CONSIDERATION OF TECHNIQUES FOR REDUCING THE ACTIVITY IN REPROCESSING WASTES PRIOR TO DISPOSAL

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ABSTRACT

Magnox cladding waste and Plutonium Contaminated Material (PCM) have been generated at Sellafield from fuel reprocessing operations and from Fast Reactor fuel fabrication and will continue to be generated into the next century. A range of techniques has been considered to restrict the amount of activity lost to these waste streams or to remove activity from those wastes which already exist. Technical feasibility, operator and public dose uptake and cost have been used as the main criteria to judge whether any particular method should be implemented.

INTRODUCTION

Radioactive waste has been accumulating at BNFL Sellafield in the UK for over 30 years as a result of reprocessing natural uranium metal fuel from a gradually increasing number of Magnox gas-cooled power stations, which now number thirteen. To date, over 30,000 tU has been reprocessed and an additional 15,000 tU will be reprocessed before the end of the programme in 2005/06. In the early 1990's, the Thermal Oxide Reprocessing Plant (THORP) will begin to reprocess Advanced Gas-cooled Reactor (AGR) fuel from the UK together with a substantial quantity of overseas fuel from PWR and BWR reactors.

An overview of radioactive waste management has been given recently (1) and this showed that all the various waste streams containing significant quantities of activity (classified in the UK as High Level Waste (HLW) or Intermediate Level Waste (ILW)) are presently stored on site in their raw, untreated form. In contrast, the larger volumes of lower contaminated wastes (classified as Low Level Waste (LLW)) are disposed of as they arise by shallow land burial. The intention is that following vitrification, HLW will be stored in engineered facilities for at least 50 years, to allow radioactive decay and plans are progressing to open a deep repository for ILW and LLW in the period 2001-2006. In preparation for the disposal of ILW, BNFL is designing and constructing facilities to treat and package the stored wastes as appropriate. Such facilities will also be employed to package the wastes which continue to be produced, as they arise.

In an effort to reduce the activity content of wastes which will ultimately be disposed of in the environment and thereby reduce the long term doses resulting from disposal, BNFL has considered, in the context of new plants, techniques for reducing the amount of activity transferred to waste streams. In parallel with this approach, consideration has also been given to the possibility of removing activity from waste which has already been generated. This paper considers two specific waste streams:

(i) Magnox cladding material, which is contaminated with irradiated fuel, and,

(ii) Plutonium Contaminated Material (PCM) which is similar to TRU waste in the US and which, as its name implies, is principally contaminated with plutonium.

These two waste streams were selected for study since, at the completion of the existing Magnox and oxide reprocessing program, they would contain a very large percentage of the total actinide content of all Sellafield wastes; using plutonium as the measure they would contain over 90% of the total.

WASTE PRODUCTION, CHARACTERISTICS AND EXISTING MANAGEMENT

Magnox Cladding

Prior to the dissolution of the uranium metal fuel in nitric acid, and the subsequent chemical separation processes which give rise to the U and Pu products, the magnesium/aluminium alloy cladding is mechanically removed from the fuel rod. A very small proportion of fuel remains with the stripped cladding, either adhering to the cladding or as small chips and pieces of fuel. Until a plant to package the cladding waste, by encapsulation in cement, becomes operational in 1990, the material will continue to be tipped into one of a series of water-filled storage compartments constructed of reinforced concrete, each able to accommodate some 500 m^3 of material.

In contact with water the cladding slowly reacts, with the liberation of hydrogen, to form a sludge consisting mainly of magnesium hydroxide. For the compartments which contain fresh, relatively unconverted cladding, BNFL is assessing the feasibility of inhibiting this reaction in order to improve the safety of storage. However, until this inhibition is put into practice, the cladding will continue to react at rates of about 2% per annum until an equilibrium level of about 85% conversion is reached, as in the case for the earlier storage compartments.

The processes which have been considered for removing activity from this existing cladding waste will separate the very small proportion of fuel from the bulk of the cladding. If the fuel, containing plutonium, other actinides and fission products can be successfully removed it would be possible to route it into the reprocessing plant, allowing the uranium and plutonium to be recovered for recycle into reactors with the remaining actinide and fission product activity routed to the vitrified HLW stream.

Plutonium Contaminated Material

PCM arises as a waste from plutonium processing operations and comprises a wide variety of materials, including combustibles such as plastics, rubbers and cellulose, and non-combustibles such as tools and equipment. The

majority is either packaged in PVC bags and stored in 200 litre mild steel drums, or crated and overwrapped.

