INNOVATIVE MATHEMATICAL MODELLING IN ENVIRONMENTAL REMEDIATION

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Abstract

Subsurface contamination problems of radionuclides, metals and organic co-contaminants are ubiquitous. These contaminants may exist in the solute phase or may be bound to soil particles and interstitial portions of the geologic matrix. Innovative tools to reliably predict the migration and transformation of these radionuclides, metals and co-contaminants in the subsurface environment enhance the ability of environmental scientists, engineers and decision makers to evaluate the efficacy of alternative remediation techniques and to analyse their impact prior to incurring expense in the field. A realistic mechanistically based numerical model that considers feedback between fluid flow, thermal transport and reactive transport could provide such a tool. This paper communicates the development and applications of a mechanistically coupled fluid flow, thermal transport, hydrologic transport and reactive biogeochemical model where both fast and slow reactions occur in porous and fractured media. Four example problems are employed to demonstrate how numerical experimentation can be used to evaluate the feasibility of different remediation approaches.

1. INTRODUCTION

Groundwater has always played an important role in human history and groundwater contamination has been subject to intensive investigations since the mid-1980s. Contaminants in the water environment undergo changes in concentration resulting from physical, chemical and/or biological processes, and a capability to understand and model these processes is at the core of water quality management. Accurate tools for the reliable prediction of contaminant migration and transformation are necessary to support the task. Consideration of equilibrium chemistry, kinetic chemistry, hydrologic transport and the interaction between fluid flow and reactive transport is necessary in order to reflect the complexity of the many systems. For example, solid phase reactions including precipitation and dissolution can potentially plug pores or open fractures reducing matrix diffusion and promote rapid flow through fractures.

The development of mechanistically based reactive chemical transport models has increased dramatically in the last two decades [1–8]. These numerical reactive transport models have had varied scopes. This paper describes the development and application of the latest versions of HYDROGEOCHEM [7], a mechanistically based numerical model for the simulation of coupled fluid flow, thermal transport and reactive chemical transport in variably saturated porous and fractured media. These latest versions are among the most versatile codes for dealing with biogeochemical processes under variably saturated flow conditions.

2. MATHEMATICAL BASIS

The reactive transport equation of any species can be derived based on the conservation law of material mass stating that the rate of mass change is due to biogeochemical reactions and hydrologic transport [7]. This statement would result in M partial/ordinary differential equations (PDEs) involving M species concentrations and N reaction rates. The number of unknowns is $(M + N)$, which is more than the number of PDEs. Thus, N more equations are needed. We will assume that the N reactions are made of N_E equilibrium and N_K kinetic reactions. For each of the N_K kinetic reactions, its rate is explicitly formulated based on experimental evidence. For each of the N_E equilibrium reactions, its rate is implicitly defined with an algebraic equation, for example, a mass action equation. The substitution of explicit rate equations for kinetic reactions into the system of PDEs results in $(M + N_E)$ unknowns in M PDEs. This coupled with N_E algebraic equations of thermodynamic relationships forms a closed system of $(M + N_E)$ mixed differential algebraic equations. Decoupling of the N_E unknowns of equilibrium rates from the M unknowns of species concentrations can be made via the Gauss–Jordan reduction of reaction networks [2]. Performing matrix decomposition of the reaction matrix, we obtain two subsets of equations as described below:

(a) $M - N_E$ transport equations for $M - N_E$ reaction extents

$$\frac{\partial \theta E_i}{\partial t} = L\left(E_i^m\right) + \theta \sum_{j \in \{N_K\}} D_{ij} f_j,\ i \in \{M - N_E\} \text{ in which } E_i = \sum_{j \in \{M\}} a_{ij} C_j \tag{1}$$

where E_i is the ith reaction extent [M/L^3]; L is the hydrologic transport operator; E_i^m is the portion of E_i which contains the linear combination of only mobile species; θ is the moisture content [L^3/L^3]; $\{N_K\} = \{1,2,..,N_K\}$; $f_j = f_j(C_i{:}i \in \{M\})$ is an explicit function of M C_i's that represents the rate equation of the jth reaction; D_{ij} is an element of decomposed reaction matrix; $\{M - N_E\} \subset \{M\}$ having $(M - N_E)$ members is a subset of {M} where $\{M\} = \{1,2,..M\}$; and a_{ij} is the element of an M × M matrix resulting from the matrix decomposition of a unit matrix and it represents the coefficient of the linear combination of C_j in E_i.

(b) N_E rate equations for N_E fast/equilibrium reactions

$$\theta D_{ik} R_k = \frac{\partial \theta E_i}{\partial t} - L\left(E_i^m\right) - \theta \sum_{j \in \{N_k\}} D_{ij} f_j,\ k \in \{N_E\},\ i \in \{M_E\} \tag{2}$$

where D_{ik} is an element of decomposed reaction matrix corresponding to an independent equilibrium reaction; E_i, the *i*th reaction extent, is called an equilibrium variable since it corresponds to an independent equilibrium reaction; $\{N_E\} = \{1, 2, ..,N_E\}$; and $\{M_E\}$, having M_E (=$M - N_E$) members, is a subset of $\{M\}$.

The $(M - N_E)$ PDEs in Eq. (1) are coupled with N_E non-linear algebraic equations,

$$F_k\left(C_i : i \in \{M\}\right) = 0,\ e.g.\ \beta_k^E - \prod_{i \in \{M\}} \left(C_i\right)^{\nu_{ik}} / \prod_{i \in \{M\}} \left(C_i\right)^{\mu_{ik}} = 0,\ k \in \{N_E\} \tag{3}$$

which implicitly define the rates of N_E equilibrium reactions, to form a system of M equations for the unknowns of M species concentrations, C_i's. In Eq. (3), β_k^E is the modified equilibrium constant of the *k*th equilibrium reaction and μ_{ik} and ν_{ik}, respectively, are the reaction stoichiometries of the *i*th species in the *k*th reaction associated with reactants and products, respectively.

3. EXAMPLE PROBLEMS

Example 1: This problem considers the release and migration of uranium from a simplified uranium mill tailings pile. The mill tailings pile was located adjacent to a surface that slopes down to a river. The problem consisted of a reaction network of 35 aqueous complexation and 14 precipitation–dissolution reactions involving 56 species [6]. Diagonalization of the reaction network resulted in seven major chemical components: calcium, carbonate, uranium, phosphate, sulphate, proton and ferrous [6]. Simulation results on the migration of uranium and other chemical species over 300 days were reported in Yeh et al. [7]. The same 56 species uranium tailing problem was applied to a proposed waste disposal site at Melton Branch Watershed. The parallel version of the code was employed and computations were distributed over a number of processors to speed up the computations. Migrations of uranium, proton, carbon and iron are given elsewhere [9].

