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A LITERATURE REVIEW OF METHODS OF ANALYSIS OF ORGANIC
ANALYTES IN RADIOACTIVE WASTES WITH AN EMPHASIS ON
SOURCES FROM THE UNITED KINGDOM

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SUMMARY

In Hanford nuclear wastes, the nature of the organic material is an important factor in safety issues and the ultimate disposal of the waste. The task of developing the necessary procedures for analyzing waste is both expensive and time consuming. In an attempt to reduce development time, literature reviews have been conducted on the analysis of organic constituents in radioactive waste. Analytical methods described in the open literature have been previously reported in *Methods of Chemical Analysis for Organic Waste Constituents in Radioactive Materials: A Literature Review* (Clauss and Bean 1993). Because of the paucity of methods found in that review, the search was continued for analytical technology developed in other countries. The first country approached was the United Kingdom (U.K.). Researchers at Harwell Laboratory of the United Kingdom Atomic Energy Authority aided Pacific Northwest Laboratory (PNL) in the literature search. This document reviews reports from the U.K. and secondary references found in their reports from the U.K. and various other countries.

The British have kept very good records of their waste's composition. Consequently, they have developed little analytical methodology that would apply to our needs. A majority of their papers have focused on the fate of solid organic wastes entrained in concrete wastefoms for permanent storage. The main areas of concern were

- formation of chelators
- microbial degradation
- wastefom destruction
- gas formation.

No direct method of analysis from the British literature was found. This was also the conclusion reached by Harwell Laboratory. The British references describe experiments that indirectly determine the amount of chelators in aqueous solutions leached from cementous wastefoms. Typically, the increase in a radionuclide's rate of dissolution was measured, and the amount of chelating leachates was inferred from this measurement. This probably would

not be a useful approach in analyzing Hanford's waste, since Hanford waste already contains large amounts of chelators and radionuclides.

References secondary to the British reports were also investigated. Some Canadian, French, Japanese, and American references were discovered. Some of these papers described methods that were not recovered in the previous search of the open literature. Three of the most significant reports are summarized in the following paragraphs.

Japanese researchers have developed a method for analyzing tributyl-phosphate degradation products using ion-exchange chromatography. These degradation products were dibutyl phosphate (DBP), monobutyl phosphate (MBP), and phosphoric acid. They had a linear responses over a range of 2 to 150 ppm for DBP, 3 to 200 ppm for MBP, and 3 to 100 ppm for H_3PO_4 .

At Savannah River, researchers developed a solid-phase extraction method. This method described the clean-up and analysis of tributyl phosphate and normal paraffin hydrocarbons found in the aqueous portions of the PUREX process matrix. The analytes were trapped and concentrated on an octadecyl-phase column. The analytes were then eluted from the column with tetrahydrofuran. The clean-up was on a scale workable within a glovebox. Analysis was by gas chromatography.

Brookhaven researchers evaluated the groundwater chemistry at radioactive waste sites throughout the United States. They developed a liquid extraction scheme for isolating acidic, basic, and neutral organic components in the groundwater. The analysis was by gas chromatography/mass spectrometry.

The review of literature from the U.K. has not significantly increased the number of analytical methods available to researchers at Hanford.

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Clauss, S. A., and R. M. Bean. 1993. *Methods of Chemical Analysis for Organic Waste Constituents in Radioactive Materials: A Literature Review*. PNL-8266, Pacific Northwest Laboratory, Richland, Washington.

ACRONYMS

BNFL	British Nuclear Fuels, plc.
CEGB	Central Electricity Generating Board
DBP	Dibutyl Phosphate
DoE	Department of the Environment (U.K.)
EDTA	Ethylenediaminetetraacetic Acid
EPA	Environmental Protection Agency
GC	Gas Chromatography
HATCHES	Harwell/Nirex Thermodynamic Database for Chemical Equilibration Studies
ICP/MS	Inductively Coupled Plasma-Mass Spectrometer
LIPAS	Laser Induced Photoacoustic Spectrometer
MBP	Monobutyl Phosphate
MS	Mass Spectrometer
NPH	Normal Paraffin Hydrocarbons
PNL	Pacific Northwest Laboratory
PUREX	Plutonium-Uranium Extraction
ORNL	Oak Ridge National Laboratory
R&D	Research & Development
TBP	Tributyl Phosphate
TMS	Trimethylsilyl
U.K.	United Kingdom
U.K.A.E.A.	United Kingdom Atomic Energy Authority

CONTENTS

SUMMARY	iii
INTRODUCTION	1
METHOD OF SEARCH	3
RESULTS OF THE LITERATURE SEARCH	5
OVERVIEW	5
COMPLEXANTS	6
DEGRADATION OF WASTEFORMS	9
GAS FORMATION	10
SECONDARY REFERENCE FROM OUTSIDE THE UNITED KINGDOM	10
CONCLUSION	16
REFERENCES	17
APPENDIX A - STATEMENT OF WORK TO HARWELL LABORATORY	A1
APPENDIX B - THE REPORT ISSUED TO PNL FROM HARWELL LABORATORY	B1
APPENDIX C - FURTHER REFERENCES NOT CITED IN THIS REPORT	C1

TABLES

1.	Anaerobic Degradation of Organic Compounds Present in Maxey Flats Trench 26 Leachate Sample by a Mixed Culture of Bacteria (Francis et al. 1980)	13
2.	GC Conditions for the Analysis of Trench Water Organics (Weiss and Colombo 1980)	14

FIGURES

1.	Schematic of Organic Extraction of Trench and Well Waters (Weiss and Colombo 1980)	15
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INTRODUCTION

Most of the waste generated while producing defense materials at Hanford is presently stored in 177 underground tanks. Little is known about the organic constituents in the tanks because of the many waste treatment processes, the operations conducted to move and consolidate the waste, and the long-term storage conditions at elevated temperatures and radiolytic conditions.

This report, compiled by Pacific Northwest Laboratory (PNL)^(a), examines literature originating through the United Kingdom (U.K.) nuclear industry relating to the analyses of organic constituents of radioactive waste. Additionally, secondary references from the U.K. and other countries, including the United States, have been reviewed. The purpose of this literature review was to find analytical methods that would apply to the mixed-waste matrices found at Hanford.

To solve the problems associated with the stabilization and ultimate remediation of the wastes found in Hanford's storage tanks, understanding the constituents in these tanks is essential. The Tank Waste Science Panel has recommended that "Tank 101-SY be physically and chemically characterized as fully as possible and as expeditiously as safety considerations allow" and that "no remediation steps be taken until there is a better understanding of the chemical and physical phenomena connected with gas generation and release in Tank 101-SY" (Dunning and Horowitz 1991). There is little doubt that other Hanford remediation activities will focus on characterization before cleanup. Regulations, Tri-Party Agreement provisions, and environmental impact statement requirements also require comprehensive knowledge of waste constituents.

The tanks at Hanford contain a large variety of organic compounds, including solvents, extractants, complexing agents, process chemicals, and cleaning agents (Gerber et al. 1992). These organic compounds intermingle with aqueous solutions that are very high in pH, salinity, and radioactivity.

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Standard methods available for analyzing organic compounds in other matrices are usually inadequate for Hanford's needs. Methods that work in high-level waste are needed to support the tank characterization effort. Methods provided by the U. S. Environmental Protection Agency (EPA) (e. g., SW-846) are not effective or implementable to many types of samples found at Hanford because of the complex and unique matrix. The EPA methods do not target many chemicals found, such as organic chelators, in high concentration in certain Hanford wastes. Standard analytical methods have, in some cases, been entirely ineffective for some tank-waste samples because of interferences (Hoppe et al. 1992a; Hoppe et al. 1992b). Therefore, it is essential to have at Hanford a comprehensive program for characterizing the organic species in waste tanks.

