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ABSTRACT
This paper details the development (and implementation) of a novel, low-cost electrokinetic soil clean-up method for treatment of Pu-labelled soil wastes at the AWE Aldermaston site, Berkshire, U.K. Nuclear weapons manufacture and maintenance, and related research and development activities, have been carried out at the Aldermaston site for over 50 years, and these historical operations have generated a number of contaminated land legacy issues, including soils which contain above background (although radiologically insignificant) specific activities of Pu. Much of the Pu-labelled soil has been removed (via soil excavation), and is held in containment units on site, prior to remediation / decommissioning. Based on initial small-scale laboratory trials examining the potential for Pu removal and directed migration under a low intensity electrical field, a two year project (funded by the former UK Department of Trade and Industry and AWE PLC) has been implemented, and is reported here, involving a focussed programme of laboratory trials followed by a full-scale field trial to examine the potential of low-cost electrokinetic techniques to reduce the activity of Pu in clay-rich site soils, and reduce site waste disposal costs. Pu (and U) exhibited relatively complex behaviour in the laboratory trials, with Pu forming mobile soluble oxyanionic species under the high pHs generated by the electrokinetic treatment technique. Clear mobilisation of Pu and U (along with a range of other elements) was however observed, in a range of soil types. The relative efficiency of remobilisation was element-dependant, and, in terms of heavy metal contaminants, radionuclides, and the stable analogues of radionuclides known to be problematic at other nuclear sites, was (from most to least mobile) Cl > Zn > Sr > U > Pu > Pb. Both Pu and U showed enhanced mobility when the low-cost soil conditioning agent citric acid was added prior to electrokinetic treatment. Full-scale field trials of the treatment method during summer 2008 involved ex-situ, but on-site, treatment of soil wastes in a lined steel cell, using low-cost materials (e.g. portable 12V batteries, cast iron electrodes), over a 2 month period. The development and field-scale implementation of the remediation technique on a working nuclear site involved the development of a detailed safe system of work, with standard operating and Quality Assurance procedures, and the involvement and cooperation of a range of on-site and off-site organisations. The implications of:
- the laboratory and field trial data; and
- the site and regulatory requirements for the implementation of the clean-up process
for the application of similar remediation or waste management methods on other nuclear sites are described and evaluated here.

INTRODUCTION
The Atomic Weapons Establishment (AWE) has manufactured, maintained and decommissioned the UK’s nuclear deterrent for over 50 years. During this time the AWE Aldermaston Site, Berkshire UK has accommodated weapon manufacture, maintenance and related research and development activities. The historical activities and operations undertaken at AWE have generated a number of contaminated land legacy issues, including soils which contain above background (although radiologically insignificant) specific activities of Plutonium (Pu). Much of the Pu-labelled soil has been removed (via soil excavation), and is currently held in containment units on site, prior to remediation / final disposal.
With increasing emphasis on sustainable waste management practices and increasing costs of disposal of wastes to specialist landfill sites, low cost effective remediation / waste minimisation techniques have become increasingly attractive to AWE, some of which may generate significant cost savings. As such AWE has invested significant resource investigating the feasibility of numerous waste minimisation techniques. One remediation technique which was identified as having significant potential was the Ferric Iron Remediation and Stabilisation (FIRS) technique. Conceived by academics at the University of Brighton (Prof. Andrew Cundy and Dr L Hopkinson) this novel, low cost, robust, non selective electrokinetic method of contaminant remediation and stabilisation is currently under development as a potential in-situ and ex-situ remediation technology. Since FIRS is a non-selective technique for trace element remediation it also has potential to address high volume, low level radioactive contaminated soils and sediments (Cundy and Hopkinson 2005).

