Development of a Direct Encapsulation Technique for the Treatment of a Mixed Sludge / Solid Waste

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ABSTRACT

This paper describes development studies being undertaken by British Nuclear Group Sellafield Limited (BNGSL) to develop a technique for the direct encapsulation of waste from the Magnox Swarf Storage Silo at Sellafield. The waste consists mainly of debris from the decanning of Magnox fuel elements, miscellaneous beta gamma waste (MBGW), and graphite. All the waste is stored underwater to eliminate potential fire risks and under these conditions Magnox metal corrodes over time to yield a magnesium hydroxide sludge and hydrogen. The liquor covering the waste is highly radioactive and represents a considerable risk. The volume of waste in the Silo is considerable, and represents the largest individual packaged volume of the total UK Intermediate Level Waste (ILW) as well as being considered to be one of the most technically challenging wastes in the ILW inventory. In order to facilitate the prompt emptying of the Silo and processing of the waste into a passively safe form suitable for long-term storage and disposal, a method for the cementation of waste has been developed that does not require control of the water content in the waste or extensive size segregation.

INTRODUCTION

The Magnox Swarf Storage Silo at Sellafield is an Intermediate Level Waste (ILW) storage facility built to support the UK Magnox reprocessing programme. In its current state, it consists of multiple concrete compartments that store the solid waste under water. Originally, six concrete compartments were constructed and commissioned in 1964, but in order to keep pace with the Magnox programme further compartments were added in three extension phases. The last tippings of waste in to the Magnox Swarf Storage Silo occurred in 2000 and the building is now in a care and maintenance mode. Since the waste requires continuous ventilation and periodic cooling, and because of concerns that the containment function will diminish with time, British Nuclear Group Sellafield Limited (BNGSL) aim to empty the Silo and process the waste into a passively safe form suitable for long term storage and disposal. The recent progress made in preparing the facility for waste retrieval and clean-up was presented at WM 2006 [1].

This paper describes the experimental work that has been undertaken to aide the underpinning of a treatment process for the waste in the silo. That experimental work is one part of an extensive development programme that is being undertaken to support the construction of a process plant by 2010.

Waste Description

The waste consists mainly of fuel element debris from the decanning of Magnox fuel elements (some fresh Magnox swarf is shown in Figure 1) and a variety of contaminated process equipment classified as miscellaneous beta gamma waste (MBGW). A small amount of stainless steel and zircaloy waste arising from the shearing of uranium oxide fuel is also present but is segregated in a separate compartment.

The waste in the silo is stored underwater to eliminate the fire risk associated with potentially pyrophoric uranium compounds and under those conditions; Magnox swarf corrodes over time to yield a magnesium hydroxide sludge (see Figure 1) and hydrogen. The liquor covering the waste is highly radioactive and, being more mobile than the waste, is the main driver for early remediation of the silo contents.

Figure 1 Fresh Magnox swarf and corroded Magnox sludge

In the earliest compartments the corrosion process is almost complete, whilst the later compartments contain a much higher proportion of uncorroded swarf. As a consequence the consistency of the sludge varies from compacted clay-like material (as shown in Figure 1) to much more mobile slurries, but all types are associated with residual Magnox metal that may be present as small grit-like kernals surrounded by sludge or large pieces of metal. The sludge also contains pieces of uranium and uranium oxidation products; there was considerable carryover of uranium from the decanning process with the swarf consigned to the silo, in the form of small pieces trapped in the swarf or as whole or broken fuel rods.

Individual categories of MBGW items in the Magnox Swarf storage silo run to several hundred and include items such as redundant machinery, pumps, scaffolding poles, filters and graphite. The total displacement volume of MBGW is estimated to be about 700 m^3. The silo compartments tended to be filled with MBGW and swarf waste in campaigns, resulting in a layered structure. Some items of MBGW are large and/or long and will require size reduction prior to export from the silo. There are a large number of cans that were used to containerise small waste items before consignment to the Silo. These cans are considered especially problematic since a small number of them could contain an environment conducive to the formation of compounds that have pyrophoric properties (e.g. uranium hydride) when exposed to air. Such materials could be the ignition source for a Magnox fire or could release hydrogen that was generated during the period of storage in the Silo.