Example 2: This problem simulated Monitored Natural Attenuation (MNA). In addition to the processes of the previous problem, adsorption–desorption processes were also included. The objectives were to conduct a parametric study of the adsorption–desorption of uranium. Different sorption mechanisms, including fast (or reversible), slow and irreversible sorption, were simulated. Three cases were studied: equilibrium sorption, kinetic limited sorption with slow uptake and rapid adsorption with slow desorption. For Case 1, fast adsorption only, four equilibrium reactions were included. For Case 2, mixed fast and slow adsorption, two more equilibrium reactions and one reversible kinetic reaction were included. For Case 3, mixed reversible and irreversible reactions, the slow kinetic reaction was considered partially irreversible. Simulation results indicated that: (a) a dissolved uranium plume moves faster when sorption processes are not included; (b) the amount of sorbed uranium on the fast site is higher than on the mixed site; (c) since less uranium is sorbed on to the mixed site, the intensity of the dissolved uranium plume is lower than at the fast site during the desorbing period; (d) the separation and alteration of the mass centre of the dissolved uranium plume is the effect of non-linear sorption–desorption reactions; (e) during the sorbing period, the irreversible site can provide almost the same sorption ability as the reversible site; (f) during the desorbing period, the irreversible site partially confines the migration of uranium; and (g) the complete removal of adsorbed uranium from the irreversible site requires more time to achieve than at the reversible site.

Example 3: This example investigated laboratory experiments involving extremely high concentrations of uranium, technetium, aluminium, nitrate and toxic metals [10]. The experiment was modelled with a reaction network of 92 equilibrium and 5 kinetic reactions involving 138 chemical species. The conceptual model involving 12 chemical components was proposed for the experiments: nitrate, Na, K, Al, Si, sulphate, Ca, Mg,

Mn, U Co, and Ni [10]. An equilibrium reaction model that considers 72 aqueous complexation reactions was first used to perform the speciation calculation for each data point to determine the concentrations of individual species given the pH and the total aqueous concentrations of nitrate, Na, K, Al, Si, sulphate, Ca, Mg, Mn, U, Co, Ni and Cl. Based on the calculated aqueous species concentrations, the saturation index was calculated for each of the 26 minerals considered and a decision was made to include only five precipitation–dissolution reactions. Finally, soil buffering capacity was modelled with six ionization reactions of a polyprotic acid (H_4X) and a polyprotic base ($Y(OH)_2$). Simulation results indicated good agreement between experiments and theoretical predictions using the proposed reaction network.

Example 4: This example modelled bioremediation field experiments conducted at a Uranium Mill Tailings Remedial Action (UMTRA) site using acetate amendment to stimulate microbially mediated immobilization of uranium in the unconfined aquifer. Experiments at the Rifle site showed that the growth of acetate-oxidizing Fe(III)-reducers dominated by Geobacter sp., was accompanied by significant uranium removal from groundwater. An important feature of these field experiments was the eventual onset of sulphate reduction, which was characterized by a decrease in aqueous sulphate, near complete consumption of acetate and less efficient U(VI) removal from groundwater. A key observation from field experiments at the Rifle site was that longer term, post-biostimulation U(VI) removal from groundwater was associated with longer periods of sulphate reduction. This led to the inclusion of abiotic chemistry for the bioreduced U(IV), Fe(II) and sulphide products of the principal terminal electron accepting processes (TEAPs), to address their potential roles in long term uranium immobilization. The conceptual model was developed to facilitate understanding of the principal processes and properties controlling uranium biogeochemistry. The model included four TEAPs involving two pools of bioavailable Fe(III) minerals (phyllosilicate, oxide), aqueous U(VI) and aqueous sulphate, two distinct functional microbial populations (iron, sulphate reducers), as well as aqueous and surface complexation and mineral precipitation and dissolution. The model assumes: (a) co-metabolic uranium bioreduction occurs via active iron reducers; (b) the onset of sulphate reduction is controlled by a bioavailable Fe(III) threshold; (c) iron, sulphate and uranium TEAPs occur simultaneously during sulphate reduction; and (d) there is no abiotic U(VI) reduction. The conceptual model reflects findings from laboratory studies that during biostimulation, 90–99% of the Fe(III) initially reduced is in the phyllosilicate clays [11] and biogenic Fe(II) resulting from phyllosilicate iron reduction generally remains in the layer silicate structure. Simulated and measured breakthrough at several locations down-gradient of the injection gallery show good agreement.

ACKNOWLEDGEMENTS

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ADVANCES IN THE APPLICATION OF ELECTRICAL TECHNIQUES FOR SITE REMEDIATION

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Abstract

Electrical techniques in site remediation have advanced over the past 10–15 years as a result of the experience gained in their application to various types of waste and sites. The main advances have been in equipment design and construction combined with improvement in the understanding of the vitrification process. An overview is given of the advances together with an account of an application to a particular remediation problem.

1. INTRODUCTION

GeoMelt is a technique that has been in commercial use since 1989. It was invented by the Battelle Institute for the United States Department of Energy (DOE) for use in the in situ treatment of radioactively contaminated sites. Until recently, the process was used exclusively in a mobile form with the equipment being assembled on site. Now, permanent treatment facilities have been established in which the contaminated soil is brought to the plant for treatment — this is the case at the Japanese Daiei Kankyo facility.

The initial design was for fixed electrodes (initially six molybdenum electrodes) to be drilled into the area to be treated. Then electricity was applied to the fixed electrodes to promote the melting process. Over the years, the equipment has been modified with items such as the electrodes being changed to have graphite collars fixed over molybdenum inner rods. Nowadays, commercially available 'off-the-shelf' type graphite electrodes are used. The number of electrodes has been reduced to four, and sometimes only two electrodes are used for specific 'in container' type melts.

The off-gas capture hoods were initially made from a heat resistant fabric but after a fire they were replaced by hoods of fabricated stainless steel. These were effective but not easy to assemble. Later, a change to modular type panel hoods was made; this allows ease of assembly and reduces the requirements for lifting equipment on-site to move the hoods between melts.

Today the technology is used in different configurations (in situ, in container, staged and planar (starting to melt subsurface)) and the basic technology has become a very flexible and adaptable process capable of many different applications. Individual melts have been achieved in excess of 1000 tons in total.

2. PROCESS DESCRIPTION

GeoMelt vitrification uses graphite electrodes to supply alternating current from a GeoMelt transformer through the electrodes and into the contaminated soil or waste being treated. Gases generated by the vitrification process are captured in a hood covering the treatment area and drawn through an 'off-gas' treatment system before being released to the atmosphere (Fig. 1).

The temperatures reached in the process can be as high as 2000ºC. Organic materials in the soil are destroyed and heavy metals and radionuclides are incorporated into the vitrified product and immobilized.

