 0.2 μm micropore filter film. The filtrate was used for these experiments.

The results of the influence of pH on the adsorption ratio are shown in Table VII. It can be seen that Rd value increases with the increasing pH value. Two kinds of a mechanism may exist: (1) competitive adsorption from H^+ decreases while pH value increasing; (2) absorbent dissolves partially resulting in a rise in pH due to H^+ consumption, hydrolyzable metal ions form precipitates which carry actinides.

TABLE VII. INFLUENCE OF pH on Rd VALUES

No.	Initial pH	Final pH	Rd (mL/g)
1	1.09	1.94	8.1×10^2
2	1.52	2.70	1.0×10^3
3	2.00	3.44	1.1×10^3
4	2.50	4.02	2.4×10^3

2.2.4. Removal of actinides by absorbent precipitation

The results of the actinide removal by absorbent precipitation are shown in Table VIII. It is clear that the removal of gross alpha activity increases with increasing of the amount of the absorbent.

TABLE VIII. RESULTS OF ABSORBENT PRECIPITATION EXPERIMENTS

No.	Liquid waste (mL)	Addition of absorbent (g)	Initial pH	Final pH	Removal of gross alpha-activity (%)
1	100	1.50	2.0	3.62	95.8
2	100	3.25	2.0	4.01	97.6
3	100	5.00	2.0	4.24	98.7

When the absorbent addition percentage of the liquid waste was higher than 3.25wt%, the removal of gross alpha-activity was above 97%. In this case, the gross alpha-activity of the liquid waste was below 3.7×10^3 Bq/L that meets the acceptance requirements of the LLRTP.

3. CEMENTATION OF THE ALPHA BEARING ABSORBENT SLUDGE

The alpha bearing absorbent sludge produced from the treatment process needs to be immobilized to meet the requirements for interim storage, transport and shallow land disposal according to the Waste Management Programme. Inorganic cements are considered attractive matrices for waste solidification as they satisfy a number of process and waste form requirements [3]. Cementation is considered to be suitable for this purpose because cements are inexpensive, tolerant to wet materials and durable in the natural environment [4]. Moreover we had an experience in immobilization of the intermediate level wastes from reprocessing plants by cementation[5]. Therefore, we have decided to adopt this technique.

3.1. EXPERIMENTAL ARRANGEMENTS

3.1.1. Preparation of a simulated alpha bearing absorbent sludge

A simulated decontaminating feed prepared for this study was composed of the main chemical constituents listed in Table I. Certain amounts of chemical reagents were dissolved in distilled water and poured into a 20 L polyethylene container, subsequently adjusting pH of feed with HNO_3 up to 1.07 that is the same as the pH of the actual decontaminating waste. This feed was used for the preparation of the absorbent sludge.

The absorbent sludge was prepared precipitation. To 10 L simulated decontaminating feed preadjusted to pH2.0 with 4 mol/L of NaOH solution was added 500 g of apatite absorbent-D (particle size 60-120 mesh). Phase mixture was carried out by electric power stirring for 15 minutes, the mixture was allowed to stand overnight and then the supernatant was decanted. The residue as dilute simulated alpha bearing absorbent sludge was conserved for further tests.

The diluted simulated alpha-bearing absorbent sludge needs to be dewatered in order to improve the loading of a solidified waste form. Two dewatering technologies including vacuum filtration and centrifugation were adopted on a laboratory scale. Vacuum filtration was performed by transferring absorbent sludge to a 150 mm diameter Buchner funnel; centrifugation was carried out by using a centrifuge with 4000 rpm for 30 min.

The water content of the absorbent sludge was determined by a weight method. The absorbent sludge was fully mixed by manual stirring and sampled into weighed bottles. Samples were dried in an oven at 105°C and weighed up to a constant weight. The water content of the absorbent sludge sample was calculated, and an average value of the water content was reported.

3.1.2. Preparation of a specimen of the cemented absorbent sludge

A general procedure for the solidification of the absorbent sludge with cement can be as follows:

Weigh a calculated amount of the fully mixed absorbent sludge and put into a plastic beaker (if necessary, add a calculated amount of supernatant), add some amount of weighed cement, mix manually for 5 minutes, fill the mixture into cylindrical plastic molds (diameter and height are equal to 40 mm) to make an individual form. The molds should be mechanically vibrated for 2 minutes before cure. Two replicated specimens for each condition were prepared.

