

# EXPANSIVE FAILURE REACTIONS AND THEIR PREVENTION IN THE ENCAPSULATION OF PHENOL FORMALDEHYDE TYPE ION EXCHANGE RESINS IN CEMENT BASED SYSTEMS

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## ABSTRACT

Lewatit DN is a phenol formaldehyde based ion exchange resin used to remove radioactive caesium from liquid waste streams such as fuel cooling ponds and effluents. This paper presents the results of a study of the encapsulation of the bead form of the resin in cement with particular reference to the mechanisms of its interaction with the encapsulant. When incorporated in pure ordinary Portland cement (OPC) at loadings in excess of 15 wt% an unstable product results due to expansion of the system and at higher waste loadings failure results after only a few days. The resin beads swell on contact with the alkaline pH environment of the cement but this occurs too rapidly to be the cause of the expansive failure reaction. Increased production of ettringite can also be ruled out as the sulphate concentrations in the resin are too low. Blending the OPC with blast furnace slag (BFS) gives a satisfactory product up to 25 wt% loading and addition of sodium hydroxide to the mix water enables loading of up to 36 wt% to be employed. Evidence from differential scanning calorimetry, X-ray diffraction and scanning electron microscopy all indicate the cause of the expansive reaction to be the formation of crystals of calcium salts around and within the resin beads. Calcium hydroxide, calcium oxalate and calcium carbonate were observed. Addition of BFS and sodium hydroxide prevent the formation of these salts by removal of calcium hydroxide from the system in other reactions.

## INTRODUCTION

Ion exchange materials have been used since the earliest days of the nuclear industry for the control of levels of radioactivity in aqueous solutions. Typical applications include boron control in pressurized water reactors, polishing condenser water and activity control in fuel storage ponds and in liquid effluent discharges.

At the Magnox gas-cooled reactors operated in the UK by Nuclear Electric the principle contaminant in aqueous waste streams is caesium 137 and to control levels of this radioisotope the waste streams are treated using a phenol-formaldehyde ion exchange resin. This exchanger has high selectivity for caesium, an important consideration given that the solutions have a pH of ca 11 adjusted through the addition of sodium hydroxide.

The resins are not easily regenerated and when caesium 137 breakthrough begins to occur the resins are discharged to special radwaste accumulation facilities at the power station sites. Eventually the resins will be retrieved, encapsulated in cement and offered for disposal by deep land burial. The encapsulation of these resins has proved to be quite difficult for under certain circumstances an expansive failure reaction occurs. This paper describes work undertaken to identify a suitable cement formulation and to investigate the nature of the resin-cement interactions that occur.

## PHENOL FORMALDEHYDE RESINS: MANUFACTURE AND USE

Phenol formaldehyde resins were the first synthetic ion exchange materials to become commercially available (1).

They are prepared by a number of manufacturers and have been sold under various trade names including Amberlite 1 or 100, Duolite C3 and Lewatit DN. The material used for this work was Lewatit DN which has been used by power station operators in the UK. The resin has been supplied in two forms: Bead resin, prepared by suspending the monomers in water followed by heat treatment; or Granular resin, prepared by crushing solid blocks of polymeric phenol formaldehyde. These materials are then functionalized by treating with concentrated sulphuric acid. The bulk of the work described here has been undertaken with the bead form of the resin.

## CEMENT SYSTEMS USED

The cementitious materials used are those readily available in the UK, however, they have analogues in most countries. The main cementitious material used was Ordinary Portland Cement (OPC) (2) which is similar to Type I cement used in the USA (3). Blast Furnace Slag (BFS) (4) was also used primarily to control the cement chemistry and therefore increase the waste loading. These materials are widely used within the UK nuclear industry for the cementation of radioactive waste including inorganic ion exchangers and sludges (5, 6).

## WASTE LOADING

The waste loadings of ion exchange resin in cement systems can be expressed in a number of different ways. For the purposes of this work weight percent (wt%) of resin in the fully saturated drained form was used. Waste loadings of 30 wt% correspond to approximately 70 % by volume (taking

resin density to be 0.76) or a conditioning factor by volume of 1.4.