Previously, we have reported the results of a literature search for applicable analytical methods in the open literature. Most of the references reported were from American sources (Clauss and Bean 1993). The conclusion of this report was that only a small body of work related to this subject. Most of this work was done at Hanford or Oak Ridge. To gain further insight on possible useful analytical methods, international sources were investigated.

To expedite the literature search in the U.K., researchers from the United Kingdom Atomic Energy Authority (U.K.A.E.A) at the Analytical Sciences Centre, AEA Technology, Harwell Laboratory (AEA is the trading name of the United Kingdom Atomic Energy Authority) were contracted to do the initial search. The statement of work is found in Appendix A. Our report was developed using the references that were provided by Harwell. Potentially useful secondary references found in Harwell's references were also examined.

METHOD OF SEARCH

Records at Harwell date back to 1946. Records and abstracts of publications dated from 1946 to 1980 are filed on a card-index system. Records created after 1980 are filed on a computer system. These file systems were searched for the key words

- analysis
- determination
- organics
- radioactivity

separately and in combinations.

In addition to the formal searches of these index systems, the researchers at Harwell sought out staff members that they believed would have first-hand knowledge of less formal methods or publications. Appendix B, which is the report delivered to PNL by Harwell (Brown and Monahan 1993), lists these senior staff members and their positions. Harwell's report contained the abstract of each reference that they found. Harwell also provided copies of each reference. The Harwell report cited fourteen publications.

Each of the references provided by Harwell was examined for secondary references. Secondary references were selected based on the discussion in the text preceding their citation or, on some occasions, based on the title listed in the primary reference's bibliography. Sixty-eight additional references were found by this method.

The secondary references were not limited to documents prepared in the U.K. Documents cited in the primary references came from the United States, Canada, France, Japan and Austria. Our domestic review (Clauss and Bean 1993) discussed most of the American references cited by British publications; however, there were some new reports to examine.

All potential references were placed into a computer database. The database ultimately contained 83 references. Of the 83 references, 45 were selected for review. The publications that were not procured for review were discounted because their titles indicated that their focus was either radionuclide

analysis, or the matrix was not radioactive, or they were not analytical papers. Appendix C contains an annotated listing of reviewed database references not cited in this report.

RESULTS OF THE LITERATURE REVIEW

OVERVIEW

A review of the British reports indicates that the British have documented the content of their wastes very well. A report, titled *The Physical and Chemical Characteristics of Radioactive Wastes*, lists the characteristics of high-level, intermediate-level, and low-level wastes found in the U.K. (Electrowatt 1990). The report, over 1000 pages in length, covers the civil nuclear industry, R & D, medical, and industrial sources. This report lists wastes stored by British Nuclear Fuels plc. (BNFL), the Central Electricity Generating Board (CEGB), the South Scotland Electricity Board, and the U.K.A.E.A. Each waste is assigned an identifier, and its history, physical state, organic and inorganic content, and future disposition are tabulated. No indication is given of how the chemical content is determined, but it is most likely from record keeping, not chemical analysis.

Because their waste's make-up is well documented, the British have focused on the fate of their waste once it is placed into permanent storage. A bulk of the reports recovered in this literature search discussed the behavior of waste and its encapsulating material in storage.

The storage concerns can be categorized into three main topics:

- the formation of complexants that will enhance radionuclide mobility in the environment from organic materials in the waste
- the degradation of the waste's containment structure, or wasteforms (this is usually cement or cement with added polymers or bitumens)
- the formation of gas, which could rupture the waste's containment.

A good overview of British concerns of organics in mixed waste can be found in *Organics in Radwaste, Proceedings of the one day technical seminar held at Harwell on 22nd September 1987* (Taylor 1988). This reference

presents some tabulated data of wastes generated by various sites and describes some experiments developed to study these wastes.

Another good overview of research in this area is a report by Greenfield, et al. They reviewed the microbiological, chemical, and radiolytic degradation of solid organic materials in intermediate and low-level radioactive wastes. Their focus was directed at the formation of water-soluble complexing agents (Greenfield et al. 1990).

COMPLEXANTS

The bulk of the references recovered in this review addressed the discussion and study of the formation of complexants, or leachates, in the radioactive waste-storage environment. The complexants arise from chemical, radiolytic, or microbial degradation of organic materials in the waste; from the direct addition of complexants, such as EDTA; or from materials present in the near-field environment (Greenfield et al. 1990).

Guest (1987) and Ewart and Williams (1986) both conducted early literature reviews to determine the effects of degradation products and environmental compounds that may influence the migration of plutonium out of the waste-storage repositories. In his eight point conclusion, Guest theorized that most major polymers found in the probable waste environment would not undergo chemical degradation to smaller water-soluble organic molecules; however, they may slowly undergo some change by free radical reactions. Some polymers, such as polyesters, could hydrolyze back to their monomers in the alkaline waste environment. Cellulosic materials would be the most problematic because they would degrade to smaller carboxylic acids, which could form complexes with actinide ions. Ewart and Williams discussed the effect humic and fulvic acids might have on migration of actinide out of the waste repositories. They concluded that very little data existed on which to make a solid conclusion; however, the significance of these soil acids in radionuclide migration is "open to doubt."

Wilkins (1987) indirectly determined the formation of complexants by measuring the enhanced solubility of plutonium in water containing

decomposed organic material. Both chemical and radiolytic decomposition were studied. To test for chemical decomposition, polyvinyl chloride, neoprene, hypalon, polyethylene, cellulose, and mixtures of these were immobilized in concrete as they would be in waste storage. The concrete was then crushed and heated at 80°C for 200 days under water. A spike of plutonium nitrate was added, and after equilibrium was reached, the amount of dissolved plutonium was measured. The plutonium was measured by a standard procedure developed for solubility experiments. A sample of the mixture at equilibrium was filtered through a pre-conditioned Amicon Cetriflo CF 25 ultrafiltration cone into 100 μ L of 10 M nitric acid. This filter has a nominal molecular weight cutoff of 25,000. After filtration, the solutions were assayed by a standard α -counting method. This result was compared to results from a concrete sample that contained no organics. The radiolytic decomposition was tested in much the same way. However, in place of heating, the organic materials were doped with $^{241}\text{AmO}_2$ at 10g/kg and held for 700 days. This gave an estimated radiation dose of 10^8 Gray. Again, the dissolved amount of equilibrated plutonium was measured. In both cases, the organics increased the solubility of plutonium by an average of about 2000 fold. The greatest enhancement came from degraded cellulose. Wilkins did not attempt to identify the solubility-enhancing complexants in this paper. Wilkins et al. also studied the effect of γ -irradiation on these types of samples (Bradshaw et al. 1986a).

Later Wilkins et al. (Bradshaw et al. 1986b) attempted to identify the compound responsible for the enhanced solubility of plutonium in these cement/organic leachates. To do this, they substituted thorium for plutonium in simulated wasteforms. After aging, the samples were passed through a gel permeation column, through a standard ultraviolet detector, and on to an inductively coupled plasma/mass spectrometer (ICP/MS). They were not successful in identifying the solubility enhancing component of the leachate. However, they concluded that the component that is responsible for the solubility increase is a minor component of the leachate.

Lacking positive identification of the plutonium solubility enhancing component in the experiments cited above, Cross et al. (1989) assessed different carboxylic acids for similar solubility patterns. This was because carboxylic acids were thought to be plausible degradation products of cellulose.

They found that solubility was greatly influenced by the number of carboxylate, hydroxyl, and carbonyl groups found on the molecules studied. They found that D-saccharic acid most closely simulated the solubility enhancement found in the earlier cement/organic leaching experiments. Additionally, they discovered that the presence of calcium appeared to suppress the solubility of plutonium. They believed these modeling studies would enable them to describe plausible reaction mechanisms and better understand the decomposition products in the earlier experiments.