Following a small scale initial feasibility study examining the potential for actinide mobilisation and directed migration under a low intensity electrical field the decision was made to invest in FIRS development, and attempt to develop FIRS from a prototype to a field scale remediation technology on the AWE site, to reduce the activity of Pu in clay-rich site soils, and reduce site waste disposal costs. A two year work programme was developed with joint funding from AWE and the UK government, under the Knowledge Transfer Partnership Programme (KTP), a government incentivised scheme to encourage collaboration and knowledge transfer between academia and industry.

The work programme included a focussed series of laboratory trials to investigate controlling variables within the system, followed by an intermediate scale trial to inform development of a field scale trial. Finally a full-scale field trial was implemented to examine the potential of the low-cost electrokinetic technique to act as a waste minimisation technique, i.e. to concentrate actinides into a small volume of soil, leaving the bulk of the soil waste beneath the Radioactive Substances Act Substances of Low Activity (RSA93 SoLA) exemption order levels to reduce waste disposal costs.

Here, we detail the development and implementation of the FIRS technology on the AWE Aldermaston site, and discuss the implications of:

- the laboratory and field trial data; and
- the site and regulatory requirements for the implementation of the clean-up process for the application of similar remediation or waste management methods on other nuclear sites.

BACKGROUND

Low-energy electrokinetic remediation, Ferric Iron Remediation and Stabilisation (FIRS). Electrokinetic remediation is an emerging technology that has generated considerable interest as a technique for the in-situ remediation of low hydraulic conductivity, clay-rich, soils and sediments (e.g. Acar and Alshawabkeh, 1993; Probst and Hicks, 1993; Reddy et al., 1997; Virkutyte et al, 2002, Cundy and Hopkinson 2005, Hopkinson et al 2008). Despite a variety of promising experimental results, however, at present there is no standardised universal electrokinetic soil/sediment remediation approach. Many of the current electrokinetic technologies are technically complex and energy intensive, and geared towards the removal of 90% or more of contaminants, under very specific field or laboratory-based conditions. However, in the real environment a robust, low-energy contaminant reduction / containment technique may be more appropriate and realistic. The Ferric Iron Remediation and Stabilisation (FIRS) technique (Cundy and Hopkinson 2005, Faulkner et al 2005) is an alternative electrokinetic method based on naturally-occurring geological reactions, and involves the application of a low magnitude (typically less than 0.2V/cm) direct electric potential between two or more sacrificial, iron-rich, electrodes emplaced either side of a contaminated soil or sediment. The electric potential is used to generate a strong pH (and Eh) gradient within the soil column (ca. pH 2 – 13) (figure 1), mobilise dissolved iron into the soil via anodic dissolution, and force the in-situ precipitation of an iron-rich barrier or “pan” in the soil between the electrodes. This iron-rich barrier, consisting (dominantly) of amorphous ferric oxyhydroxides,
goethite and other Fe phases (Faulkner et al 2005) is effectively impermeable (permeability = $10^{-9}$ m/s or less), and can be generated in a variety of geometries (including horizontal geometries) to allow creation of protective layer(s) between sensitive receptors and sources. During the electrokinetic treatment, soil contaminants are:

(a) remobilised and concentrated on or around the precipitated iron-rich barrier (which can then be excavated), or

(b) (in the case of redox-sensitive contaminants such as Cr) reduced and stabilised with Fe-oxide and oxyhydroxides phases in the soil.

The system uses approximately a tenth of the energy requirements of most conventional electrokinetic systems, and has been successfully applied at laboratory bench top scales in a range of soil and sediment wastes, containing a variety of common contaminants (e.g. As and $^{60}$Co (Cundy and Hopkinson (2005), Cr (Hopkinson et al 2008)).

Figure 1. Schematic diagram of FIRS setup and key processes including development of pH regions in treated soil.
EXPERIMENTAL PROGRAMME

An 18 month programme of experimental work (figure 2) was devised to rigorously and robustly assess controlling variables within the system and to identify the operating parameters at which remediation using FIRS is most effective in AWE site material.

