

**A REVIEW AND UPDATE OF THE BNFL CEMENT FORMULATION DEVELOPMENT PROGRAMME
FOR THE IMMOBILISATION OF INTERMEDIATE LEVEL WASTES FROM MAGNOX POWER
STATIONS**

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ABSTRACT

For several years BNFL has carried out a cement formulation development programme for the immobilisation of intermediate level wastes from decommissioning Magnox power stations. This has been supported by programmes of waste characterisation, simulant development and characterisation, retrieval and de-watering technology, and latterly the predicted behaviour of containers of cemented waste under conditions of interim storage and deep geological disposal. This paper discusses the above strategy in the context of a wide range of waste types, and updates previously published information now that the dates for initial retrieval and immobilisation are approaching.

The paper identifies some of the challenges met during the simulant and formulation development programme, and in particular the storage and disposal sensitive issues, which have evolved as wasteform specifications have developed. Examples are given with reference to particular wastes showing how the available information is discussed and assessed, and then applied and extrapolated to similar waste streams. This is particularly important where mixtures of wastes arise in the same storage facility, and a fully developed methodology will be explained for the successful treatment of such waste streams. The question of changes in raw materials sources and properties is also discussed where it influences the detailed cement formulation and encapsulation plant operation.

Due to the age of some of the accumulated Magnox wastes, the question of physical and chemical ageing is discussed for resins, sludges and metallic wastes. Sludge characteristics are particularly important and examples are given of how waste ageing influences the retrieval and encapsulation strategies.

Specifically, the use and limitations of long-term monitoring of samples is discussed, giving example of the wastes under test. Overall, it is considered that the results from this part of the programme underwrite the current reference formulations for all the waste streams considered.

The container corrosion work is important as the time for retrieval, packaging and interim storage is reached. Container corrosion related data is discussed, including effects of wasteform degradation and gas generation mechanisms, which can be influenced by interim storage environments and eventual transport and disposal strategies. Predicted container lifetimes are given and the uncertainties discussed in terms of non-uniform corrosion mechanisms. The situation for the related mechanism of Galvanic corrosion is updated in the context of the high pH cement environment.

There is a brief account of the development process for two fairly intractable wastes, namely borated ion exchange resins and phenolformaldehyde based ion exchange resins. The reference formulations are identified and the process is then extended to mixtures of wastes which if separate would require two different formulations.

Finally a number of issues are discussed, including gas generation, migration of actinides, materials specifications, retrieval of wastes, simulants, monitoring of waste packages in interim storage and the tolerances expected on the operation of an encapsulation plant. All these issue (and others) need to be considered when the reference formulation is being developed and when it is finally optimised just prior to operations.

The overall conclusions are that the BNFL programme of cement formulation development for a wide range of intermediate level waste types has been successful in leading to tailored stabilization formulae for diverse waste types. As the time approaches when some retrieval and immobilisation is to begin there is confidence that the wasteform specifications can be met. It is acknowledged that there will always be the need and incentive for final optimisation of the processes of retrieval and immobilisation and to assist in this formulations have been developed to be as robust as is practicable. In the UK context, a careful analysis of the response of immobilised radioactive waste in stainless steel vented containers to the minimum 50 year envisaged interim storage regime, is being carried out with emphasis on those with the greatest potential for internal corrosion.

BACKGROUND

For a number of years BNFL has proceeded with a strategy for waste management (1) and a programme of cement-based formulation development for the eventual immobilisation of retrieved intermediate level wastes from decommissioning nuclear power stations. Historically this has included wastes from Magnox and AGR gas cooled reactors and the PWR at Sizewell B. This programme has been supported by parallel programmes of waste characterisation by sampling and analysis, simulant development and characterisation, retrieval and de-watering technology, and latterly the predicted behaviour of containers of cemented waste under conditions of interim storage and deep geological disposal. This paper discusses the above strategy in the context of a wide range of waste types, and updates previously published information (2, 3) now that the dates for initial retrieval and immobilisation of some Magnox wastes are approaching.

TYPE OF WASTES

Only LLW and ILW arises during operations and decommissioning at Magnox power stations, and the former is routinely packaged and disposed of to a shallow land burial site at Drigg in Cumbria. The liquid and solid ILW, which arose during operations, is held in special accumulation facilities at the stations. On the three decommissioning stations at Berkeley, Trawsfynydd and Hunterston A it is these wastes that are being considered for retrieval and encapsulation. The dominant wastes are sludges, organic ion exchange resins, and metallic debris. The metallic debris consists primarily of Magnox alloy gas flow splitters removed from the spent fuel assemblies, together with small amounts of zirconium. In the case of Berkeley and Hunterston A there are also graphite components associated with the fuel element design, which are removed during the splitter removal process. The stored metallic debris from these two facilities ranges from mainly Magnox, through mixtures of Magnox and graphite, to predominantly graphite.

The sludges have arisen from a number of sources from the clean-up of the fuel pond water and other effluents. They contain corrosion products from the Magnox alloy, which is mainly magnesium oxide in a range of particle size distributions. These sludges also contain traces of sand from filters and in some cases oil. In detail about twenty materials associated with station operations (*e.g.* effluent treatment, wash rooms, laundry and decontamination work) can be identified in the sludge and most of these must be considered in any viable simulant. Sludges also suffer from the long-term characteristics of ageing and consolidation. Ageing can result in a sludge, which is difficult to simulate in terms of chemical properties, physical properties and rheology in the one simulant. Consolidation can make the retrieval process – generally hydraulic transport and homogenisation – difficult. It should be noted that some accumulation facilities contain a number of sludge materials, which might be different in physical and chemical characteristics and may also be present as consolidated layers.