After aging in a curing box with the relative humidity above 95% at 25°C for 1 day, the specimens were demoulded, and cured in the same curing box for an extended cure period of 7 days. Testing of compressive strength was then conducted on the specimens.

3.1.3. Caracterization of the cemented waste forms

Various characteristics of the cemented waste forms were determined according to the the Chinese Standard [6].

- *Compressive strength*

Mechanical stability of waste forms is an important parameter for safe disposal of waste. The compressive strength of the cemented absorbent sludge waste forms was tested using a compression tester (home made) with a loading rate of 4900 N/S in order to examine the effects of water/cement and solid/cement ratios, pH, range of a size of absorbent, immersion, radiation damage etc. on mechanical stability.

- *Impact resistance*

The specimens prepared as described in Section 3.1.2 were used for an impact test. From a height of 9 m, specimens were made to fall freely upon the concrete floor to examine whether they would break into pieces.

- *Leach resistance*

Leach testing was performed in accordance with the Chinese Standard GB 7023-86 [7].

- *Immersion resistance*

After specimens were immersed in tap water for a period of 90 days, compressive strength was measured.

- *Freeze-thaw resistance*

Freeze-thaw cycle tests were carried out as follows:

The specimens sealed in a plastic bag were immersed into a 15-20°C cold water bath for 4 hours, then taken out and placed in a refrigerator at a temperature of -20°C for a period of over 2 hours. After that the specimens were removed from the refrigerator and placed into a plastic bag, sealed, and immediately placed into a 15-20°C cold water bath to thaw out for above 4 hours. Thus far, the first freeze-thaw cycle was finished. The second freeze-thaw cycle was started in the above manner. After 25 freeze-thaw cycles, compressive strength of specimens was measured.

- *Radiation stability*

The specimens were gamma-irradiated in an annular Co-60 facility at a dose rate of 10 kGy/h. Six specimens sealed in a plastic bag were annularly emplaced in the center of the facility to make each specimen situated nearly in the same irradiation field condition. After the dose of 1000 kGy the compressive strength of specimens was measured.

3.1.4. Long term leach testing of the solidified actual radioactive waste forms

- *Preparation of specimens*

Alpha bearing absorbent sludge produced from absorbent precipitation of the actual liquid waste was mixed with cement manually. The cement-waste mixture was filled into a cylindrical polyethylene container of 40 mm diameter and treated for the elimination of air bubbles by vibrating during 15 minutes. The mixture was cured in a water-vapour saturated atmosphere for 28 days, and then the cement block was withdrawn from the container. The upper and lower surface of the cylindrical block was polished with 200 grit paper and cleaned from dust particles with cotton. All specimens were measured and weighed before leach testing.

- *Leach testing*

The cylindrical polyethylene bottles of 90 mm in diameter were used as leachant containers. The bottles were thoroughly cleaned with deionized water prior to use. The specimens (diameter to height ratio is about equal) were suspended in containers filled with 900 mL of deionized water. After certain intervals (as specified in the standard [7]), the specimens were withdrawn from the containers and immediately transferred to the next leachant container filled with a fresh leachant. The used leachant containers containing all leached material were closed and allowed to stand for analysis.

- *Analysis of the leachant solution*

Both ^{239,240}Pu and ^{241}Am in the leachant solution were determined by using a low background large area gridded ionization chamber [8]. The technological process of preparing 1400 cm^2 α-spectrometric source and method of determination of α-nuclides in a sample is described in Ref. [9].

After determination of pH and conductivity, the leachant solution was acidified with HNO_3 to about pH1. An aliquot containing about 100 mg of solids in the leachant solution was taken into a beaker and evaporated to dryness, the residue was dissolved in a suitable amount of deionized water. The beaker was placed in a supersonic breaker to grind non-soluble solids in the sample and then the sample was stuck on aluminized polyester film in a vacuum drying oven.