Greenfield et al. (1991) also conducted experiments similar to those cited above. They tested ion-exchange resins for degradation and solubility enhancement of plutonium. They also tested lower levels of cellulose than previously studied. They found that the ion-exchange resins' degradation products did not significantly increase solubility. They also found that when lowering the cellulose loading in the cement from the 10% used in previous experiments to 0.1 to 0.5%, the solubility enhancement effect was significantly reduced, more than would be accounted for because of the reduced concentration. They theorized that at lower concentrations, the cellulose's degradation products are absorbed on active sites on the cement. Only after the amount of the cellulose's degradation products exceeded the number of these active sites would solubility enhancement take place. In the same paper, they discussed the successful computer modeling of the solubilities of plutonium in the presence of D-saccharic, D-gluconic, and glyceric acids. The simulations were carried out using data from the Harwell/Nirex thermodynamic database for chemical equilibration studies (HATCHES).

Berry et al. (1989) conducted experiments to test the effect of the cellulosic decomposition products on the sorption of uranium and plutonium onto London clay and Caithness flagstone. They also tested gluconate as a comparison. They found that these do indeed lessen the sorption of the two radionuclides onto these soil types. This would lead to more facile migration through soil. Two different pHs were tested, pH=11, thought to be similar to the pH near the cement repository, and pH=8, which simulates the pH near the edge of the zone of migration. They found that at the higher pH, the gluconate had a much greater influence in suppressing sorption (i.e., enhanced solubility) for both nuclides in both materials. At the lower pH, the gluconate and

cellulosic decomposition products were similar in behavior. The technique for measurement was the same as the previously cited papers. That is, they indirectly measured the amount of leachate by measuring the amount of radionuclide that was complexed by it.

Pollard and co-workers (Cross et al. 1988) were able to distinguish between plutonium complexes of gluconic acid and citric acid using Harwell's laser-induced photoacoustic spectrometer (LIPAS). These acids could be present in waste repositories, in the case of gluconic acid from degradation of cellulose, and in the case of citric acid as a decontamination agent. The experimental procedure dissolved the sodium salts of gluconic and citric acid in dilute hydrochloric acid and then neutralized them with sodium hydroxide. Cement leachate was prepared by leaching a block of concrete with water. Each acid was added to separate 10-mL aliquots of the cement leachate to give a 10^{-3} -M solution of gluconic acid and a 10^{-2} -M solution of citric acid. The pH of both solutions was between 12 and 12.5. These solutions were spiked with $5\ \mu\text{L}$ of $6\ \text{g}\cdot\text{L}^{-1}\ \text{Pu}(\text{NO}_3)_4$ and equilibrated for 48 hours. The solutions were then filtered through 25,000 molecular weight cut-off Amicon YM25 ultrafiltration membranes. The filtered solutions contained plutonium at concentrations between 8.2×10^{-6} and 10^{-7} M and were measured against unspiked blanks by LIPAS. The complexes of citric acid and gluconic acid were readily distinguishable. The citric acid complex had an absorption band at 493 nm. The gluconic acid complex absorbed at 506 nm. In addition to these complexes, they could easily distinguish between different oxidation states of plutonium.

Another route of decomposition of organic materials in mixed waste considered by researchers in the U.K. is microbial degradation. Various researchers have compiled examples of impressive bacterial and fungal tolerances (West et al. 1985; McCabe 1987). The best overall discussion of microbiological factors in mixed waste is found in West et al. (1985).

DEGRADATION OF WASTEFORM STRUCTURES

Cement encasement and burial of solid mixed wastes appears to be the choice for long term disposal in the U.K. While cement is not organic and

therefore would not be considered in this review, experiments have been conducted where cement is mixed with plastics or bitumen in an attempt to create a more stable wasteform. Duddridge (1986) presents a review of the problems associated with the inclusion of organic materials into the wasteforms, and suggests further studies. Other references discuss in more general terms the effect of radiation of polymers (Phillips 1988; Rudd 1988)

Johnson et al. (1986) studied the swelling associated with irradiating bitumens. Apparently gases form upon the radiolytic decomposition of bitumens. These gases are trapped in the structure of the material and cause the swelling. To do this experiment, they created simulated bitumen wasteforms and irradiated them with a ^{60}Co source that was capable of delivering up to 5 kGy/hour. They determined from their experiments that keeping the activity of the waste entrained in the bitumen to less than 75 Bq/L should ensure that no significant pressure build-up occurs.

GAS FORMATION

While apparently no formal methods exist for evaluating gas generated from buried mixed waste, Rees (1989) does present information on the subject. He cites two sources of gas generation from solid wastes: the corrosion of metals, releasing hydrogen, and the microbial degradation of organics, creating carbon dioxide and methane. He goes on to say that radiolysis is thought to play only a small part in generating of gases.

SECONDARY REFERENCES FROM OUTSIDE THE UNITED KINGDOM

Canada

Stroes-Gascoyne (1990) gave the requirements for microbial growth in a disposal site. The four factors given were physiological tolerance of the microbes, fluid movement into the vault, availability of nutrients, and availability of energy sources.

Buckley, et al. (1985) attempted to grow *Pseudomonas* sp. on bituminized waste to determine if this would affect the release of complexants

and therefore radionuclides. They saw no increase in the release of ^{60}Co or ^{137}Cs . From this, they concluded that the microbial degradation of bituminized waste would be insignificant.

Japan

In a Japanese paper, Shoji and co-workers (1987) presented a new method for determining the degradation products of (TBP). Tributyl phosphate decomposes into dibutyl phosphate (DBP), monobutyl phosphate (MBP), and phosphoric acid (H_3PO_4) by hydrolysis and radiolysis. They tested the procedure on an irradiated simulated sample. The sample, which was TBP (30 vol. %) in n-decane was irradiated with a ^{60}Co γ -ray source at a dose rate of 2×10^3 Gy/h. The sample was then extracted with 0.001 to 0.1 M sodium hydroxide, and the aqueous layer was analyzed by ion-exchange chromatography. The equipment used was Dionex. The column, which is assumed to be an anion exchange, was not specified. The mobile phase was 4 mM Na_2CO_3 and 1.5 mM NaHCO_3 . They had linear responses over a range of 2 to 150 ppm for DBP, 3 to 200 ppm for MBP, and 3 to 100 ppm for H_3PO_4 .

France

A joint French and Japanese paper (Madic 1991) gave suggestions for reducing "troublesome" solvents in their analysis of TBP and decane in water. They suggested substituting hydrochloric acid with nitric acid. This nitric acid could then be recycled into the decladding process. They also replaced carbon tetrachloride with xylene hoping that xylene would be easier to dispose of. After this modified extraction technique, the TBP and decane were analyzed by an unspecified gas-chromatography technique.

United States

Means and Alexander (1981) provide a good review of the biogeochemistry of chelators in the environment. While it contains no analytical methods, we have included it in our report to call it to the attention of any researcher looking for information on many of the common chelators used in the nuclear industry.

Boggs and Seitz (1984) conducted partitioning experiments to measure the influence of humic and fulvic acids on the sorption of americium and neptunium. This is another indirect method of measuring organic complexants by measuring their effect on the solubility of radionuclides. Details of this method are not presented here because they are so similar to the method of Wilkins reported earlier, and it is not a true organic analysis. However, their conclusion is quite the opposite of that arrived at by Ewart and Williams (1980). Boggs and Seitz believe humic and fulvic acids would significantly increase the mobility of radionuclides through groundwater rock environments.

Francis et al. (1980; 1979) reported on the changes of organic-compound concentrations present in trenches at Maxey Flats upon exposure to microbes found in the trenches. Some of the compounds, which are listed in Table 3, increased, and others decreased. These compounds were extracted out of an aqueous layer into methylene chloride and analyzed by GC/MS. No details of the GC conditions were given. The compounds were identified by comparing spectra with EPA-National Institute of Health computer libraries. They also reported that 10 kBq/mL completely inhibited microbial growth.