A range of organic ion exchange resins have been used over the years for treatment of a number of plant effluents. Some will contain corrosion products from metals and some will contain fission products from the clean-up of pond water when there was leaking fuel. One or two ion exchange resins dominate these arisings, although there are a significant number of small arisings of less common resins and some inorganic ion exchange materials. A particular feature of the AGR ion exchange resin arisings is the loading of boron from the pond water. In the case of the Sizewell B PWR there are also organic ion exchange resins with high boron loadings and in addition the boric acid concentrate from primary circuit operations.

There are a number of other materials, which need to be considered in their own right, although they may be the dominant components of mixtures. Materials such as filter aid and corrosion products from specific metals such as aluminium are typical examples. All wastes are documented in the UK Inventory (4).

REQUIREMENTS OF THE WASTE ENCAPSULATION PROCESS

Over the years a number of critical areas have been continually addressed as the detailed strategy for retrieval and encapsulation was developed. Solid wastes, such as the fuel element debris, will be mechanically retrieved with a grab, and after a process of sorting will be placed in a suitable stainless steel container prior to grouting and lidding. The sludges and resins will have to be retrieved hydraulically and in order to meet the waste disposal criteria the material will have to be homogenised. The UK wasteform specification identifies local areas of waste concentration as possibly leading to wasteform degradation due to enhanced corrosion, expansion, gas and heat generation and loss of mechanical strength. Depending upon the characteristics of the waste, the homogenised and retrieved sludge may require de-watering to reach the optimum waste loading and minimise the arisings of packaged wastes. Similarly, organic ion exchange resins, which are known to be mixtures of resins in some cases, will be homogenised and retrieved hydraulically. Excess water in the resin wastes will probably be removed by simple settlement and decanting in order to reach the required waste loading.

Once the waste has been transferred to the container in the appropriate amount, the process of cement addition follows, using a previously proven formulation. The fuel element debris, and other solid waste, will require grouting using a formulation, which has been shown to result in minimal voidage in the wasteform. To this end various types of superplasticising materials have been considered together with alternative non-superplasticised formulations. Wet wastes such as sludges and resins will require a process of in-drum mixing (with a lost paddle) to ensure that the wasteform is homogeneous and meets the disposal criteria for strength and integrity. The objective is to achieve a high degree of homogeneity before the viscosity of the mix increases and the process of setting begins. This is usually achieved by using a slow mixing speed during addition of the components of the formulation, in order to avoid splashing and contamination, followed by a higher speed to ensure good mixing on a short timescale.

UK SCENARIO FOR ENCAPSULATED WASTES

Since the decision was made not to proceed with the construction of a UK deep repository in the near future, the question of storage of packaged ILW has had to be addressed. The current assumption is that wastes will be retrieved and encapsulated from early 2001, noting that some packaged ILW is already in storage at Trawsfynydd Power Station, and placed in interim storage for a minimum of 50 years. The storage facilities will be based upon a generic design as far as possible, but will inevitably have several site specific features. For example, some storage facilities will utilise existing reactor buildings and some will be new free-standing facilities. For interim storage on this timescale it is vital that the integrity of the wasteform and the waste package can be assured to a high standard and that environmental control within the store can also be assured over the required timescale. The preference is for passive environmental control with an agreed minimum level of package monitoring and periodic inspection. The outcome of such monitoring and inspection may be limited as the preference would be for non-intrusive methods where possible. The end point of such storage will be the eventual inspection of the packages prior to transport to the repository, and in making the transport safety case it may be advantageous to have had dummy packages in the store from the start. Such packages would be identical in preparation and contents to the real containers, but would contain inactive simulant for the waste and would therefore be available for intrusive inspection.

There is currently a wide ranging debate involving the UK waste producers and regulators to agree on the criteria for the optimum interim storage environmental conditions and the degree of monitoring and inspection during the storage period. Some thought also has to be given to the currently perceived options available for dealing with non-compliant packages. This includes the remote possibility that some packages will have deteriorated to the extent that they require reworking before handling, transport and disposal.

BASELINE DATA

The cement formulation development programme has, for a number of years, accumulated baseline data for the characterisation of cement formulations in terms of the standard product properties. These are a setting time of less than 24 hours, an absence of significant surface water on the surface of the setting cement, viscosity of the mix during the in-drum mixing process, an acceptable exotherm and a number of mechanical properties of the cured wasteform. The latter would include tensile strength and dimensional stability. In addition the wasteforms are subjected to freeze/thaw cycles, total water immersion and exposure to gamma radiation up to a total dose of 9 MGy. Where appropriate measurements of the leaching rate for identified chemical species are carried out.

This data has been accumulated on a number of waste streams encapsulated in a 9:1 blast furnace slag and ordinary Portland cement (BFS/OPC) mixture. Similar data exists for grout mixtures based upon pulverised fuel ash and ordinary Portland cement (PFA/OPC). More recently data has been accumulated for a formulation based upon condensed silica fume and sulphate resisting Portland cement (CSF/SRPC) and formulations with high alumina cement (HAC) added.

