UK DEPARTMENT OF ENVIRONMENT QUALITY CHECKING FACILITY

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ABSTRACT

In June 1986 Taywood Engineering Ltd was awarded a three-year contract by the Department of Environment to set up an independent Radioactive Waste Quality Checking Laboratory. This contract was subsequently supported by the Commission of European Communities.

The purpose of the Laboratory was to develop and evaluate techniques for the non-destructive and destructive examination of both low- and intermediate- level radioactive waste packages. Some of these techniques were then used during 1988/89 for the Quality Checking of low level waste packages obtained by Her Majesty's Inspectorate of Pollution (HMIP) from UK sites. The contract included a study on the conceptual design and costing of a permanent facility for Quality Checking of radioactive waste packages.

This paper summarizes the progress achieved during 1986-89.

INTRODUCTION

The UK Department of Environment's policy on Quality Assurance in radioactive waste management is detailed in its publication "Radioactive Waste Management, Information Note 2"(1) which states that:

> "It is the intention of the authorizing Departments that an assessment will be made of the product material independently of the waste processing organizations. In practice this appraisal will range from the scrutiny of plant records and documentation to a check on the quality of the product in a Waste Form Quality Checking Center."

In June 1986, the Department of Environment awarded a three-year contract to Taywood Engineering Ltd (one of the Taylor Woodrow group of companies) to evaluate methods for Quality Checking (QC) of packaged radioactive wastes. This contract was subsequently supported by the Commission of the European Communities.

The key objectives were the development of a Quality Assurance system to enable the contract research schedule to:

- Procure, manage and operate appropriate facilities for the destructive and non-destructive examination of radioactive waste packages.
- Develop and demonstrate appropriate test methods for examination of radioactive waste packages.
- Design and cost permanent facilities for the examination of low and intermediate level radioactive waste packages.

During 1987/88, experimental facilities meeting the requirements of the Radioactive Substances Act (1960) and the Ionizing Radiations Regulations (1985) were set up and a Quality Checking team established on the AEA Technology site at Winfrith, Dorset. This paper summarizes the technical progress achieved during the contract duration; interim progress statements are contained in Refs. 2 - 4.

ASSESSMENT OF NON-DESTRUCTIVE TECHNIQUES FOR ASSAY OF CONTENTS OF DRUMS OF LOW LEVEL WASTE

The requirement was to assess the availability/suitability of non-destructive test methods for examination of the contents of 200 litre drums of low level waste (LLW). The following non-destructive techniques were evaluated:

- X-Radiography
- Neutron Radiography
- Passive Neutron Counting
- High Resolution Gamma Spectroscopy.

Tests were carried out using both simulant and genuine low level wastes and the results and conclusions are summarized below.

Waste Composition

Provided the waste components are not shielded, X-radiography will differentiate between the hard (eg metals, glass, concrete) and soft (eg paper, plastics) components of the waste. Film X-radiography gives the sharpest images but X-ray fluoroscopy (with the LLW drum on a rotating turntable) proved to be the most convenient technique. X-radiography will detect free liquids inside glass and plastic containers and items which can be recognized by shape (eg batteries, wire, filters). The technique is also useful for identifying items (eg bulky pieces of pipework and broken glass) which could make destructive sampling more hazardous for operators.

The technique is not generally useful for characterization of soft wastes but an experienced operator can in some circumstances differentiate between paper, cardboard and plastics. The technique cannot identify materials surrounded by dense, high molecular weight materials (for example, vials of liquids inside lead pots) and neutron tech-

niques must then be considered. Neutron radiography can detect liquids inside lead pots, but further work is necessary before this technique is suitable for routine application to drums of LLW.

Alpha-emitter Content

Some isotopes emit both alpha particles and neutrons, and this allows neutron counting techniques to be used for alpha-emitter assay. For example, the transuranic alpha-emitting isotopes Pu-238, Pu-240 and Cm-242 also decay by spontaneous fission and this allows them to be detected inside 200 litre drums of LLW by passive neutron coincidence counting techniques. Interaction of alpha particles with light elements inside LLW drums also produces neutrons, and this allows the above neutron counting techniques (in the non-coincident mode) to be used for alpha-emitter assay.