As it arises, PCM is generally categorised according to material type (combustibility and shreddability) and by plutonium content. Drums containing less than about 15g of Pu are classified as "low", while those containing 15-200g are classified as "high". As a result of this segregation, about 85% of the plutonium is contained in as little as about 10% of the PCM volume.

Since plutonium is the principal contaminant of PCM the activity removal processes which have been considered have been specifically chosen to separate out the plutonium, from the essentially inactive waste, ideally into a form which could be readily routed back into the reprocessing plant.

Quantities and Activities of Wastes

The raw volumes of cladding wastes, PCM and other wastes in the general category of 'intermediate level wastes' (ILW) which will be produced at Sellafield by the completion of the Magnox and oxide fuel reprocessing programmes, are shown in Table I (based on Ref. 2).

The original activity content of these waste streams, expressed using their plutonium content, is also given. At the outset of the considerations to reduce the activity content of these two waste streams a preliminary evaluation was undertaken which indicated that up to 65% of the original total activity (in the form of Pu) might be recovered. The values corresponding to this 'target' recovery are given in Table I.

TABLE I

Volumes and Activity content of Sellafield Wastes.

Waste Streams (ILW)	Volume (m3)	Activity Content (kgPu)	
		Original	Target for Recovery
Magnox Cladding	17000	2350	1500
PCM	15000	1250	850
Others	30000	300	0
62000	3900	2350	

CONSIDERATIONS FOR REDUCING WASTE ACTIVITY

The principal advantage which would be gained by *reducing* the uranium and plutonium content of the two wastes under consideration is that the long term dose to man following disposal would, theoretically, be reduced. A cost-benefit type assessment, balancing the reduction in potential future doses against the immediate cost and dose up-take of processing the waste before disposal would help in reaching a decision on whether such actions were justified or worthwhile. However, even if such a justification cannot be made for activity removal, there may be benefit in pursuing such actions as an aid to secure public acceptance of disposal.

Magnox Cladding Wastes

Table II gives the range of options which has been considered for reducing the fuel content of the cladding. For fresh arisings of cladding the most obvious course of action is to improve the mechanical de-cladding operation itself so that less fuel is carried over into the waste stream and is instead routed with the bulk of the fuel into the reprocessing plant.

Since consideration was first given to this issue of activity reduction, a new de-cladding and fuel storage facility (the Fuel Handling Plant (FHP)) has been brought on-line. In comparison with the earlier equivalent facility, more efficient mechanical equipment has been installed which reduces the amount of mechanical damage to the uranium fuel rod and hence achieves the objective of reducing the quantity of fuel which is lost to the cladding waste stream. In addition, gamma spectrometry systems are now used to monitor the waste as soon as it is produced such that larger pieces of fuel can then be removed when they are detected. Introduction of this system will mean that until completion of Magnox reprocessing, in excess of 100 ton of additional fuel, containing approximately 300 kg of plutonium, will be routed back to the fuel cycle rather than to disposal.

The remaining six basic options shown in Table II are all applicable to removing fuel from stored cladding, some of which will be in the form of magnesium hydroxide sludge. Options 2-5 (gravity settling, magnetically enhanced settling, froth flotation and hydrocyclone) were rejected at an early stage in favour of High Gradient Magnetic Separation (HGMS). It was concluded that HGMS would be superior to all of these four options as each of them had a greater dependence on the properties of the sludge constituents, such as particle size and rheology, particle density and general chemical properties.

Development of HGMS has, however, not proved particularly successful, despite the promising laboratory scale results obtained on simulated waste. Results from work performed using fully active material have shown that the fuel is intimately associated with the magnesium hydroxide and therefore any fuel which was recovered was heavily contaminated. Such fuel could not therefore have been transferred to the reprocessing plant, without having a significant impact on its operation. In addition, the efficiency of separating the fuel was poor, with at best only 40% being extracted. Although efforts were made to improve both the separation efficiency and product purity, these were unsuccessful and development work on the HGMS techniques has therefore been abandoned.

