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FIRS (Ferric Iron Remediation and Stabilisation): A Novel Electrokinetic Technique for Soil Remediation and Engineering

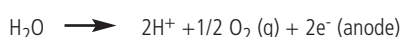
1. INTRODUCTION

A novel **electrokinetic** technology for groundwater protection, soil remediation and engineering called Ferric Iron Remediation and Stabilisation (FIRS), has been developed at the Universities of Brighton and Sussex. The technology involves the strategic, *in situ* precipitation of an iron-rich band, which provides a physical and chemical (i.e. sorptive) barrier to the migration of contaminated waters and liquids. In addition to the precipitation of the barrier, the applied electric field causes acid front generation and contaminant desorption, from soil/aquifer materials and **electro-osmotic** purging of **non-polar** contaminants.

This bulletin describes the theory and rationale behind the FIRS technique; details the developmental work carried out to date; discusses the potential applications of FIRS to contaminated land remediation and leachate containment, and evaluates the costs and benefits of the technology in relation to existing commercial remediation techniques.

2. ELECTROKINETIC REMEDIATION TECHNIQUES

Although clays and silts tend to **sequester** large quantities of heavy metals, radionuclides, and selected organic contaminants (Kovalick et al., 1995) they are relatively resistant to remediation with traditional technologies (e.g. pump and treat, soil washing) because of their low **hydraulic conductivities**. This has stimulated a considerable amount of research into cost-effective, *in situ* techniques that can be used to remediate low-permeability, high clay content soils. One emerging technology that has received much attention is electrokinetic remediation. Electrokinetics is a process that separates and extracts heavy metals, radionuclides, and organic contaminants from **saturated** or **unsaturated** clay-rich soils, sludges, and sediments under the influence of an applied electrical field. Experiments have shown its applicability to a variety of organic, inorganic and radioactive wastes (Acar et al., 1993; Kovalick et al., 1995; Virkutyte et al., 2002). The electrokinetic process involves the application of a low intensity direct current across **electrode** pairs that have been implanted in the ground on each side of a contaminated soil mass. Groundwater is **dissociated** at the electrodes via the reactions:



producing an acid front (due to excess H^+ ions) around the **anode** and an alkaline front (due to excess OH^- ions) at the **cathode**. The electric current causes electro-osmosis and ion migration, which moves both water and aqueous phase contaminants in the subsurface from one electrode to the other, and **electrophoresis**,

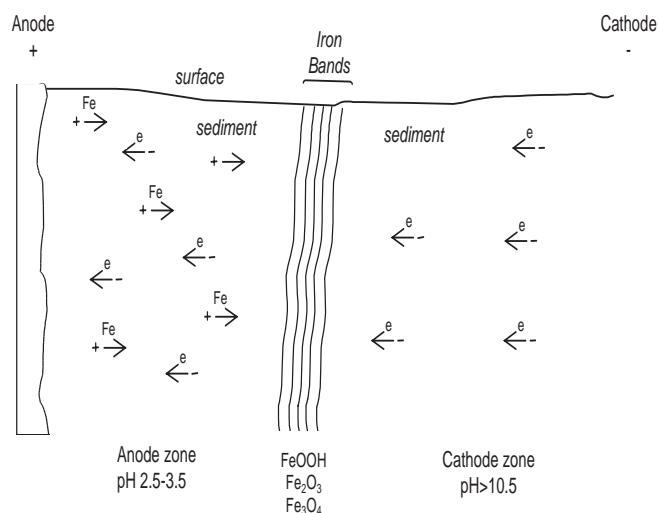


Figure 1: Adapted from Jacob et al., (1996) showing how electrolysis in the presence of iron sources (represented by vertical electrodes) buried in a sediment column can result in the spontaneous generation of iron bands.

which results in the migration of **colloidal** fractions. **Sorption**, precipitation and dissolution are accompanying reactions. Aqueous phase contaminants, and contaminants desorbed from soil particles, are transported towards the anode or cathode depending on their charge. In existing commercial electrokinetic systems, contaminants are commonly extracted by a secondary recovery system or deposited at the electrode. **Surfactants**, **complexing agents**, and other reagents are frequently used to assist contaminant movement (Acar et al., 1993; Virkutyte et al., 2002). However, most contaminated sites contain mixtures of contaminants rather than single contaminants, which makes remediation more complicated.