The limit of detection of the technique both for spontaneous fission and alpha-n events will depend on the waste matrix, background neutron levels and counting times. The method is capable of detecting LLW drums with alpha concentrations above the authorized UK (Drigg) LLW disposal limit of 4 Gigabecquerels per tone. The technique gives low results if neutron-absorbers like cadmium or gadolinium are present, does not indicate the spatial distribution of the alpha- or neutron-emitters inside the drum, and is not isotope-specific. Interpretation of the results depends on the isotopic composition of the alpha-emitters in the waste stream being available.

Only a limited amount of information on the alpha content of a drum is available from neutron counting techniques. This could be used in conjunction with knowledge of the isotopic composition of the waste stream and/or gamma spectrometry results to build up a more detailed alpha-content picture.

Gamma-emitter Content

Gamma spectroscopy will identify a wide range of fission and neutron-activation products. If the waste is soft, on-line transmission corrections (for attenuation of the gamma photons by the waste matrix) are not necessary, and a standard gamma spectrometer system can be adapted for the NDT of LLW drums. If the drum contains hard waste, a Segmented Gamma scanner (SGS) with an external transmission source should be used.

Problems arise when the abundance of the gamma photons is low, their energies are low or the isotopes are shielded. Thus, for example, Pu-239 inside a lead pot would be difficult to detect. If X-ray analyses or the external transmission source suggest the presence of dense materials inside a 200 litre drum, neutron counting techniques could be used in conjunction with SGS to build up a more representative picture of the alpha/gamma content of the drum.

QUALITY CHECKING OF LLW PACKAGES PROVIDED BY HMIP

Between July 1988 and March 1989 nine LLW packages were obtained by Her Majesty's Inspectorate of Pollution for independent examination at the QC Laboratory. The drums were non-destructively examined and opened in the QC Laboratory; selected contents were then removed for additional analyses.

Typical results obtained by NDT of the drums included:

X-radiography

- One drum was shown by X-ray analysis to contain two large sections of pipe instead of the concrete rubble informally declared by the waste producer.
- One drum was shown by X-ray analysis to contain syringe needles and ampoule knives. X-rays showed that this drum contained lead pots, and when the pots were opened, glass ampoules - containing free liquids - were found inside. (This drum had been obtained from decay-storage to assist in the development of Quality Checking techniques. It was not destined for disposal in the form tested at the QC Laboratory.)

Passive Neutron Counting

Six of the LLW drums were assayed by passive neutron counting but only two showed net total count-rates three standard deviation above the background level. One of these drums did not contain transuranics but the other contained almost 480kBq Am-241. A third drum containing 2kBq (Pu-239 + Pu-240) and 2kBq Am-241 did not give positive neutron signals.

Gamma spectroscopy

Gamma Spectroscopy provided unequivocal identification of a large number of fission products (eg Zr-95/Nb-95, Ru-106/Rh-106, Sb-125, Cs-134, Cs-137, Ce-144/Pr-144, Eu-152, Eu-154, Eu-155), activated corrosion products (eg Mn-54, Co-60, Zn-65) and actinides (eg U-235/U-238 and Am-241) inside the drums.

Six LLW drums were assayed by both Harwell (Segmented Gamma Scanning) and the QC Laboratory (gamma scanning and destructive analysis), but correlation between the two sets of results was not always good. The exercise highlighted the difficulties involved in assaying waste drums containing a wide variety of matrices and gamma isotopes.

Destructive Sampling and Analysis

All nine 200 litre waste drums were destructively sam-

pled and analyzed. Most wastes were packed in polythene bags inside the drums and these presented no sampling problems. Samples were monitored for radioactivity using probes inside the sampling glove-box and a selection of reference sources were available to check the probe efficiencies. The wide range of items found inside the nine drums of LLW included:

Lead pots with glass ampoules containing liquids, vermiculite, metal staples, dry-cell batteries, paper clips, film cassette, plastic box, coils of wire, cardboard boxes, tissue boxes, glove wrappers, newspapers, photographs, screw nails, soil-like material, filter papers, tissues, mineral fibre, 65kg valve, 25kg J-shaped pipe, gaskets, coveralls, spitzer teats, cleaning cloths and rags, plastics, incinerator ash, nuts, bolts, halogen lamps, steel bar, sticky tape (contaminated), polythene sheets, 945cm hemp rope (heavily contaminated), overshoes, damaged respirator, paper, gloves, polythene bottles, clamp stand, electrical wire, pesticide analysis kit, broken glass, sharp metal turnings (swarf), filter units, can of oil, metal containers, syringe needles, cotton wool.