The final option considered, which would be capable of removing fuel from both fresh cladding and converted cladding was the complete dissolution of the waste stream followed by solvent extraction or ion exchange decontamination to remove the fuel. Early development concentrated on the use of nitric acid as the solvent, allowing the direct return of dissolved fuel to the reprocessing

TABLE II

Options for Fuel Reduction in Magnox Cladding

WASTE TYPE	OPTION	COMMENT
Fresh arisings	1. Reduce loss of fuel to cladding at source	Successfully developed
Existing stored waste (large proportion converted to sludge)	2. Gravity settling	)
	3. Magnetically enhanced settling	)
	4. Froth flotation	) Inferior to HGMS
	5. Hydrocyclone	)
	6. High Gradient Magnetic Separation (HGMS)	Low recovery efficiency and product purity
	7. Dissolution - nitric acid - carbonate	Technical difficulties, requirement for extensive downstream effluent clean-up, very high total cost

plant. However, technical difficulties, associated particularly with the prevention of runaway reactions and off-gas production, precluded the adoption of nitric acid dissolution.

A review of alternatives identified carbon dioxide based solvents as having potential, even though oxidising and complexing agents would be required to ensure complete dissolution. In preference to the more usual approach of solvent extraction to recover the uranium and plutonium, ion exchange materials were identified for actinide recovery mainly because of the complex nature of the dissolved material.

However, after detailed experimental work and assessments, this option was rejected for the following reasons:

(a)difficulties associated with recovery of actinides in a sufficiently pure form to allow return to the fuel cycle;

(b)the need for extensive downstream effluent clean-up in order to reduce the radiological impact of discharge liquors to acceptable levels;

(c)other unresolved technical difficulties, such as those associated with the formation of agglomerates during the dissolution process.

Assuming that the technical uncertainties could be resolved relatively easily, the capital cost of a suitable facility was estimated to be in the range $700-900M. Taking into account the financing charges and operational costs, the total cost of the option would exceed $2000M. Because of the technical problems and high cost this solution was therefore abandoned.

Plutonium Contaminated Material

Given that about 10% by volume of the PCM contains about 85% of the activity in PCM, it was decided from the outset that only the "high Pu" streams would be assessed when considering activity (ie Pu) removal processes.

Starting with raw waste, the steps which are required in order to route plutonium back into the reprocessing plant, for example at the plutonium purification stage, are:

(i)Physical Preparation of the waste, if required. For combustible PCM this would involve shredding and for non-combustible PCM, size reduction would be undertaken if required.

(ii)Plutonium/Waste Segregation, to separate the bulk of the plutonium from the bulk of the inactive waste. Washing, using 1M sodium hydroxide or a non-hydrogenous solvent (Arklone) has been studied. Because of the poor Pu removal efficiencies achieved for washing non-combustible PCM, melt refining has also been assessed.

(iii)Intermediate Treatment. Following washing, the Pu fines are filtered and pyrolysed (to enable subsequent Pu leaching) and following melt refining the slag must be removed.

(iv)Plutonium Leaching, to extract the plutonium into a form which can be routed into the reprocessing plant. Two leaching processes, nitric acid/fluoride and

silver-catalysed electrochemical dissolution have been studied.

Table III summarises these stages and quantifies the segregation efficiencies and leaching efficiencies which were achieved. For combustible PCM, the most efficient route was found to be sodium hydroxide washing followed by nitric acid leaching of the pyrolysed fines which would, overall, recover about 85% of the plutonium. Washing of non-combustible PCM was not particularly successful and melt refining followed by silver-catalysed electrochemical dissolution would need to be adopted in order to provide a reasonable overall plutonium recovery of about 85%. Thus in order to achieve such high recoveries two separate segregation processes and two separate leaching processes would need to be employed.

The implications of implementing plutonium recovery are given in Table IV in terms of capital cost, peak and collective operator dose uptake, peak critical group doses and collective effective doses to the UK population. Three different management options are illustrated. Option A is the simplest (base-line case) and comprises encapsulation of all PCM by grouting using a suitable cement matrix without any attempt to recover plutonium. Option B assumes all high plutonium content PCM is washed and Option C is an extension of B comprising washing for combustible PCM, but melt refining for non-combustible PCM.