A number of sampling campaigns, giving rise to approximately 200 sludge and swarf samples have been carried out, mostly directed at characterizing the waste in the earliest silo compartments. Less samples have been taken from the later compartments therefore there is less confidence in the data available, although approximately 1000 m^3 of swarf has been successfully retrieved from the later compartments and encapsulated in grout in the Magnox Encapsulation Plant (MEP) at Sellafield, hence proving the retrieval concept. However, the MEP uses a vibro-grouting process designed for the encapsulation of fresh swarf [2], so once significant quantities of sludge were encountered processing through MEP had to stop.

DEVELOPMENT STRATEGY

From quite early on it was recognised that the bulk storage of ILW such as that in the Magnox Swarf Storage Silo, whilst not foreclosing options, was not sustainable indefinitely and that a treatment process was required. Early studies were very wide ranging including dissolution, thermal oxidation and encapsulation in a variety of media, but by 1982 the focus was on encapsulation with cement being eventually chosen as the preferred matrix for MEP which was commissioned in 1989 and for the Waste Encapsulation Plant (WEP) which was designed to encapsulate the waste arising from THORP operations, namely hulls and slurries. However, the cementation processes used successfully in MEP and WEP (and subsequent encapsulation plants at Sellafield) for fresh waste arisings could not be translated for application with the stored wastes. As can be seen from the description of the waste, the contents of the Magnox Swarf Storage Silo impose significant challenges for any treatment process; namely:

- High activity levels
- Variable water content.
- Reactive metals (e.g. Magnox, uranium and aluminium)
- Organic material
- Graphite
- Material composition ranging from thick sludge to thin sludge, through small solids (<20cm) to very large solids (100’s of cm maximum dimension).

The original attempts to identify a cementation process for the silo waste failed because it was not possible to control the water content and segregate the waste in to size fractions compatible with the then preferred treatment methods of either In-Drum Mixing (IDM) or vibro-grouting without greatly increasing the packaged waste volume. Alternative processing options using high temperature treatment also proved problematic so as a consequence BNGSL initiated a fundamental review of treatment methods for legacy wastes such as those in the Magnox Swarf Storage Silo. That review involved a worldwide search of technologies and techniques, from which potential process options were selected for feasibility studies. The deselection process culminated in a recent Best Practical Environmental Option (BPEO) study that identified Direct Encapsulation as the preferred treatment option.

DESIRED PRODUCT QUALITY AND SUSTAINABILITY

UK policy (Command 2919) [3] requires that whenever possible nuclear waste be dealt with now and not left as a burden to future generations, in keeping with this the preference will be to produce a product that is suitable for disposal. However, where that is not practical either due to current technical difficulties or pressing time constraints to reduce risks posed by current storage conditions an interim product may need to be made. These may or may not be deemed to be compatible with the current disposal concept as established by UK Nirex (i.e. Nirex ‘Letter of Compliance’ products), but where they are not then there should be a credible means by which an interim product can be reworked in order to move towards a disposable product.

In considering the potential product forms against the current Nirex criteria, the main issues for product performance tend to be as follows:

- **Immobilisation of radionuclides and particulates.**
  A requirement to ensure that the radioactivity is retained in the package under normal and accident conditions such as an impact or fire incident. Thus solid products where the waste is intimately bound in to a matrix are preferred.
- **Chemical containment**.
  The ability of the product to contain the final waste-form or break down products from the waste that may occur over time. This is typically assessed by the measured or estimated strength, quantity and type of corrosion product formed and gases released. The ease with which material can be leached from the product is also considered.
- **Mechanical and physical properties.**
  The product should have sufficient robustness to permit handling within plant, store and ultimately removal to a repository. This is typically assessed by the measured or estimated strength of the waste-form, the presence of any voidage and its mass etc. However, the contribution in performance from the container (e.g. box, drum, etc.) should also be considered.
- **Hazardous materials**.
  Materials that by virtue of their intrinsic properties (e.g. flammability, pressure etc.) have potential to disrupt/damage the waste-form or package. Assessment is based on the inventory and chemistry of the waste.
- **Degradation processes and wasteform stability.**
  The potential for changes in stability (chemical and physical) of the waste-form, as a result of corrosion reactions, thermal changes or radiation exposure to adversely affect the integrity of the product. Assessment is based on measured or estimated dimensional changes, corrosion rates etc.
- **Gas Generation.**
  The potential for the final waste-form to generate gases as a break down product (via corrosion or radiation mechanisms) over time is considered, both in terms of the ability of the product to release the gases and not become pressurised, as well as the impact these gases may have on the storage or disposal environment.

