

A Cradle to Grave Decontamination Process – 15266

Steven Black *, Matt Tuck *, Neil Foreman *
* MDecon

ABSTRACT

As the rate of decommissioning of nuclear facilities is accelerating there is an ever increasing need for technologies which will decrease dose to operators, reduce overall cost and allow minimization of waste volumes. A new fully integrated decontamination and waste management process is described herein. This method approaches surface decontamination in an integrated fashion in that it deals with the full cycle of the process including the final disposition of the secondary wastes generated during the cleaning cycle. This approach also simplifies decontamination in that it addresses issues observed in previous chemical decontamination applications such as generation of orphan wastes and the requirements for multi-step reagent additions over repeated cycles. The waste management aspect of this system is key to providing a fully integrated process and deals with the issues related to grout formulations in the presence of high waste loadings.

INTRODUCTION

The deployment of a chemical decontamination process prior to the dismantling of nuclear facilities and large items such as fuel casks allows the techniques used for the decommissioning process to be simplified. Application of a chemical surface decontamination process will remove loose activity and as much depth of the surface as required to lower dose rates and hence lower the burden on the site staff for decommissioning. The streamlined nature of the process where no regular chemical cycles are added also lowers the deployment and operational complexity of the system.

The process uses a moderate strength acid with a ion exchange activity capture system. In order to minimize waste generation the ion exchange media are not disposed of when spent and are instead regenerated in order to present a waste stream suitable for direct processing on existing site disposal/treatment routes or as a solidified material suitable for sentencing.

The decontamination process etches micron by micron layers off the surface oxide layers and associated contamination and can also remove metal where contamination is entrained. The dissolved material and contamination is then captured on a cation exchange resin column which in turn regenerates the acid solution allowing the decontamination process to continue.

The regeneration and immobilization process is the essential factor in the management of the overall decontamination procedure and is described in terms of how it is applied to high salt loadings and minimization of waste volumes.

Industry Principles for Cementation

The requirement to produce a 'passively safe' wasteform to allow radioactive waste to be sentenced to a repository for interim storage and ultimate disposal is a common theme throughout the nuclear industry worldwide. In order to successfully treat radioactive wastes it is necessary to manufacture environmentally acceptable packages that minimize or eliminate the possibility of radioactive and/or toxic contaminants being released from the package. The concept of stabilization/solidification of wastes has evolved considerably over the past four decades and is now in a mature state.

Stabilization generally refers to the chemical treatment of the waste in order to convert the contaminants to less mobile, insoluble forms. The solidification phase is where a waste is converted to a solid form such as a grout, vitrified glass or polymer immobilized monolith. This is achieved by a process of chemically treating the waste to a form that is suitable for mixing with an inert binder that is capable of delivering waste packages that fulfill the requirements imposed by the relevant regulatory bodies.

Where a raffinate or slurry contains high levels of salts, such as sodium sulphate, the conditioning and stabilization steps need to account for this or a poorly formed and unstable wasteform can result.

High Sulphate Wastes and their Challenges

Where high concentrations of inorganic salts are present in a pre-grout waste stream there exists the possibility that these will interfere with the properties of the grouted product. These interferences can be manifested in the final wasteform, for example, effects on set time, variations in durability, expansive degradation or unwanted changes in porosity as the product undergoes hydration. In the case of a regeneration liquor there will be a dominant species present in the form of sodium sulphate with a lower but significant portion of iron sulphate.

Sulphate, when present in dilute solutions in water, does not have a marked effect on cement set characteristics and calcium sulphate is often used as a moderator of the rate of set and hydration of aluminate phases [1]. However it is possible to use sulphates as regulators of set in grouts and this is usually controlled at the manufacture stage of the cement powders by addition of gypsum to the mixture prior to grinding to attain the final desired formulation.