Samples were selected for radiochemical analysis if activity was detected by the glove-box probes. Where the activity was spread throughout the drum (incinerator ash, contaminated mineral fibers) either all of the sample or representative sub-samples were selected. There was some stratification of the waste in a drum containing incinerator ash; the top layers contained heavier objects which were less radioactive.

Sample preparation

The following techniques were used for preparation of samples for analyses:

- The sample was stirred in mineral acids (eg nitric, hydrochloric, aqua-regia), the solution filtered and then made up to a known volume. Gamma spectroscopy measurements were made on the sample before and after dissolution to give an indication of the percentage of the sample taken up into solution.
- The sample, suspected of containing tritiated water, was treated with deionized water, and the solution distilled. Tritium was found in the distillate and the majority of the other remaining isotopes remained in the distillation flask.
- The sample was placed inside a stainless steel wire cage and solvent (water, acid or organic compounds) was refluxed to leach out the radioactive species. This method was used where it was difficult to bring the waste constituents into solution.
- The waste was heated (in a microwave oven) to reduce its volume and treated with acid to bring the radioactive species into solution. This method was used for contaminated PVC and polythene samples.
- The sample was dissolved and chemical separations carried out to isolate the isotopes of interest. This method was used for alpha- and beta-emitters (eg uranium and plutonium isotopes, strontium-90 and technetium-99).

Sample measurement

A variety of techniques was used to analyze samples from the nine HMIP drums. These included:

- Gamma Spectroscopy
- Liquid Scintillation Counting
- Alpha Spectrometry
- Atomic Absorption Spectrometry
- Inductively Coupled Plasma Emission Spectroscopy
- X-ray Diffraction
- Mass Spectrometry
- Fourier Transform Infra-red Spectrometry
- Microscopy.

The following isotopes were detected inside the drums:

Mn-54, Co-57, Co-58, Co-60, Zn-65, Se-75, Sr-90, Zr-95/Nb-95, Tc-99, Ru-106/Rh-106, Ag-110^{m}, Sb-125, Cs-134, Cs-137, Ce-144/Pr-144, Eu-152, Eu-154, Eu-155, U-235, U-238, Pu-239, Pu-240, Am-241.

Results

A summary of the drum examination results is given below.

- Two LLW drums contained about 98% of apparently non-contaminated items.
- The activity of two of the nine drums was underestimated by the waste producers by a factor of 1.5 to 3. The activity of the other drums was overestimated by factors ranging from 1.5 to more than 20,000.
- One of the drums contained free liquids in glass ampoules inside lead pots. These were acidic solutions of radioisotopes and a total of 1 litre free liquid was found.
- A 250ml can of oil was found inside one drum.
- Another drum contained small amounts of an acid-based liquid which had chemically corroded the inner base of the drum.

Discussion

The LLW NDT assessments and examinations of the HMIP drums helped in the identification of equipment and

development of Quality Assurance procedures and Work Instructions for the pilot LLW QC facility now in operation at Winfrith.

DESTRUCTIVE SAMPLING OF CEMENTED INTERMEDIATE LEVEL WASTE

The Quality Checking of encapsulated Intermediate Level Waste (ILW) could involve the destructive sampling of packaged (cemented) ILW to provide specimens for chemical analysis. The requirement was, therefore, to develop equipment to core and extract samples from steel waste drums by techniques compatible with eventual remote-handling operations in a hot-cell.

