

CLASSIFICATION OF CONTAMINATED AND NEUTRON-ACTIVATED CONCRETES FROM NUCLEAR FACILITIES PRIOR TO THEIR DECONTAMINATION OR DECOMMISSIONING

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ABSTRACT

A good estimate of the radioactivity in a nuclear facility is required to define the approach to decommissioning in terms of method and timing. A series of concrete core samples have been taken from various aging nuclear facilities. These include a cooling pond, a dry concrete facility and a reactor bioshield. These samples have been examined to determine radiation levels, distribution of surface activity, depth of penetration of specific radionuclides, compressive strength as well as some microstructural examination by a scanning electron microscope. The results will provide useful information in planning decommissioning. Although activity can penetrate some distance into the concrete, the levels are very low compared to surface activity. The amount of penetration depends on the surface condition of the concrete.

INTRODUCTION

In the UK, many of the early nuclear facilities are now redundant. These facilities, particularly reactors, fuel handling plants (e.g., cooling ponds) and reprocessing plants contain large amounts of concrete in their construction to provide adequate shielding.

A series of studies on concrete samples taken from aging nuclear facilities has been carried out. As these structures are dismantled, much of the debris will constitute radioactive waste. It is important to establish the physical condition of such structures to determine their likely durability and the extent of any contamination or physical changes resulting from irradiation. The purpose of this work is to gather essential information prior to either;

(a) Decontamination of a physically sound structure such as a fuel storage pond or silo in order that it may be reused, removal of a thin surface layer followed by resealing may be sufficient, or

(b) Decommissioning for disposal, activity measurements at the surface and at depth can define whether decontamination would reduce the category of waste for the bulk of the concrete and whether decontamination would be effective in simplifying the decommissioning methods.

A good estimate of the amount and type of radioactivity in a nuclear facility is important because it can directly affect the whole approach to decommissioning including the choice of the time to start decommissioning and the desirability of delay between stages. In addition, such an estimate will be a great asset in the planning and execution to ensure that the facility is decommissioned safely, economically and to schedule. This information will assist the planners in determining factors such as the need for decontamination, shielding or remotely-operated equipment, transport and disposal, and potential radiation exposure to the workforce during decommissioning.

The radionuclide inventory in a nuclear facility can be

divided into two categories:

(a) Radionuclides induced by neutron activation of certain elements in reactor components and adjacent structures. Isotopes of interest in neutron activated concrete include ^{36}Cl , ^{41}Ca , ^{14}C , ^3H , ^{60}Co and ^{152}Eu .

(b) The radioactive material deposited on internal surfaces of various systems as contamination in reprocessing facilities for example. This includes fission products such as ^{137}Cs and ^{90}Sr as well as actinides.

The information obtained in these concrete investigations is intended to assist those responsible for decommissioning. Concrete cores or drillings are examined to provide information in the following categories:

Radiation Levels - the radiation levels, particularly at the contaminated or outside surfaces of the concrete can be used to assess the surface radiation and the need for shielding or remote operation.

Surface Activity - in some cases, particularly where there is no neutron activation and the concrete surface has not been exposed to contaminated water, contamination may be restricted to a relatively thin surface layer. In such cases, removal of this layer by a relatively simple process leaves the bulk of the concrete essentially non-active such that it can be reused or possibly disposed of as very low level waste. Although the de minimis concept has not yet been adopted in the UK (1), many large volume concrete wastes would be ideally suited for de minimis disposal.

Penetration Depth - in many cases activity will be present in the bulk of the concrete either due to neutron irradiation or by diffusion of active solution through the cement pore structure. For the purposes of economic disposal, it is important to classify the waste accurately and in such cases, it is beneficial to establish a cut-off depth for intermediate level waste (ILW), low level waste (LLW) and inactive waste. The decommissioning plan can then allow for re-

removal of a predetermined depth of concrete for active disposal leaving the remainder as low active waste.

Durability and Stability - a condition survey of the concrete may establish a desired timescale for decommissioning. If the structure shows signs of distress, it may be desirable to hasten the decommissioning program. Alternatively, a sound structure may be safely left for some time before decommissioning or may be decontaminated and reused.

Chemical or Radiation Effects - the condition survey may also provide information relating to any deleterious effects of high radiation fields or contact with corrosive chemicals.

This paper describes the results of concrete examinations from three separate facilities. In each case, the concrete was subjected to very different conditions during the operating life of the plant. The concretes examined were from:

Cooling Pond - a series of cores have been taken at various points of the internal surface of a cooling pond below the water level. The internal surface is uncoated concrete in good condition, which has been in contact with contaminated water for over thirty years. In some parts of the complex, efflorescence has occurred due to leaching of the concrete. Samples of this have also been recovered using a remotely operated underwater vehicle.