LONG TERM MONITORING OF SAMPLES

Underwriting the whole cement formulation development programme, is the accumulation of sample wasteforms of each formulation together with appropriate control samples in order that changes from the baseline characteristics over time can be measured. A large number of samples are stored, under appropriate conditions of temperature and relative humidity and examined yearly for dimensional stability, pulse velocity, elastic modulus and visual appearance. It is accepted that such samples have a limited value after about 5 years as some degree of shrinkage due to desiccation occurs as a function of the sample size and the absence of a sealed container. The sample therefore becomes less representative of a full-scale wasteform. However, some credit is claimed if a formulation sample is still monolithic after 5-10 years despite the limitations of the sample geometry (surface area/volume ratio for a prism sample is 0.16 compared to 0.005 for a full scale 500 litre or 2.6 m³ wasteform.). The intention is to have sufficient samples in long-term storage to cover all the reference formulations plus some, which bound the reference conditions and even support non-reference formulations in case a re-

think is necessary due to unexpected circumstances. Long-term photographic evidence is also used as an appropriate means of indicating either degradation of a formulation or continuing satisfactory performance.

A large number of cemented samples are included in this long term monitoring programme. Dimensional stability and other physical properties are updated annually for the following cemented wastes:

- Fine and coarse Magnox sludge
- Bead and granular phenolformaldehyde ion exchange resin
- Ammoniated divinylbenzene ion exchange resin
- Inorganic filter media and aids
- Granular carbon
- Inorganic ion exchange material
- Magnox alloy splitters
- Borated wastes such as ion exchange resins
- PWR primary ion exchange resin
- Silica gel resin
- PWR wastes such as boric acid concentrate

Overall, it is considered that the results from this part of the programme underwrite the current reference formulations for all the waste streams considered.

CONTAINER CORROSION

A vital component of the waste package, and one, which is required to meet several sets of criteria for handling, storage, transport and disposal, is the container. A number of approved waste containers are available to BNFL for Magnox power station wastes, including a 500 litre drum, a 3 m³ box and drum, and a larger box essentially for solid and decommissioning wastes. The Sizewell B PWR will use Ductile Cast Iron (DCI) drums of significant and varying wall thickness to accommodate the most active wastes and provide appropriate shielding. The wet mobile wastes will be encapsulated mainly in the 3 m³ drum.

In order to examine the propensity of the container for internal corrosion, mainly due to interactions with the wasteform components, a 10 year programme has been followed. Selected waste simulants are cemented in cylindrical 50 litre stainless steel containers incorporating a number of monitoring devices. There are embedded electrodes for measuring the corrosion potential and oxidation potential, the galvanic current between the stainless steel container and carbon steel paddle is measured with a zero resistance ammeter, relative humidity is measured in a sealed cavity in the cement matrix and temperature is measured both within the wasteform and the cavity. Corrosion rate measurements are made on mild steel, stainless steel, cast iron and aluminium coupons embedded in the cement using two different methods. In some containers a stainless steel crevice corrosion assembly, manufactured to ASTM standards, has been embedded in the cement matrix in order to monitor for the enhanced effects of crevice corrosion.

Table 1 shows the wide range of waste simulants used. One container, simulating cemented borated mixed bed resin, has been maintained at 60°C for three years in order to measure the increased corrosion rates. This is to simulate the exotherm which will occur when the repository is backfilled.

During the 10 years of the container corrosion monitoring programme the corrosion rates measured have always been low enough to give an acceptable predicted container lifetime, based upon uniform corrosion. However, it is of interest to consider the more recent data. During 1998/1999 the measured corrosion rates varied between 0.001 and 2.38 $\mu\text{m y}^{-1}$ for the mild steel coupons, between 0.002 and 1.62 $\mu\text{m y}^{-1}$ for the stainless steel coupons and between 0.012 and 2.5 $\mu\text{m y}^{-1}$ for the cast iron coupons.

The measurements during April 1999 show a general increase in corrosion rates for the stainless steel coupons, which has been linked with a move of the containers from Harwell to Culham. The implication is that there was damage to the passive film on the surface of the stainless steel coupons during the move. The increase in corrosion rate for the stainless steel coupons was by a factor of 20 to 30, with an enhanced risk of the initiation of pitting corrosion until the passive film was repaired. This could occur every time a container is moved. Further work is proposed to verify whether this is a real and significant effect as some movement of the containers is inevitable if a programme of frequent monitoring is required.

Table I. Container Corrosion Monitoring Programme

Container No. (Date prepared)	Simulant Contents	Sealed (S) Vented(V)	Container Type
1(12/90)	Boric acid evaporator concentrate 9:1 BFS/OPC	Sealed	SS
2(12/90)	Boric acid evaporator concentrate 9:1 BFS/OPC	Sealed	CS
3(8/91) (Sectioned 2/94)	Boric acid evaporator concentrate 9:1 BFS/OPC	Vented	SS
4(8/91) (Sectioned 4/94)	Boric acid evaporator concentrate 9:1 BFS/OPC	Vented	Carbon Steel
5(3/92) (Sectioned 10/93)	Borated mixed bed resins 9:1 BFS/OPC	Sealed	SS
6(1/93)	Dicalite Speedplus 9:1 BFS/OPC	Sealed	SS
7(1/93) (Sectioned 12/95)	Lewatit DN 9:1 BFS/OPC	Sealed	SS
8(3/94) (Curing at 60°C)	Borated mixed bed resin 9:1 BFS/OPC + 6% HAC	Vented	SS
9(12/94)	20 wt% bead Lewatit DN ion exchange resin in 1:1 CSF/SRPC	Vented	SS
10(12/95)	20 wt% bead Lewatit DN ion exchange resin in 1:1 CSF/SRPC (2000 ppm chloride as NaCl in the mix).	Vented	SS
11(2/96)	20 wt% Decalso Y in 1:1:0.5 CSF/SRPC/lime and 1.5 molar mix water	Vented	SS
12(2/97)	20 wt% bead Lewatit DN ion exchange resin in 1:1 CSF/SRPC (2000 ppm chloride as NaCl in the mix).	Vented	SS
13(2/97)	8 wt% dry Magnox AETP simulant in 9:1 BFS/OPC (w/c = 0.61)	Vented	SS
14(12/97)	1:1 wt% aluminium hydroxide floc:mixed corrosion product, pre- treated with 10 wt% lime, 3:1 BFS/OPC:waste.	Vented	SS
15(12/97)	20 wt% dry waste of 1:1 wt% Magnox./AGR AETP sludge simulant and Borated DVB mixed bed ion exchange resin, 1.5 molar NaOH pre-treatment, 9:1 BFS/OPC + 6 wt% HAC, w/c = 0.50 with 20 wt% oil wrt dry solids.	Vented	SS
16(12/97)	3:1 PFA/OPC, w/c = 0.42	Vented	500 litre thin walled cast iron
17(12/97)	25 wt% CVCS resin in 9:1 BFS/OPC, w/c = 0.36 with 1.8 wt% NaOH(s).	Vented	500 litre thin walled cast iron
18(2/99)	30 wt% solids slurry content Magnox Dissolution Plant sludge, 1.5 molar NaOH, 9:1 BFS/OPC, w/c = 0.55	Vented	316L Stainless