The main components of the experimental program were:

- to design and fabricate a full scale rig to carry out coring trials on drums of cemented simulant ILW
- to demonstrate techniques for containment of cooling water and the cement sludge generated by the sampling operations
- to evaluate the use of air cooled techniques for the coring of cemented waste
- to develop methods for the extraction of cores from the waste drum
- to develop and demonstrate methods of taking subsamples (for chemical analysis) from cores removed from the cemented simulant waste drum.

Sampling Rig

A sampling rig was designed to carry out the coring trials on the drums of cemented waste; it allowed the waste drums and the coring equipment to be mounted in either vertical or horizontal positions. The rig was commissioned in early 1988 using 200 litre mild steel drums filled with a mix of 3 parts of sand and 1 part of Ordinary Portland Cement (OPC). After the initial trials the work was continued using a matrix of 3 parts of Blast Furnace Slag cement (BFS) and 1 part OPC with a water/solids ratio of one to 0.35. The latter is the reference cement formulation which will be used for the encapsulation of several types of UK ILW waste streams. The coring trials carried out were restricted to simulant homogeneous wastes. The sampling of cemented solid waste (for example encapsulated fuel hulls) was not included in the programme. The coring equipment was hydraulically powered and as supplied, the machine had a drill rotation speed in the range 400 rpm to 1000 rpm. The coring machine was driven from a recirculating hydraulic oil system in the power pack unit.

Water Containment

In conjunction with an industrial consultant a water containment unit was developed to provide a water seal at the interface between the core drill and the top of the waste drum. The main design feature was that the unit was held on to the surface of the drum by a vacuum system. This eliminated the use of mechanical clamps which would be difficult to use under active handling conditions. Two 60 litre bins were each attached via two hoses to the water containment device and two vacuum pumps per bin provided the suction needed to evacuate the water containment device.

Coolant Water - Rate of Flow

Trials were carried out to establish the optimum water flow rate required for coring drums of cemented waste. It was established that the optimum water flow rate to cool the core bit and remove the sludge was in the range 6 to 10 liters per minute.

Core Drill Bits

Core drills fitted with either diamond impregnated cutting segments or tungsten carbide teeth were used for the horizontal coring tools. For the BFS/OPC cement matrix used in these tests the tool wear for both types of cutting tool was negligible. The tungsten carbide cutter demonstrated a higher cutting rate than the diamond tipped cutter without evidence of tool chipping or wear.

Air-cooled Coring

Research work is currently being conducted in France and Germany on the development of destructive methods for the Quality Checking of packaged wastes. This work has indicated that air can be substituted for water for cooling the coring tools used for sampling cemented wastes. For comparison purposes a limited development programme commenced in May 1989 on the assessment of air cooled coring tools; the trials were carried out with waste drums filled with BFS/OPC grout. The same types of coring tools were used for the air cooled trials as used previously in the water cooled programme. The trials have confirmed that air cooled tools can be used for drilling cores in cemented homogeneous wastes. The substitutes of air for water ensures that the chemical composition of the core is not changed by the sampling process; for example by the leaching of radionuclides by the coolant water. The use of air-cooled tools has still to be demonstrated for the sampling of solid waste, for example encapsulated fuel hulls.

Extraction of Core from Waste Drum

Two different core extraction tools were developed and tried in conjunction with an industrial consultant. The first one developed was a core drill and a 'matching' core extraction tool. The next stage was the development of a single tool to carry out both core drilling and extraction. The

combined tool was capable of drilling and extracting cores in the vertical mode but a more consistent set of results was achieved with the drum and coring equipment mounted in a horizontal position on the rig. One of the main advantages of coring in the horizontal position is that a fractured core remains in the tool when it is retracted from the drum. These trials were carried out using both water and air to cool the core drill bit.

Comparison of Vertical and Horizontal Coring Methods

Trials were carried out with the drum and coring equipment mounted in the vertical and horizontal positions. The advantages and disadvantages of the two systems were evaluated and, based on this work, the preferred orientation of the drum and equipment was the horizontal position.