Both the leachant solution sample and the blank solution sample that resulted from leaching of a blank cemented waste form were measured in an ionization chamber. Usually, a measured time was 30 hours and then α-spectrum was plotted. The activities of ^{239,240}Pu and ^{241}Am were calculated from the following equation:

$$C = \frac{N}{60 W \eta P f} \qquad \textbf{(2)}$$

where

C is the specific activity of sample (Bq/g or Bq/L),
N is the net counting rate (cpm),
W is the amount of sample (g or L),
η is the counting efficiency of the ionization chamber (48%),
P is the branching ratio of nuclide, and
f is the chemical recovery.

- *Expression of the leach testing results*

The results are expressed for each constituent by plots of leaching rates, R'_n , and cumulative leaching fractions, P_t^i , as a function of time, *t*, of leaching:

$$R_t^{i} = \frac{a_n^{i}/A_o^{i}}{(F/V)t_n} \qquad (3)$$

where

R_n^i is the leaching rate for the i-th constituent in the n-th leaching period ($cm \cdot d^{-1}$),
a_n^i is the activity for the i-th constituent leaching in the n-th leaching period (Bq),
A_0^i is the initial activity for the i-th constituent in the specimen of leach test (Bq),

$$P_t^{i} = \frac{\sum a_n^{i}/A_0^{i}}{F/V} \qquad (4)$$

where

F is the geometric surface area of the specimen in contact with leachan (cm^2),
V is the volume of the specimen (cm^3),
t_n is the duration of the n-th leaching period (d);
P_t^i is the cumulative leaching fraction of the i-th constituent when the time equal t (cm), and
t is the cumulative leaching time (d). $t = \sum t_n$.

3.2. RESULTS AND DISCUSSION

3.2.1. Preparation of the simulated alpha bearing absorbent sludge

Simulated decontaminating feed used for the tests was prepared with non-radioactive chemical agents so that experiments can be carried out in a non-radioactive chemical laboratory. The chemical composition of the simulated decontaminating feed was about the same as the actual decontaminating liquid waste (See Table I). The range of pH value of supernatant produced from a series of absorbent precipitation processes using simulated decontaminating feed was 3-4, which was similar to that from the same process using the actual decontaminating liquid waste. This suggested that properties of both the simulated feed and the actual waste liquid were approaching each other. The water content of the dilute absorbent sludge was about 80%, which could be dropped to about 40% by means of vacuum filtration or centrifugation (see Table IX).

TABLE IX. DEWATERING OF SIMULATED ABSORBENT SLUDGE

Dewatering	water content of the absorbent sludge (%)					
	1	2	3	4	5	average
Centrifugation	42.1	38.0	40.2	35.2	36.7	38.4
vaccum filtration	44.2	44.6	44.2			44.3

3.2.2. Selection of cements for the solidification of the absorbent sludge

Cement has been used for many years for solidification of a wide variety of low and intermediate level radioactive wastes. However, immobilization of apatite absorbent sludge with cement has not been reported. Therefore, compatibility of the absorbent sludge with different types of cements needs to be investigated. Seven types of home-made cements, including Portland cement, Portland-pozzolana cement and moderate heat Portland cement were used for tests, and selection criteria were defined as follows.

When water/cement ratio of the solidified waste form was 0.5-0.55, depending on the mixing workability, loading of the absorbent sludge in the solidified waste form was about 30%, which makes the solidified waste form to have an α-activity less than 4 kBq/g suitable for near surface disposal. The compressive strength of the specimens should be greater than 5 MPa after curing for 7 days. The results of the experiments are shown in Table X.

From Table X, it can be seen that 325 type Portland cement, 425 type Portland blast furnace-slag cement and ordinary Portland cement seem to be unsuitable for solidification of the absorbent sludge from the point of view of mechanical stability. The solidified forms possess low compressive strength, whereas 525 type Portland cement and moderate heat Portland cement appear to be compatible with the absorbent sludge. Their solidified forms possess high compressive strength. 325 type Portland pozzolana cemented waste forms have also higher compressive strength and meet the selecting criteria. In the present study, the Qinghai 525 type moderate heat Portland cement was the first choice for further formulation study. Its chemical composition is shown in Table XI.