The above corrosion rates predict a time to penetration of between 2,100 and 5,000,000 years for the mild steel containers (minimum wall thickness 5 mm), between 1,600 and 1,300,000 years for the stainless steel containers (minimum wall thickness 2.6 mm) and between 30,000 and 7,500,000 years for the cast iron containers (minimum wall thickness 75 mm). This is based upon uniform corrosion rates as determiner during the programme. If the highest corrosion rates measured during the exposure period are taken as a worst case example, the predicted times to penetration of the container are between 200 and 83,000 years for mild steel, 1,600 and 130,000 years for stainless steel and 18,000 and 500,000 years for cast iron based upon uniform corrosion rates. If the mean corrosion rates are used the predicted times to penetration of the container are between 700 and 100,000 years for mild steel, 3,600 and 260,000 for stainless steel and 33,700 and 938,000

for cast iron, again based upon uniform corrosion rates. The range of predicted times to container penetration are a result of strict interpretation of the corrosion rate data together with allowance for peaks and error bands.

The containers being monitored for crevice corrosion have shown no evidence for the initiation of this type of corrosion. However, pitting attack or stress corrosion cracking also represent a potential threat. In the case of some fuel element debris for early Magnox power stations, there is graphite present as part of the fuel element design. Experimental work has shown that in a cementitious high pH environment, the nature of graphite with respect to stainless steel implies that galvanic corrosion could be a potential mechanism. This could result in penetration of the stainless steel container over a relatively short timescale. Work is in hand to offset this potential problem.

As can be seen from Table I one of the stainless steel containers with a simulated borated mixed bed ion exchange resin in a 9:1 BFS/OPC mix with 6 wt% HAC has been subjected to an increased temperature of 60 °C since February 1977. The corrosion rates of the coupons have continued to increase during this period, which is believed to be due to an increased rate of resin breakdown leading to an increase in the chloride concentration in the system. However, it should be stressed that even such increased corrosion rates still give acceptable and realistic container lifetimes in terms of the time to penetration.

At present external corrosion has not been considered and would be assumed to be minimal due to the environmental conditions in the interim store. However, chloride ingress during the store filling phase would need to be controlled and monitored and post-emplacement in the repository prior to backfill could also generate a hostile environment.

GALVANIC INTERACTIONS

Studies were undertaken to identify any particular combinations of materials that could give rise to enhanced rates of corrosion when electrically/chemically coupled. The materials used to set-up galvanic couples with Magnox were graphite, cast iron, zirconium, 316 stainless steel and Nimonic springs, as shown in Table II, all with appropriate degreasing and surface treatment. In addition two 50 litre stainless steel containers were instrumented to monitor the galvanic corrosion current between Magnox and graphite, corrosion and oxidation potential, relative humidity of the air in the container void, temperature within the wasteform and on the container surface, and the corrosion rate of a single Magnox electrode. In all cases the containers were filled with 3:1 BFS/OPC with a waste/cement ratio of 0.39.

Table II. Galvanic Corrosion Experiments In a 3:1 BFS/OPC MIX

Sample Reference	Galvanic Couple	Surface Area Ratio	Test Temperature °C
Cell 1	Nimonic Springs/Magnox	10:1	80
Cell 2	Stainless Steel/Magnox	10:1	80
Cell 3	Cast Iron/Magnox	10:1	80
Cell 4	Zirconium/Magnox	10:1	80
Cell 5	Graphite/Magnox	1:1	80
Cell 6	Graphite/Magnox	4:1	80
Container 1	Graphite/Magnox	4:1	Ambient
Container 2	Graphite/Magnox	4:1	Ambient

It was concluded that galvanic coupling of Magnox to graphite is unlikely to result in significantly higher rates of hydrogen gas generation, the long term corrosion rate for Magnox/graphite couples is $<0.01 \mu\text{m year}^{-1}$ and that the oxidation potential of the wasteform indicated that conditions in the cement were oxidising throughout the test duration. Physical examination showed that exposure of Magnox to a cement environment resulted in a protective surface film of $\text{Mg}(\text{OH})_2$ and the inside walls of the stainless steel container showed no signs of corrosion after greater than 6000 hours exposure to a 3:1 BFS/OPC (w/c = 0.39) grout. Over the test period of up to 250 days, mixed graphite and Magnox in a cemented matrix showed no propensity for enhanced corrosion.

