Development of the Use of Alternative Cements for the Treatment of Intermediate Level Waste.

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ABSTRACT

This paper describes initial development studies undertaken to investigate the potential use of alternative, non ordinary Portland cement (OPC) based encapsulation matrices to treat historic legacy wastes within the UK's Intermediate Level Waste (ILW) inventory. Currently these wastes are encapsulated in composite OPC cement systems based on high replacement with blast furnace slag of pulverised fuel ash. However, the high alkalinity of these cements can lead to high corrosion rates with reactive metals found in some wastes releasing hydrogen and forming expansive corrosion products. This paper therefore details preliminary results from studies on two commercial products, calcium sulfoaluminate (CSA) and magnesium phosphate (MP) cement which react with a different hydration chemistry, and which may allow wastes containing these metals to be encapsulated with lower reactivity. The results indicate that grouts can be formulated from both cements over a range of water contents and reactant ratios that have significantly improved fluidity in comparison to typical OPC cements. All designed mixes set in 24 hours with zero bleed and the pH values in the plastic state were in the range 10-11 for CSA and 5-7 for MP cements. In addition, a marked reduction in aluminium corrosion rate has been observed in both types of cements compared to a composite OPC system. These results therefore provide encouragement that both cement types can provide a possible alternative to OPC in the immobilisation of reactive wastes, however further investigation is needed.

INTRODUCTION

Composite cementing systems containing high replacement levels of ordinary Portland cement (OPC) with blast furnace slag (BFS) or pulverised fuel ash (PFA) is currently the dominant technical solution for the treatment of low and intermediate level (L/ILW) radioactive wastes in the UK. These composite systems offer several advantages over OPC alone, including lower heats of hydration, reduced permeability and greater long term durability. However, despite these advantages, significant quantities of historic legacy wastes within the UK are known to be heterogeneous, and comprise of reactive metals such as aluminium, Magnox and uranium. The relatively high internal pH of OPC based composite cements, coupled with a relatively high free water content within the hardened matrix structure, leads to corrosion of such metals when immobilised in cement with the generation of hydrogen gas and the formation of expansive corrosion products. This process can result in possible cracking of the cemented wasteform and

could ultimately place a restriction on product lifetimes. This factor is likely to become more onerous as the timescales for demonstrating stable product properties are likely to increase over those originally envisaged for cemented ILW wasteforms. As a result, alternative cement systems are under investigation to provide innovative solutions for the treatment of reactive metal containing historic wastes which may yield wasteforms with superior longer term properties than those currently deployed for ILW encapsulation. Two such systems are magnesium phosphate (MP) and calcium sulfoaluminate (CSA) cements, which offer potential advantages over OPC based cements regarding reactive metal encapsulation in terms of their lower internal pore solution pH, and a potentially higher water binding capability.

This paper therefore outlines preliminary work and presents initial results on both CSA and MP systems covering 2 areas of study; namely:
- Processing characteristics
- Initial corrosion studies incorporating aluminium metal

REACTIVE METAL REACTIONS IN GROUT

Aluminium is a reactive amphoteric metal, readily forming a protective oxide layer on contact with air or water. This layer is generally regarded as stable in the pH range 4.5 - 8.5 [1]. However, in strong alkali, such as that encountered in conventional OPC grouts, this layer is soluble resulting in continued corrosion with associated liberation of hydrogen and subsequent formation of expansive metal hydroxides, in addition to calcium based aluminosilicate hydrates [2]. Additionally, corrosion of other reactive metals, such as Magnox and uranium, also occurs due to a combination of the internal pH (primarily affecting Magnox corrosion rates) and the availability of free water within the pore structure of the system. As a result, alternative cementitious systems with differing internal pH or water binding capability may reduce corrosion rates, improve wasteform product quality, enhance waste loadings and simplify safety issues during processing and storage.
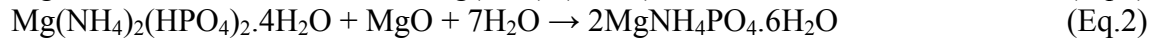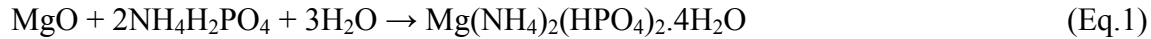
MAGNESIUM PHOSPHATE CEMENTS