Table 1. Anaerobic Degradation of Organic Compounds Present in Maxey Flats Trench 26 Leachate Sample by a Mixed Culture of Bacteria (Francis et al. 1980).

Compound	Initial Concentration (mg/L)	Percent Change
2-Methyl propionic acid	3.5	+31
2-Methyl butanoic acid	18.7	+16
Valeric acid	4.6	-100
C6 acid (unidentified) ^a	NQ	+5.8
C6 acid (unidentified) ^a	NQ	+3.6
Hexanoic acid	1.8	-100
2-Methyl hexanoic acid	1.3	+8
Cresol	1.8	+11
C8 acid (unidentified) ^a	NQ	-4
C8 acid (unidentified) ^a	NQ	-0.5
Benzoic [acid?]	1.1	0
Phenyl acetic acid	1.4	-7
Phenyl propionic acid	1.2	-100
α -Terpineol	0.16	-6

^a Percent changes in concentration were determined on the basis of the ratio of the compound with the internal standard. NQ, not quantified.

Shook (1987) reported on a new solid-phase extraction technique that concentrates organic analytes from an aqueous stream and separates them from radioactive species for analysis by GC. This technique was designed to use with the aqueous effluent from the Savannah River Plant's Purex process. Tributyl phosphate in normal paraffin hydrocarbons (NPH) is used as an extractant for uranium and plutonium. These organics can contaminate the aqueous effluent. The TBP slowly hydrolyzes to DBP (see Shoji (1987), above). The presence of DBP can cause filter and resin bed clogging in subsequent steps of the process, so this analysis was very important. To prepare a sample, an octadecyl column was attached to a vacuum manifold in a glovebox. The column was washed with methanol and then water. An aliquot of radioactive

sample was slowly passed over the column bed, which was then washed with water and allowed to dry for 2 minutes by aspirating air. The analytes were then flushed from the column with tetrahydrofuran. This eluant was adjusted to a known volume for analysis by GC. The GC conditions are not detailed in this paper. The recoveries by this method were >90% for TBP and ranged between 30 and 50% for NPH. Shook found that eluting the octadecyl column with methanol resulted in poorer NPH recovery, and elution with hexane did not recover any TBP.

One of the earlier reports comes from Weiss and Colombo of Brookhaven National Laboratory (Weiss and Colombo 1980). It evaluates the groundwater chemistry and isotope migration found at radioactive waste disposal sites in Maxey Flats, Kentucky; West Valley, New York; Sheffield, Illinois; and Barnwell, South Carolina. Among the analyses performed was organic analysis of trench and well water from the sites. A liquid extraction technique was used to isolate the acidic, basic, and neutral constituents of the samples. The technique is pictured schematically in Figure 1. The TMS derivitization used N,O-bis-(trimethylsilyl)-trifluoroacetamide as the reagent. The GC/MS analysis used a Hewlett Packard 5983 mass spectrometer interfaced to a Hewlett Packard 5700 gas chromatograph and a 5933 data system. The GC conditions are listed in Table 4.

Table 2. GC Conditions for the Analysis of Trench Water Organics
(Weiss and Colombo 1980)

Column:	1.8 m x 2.0 mm glass, packed with 10% SE-30 on Chromosorb-W
Carrier:	Helium at 35 mL/minute
Temperature:	Initial 60°C for 4 minutes, then 4°C/minute to 240°C
Interface:	The column was interfaced to the MS via a jet separator.

Figure 1. Schematic of Organic Extraction of Trench and Well Waters (Weiss and Colombo 1980).

CONCLUSIONS

We have examined literature found in the U.K. Not much information appears to be pertinent to the types of radioactive wastes found at Hanford (waste containing large volumes of liquid and salt slurries).

The nuclear industry in the U.K. appears to have kept very good records of their waste materials. This has made development of complex analytical techniques unnecessary.

Most of the information found in this search pertains to the fate of solid waste entrained in cement for long-term burial. The British researchers are primarily concerned with the formation of complexing leachates that would assist the migration of radionuclides out of the cement wasteforms and through the soil. The other prime concern was the integrity of the wasteform. One new aspect of waste fate uncovered in this literature search is the role of microorganisms in creating complexants.

Useful secondary references describe determination of TBP degradation products, GC/MS analysis of organic acids, and a solid-phase extraction method. A scheme for the organic analysis of groundwater samples from radioactive waste sites was also described.

The methods referred to in the preceding paragraph are the only methods uncovered in this literature search. The final conclusion of this and the earlier literature search (Clauss and Bean 1993) is that the nuclear industry has not made a major effort to examine its waste streams for organic waste.

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APPENDIX A

STATEMENT OF WORK TO HARWELL LABORATORY

STATEMENT OF WORK

Literature Search for Methods of Analysis for Organic Analytes in Radioactive Waste.

BACKGROUND

Pacific Northwest Laboratory (PNL) is a contractor for the US Department of Energy and is working closely with Westinghouse Hanford Company in the management and cleanup of nuclear defense waste at the Hanford Reservation in the State of Washington. PNL is seeking methods developed in other countries on the analysis of organic compounds in nuclear wastes. The literature retrieved will be evaluated by PNL, summarized, and compiled into a publicly available report.

There is a need for this information at Hanford so that the final treatment and disposal of the nuclear wastes can be accomplished efficiently. Although there are published methods for analysis of organics in wastes, notably methods from our US Environmental Protection Agency, they do not include provisions for handling radioactivity, do not include all compounds of interest, and often are not applicable to the sample matrices found in nuclear wastes.

SPECIFIC TASKS

1. Search UKAEA databases, abstracts, and documents on hand for methods that are specifically written for the sampling or analysis of organic compounds in radionuclear waste, reprocessing streams, sites contaminated with radioactivity, or any other areas where organic material and radioactive material have commingled.

2. Search UKAEA databases, abstracts, and documents for publications that describe:

- experiments using simulated radioactive waste matrices.
- organic composition of radionuclear wastes and process streams.

3. Provide PNL with other contacts; either persons, companies, or government agencies that may contribute additional sources of information.

SEARCH SUGGESTIONS

A similar search in the United States has found information on subjects listed below. The list below provides the searcher with subject headings that

might prove useful in initiating a search. It is not, however, meant to be inclusive of all the possible subjects that could be found in the search.

- Total organic carbon
- Molecular weight distribution of organics
- Solvents (carbon tetrachloride, tetrachloroethylene, hexone, saturate hydrocarbons, etc.)
- Volatile organics (e.g., purge & trap and related methods)
- low molecular weight acids and aldehydes (glyoxylic acid, oxalic acid, glyoxal, acetic acid, etc.)
- Chelators and chelator breakdown products (EDTA, HEDTA, NTA, IDA, ED3A, etc.)
- Phenolic compounds
- General methods for determination of semivolatile acid, base and neutral organic compounds
- Higher molecular weight organics (polymers, humic acids, condensation products)
- Organometallic compounds
- Nitro and nitroso compounds

PNL is also interested in publications specifically directed to the use of mass spectrometry (MS), gas chromatography/MS (GC/MS), liquid chromatography/MS (LC/MS), and LC/MS interfaces that are particularly applicable to radioactive wastes. Other methods of interest include ion chromatography applied to organics in radwastes, and simultaneous detection of organic and inorganic eluants from separation columns, for example by combined ICP/MS and GC/MS or LC/MS.

The work envisioned by PNL is a brief search to determine the extent of the available material. This includes a listing of report titles or other indication of content.

DELIVERABLES

The draft report shall consist of all documents that have been identified. This list shall include the title and date, applicability (sample types, analyses, etc.), current status (in use, withdrawn, etc.), and contact (name, location, etc.). The draft copy shall be faxed to the PNL for comment.

The final report shall consist of all documents that have been identified. This list shall include the title and date, applicability (sample types, analyses, etc.), current status (in use, withdrawn, etc.), and contact (name, location, etc.). The original and two copies of the final report shall be mailed to PNL.