Substantial volume reduction is achieved, usually a minimum of 50% and, depending on the contents of the soil/waste mixture, the volume reduction can be as high as 75–80%. Soil is the normal medium to which the technique is applied, but when it is applied to materials containing high levels of asbestos or fly ash, little or no soil is required in the melting process.

The off-gas treatment system used is varied depending on the waste being treated and the regulatory requirements applicable to the project. Usually, the configuration consists of a pre- or roughing filter, a thermal oxidizer (if required), a scrubber and mist eliminator, a heater and high efficiency particulate air (HEPA) and/or carbon filters. Specific additional requirements can be added if materials containing mercury and arsenic, for instance, are encountered.

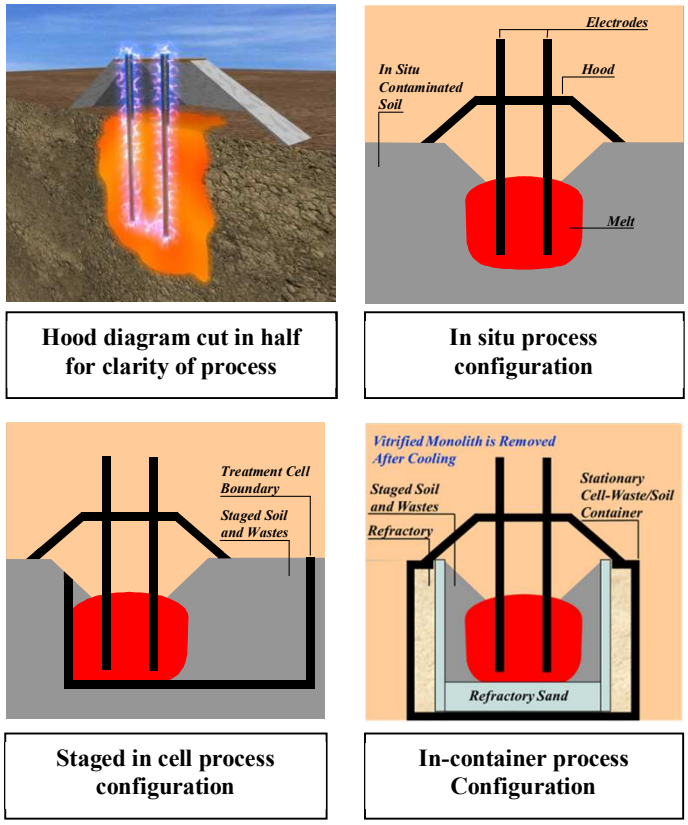

FIG. 1. Diagrams of the GeoMelt process application.

3. APPLICATIONS

GeoMelt has been applied to many varying types of waste containing organic and heavy metal contaminants or combinations of radionuclides and mixed waste. Summary tables (Tables 1 and 2) show previously treated waste types and radionuclides.

TABLE 1. SUMMARY OF SOME MATERIALS PREVIOUSLY TREATED

Heavy metals	Liquid organics	Solid organics	Solid debris
Pb	PCBs	Wood	Concrete
As	Dioxins	Rubber	Steel plates
Cd	Furans	Asphalt	Structural steel
Cr	TCE	PVC	Tyres
Ni	PCE	Polyethylene	Drums
Ba	Benzene	Neoprene	Rocks
Zn	Toluene	Paper	Bricks
Hg	Acetone	Cotton	Clay pipe
Cu	Formaldehyde	Polypropylene	Glass bottles
Al	Methylene chloride	DDT, DDD, DDE	Ash
Fe	Ethylene glycol	TBT, RDX, HMX	Tanks
Nd	MEK	Hexachlorobenzene	
Rb	Carbon tetrachloride	Ion exchange resins	

The materials in Table 1 have been treated either as part of an overall waste stream or individually, for example with items such as hexachlorobenzene or ion exchange resins.

TABLE 2. EXAMPLES OF RADIONUCLIDES TREATED

Am-241	Co-60	Pu-238	Tc-99
Ag-110m	Eu-152	Pu-239	U-234
Cs-134	Eu-154	Pu-240	U-237
Cs-137	Eu-155	Ru-106	U-238
Co-57	Mn-54	Sr-90	Zn-65
Co-58	Ni-59	Sb-125	Zr-95

4. PROJECT EXAMPLE

The rehabilitation of the Maralinga nuclear test site (Fig. 2) is representative of contaminated soil remediation at a large scale and in a remote location. The traditional in situ technique was applied; this allowed the greatest sized batch to be achieved.

FIG. 2. Layout of application at the Maralinga site (Taranaki burial pits).

The Maralinga site is a former nuclear weapons test range in South Australia used by the British Government in the 1950s and 1960s for above ground nuclear testing. Several hundred experiments involving conventional explosives resulted in plutonium (Pu), uranium (U) and beryllium (Be) being dispersed in the environment.

At the Taranaki area of Maralinga, 12 minor tests were performed that involved the explosive dispersal of 22 kg of Pu, resulting in large amounts of contaminated debris and soil that were placed in burial pits. The Taranaki pits were typically excavated by blasting in the native limestone. Several years later, concrete caps were placed on tops of the pits.

The cleanup of the Taranaki burial pits was part of the Maralinga Rehabilitation Programme managed by the Commonwealth of Australia. In 1989, GeoMelt was identified as the preferred technology for remediating the burial pits in a cooperative British/Australian study by the Maralinga Technical Assessment Group. Confirmatory testing and radioactive demonstrations were performed before dedicated equipment was designed and manufactured for remediating the pits. The pits were believed to contain ~ 2–4 kg of Pu; a similar amount of U; various metals including lead (Pb), barium (Ba), and beryllium (Be); and large amounts of debris (e.g. massive steel plates, steel beams, lead bricks, barytes shielding bricks, cable, and organic based materials).

A mound of silica sand was placed over each pit, and the GeoMelt equipment was positioned for treatment. The sand provided a level and uncontaminated base for workers to prepare the system. Melting was

initiated in the sand layer. The sand augmented the melt chemistry by providing more glass forming ions, which improved the chemical and physical characteristics of the vitrified product.

This project was completed in 1999 and achieved its primary objective of converting the loose, friable, radioactive contamination in the pits into dense, hard, intrusion resistant vitrified masses, eliminating the long term hazards of subsidence or human intrusion. The resulting vitrified monoliths (Fig. 3) of each pit were intrusively sampled and examined to characterize the vitrified product and confirm the completeness of treatment.