The annual critical group doses from deep land disposal are all very low when considered in the context of the appropriate target laid down by the UK Department of the Environment (3); this is a limit equivalent to 0.1 mSv (or 100 microSv) to any individual in any one year. The doses derived following land disposal have been calculated using a relatively unsophisticated model but one which is nevertheless adequate to show the differences in dose which could potentially be achieved by recovering a substantial amount of the plutonium. On the other hand, the critical group doses from the liquid discharges which would be associated with implementing the three options are based on the known and measured effect on populations local to Sellafield from the present liquid discharges. In calculating these values, it has been assumed that in order to limit the doses from liquid effluent discharges to very low levels a sophisticated treatment plant can be provided which will be capable of very high decontamination factors (of the order of 5000) for plutonium. It has been demonstrated that, based on the process to be used in a new facility due for

TABLE III

Options for PU Removal From PCM

	PREPARATION	PLUTONIUM/WASTE SEGREGATION		INTERMEDIATE TREATMENT	PLUTONIUM LEACHING	
		TECHNIQUE	EFFICIENCY		TECHNIQUE	EFFICIENCY
Combustible PCM	Shred	Wash - NaOH	95%	Filter and pyrolyse fines	HNO_3/F	> 90%
					Ag	30/40%
Non-combustible PCM	Size reduce (if req'd)	Wash - NaOH - Arklone	40/50% 5%	Not assessed		
		Melt refine	100%	Remove slag	HNO_3/F	50%
					Ag	80/90%

TABLE IV

Comparison of PCM Management Options

OPTION (SEE TEXT)	PU REMOVAL PROCESS (a)	OVERALL PU RECOVERY	CAPITAL COST ($M) (c)	PEAK CRITICAL GROUP DOSE (MICRO SV/YEAR)		UK COLLECTIVE DOSE (MAN-SV)	COLLECTIVE OPERATOR DOSE (MAN-SV)
				LIQUID DISCHARGES	LAND DISPOSAL		
A	None (b)	0%	130	0.04	0.15	0.40	1.5
B	Wash/Wash	50%	300	7	0.12	0.46	2.6
C	Wash/Melt Refine	75%	450	8	0.11	0.43	2.6

(a) The first process relates to combustible PCM, the second to non-combustible PCM

(b) Assumes PCM is encapsulated in cement

(c) Excluding financing and operating charges

operation in 1992 (the Enhanced Actinide Removal Plant (EARP)) (4) this would be achievable using a two cycle floc precipitation process with ultrafiltration.

It can be seen from Table IV that even allowing for sophisticated liquid effluent treatment, the critical group doses of options B and C from liquid discharges are approaching 10 microSv/year or one tenth of the limit set for the (long term) doses from a single deep repository containing all UK waste.

Both washing and melt refining of PCM (options B and C) to remove significant amounts of plutonium have therefore been rejected and the main reasons can be summarised as:

(i) The long term reduction in critical group dose resulting from land disposal would be marginal (about 25%) and small in absolute terms (less than 0.1 microSv/year).

(ii) By implementing the processes there would be a significant increase in short term critical group dose resulting from liquid discharges (about 10 microSv/year). This compares unfavourably with the small reduction in critical group dose which may be achieved in the long term following land disposal (ie the 0.1 microSv/year in (i)).

(iii) Relative to the base-case, options B and C would increase collective operator dose commitment by over 1 man-Sv (70% increase) which is substantially in excess of the total UK collective dose following disposal for any of the options.

On balance, the very limited (and somewhat speculative) benefits which may be secured in the longer term are offset by relatively large and unavoidable short term detriments. Coupled with the fact that the total cost of implementing washing/melt refining (including financing and operational costs) would be in the range $800-1200M, there is no justification to recover plutonium from PCM.

CONCLUSIONS

Success in reducing the fuel loss to Magnox cladding will in the future divert about 100 tU, containing almost 300 kg of plutonium, away from waste, and thus disposal, and back into the fuel cycle.

All of the techniques to remove fuel from existing cladding waste suffer from major technical difficulties and/or very high cost and will not be pursued.

Techniques which initially appeared to offer the prospect of easily recovering substantial amounts of plutonium from PCM have been investigated experimentally. The results show that, from a technical viewpoint, segregation and leaching methods exist which may be capable of implementation at the full scale. Substantial additional development of the four processes required to give optimum plutonium recovery would be necessary. However, even if successfully implemented for PCM, this would still leave a very significant quantity of plutonium with the Magnox cladding and other Sellafield wastes.

Moreover, the potential long term benefits are very marginal and would be offset during and immediately

following the processing operations by significant increases in operator and critical group doses. It has therefore been recommended that the techniques which have been investigated should not be implemented and no further work is envisaged in these areas.

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