There are no guarantees that any relevant methods exist. It is possible that UKAEA may not be able to disclose information on the grounds of confidentiality.

Schedule

The draft report shall be due by 12 February 1993.

PNL shall fax and then mail a copy of the draft report with PNL's comments to UKAEA 5 March 1993.

UKAEA shall fax the final report and then mail the final report and its two copies by 19 March 1993.

APPENDIX B

THE REPORT ISSUED TO PNL FROM HARWELL LABORATORY^(a)

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COMMERCIAL IN CONFIDENCE

AEA-EE-0489

LITERATURE SEARCH FOR U.K.A.E.A.
METHODS OF ANALYSIS FOR ORGANIC
ANALYTES IN RADIOACTIVE WASTE

R M Brown and J Monahan.

Analytical Sciences Centre
AEA Technology
Harwell Laboratory

March 1993

ABSTRACT

Under contract to Battelle's Pacific Northwest Laboratory, a search of AEA databases, records and working documents has been performed to search for written methods of analysis of organic analytes in radioactive waste. Locations searched have included AEA libraries and departments performing analytical chemistry. Discussions have also been held with senior members of AEA staff.

The search has not located any formal or informal documents that detail analytical procedures. Related documents have been found however, that either give details of the organic composition of radionuclear wastes or that give details of experiments to characterise thermal or radiolytic degradation products of organic polymeric wastes such as cellulose and various plastics. References to and the abstracts from these unclassified related publications are listed in an Appendix.

1. INTRODUCTION

The safe decommissioning of nuclear facilities and disposal of nuclear waste is dependant upon reliable measurement of the composition and quantities of materials present. In the context of nuclear waste the prime interest for many decades has been the radionuclide content. In more recent years there has been a growing understanding of the effects of the presence of co-disposed non-radioactive materials. The reasons for this are:

- Some of the co-disposed materials may themselves be chemically toxic,
- co-disposed materials may influence the release or retention of radionuclides in waste reprocessing and disposal,
- co-disposed materials particularly organics may be decomposed radiolytically.

The analytical chemist therefore plays a pivotal role in identifying and quantifying species present in waste.

Battelle's Pacific Northwest Laboratory (PNL) is collaborating in the management and cleanup of nuclear defence waste at the Hanford Reservation. PNL is producing methods for the analysis of nuclear waste in order to determine organic analytes. This information is required to enable the efficient treatment and disposal of waste.

Under contract to PNL, we have searched the libraries of AEA Technology (AEA, the trading name of the United Kingdom Atomic Energy Authority) and have talked to a number of senior analytical chemist within AEA. We have sought methods currently in use or withdrawn from use that may be of use in the Hanford Reservation cleanup.

Our prime objective has been to locate information relating to analytical methods appropriate to identifying and/or quantifying organic species in nuclear wastes. Although many published method exist including some fully validated, they generally do not include provision for the safe handling of radioactive species do not include all species of interest to the nuclear industry and are often not applicable to the matrices encountered with nuclear waste.

In addition, the opportunity has been taken to search for information on AEA experiments using simulated radioactive waste matrices together with data on the organic composition of radionuclear wastes and process streams.

From the outset it has been made clear that there are no guarantees that any relevant analytical method or publications exist, nor even if they do exist, that they can be made available to PNL. Much of the early work of the AEA is still covered by its original grading and much of the more recent work is covered by terms of commercial confidentiality. The search has taken these limitations into account.

It has been assumed throughout that PNL have access to all published AEA documents via use of international databases such as Chemical Abstracts and the International Nuclear Information System. No attempt has been made therefore to list or review any documents already in the public domain such as refereed papers in scientific journals.

Instead this search has been restricted to internal publications and unpublished informal documents that PNL would otherwise not have access to. This report details the findings of our search.

2. RECORDS SEARCHED

The Harwell Library contains copies of or references to all published external and internal documents of the AEA since its formation. Records and abstracts of publications between 1946 and 1980 are held on an extensive card-index system. This system is ordered by subject and contains in excess of 50,000 individual cards. The system has been searched by subject using the keywords

- analysis
- determination
- organics
- radioactivity

individually and in combination. Since 1980 the records have been fully computerised and this database has also been searched in the same way.

The search for less formal documents has involved discussion with senior staff of analytical departments throughout AEA. This aspect of the search was designed to find work instructions or other written documents held at a local level. The AEA has staff at six laboratory locations spread across the UK although not all sites have an analytical department. For example our staff at the Sellafield reprocessing site in Cumbria use the analytical resources of BNFL on the same site. Principle staff contacted have been:

• Dr J S Hislop	- Divisional Manager of Harwell's Analysis and Diagnostics Division which includes the Analytical Sciences Centre. His department is responsible for providing analytical support to a wide range of internal (AEA) and external customers. This department houses AEA's main organic analytical resources.
• Mr C G Allen	- Chemist in charge of AEA's nuclear reprocessing plant at Dounreay, Scotland.
• Dr J D Wilkins	- Divisional Manager of Harwell's Process Services Division. His responsibilities include analytical facilities in Harwell's Actinide Chemistry and Reprocessing Development departments. Additionally he was formerly Division Head of Harwell's Chemistry Division

In addition, discussions have taken place with a number of their staff and others who may be more aware of the existence of informal work-instructions or other local documents.

Finally a number of current senior managers of the AEA have been consulted. These staff because of the current or past roles have or have had responsibility for active wastes. These senior staff include:

- Dr R H Flowers - Chief Technologist, Nuclear.
- Dr R L. Nelson - Director of Decommissioning and Radwaste Operations.
- Dr P Hawtin - Formerly Head of Harwell's Chemical Engineering Division responsible for nuclear waste R&D programmes.
- Dr K W Carley-Macauley - Programme manager in Decommissioning and Radwaste Operations whose duties include responsibility for the preparation of inventories of all Harwell's radioactive wastes and their composition.

3. ANALYTICAL METHODS

No formal or informal written analytical methods have been found. Discussions with analytical departments throughout AEA have given similar answers, namely that no formal methods are now or have been regularly used in the past. Whenever a particular organic analysis has been required then the analytical methods available at the time for use on inactive samples are applied, with suitable modification where necessary. Examples can be found covering GC, HPLC, GCMS, FT-IR, Total Organic Carbon etc, but none of these have been written into a form suitable for external release. Some will exist only as handwritten comments in laboratory notebooks for example.

One publication has been identified which details the application of Laser Induced Photoacoustic Spectroscopy to the study of Plutonium (IV) complexes with organic ligands. This paper (AERE-R13299) is detailed in the Appendix.

4. EXPERIMENTS USING SIMULATED RADIOACTIVE WASTE MATRICES.

Harwell has an on-going research programme to investigate both thermal and radiolysis degradation products of common polymers likely to be consigned with low level radionuclear waste. Several available reports have been produced and their references titles and abstracts are listed in the appendix.

5. ORGANIC COMPOSITION OF RADIOACTIVE NUCLEAR WASTE

At the moment, information on the organic materials present in active waste is usually derived from a detailed knowledge of the source of the waste. For solid wastes reliable estimates of the quantities of cellulose and synthetic organic

polymers and rubbers can readily be made this way. For liquid waste streams data derived this way for solvents, complexing agents etc is likely to be less reliable.

In the UK, the Government agency responsible for formulating policy relating to nuclear waste is UK Nirex Ltd, who report to the Government's Department of the Environment (DoE). Nirex commission research from a number of commercial and Government organisations including AEA. One relevant report identified during the search is Nirex Report No 96. The full title, abstract and reference are given in the Appendix.

It is possible that Nirex have other relevant information relating to the organic composition of UK nuclear wastes and it may therefore be appropriate for PNL to contact them directly.

UK Nirex Ltd
Curie Avenue
Harwell
Didcot
Oxfordshire OX 11 ORH
United Kingdom

phone +44-235-835153 (switchboard)
fax +44-235-831239

UK Nirex Ltd's Information and Public Relations Manager is a Mr P J Curd on telephone extension 515.