TABLE X COMPRESSIVE TESTS OF THE CEMENTED ABSORBENT SLUDGE

Test No	Type of cement	Water/cement ratio	Loading %	Compressive strength (MPa)
1	Liulihe 425 type Portland blast furnace-slag cement	0.5	29.6	2.4*
2	Zhoukoudian 325 type Portland pozzolana cement	0.55	31.4	5.8
3	Taiyuan 325 type Portland cement	0.5	35.4	1.7
4	Shanxi 425 type ordinary Portland cement	0.5	33.2	2.0
5	Qinghai 425 type ordinary Portland cement	0.5	37.9	1.0
6	Qinghai 525 type moderate heat Portland cement	0.5	33.9	18.3
7	Lasa 525 type Portland cement	0.5	36.5	16.7

* data measured after curing for 15 days

TABLE XI CHEMICAL COMPOSITION OF 525 TYPE MODERATE HEAT PORTLAND CEMENT(MHPC) AND 325 TYPE PORTLAND POZZOLANA CEMENT (PPC)

Constituent	Content (wt%)		Constituent	Content (wt%)	
	MHPC	PPC		MHPC	PPC
SiO_2	20.55	33.33	P_2O_5	0.32	0.08
Al_2O_3	5.17	8.14	TiO_2	0.26	0.52
CaO	61.86	40.05	MnO	0.07	0.08
MgO	1.50	3.35	TFe_2O_3	5.10	2.59
K_2O	0.98	1.38	SO_3	2.68	1.92
Na_2O	0.26	0.53	Loss on ignition	1.92	7.61

3.2.3. Formulation of the cemented waste form

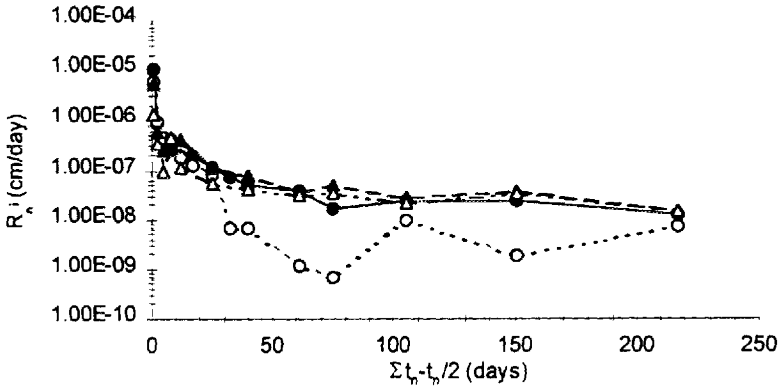
Performance of the cemented waste forms depends on many factors, such as a water/cement ratio, waste loading, grain size of waste, pH of liquid waste, etc. A number of formulations for the solidified waste forms with above variables were investigated by testing the compressive strength of the specimens. The data obtained are given in Table XII.

The results indicated that the compressive strength of the specimens of solidified waste forms increased as the water/cement ratio increased, the loading decreased, and pH value of the liquid waste increased. The effect of the grain size of the absorbent on the compressive strength of a specimen of the solidified form was clearly understood.

TABLE XII. COMPRESSIVE STRENGTH TESTS OF THE CEMENTED WASTE FORMS OF DIFFERENT FORMULATIONS

Test No.	Water/cement ratio	Loading %	Grain size of absorbent, mesh	Initial pH of absorbent sludge	Compressive strength (MPa)
1	0.5	30.0	60-120	4	19.1
2	0.5	33.9	60-120	4	18.3
3	0.5	39.0	60-120	4	13.1
4	0.5	30.0	120-200	4.5	20.7
5	0.5	30.0	30-60	4	24.2
6	0.55	30.0	60-120	4	16.4
7	0.5	30.0	60-120	8	30.0

To sum up, the compressive strength of all the specimens prepared for the formulation tests met the criteria.



● ^{239,240}Pu, ○ ^{241}Am. Intermediate heat Portland cement as matrix
♦ ^{239,240}Pu, Δ ^{241}Am. Portland pozzolana cement as matrix

Fig.2 Leaching rate of ^{239,240}Pu and ^{241}Am in both cement-silidified waste forms