As noted above, it has subsequently been shown that in the high pH cementitious environment galvanic coupling will occur between graphite and the stainless steel container to the detriment of the latter. The ease with which such couples can arise, when graphite containing waste is packaged and grouted, is being assessed in terms of the long-term implication of container penetration.

NOVEL FORMULATIONS

A significant fraction of the organic ion exchange resins derived from the operation of Magnox power stations has been of the divinylbenzene type, and these have been satisfactorily encapsulated in a 9:1 BFS/OPC mixture. The wasteform products have been acceptable in terms of all the product evaluation tests and this is therefore a reference formulation. It has been reported previously (2) that early experimental work with a particular phenolformaldehyde based organic ion exchange resin, used extensively for pond water clean-up, showed unacceptable wasteform properties in the above mixture. Early test work established that encapsulation in OPC alone was unsatisfactory due to the deleterious effects of leached organic acids from the resin, probably oxalic acid. This caused enhanced precipitation of calcium hydroxide in the vicinity of the resin beads, where presumably the leached acid concentration was depleted, and the formation of crystals of other calcium salts such as calcium oxalate. This in turn leads to mal-formation of calcium hydroxide crystals as massive plates rather than needles. The latter in particular led to expansive phase failure of the wasteform.

Replacement of some of the OPC with BFS alleviated this problem, due to the consumption of some calcium hydroxide by the BFS during the hydration reactions to form more calcium silicate hydrate based gel (C-S-H gel) which gives the wasteform strength. However, although all the mechanical properties of the wasteform were satisfactory the product did not survive irradiation at about $3,000 \text{ Gy h}^{-1}$ to a total dose of 9 MGy. Development work showed this to be due to the formation of the expansive phase ettringite, from radiolytic scission of the sulphonic acid functional group under irradiation releasing sulphate ions. The sulphate ions then react with Al_2O_3 to form the ettringite expansive phase with a solid volume increase by a factor of 3. This imposed large internal tensile forces on the wasteform giving a dramatic failure mode, reducing the wasteform to powder over a period of weeks.

Further development work suggested the use of a formulation, which was both low in Al_2O_3 and contained the capability of removing calcium hydroxide from the system. This was achieved by a 1:1 formulation of condensed silica fume and sulphate resisting Portland cement (CSF/SRPC), where calcium hydroxide is removed by reaction with the silica and the low Al_2O_3 inhibits the formation of ettringite. Although there is still a significant release of sulphate ions to the pore water under irradiation, this formulation has proved to be satisfactory for a 20 weight % waste loading of the phenolformaldehyde resin. Reaction between the calcium hydroxide and the silica framework of the mixture results in a decrease in pore water pH from about 13 to about 10, and this can be offset by the further addition of a suitable additive.

Because of the importance of the phenolformaldehyde ion exchange resins as a waste, and the known problems with swelling and expansive phase formation, it was decided to subject the CSF/SRPC system to more fundamental study. This was carried out under a PhD project, and started with an investigation and quantification of the short and long-term stability of CSF/SRPC mixes encapsulating the ion exchange resin at 25°C, 55°C and 85°C. This was followed by an assessment of the thermodynamics of hydration, an identification of the main phases present in the system and their equilibria. It was also important to assess the leaching characteristics of the system for caesium and the potential for magnesium sulphate attack from simulated ground waters and release of the sulphonic acid groups on the resin under radiation. This work supported the use of a CSF/SRPC blended cement for the phenolformaldehyde resins mainly due to dimensional stability, relatively low heat evolution and low leachability. It was also concluded that the pore water pH, susceptibility to magnesium sulphate attack and the long-term effect of increased temperature should be examined. This has led to further investigations into the long-term changes in the morphology of the system. Rather like the ageing of wastes, the long-term evolution of a wasteform, with changes to the morphology and crystal development, may represent a degradation mechanism which it is impossible to simulate on a short timescale. In this context the short timescale of experimental data is of the order of tens of years whereas the timescale for the ageing of wasteforms is hundreds if not thousands of years.

BORATED WASTES

The operation of an Advanced Gas Cooled Reactor (AGR) and a Pressurised Water Reactor (PWR) generates borated ion exchange resins from the pond water treatment plant, as the pond water contains boron for criticality reasons. In addition the PWR generates highly borated resins from the primary circuit Chemical and Volume Control System (CVCS) and boric acid concentrate from the evaporators. It is the intention to encapsulate these wastes in the reference 9:1 BFS/OPC formulation and it was recognised from the start that all these boron containing materials will cause cement to exhibit delayed time to set and in extreme cases a complete inhibition to setting. This is known to be due to the formation of amorphous calcium borate around the cement grains inhibiting the normal hydration process. The approach to avoiding this mechanism is to either keep the boron in the aqueous phase or form a solid phase other than calcium borate, which incorporates the boron.

The approach initially taken was to use a high hydroxyl ion concentration in the calcium borate/calcium hydroxide system and thereby enhance the solubility of calcium borate and replace it as a solid phase with calcium hydroxide

through which the pore water can diffuse. This required the use of high concentrations of sodium hydroxide, initially 47 weight % and later 5.5 weight % for a waste loading of 20 weight % and 10 weight % respectively. In order to move away from high sodium hydroxide concentrations, which would have process implications, and to increase the waste loading above 10 weight %, high alumina cement (HAC) was added. The calcium aluminate in the HAC would react with boric acid to produce a solid boron containing phase which would not hinder pore water access to the cement grains. This also enabled the sodium hydroxide concentration to be reduced to about 1.5 molar.

