REMEDIATION OF SOIL AT NUCLEAR SITES

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ABSTRACT

As the major nuclear waste and decontamination and decommissioning projects progress, one of the remaining problems that faces the nuclear industry is that of site remediation. The range of contamination levels and contaminants is wide and varied and there is likely to be a significant volume of soil contaminated with transuranics and hazardous organic materials that could qualify as mixed TRU waste. There are many technologies that offer the potential for remediating this waste but few that tackle all or most of the contaminants and even fewer that have been deployed.

This paper outline the progress made in proving the ability of Supercritical Fluid Extraction to remediate soil, classified as mixed transuranic (TRU) waste.

INTRODUCTION

The nuclear industry has been in existence for more than 50 years. Many of the facilities that served the nuclear industry from those early days have now been decommissioned, for example the diffusion plant, formerly used to enrich uranium and located at Capenhurst in the UK [1]. In addition, some sites that have been used by the nuclear industry have been returned to public use or are now 'brown field sites' (i.e. still under some level of institutional control.) To date the majority of the nuclear sites that have been restored have either tended to house facilities that handled relatively small quantities of radioactive material or been restricted to specific radionuclides. With the dawning of the new millennium there are plans to tackle some of the more challenging sites, for example Rocky Flats is to be closed by 2006 [2]. Despite the successes and the plans that are in place there still exist a number of major challenges in the remediation area.

In the US, for example, there are major tasks at Hanford as part of the River Protection Project (RPP) [3] and at the Idaho National Engineering and Environmental Laboratory (INEEL) [4], remediating legacy tank waste and stored mixed waste respectively. Notwithstanding the care taken during the operation of the sites and the facilities on the sites, there have been spillages or leaks of active material resulting in contamination of soil. As well as spillages or leaks of active material, soil has also become contaminated by disposal and storage practices that do not meet the current standards for waste management or are past their design lives. In the US, the leakages from the Hanford Tanks are well known and a matter of public record, as are some spillages at the Sellafield site in the UK. In addition, it is widely held that there is extensive environmental contamination within the Commonwealth of Independent States (CIS) which has

yet to be quantified or addressed. As thoughts turn to remediating these sites, the consideration is being given to treating or managing contaminated soil.

In parallel, indeed perhaps a little ahead of the nuclear industry, remediation of sites contaminated with hazardous materials like volatile organics (VOCs) and long lived polychlorobiphenyls (PCBs) has already begun and achieved some successes [5]. This paper describes one of the techniques, supercritical fluid extraction, that has been deployed on the remediation of sites contaminated with hazardous material and that might be applicable to radioactive or mixed contaminants [6].

SOIL CONTAMINATION

The activities in the nuclear industry are many and varied and virtually the full range of the periodic table is involved, with combinations ranging from tritium (^{3}H) to the heavy transuranic elements including plutonium. Potential contaminants also include activation products generated in the radiochemical industry and fission products encountered in irradiated nuclear fuel and its management. The contamination can arise from aqueous materials, e.g. spillage or leakages of highly active liquid wastes. It can also arise from solid material, particulates such as oxides and hydroxides, either deposited directly from processes or subsequently formed in the environment.

The behavior of contaminants in soil is a complex topic that has challenged the scientific community over a number of years. There are a number of ways inorganic contaminants might interact with soils [7]. These include, but are by no means limited to, the following mechanisms:

- Dissolution in pore water in soils;
- Physical sorption of charged species (e.g. double layer systems);
- Chemical sorption of charged species (e.g. ion exchange);
- Physical sorption of particulates or neutral species by electrostatic forces;
- Inclusion in mineral matrices (mineralization);
- Co-precipitation with other species (e.g. natural flocculation by ferric oxyhydroxides);
- Complexation with natural organic species (e.g. humic acids);
- Precipitation or sorption by indigenous bacteria.

The contaminants span the range from conservative species (i.e. mobile and easily solubilized) like ^{3}H, ionic iodine, alkali metal cations to the intractable (i.e. difficult to move or solubilize) such as the species included in mineral matrices or chemically stable species, for example oxyhydroxides of plutonium.