The key controlling variables are

- The Potential Difference across the electrodes
- The ionic strength of the pore water / water / conditioning agents added to the system
- The mineralogical and physical characteristics of the soil

In addition to investigation of variables within the system, testing to assess field scale trial design was undertaken; specifically electrode placement and arrangement were assessed, and field monitoring equipment and electrical distribution systems were tested before use in the field.

All laboratory-scale trials were undertaken at the National Oceanography Centre, Southampton UK, using samples of AWE contaminated soils and sediments.

Analytical techniques employed included:

- X-ray Fluorescence, to assess elemental composition of soil samples;
- X-ray Diffraction, to assess mineralogy of soil samples;
- ITRAX (scanning X-radiography / X-ray Fluorescence), used for mapping trace element distribution within a mass of soil;
- Low background Gamma Spectroscopy, to measure low levels of specific actinides and other radionuclides;
- Alpha Spectroscopy, to measure activities of specific actinides;
- Gross Alpha Beta analysis, to assess the total alpha and beta activity in a given sample.

Each experiment was designed to assess a particular variable and identify optimum operating parameters that increase FIRS effectiveness.

Field Scale Trials were undertaken onsite at AWE Aldermaston. Analytical techniques employed for the field scale trials to assess trace element and actinide mobilisation and redistribution were;

- Portable X-ray Fluorescence; to assess elemental composition of soil samples
- Gamma Spectroscopy
- Gross Alpha Beta analysis
- Radiochemical analysis for Pu and Am
Each stage of experimentation was dynamic; the experimental design was revised to ensure that the data sets obtained address individual variables and the design of the experiments was revised to ensure time and resources were used efficiently, allowing for multiple trials to be conducted simultaneously.

Full details of the laboratory trials are beyond the scope of this paper and will appear elsewhere, but the following section summarises the key findings in terms of the evolution of the testing process and informing field scale design and implementation of the remediation technology.

**FEASIBILITY STUDY; PROOF OF CONCEPT TRIALS**

Objective: to prove initial proof of concept / applicability of FIRS to AWE site material, prior to initiation of full technology development programme. Treatment of two 21 cm test cells for 42 days at 2V, one conditioned via addition of citric acid powder.

Findings
1. Clear development of pH gradient observed in treated material
2. Range of trace elements and actinides were mobilised and concentrated during treatment. Relative efficiency of mobilisation Cl > Zn > Sr > U > Pu > Pb
3. Significant release of Pu into pore waters occurred during treatment
4. Enhanced mobility of Pu and U was observed when citric acid was used as preconditioning agent

**MAIN LABORATORY DEVELOPMENT PHASE: INVESTIGATION OF CONTROLLING VARIABLES**

**Voltage Trials**
Objective: to identify operating voltages across the electrodes which induce significant trace element and actinide mobilisation.

Experimental Setup: Four cells (measuring 24 x 16 x 14 cm) each with a pair of electrodes emplaced in soil at 15 cm separation (see figure 1) were connected to power supplies set to 20V, 10V 3V and 0V. The soils were treated for 70 days before the experiments were terminated and the soils destructively sampled and analysed.

Findings
- pH and periodic monitoring suggested the carbonate content of the soil was buffering the establishment of the acidic pH region around the anode.
- Visually, there was evidence of Iron and Manganese mobilisation and redistribution at higher voltages 10v and 20v.
- White salts were precipitated on the cathode.
- ITRAX analysis confirmed significant trace element mobilisation had occurred at approx 20v potential difference across the electrodes (figure 3).
- Gamma Spectroscopy and Radiochemical analysis confirmed mobilisation and redistribution of actinides within the mass of soil.

**Figure 3. Data from ITRAX analysis showing Trace Element Mobilisation at 20V**

X axis shows distance; Y axis shows X-ray response. Anode:cathode separation = 15cm.
Ionic Solution Experiments
Objective: To assess the effect of porewater ionic strength, and use of conditioning solutions on FIRS effectiveness at mobilising trace elements and actinides.