Specific project results are as follows:

- No partitioning or elevated concentrations of Pu were found in any of the monoliths;
- There was no indication that Pu was present in the melted steel phase, when such a phase was present at the base of the vitrified monoliths;
- Pu retention in the melts was >99.99%, which minimized the level of equipment contamination and the radiological hazard to workers. The hoods and off-gas piping did not require decontamination after any one melt;
- Samples of vitrified product from two of the full scale melts were subjected to the Product Consistency Test (PCT). The normalized release rates for the major oxides from the 28 day tests were substantially <1 g/m^2.day, with most release rates <0.1 g/m^2.day. Long term leach rate measurements (4.5 years) established that the normalized leach rates decline with time. The normalized leach rate for Pu decreased by over 1000 times during the leaching period, demonstrating that the vitrified product has outstanding leach resistance.

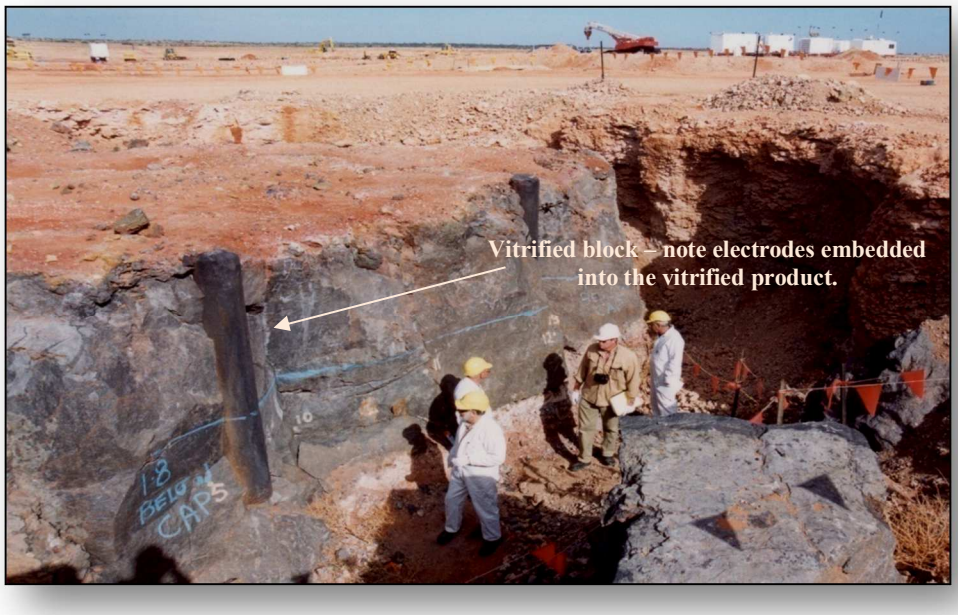

FIG. 3. Vitrified monolith of what was previously a burial pit.

The costs (Fig. 4) associated with traditional methods of containing waste such as uranium mine tailings are initially less than those of the GeoMelt process, but the ongoing costs of maintenance, dewatering, monitoring and repair/replacement of the containment media are substantially more than a permanent solution such as vitrification.

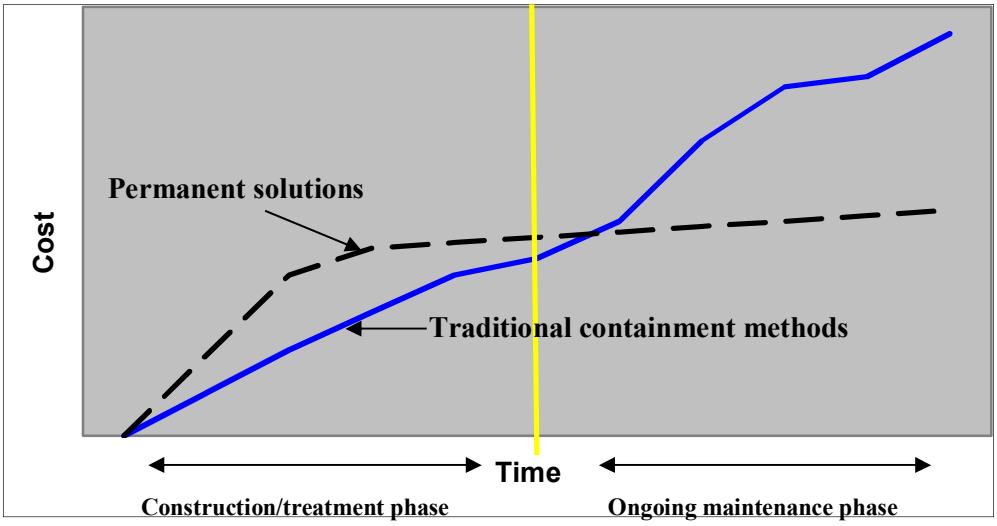

FIG. 4. Comparison of costs of remediation solutions.

5. SUMMARY

Advances made in the GeoMelt process of electric vitrification since its initial commercialization in 1989 have greatly increased its capability and flexibility. Projects such as that at Maralinga clearly show that the GeoMelt process of vitrification can be used for radioactively contaminated soil sites such as mine tailings.

SITE REMEDIATION IN PRACTICE

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Abstract

This paper describes the remediation of a former uranium mining area in Hungary. The work was carried out using stringent quality controls and special attention was paid to the radiological survey during the cleanup works on the roads, on pipe lines and yards, on the mill site and places used earlier for heap leaching. Groundwater quality control and the related groundwater quality restoration were the most important aspects of the post remediation phase which was aimed at the long term protection of the nearby drinking water aquifer. The expenditure for the remediation was approximately $100 million. The estimated cost for long term monitoring and water treatment is about US $4 million/year.

1. INTRODUCTION

Uranium mining and processing were developed in the southern part of the country in the Mecsek Hills, near to the county town of Pecs. The uranium mining activity lasted from 1958 to 1997. Approximately 47 million tonnes of rock were mined from 5 shafts and 19 million tonnes of ore were processed using acid leaching. Approximately 7.2 million tonnes of low grade ore were heap leached by an alkaline process. The uranium mining and processing was terminated in 1997 because of the high production cost. Remediation of the site started immediately after the termination of the production and was practically finished by 2008.

The mine ore, after radiometric sorting, was divided into three grade groups according to its uranium content:

- Waste rock (U < 100 g/t), dumped into three major waste rock piles (WP1, WP2 and WP3) and six smaller piles;
- Low grade ore (processed by alkaline heap leaching);
- Upgraded ore (processed in the mill using sulphuric acid leaching).

Elaboration of the remediation plan for the waste rock piles (WPs), heap leaching residues, mill tailings, etc. started with the estimation of the quantity and quality of waste, the composition of the seepage from the waste rock piles, the expected mine water composition and groundwater contamination in the immediate vicinity of the WPs. Based on preliminary site investigations and appropriate laboratory studies, field trials and feasibility studies, the general remediation plan was compiled. The overall plan comprised ten sub-projects according to the type of work to be carried out. In the separate sub-projects, the main technical data and schedules regarding the planned work were determined together with the arrangements for quality assurance. The expenditure for the remediation was provided from the State budget. During the remediation operations, particular attention was paid to the protection of the groundwater quality.