The final formulation produces wasteforms, which are satisfactory in terms of all the usual process and mechanical parameters, including water immersion and exposure to radiation at modest (200 Gy h^{-1}) dose rates. The latter two points are significant for two reasons. Wasteforms made using the early high sodium hydroxide formulations disintegrated under water immersion, due to large sodium hydroxide concentration gradients and significant swelling of the resin beads. Wasteforms made using the final formulation with HAC have a much lower sodium hydroxide concentration (1.5 molar) and therefore did not exhibit this phenomenon. However, they did exhibit spalling and cracking into several large pieces in some cases, when subjected to gamma radiation in the dose rate range of $2,000 \text{ Gy h}^{-1}$ to $10,000 \text{ Gy h}^{-1}$. This has been shown to be due to significant gas evolution rates at the higher dose rates, where the diffusion rate was limited, the internal pore structure became pressurised and the wasteform failed in a characteristic way. When the dose rate was decreased to 200 Gy h^{-1} the failure mode did not occur, although it took significantly longer to achieve a total dose of 9 MGy.

MIXTURES OF WASTES

It became apparent from the waste accumulation records and sampling and analysis that in some cases a facility was likely to contain a number of waste materials, which would probably be segregated in layers or zones. As the separate removal of each waste material was not a likely option it was concluded that the cement formulations would have to cater for homogeneous mixtures of wastes, the extremes of each waste material alone and all possible mixtures in between. Accordingly a methodology was developed to facilitate the identification of the type of formulation required and the optimum waste loading. If two waste materials are mixed, for example a divinylbenzene resin and a sludge, and each material alone would be encapsulated in a 9:1 BFS/OPC formulation, the methodology only requires to establish the optimum waste loading. However, if the mixture is a phenolformaldehyde resin and a sludge (which is likely) then there are two contending formulations, 9:1 BFS/OPC and 1:1 CSF/SRPC. In this case the methodology is used to establish which is the dominant waste in terms of the resultant wasteform properties and what is the optimum waste loading. In this case, if the phenolformaldehyde resin is above about 30 weight % it must be considered dominant and the CSF/SRPC formulation used at the determined waste loading.

GAS GENERATION

One of the important wasteform parameters is the gas generation rate, which is relevant to the long-term interim storage period, the operational or loading period at the repository and the post-closure period. In each case it is the influence of the gas generation rate on the ventilation and as an indicator of any enhanced degradation mechanisms within the package. A model has been developed based upon the mechanisms of corrosion, radiolysis and microbiological processes. Waste streams have been classified into about ten generic groups, and not surprisingly the grouted Magnox metal has the greatest potential for gas generation, although significant amounts can be produced from oily sludges.

Gas generation rates are predicted in a fairly straightforward way for the encapsulation process itself and both early and long-term interim storage. This will be based on the assumed chemistry for the system, corrosion rates, the disposition of the materials in the wasteform, temperature and radiation field. Where a parameter is difficult to establish, such as the total surface area in a container of compacted and grouted Magnox alloy fuel element debris, the model would use bounding values. Where appropriate acute and chronic corrosion rates are used from verified databases.

The model can go on to predict gas production rates following emplacement in a repository, say about 100 years after encapsulation, both for a period before the repository is backfilled and after backfilling. The same general assumptions are made concerning the system chemistry and external environment, although on the longer timescales the actual consumption of some materials, such as oxygen, water and Magnox metal needs to be taken into account. Once the repository is backfilled there is the potential for the wasteform to re-saturate with water either through the engineered vent or, after much longer timescales, via any penetrations in the container due to corrosion. As expected the timing of the re-saturation is important as it dictates the change in corrosion rates and therefore gas production rates.

The model has also been used to investigate the effect of a blocked vent due to corrosion of the filter mesh, the production of radioactive gases such as tritium from metals, cellulose degradation and the production of gases other than hydrogen. As with all work in support of radioactive wastes, care has to be taken to ensure that the simulant accurately reflects the actual waste under all conditions. For some wastes this is just a case of using the virgin material

but for sludges and some mixtures of wastes this can be a major problem and places a limitation on the value of the output data.

The model has been verified and validated as far as possible using established experimental data and is now used routinely to investigate the gas production from identified packaged wastes. Packages investigated in this way are Magnox metal in 500 litre and 3 m³ containers, oily sludges and pond water clean-up resins in 3 m³ containers, ion exchange resins in non-vented ductile cast iron drums and resin encapsulated in a vinyl polymer. Sensitivity studies are carried out where appropriate and the gas production rates can be expressed on a single container basis or for a complete storage facility.

MIGRATION OF ACTINIDES

An issue identified early in the repository design phase was the possibility that actinides could migrate through the repository backfill and exhibit a preferential uptake on ion exchange materials, which by that time, would be degraded into potential chelating agents by radiation and time. The time at which this could realistically occur would be when the containers have been significantly penetrated as indicated above. A programme of measurements has therefore been undertaken using the accepted groundwater chemistry and ion exchange materials which were in the as received condition and which had been subject to at least 9 MGy of gamma radiation in order to degrade them. The resultant data, which has been peer reviewed, indicated that this is not a waste specific problem and that the uptake of plutonium by the ion exchange materials, is no greater than would be expected by the backfill or the host geology.