Industry has also used a number of materials that are chemically toxic in their own right and are designated hazardous, like VOCs and PCBs. Whilst the chemistry of these contaminants tends to be less complex than the inorganic contaminants, there is the potential for co-contamination of soils on nuclear sites with both toxic inorganic and organic species [8].

SCOPE OF CONTAMINATON

Just as the range of chemistry is large, the range of the level of contamination is broad. It covers the spectrum from very low-level waste management thresholds (e.g.<12 GBqte^{-1} $\beta\gamma$ and <4 GBqte^{-1} α in the UK) to wastes that require special treatment (e.g.>100 nCig^{-1} for TRU waste in the US).

It also notoriously difficult to predict the volumes of contaminated soils that might be encountered during site remediation as this will depend on factors such as:

- Amount of material spilled or leaked to the soil (often this can only be inferred);
- Chemical form of the contaminant and the chemistry of the soil system, (again, this can often only be estimated);
- Mobility of the contaminants. This again is difficult to determine because of the variety of mechanisms for transport of contaminants.

Generally, the volumes of the higher categories of waste (e.g. TRU) will be relatively small compared to the lower levels of contaminants, (possibly 2 to 3 orders of magnitude lower). There is also an understandable tendency to produce conservative (i.e. high) estimates of contamination levels that are often not found in practice when the remediation task is underway.

AVAILABLE TECHNIQUES

Over the past few years, few areas have excited as much interest as soil remediation [9]. There is a multitude of techniques for remediating soils contaminated with organic materials [5]. There are however, fewer that can be deployed against inorganic contaminants, including radionuclides as unlike organic contaminants, inorganic contaminants cannot be degraded or destroyed and therefore pose a more difficult problem for remediation.

There exist numerous remediation technologies although they all fall within three of broad categories, namely:

- Immobilization:
  This includes the stablization, solidification or containment of the contamination either in situ (e.g. engineered barriers [10], vitrification [11]) or ex situ (e.g. grouting [12] or vitrification [13]);
- Extraction:
  This involves the extraction and/or separation of the contaminant species from the soil matrix and includes techniques like soil washing, chemical/solvent extraction [14];
- Destruction:
  As the name implies, technologies in this category destroy the contaminants using techniques such as thermal process [15] or oxidative techniques.

Of the technologies that have been researched to date relatively few have been deployed at scale and can be considered to be mature. Others are specific to individual contaminants or families of contaminants; for example, air purging is only effective against volatile contaminants [16].

Table 1 outlines some of the available technologies. As a rule, the high volume/low-level of contamination projects attract simple technological solutions such as removal and disposal. Whereas the low volume/high-level contamination challenges tend to justify the high technology solutions.

Some Remediation Technologies for Soil Classified as Mixed TRU Waste.

TECHNOLOGY	USES	LIMITATIONS
Sparging	Removes volatiles	Ineffective for high boiling point materials or inorganic materials
Steam Purging	Removes volatiles	Will not remove inorganic materials
In-Situ Vitrification	Destroys organics and immobilizes inorganics	Off-gas problems. Does not remove contaminants.
In-Situ Grouting	Immobilizes contaminants	Does not remove contaminants
Bioremediation	Used for specific organics. Suggested for metal removal.	Inorganic removal at research stage.
Acid Washing	Removal of acid soluble materials.	Often poor recovery. Not used for organics. Secondary waste formed.
Incineration	Destroys organics	Leaves inorganics in residues.
Soil roasting	Removes volatiles	Leaves inorganics in residues .
Oxidative/Reductive Process	Remove some or all organics	Leaves inorganics in residues. Secondary waste formed.
Segregation techniques	Volume reduces the contaminated soil if the contaminant is found predominately on one soil fraction (e.g. small or magnetic particles)	May generate volumes of secondary waste. No use if the contamination is homogeneously distributed.

Table 1.

SELECTION OF TECHNOLOGIES

In considering the deployment of technologies for remediation there are a number of factors that need to be considered in an integrated manner. These include:

- **Functionality**
  Ideally the selected technology should be capable of removing the contaminant(s) to the required level.

- **Risk**
  Any technology selection process should evaluate the effects on the safety of the onsite worker and the public within the vicinity of the radioactively contaminated site to be remediated. This includes not only the radioactivity safety aspects but also the physical (e.g. equipment safety) and exposure to other hazardous materials.