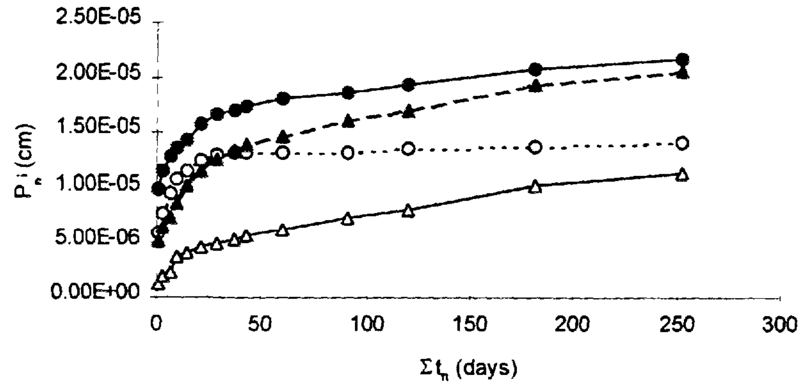
TABLE XIII CHARACTERISTICS OF THE SELECTED CEMENTED WASTE FORMS

Stability Criteria	Acceptance criteria for cemented waste forms as specified in the Chinese Standard	Waste form with moderate heat Portland cement matrix	Waste form with Portland pozzolana cement matrix
Compression impact resistance	CS ≥7MPa No breaking into pieces	CS 54.3 MPa No breaking into pieces (CS 34.4 MPa)	28.1 MPa No breaking into pieces (CS 17.8 MPa)
Leachability	R_n' for each nuclides, ^{239}Pu, ^{241}Am and other actinides (42th day) $\leq 1\times10^{-5}$ cm/d	R_n' of ^{239,241}Pu and ^{241}Am are 5.1×10^{-8} and 7.0×10^{-9} cm/d (42th day), respectively	R_n' of ^{239,241}Pu and ^{241}Am are 8.3×10^{-8} and 4.1×10^{-8} cm/d (42th day), respectively
Immersion resistance	CS ≥5.25 MPa with reduction in strength<15%	CS 51.7 MPa Reduction in strength 4.8%	CS 25.9 MPa Reduction in strength 7.8%
Freeze-thaw resistance	CS>7 MPa with reduction in strength<15%	CS 48.0 MPa Reduction in strength 11.6%	CS 24.8 MPa Reduction in strength 11.7%
Radiation stability	No requrements	CS 47.9 MPa Reduction in strength 11.8%	CS 26.0 MPa Reduction in strength 7.5%

Note CS refers to compression strength

TABLE XIV RESULTS OF Pu AND Am LEACHING

Sample No	pH	Conductivity (ms/m)	Specific activity (Bq/L) ^{239,240}Pu	Specific activity (Bq/L) ^{241}Am
1-1	8.43	48	4.3×10^{1}	2.8×10^{1}
1-2	8.43	58	7.6×10^{2}	9.2×10^{2}
1-3	8.55	52	5.5×10^{2}	9.0×10^{2}
1-4	8.33	37	3.5×10^{2}	5.7×10^{2}
1-5	8.39	38	3.6×10^{2}	3.5×10^{2}
1-6	8.41	38	5.7×10^{2}	4.3×10^{2}
1-7	8.42	35	3.8×10^{2}	2.9×10^{2}
1-8	8.39	33	2.4×10^{2}	2.4×10^{3}
1-9	8.34	28	1.4×10^{2}	2.0×10^{3}
1-10	8.35	33	2.9×10^{2}	1.0×10^{3}
1-11	8.46	34	2.4×10^{2}	1.0×10^{3}
1-12	8.56	28	3.2×10^{2}	1.4×10^{2}
1-13	9.69	45	6.8×10^{2}	5.3×10^{3}
2-1	8.65	80	2.1×10^{1}	5.8×10^{2}
2-2	8.55	55	4.4×10^{2}	2.9×10^{2}
2-3	8.56	62	3.9×10^{2}	1.7×10^{2}
2-4	8.40	43	4.5×10^{2}	5.9×10^{2}
2-5	8.40	42	6.4×10^{2}	2.0×10^{2}
2-6	8.43	43	5.3×10^{2}	2.0×10^{2}
2-7	8.43	37	4.1×10^{2}	1.9×10^{2}
2-8	8.39	37	3.1×10^{2}	1.5×10^{2}
2-9	8.30	34	2.0×10^{2}	1.1×10^{2}
2-10	8.40	43	2.7×10^{2}	2.3×10^{2}
2-11	8.39	43	6.4×10^{2}	5.0×10^{2}
2-12	8.36	30	3.6×10^{2}	3.0×10^{2}
2-13	8.59	30	9.7×10^{2}	9.2×10^{2}
leachant (deionized water)	6.25	0.15		