PREPARATION OF SUB-SAMPLES FROM CORES

The total weight of a 100 mm diameter, 1500 mm long combined core drill/extraction tool enclosing a core sample 1200 mm long is approximately 30 kg. This is above the upper working limit of the standard Master Slave Manipulator, therefore sub-sampling at an early stage is necessary. The sub-sampling experimental programme consisted of two main parts:-

- demonstrating that the core could be cut into shorter lengths
- establishing a technique for taking small powder samples along the length of the core.

Core Sectioning Trials

A 240 mm stroke reciprocating hacksaw was used for the core sectioning trials. It was established that a core enclosed in a mild steel core/extraction tool can be sectioned in less than ten minutes using a high speed steel saw blade and that cemented homogeneous waste cores can be sectioned using a hacksaw without the use of a lubricant.

Preparation of Powdered Samples by Hollow-drilling Techniques

The drilling tests were carried out on 100 mm diameter cores removed from a drum of 3:1 BFS/OPC grout. The suction system for the collection of the cement dust was provided by a vacuum pump connected by a tube to the vacuum head on the drill stand via an inlet filter housing. This contained a replaceable high retention filter element. In operation the dust generated by the action of the hollow drill on the cement core is sucked through the hollow drill and vacuum head and is collected by the filter element.

The results showed that small powdered samples (ie several grams) can be taken from cemented homogeneous waste cores using a hollow drill/vacuum suction technique. Further work is required to develop the hollow-drill sub-sampling apparatus for sequential drilling through a steel core barrel and the cement core.

DISSOLUTION OF CEMENTED INTERMEDIATE LEVEL WASTE

The requirement was to assess and/or develop methods for the dissolution of encapsulated intermediate level waste for subsequent chemical and radiometric analysis. Early literature searches indicated that it might be relatively easy to partially dissolve the sample, but substantially more difficult to completely dissolve cement blends. Partial dissolutions were considered undesirable because of the possibility that radioactivity could partition between undissolved solids and solvents.

Preparation of Samples and Experimental Apparatus

The majority of samples for dissolution trials were produced by mixing the cement ingredients with water and leaving to cure for at least 3 months. The cement specimens were then hammered to produce discrete lumps (weighing between 1 and 20 grams) or reduced in size still further to powders by either drilling followed by sieving (powder size less than 250 microns) or ball-milling (less than 125 microns).

Hydrochloric Acid

The initial experiments were conducted with hydrochloric acid and microwave heating, and the results were encouraging. The optimum conditions for microwave dissolution were as follows:

- Cement blend particle size: less than 125 microns
- Cement weight: 0.5g
- Acid concentration: 6M
- Acid volume: 20 ml
- Microwave conditions: 1 minute at 100% power (650 watts)
- Estimated Temperature: 130°C.

Under these conditions the resultant solutions had no visible turbidity and were stable to gelling for periods in excess of 3 days. A silical gel usually formed after several weeks' storage.

Other Mineral Acids

The above experiments were repeated using microwave heating and nitric acid and acceptable results were obtained. Neither hydrochloric/nitric acid (aqua regia), fluoboric acid nor nitric/fluoboric acid were as promising as

either hydrochloric or nitric acid, using the above technique.

Organic Acids

Powdered 3:1 BFS:OPC samples were treated with the acids shown below:

- maleic
- citric
- trichloroacetic
- butyric
- salicylic
- tartaric.

Insoluble residues remained after both cold and hot acid treatments and there was no evidence that organic acids would make good solvents for these cement blends.

DISCUSSION

Effective dissolution was dependent on hydrochloric acid concentration. If the acid concentration was higher (9M) than optimum (6M) turbid solutions which gelled rapidly were produced. As the acid concentration was reduced, the solutions became clearer, suggesting that water plays a role in the dissolution of some of the cement blend constituents. The solution however still tended to gel. At concentrations lower (4M) than optimum (6M) the solutions were clear and stable to gelling for at least several days, but sedimentation tended to occur.

The smaller the cement particle size, the more efficient the dissolution. The most successful dissolutions were carried out using particle sizes less than 125 microns.

Gelling was dependent on acid volume. The more reagent volume used per given mass of cement, the less gel formation occurred. Increased stability to gelling was achieved either by using more reagent volume or by diluting after dissolution. Gel formation could be retarded by a number of methods (storing in cold, addition of acetic acid, dilution with water) but never completely prevented. Preliminary experiments indicate that radioactivity could be eluted from the gels but further work is necessary on cured and aged cements.