2. CHARACTERIZATION OF WASTE

Some important data for the characterization of solid waste are presented in Table 1. It can be seen that the uranium content and other radiological characteristics of the waste are much higher than those due to the naturally occurring radionuclides in the region; therefore the waste had to be remediated. First of all, it had to be covered with non-radioactive earth to isolate it from the possible direct contact with humans and to reduce further pollution of the environment.

The composition of the liquid waste is summarized in Table 2. The waters can be divided into two main groups:

- Waters with elevated uranium concentration (mine water, seepage from the waste rock piles);
- Groundwater with elevated dissolved solids (TDS) in the vicinity of the tailings ponds (TPs).

Remediation measures included water treatment for removing the uranium and quality restoration for groundwater in the vicinity of the tailings ponds. The groundwater restoration was a task of great importance because the water aquifer is situated almost in the immediate vicinity of the tailings ponds.

TABLE 1. CHARACTERIZATION OF THE ORIGINAL SOLID WASTE

Type of waste	Volume (million tonne)	Uranium content (g/t)	Radium concentration (Bq/g)	Gamma dose rate (mGy/h)
Waste rocks	19.2	50	~0.6	~0.5
Heap leaching residues	7.2	65	~1.2	~1
Mill tailings	20.3	68	~12	3–8*
Background in the region		~4–10	$\sim 5 \times 10^{-2}$	~0.1–0.2

* Depending on the tailings pond area selected.

TABLE 2. COMPOSITION OF THE LIQUID WASTE

Type of water	U (mg/L)	TDS (mg/L)	pH	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Ra (Bq/L)
Mine water* (Shaft N1 2001)	8	1600	7.1	260	205	140	890	120	0.7
Contaminated groundwater in the vicinity of WP (2001)	0.7	1250	7.3	160	320	160	390	60	0.02
Contaminated groundwater in the vicinity of tailings pond (1998)	0.02	14 700	7.2	740	490	1580	6680	1500	0.06

* Including collected seepage from waste rock piles.

3. SITE REMEDIATION AND MONITORING

3.1. Preliminary investigations

To determine the appropriate remediation measures it was necessary to carry out preliminary investigations. It was considered that the determination of the water contamination (groundwater and runoff waters) on and around the sites had the highest priority. For screening, for example on the tailings ponds site, a geophysical multi-electrode survey was used (Fig. 1). This measurement provided valuable information on the electric conductivity of the soil, and consequently on the contamination of the groundwater with inorganic compounds originating from the tailings water. This method proved to be very useful for determining the extent of the contaminated area and the depth penetration of the inorganic contaminants from the tailings ponds. Low resistive zones around the tailings ponds were found not only in the shallow zones but also in deeper zones because of the penetration of highly contaminated tailings water into these zones.

For the estimation of the amount of the contaminants in the groundwater, data from the material balance of the mill process was used. Taking into account the amount of the consumed acid (sulphuric acid for leaching, hydrochloric acid for the ion exchange process) and the amount of the neutralizing agents (lime, dolomite of the processed ore, etc.) and some other data, the loading of the tailings ponds with dissolved solids during the mill process was calculated. On the basis of these data, the concentration of the total dissolved solids in process water was estimated for the full period of the ore processing. The data are presented in Fig. 2.

These data show that on average the total dissolved solids in water was about 20 g/L and in total about 700 thousand tonnes of dissolved compounds (mainly $MgSO_4$, and NaCl) have been discharged into the tailings ponds. The dispersion of these dissolved solids around the tailings ponds was detected by means of the geoelectric survey.

3.2. Environmental monitoring

The environmental monitoring consisted of radiological, hydrological, geochemical, geotechnical and geophysical monitoring, as presented in Fig. 3.

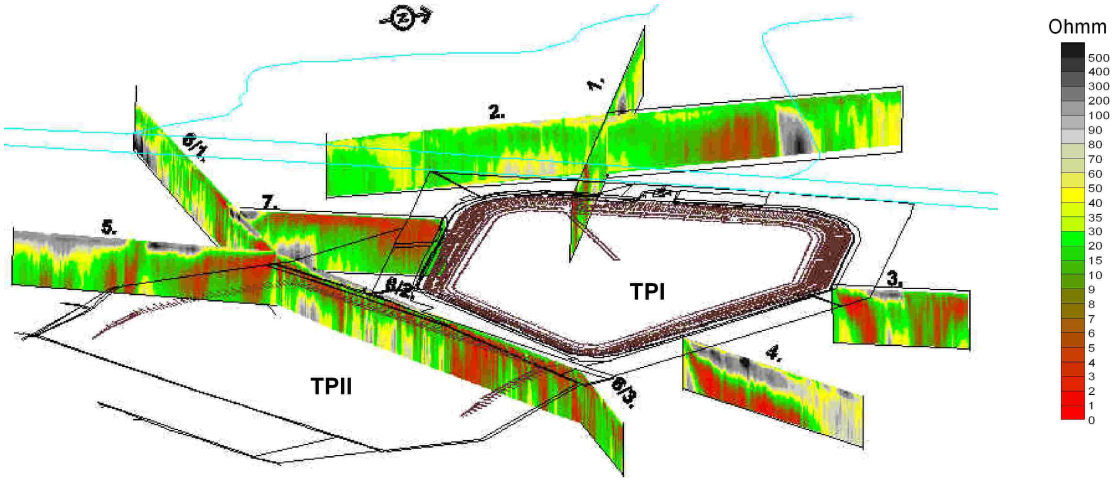

FIG. 1. Geophysical multi-electrode profiling of the tailings ponds site.

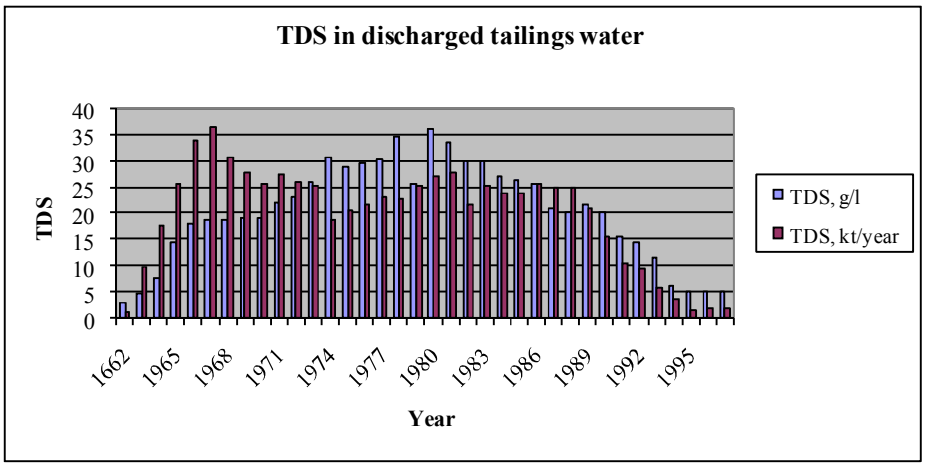

FIG. 2. TDS in process water discharged into the tailings ponds.