Experimental Setup: Experimental design was revised to increase experimental efficiency. The soil was physically separated into its component size fractions. The < 710 µm (fine) fraction was transferred into 50cm long; 15mm bore flexible plastic tubing bent into a U-shape. A glass tube fitted with a frit was attached to an end and filled with water. The anode was positioned in the soil while the cathode was positioned in the water (figure 4). The U Tubes were then connected to power supplies set at 10V and 20V.

Figure 4. U Tube Experimental Design

Findings
- The revised design was extremely effective, experimental duration was quartered.
- Well-defined pH regions were established at both the Anodic and the Cathodic electrodes.
- Visual observations confirmed significant trace element mobilisation, iron and salt precipitates were observed.
- Gamma Spectroscopy and Radiochemical analysis confirmed significant mobilisation of actinides had occurred in experiments treated with citric acid, AWE ground water and saline water.
- Experimental design limited the application of ITRAX to analyse trace element mobilisation and redistribution, i.e. the U-shape plastic tube could not be analysed as the geometry was inappropriate.

Acrylic Tube Experiments
Objective: to assess FIRS effectiveness at mobilising trace elements and actinides using a combination of soil pre-treatment and conditioning agents.
Experimental Setup: The experimental setup was revised, this time to facilitate trace element analysis. Similar to the U tube arrangement, the < 710 micron fraction was transferred to a 30cm long rigid horizontal acrylic tube which had been modified so that the ends of the tube were vertical. Prior to transfer the soil was also pre conditioned with citric acid to neutralise the carbonate in the soil. In these experimental trials the electrodes were sited in heads of water at either end of the soil mass.

Findings:
- Pre-treatment to neutralise the carbonate content of the soil aided rapid development of distinct low and high pH regions around anode and cathode.
- The citric acid also dissolved contaminants into the aqueous phase, an excess of citrate formed negatively charged complexes with actinides and significant mobilisation and redistribution of actinides was confirmed by radiochemistry and gamma spectroscopy (figure 5). Plutonium formed oxanionic species.

Figure 5. Pu, U, Fe and Mn distribution in electrokinetically treated soil material. The horizontal line on the upper graph shows baseline specific activities in homogenised, untreated material.
- The revised experimental design allowed trace element analysis to be employed; XRF analysis confirmed significant trace element mobilisation and redistribution (illustrated by iron and manganese data, which show clear migration of each element to, and concentration at, the cathode).

**Soil Composition Experiments**

Objective: To assess the role of varying soil composition on FIRS effectiveness.

Experimental Setup: Reverting back to an experimental design similar to the original experimental setup, three different soils / sediment types from the AWE site (each representing different soil types present on site) were transferred to treatment cells measuring 24 x 16 x 14 cm. The anode and cathode in each cell were sited in sand wells to facilitate water movement around the electrodes. Each pair of electrodes was separated by 15 cm of sand and soil. The electrodes were connected to a 20 V power supply. The soils were treated for 50 days, following which trace element and radiochemical analysis was undertaken to assess FIRS effectiveness at remediation of varying types of contaminated soils and sediments.
Findings:
- The revised experimental design increased FIRS efficiency at establishing pH regions around the anode and cathode. The increased porosity and permeability of the sand increased water ingress and dissociation at the respective electrodes.
- pH gradients were established in every soil type once the buffering capacity of the soil had been overwhelmed.
- Periodic monitoring and visual observation suggested significant iron and manganese mobilisation.
- One particular batch of soil showed marked trace element mobilisation and redistribution, so much so that a Manganese / Iron band was emplaced in the soil mass toward the cathode.
- Gamma Spectroscopy and Radiochemistry are currently work in progress.

INTERMEDIATE SCALE TRIAL
Objective: to assess / prove the experimental design prior to full scale testing

Experimental Setup: An intermediate-scale trial was employed on AWE site material at greater electrode separations, using a parallel electrode array (figure 6), to prove the experimental design at larger scales prior to full-scale testing. Electrodes were sited in sand wells following the observed increase in FIRS efficiency induced by this approach (see above). The experiment was run for 3 months at 24V.