Magnesium-phosphate cements have been used industrially for over 60 years in the casting of alloys and as dental cements, however it is only in the last 20-30 years that they have been considered with respect to producing materials suitable for repairing runways, roads and other industrial flooring applications where early high strength and rapid setting is required [3]. Commercially, MP cements are available as pre-mixed dry powders which just require the addition of water, although powdered admixtures are often added to accelerate or, more usually retard cement set depending upon the conditions in which they are required.

MAGNESIUM PHOSPHATE CEMENT REACTION

The principal reaction upon which typical commercial MP cements are based involves magnesium oxide reacting with ammonium dihydrogen phosphate in the presence of water. This reaction yields schertelite $Mg(NH_4)_2(HPO_4)_2.4H_2O$ (Equation 1) and struvite $MgNH_4PO_4.6H_2O$ (Equation 2) as the main reaction products, though other crystalline species such as dittmarite, $MgNH_4PO_4.H_2O$ have been found in small amounts [3].

It has been agreed by many workers [3] that during the reaction the crystalline tetrahydrate, schertelite, is formed first and hydrated further to the hexahydrate struvite, but only if sufficient water is present, (Equation 3).

$$MgO + 2NH_4H_2PO_4 + 3H_2O \rightarrow Mg(NH_4)_2(HPO_4)_2.4H_2O \qquad (Eq.1)$$
$$Mg(NH_4)_2(HPO_4)_2.4H_2O + MgO + 7H_2O \rightarrow 2MgNH_4PO_4.6H_2O \qquad (Eq.2)$$

Overall reaction:

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad (Eq.3)$$
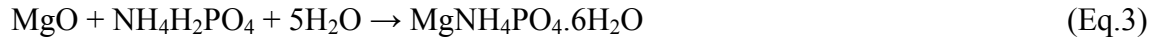
Whilst the above reaction utilises the ammonium salt, a common alternative is to use the potassium or sodium dihydrogen phosphate salt to give the alkali metal analogue of struvite as follows:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow KMgPO_4.6H_2O \qquad (Eq.4)$$

The MP cements produced have a significantly reduced internal pH compared to conventional OPC cements. In addition, the formation of struvite, or analogues, results in the chemical binding of a greater proportion of mix water than that which occurs during OPC hydration and therefore potentially reduces its availability to support ongoing metal corrosion reactions. From equations 3 and 4 it can be observed that the stoichiometry of the reaction is 1:1 with regards magnesium to phosphate ratio, however commercial cements tend to be based on ratios closer to 4:1, which serve to reduce setting times down to approximately 20 minutes.

CALCIUM SULFOALUMINATE CEMENTS

Calcium sulfoaluminate (CSA) cements were developed in the 1970's by calcining natural materials such as limestone, bauxite and clay together with a sulfate source such as gypsum or anhydrite at $1250 \sim 1350^o$C, in a composition which produces calcium sulfoaluminate, or yeelimite, ($3CaO.3Al_2O_3.CaSO_4$ denoted as $C_4A_3S''*$) as the principal reactive component. The CSA manufacturing process also results in significantly reduced CO_2 emissions in comparison to the OPC manufacturing process (approximately 40% reduction) due to a reduction in limestone utilisation, and various types are available, depending on their intended use. They have been extensively used in civil engineering projects in China [4] [5], although the reactivity of these cements is typically lower than the UK source used in this study, which has primarily been produced for the production of rapid setting cements.