### PROPERTIES OF PHENOL FORMALDEHYDE RESINS

The physical properties of ion exchange resins have been extensively studied and Lewatit DN bead resin, in common with most resins, will change volume depending on its water content and the ions present. Experiments to determine the rate of expansion of Lewatit DN have shown that the expansion of the resin in unconstrained systems is complete after 2 hours when soaked in pore water (7) or alkaline solutions. Granular resin, however, as it is less porous can take up to 24 hours to reach its expanded state. This would indicate that bead resin has sufficient time to reach its fully expanded state before cement hydration commences but granular resin does not. As these resins are used to remove caesium from aqueous wastes the resins will almost certainly be in the fully expanded state near to the end of their useful life.

### CEMENT PRODUCT PROPERTIES

Experimental work by a number of groups (8) has shown that polystyrene resin systems cemented in neat OPC result in an unstable product due to expansion of the system. With phenol formaldehyde resins at waste loadings of 15 wt% the situation is similar with expansions of 0.2% to 0.4% after 90 days. Some systems investigated at higher waste loadings failed completely after only a 2 day period. If OPC is blended with BFS, waste loadings can be increased to 25 wt% before the product fails to hydrate correctly or is dimensionally unstable. Further improvements in the waste loading up to 36 wt% can be achieved by the addition of sodium hydroxide to the mix water prior to cementation (Table I).

### INVESTIGATION OF CEMENT PHASES

Differential scanning calorimetry was used to investigate the differences between various cement phases present in stable and unstable cement systems.

The traces for 15% Lewatit DN in OPC (Fig. 1) exhibited dehydration endotherms characteristic of the dehydration of several products of cement hydration. The endotherm at 94°C is due to  $AF_t$  and the peak developing at 170°C in later age samples is characteristic of  $AF_m$  phases, levels of which are much smaller than those observed in the 30% Lewatit DN in OPC system. These peaks both lie on a broad endotherm from ambient temperature to 250°C which is due to the C-S-H phase present. Calcium hydroxide is indicated by the double endotherm at 465 to 490°C. Levels of calcium hydroxide showed no trends with respect to age, being within the range 71 to 119 J g<sup>-1</sup>. Systems containing only OPC show similar traces except there is only a single peak at 465°C due to calcium hydroxide.

Samples taken from resin encapsulated in 9:1 BFS/OPC at a waste loading of 30 wt% containing 1.5 M sodium hydroxide in the mix water have endotherms due to C-S-H,  $AF_t$ ,  $AF_m$  and hydrotalcite phases but a total absence of calcium hydroxide. There is no evidence of sodium hydroxide endotherms at 296°C and 318°C. This is probably due to sodium hydroxide being removed when the sample is washed with propanol.

### ANALYSIS OF SYSTEM BY SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy of resin cemented in neat OPC showed hexagonal crystals up to 100 μm within the craters left by the resin beads (Fig. 2). Examination of the matrix revealed the presence of no unusual cement phases.

TABLE I

Summary of Mix Details and Product Evaluation Data for Cemented Lewatit DN

Reference No. Formulation	90/168 Neat OPC	89/100 BFS/OPC Blend	90/169 Lewatit Neat OPC	91/067 Lewatit BFS/OPC NaOH	90/155 Lewatit BFS/OPC Blend	90/212 Lewatit BFS/OPC NaOH
Wt% Composition						
Cement	68.8	76.9	58.5	58.0	51.5	50.6
Resin	0.0	0.0	15.0	15.0	30.0	30.0
Water	31.2	23.1	26.5	25.5	18.5	18.3
Sodium Hydroxide	0.0	0.0	0.0	1.5	0.0	1.1
Water/Cement Ratio	0.45	0.33	0.45	0.44	0.36	0.36
Compressive Strength (N mm <sup>-2</sup> )						
Days						
7	--	35.9	--	3.6	4.0	6.8
90	--	60.0	--	8.1	9.8	10.4
Dimensional Movement (Microstrain)						
Days						
7	-180	-420	+2000	-40	0	+220
90	-1030	-1100	+2020	+370	-250	+120

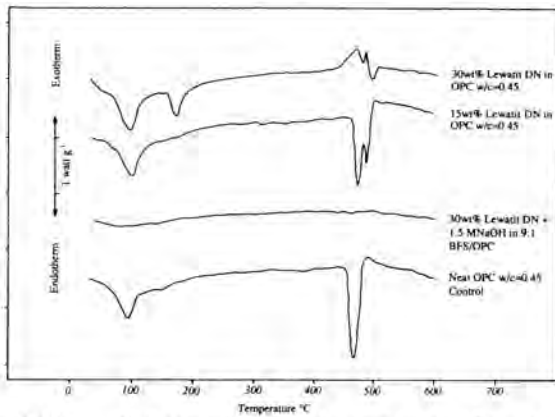


Fig. 1. Differential scanning calorimetry curves for cemented resin systems at 28 days.