SUMMARY REPORTS

Many of the cement formulation development areas have been the result of a number of years research and development, sometimes by different organisations. The result is a number of reports with different formats, different emphasis and some replicated data. The decision was made to commission a series of summary reports on all the major waste streams studied. The objective was to produce a "stand alone" document, with all the appropriate references, which summarised all the information underwriting a particular cement formulation for a specified waste stream. The document should contain sufficient technical information to satisfy regulators, at least in the first instance, and also carry detailed information for the encapsulation plant operator as to the actual formulation to be used in terms of quantities per container. This approach has been used with some success in the application for "Letters of Comfort" for the encapsulation of wastes for eventual deep disposal in the UK.

MATERIALS SPECIFICATION

Within the current cement formulation development programme within the UK there has been a change in one of the prime sources of BFS due to the closure of a steelworks. The most important parameter in the specification of a BFS, from the point of view of the cementation of radioactive wastes, is the particle size range. This determines its reactivity and water uptake, which in turn determines the water/cement ratio. In the UK BFS is covered by a British Standard (BS), which is directed predominantly at the civil engineering industry. The acceptable particle size band is wide and will include a number of BFS sources, although each will have its own narrow band within the BS. It is clear that within the envisaged timescale of the total programme of retrieval and encapsulation of Magnox power station wastes, the source of BFS may have to change several times. By implication, other materials, which are predominantly supplied to the civil engineering industry (e.g. cement and pulverised fuel ash), may suffer similar changes. Other materials, such as condensed silica fume, which are the products of other industrial processes, would not be immune from such changes in specification. Accordingly, it was decided to carry out a study of the implications of such changes, both in the context of a change, which was announced or anticipated or one which was not known about until raw materials were delivered to encapsulation plants. Fortunately, the implications are nearly always confined to the particle size distribution, and this can be responded to by minor modifications to the water/cement ratio. If other more significant changes occur, such as the chemical composition of the raw material or the appearance of an additive, this would have to be the subject of prompt development work.

RETRIEVAL

The encapsulation process itself is designed and engineered to be as simple as possible. For the Magnox reactor wet waste a mobile encapsulation plant has been constructed, which can visit all Magnox reactor sites as required. Magnox power stations will have dedicated encapsulation facilities for the management of fuel element debris (FED), which involves retrieval and grouting in a cement matrix. However, even with wet wastes certain constraints have to be taken into consideration, dictated mainly by the characteristics of the waste stream. Some wet wastes, mainly sludges, will require de-watering after hydraulic retrieval. Therefore, it has been necessary to construct a mobile de-watering plant to accompany the mobile encapsulation plant.

The main problem is that the design of retrieval and de-watering processes is essentially a function of the rheology of the system, whereas satisfactory long-term encapsulation in a cement based matrix is a function of the physics and chemistry of the system. For some Magnox sludges these two criteria are incompatible (*i.e.* a simulant that has the desired rheological properties will not have the desired physical chemical properties and vice versa). This is because ageing has introduced rheological and chemical/physical characteristics to the sludge which are unique and not readily simulatable in one mixture. These sludge types therefore have to be represented by two simulants, one for the rheology and one for the physics/chemistry.

The retrieval and encapsulation process itself, although designed to be simple, does have certain constraints to accommodate. For example, some waste streams such as filter media are dense enough to settle and consolidate in the waste container if agitation is lost for a period of time. The settled mass will be too dense for the paddle to re-suspend without damage. Over-filling the container due to adventitious water held up in the pipework system is also a potential issue. The plant must be able to store containers while they undergo the 24-hour period of curing prior to moving. This is to attain the minimum tensile strength needed to prevent cracking of the wasteform and loss of monolithicity. The plant must also be able to accommodate any container, which as a result of mal-operation or change in the waste stream characteristics, do not set within the 24-hour period.

In all encapsulation processes there is the criterion that the wasteform shall contain minimal (and preferably zero) voidage. For wet wastes, subject to the potential problems discussed, this is not a problem. However, with FED and any other component based waste streams, where the process is essentially one of grouting, the potential for voidage is clearly present, possibly enhanced by the degree of compaction of the wasteform. The obvious solution is to use a superplasticiser and experiments have shown that this results in effectively zero voidage. However, concern has been expressed over the use of such superplasticisers, which are organic in character. The reference material is a sulphonated naphthalene formaldehyde which may contain other organic materials such as fungicides. Such materials are manufactured for the civil engineering industry where a high degree of product quality control is not required. The problem arises because such materials can be assumed to degrade to organic chelating agents, which will enhance the transport of actinides within and out of the repository, post-closure when the containers have been breached. It is necessary to show that such materials remain locked up in the morphology of the wasteform and do not degrade in the proposed way on any timescale that is likely to threaten the integrity of the repository. The alternative is to develop non-superplasticised grouts, which do penetrate typical partially compacted FED wastes.

Another issue, which has arisen in the retrieval of FED is the question of fire. The scenario is that it is not possible to guarantee the 100% absence of fuel (metallic uranium) in the FED vaults. If fuel is present it must be assumed that it could have formed uranium hydride due to the hydrogen environment generated by corrosion over the years. Uranium hydride is susceptible to combustion if disturbed, which is exactly what will occur during retrieval. The implications of such a fire must be considered as it would lead to the combustion of the Magnox alloy. Such a scenario has been modelled in terms of the fire initiation, smoke production, fire detection and fire control by means of argon injection. The result is that for a given site specific set of conditions the fire can be detected and controlled on a timescale that prevents an un-controlled situation where the fire continues to destroy the integrity of the containment and result in an unacceptable off-site release of activity.

SIMULATION

This is not normally considered an issue, as a waste stream is simulated by "as received" material of the identical type. However, in the case of Magnox power station wastes a large number of ion exchange and filter materials have been used over the years. Most of these materials are not in current production and supplies of the inactive material are therefore limited. Such issues have to be addressed by means of a generic approach, in which a material is characterised in terms of its chemical structure and functional groups in the case of an ion exchange resin, and experiments carried out on a suitable and available substitute.