Figure 6. Intermediate Scale Trial Experimental Setup. Scale bar is 30 cm (12 inches)

Outcome:
- The experimental design was confirmed effective, pH gradients were established more rapidly using sand wells.
- Iron mobilisation was apparent visually.
- Although the experiment has been completed analysis and interpretation of the trace element and radiochemical data sets is currently work in progress.
- The intermediate scale trial confirmed the applicability of the revised electrode configuration, and the applicability of the electrokinetic effect over larger electrode separations.

FIELD SCALE TRIALS
Objective: To assess FIRS effectiveness at mobilising, redistributing and remediating actinide contamination in large masses of soil. To assess FIRS effectiveness as a field scale remediation technique.

Experimental Setup: For the past decade the contaminated soil has been stored in a weather proof containment units, resulting in drying and desiccation of the soil material. To homogenise and wet / precondition the soil prior to electrokinetic treatment, the soil was disaggregated by passing it through a scaffolding mesh and saturated using AWE groundwater / weak citric acid in a lined treatment cell (i.e. a metal containment unit, lined with plastic sheeting to avoid electrical conductivity effects in the container itself) (figure 7 and 8).

- Approx 4 tonnes of soil was transferred to the treatment cell in a secure working compound, approx 100 l of AWE groundwater and approx 60 l of 0.1M citric acid were added during transfer.
- Once in place a pit was dug and filled with sand, the sand was then saturated and the electrodes emplaced vertically in the sand.
- 10 iron electrodes (5 Anode, 5 Cathodes) were inserted into the sand wells within the soil
- The electrodes were connected to five 110 Ampere hour, 12Volt leisure batteries (wired in series) using IP rated wiring.
- The electrode separation was approx 1.5m (approx 5ft)

Figure 7. Field Scale Trial Experimental Design
Findings:

- The working compound and experimental trials were established and implemented safely, to schedule and to budget.
- Evidence of electrokinetic effects was evident in the field scale trial as gas release was observed at the cathodes.
- Periodic monitoring confirmed a significant pH gradient was established in the sand wells and treated soil (figure 9).
- Portable X-ray fluorescence analysis, gamma spectroscopy and radiochemical analysis is ongoing, and will be reported elsewhere.

Figure 9. pH Gradient Established in Field Scale Trial
SITE AND REGULATORY REQUIREMENTS
As AWE is a Nuclear Licensed site it is subject to stringent regulatory scrutiny, and as a result AWE is very safety and procedurally orientated creating a safe and secure working environment and exceptional safety performance.

The following is a summary of the process which the project team had to undertake to initiate field trials of FIRS at AWE (figure 10).

Step 1; Introduction
The project team introduced the aims and objectives of the project to key stakeholders and made an initial proposal on how, when and where the project team intended to deliver the project. Stakeholder buy-in was attained by selling the benefits of the project to stakeholders, encouraging stakeholder input and by undertaking engagement early.

Step 2; Documentation and approvals
The project team produced all relevant documentation for the works to commence. Key documents included
- Method statements detailing each task to be undertaken
- Risk assessments for each stage of the work.
- Dose assessments for the workers
- Environmental Assessment
- Project Waste Management Strategy

Once these documents (and others) were produced and verified by respective assurance groups the required amendments to the facility safe case were undertaken to ensure the scope of works were within the safe operating envelope of the facility.
With facility management approval the works to commence the Safe System of Work for the project was complied. Detailing every aspect of works (from emergency procedures, work instructions to equipment specifications) the safe system of work provides operators with the instructions and all required information to undertake the work safely. Once the Safe System of Work had been produced and approved work commenced.