Fig. 2. SEM micrograph of 30 wt% Lewatit DN in OPC w/c = 0.45 at 28 days, bead crater.

Indentations in the resin bead surface (Fig. 3) were also observed as well as crystal growth on the surface of the bead. Results from quantitative electron dispersion spectroscopy (EDS) show that the crystal formed in the bead craters and on the resin surface contain 40 to 50% calcium. These results suggest that these crystals are calcium hydroxide, in the case of the hexagonal plates, and other calcium salts including calcium hydroxide present on the resin surface. Sectioning the resin bead also revealed crystals growing within the bead which showed a calcium content of approximately 16 % by EDS analysis (Fig. 4). This figure is more indicative of the presence of calcium oxalate and carbonate rather than calcium hydroxide.

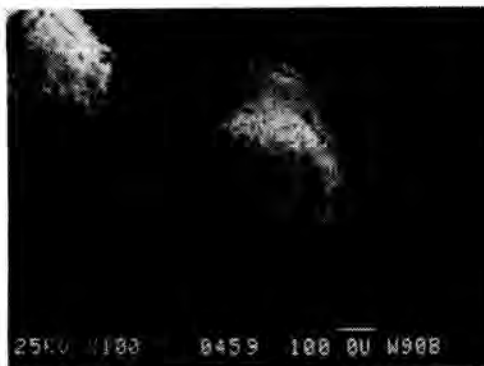


Fig. 3. SEM micrograph of 30 wt% Lewatit DN in OPC w/c = 0.45 at 28 days, resin bead.



Fig. 4. SEM micrograph of Split Lewatit DN resin bead removed from 15 wt% Lewatit DN in OPC w/c = 0.45 sample.

Scanning electron micrographs of samples prepared using 9:1 BFS/OPC with sodium hydroxide in the mix water gave a very different picture. There were no large crystals within the craters left by the resin beads and no crystals on the surface of the resin bead (Fig. 5).

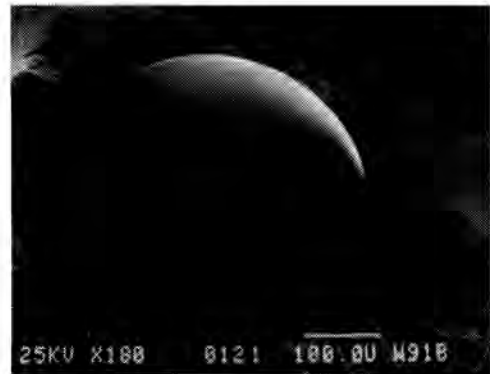


Fig. 5. SEM micrograph of 30 wt% Lewatit DN in 9:1 BFS/OPC w/c = 0.44 with 1.5 Molar NaOH at 120 days, resin bead.

#### POWDER X-RAY DIFFRACTION ANALYSIS

X-ray diffraction of cement samples removed from 28 day old specimens containing resin show the expected patterns for alite, brownmillerite, ettringite and calcium hydroxide. The main difference between resin treated OPC and an OPC control was the larger diffraction due to calcium hydroxide at  $2\theta = 18^\circ$ . Also present in the resin cement system was calcium oxalate. Investigations of systems containing 9:1 BFS/OPC showed the expected peaks associated with normal BFS/OPC hydration, however, only small quantities of calcium hydroxide were observed.

Resin particles cemented in OPC were also removed and examined by x-ray diffraction. The main crystalline material identified in the resin was calcium oxalate.

#### DISCUSSION

One theory of the cause of the expansions observed when immobilizing Lewatit DN in cement was that the resin expanded within the hardened cement paste as ion exchange occurred between species initially on the resin and those present in the cement pore water. This ion exchange does occur, but the results of the Lewatit DN expansion trials demonstrate that the physical and chemical changes in the

resin occur too rapidly for this to be the only mechanism for failure of the cement system. Since the resin will probably be in a flooded form prior to encapsulation, the worst case for expansion is that of resin soaked in 1.5 molar sodium hydroxide. Even in this case, the observed expansion is complete within one hour which is far quicker than cement setting occurs.