6. CONCLUSIONS

The search for AEA internal documents detailing analytical methods for the determination of organic analytes in radionuclear wastes has not identified a single directly relevant document although a number of related reports have been identified and details provided in Appendix 1. Formal quality assurance designed to comply with ISO9001 is currently being implemented throughout AEA and many analytical Standard Operating Procedures exist or are being written. At the present time none have been identified which relate to PNL's specific interest in validated analytical methods for determination of organic analytes in radio-nuclear wastes.

The search has however highlighted a number of related AEA internal publications which either give the results of application of analytical methods, or which detail experiments to identify radiolysis degradation products and their effect on actinide solubility, or which give indications of the organic composition of UK nuclear wastes. These predominantly concentrate on the presence in waste of solid organic polymers including cellulose and the man-made rubbers and plastics. Reference to, and the abstracts from, these publications are appended. Other work and additional reports have been identified but can not be provided to PNL for reasons of commercial confidentiality.

APPENDIX I

**REFERENCES TO AND ABSTRACTS FROM REPORTS AND
PUBLICATIONS IDENTIFIED DURING THE SEARCH**

TITLE: α -irradiation of combustible plutonium contaminated material.

AUTHORS: W G Burns, C E Lyon, W S Walters & J D Wilkins.

DATE: November 1985.

REFERENCE: Harwell Report No. AERE R 11696.

AVAILABILITY: ISBN 0-7058-1382-7 from HMSO, PO Box 276, London SW8 5DT, England.

ABSTRACT I: A survey has been carried out of α -irradiation effects on the components of combustible plutonium contaminated material (ie plastic and rubber) with particular emphasis on the possible formation of water soluble species that might form complexes with plutonium. The composition of combustible PCM and the possibility of chemical contaminants are discussed. Materials discussed include polyvinyl chloride, Hypalon, neoprene, latex, polyethylene and cellulose.

TITLE: A literature survey of the possible effects of humic acid on the disposal of low level waste and intermediate level waste.

AUTHORS: F T Ewart and S J Williams.

DATE: March 1986.

REFERENCE: Harwell Report No. AERE-R12023.

AVAILABILITY: ISBN 0-7058-1293-6 from HMSO, PO Box 276, London, SW8 5DT, England.

ABSTRACT: A review has been made of the literature on the interactions of radionuclides with humic acids taking note of the chemical conditions which may be present under possible land disposal options for low and intermediate level wastes. The quantities and molecular weights of dissolved organic carbon are determined by the nature of the site under investigation. Complexation data is limited and can not be used to reliably predict solubilities. No work on the influence of humic acids on the sorption properties of the actinides or technetium on near-field components has been reported. In the far-field of a repository constructed in a clay bed only a small fraction of the total organic carbon may be mobile under natural conditions. The majority may be bound to clay minerals and provide a significant sink for radionuclide sorption. It is concluded that there is a requirement for further work in this area and some possible experimental investigations are discussed.

TITLE: Preliminary experimental studies on the chemical and radiation degradation of combustible plutonium contaminated material.

AUTHORS: S Bradshaw, S C Gaudie, B F Greenfield, C E Lyon, J H Rees, M W Spindler and J D Wilkins.

DATE: October 1986.

REFERENCE: Harwell Report No. AERE R 12223.

AVAILABILITY: ISBN 0-7058-1444-0; HMSO, PO Box 276, London, SW8 5DT, England.

ABSTRACT I: The chemical and radiation degradation of combustible plutonium contaminated material (PCM) in a cement matrix has been investigated.

Experimental studies have been carried out to establish the influence of any water soluble chemical and radiation degradation products on the solubility of plutonium at high pHs. The influence of complexing agents (eg EDTA, citric acid) which may be present in wastes on plutonium solubility has been assessed. The extent of sorption on cement in the presence of organic degradation products has been measured.

TITLE: Cement and polymer matrices for the immobilisation of intermediate level waste a preliminary assessment of their potential deterioration during storage and disposal.

AUTHORS: J E Duddridge.

DATE: November 1986.

REFERENCE: Harwell Report No. AERE-R11862.

AVAILABILITY: Publications Office, Harwell Laboratory, Oxfordshire, OX11 0RA, England.

ABSTRACT: As part of the jointly funded BNF plc/DoE intermediate level waste product evaluation programme a review of the literature relevant to the microbiological deterioration of cement, polymer-modified cement and polymer matrices considered for intermediate level radioactive waste immobilisation has been undertaken. In the absence of experimental or field data a speculative assessment has been performed which identifies those factors likely to influence or direct the extent of matrix biodeterioration and the overall microbiology of the storage and disposal systems.

Subject to the qualifying conditions and arguments presented within the report, some tentative conclusions on repository design and operation have been reached.

TITLE: Survey of chemical degradation processes in immobilised plutonium contaminated material.

AUTHORS: M J Guest.

DATE: September 1987.

REFERENCE: Harwell Report No. AERE-R12083.

AVAILABILITY: ISBN NO-7058-1406-8, HMSO, PO Box 276, London, SW8 5DT, England.

ABSTRACT: The possible decomposition routes for organic waste materials (eg cellulose, polvvinylchloride, neoprene, polyethylene) under the high pH conditions expected in concrete pore water have been reviewed. The different types of organic material present in radioactive waste have been categorised according to their susceptibility to attack by alkali. Where possible the decomposition products have been identified and where possible their ability to form complexes with long lived radionuclides has been reviewed.

TITLE: Experimental studies on the chemical and radiation decomposition of intermediate level wastes containing organic materials.

AUTHORS: S Bradshaw, S C Gaudie, B F Greenfield, S Long, M W Spindler and J D Wilkins.

DATE: November 1987.

REFERENCE: Harwell Report No. AERE R 12806. Also published as UK Department of the Environment Report No. DOE/RW/89/049.

AVAILABILITY: Publications Office, Harwell Laboratory, Oxfordshire, OX11 0RA, England.

ABSTRACT: Further studies on the radiation and chemical decomposition of combustible plutonium contaminated material (PCM) in a cement matrix have been carried out. A wide range of organic materials has been investigated both as individual materials and as representative mixtures. The formation of water soluble complexing agents has been monitored through the measurement of plutonium (and in some cases americium) solubility and sorption on cementitious materials.

TITLE: The influence of organic materials on the near-field of an intermediate level waste radioactive waste repository.

AUTHOR: J D Wilkins.

DATE: February 1988.

REFERENCE: Harwell Report No. AERE R 12719.

AVAILABILITY: Publications Office, Harwell Laboratory, Oxfordshire, OX11 0RA, England.

ABSTRACT: The encapsulation of a range of intermediate level wastes in cementitious materials is being planned by the nuclear industry. Although potential sites for the disposal of intermediate level wastes have not yet been identified they will be situated in regions of low water flow. Under these conditions the concentrations of radionuclides in water leaving the repository will be controlled by their solubility and sorption on the solid materials present. The cementitious materials which are used as waste matrix and can be used as backfill have been found to be particularly beneficial. Experiments with intermediate level wastes have shown that these chemical processes can reduce the concentrations of key radionuclides such as neptunium and plutonium to very low levels.

Some wastes contain organic materials which may decompose to form water soluble complexing agents. These could complex with the radionuclides thereby reducing the extent of sorption and increasing the solubility which would lead to an enhanced release from the repository. Decomposition as a result of the chemical conditions, the radiation field and microbiological activity in the repository are being investigated through accelerated experiments in the laboratory. The solubility of plutonium is being measured as a key marker element to give an indication of the effects of any decomposition products. A modest enhancement of solubility (up to a factor of 100) has been observed with some materials but the solubilities have been increased by about a factor of 10^4 with a few materials (e.g. cellulose). The change of solubility with time in the accelerated experiments is being monitored and it appears that the rate of increase is falling.