- **Nuclear Properties**.
  The external dose rate and criticality potential of the final waste form. Assessment is based on the inventory and construction of the product.

The measurements referred to above are seldom a simple ‘must meet’ value, but rather indicators of the performance of the product from which an overall argument for the acceptability of the product is deduced.

Multibarrier approach

In developing a new approach for the treatment of this waste one of the key developments has been the recognition of the contributions of the individual components of the waste package to the overall performance of the package. Historically, the cemented waste form delivered a large amount of the performance of waste products with the container itself being often viewed as just the ‘outer skin’. However, the multi-barrier concept supported by the development of enhanced containers, such as double-walled boxes with the annulus pre-filled with a performance grout, has enabled the development programme to consider new waste forms that do not need to provide all the performance characteristics on their own.

Product Evolution

A key factor in the overall assessment is the predictability of the performance of the product with time. Essentially, this means understanding the potential degradation processes and mechanisms by which the product is deemed to depart from the original specification. The ideal situation is one where a product does not degrade, but this is extremely unlikely unless all chemical potential within the product is removed. More commonly, one is faced with a situation where there is material in the product that will undergo some form of degradation whether due to chemical reaction (e.g. corrosion of Magnox) or radiolytical effects. Thus one needs to examine these mechanisms and ascertain that they proceed in a very slow and consistent manner and do not suddenly accelerate. In a similar manner the consequences of this degradation must be considered against the ability of the product (through a combination of the waste form and container) to satisfy its fundamental function of keeping the radioactive species immobilised and contained.

When this deterioration in product performance is likely to occur before the product is finally disposed of or to allow it to meet future disposal requirements, appropriate rework strategies will be developed.

THE DIRECT ENCAPSULATION PROCESS AND PRODUCT DESCRIPTION

The proposed plant concept is that the waste is imported in to the plant in skips contained within flasks. The skip is removed from the flask and is transferred to a separation cave where its contents are tipped onto a coarse vibrating screen, which is nominally sized at a mesh size of 350 × 350 mm. The coarse vibrating screen separates the waste into an undersize and oversize fraction.

The undersize portion of the waste passes through the coarse vibrating screen into an undersize mixing vessel, which is then transferred to the encapsulation cave for intimate mixing with matrix grout and the mix poured into an enhanced $3m^3$ box. The matrix grout is prepared in an inactive grout preparation facility by mixing pre-determined ratios of Blast Furnace Slag (BFS) with Ordinary Portland Cement (OPC) and water.

The oversize waste remaining on the coarse vibrating screen is removed using a heavy-duty hydraulic manipulator and placed inside an enhanced $3m^3$ box. The box is then transferred to the encapsulation cave for matrix grout addition in the same ratio as for the undersize.

Once the matrix grout has been added and the box contents cured, the boxes (containing either grouted undersize or oversize waste) have capping grout added. The cap, which has been prepared in the grout preparation facility by mixing pre-determined ratios of water, Pulverised Fuel Ash (PFA) or BFS with OPC, is allowed to cure and the box lidded.

The lidded box is then transferred into the decontamination and monitoring cave where the external surfaces of the box are decontaminated, dried and swab monitored to ensure the boxes are suitable for export. Once the boxes are deemed suitable for export they are transferred to a store.

During the process operations effluents are produced. These effluent streams are collected in local sumps / vessels before transfer to an effluent tank. The effluent collected within this tank is either recycled back into the process for re-use or transferred to the effluent treatment process.

The key features of the approach are:

- One skip in one box out
- A simple process with minimum operational steps and avoiding complicated segregation processes – experience has shown that the operability of complex segregation processes with this waste rapidly deteriorates and the waste cannot be processed in the timescales required.
- No complicated adjustment of the cement grout – the same fixed quantity of the reference grout is added to a fixed volume of waste irrespective of the waste composition. It is recognised that this approach will result in bleed production, which is subsequently removed and a capping grout added to seal the product surface and fill the void.
- A low temperature process to avoid issues with graphite oxidation.
- The product is compatible with the UK Nirex disposal concept.