At present there is no standardised universal soil/sediment remediation approach. Instead there are numbers of technologies (e.g., Lasagna™, Electro-Klean™, electrochemical geooxidation), each of which has its own operational and design requirements, and limitations (Virkutyte et al., 2002). Many of these technologies are technically complex and energy intensive, and geared towards the removal of 90 % or more of specific contaminants, under very specific field or laboratory-based conditions. However, in the real environment a low-tech, low-energy contaminant reduction / containment technique may be more appropriate and realistic.

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This bulletin outlines work into a novel, natural analogue-based electrokinetic process for contaminant removal and containment at contaminated sites. This technique (FIRS - Ferric Iron Remediation and Stabilisation) involves:

- the strategic and remote electrokinetic placement of an iron-rich barrier to a required geometry, which provides a physical and/or chemical barrier to contaminants;
- the generation of a pH gradient to remobilise and/or trap contaminants within soils, sediments and slurries;
- the stabilisation and strategic dewatering/rewatering of soils / sediments/ slurries, and the forced and directed migration of contaminated leachates.

Unlike existing electrokinetic techniques FIRS provides a robust, non-selective and low energy approach to contaminant reduction and containment, and is based on natural iron mineralisation processes that occur in the near-surface environment. In addition, since the system mimics nature (e.g. the formation of iron pans), and iron is a common major element in rock and soil systems and is relatively non-toxic, the environmental impacts are minimal. Moreover, iron itself has well-documented contaminant-trapping properties.

3. BACKGROUND

Internal electric fields of the scale used in the FIRS technology (i.e. < 2 volts (V)) commonly occur naturally in rock and soil bodies and can arise from a variety of conditions. A common result of this phenomenon is the electrical generation of bands of iron-stone in uncemented sediments (e.g., Jacob et al., 1993). Such bands, which are found in many geological systems, can result when the electrolytic dissociation of water takes place, with the formation of an anode zone characterised by acidic ions (pH 2.0-2.5), and a cathode zone characterised by alkaline ions (pH 10.5-11.5). As a consequence of the potential difference a sharp boundary zone is developed within which an abrupt pH change from 2.5 to 8 occurs (Figure 1). Where sufficient iron is present in the system, spontaneous precipitation of insoluble metal (mainly iron) hydroxides occurs at the point of the pH "jump" (Jacob et al., 1993). In natural settings, such **ferric iron** bands are commonly poorly crystalline or amorphous (e.g., Hopkinson et al., 1998). Freshly precipitated amorphous or poorly crystalline Fe-rich solids are extremely effective scavengers of a range of heavy metals, radionuclides and organic contaminants in a variety of environments (Bendell-Young and Harvey, 1992; Cundy and Croudace, 1995). Moreover, **zero valent iron** itself is an important catalyst for the dechlorination of toxic chlorinated aliphatic compounds (Haran et al., 1996). The FIRS technique emulates these natural iron^{III} mineralisation processes, but over experimental rather than geological timescales, by applying a direct electric potential to electrodes to grow bands of iron^{III} mineral phases in sediment and soil columns, and to harness their adsorptive properties, to trap or break down contaminants from the aqueous phase, or extracted from soil particles.

4. EXPERIMENTAL WORK

Pilot studies have been applied at laboratory scales in 25 x 2 x 15 cm and 30 x 50 x 40 cm open topped perspex cells (i.e. effectively in two-dimensional and three-dimensional space). All experiments have been run at < 5 V, using sacrificial cast iron electrodes, in a variety of sands and contaminated muds, with groundwater and seawater interstitial pore waters, under unsaturated and saturated conditions. Timescales ranged from 3 - 400 hours. In every case, a strongly acidic zone was generated around the anode (approx. pH 2), and an alkaline zone around the cathode (approx. pH 13). At the point of abrupt pH change, approximately equidistant between cathode and anode, a 1 - 4 cm thick, coherent, iron stone was precipitated (Figure 2) having an approximate uniaxial compressive strength comparable to a moderately **lithified** sandstone (or the strongest Chalks in southern England). The iron stone generated consists of an amorphous iron band (see Figure 3a), or, in sandy sediments, a coating of zero valent iron and iron oxides which cement mineral grains. The presence of zero valent iron in the Fe-rich band is noteworthy since a large proportion of permeable reactive barriers employed at contaminated sites are based on the use of zero-valent iron to act as a powerful chemical reductant for **chlorinated aliphatic compounds** dissolved in groundwater (Younger, 2002). It is also possible to rapidly generate a dispersed sorptive coating of iron on a pre-defined area of soil without significant loss of **porosity**, simply by switching off the current before the Fe-



Figure 2: Sub-vertical, 1 cm thick Fe-rich band generated in water-saturated sands after 30 hours application of a 1.5 V potential difference between cast iron electrodes.

band fully develops (Figure 3b). Such an approach may be desirable in situations where the sorptive properties of iron can be harnessed to reduce the concentration of specific contaminants, such as arsenic (As), in groundwater.