The experimental results obtained to date indicate the need to examine the effect of organic materials on the performance of the near field of a radioactive waste repository.

TITLE: Organics in Radwaste - Proceedings of the one day technical seminar held at Harwell on 22 September 1987.

AUTHOR: N K Taylor. (ed)

DATE: October 1988.

REFERENCE: Harwell Report No. AERE R 13079.

AVAILABILITY: Publications Office, Harwell Laboratory, Oxfordshire, OX11 0RA, England.

ABSTRACT: This 173 page report contains the 15 papers presented by representatives of AEA British Nuclear Fuels Ltd and the Central Electricity Generating Board. The papers were grouped around three topics:

- types of organic materials in radioactive waste (3 papers)
- the effects of organics on repository performance (5 papers)
- destruction of organics (7 papers).

TITLE: Actinide Speciation; further development and application laser induced photoacoustic spectroscopy and voltametry.

AUTHORS: J E Cross, D Crossley, J W Edwards, F T Ewart, M Liezers, J W McMillan, P M Pollard & S Turner.

DATE: December 1988.

REFERENCE: Harwell Report No. AERE-R 13299.

AVAILABILITY: Publications Office, Harwell Laboratory, Oxfordshire, OX11 0RA, England.

ABSTRACT: Further work is reported on the sensitive determination of actinide species in solution using the Harwell laser induced photoacoustic spectrometer (LIPAS). To permit speciation and solubility measurements under well controlled pH and Eh conditions a combined LIPAS/electrochemical loop has been developed and is described in detail. The new equipment has been used to study uranium and neptunium species at several pH s and Eh s between +280 and -400mV. Comparison of observed species with those predicted by the thermodynamic geochemical modelling code PHREEQE has revealed differences. These in part can be reconciled by database refinement but in part have revealed deficiencies in knowledge that require further study. The sensitivity of LIPAS for the measurement of U, Pu, Np and Am species has proved to be high up to ca 10^{-9} M sensitivities generally being higher for alkaline solution conditions. Preliminary work indicates that LIPAS can be used to distinguish between Pu(IV) complexes with possible cellulose degradation products typified by gluconic acid and other organic acids likely to be present in a waste repository.

TITLE: Modelling the behaviour of organic degradation products.

AUTHORS: J E Cross, F T Ewart & B F Greenfield.

DATE: March 1989.

REFERENCE: Conference presentation at 12th International Symposium on the Scientific basis for nuclear waste management (Berlin, Germany October 1988). Published as UK Nirex Ltd Report No. NSS/R-151.

AVAILABILITY:

ABSTRACT: Results are presented from recent studies at Harwell which show that the degradation products which are formed when certain organic waste materials are exposed to the alkaline conditions typical of a cementitious environment can enhance the solubility of plutonium, even at pH values as high as 12, by significant factors. Characterisation of the degradation products has been undertaken but the solubility enhancement does not appear to be related to the concentration of any of the major organic species that have been identified in the solutions. While it has not been possible to identify by analysis the organic ligand responsible for the increased solubility of plutonium, the behaviour of D-Saccharic acid does approach the behaviour of the degradation products. The PHREEQE code has been used to simulate the solubility of plutonium in the presence of D-Saccharic acid and other model degradation products in order to explain the solubility enhancement. The extrapolation of the experimental conditions to the repository is the major objective but in this work the ability of a model to predict the behaviour of plutonium over a range of experimental conditions has been tested.

TITLE: The Measurement of Molecular Weight of Humic Acid by Ultracentrifugation.

AUTHOR: M P Gardner.

DATE: July 1989.

REFERENCE: Harwell Report No. AERE-M3730.

AVAILABILITY: ISBN 0-7058-1539-0 from Her Majesty s Stationary Office,PO Box 276, London SW8 5DT, England.

ABSTRACT: This report is concerned with the application of ultracentrifuge methods to the determination of humic acid molecular weights. The work has been undertaken as part of the COCO Club intercomparison exercise on humic acid characterisation. Knowledge of the molecular weight distribution of humic acid will be an important parameter in assessing the likely physical and chemical behaviour under the near-field environment. Molecular weights of a sample of purified Aldrich humic acid have been obtained by sedimentation velocity and sedimentation equilibrium studies using an analytical ultracentrifuge. The results have shown the material to be polydisperse with a weight average molecular weight in the region 2700-4000.

TITLE: The Physical and Chemical Characteristics of Radioactive Wastes.

AUTHORS: Electrowatt Engineering Services (UK) Ltd.

DATE: May 1990

REFERENCE: UK Nirex Ltd. Report No. 96 (also issued as UK Department of the Environment Report No. DOE/RW/90-038)

AVAILABILITY: From UK Nirex Ltd, Curie Avenue, Harwell, Didcot, Oxfordshire, OX11 0RA, United Kingdom.

ABSTRACT: This report presents information on the physical and chemical characteristics of low, intermediate and high level radioactive waste in the United Kingdom and on the current storage conditions and anticipated conditioning process. Operational and decommissioning wastes are considered for both committed and prospective plant. Arisings are from power reactors, commercial reprocessing, fuel manufacture, medical and industrial sources and research development.

TITLE: Review of the microbiological, chemical and radiolytic degradation of organic material likely to be present in intermediate level and low level radioactive wastes.

AUTHORS: B F Greenfield, A Rosevear & S J Williams.

DATE: November 1990.

REFERENCE: AEA Decommissioning & Radwaste Report No. AEA-D&R-0120 also issued by UK Department of Environment as DoE Report No. DOE/HMIP/RR/91/002.

AVAILABILITY: From Decommissioning & Radwaste Registry, AEA Technology, Winfrith, Dorset, DT2 8DH, England.

ABSTRACT: A current option for the disposal of intermediate-level and low-level radioactive wastes is their consignment to a deep mined, underground repository. After the closure of the repository, resaturation of the near field will take place and all the wastes will be progressively exposed to groundwater which has been in contact with a cementitious backfill. Any effects which may alter the expected solubility and sorption behaviours of radioelements under these conditions should be considered.

One possible influence on radioelement behaviour is the release of water soluble complexants by the degradation of the solid organic polymers which will be present in the wastes eg cellulose, polyvinylchloride and polyethylene. These may be subjected to chemical, microbiological and radiolytic attack. The objective of this report is to review the present state of knowledge of these topics and the implications for radioelement solubilities.

An estimate has been made of the likely quantities of organic materials which may be disposed of in the proposed UK repository for ILW/LLW. Their chemical degradation is considered and specific attention paid to cellulose whose degradation products have been found to cause considerable increases in plutonium solubility under alkaline conditions. Radiolytic degradation of organic polymers is described and the results of experimental studies on the influence of alpha and gamma irradiated materials on plutonium solubility reviewed. The nature of microbial degradation is outlined and the specific case of organic degradation under repository

conditions is detailed. Potential interactions between microbial, chemical and radiolytic processes are described with attention concentrated on the biodegradation of chemically and radiolytically derived organic intermediates. The effects of organic degradation products on the solubilities of plutonium, americium, thorium, technetium and nickel under near-field conditions are reviewed and some consideration is given to the effects on sorption.

A number of recommendations for further research on the degradation of organic materials under repository conditions are made. The report contains 160 references.

TITLE: The effects of degradation of organic materials in the near-field of a radioactive waste repository.

AUTHORS: B F Greenfield, A D Morton, M W Spindler, S J Williams & D R Woodwark.

DATE: 1992.

REFERENCE: Mat. Res. Soc. Symp. Proc. V257, p299-306 (1992) presented at the Materials Research Society Symposium, Strasbourg 1991.