The presence of sulphates is beneficial to the set and cure of cementitious grouts, but can also present a significant risk to their long term stability due to the potential to form the mineral ettringite. This occurs through an expansive process as the product undergoes full hydration and cure following the initial set. Ettringite is a highly hydrated calcium aluminosulphate phase which has the formula $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$. During the initial set of cementitious materials the tricalcium aluminate portion of the system will react with available sulphates to form ettringite, and if the mixture is still plastic in nature the stresses caused by the expansion (approximately 77% increase in volume over the precursors [2]) will be accommodated.

However if the material has set then the formation of the ettringite can cause damage to the matrix through cracking caused by the expansive nature of the ettringite phase [3]. The presence of a large excess of sulphate in the matrix can lead to the ettringite formation occurring post set and this 'internal attack' of the expansive product formation leads to product instability and breakup.

Sulphate Effects on Set and Solutions

The effect of adding increased amounts of sodium sulphate to grout has been observed when a solution of sulphuric acid that was neutralized and then evaporated to obtain a sodium sulphate salt was tested with Ordinary Portland Cement (OPC) [4]. Palmer and Smith observed an acceleration effect caused by the sodium sulphate on the set time as shown by conduction calorimetry and a marked increase in compressive strength over control materials at 48 hours post set. They also noticed that this acceleration effect resulted in a very high temperature (120°C) on a 220 liters-scale test. As a result, they modified their formulation to a 10% OPC - 90% Blast Furnace Slag (BFS) blended cement to minimize this effect.

A series of experiments in the EU on Boiling Water Reactor (BWR) liquor concentrates demonstrates that a high level of salt in solution (approximately 21%) can be tolerated in OPC blends [5]. These tests showed that while there was some surface cracking of the leach monoliths they remained intact and that the blending procedure of the wastes into the grout was the critical factor and tight control of this was key to controlling product quality.

The effects of ettringite formation on construction materials has been investigated by the US Federal Highways Administration and the destructive nature of the material effects led to the use of fly ash materials to mitigate this. Addition of 20% PFA to the cement blend in concretes inhibits or prevents the ettringite effects on the matrix successfully [6].

The development of new solidification regimes using aluminate cements and pre-casting treatment with barium hydroxide has been shown to prevent destructive ettringite formation by scavenging the excess sulphate prior to full set. This method

does add in a treatment step to the grouting process but can tolerate up to 25% sodium sulphate in solution [7].

Silica fume and sodium silicate are known to reduce the permeability of grouts and increase the sorption of metals within the matrices [8]. Silicates can cause higher strengths as a consequence of closing off the pore structures but can also accelerate cure leading to temperature increases at large volumes.

Vejmelka and Sambell reported good results in achieving set from a solution containing 22.5% sodium sulphate in Portland cement and that they observed no ettringite presence after 30 days [9] and that anhydrous sodium sulphate was present instead.

As most waste streams are mixtures of many species that can include inorganics, organics and radionuclides carrying out cementation trials is essential. When considering such complex mixed waste theoretical knowledge is of limited value, and tests need to be performed in order to determine the properties of the waste and its effect upon the host waste form.

In order to establish that the wastes in question can be immobilized using blending with a grout matrix it must be proven that suitable immobilization envelopes can be produced within which acceptable waste products can be formed. Such envelopes are established by performing a number of trials on the waste surrogate solutions that have been conditioned or neutralized.

Methods

In order to establish that the ion exchange regeneration wastes can be safely immobilised using grout it must be proven that suitable immobilisation envelopes can be produced within which acceptable waste products can be formed. The trials incorporate variation of cement powders by type and ratio along with amount added until a range of formulations are obtained that are acceptable. Figure 1 shows this principle in graph form, note that real grout envelopes are rarely as symmetrical.