Dry Concrete Facility - cores have also been obtained from a concrete in direct contact with deposited airborne contamination over thirty years. Some of the concrete specimens we have studied from facilities in this category have been of sufficiently low activity to be classifiable as non-active waste with the exception of the first few millimeters. This paper concentrates on samples taken from a more heavily contaminated concrete with significant penetration of activity.

Reactor Bioshield - a core was taken through the concrete bioshield of the Windscale Advanced Gas-Cooled Reactor at the point of highest neutron flux. The core length was approximately 2.7 meters. The neutron flux at the inside face of the bioshield during reactor operation was $1E10n/m^2/s$, dropping to $100n/m^2/s$ at the outer face. The operating temperature at the inner face was not greater than $70-80^{\circ}C$.

TECHNIQUES USED

Sampling Methods

In all cases, the primary samples were obtained using standard concrete drilling equipment, i.e., cylindrical bits (diameter 70 or 100mm). The contaminated (inner) surfaces of the cores were sampled by scraping a mass from a known area of surface to give an average surface activity in

Bq/g. Samples have also been taken at various distances from the inner surface by drilling into the wall of the core using a hammer drill and collecting the drillings. The first 10mm of this subsample was always discarded to avoid the possibility of cross-contamination. These subsamples can be taken using a hollow drill-bit attached to a vacuum line with a filter to collect the drillings. Subsamples will always include a mixture of drillings from coarse aggregate, fine aggregate and cement, in varying quantities, particularly if the sample is small. Since the activity will not be evenly distributed among these components, this can introduce some scatter in the Bq/g results. In case of doubt, sampling was duplicated to confirm the result. In the future, it is intended to use experimental design methods to select appropriate sampling points on large structures.

The hollow bit method can also be used as a rapid, economical method of obtaining the primary sample, particularly where space is limited or radiation levels restrict working times.

Sample Preparation and Analysis

Immediately after sampling, radiation measurements were made on the cores using both ratemeter and radiation film attached to the inner surface for an appropriate length of time. (One of the purposes of the later radiochemical assay was to correlate activity levels with radiation measurements.) At this stage, autoradiographs using Polaroid film were also taken to give some indication of the distribution of activity across the contaminated mortar. Figure 1 is an autoradiograph of a core taken from the dry concrete facility. The dark, exposed lines are runs of contaminated mortar. Although these mortar runs were actually similar in activity to the rest of the surface (the difference in exposure being due mainly to a distance effect), the white, unexposed sections where the mortar runs were broken off indicate that the bulk of the activity in this sample was within 1-2mm of the contaminated surface.

When these initial investigations were complete, subsampling was carried out for more detailed isotopic analysis. Gamma-spectrometry was done by direct counting on samples of powdered drillings. For detailed isotopic analysis of alpha and beta isotopes it was necessary to completely dissolve the concrete using either hydrofluoric acid or a suitable flux such as lithium metaborate (2). The resulting solutions were analyzed as appropriate for the required isotopes. The reason for complete dissolution of cement and aggregate is that the activity is not associated entirely with the cement pore structure: A significant fraction can also be associated with the aggregate. Results quoted in this paper for strontium-90 and alpha isotopes were obtained by



Fig. 1. Autoradiograph of Contaminated Core.

Note unexposed line, where a 1mm thick layer of mortar has been broken off. This demonstrates that most of the activity is confined within 1mm of the surface.

precipitation in fuming nitric acid and solvent extraction in thenoyltrifluoro acetone (TTA) (3) respectively.

Additional methods such as scanning electron microscopy (SEM) and X-ray Diffraction (XRD) were also used to provide an understanding of the processes involved in contamination and transport of the activity into the bulk of the concrete.

PENETRATION OF CONTAMINATION

Soluble isotopes in contact with an unprotected concrete surface will migrate through the water-filled pore network and contaminate the concrete to a depth dependent on the rate of diffusion and the extent to which that isotope is sorbed in the cement. Sorption of a radioisotope on the solid phase of cement will reduce the depth of penetration (4), although it will also increase the activity per unit weight of those parts which have been contaminated.

Figure 2 shows the variation in activity levels of cesium-137 with distance from the contaminated face. This graph is based on average activities of many individual analyses. The activities of all the concretes examined exceeded the limit FOR LLW in the UK set by NIREX (5), i.e., 12 GBq/t (or 12 kBq/g) beta plus gamma. In all cases, the activity falls rapidly with depth. The decrease with depth was most rapid with the dry concrete even though the surface activity was similar to the cooling pond concrete. The reason for this is likely to be that the pore network of the dry concrete has

dried out close to the surface. The aqueous transport mechanisms required for transport of the activity into the concrete are therefore limited. In the cooling pond, the pore network is obviously fully saturated, allowing full access to dissolved radionuclides.