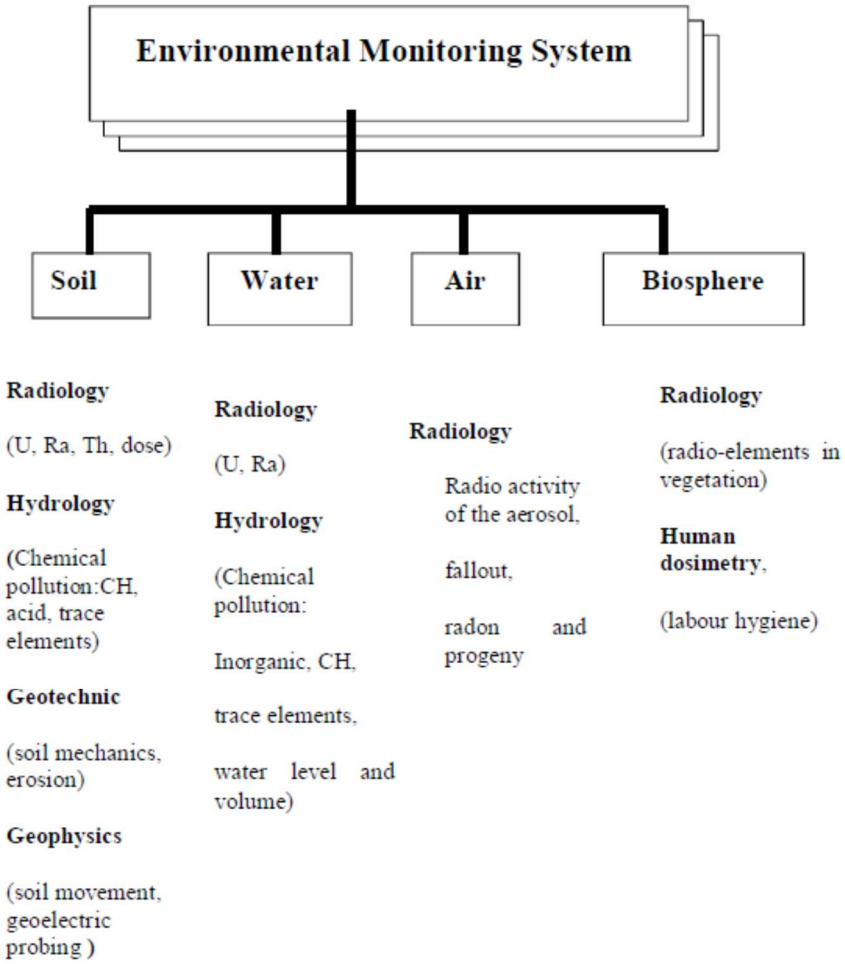

FIG. 3. Scheme of the environmental monitoring system.

Radiological monitoring was essential during the cleanup of different areas (yards, pipeline areas, roads, heap leaching sites, the mill site, etc.) in order to meet the cleanup standards. In practice, the excavation of the contaminated soil was carried out at the same time as gamma dose rate monitoring and the measurement of the specific activity of the soil. The cleanup procedure was continued until the relevant standards were met.

The radiological monitoring was important also for the estimation of the equivalent radiation dose to the population living in the vicinity of the remediated areas; this work was carried out using an automatic monitoring station placed in the village.

Hydrological monitoring was essential for protecting the surface and groundwater quality. The results were used for the cleanup of the contaminated sites, the planning of groundwater restoration systems, etc. The monitoring provided input data for the integrated water management of the former uranium mining and ore processing site, allowing the controlled discharge of all kinds of waters from the former uranium mining site through one common discharge basin. There were 612 sampling points in 2007, from which 1472 samples were collected and analysed for radioelements and other components.

3.3. Basic methods of radiological and hydrological monitoring

- In situ measurements and investigations (ambient gamma dose rate, ^{222}Rn, short lived radioactive aerosols etc., pH, Eh, electrical conductivity, etc.);
- Sampling and laboratory analyses of samples (soil, plant, aerosol, fallout, specific activity, gamma spectrometry, U, Ra concentrations in water, chemical composition, etc.);

– Automatic monitoring stations (dose components, different water parameters).

4. WATER TREATMENT

An inevitable part of the remediation is water treatment. This consists of the treatment of the mine water to remove the uranium (in the form of commercial concentrate) and the treatment of the extracted groundwater to reduce the total dissolved solids in the discharged water. The methods used are described in some earlier publications [1-3].

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MONITORED NATURAL ATTENTUATION OF METALS AND RADIONUCLIDES IN SOIL AND GROUNDWATER

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Abstract

Natural attenuation processes, which include a variety of physical, chemical or biological processes, can work to bring about the remediation of a contaminated site. Monitored natural attenuation (MNA) is a remediation approach which relies on these processes. The United States Environmental Protection Agency has established a four tier system for demonstrating that MNA is a viable solution for metal and radionuclide contaminated sites. To meet the criteria specified by this guidance requires a fundamental understanding of how geochemical conditions will change in the future. The United States Department of Energy has funded an applied research initiative led by the Savannah River National Laboratory aimed at increasing the understanding of the geochemical evolution of sites in the context of remediation. This paper describes the relevant regulatory framework and the use of geochemical gradients established by plumes as a framework for understanding waste site evolution.

1. INTRODUCTION

Although it has been ten years since Monitored Natural Attenuation (MNA) first became recognized as a viable remedy for groundwater remediation, there are relatively few records of decisions involving MNA being implemented for sites with metal or radionuclide contaminants. In the past, remediation has primarily consisted of attempts to remove contaminants from the subsurface by excavation or 'pump and treat' systems. Increasingly these approaches have come to be seen as inefficient and in situ immobilization of contaminants is now the favoured remedy at most sites. Whether explicitly stated or not, in situ remedies must ultimately rely on natural attenuation processes to keep contaminants immobile; this is, in fact, the desired end state of MNA.