Two specific studies are presented here which illustrate the applicability and potential of the FIRS technique for containing leachate and dissolved phase contaminants and remediating contaminated land.

4.1 Hydrocarbon and heavy metal contaminated sediments, Southampton Water

An estuarine mud sample, contaminated with copper (Cu) and petroleum hydrocarbons from the nearby Fawley oil refinery and from discharges from local shipping, was treated using a voltage of 2 V, in a three-dimensional cell using a

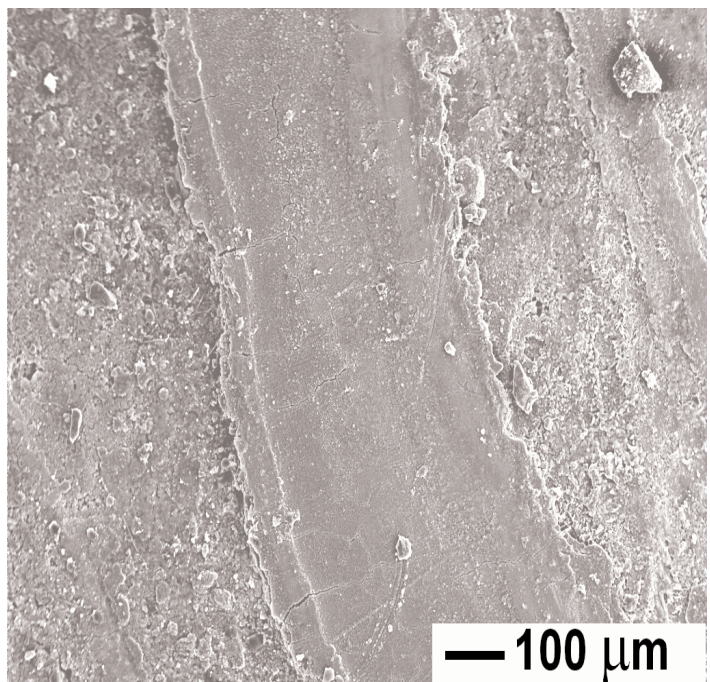


Figure 3a: Generation of amorphous Fe band in clay soil medium using FIRS technique.

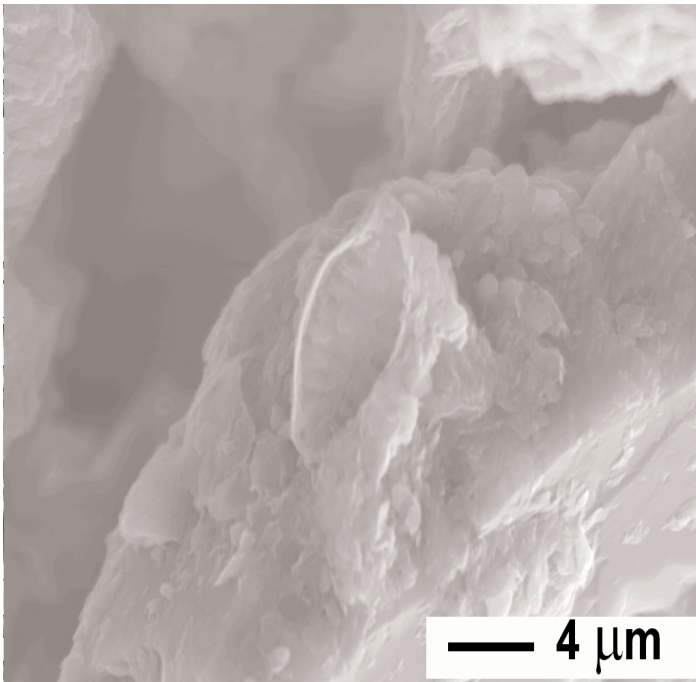


Figure 3b: Diatom (marine micro-organism) which, together with the underlying silt particle, has been coated and cemented by iron.