The hydration of CSA cement occurs along a number of reaction paths depending on the components present [6]. Principally yeelimite reacts with gypsum or anhydrous calcium sulfate in the presence of water to form ettringite ($C_6A S''_3H_{32}$) and alumina gel:

$$C_4A_3S'' + 2CS''H_2 + 34H \longrightarrow C_6AS''_3H_{32} + 2AH_3 \qquad (Eq.5)$$
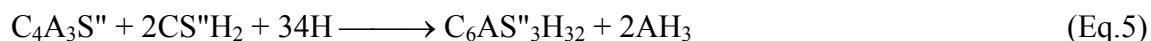
If reduced quantities of sulphate are present, monosulphate ($C_4A S''H_{12}$) is also produced:

$$2C_4A_3S'' + 2CS''H_2 + 52H \longrightarrow C_6AS''_3H_{32} + C_4AS''H_{12} + 4AH_3 \qquad \text{(Eq.6)}$$
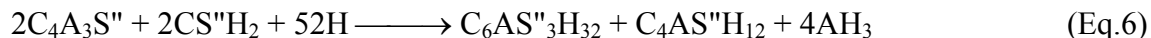
*Cement Nomenclature used above:
$C=CaO$, $S=SiO_2$, $A=Al_2O3$, $S''=SO_3$, $H=H_2O$

From equations 5 and 6 it can be observed that the main hydration product formed from hydration is ettringite with alumina gel co-existing, if the cement is correctly formulated. Due to the high associated chemically bound water content of ettringite, CSA cements also provide a potentially high water binding capability, which may serve to limit long term reactive metal corrosion rates. Several studies [7] [8] have also shown that ettringite can act as host to a number of ions in its crystal structure with substitution at the calcium, aluminium, hydroxide and sulphate sites. This property, together with its low pH (unlike OPC $Ca(OH)_2$ is not formed during the hydration reaction) means that CSA cement could also offer a potential advantageous alternative to OPC for waste immobilization applications.

PROCESSING CHARACTERISTICS

Both commercial MP and CSA cements are typically designed to react rapidly. However, for waste encapsulation applications it is generally essential for the grout to remain fluid for 2-2.5 hours in order to ensure adequate infilling of wastes, which are often complex in shape, and hence minimise overall voidage in the resultant wasteform. A further desired criteria is to minimise the hydration exotherm from the cement curing reactions as excessive temperatures ($>100^oC$) could result in steam pressurisation of the wasteform and hence compromise final product quality. As a result small scale mixing trials have been conducted on both MP and CSA cements to assess the flow, set, bleed (residual liquor on top of the cement after set) pH in the plastic state, and temperature rises during mixing with changing reactant ratios and water/solid ratios. This latter factor is important for ILW encapsulation processes since for plant operations it is necessary to demonstrate that a grout meets the required processing criteria over a range of formulations such that an operating envelope can be developed.

Magnesium Phosphate Cement Flow Studies

A series of small scale (3 litre) mixes have been undertaken using two separate batches of dead burned magnesia (DBM) (MgO) obtained 1 year apart (batch 1 received in 2005, batch 2 in 2006) of particle size DBM 60 mesh. Typical chemical and physical characteristics for the MgO are shown in table I:

Table I. Product Specification for DBM 60 MgO

Chemical composition	%
MgO	98.5
CaO	0.74
Fe_2O_3	0.44
Particle Size Distribution	**Typical**
>0.250 mm	4 %
<0.063 mm	60 %

<0.032 mm	36 %

This material was mixed with standard laboratory grade potassium dihydrogen phosphate and boric acid, whilst the PFA was a commercial grade powder conforming to British Nuclear Group Sellafield Limited (BNGSL) specifications. The reagents were mixed in the following proportions:

- 1.25:1 molar ratio $MgO:KH_2PO_4$, + 50 wt % PFA and 2 wt% boric acid based on total weight of reactive mix components ($MgO + KH_2PO_4 + H_2O$)
- 1.5:1 molar ratio $MgO:KH_2PO_4$, 50 wt % PFA and 2 wt% boric acid

The molar ratios of $MgO: KH_2PO_4$ were chosen based on equation 4, with the addition of PFA and boric acid deemed necessary to both retard the cement set and potentially reduce the heat of hydration, with PFA acting as a filler in the mix design. Initial scoping studies showed that adding water at a ratio of 5 moles to 1 mole of KH_2PO_4 (eq.4) gave insufficient workability due to the additional solid PFA component, and therefore an additional 0.5 moles of water was added to give an overall water/solids ratio of 0.30 based on total powder weight. A further water/solids ratio of 0.32 was also investigated for both molar ratios studied.