DEVELOPMENT STUDIES

To underpin the Direct Encapsulation process and product quality a programme of development studies was initiated that aligned with the requirements of the FEL-Gate process. The scope of these studies is defined by Issue Resolution Strategies developed for each technical or process risk. The overall scope of these studies is far reaching and covers all aspects of the intended processing of this waste stream from initial receipt of the skips of waste into the plant through storage of the product and eventual disposal. The development programme draws upon extensive historical work as well as new practical work in order to model and predict the performance of the process and product. This paper describes the results from recent formulation studies using simulated waste to underpin the Direct Encapsulation mixing process.

Recent Experimental Work

To test the Direct Encapsulation mixing process the trials to date have used a conventional cement truck type mixer. The mixer is a Ritemixer model RTE3 consisting of the mixing drum and hydraulic drive unit of a road going cement mixer. The barrel has a working volume of 3.6 cubic metres and is inclined at 14 degrees from the horizontal with the barrel throat uppermost. Internal 'blades' within the barrel are configured to form an Archimedean screw. The barrel rotates at a variable speed of 0 to 15 rpm along its centre axis. In normal operation the feed is via the barrel throat but because the desired feedstock for the un-segregated mixes was non-standard for this type of mixer the simulant was imported into the barrel via side inspection ports. Discharge from the blender barrel is achieved by driving the barrel in reverse (see Figure 2). The mixing system has been tested using simulated sludges manufactured from commercially available grades of magnesium hydroxide that are blended with water to produce sludges with the desired consistency and rheological characteristics.

Figure 2 Tumble mixer

Over the last year more than 40 full-scale ($2m^3$) wasteforms have been made which cover the following range of conditions:

Parameter	Range
Waste types	Pure liquor (i.e. 100% water, no solids) Pure sludge (with variable solids content up to 70%w/w) Variable amounts of MBGW with water or sludge.
Reactive metals	Magnox metal

	Aluminium
Waste to grout ratio	1:1, 3:2, 3:1
Cement grout.	BFS:OPC or PFA:OPC mixtures with 10 to 100% OPC content with water/cement ratios between 0.25 (with superplasticiser added) to 0.41.

Additionally some scoping trials using alternative inorganic cement systems have also been undertaken.

The large scale inactive trials with simulated waste have been used to demonstrate the mixing efficiency of the tumble mixer, the ability of the mixer to discharge the resulting mixture and to generate a full set of product quality tests. The product quality testing has included measurement of:

- **Curing exotherms** and **setting characteristics** of full-scale products.
- **Compressive strength** (of core specimens taken from full-scale products as well as of cube specimens cast from wet mixes).
- **Dimensional stability** (from in-situ strain gauges within full-scale products as well as of prism specimens cast from wet mixes).
- **Homogeneity** of products.

In addition, the corrosion of Magnox and aluminium metal in full-scale products as well as small-scale specimens has been examined. The mix compositions covered by these trials are shown in Figure 3 along with effective envelopes for various types Magnox.