● ^{239,240}Pu, ○ ^{241}Am. Intermediate heat Portland cement as matrix
♦ ^{239,240}Pu, △ ^{241}Am. Portland pozzolana cement as matrix

Fig.3 Cumulative leaching fraction of ^{239,240}Pu and ^{241}Am in cement solidified waste forms

3.2.4. Characterization of the selected cemented waste forms

The specimens composed of 0.5 (or 0.55 for 325 type Portland pozzolana cement) of the water/cement ratio, 30% loading, 60-120 mesh grain size of absorbent, initial pH8, were used for the characterization. These specimens were prepared by using a simulated absorbent sludge mixed with the moderate heat Portland cement (or Portland pozzolana cement) except that the specimens used for leach tests were prepared by using actual waste sludge produced from the absorbent precipitation process. Several tests that included the determination of compressive strength, impact resistance, immersion resistance, freeze-thaw resistance, radiation stability, have been completed. The results are shown in Table XIII. For comparison with the Chinese Standard [4], the acceptance criteria are listed in the same Table. From Table XIII, it can be seen that the selected cemented waste forms meet the acceptance criteria.

3.2.5. Leach testing

Analytical data obtained for leaching of ^{239,240}Pu and ^{241}Am are given in Table XIV.Two kinds of leaching curves for ^{239,240}Pu and ^{241}Am, where the leaching rate R is plotted against a time function $\sum t_n\text{-}t_n/2$, and the cumulative leaching fraction P is plotted against the total time of leaching $\sum t_n$, are shown in Fig. 2 and Fig. 3, respectively. From the examination of these curves it can be concluded that the leaching of ^{239,240}Pu and ^{241}Am from the cemented radioactive waste is low, the leaching rates of them are of the order of magnitude of 10^{-8} cm·d^{-1} and the cumulative leaching fraction of them are of the order of magnitude of 10^{-5} after 100 days.

4. CONCLUSIONS

The main conclusions which can be drawn from the experiments are the following:

(1) Experiments of batch equilibrium with actual liquid waste show that the apatite (code name D at the present experiments) from Guizhou Kaiyang Phosphorous Mineral Prospecting Burean possesses higher adsorption capacity for actinides. The Rd of actinides increases with increasing of temperature, pH value and contact time, and decreasing of the range of particle size. At a temperature of 38℃, initial pH2, contact time 24 hours, and the range of particle size 60-120 mesh, Rd of 1.1×10^3 mL/g can be achieved. Therefore, it can be used as an inorganic absorbent for actinide

removal from the liquid decontaminating waste stream. The removal of gross alpha-activity was above 97% when the adsorbent addition percentage of liquid waste was more than 3.25 wt%. The gross alpha-activity level of the liquid decontaminating waste stream dropped to below 3.7×10^3 Bq/L which can meet the acceptance requirements of LLRTP.

(2) Dewatering of the absorbent sludge can be achieved by centrifugation or vacuum filtration. In laboratory tests, the water content of the sludge decreased from 80% to 40%, which is suitable for the formulation of cemented waste forms.

(3) From the point of view of mechanical stability, three types of cement, which include 525 type moderate heat Portland cement, 525 type Portland cement and 325 type Portland pozzolana cement are compatible with the absorbent sludge and possible to be used for its immobilization.

(4) Formulation tests show that specimens prepared with 525 type moderate heat Portland cement have good mechanical properties when water/cement ratio is 0.50-0.55, loading of absorbent sludge in solidified form 30-39%, grain size of absorbent 60-120 mesh and pH of absorbent sludge 4-8. Compressive strength of these specimens are above 13 MPa that exceeds the minimum criterion (7MPa) in the Chinese Standard.

(5) The selected cemented waste forms meet the requirements for solidified waste forms as specified in the Chinese Standard. Therefore, cementation of absorbent sludge with either 525 type moderate heat Portland cement or 325 type Portland pozzolana cement is feasible.

(6) Leaching of ^{239,240}Pu and ^{241}Am is low for the cemented radioactive waste forms. As far as its leachability is concerned, both the cemented waste formulations are suitable for the solidification of the alpha-bearing absorbent sludge resulted from absorbent precipitation of the liquid decontaminating waste stream.

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