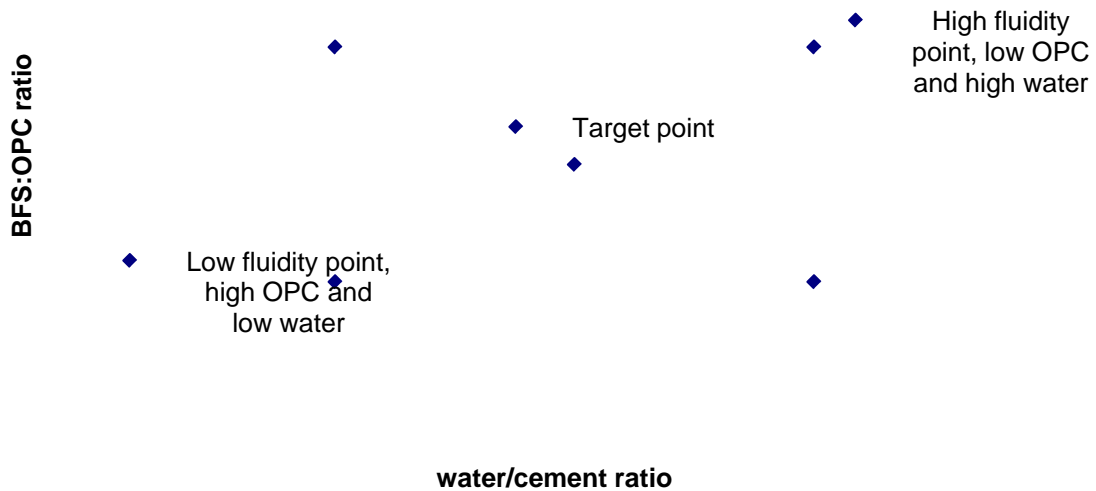


Figure 1: A typical grout immobilisation envelope

The first stage for any cementation trials is to define a starting point by mixing standard blends of 1:1 PFA:OPC or 3:1 BFS:OPC with a known mass of neutralized surrogate. The known mass will have a known associated water content. The amount of cement powder added to give a ‘thick’ mixture (around 4-5 Pas or by observation which is where no further powder can be added reasonably), at this time the consistency is to be recorded.

The setting time and the determination of any bleed water is to be measured on the initial samples. Providing that the sample achieves final set in a reasonable time (e.g. within 48 hours) then further formulations can be investigated using the same powder ratios (PFA:OPC, BFS:OPC) with a variation of the water to cement ratio. At this stage the density of the samples can also be measured by using their mass and approximate volume.

A number of internationally accepted standards for grout testing exist, however the UK BSI (British Standards Institute) and the ASTM (American Standard Test Methods) are the main ones used for product quality testing. The key standards employed for the testing of samples for wasteform product quality in the UK, Europe and North America are:

1. Set is measured using the Vicat-needle penetration test. The procedure is based on BS EN 196-3:2005 [10] or ASTM C191-07 [11].
2. Compressive strength can be determined in two ways: destructively by crushing the sample till the yield point is reached and non-destructively through use of ultrasonic pulse velocity measurement. Destructive testing is based on BS EN

196-1:2005 [12], and ASTM C109/C109M-07 [13] (destructive testing) and BS EN 12504-4:2004 [14] and ASTM C597 [15] (ultrasonic testing) as guidance.

3. Dimensional stability is a product evaluation property and examines the shrinkage or expansion of a grout formulation throughout the length of time it is measured. It is measured using the manual measurement of length of a prism at predetermined intervals over the long term. This test method is based on and ASTM C157 and C490 [16,17] specifications.
4. Viscosity can be measured on the grout mixes by use of a torque meter on the mixing paddle or by taking samples to a recently calibrated viscometer.
5. Leach testing should be carried out to the standards of either the American National Standards Institute; ANSI/ANS-16.1-2003;R2008 (R=Reaffirmed), [18], or the NEN 7345 (Dutch standard commonly used in Europe), NEN 7345:1995.nl, [19].

Sample Preparation

Samples of a high sulphate sludge cake typical of that yielded from the precipitation of a regenerant liquor were prepared with approximately 75-90% water by mass. This level of moisture in the cake is sufficient to allow direct blending of the grout powders with the sludge as on mixing the high affinity for water present in the powders will sequester the water and a cement hydration reaction occurs.

Whilst blending powders in this way in a laboratory setting is difficult once they are incorporated the mix becomes a high viscosity mixture which will self settle under agitation such as vibration. The samples set in an acceptable timescale and offered no concerns in terms of their cure exotherm for scale up.