- **Cost**
  Given the volumes of waste or contaminants, cost is a significant factor although it should always be weighed against the benefits of using the technology. If the technology is new then it may be necessary to evaluate development costs etc. in addition to budgeting for decontamination and decommissioning.

- **Environmental Impact**
  Whilst there may exist techniques that can treat contamination there must be a net overall benefit from doing so. There is, for example, little benefit in removing a contaminant that is well fixed on a low volume of soil, only to produce a high volume of an aqueous waste with the contaminant in a soluble or mobile form. In addition, the techniques should not generate large quantities of secondary waste or should not pose risks of exposure to the public or operators that exceed the risks of quiescent contamination.

- **Availability**
  In an ideal world, the selected technology would be well established and proven in practice. However it is often necessary for a number of reasons, to consider innovative and unproven technologies. If this is the case then due consideration should be given to whether the engineering problems of deploying the core processes have been solved or whether the components parts of the technology are at similar states of maturity. For example, often the core of the technology has been well researched (e.g. the extraction process) but the material handling problems have not been resolved.

WHY SUPERCRITICAL FLUID EXTRACTION?

The above criteria were applied to consideration of remediating significant volumes ($\underline{ca.}10^3$ m^3) of soils contaminated with transuranic elements, such as plutonium. It was assumed that any contamination would be in an intractable form, (e.g., oxide, ceramic oxide or oxyhydroxide), based either on the origin of the contamination or because of subsequent reactions in the

environment. It was also expected that the radioactive contamination would be accompanied by organic co-contaminants (e.g. PCBs, VOCs), fission products and hazardous inorganics. The main challenge posed in the assessment of potential remediation technologies was to generate a bulk product that could at least be disposed of as low-level waste (LLW) without recourse to TRU or mixed categories for disposal. Other constraints were that the technology had to be deployable in the short-term (within 1-3 years) and therefore have some track record or considerable background in development.

Upon evaluation of potential technologies, it was found that there was no single technology that would satisfy the generic criteria and meet the specific challenge outlined above. At this point, it was decided to invest some effort in testing one of the prospective technologies, supercritical fluid extraction (SFE), to meet the required functionality. Initially supercritical fluid extraction recommended itself as it has already been deployed on organic hazardous waste (soil) at scale with some success and thus many of the engineering problems have already been tackled. For instance, it was successfully demonstrated at an EPA Superfund in Conroe in Texas [6] to extract toxic organics (oil, grease and polyaromatic hydrocarbons) from soil at rates of 150+ tons per day. This large-scale application gave confidence that it could be engineered and nuclearized to remove radionuclides from soils.

The solvent systems used for removal of organic materials (i.e. hydrocarbons) may have resolved many of the engineering problems of soil and product handling but unfortunately they are not chemically able to remove inorganics and transuranics. Although hydrocarbons were used to remove the organics from soil, there is a range of materials that have accessible supercritical properties (see Table 2.) The properties they exhibit are particularly attractive as they offer the following [17]:

- Rapid rate of extraction due to the high diffusivity of the supercritical fluid;
- Potentially high loading of contaminants;
- Ease of recovery of the contaminant at low volume if a fluid that is gaseous at STP is used;
- No aqueous or high volume secondary effluent is produced;
- The soil is not denatured by the treatment.

Physical Parameters of Selected Supercritical Fluid

Fluid	Molecular Formula	T_c (°C)	P_c(atm)
Carbon Dioxide	CO_2	31.1	72.9
Nitrous Oxide	N_2O	36.5	71.7
Ammonia	NH_3	132.5	112.5
η-Pentane	C_5H_{12}	196.6	33.3
η-Butane	C_4H_{10}	152.0	37.5
η-Propane	C_3H_8	96.8	42.0
Sulfur hexafloride	SF_6	45.5	37.1
Xenon	Xe	16.6	58.4
Methanol	CH_3OH	240.5	78.9
Ethanol	C_2H_5OH	243.4	63.0
Isopropanol	$(CH_3)_2 CHOH$	235.3	47.0
Diethyl ether	$(CH_3CH_2)_2O$	193.6	36.3
Water	H_2O	374.1	218.3

Table 2.