ABSTRACT 1: UK Nirex Ltd are seeking to develop a deep underground repository for the disposal of solid ILW and LLW in the UK. The formation of water-soluble complexants from the degradation of the solid organic polymers and cellulosic materials present in such wastes may influence the solubility and sorption properties of a number of radioelements. A number of materials have been chemically degraded under alkaline, anaerobic conditions representative of the near field of the repository. Measurements of plutonium solubility in the leachates obtained show that the degradation of cellulose is of particular concern; the effects on the solubility can be several orders of magnitude greater than those of other organic materials. Products formed from the degradation of ion-exchange resin were found to have little effect. Solubilities of a number of other radioelements in aerobically degraded cellulose leachates are also given. The effect of reducing the ratio of cellulose to cement in the degradation experiments results in a decrease in plutonium solubility in the corresponding leachate. Several of the likely degradation products of cellulose have been individually synthesised including isosaccharinic acid, a key degradation product of cellulose. Enhanced plutonium solubilities have been measured in 10^{-3}M solutions of these compounds. Sorption of plutonium onto cement from leachates obtained by the degradation of 10% cellulose in cement is reduced by about two orders of magnitude. Interaction with cement removes significant concentrations of complexants from solution. Thermodynamic modelling studies show that hydroxyl groups present in the compounds which result from the alkaline degradation of cellulose can strongly complex with plutonium.

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APPENDIX C

FURTHER REFERENCES NOT CITED IN THIS REPORT

This appendix lists in bibliography form references found in this literature search that were not cited in the main text. This list contains references that were ordered and reviewed, and a brief comment as to why they were not cited. The comment may be useful for those attempting to find further information. These references are arranged in descending order by year, and are alphabetized within each year.

1. Cooper, M. J. 1991. *Nirex Safety Assessment Research Programme Bibliography*. NSS/G116 AEA-D&R-0235, Harwell Laboratory, Oxfordshire OX11 0RA, U.K.

Comment: This is a list of references from Harwell. While it contains no discussions, it is a good starting point when doing a literature search of the British nuclear industry.

2. Ceo, R. N., M. B. Sears, and J. T. Shor. 1990. *Physical Characterization of Radiation Sludges in Selected Melton Valley and Evaporation Facility Storage Tanks*. ORNL/TM-11653, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Comment: Measured radioactivity, density, viscosity, yield stress, and sedimentation of Oak Ridge tank samples. No organic analysis was discussed.

3. Green, D. W. 1990. *Analytical Chemistry Laboratory, Progress Report for FY 1990*. ANL/ACL-90-2, Argonne National Laboratory, Argonne, Illinois.

Comment: This paper is, as the title implies, a progress report, and contains no methods.

4. Mackay, C.N.N., C. L. Mills, and T. W. Kyffin. 1990. *On-Line Fibre-Optic Spectrophotometry in Plutonium Pulsed Column Pilot Plant*. DNE-R--23, ry9000145(BNFL), UKAEA, Dounreay Nuclear Power Development Establishment, Thurso, Caithness, Scotland, U.K.

Comment: This paper reported the analysis of radionuclides.

5. Sears, M. B., J. L. Botts, R. N. Ceo, J. J. Ferrada, W. H. Griest, J. M. Keller, and R. L. Schenley. 1990. *Sampling and analysis of radioactive liquid wastes and sludges in the Melton Valley and evaporator facility storage tanks at ORNL*. ORNL/TM-11652, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Comment: This report referenced analytical techniques previously described in our earlier report, *Methods of Chemical Analysis for Organic Waste Constituents in Radioactive Materials: A Literature Review*. PNL-8266.

6. Carlsen, L. 1989. *The Role of Organics on the Migration of Radionuclides in the Geosphere*. CEC REPORT EUR 12024 EN.

Comment: Discussion of radionuclides migration. No analytical methods.

7. Colasanti, R., D. Coutts, S.Y.R. Pugh, and A. Rosevear. 1989. *Microbiology and Radioactive Waste Disposal; Review of the Nirex Research Programme- January 1989*. UKAEA Report NSS/R131, Biotechnology Group, Harwell Laboratory, Oxon OX11 0RA, U.K.

Comment: Discussed Harwell's attempts to model the behavior of microbes with respect to buried solid low-level waste. No pertinent analytical methods.

8. Gardiner, M. P. 1989. *The Measurement of the Molecular Weight of Humic Acid by Ultracentrifugation*. Harwell Report AERE M3730, Chemical Division, Harwell Laboratory, Oxfordshire OX11 0RA, U.K.

Comment: This reference does not pertain to radioactive samples.

9. International Atomic Energy Agency. 1989. *Options for the Treatment and Solidification of Organic Radioactive Wastes*, IAEA Technical Reports Series No. 294. International Atomic Energy Agency, Vienna, Austria.

Comment: Discussion on various methods of treating waste, but no analytical methods.

10. McGahan, D. J. 1987. *Survey Of Microbiological Effects in Low -Level Radioactive Waste Disposed of to Land*. UKAEA Report AERE R12477, Environmental Safety Centre, Environmental and Medical Sciences Division, Harwell Laboratory, Oxfordshire OX11 0RA, U.K.

Comments: A literature review on the state of research into the microbiological effects in low-level radioactive waste repositories. No analytical methods.

11. Oblath, S. B. 1987. *Characterization of organics in the feed streams for the H/F effluent treatment facility*. DPST-87-690, Technical Division, Savannah River Laboratory.

Comment: This paper cites Shook's paper (reference 34 in the main text) for its analytical technique. It does, however, have many lists of results.

12. Dayal, R., R. F. Pietrzak, and J. H. Clinton. 1986. Source Term Characterization For Maxey Flats Low-Level Radioactive Waste Disposal Site. Nucl. Tech. 72, 158, (1986), pp. 158-177.

Comment: Reports the results of work done by Brookhaven National Laboratory at Maxey Flats. This paper cites the Weiss and Colombo paper (Weiss and Colombo [1980] in the main text) for its analytical technique. It does, however, have many lists of results.

13. Peretz, F. J., B. R. Clark, C. B. Scott, and J. B. Berry. 1986. *Characterization of Low Level Liquid Wastes at the Oak Ridge National Laboratory*. ORNL/TM-10218, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Comment: Used EPA method 8270 for analysis of semivolatiles. Quite a complete set of other, non-organic analyses.

14. Pillay K.K.S. 1986. "The Effect of Ionizing Radiation on Synthetic Organic Ion Exchangers", *J. Radioanal. Nucl. Chem.*, Art., 97/1, pp 135-210.

Comment: Discussed the loss of exchange capacity of ion exchange resins upon exposure to radiation.

15. Burns, W. G., C. E. Lyon, W. S. Walters, and J. D. Wilkins. 1985. *α -Irradiation of combustible plutonium contaminated material*. AERE R 11696, Chemistry Division, Harwell Laboratory, Oxfordshire, OX11 0RA, U.K.

Comment: This was a literature review, and therefore contained no methods. It was used a source of secondary references.

16. West, J. M., I. G. McKinley, H. A. Grogan, and S. C. Arme. 1985. *Laboratory and Modeling Studies of Microbial Activity in the Near Field of a HLW Repository*. Mat. Res. Soc. Symp. Proc. Vol. 50, pp 533-538.

Comment: A discussion of microbial effects on radioactive waste forms.

17. Holcomb, W. F. 1978. *A Summary of Shallow Land Burial of Radioactive Waste at Commercial Sites between 1962 and 1976, with Projections*. Nuclear Safety, Vol. 19, No. 1, (1978), pp. 50-59.

Comment: This reference presents a compilation and interpretation of the inventories of commercial shallow land burial sites in the United States. No analytical methods were discussed.

18. Dole, M. 1972. *The Radiation chemistry of macromolecules Vol. I & II*, Academic Press, New York.

Comment: A book discussing the effect of radiation on polymers. There were no pertinent analytical techniques.

19. Charlesby, A. 1960. *Atomic Radiation and Polymers*, Pergamon, Oxford, U.K.

Comment: A book discussing the effect of radiation on polymers. There were no pertinent analytical techniques.

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