Another area of uncertainty in terms of simulation is sludges, either from the Active Effluent Treatment Plant (AETP) or the FED storage vaults. Such simulants can be analysed and prescribed in terms of 20-30 ingredients. However, experience has shown that only a few of these ingredients will be a threat to the eventual wasteform integrity. In the case of Magnox power station sludges this is usually the magnesium hydroxide component, which can vary in terms of the particle size distribution and the floc as opposed to crystalline nature of the corrosion products. Again, it is sometimes necessary to resort to more than one simulant to emulate the rheology and physics/chemistry of the system.

MONITORING

As the time for the production of containers of encapsulated waste approaches, there is a wide-ranging debate within the UK nuclear industry on the criteria for monitoring of waste containers in interim storage at the power station site for up to 100

years. It should be noted that some power stations will have a store which is utilising existing reactor building facilities, such as the original gas circulator hall. Others will have new, free-standing buildings on existing locations such as the old turbine hall. Issues such as the mix of containers within a storage facility and their packing density will therefore vary.

Clearly, the most advantageous monitoring regime is to carry out very little actual container monitoring as this requires maintenance of the crane, movement of the containers and maintenance of the monitoring facility. Containers will be stacked several high and acquisition of a given container will imply the movement of several others. The simplest approach is to rely on the quality assurance of the wasteform and container preparation plus monitoring the storage environment and deduce the condition of the containers from this. However, it is acknowledged that the storage environment may be at risk during the filling phase, particularly for coastal and estuarine locations due to chloride ingress. There will also be a period of equilibration following closure of the store when critical parameters will reach their base level. The question is what to do then.

A review has been carried out of all the currently available non-intrusive monitoring techniques. Very little quantitative information can be obtained in this way beyond what is clear from a visual inspection or airborne activity measurements, which would imply penetration of a container. It is accepted that during the next 50 years some of the non-intrusive monitoring techniques may benefit from development work, which could make them more useful.

One approach to container monitoring which is to be exploited is the preparation of "reference" containers. These would contain inactive waste simulant and be prepared during the inactive commissioning phase of the encapsulation plant. Although container degradation is not anticipated to be a significant problem on the interim storage timescale, it is prudent to consider the options for re-working a waste package should it be unacceptable for handling, transport and disposal at the end of the interim storage period. Such container degradation would manifest itself as penetration (which would be visible from the outside) or loss of integrity such as loss of wall thickness (not necessarily visible from the outside) which would compromise the handling, transport and disposal safety case. It is acknowledged that such reference containers do not have the internal radiation to influence the waste ageing/corrosion mechanisms, but they will provide a simple but effective means of monitoring the progress of all other mechanisms.

If inspection of a reference container indicated loss of container integrity, the response to such a situation would be the inspection of all similar actual waste containers and those in the vicinity of the failed container. If an actual waste container was found to have a serious loss of integrity the response would have to be remediation such as patching, over-packing or complete destruction of the package, comminution of the wasteform and re-encapsulation. As the standard packaging and transport containers for ILW have been designed together, over-packing could generate the requirement for a new transport container.

TOLERANCES

An important issue, which has emerged since the operation of the mobile encapsulation plant approaches is the question of the tolerances on the delivery of the components of the cement formulation. The cement formulation was developed at the 50 litre scale where tolerances were insignificant. On the full scale plant there will be tolerances on the amount of waste delivered to the container, the volume of mix water and the amount of BFS/OPC or CSF/SRPC delivered. There will be additional tolerances on any additives such as sodium hydroxide and superplasticisers. Therefore a study has been carried out on each cement formulation to determine the effects on the integrity of the wasteform of extreme tolerances on the deliverables. No requirements for re-formulation have been identified, although the demonstration of a formulation at the 50 litre scale does not necessarily guarantee a satisfactory formulation at the full scale of 3m³.

NON-STANDARD WASTEFORMS

Beyond the wet wastes and grouted FED and other component based waste streams, there are a number of waste arisings, which fall between the description of homogenised matrix and grouted components. For example the PWR primary circuit filters and the recent deployment of an inorganic caesium specific absorbent for pond water treatment. Both are examples of an engineered component, which will contain significant activity but which, when grouted, may contain voidage, will contain free water prior to grouting, and will not strictly meet the requirements for the activity to be immobilised. The concept of macro-encapsulation describes a situation where the activity is confined within a metallic component in a grouted container, but not intimately mixed with the cement matrix.

QUALITY ASSURANCE

An obvious but very important component of the cement formulation development programme is the quality assurance of the work, the auditable route to the encapsulation plant data and the records. All the work has been carried out by suitably qualified contractors using established and documented methods. In addition, BNFL has documents covering the cement

formulations, the simulants and the research and development programme. These are supported by a bibliography of relevant references and a management control document, which lays out the approach to be adopted for any future waste streams. These documents have been peer reviewed and issued within the company.

CONCLUSIONS

The BNFL cement formulation development programme has been comprehensive and gives a high degree of confidence that existing ILW can be satisfactorily immobilised. The immobilisation will be satisfactory for the duration of the envisaged interim storage of up to 100 years. There is a high degree of confidence that the packaged wasteforms will be acceptable for handling, transport and deep disposal at the end of the interim storage period. The cement formulations are robust enough to cater for changes in raw materials, changes in the predicted properties of the waste streams and tolerances on the deliverables from the encapsulation plants.

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