Visual examination of the concrete from the cooling pond suggests that across most of the surface the concrete is in extremely good condition.

In places there has been erosion of the cement component leaving a pitted surface. The results for the cooling pond concrete have been separated according to the surface appearance. The activity penetration into the eroded surface at depths up to 10mm was greater than into the smooth surface.

The effect of surface condition is further demonstrated in Fig. 3. This bar chart shows the activities of Pu-239/240, Sr-90 and Cs-137 at 10mm into the concrete as a fraction of the surface activity for smooth and eroded surfaces. For all three isotopes the activity was a small fraction of the surface activity. However, the smooth surfaces provided a better protection and the activity was about one-tenth that of the eroded surfaces. It is interesting to note that the magnitude of this effect was similar for all isotopes, despite the differences in sorption properties onto concrete for these isotopes.

It should not be assumed that if the activity of the concrete surface exceeds the limit for LLW, that classification into the LLW category is precluded. Removal of a relatively thin surface layer or even averaging of the activity over just a few millimeters may bring the waste within LLW limits.

It should also be noted that the NIREX limit quoted is for an assumed future repository not yet constructed and that the limit is for beta plus gamma. The activities in Fig. 2 are for gamma only and are included to give a rough guide to the levels of contamination rather than to identify an absolute depth cut off for ILW or LLW.

EXAMINATION OF CONCRETE SURFACE

Since the condition of the concrete surface appears to have a significant effect on the penetration of activity, it is worth looking in some more detail at the surface. Subcores of 8mm diameter were therefore taken by drilling into the contaminated face with a cylindrical bit. The subcore was then sliced longitudinally, polished and examined in a scanning electron microscope (SEM) with the facility for elemental analysis by energy dispersive X-ray analysis.

The sample taken from the smooth surface of the cooling pond is shown in Fig. 4. The concrete appeared to be of high quality with little evidence of voidage or microcracking. Of particular interest was a high density layer some 200-300 micrometers deep at the surface. This proved to be a layer

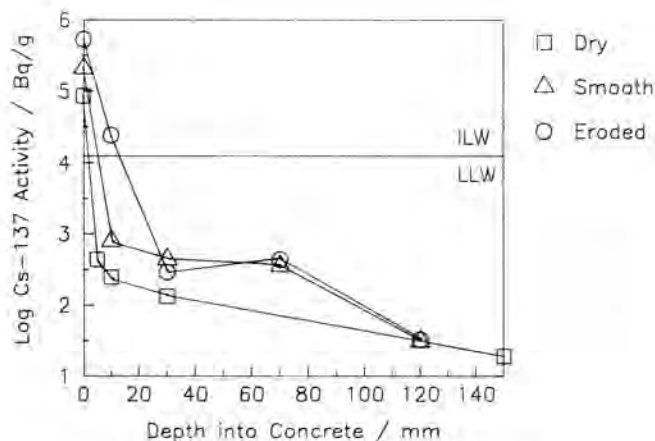


Fig. 2. Depth of Penetration of Cesium-137.

of calcium carbonate probably formed by leaching of calcium hydroxide towards the surface from the bulk of the concrete. At the surface, the calcium hydroxide is contacted with dissolved carbon dioxide in the water and calcium carbonate is precipitated. This layer effectively blocks the entrance to the pore network and restricts access of contaminated water. This layer was not present in the eroded parts of the concrete surface, where ¹³⁷Cs penetration was highest.

In some areas of the facility, there was efflorescence at the surface of the concrete, a layer of salts formed from material leached from beneath the surface. A sample of this material was analyzed by X-ray Diffractometry and identified as a mixture of calcite and aragonite (both of which are crystalline forms of calcium carbonate). A sample was dissolved and analyzed radiochemically. The results are shown in Table I alongside a typical analysis of the water in contact with the concrete surface. This analysis demonstrates the ability of calcium carbonate to concentrate strontium, the carbonated surface layer identified in the SEM studies also preferentially absorbs strontium. The aragonite component in particular is thought to be responsible for trapping the strontium (6).

An SEM micrograph of the surface of the dry concrete is shown in Fig. 5. In this case there is no dense carbonate layer at the surface. Instead, there is a thin silicate-rich layer, consisting of fine aggregate with almost no cement binder.