Undertaking rigorous and robust planning, assessment and scrutiny of the works upfront ensured that the work programme was practical, logistically feasible and ensured that work was adequately resourced at all stages. Up front assessment also ensured work was de-conflicted prior to commencement. Systematic assessment ensured foreseeable risks has been identified and control measures had been bought into place to eliminate / reduce / mitigate risks, allowing work to be undertaken in a safe manner in a safe environment.

**Figure 10. Schematic Flow Chart FIRS Implementation at AWE**
**DISCUSSION**

Pu (and U) exhibited relatively complex behaviour in the laboratory trials, with Pu forming mobile soluble oxyanionic species under the high pHs generated by the electrokinetic treatment technique. Clear mobilisation of Pu and U (along with a range of other elements) was however observed, in a range of soil types. The relative efficiency of remobilisation was element-dependant, and, in terms of heavy metal contaminants, radionuclides, and the stable analogues of radionuclides known to be problematic at other nuclear sites, was (from most to least mobile) Cl > Zn > Sr > U > Pu > Pb. Both Pu and U showed enhanced mobility when the low-cost soil conditioning agent citric acid was added prior to electrokinetic treatment.

The low-cost, robust design and approach trialled at laboratory scale was clearly applicable at field scale. While field trial data are still preliminary, and await final analysis of Pu and other radionuclides, the clear development of a strong pH gradient in the field trial cell, and clear evidence for iron migration in the cell, shows that the trial proceeded as expected, based on observations during the laboratory trial phase. The lack of on-site electrical supply necessitated the use of a recyclable battery array to provide power, which was successful, and indicated the potential to use the technique at low-cost (both in terms of power supply and materials), at relatively remote site locations. Of note is that the technology forms a relatively passive treatment process for contaminants once set-up, which can continue at relative low cost and impact to site operations until targets have been achieved. The self-contained nature of the treatment unit, and the safe system of work developed in terms of loading and decommissioning the treatment cell, meant that the risk of contamination of the surrounding area was minimised. The overall cost of materials, set-up, implementation and decommissioning for the field trial (excluding the original cost of the containment unit) was in the order of £8000, or approximately £2000 per tonne of material treated. This compares to an approximate direct disposal cost of ca. £5000 per m³ (based on current disposal costs at the low level waste repository facility at Cumbria, U.K).

The treatment system was operated on site, but *ex-situ*, reflecting (a) the form of the waste material requiring treatment (which was held on-site in waste containment units), and (b) potential problems (in terms of releasing contamination to groundwater) of mobilising Pu in the subsurface, if the technique were applied *in-situ*. While the FIRS technique has potential applicability for *in-situ* use (particularly in terms of generating subsurface containment barriers, stabilising contaminants and reductive trapping of elements such as Cr, e.g. Cundy and Hopkinson 2005, Hopkinson et al 2008) the potential for Pu release in the subsurface, and the complex behaviour exhibited by Pu in the strong pH gradients generated by the technique, mean that on-site *ex-situ* use is currently more technically and operationally feasible than *in-situ* ground application.

A major issue raised by the project, in terms of implementation of similar novel remediation technologies on other nuclear (and non-nuclear) sites was the need for significant advanced forward planning, given a relatively short two year project timescale, to ensure safety clearance prior to initiation of the field trial. This necessitated full engagement of a range of stakeholders and regulators, and senior company staff, during an approvals process that ran over the same time period as the laboratory and intermediate trials (figure 2 and 10). One of the key deliverables of the work programme, in addition to scientific deliverables, was the production of standard operating procedures documented and disseminated to relevant staff within the company. Such procedures, developed with full stake holder (including regulator) involvement are an essential prerequisite in enabling wider onsite implementation of technology on AWE operated sites.

More widely, the project illustrates the potential utility of industry: university partnerships in delivering novel solutions to onsite legacy issues. The approach used involved embedding a University of Brighton employee within the Environmental Projects Group at AWE for the full 2 year period of the project. This embedded approach ensured close communication between groups and onsite management of logistics.
and engagement of stakeholders and was essential for the successful delivery of the project and technology development and implementation.

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