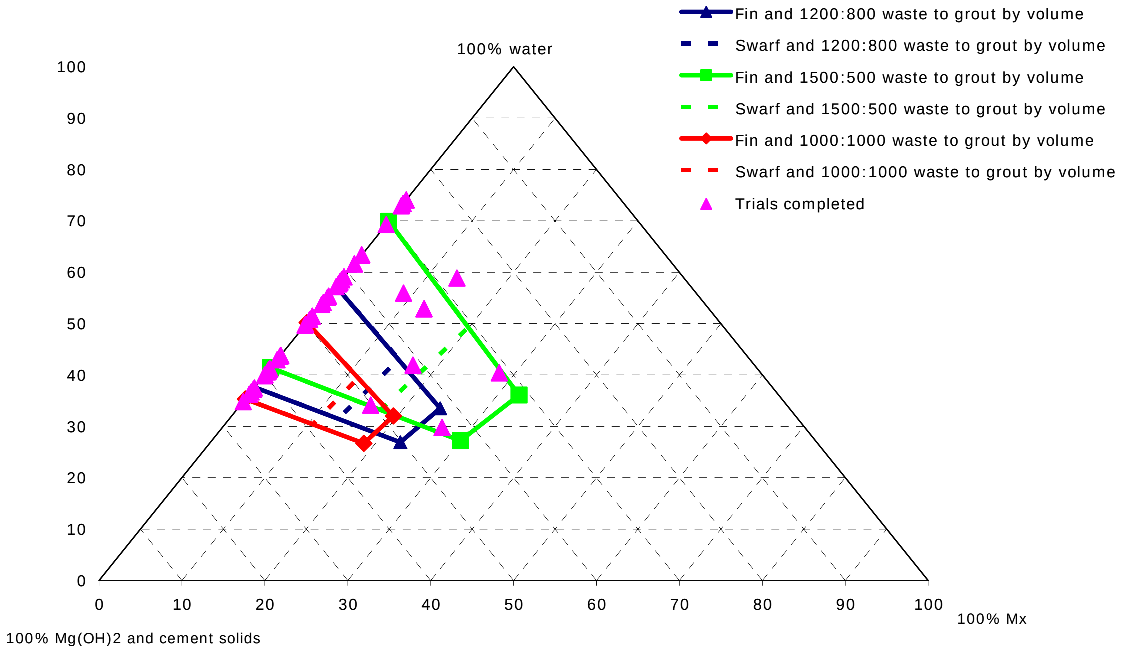

Figure 3 Theoretical envelopes for various Magnox types and different waste to grout loadings.

PROCESS AND PRODUCT PERFORMANCE

The large-scale trials have demonstrated that the Direct Encapsulation technique is a feasible process for producing cemented products that span the expected waste feed envelope. Results to date are showing the following:

Mixing efficiency

One of the biggest challenges that faced earlier attempts to encapsulate this waste was the very large variation in the sizes of the solid items co-existing with the sludge material. Hence processes such as In-Drum Mixing or other paddle mixing methods required that the waste be screened down to quite small sizes to avoid having material that might jam within the mixer. In the case of the Direct Encapsulation Mixer there are no internal moving parts and whilst there is still a potential for items to jam the size of material that may do that is orders of magnitude greater than for the other systems. The consequence of this is that any screening duty is dramatically reduced with only the very largest items needing to be routed for alternative treatment, which for this waste will be in-fill grouting.

Although the tumbling action of the Direct Encapsulation Mixer is very effective in its own right in blending the sludge waste with the cement grout, the presence of larger solid items is beneficial and enhances the mixing process, primarily through its ability to break-up larger pieces of sludge and allow more rapid dilution of the sludge by the grout. An additional benefit is that the presence of large metal items can aide the disruption of sealed containers thereby mitigating the potential of such containers to maintain or form pyrophoric material. It also minimises the potential for voids to be left within the final product. For these reasons it is conceivable that the process may be enhanced by the deliberate inclusion of sacrificial metal items.

Ability of the mixer to discharge the waste/grout mixture

Having created the waste/grout mixture it is important that the system is capable of discharging the contents in to the final container. Since the Direct Encapsulation is based on the use of a very fluid cement grout, then even with thick sludge the resulting mixture tends in the majority of cases to be very mobile. As a consequence it usually flows readily from the mixer with any metal items being pushed out by the action of the internal ‘blades’ in the mixer.

Curing exotherms

For the trials undertaken to date the wet mixes are discharged in to approximately 2m^3 demountable moulds, which matches the planned mix volumes to be used in the proposed plant. These moulds contain an array of thermocouples that allow the temperature profile throughout the full-scale product to be mapped over the duration of the curing exotherm.

Of course the peak temperature of an individual mix is dependent on many variables such as OPC content, waste to grout ratio, waste composition, and curing temperature. However, results to date are showing good predictability between the expected peak temperature and the volume fraction of cement powder in the final product. Since the concept is based on the use of less than 50%v/v cement grout the curing exotherms have in most cases been low (i.e. less than 70ºC peak temperature), which is beneficial in that the system can remain safely below the temperatures at which the graphite in waste (or other materials) might be prone to auto-oxidation or ignition.

The low curing exotherms displayed by these waste forms has the added benefit of reducing hydrogen generation during processing.

Setting characteristics

The high waste loading and relatively low OPC content of some of the resulting mixtures can tend to lead to longer setting times than the usual less than 24 hours experienced in other cementation plants. However, all mixes were set within 48 hours and this can be accommodated in the plant capacity and throughput requirements.

Bleed

As stated previously a particular problem associated with earlier attempts to develop a formulation for the encapsulation of this waste stream was the requirement that the water content of the waste had to be controlled. The Direct Encapsulation process takes an entirely different approach in that it ignores the water content of the waste and utilises the fact that cement systems can set under water and will in fact be self-controlling and expel any excess water. The consequence of this approach is that the Direct Encapsulation plant will have to accommodate potentially large volumes of bleed liquor in its effluent system and the capping grout, which in most cementation plants is a small fraction of the overall product may be the equivalent of a second matrix grout infill.