Investigations into the ability of supercritical fluid to solubilize inorganic species have been carried out at a number of locations. The main center of research was and is at the University of Idaho, where a patent was generated to extract, amongst other species, uranium [18]. Studies were also carried out at the University of Leeds, in the UK, to establish some basic scientific data concerning solubility in supercritical fluids and the V.G. Khlopin Institute in St Petersburg performed some empirical studies on decontamination using supercritical fluids.

These studies all used carbon dioxide (CO_2) as the supercritical fluid. They achieved dissolution and high solubility using soluble complexants like acetylacetone species or tributyl phosphate (TBP), and modifiers to change the polarity of the solvent (e.g. traces of methanol, water.)[19].

INVESTIGATIONS

The study of SFE as a potential technology for remediation transuranic soil was accomplished by proving the chemistry of the process for a specific contamination problem, as the efficacy of remediation technologies tend to be site (matrix) dependent. Therefore, the chemistry investigations were carried out on soils collected from the INEEL site. These soils were contaminated with plutonium in a particularly intractable form or forms (i.e. mainly oxide and oxyhydroxide species). In addition, trials were carried out on standard samples from other nuclear sites to ensure some environmentally aged samples were included to accommodate long-term interactions with the soil(s). The purpose of the trials was not necessarily to optimize the extractions to below an absolute level (for example the low-level waste boundary of <10 nCi/g) but to show that significant extraction could be achieved. This would then form the basis for treatability tests on authentic samples and further investment in the development of the SFE process.

CHEMISTRY TRIALS

The tests to demonstrate the ability of supercritical fluid extraction to remove intractable actinides from soils used both simulants and a 'standard' soil that had been fully characterized by the National Institute of Standards and Testing.

The simulant soil, a lakebed silt clay, was obtained from the INEEL site from the vicinity of the Radioactive Waste Management Complex (RWMC). This soil was initially sieved to remove macroscopic material (sagebrush, rocks etc.) and in the end sieved to below 50 mesh. The soil was radiologically characterized before further use. Three separate fractions of the soil sample were then spiked with plutonium by the methods summarized in Table 3 and designated Soils A, B and C. Each sample was measured by alpha-spectroscopy and gamma ray-spectroscopy to determine the levels of ^{239}Pu and ^{241}Am in each.

Characteristics of Soil Samples

Soil Type	Treatment	Batch	^{239}Pu nCi/g	^{241}Am nCi/g
Soil A	• Spike with Plutonium Nitrate in 8M HNO$_3$ • Dry at out 65° C for 4 days	1 2	467 ± 27 4.87 ± 26	2.46 ± 0.16 2.51 ± 0.01
Soil B	• Spike with Plutonium Nitrate in 8 M HNO$_3$ • Add Sodium Nitrate to 1000 ppm nitrate • Dry at 65° C for 4 days • Heat to 500° C for 2 hours	1 3	465 ± 56 467 ± 21	2.47 ± 0.32 2.49 ± 0.18
Soil C	• Spike with Plutonium Nitrate in 8 M HNO$_3$ • Add Fe$_2$(SO$_4$)$_3$, Na$_2$CO$_3$, Na$_3$PO$_4$ • Adjust pH to 11 • Dry at 65° C for 4 days	1	994 ± 44	5.30 ± 0.32
NIST Sol	• Environmental sample taken from the vicinity of a nuclear facility	1 2 3	0.01 x 10^{-3} 0.3 x10^{-3} 0.5 x 10^{-3}	

Table 3.

Sequential Aqueous Extraction

To fully characterize the spiked (simulant) soil samples, a sequential extraction technique was used to determine to which soil fraction and how strongly were the Pu and Am bound [21]. During the course of this procedure the soil sample is subject to different chemicals in a prescribed sequence. Each reagent is designed to remove metals associated with different soil fractions, for instance metals associated with ion exchange sites or bound by organics, (see

Figure 1.) depending on their strength of binding. Any metal remaining in the sample after extraction with all the different reagents is said to be in the residual fraction.