NEUTRON ACTIVATED CONCRETE

Low level gamma-spectroscopy was carried out on various sections of the reactor bioshield core. The results are

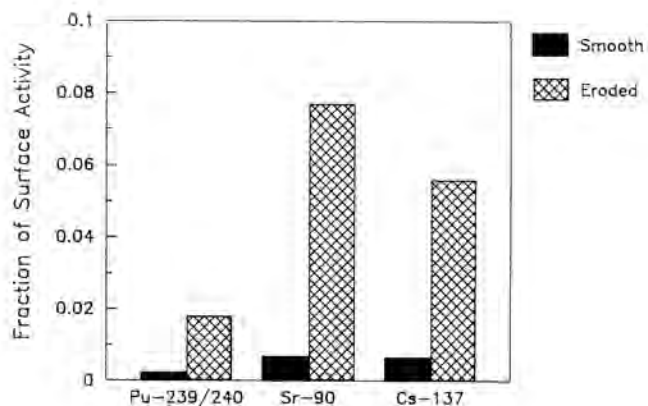


Fig. 3. Relative Activities of Smooth and Eroded Concrete at 10mm Depth.

shown in Fig. 6. The main gamma-emitting isotope is europium-152, an activation product of the trace levels of europium found in fine aggregates at ppm levels. The gamma contribution to the total activity of the concrete is sufficient to classify at least the first meter from the active face as low level waste. Compressive strength measurements have also been made throughout the core and these demonstrate that there is no weakening of the concrete as a result of the high radiation fields experienced by the concrete at the inner face.

TABLE I
Analysis of Efflorescence on Concrete Surface

ANALYSIS	EFFLORESCENCE Bq/g	TYPICAL WATER Bq/ml
pH	--	8
Total Alpha	250	0.1
Total Beta	103,000	201
Total Gamma	2,600	141
Sr-90	48,400	30
Y-90	48,400	30
Cs-137	1,700	75
Cs-134	< 50	< 0.1

CONCLUSIONS

In the decommissioning of radioactive facilities containing large volumes of concrete, successful planning and

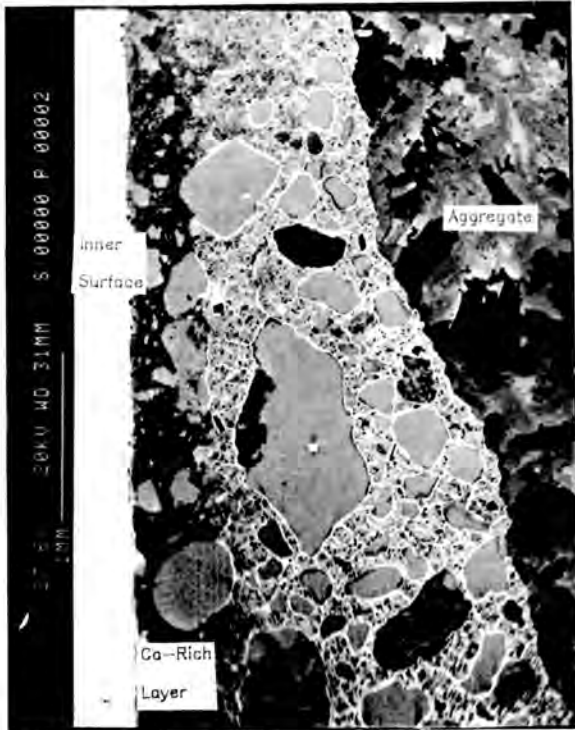


Fig. 4. Scanning Electron Micrograph of Pond Core Surface Showing Carbonated Layer.

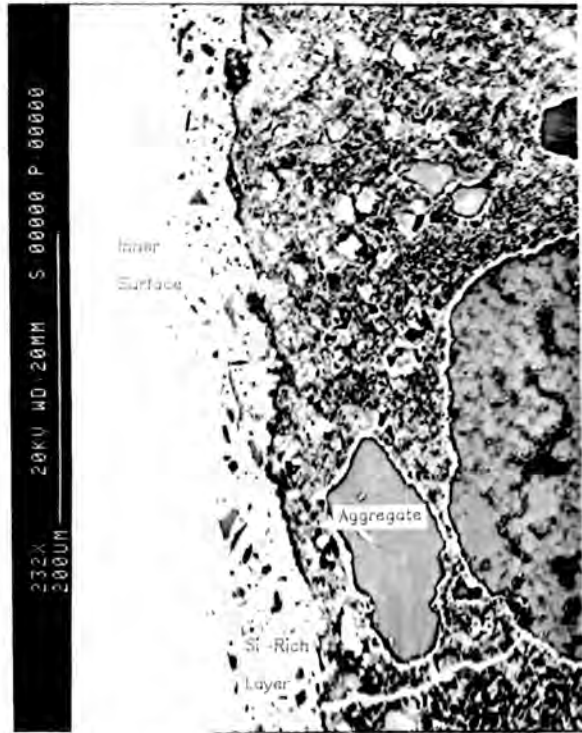


Fig. 5. Scanning Electron Micrograph of Dry Aged Concrete Showing Silica-Rich Surface Layer.