Further work is required to confirm the results on the other UK nuclear industry cement blends, ie 9:1 BFS:OPC and 9:1 PFA:OPC with and without ILW additions (magnox swarf, PWR hulls etc) and on aged cement blend samples (of the order of 10 years old).

Dissolution of Cement Blends using Fusion Techniques

Experimental Apparatus and Method

The general method was to mix the cement blend with an alkaline flux and react the mixture at about 1000°C; the fused product was then taken up into solution using water or acid. Inactive fusions were carried out in crucibles (Platinum/15% gold, or nickel or silica) inside a muffle furnace; active fusions were carried out using a wide-bore silica glass tube to insert the crucibles into a tubular furnace. Air was passed over the sample through vapor traps to catch volatile constituents. After quenching and dissolution, the resultant solution and the vapor trap were analyzed for radioactivity and the results compared to the initial measurements.

Inactive Fusions

A series of experiments was conducted using the following fluxes: sodium carbonate, sodium carbonate/boric acid, strontium metaborate, sodium hydroxide, boron trioxide, lithium tetraborate, sodium tetraborate, sodium/lithium tetraborate, lithium metaborate, sodium peroxide. The most successful fusion experiments were those using lithium tetraborate, sodium/lithium tetraborate, lithium metaborate or sodium peroxide. Cement blend powder quantities were between 0.5-1.5g.

Active Fusions

Samples of 3:1 BFS:OPC were made up, known amounts of radioactivity added, and the samples left for periods ranging from 1 week to 6 months. An example of the dissolution method is shown below.

3:1 BFS:OPC (Curing Period 6 Months)

One part by weight 3:1 BFS:OPC (containing a known quantity of Cs-137) was mixed with 4 parts by weight of lithium metaborate. The mix was placed in a platinum crucible and fused in the furnace at 880°C for 30 minutes, and the melt quenched in 3M nitric acid. Only about 0.2% of the original sample remained undissolved.

All of the initial radioactivity was found inside the final solution and none was detected in the vapor trap. The final solution was stable to gelling for at least 1 year. (On other occasions some of the initial radioactivity was also found in the nitric acid vapor trap.)

CONCLUSIONS

Cement blends can be dissolved using fusion techniques and the resulting solutions are stable to gelling for periods in excess of one year. Fusion is therefore the preferred dissolution technique. Work is underway on the adaptation of the fusion method for samples weighing up to 10-15g.

Hydrochloric acid and nitric acid are promising solvents for dissolution of cement blends using microwave

techniques. The resultant solutions however tend to form silicic acid gels.

Analysis of Intermediate Level Wastes for Beta-emitters

Methods were developed for analysis of Sr-90, Tc-99 and Ni-63 in cement blends, and have been tested on cement samples with ages less than one year. Further work is still necessary to validate the techniques for aged cements.

CONCEPTUAL DESIGN OF A PERMANENT FACILITY FOR INDEPENDENT QUALITY CHECKING OF RADIOACTIVE WASTE PACKAGES

Based on the above experience, a conceptual design was produced for an independent Radioactive Waste Quality Checking facility capable of examining the contents and characteristics of packaged low level and intermediate level radioactive wastes. The main function of the facility would be to provide an independent verification of the declared chemical and radionuclide inventory of packaged waste. This information would be used to confirm that packaged waste complies with the relevant regulations for storage and disposal. The budget cost estimate of a dedicated Radioactive Waste Quality Checking Facility on a green-field site was in the order of thirty million pounds sterling.

DISCLAIMER

The results of this work will be used in the formulation of Government Policy, but at this stage they do not necessarily represent Government Policy.

ACKNOWLEDGEMENTS

The authors thank Mrs V Sinclair (Project Coordinator) for the typing and presentation of this document and the other Taylor Woodrow team members involved in this project over its three-year duration. They are also indebted to personnel from Winfrith Technology Center, Harwell Laboratory, Rolls Royce plc and Marcrist Industries Ltd for their contribution to the project.

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