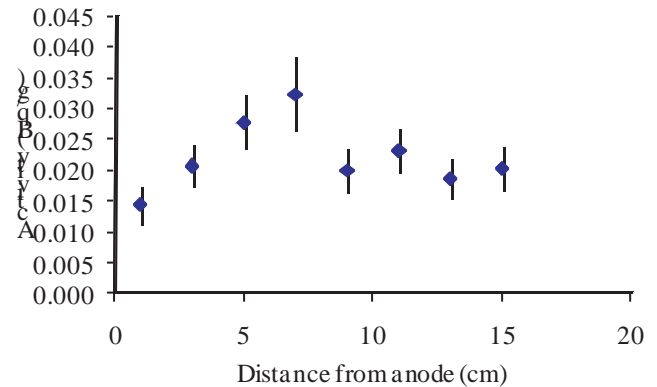
rectangular electrode array. A continuous iron band of up to 3 cm thickness was generated from the electrode point sources. Data for pre- and post-treatment Cu concentration indicate that the electrokinetic treatment resulted in an approximate reduction of 61 % in Cu contamination in the anode zone in 16.3 days (note that a small proportion of Cu is natural background Cu held within the crystal lattice of stable minerals. This naturally occurring Cu is not influenced by the electrokinetic process). Notably, liquid hydrocarbon-rich effluent was expelled from the sediment (via electro-osmotic purging) and channelled and drained at approximately 10 ml per day from the surface of the cathodic compartment. The energy requirement for the experiment was 10.9 kW/m³. These values compare favourably against commonly cited energy requirements for other electrokinetic remediation systems, e.g., 500 kW/m³ for 100 % removal of metal contaminants (Virkutyte et al., 2002). The timescale for copper decontamination and hydrocarbon purging from the sediment is comparable in duration to existing technologies which employ comparatively expensive cation-selective membranes (Van Cauwenberghe, 1997). The use of cast iron electrodes (as opposed to gold coated, platinum or graphite electrodes), means that the experimental system is low cost in terms of energy, materials and electrode construction, which typically make up ~70 % of the costs associated with any electrokinetic remediation system (Ho et al., 1997).

4.2 Radioactively-contaminated sediment, Ravenglass, Cumbria

A clay-rich sediment sample, slightly contaminated with artificial radionuclides, was collected from the Ravenglass estuary, Cumbria and treated at 1.5 V for 410 hours in a two-dimensional perspex cell, using an electrode separation of 17 cm. A 17 mm thick Fe-rich band was generated 5 cm from the anode, at the point where a major step in pH (from pH 2 to pH 13) occurred. Geochemical and radiometric analysis of the treated sediment (see Figure 4) shows clear removal of radioactive cobalt (⁶⁰Co) from the anode zone of the cell, and precipitation of the remobilised ⁶⁰Co on the iron-rich band. This was achieved in a short 17 day timescale compared with commercial systems which typically operate over durations of 20 - 100 days. Manganese (Mn), calcium (Ca) and strontium (Sr) were also remobilised from the anode zone and precipitated on, or around, the iron band. Soluble ions such as iodine (I), bromine (Br) and sodium (Na) migrated towards the appropriately charged electrode. Notably, As, present as a trace contaminant in these sediments, was highly amenable to the FIRS treatment, with desorption occurring at high pHs in the cathode zone. A 100 % enrichment of As occurred on the iron-rich band (see Figure 4), reflecting the strong affinity of As for the amorphous precipitated Fe.

The highly particle-reactive radionuclides plutonium (Pu) and americium (Am), present at elevated activities in this sediment, were not significantly remobilised over

Co-60 - radionuclide harvesting stage 1



As - radionuclide harvesting stage 1

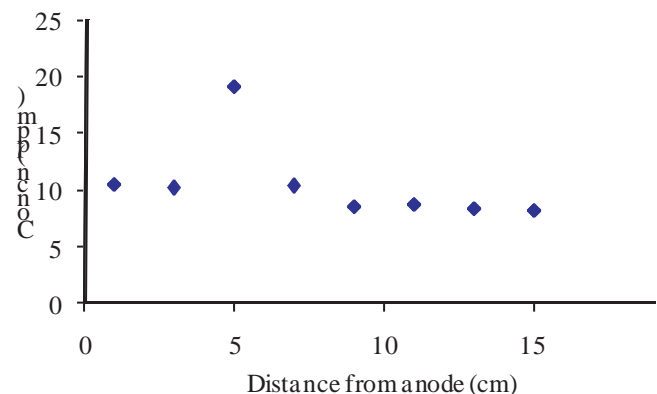


Figure 4: ⁶⁰Co and As data for treated Ravenglass mud. Fe band is located 5cm from the anode. Note change in y-axis units, with ⁶⁰Co in Bq/g (or atomic disintegrations per second per gram) and As in ppm. Error bars on As data are smaller than the diamond marker symbol used. Note ca. ~40 % reduction of As in cathodic compartment, and ~100 % enrichment in narrow iron band. Reduction in ⁶⁰Co is less notable, but still exceeds 30 % in the anode zone (compared to the untreated material). A ~50 % enrichment in the iron band compared to untreated material (which corresponds to a ~110 % enrichment in ⁶⁰Co over the anode zone) is also observed.