Trials using this standard test failed to remove any plutonium from the samples, regardless of the chemical preparation technique used, suggesting the plutonium is very firmly bound to the soil matrix,. It thought likely that the form of plutonium is either an oxide, hydroxide or oxyhydroxide; although plutonium polymerization is also a possibility. Americium was predominantly recovered (up to 80%) by the reagent that indicates the contaminant is held predominantly in a fraction consistent with precipitation in the iron/manganese phase (i.e. more readily extracted than plutonium). A small amount remained in the residual fraction.

Extractions using supercritical CO_2 were carried out using hexafluroroacetylacetone and tributyl phosphate as the complexant. A schematic of the equipment used is shown in Figure 2 and some typical results are shown in Table 4.
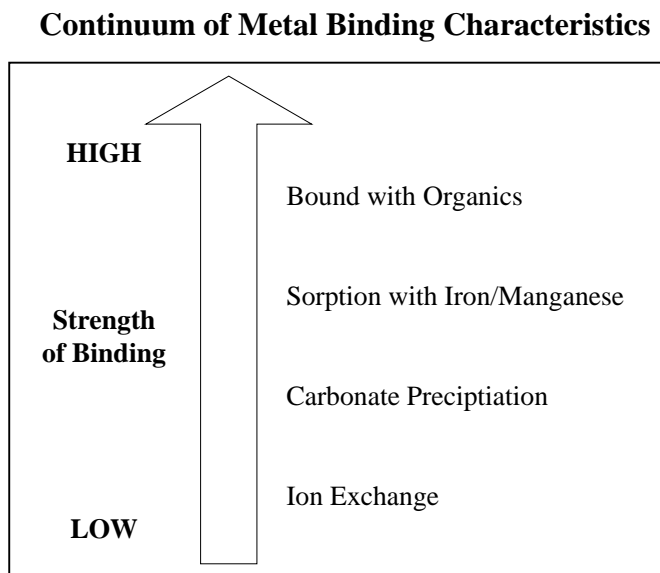
Continuum of Metal Binding Characteristics

Figure 1.

The results show that the extraction system will remove some plutonium from even very low level, aged authentic soil samples, albeit with poor mass balance. The spiked soils showed levels of extraction of up to 80%, even for the surrogates that had been subject to high temperatures and alkaline conditions where oxyhydroxides might be expected to form.

These results are encouraging enough to consider proceeding with authentic site-specific samples in treatability trials. No attempt was made to further optimize extraction on these samples as the efficacy of the process in general was proven. The plutonium, intractable to even 3M nitric acid in the aqueous extraction trials, was accessible to the supercritical fluid extraction.

DESIGN STUDIES

The design studies carried out on the SFE concept have concluded that it is feasible to engineer the process at scale to nuclear standards and no insurmountable problems have been identified.

THE WAY FORWARD

The work so far has demonstrated that it is chemically feasible to remove both organic and intractable inorganic contaminants from soils. It has also provided some confidence that the process can be optimized to site specific soils and to appropriate waste acceptance criteria. To move forward to an engineered process the following steps are required:

- Treatability trails against specific samples; authentic samples taken from contaminated sites.
- Pilot scale demonstration, perhaps $1m^3$ scale, with authentic soils to provide design data for a full scale facility and process optimization against site specific conditions and constraints.