In addition to the formulated mixes described, two batches of a commercial pre-blended MP cement were also tested. This is denoted as FEBLAB 1846 (ordered in 2005) and DEVLAB 1846 (ordered in 2006). These materials are based on the ammonium phosphate salt, and contained a proprietary retarder (borax) at 0.66 wt% in the mix blend. These materials were tested at 0.2 and 0.22 water/solids ratio, under recommendations from the manufacturer.

All powder components were weighed and added to chilled water (3-8°C) in a 3-litre standard Hobart mixing bowl at room temperature in the order, boric acid, PFA, MgO and finally KH_2PO_4. After mixing for 10 minutes, the mix was then subjected to 10 minutes high shear at 4000 revolutions per minute to simulate higher shear large scale plant mixers and, at this point (denoted as T=0 minutes) fluidity measured using a standard Colflow apparatus. This piece of equipment measures the distance that 1 litre of slurry will flow in a confined channel under gravity. The pH and temperature of the grout was measured simultaneously using a combined pH/temperature probe and measurements were repeated at 30 minute intervals up to a maximum of 150 minutes. Bleed volumes were measured by sealing the grout in a 100ml measuring cylinder and measuring the amount collected on the surface after curing for 24 hours at 20°C and >95% relative humidity. This is an important parameter because bleed liquor, if not reabsorbed, forms a secondary radioactive waste that must then be treated. Finally, initial and final set were measured according to ASTM C191 Revision A and BSEN 196-3:1995 respectively.

Results

The results of the 3 litre trials for both 1.25:1 $MgO: KH_2PO_4$ and 1.5:1 $MgO: KH_2PO_4$ molar ratios are shown in tables II and III. The results for a conventional encapsulation reference grout of 3:1 BFS/OPC at a 0.35 water/solids ratio is also given for comparison:

Table II. 1.25:1 MgO: KH_2PO_4 mix results incorporating 1532g KH_2PO_4, 50 wt% PFA (1500g) and 2 wt% boric acid (60g)

	Components				Colflow					pH	Temp (oC)	Set (hrs)	
Batch	MgO:PO$_4$	w/s ratio	MgO (g)	Water (g)	0 min	30 min	60 min	120 min	150 min			ini tial	final
1	1.25:1	0.30	567	1100	1000	1000	1000	1000	1000	5.3-6.4	10-25	6	<24
1	1.25:1	0.32	567	1165	1000	1000	1000	1000		5.4-6.3	13-21	5.5	<24
2	1.25:1	0.30	567	1100	1000	1000	1000	1000	1000	5-5.5	13-19	10	<24
2	1.25:1	0.32	567	1165	1000	1000	1000	1000	1000	5-5.6	13-17	10	<24
BFS/ OPC	**3:1**	**0.35**			**440**				**270**	**12.8**		**3.5**	**<24**

Zero bleed was measured for all mixes.

Table III. 1.5:1 MgO: KH_2PO_4 mix results incorporating 1532g KH_2PO_4, 50 wt% PFA (1500g) and 2 wt% boric acid (60g)

	Components				Colflow					pH	Temp (oC)	Set (hrs)	
Batch	MgO:PO$_4$	w/s ratio	MgO (g)	Water (g)	0 min	30 min	60 min	120 min	150 min			ini tial	final
1	1.5:1	0.30	681	1130	1000	1000	880	820	820	5.4-6.4	10-31	3	<24
1	1.5:1	0.32	681	1165	1000	1000	1000		1000	4.9-6.5	10-21	4.5	<24
2	1.5:1	0.30	681	1130	1000	1000	1000	1000	1000	5.4-5.8	13-22	8	<24
2	1.5:1	0.32	681	1165	1000	1000	1000	1000	1000	5.7-6.1	12-21	10	<24

Zero bleed was measured for all mixes.