A common misconception is that invoking MNA after active remediation is a means of abandoning the site without further obligation. To the contrary, the use of MNA in a remediation strategy requires a long term commitment to the site and can be a complicated process. Unlike organic contaminants that degrade, metals and radionuclides can persist in the subsurface indefinitely. The exceptions are radionuclides with short half-lives. However, uranium isotopes, plutonium isotopes, ^{99}Tc, ^{129}I and many of the actinides present at United States Department of Energy (USDOE) sites persist for thousands to millions of years. The continued presence of these in the subsurface following active in situ remediation requires site owners to prove, to the satisfaction of regulators and stakeholders, that the contaminants will not be a threat to human health and the environment over long time periods.

Three initiatives in the USA are directed toward facilitating the use of MNA in the context of metal and radionuclide contamination. The United States Environmental Protection Agency (USEPA) has issued two guidance documents describing the level of proof expected for demonstrating that MNA will be effective and the specific technical aspects that will ideally be considered for selected metals [1, 2]. Forthcoming documents from the USEPA are: a volume pertaining to MNA for selected radionuclides and an official policy statement on the use of MNA for inorganic contaminants. The Interstate Technology and Regulatory Council (ITRC) has convened a team to provide a framework for site owners, regulators and stakeholders to evaluate MNA as an option for metal and radionuclide contaminated sites. The third initiative, funded by the USDOE and led by the Savannah River National Laboratory (SRNL), is focused on developing approaches, tools and guidance that will facilitate achieving the required monitored natural attenuation end point for metal and radionuclide contaminated sites.

2. REGULATORY HISTORY OF MONITORED NATURAL ATTENUATION IN THE UNITED STATES

Natural attenuation strategies have been incorporated into environmental regulations and technical guidance since the early 1990s. The early guidance involved the attenuation of petroleum hydrocarbons; this was followed by guidance on chlorinated volatile organic contaminants (CVOCs), and, most recently, guidance on metals and radionuclides. From a technical perspective, the development of technical guidance has followed a logical progression from contaminants most amenable to destruction by robust and simple mechanisms to those that are not destroyed or for which destruction only occurs on the order of geologic timeframes. Many

organizations have produced technical guidance related to the natural attenuation of petroleum hydrocarbons and CVOCs. In the USA, the policy document that all natural attenuation based guidance documents are based upon is the USEPA Office of Solid Waste and Emergency Response (OSWER) Directive No. 9200.4-17P, titled 'Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites' [3]. This document lays out the groundwork for all MNA remedies. It defines MNA as:

> "…the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soils or groundwater. These 'in situ' processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay, and chemical or biological stabilization, transformation, or destruction of contaminants."

Regarding inorganics (metals and radionuclides), USEPA [3] states that:

> "…natural attenuation of inorganic contaminants is most applicable to sites where immobilization or radioactive decay is demonstrated to be in effect and the process/mechanism is irreversible."

The directive also provides guidance in terms of specific objectives that need to be considered for implementation of MNA.

The USEPA has subsequently issued two volumes that provide guidance for the implementation of MNA for inorganic contaminated sites http://www.epa.gov/ada/pubs/reports.html):

Volume 1 outlines the regulatory aspects of metals/radionuclides MNA and then describes a tiered approach for implementation and the use of modelling in the tiered screening process. After describing the chemical and microbiological controls over the fate of inorganic contaminants, Volume 1 reviews general site characterization requirements for metals/radionuclide MNA.

Volume 2 discusses the contaminant specific factors affecting the MNA of arsenic, cadmium, chromium, copper, lead, mercury, nickel, nitrate, perchlorate, selenium and zinc. Chapters are devoted to each of these and contain sections on occurrence and distribution, geochemistry and attenuation processes, site characterization, long term capacity and the application of tiered analysis for the particular contaminant.

A third volume on the MNA of radionuclides, including isotopes of americium, caesium, iodine, plutonium, radium, radon, strontium, technetium, thorium and uranium, as well as tritium, is in preparation.

The first three tiers in the approach for evaluating a site for MNA are progressive layers of evidence that contaminants will not pose a future threat [1]. If the criteria of the first tier are not met, MNA is not a viable option and the site owner can avoid the more complicated and expensive analyses required in Tier 2. Likewise, the site owner would only advance to collecting the additional data required for Tier 3 if the criteria of Tier 2 are met. The fourth tier is the design of a long term monitoring system and a contingency plan in the event that MNA fails.

The ITRC team on 'Attenuation Processes of Metals and Radionuclides' is currently developing a framework and flow chart, based on the USEPA four tiered approach, to guide users through the process of evaluating MNA for metal and radionuclide contamination.

3. USDOE APPLIED SCIENCE INITIATIVE

The USDOE applied science initiative is focused on improving understanding of the geochemical evolution of waste sites contaminated with metals and radionuclides and its use to increase the efficiency of remediation at these sites. It is fostering an approach to remediation that begins with the recognition that the desired end state of in situ remediation of metals and radionuclides is MNA. The approach encourages the idea that the characterization of a site and the selection of a remedy will ideally be consistent with the geochemical evolution of the site.

If a site meets all of the criteria up to and including Tier 3 of the USEPA approach for evaluating sites for MNA, then it has been sufficiently demonstrated that contaminants are unlikely to be significantly remobilized in the future. To achieve this requires a fundamental understanding of the future geochemical evolution of the site, since, with the exception of radioactive decay, all other mechanisms of attenuation and enhanced mobility are highly dependent on geochemical conditions within the aquifer.

To predict attenuation in the future is complicated because the factors controlling attenuation evolve with time. A contaminant plume is a transient perturbation of natural subsurface conditions that can change the chemistry, mineralogy and microbiology within the aquifer as the plume migrates. Over time, as the contamination source is depleted or contained, the plume will eventually migrate to an exposure point or dissipate and background uncontaminated groundwater will migrate through the zone traversed by the plume. The result of this sequence will be the long term evolution of the chemical, mineralogical and microbiological conditions within the affected portion of the aquifer. As these overall biogeochemical conditions evolve, attenuation processes of any contaminant metals and radionuclides will change in rate and magnitude. Thus, the long term prediction of whether natural attenuation processes can limit contaminant concentrations to below regulatory standards at exposure points requires an understanding of the overall biogeochemical evolution of the waste site.

One organizing principle to simplify the understanding of the overall biogeochemical evolution of waste sites is that the most dynamic changes in contaminant attenuation occur at biogeochemical gradients induced by the plume. Figure 1 shows a cartoon of a plume emanating from an industrial source at the surface. When the contaminant plume is introduced to the subsurface, a biogeochemical gradient is created at the leading edge of the plume, at the interface of the contaminant plume and natural groundwater. Dilution of the plume, reaction with aquifer minerals, adsorption of plume constituents, desorption of natural constituents and changes in microbiology can all occur at this gradient. In point of fact, different types of gradients move at different rates, though all are driven by the same hydrodynamic forces. For example, a leading gradient caused by dilution alone moves according to hydrodynamic forces and is unimpeded by chemical reactions. In contrast, a pH gradient is impeded by the buffering reactions associated with aquifer mineral dissolution and adsorption of free protons (H^+) to mineral surfaces. Likewise, a leading redox gradient can be impeded by microbiological reactions and reaction with redox sensitive aquifer minerals.