Compressive strength

Despite the very variable waste and cement grout contents of the test products made, the resulting waste forms have proven to be robust to handling and measured compressive strengths are comparable to those displayed by other sludge wastes that have been cemented using in-drum mixing techniques. Some typical data is shown in Table 1.

Table 1 Typical cube and core strength data

Waste / Grout ratio	% $Mg(OH)_2$	% water	BFS / OPC ratio	W/C ratio	Cube Compressive strength (MPa)		Average core strength (Mpa)	Average core density (kg/m^3)
					28 day	**90 day**		
1:1	60	40	3.44:1	0.35	11.6	18.0	15.4	1757
1:1	60	40	3:1	0.35	14.6	20.3	16.2	1720
1:1	60	40	100% OPC	0.35	27.8	Awaiting testing at 90 days		
1:1	70	30	3:1	0.35	10.9	20.8	Cores not taken	
3:1	70	30	3:1	0.35	8.3	9.8		
3:1	30	70	3.44:1	0.35	6.9	7.1	3.7	1454
3:1	45	55	3:1 PFA/OPC	0.45	1.0	1.2	1.25	1559
1:1	70	30	3:1 PFA/OPC	0.45	3.1	7.2	8.75	1606

Dimensional stability

All of the conventional cement grout products made to date have proven to be dimensionally stable with measurements from in-situ strain gauges or test prisms having shown very little dimensional movement overall (less than 500 microstrain i.e. < 0.05%) with nearly all of that movement being seen in the first few days after the product is made with negligible movement there after. This is acceptable performance comparable with similar cement products studied previously.

Homogeneity

After the waste forms have reached an age of 90 days, selected products are sectioned (by being cut through with a diamond wire) to expose the internal structure and determine if the product is uniform with no gross voidage or areas of un-immobilised sludge etc. A typical section surface is shown in Figure 4.

Figure 4 Section cut from full-scale product

Performance against Nirex Criteria

The results to date are demonstrating that the Direct Encapsulation process does produce products that meet the requirements that the waste is immobilised and that by analogy with comparable cemented wastes will perform acceptably with respect to mechanical and physical properties. With regard to issues of chemical containment, waste form degradation/stability, gas generation and product lifetime the Direct Encapsulation approach is subject to all the advantages and disadvantages of a cementation system. The high pH environment and the chemistry of BFS/OPC systems is beneficial for aiding the retention of radioactive species, but residual reactive metals such as Magnox, uranium or aluminium will continue to corrode even after the cement grout has set. It is these corrosion reactions with the associated expansive forces and hydrogen gas generation that will most likely determine the lifetime of the products. To evaluate the extent of the corrosion, trials are in progress to determine the rates of Magnox corrosion over a wide variety of compositions and curing conditions. The trials are mainly undertaken at small-scale, but full-scale lead-time products have also been made. In addition, complementary studies with uranium and aluminium have also been undertaken, and further trials are being initiated. On the basis of the work completed to date and planned future development work, it is expected that a Letter of Compliance will be issued for the Direct Encapsulation process and products.

FUTURE STUDIES

The development programme is on going and a new full-scale demonstration pilot rig will be available in January 2007 to support the project in meeting its challenging timescales. In addition to progressing the optimization of the grout formulation and further underpinning of the product longevity through corrosion studies; the development trials will also be concentrating on optimizing the process design and its overall operability.

CONCLUSIONS

To date over 40 full-scale simulated waste products have been made to underpin the process feasibility and product performance. These trials cover the full range of waste compositions and show that cemented products are made which:

- Efficiently mixed
- Are fluid enough to pour
- Set in <48 hours.
- Have exotherms less then 100°C.
- Have sufficient strength.
- Are dimensionally stable
- Have low voidage.

This can be achieved within the following conditions:

- Adding 500 - 1000 litres of grout to 1000 - 1500 litres of waste to make a 2m^3 product.
- The waste can consist of water through to sludge of ~ 30% water.
- A conventional BFS/OPC grout.

Current challenges are focused on establishing a grout that minimises bleed whilst improving product lifetimes by limiting the water in the end product that is readily available for corrosion of reactive metals.

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