This would not appear to be true in the case of granular resin as it takes at least 24 hours to adjust.

Investigation of the dimensional stability of phenol formaldehyde resin beads cemented in neat OPC have demonstrated that an expansive reaction occurs as observed with polystyrene resins (8). This expansion can be controlled and eliminated for phenol formaldehyde resins by using OPC blended with BFS or by the addition of sodium hydroxide to the mix water prior to cementation in OPC/BFS blends. With waste loadings of 25 wt % containing blended OPC/BFS systems if sodium hydroxide is added to the mix water the waste loading can be increased to 36 wt %. The limit on the waste loading results from the product failing to set after 24 hours.

Physical analysis of the cement system has shown that the addition of BFS to OPC reduces the formation of calcium crystals at the cement resin interface. These crystals have been identified by powder x-ray diffraction and scanning electron microscopy as consisting mainly of calcium hydroxide. Calcium oxalate and calcium carbonate have also been identified on the surface and within the resin bead.

These observations suggest a mechanism for destructive expansion of the cemented Lewatit DN systems is due to the formation of crystals of calcium salts. One would normally expect calcium hydroxide deposition at cement-aggregate interfaces (9), but in the case of the Lewatit DN system this is clearly enhanced. When the resin is placed into the cement system, ion exchange occurs between sodium initially on the resin and potassium and calcium formed by dissolution of free calcium oxide in the OPC. Exchange will also occur between the proton on the phenol group and  $\text{Ca}^{2+}$  due to the phenolic group acting as a weak acid ion exchanger at high pH. This exchange results in high localized calcium concentrations both at the cement-resin interface and within the resin bead itself. As the solution becomes saturated, calcium hydroxide crystals form at the cement-resin interface and calcium oxalate and carbonate crystals form within the resin bead pores. The oxalate and carbonate ions are presently thought to come from degradation of the resin beads at high pH. As these crystals grow in size and fill the space initially available to them they exert a pressure on the cement matrix. It is this pressure which causes the expansion of the matrix which has been observed.

This proposed mechanism is in agreement with the reduced expansion observed when lowering OPC concentration in the cement blend by dilution with BFS. The initial products of OPC hydration are C-S-H and calcium hydroxide. Hydration of BFS consumes calcium hydroxide to form more C-S-H phase, thus the inclusion of BFS in the cement blend not only reduces the calcium hydroxide initially produced, but also removes calcium hydroxide from the system. The effect of this is to reduce the availability of calcium ions which can exchange on the resin bead and thereby also reduces the amount of crystals formed which have the deleterious effect on the cement system.

A further measure to reduce expansion in the cemented Lewatit DN system is the use of sodium hydroxide in the mix water. Sodium hydroxide is a known accelerator of BFS hydration. This has been confirmed by DSC analysis demonstrating the enhanced removal of calcium hydroxide from the system by BFS. Both DSC and SEM analysis of a 30% Lewatit DN in 9:1 BFS/OPC, w/c = 0.36 with mix water containing 1.5M sodium hydroxide have demonstrated the absence of calcium hydroxide from the system. SEM has shown the beads and resin crater to be clean and smooth. This is a stable system and confirms that the removal of calcium hydroxide solves the problem of expansion.

## CONCLUSIONS

1. The physical and chemical changes which occur in bead form Lewatit DN resin during ion exchange occur too rapidly for this to be the only mechanism for failure of the cement system.
2. The extent of expansion of cemented Lewatit DN is reduced by reduction of OPC concentration by dilution with BFS.
3. Sulphate concentrations in the solution contained within the Lewatit DN are not sufficient to increase ettringite production in the cement system to cause expansion.
4. DSC, XRD and SEM analyses all indicate the cause of expansion to be the formation of crystals of calcium salts around and within the Lewatit DN resin beads in cement systems.
5. The proposed mechanism for expansion is ion exchange between sodium initially on the resin bead and calcium produced by cement hydration which results in increased localized calcium concentrations in and around the Lewatit DN resin. As the solutions become saturated, the growth of crystals of calcium salts results in expansion of the matrix.
6. Expansion can be reduced by using 9:1 BFS/OPC and 1.5M sodium hydroxide in the mix water to remove calcium hydroxide from the system via consumption by BFS.

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