the timescales used. The FIRS system however can still be used to contain leachates contaminated with these radionuclides due to:

- the action of the Fe band as a barrier to groundwater flow,
- the strong association of Pu and Am with freshly precipitated amorphous iron oxide phases, and
- the action of the applied electric field, which forces ionic and colloidal species to migrate towards the appropriately charged electrode.

In summary, unlike existing electrokinetic techniques which actively avoid precipitation of minerals and salts in the soil mass between the two electrodes, the FIRS technique is specifically geared towards producing an iron-rich band *in situ* between cathode and anode. This iron band simultaneously provides a physical as

well as a chemical barrier to leachate migration. FIRS also employs a low voltage (with low energy requirements) to generate a strong pH gradient within soils and sediments and can desorb a range of **polar** and **ionic** contaminants. It uses low cost, sacrificial cathode and anode materials, and can produce, through differential dewatering, water movement and electro-osmotic purging of non-polar organic contaminants.

5. ON-GOING WORK

On-going work on the FIRS technology is focusing on a detailed evaluation of its application to a range of organic contaminants, detailed geotechnical tests on treated soils, and the optimisation of electrode arrays to enable three dimensional production of iron-bands to a desired geometry. An EPSRC-funded programme will examine the applicability of the technique, and the optimisation of its remediation capacity, in a range of heavy-metal contaminated soils and sediments. In addition, following the promising results on decimetre-scale soil cells outlined above, the system will be scaled up to metre-size soil cells in "field-scale" laboratory trials. Since a critical consideration both for electrokinetic techniques and remediation technologies in general is the impact of site and contaminant heterogeneity, the soils used will contain natural and/or introduced sediment heterogeneity (i.e. through additional of sand, rubble and other debris) to simulate environmental heterogeneity or conditions in made-ground. Following optimisation of electrode configuration and depth, applied voltage etc. in these larger cells, a system will be tested at field scale.

6. POTENTIAL FOR FIELD USE

The FIRS technique has significant potential for field-scale use, as it has already been successfully applied in decimetre-scale three-dimensional cells, in a range of soil and sediment types, in low and high-ionic strength groundwaters, and in the presence of a range of contaminants. FIRS also mimics a natural system that operates over scales in excess of 10 m in geological systems. The low voltage and current used mean that power requirements are likely to remain low even when the system is scaled up, and, coupled with the flexibility provided by the use of multiple, low cost electrodes means that contaminated land can be sequentially treated with a series of electrode arrays, whereby the distance between individual electrodes does not exceed a few metres. In addition, the current is sufficiently low to avoid soil heating and large-scale gas generation at the electrodes. More generally, a key feature of the technique is that it can be used cost-effectively on small sites, and on active sites or sites with infrastructure. Adjustable electrode geometry means that the technique can be adapted to suit site-specific conditions, and large areas of land can be sequentially treated. Following treatment, the iron band can simply be excavated as a coherent mass, or left *in situ* to provide a long-term, inert, and, via reapplication of current, resealable, barrier.

Importantly, the mimicking of natural geological processes, coupled with the system's low power requirements and use of low cost materials (e.g. scrap iron), mean that the FIRS technique has the capability of forming a cost-effective, sustainable technology, with chemical and engineering applications, ideal for field use both in developed and developing nations.

7. SUMMARY

The FIRS technology, while currently still at prototype, bench scale, shows considerable promise as a technique for groundwater protection and contaminated site remediation. The FIRS technology generates a resealable iron-rich barrier, which can be remotely placed (without engineering) at working sites and sites with infrastructure to physically and chemically inhibit subsurface contaminant migration, and can redirect subsurface pollutant flow. In comparison with commercial electrokinetic remediation techniques, FIRS has an order of magnitude lower energy requirements and electrode cost, and does not involve the use of potentially toxic conditioning solutions. The system can be operated in combination with, or as an alternative to, existing land remediation technologies. The technique is applicable to small sites, as well as to larger areas of contaminated land, and can be implemented

in ground where man-made structures are present, or where there is on-going site activity.

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