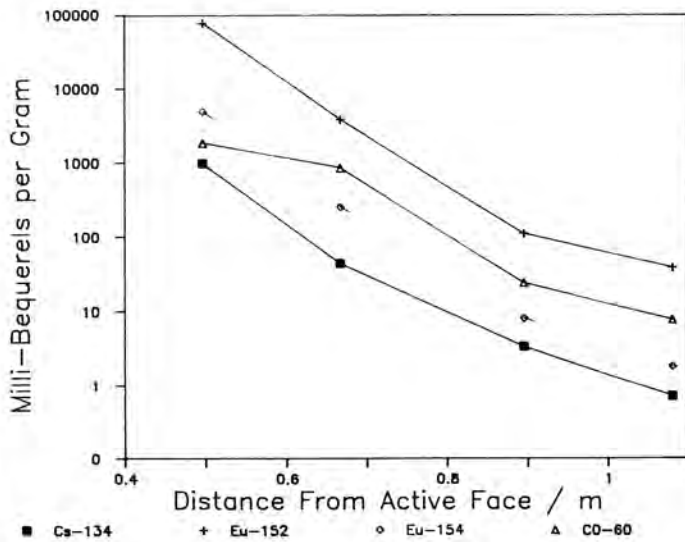


Fig. 6. Reactor Bioshield Sample Analysis

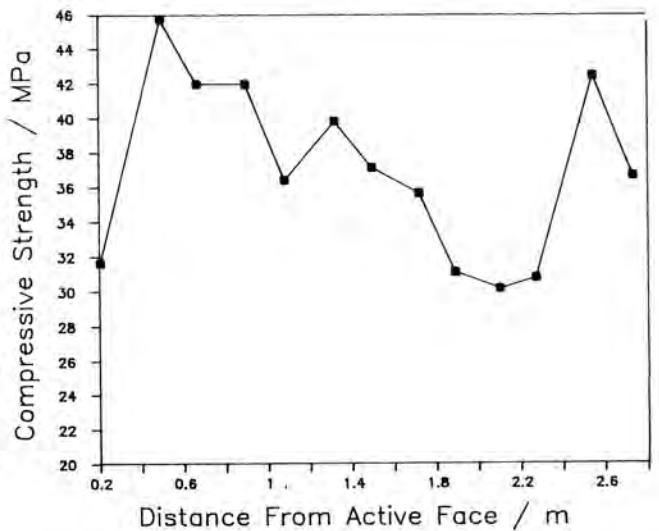


Fig. 7. Compressive Strength Results

accurate costing of the program requires analysis of the concrete and classification into appropriate categories.

Standard coring and drilling equipment have been used to obtain cylindrical core samples and powdered drillings for such analysis.

Various analytical methods have been applied to identify the levels of individual isotopes in the concrete. More basic methods can also be applied such as autoradiography to determine surface distribution of activity.

Additional methods such as SEM and XRD are useful in helping to understand the contamination processes.

REFERENCES

1. GOODILL, D. R. and TYMONS, B. J., "Do We Need the de Minimis Concept in the UK?", *Radioactive Waste Management* 2, 7, BNES (1989).
2. GREEN, T. H., SMITH, D. L., NORRIS, G. H., BURGOYNE, K. E., MAXWELL, D. J. and BILLINGTON, D. M., "The UK Department of Environment Quality Checking Laboratory," *Waste Management '90*.
3. MOORE, S. L. and HUDGENS, J. E., "Separation and Determination of Plutonium by TTA Extraction," *Anal. Chem.* 29, 1767, (1957).
4. ATKINSON, A. and NICKERSON, A. K., "Diffusion and Sorption of Cs, Sr and I in Water-Saturated Cement," AERE-R-12124, AEA Technology (1986).
5. UK NIREX, "Deep Repository Project: Preliminary Environmental Radiological Assessment and Preliminary Safety Report," NIREX Report No. 71 (1989).
6. FUHRMANN, M. and COLOMBO, P., "Radionuclide Releases From Cement Waste Forms in Seawater," *Radioactive Waste Management and the Nuclear Fuel Cycle*, 11, 365 (1989).