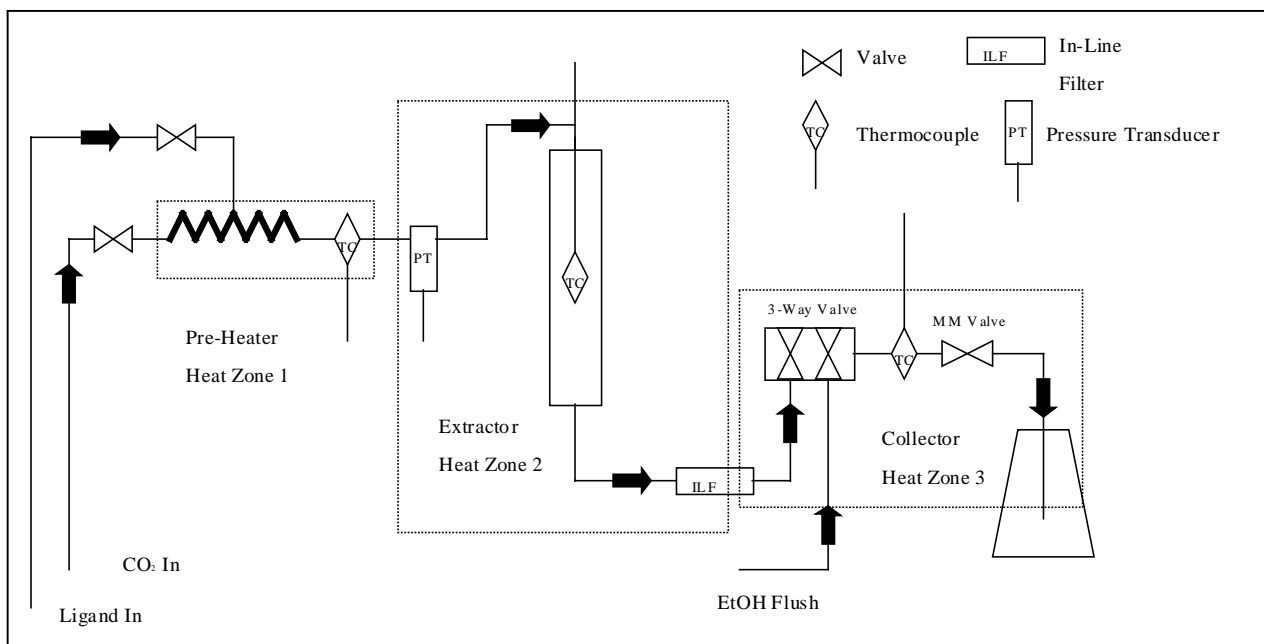### Process Schematic for Supercritical Fluid Extraction

Figure 2.

SUMMARY

Supercritical Fluid Extraction (SFE) is a technology for treating TRU and mixed TRU waste that offers benefits and capabilities not offered by other technologies and combinations of technologies. BNFL is, therefore aggressively pursuing further development of the technology.

Supercritical Fluid Extraction of Contaminated Soil Samples

	Condition #1									
	Radiological Activity (nCi)								% Extracted	
	Pre-Soil		Post-Soil		Difference		Recovered Material			
Soil	Pu	Am	Pu	Am	Pu	Am	Pu	Am	Pu	Am
A1	5151	27.1	1614	4.97	3537	22.1	3300	22.0	64	81
A2	4460	23.0	1408	4.00	3052	19.0	3270	21.0	73	91
A3	4565	23.5	1342	4.60	3223	18.9	3215	21.7	70	92
B1	4453	23.7	2457	8.8	1997	14.9	2295	16.4	52	69
B2	4249	22.7	2572	10.1	1677	12.6	1816	13.7	43	60
C1	10189	54.3	3946	11.8	6243	42.5	5548	37.0	54	68
C2	10393	54.3	3508	10.6	6885	43.7	6580	45.4	63	84

	Condition #2									
	Radiological Activity (nCi)								% Extracted	
	Pre-Soil		Post-Soil		Difference		Recovered Material			
Soil	Pu	Am	Pu	Am	Pu	Am	Pu	Am	Pu	Am
A1	4516	23.3	2153	6.84	2363	16.4	2961	15.8	66	68
B1	4440	23.6	2426	9.2	2014	14.4	1953	14.6	44	62
B2	4126	21.9	2285	9.1	1841	12.8	1865	13.6	45.2	62
C1	10894	58.1	4967	13.8	5927	44.3	5158	42.5	47	73
C2	9578	51.1	4603	13.6	4975	37.5	4190	35.5	44	69

	Condition #3									
	Radiological Activity (nCi)								% Extracted	
	Pre-Soil		Post-Soil		Difference		Recovered Material			
Soil	Pu	Am	Pu	Am	Pu	Am	Pu	Am	Pu	Am
A1	4437	22.9	934.7	1.5	3502	21.4	5316	21.5	80	93

Conditions 1 through 3 represent different concentrations of ligands, exposure times, etc.

Extractions were carried out on the NIST samples and although significant quantities of plutonium were removed the variation between the measured residual plutonium on the soil and the recovered plutonium in the extractant were sufficiently large (due to the low initial plutonium concentrate to render any calculation of % extraction unreliable.

Table 4.

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