For full scale application the process of blending the powders direct to the sludge would be a simple one. An air fed powder hopper with an Auger type mono pump would provide the necessary blending ability and the pump shaft/blender unit could be disposed of in the waste package if cleaning was deemed difficult.

CONCLUSIONS

A surface chemical decontamination that is progressed from the initial activity trapping on ion exchange media through to the final wasteform in an integrated process is demonstrated. The regeneration liquor can be successfully precipitated and the resulting slurry material can be isolated as a cake and directly blended with grout powders. The sludge cake preparation with the water content described above is essential to the waste minimisation concept in this process as it prevents the generation of larger waste conditioning factors common to raffinate treatment.

The cradle to grave approach presented allows sites to reduce the risk and cost of decommissioning activities and provides a wasteform suitable for direct disposal or interim storage that is passively safe.

REFERENCES

- 1 Lea, F.M. 1971. *'The Chemistry of Cement and Concrete'*, Chemical Publishing Company, Inc., New York.
- 2 Roy, D.M. 1986. "*Mechanisms of Cement Paste Degradation Due to Chemical and Physical Factors*", pp. 362-380 in Proceedings of the International Congress on the Chemistry of Cement, Vol. I, Rio de Janeiro.
- 3 Taylor, H.F.W., "*Cement Chemistry*", 2nd Edition, Thomas Telford Publishing, London, 1997, pp. 459.
- 4 Palmer, J.D. and Smith, D.L.G. 1986. The Incorporation of Low and Medium Level Radioactive Wastes (Solids and Liquids) in Cement, EUR 10561 EN, Commission of European Communities, Luxembourg.
- 5 De Angelis, G., Marchetti, A. and Balzamo, S. 1992. "*Leach Studies: Influence of Various Parameters on the Leachability of Cesium from Cemented BWR Evaporator Concentrates*", pp. 182-192 in Stabilisation and Solidification of Hazardous, Radioactive and Mixed Wastes, Vol. 2, STP 1123, ed. T.M. Gilliam and C.C. Wiles, American Society for Testing and Materials, Philadelphia.
- 6 " *Mitigation of delayed ettringite formation using class F fly ash or mix water conditioner* ", A M Amde, A Azzam, R A Livingston, 30th Conference on our world in concrete structures. 23 - 24 August 2005, Singapore.
- 7 Cement Solidification Method For Intermediate-Level Liquid Waste Containing Sodium Sulphate (Na_2SO_4), WM 2009, 9365.
- 8 Langton, C.A. 1989. "*Slag-Based Materials for Toxic Metals and Radioactive Waste Stabilisation*", 3rd Annual International Conference on the Use of Fly Ash, Slag and Silica Fume in Concrete, Trondheim, Norway, 1989.
- 9 Vejmelka, P. and Sambell, R.A.J. 1984. Characterisation of Low and Medium-Level Radioactive Waste Forms: Joint Annual Progress Report, 1982, EUR 9423 EN, Commission of European Communities, Luxembourg.
- 10 BS EN 196-3:2005 – Methods of Testing Cement – Determination of Setting Times and Soundness.
- 11 ASTM C191-07: Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle
- 12 BS EN 196-1:2005 – Methods of Testing Cement – Determination of Strength
- 13 ASTM C109/C109M-07: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)
- 14 BS EN 12504-4:2004 – Testing Concrete – Determination of Ultrasonic Pulse Velocity

15 ASTM C597: Standard Test Method for Pulse Velocity Through Concrete

16 ASTM C157/C157M-08 Standard test method for length change for hardened hydraulic cement paste, mortar and concrete.

17 ASTM C490/C490M-08 Standard practice for use of apparatus for the determination of length change in hardened cement paste, mortar and concrete.

18 ANSI/ANS-16.1-2003;R2008 (R=Reaffirmed): Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure.

19 NEN 7345:1995.nl; Leaching characteristics of solid earthy and stony building and waste materials - Leaching tests - Determination of the leaching of inorganic components from buildings and monolithic waste materials with the diffusion test.