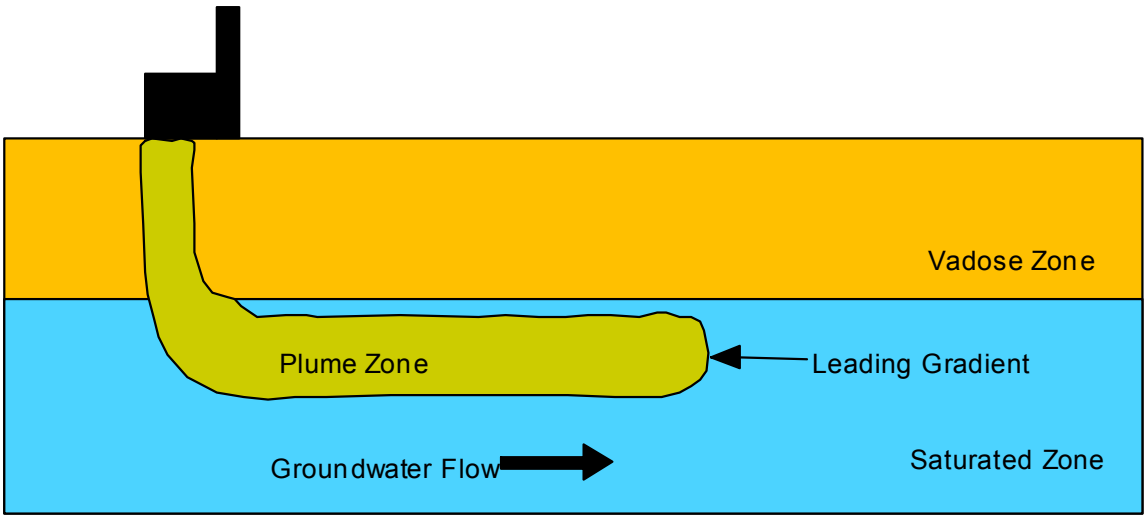

FIG. 1. Diagram showing a leading gradient at the front of a contaminant plume.

Trailing gradients form where natural up-flow groundwater meets the infiltrating plume or enters the zone affected by the plume. As long as plume infiltration is relatively constant, the trailing gradient is stationary. Once the plume flux from the vadose zone to the saturated zone is eliminated or substantially reduced, the trailing gradient migrates into and through the plume zone (Fig. 2). Trailing gradients are controlled by hydrodynamic forces, dilution, reaction with plume altered minerals, and the influx or elimination of nutrients to sustain microbial growth.

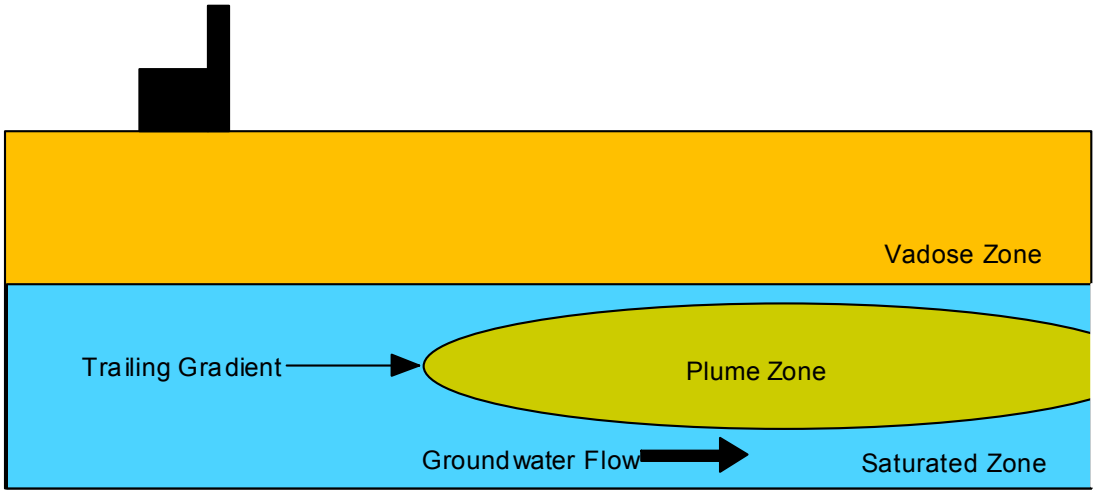

FIG. 2. Diagram showing a trailing gradient at the back end of a contaminant plume.

Examples of reactions with plume altered minerals are desorption of free protons from plume zone minerals or oxidation of reduced minerals created within the plume zone.

One way in which consideration of biogeochemical gradients simplifies the long term prediction of natural attenuation is that, for sites with multiple contaminants, the contaminants can be grouped according to how their migration is controlled. Some contaminants will be controlled only by dilution, some predominantly by pH and others predominantly by redox conditions. Large changes in contaminant mobility only occur across sharp gradients in these factors. Thus, the attenuation of contaminants is controlled by the migration rates of these gradients.

The other way in which consideration of biogeochemical gradients simplifies long term prediction of natural attenuation is that it compartmentalizes characterization and modelling into zones of importance. This is because large changes in mobility only occur across controlling gradients. Characterization and modelling will ideally be focused on the leading and trailing gradients, which are most important in controlling overall contaminant mobility. Consider, for example, an acidic plume with contaminants that are predominantly controlled by adsorption, which in turn is controlled by pH. It is more important to characterize what is present and down flow of the leading pH gradient than what is between the leading and trailing gradient. Likewise, it is more important to understand and model the processes occurring in those parts of the aquifer in the vicinity of the gradients; less emphasis can be given to parts of the aquifer between these gradients.

The use of geochemical gradients in the remediation of a waste unit at the Savannah River Site is discussed in Ref. [4]. At the waste unit site there is an acidic plume containing concentrations of uranium isotopes, ^{90}Sr, and ^{129}I that exceed regulatory limits. A remediation system that is consistent with the evolution of the waste site has replaced a costly 'pump and treat' system. The pH of groundwater passing through the gates of a hybrid funnel and gate system is neutralized, resulting in stronger adsorption of ^{90}Sr and uranium. Essentially, an artificial pH gradient has been installed that accelerates the return of the groundwater to its natural pH of 6; this system will be active until the natural trailing pH gradient reaches the funnel and gate. At this point, additional treatment will not be required and the desired end state of MNA will be achieved. An injectable amendment to immobilize ^{129}I in a way that is consistent with the evolution towards higher pH has been developed by SRNL and field testing is currently in progress.

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