Results for 3 litre trials using commercial MP cement are shown in table IV:

Table IV. Mix results for commercial MP cements at 3 litre scale

	Components				Colflow					pH	Temp (oC)	Set (hrs)	
Name	Powder (Kg)	w/s ratio	Borax (g)	Water (g)	0 min	30 min	60 min	120 min	150 min			ini tial	final
Feblab 1846	3	0.20	19.8	600	960		420	0		6.3-6.4	17-23	3.	<24
Devlab 1846	3	0.20	19.8	600	1000		720	860		6.4-6.9	20-21	3	<24
Devlab 1846	4.5	0.22	29.7	1000	1000	1000	950	860	830	5.5-6.4	15-20	4	<24

Zero bleed was measured for all mixes.

Conclusions from MP Flow studies

The results of the trials indicate that all MP formulations tested produced grouts with significantly higher flow properties than those obtained with conventional BFS/OPC grouts, all of which set within 24 hours with zero bleed. The measured pH of the system is significantly lower than that obtained with the BFS/OPC system (lying in the stability range for aluminium) and whilst mix temperatures rose during mixing, this appears not to be onerous at this stage of testing. However, due to the potentially large volumes of cement used in nuclear waste encapsulation, subsequent testing of hydration exotherms will be required, although the introduction of PFA is anticipated to lower such hydration temperatures.

In terms of the commercial grouts, older batches of MgO appeared to have enhanced reactivity, and hence reduced fluidity, compared to newer batches at the water contents tested, which may be a result of partial hydrolysis of MgO in storage forming $Mg(OH)_2$, although further studies will be required to confirm this hypothesis. Hence the effect of storage time on grout mixing properties will need to be assessed further. With respect to formulated grouts, systems at 1.5:1 molar ratio appeared to react marginally faster than the 1.25:1 mixes, which could be anticipated from increasing the availability of magnesia to support the reaction scheme depicted in eq.4, although as noted, all flows were considerably above those for current grouts and, at this stage, no attempt has been made to optimise the grout formulation or reactant specifications.

However perhaps the most important aspect regarding the long term product quality of encapsulated reactive metals from these initial trials is that the high fluidities measured have been achieved at very low water contents with respect to commercial MP products, or at water contents that approximate to the required molar ratios to form the alkali metal analogue of struvite in the formulated products. As a result it could be anticipated that the mix water may rapidly become chemically bound in the system and hence may not be available to support longer term corrosion. This assumption needs to be tested in future work.

Calcium Sulfoaluminate Flow Studies

A series of 3 litre mixes have been undertaken in which a commercial CSA cement, Rockfast 450, supplied by Lafarge Cement UK, has been blended with different proportions of gypsum to activate the cement according to the reaction schemes outlined previously. PFA has also been added to selected mixes at varying water/solid ratios and fluidity, bleed, internal pH, temperature rise during mixing and set time measured as described for MP cements. The Rockfast had a specific surface area of 450 m^2/kg, and the compound composition is shown in table V:

Table V. Phase Composition of Rockfast CSA

Cement Phase	Compound composition (wt%)
C_4A_3S''	58
CA	17
C_2AS	16
C_4AF^*	4
CT^*	4
$C_{12}A_7$	1

* $F=Fe_2O_3$, $T=TiO_2$

Gypsum was supplied by Albion chemicals, had a chemical assay of 98% and a particle size distribution of 86% <75 µm. PFA was a commercial grade powder conforming to BNGSL specifications.

Based on theoretical calculations, 36 wt% gypsum is required at a w/s ratio of 0.54 to ensure complete hydration of the clinker to produce ettringite and alumina gel according to equation 5. This is the desirable product for metal encapsulation as the crystal structure of ettringite contains 32 molecules of water and, as a result, a large amount of mix water will be chemically bound within the cement hydrate structure. However, meeting this ideal condition may not give ideal grout properties in terms of flow or sufficient working times. As a result various ratios of Rockfast and gypsum were mixed at w/s ratios around and above the theoretical value. In selected mixes 25wt % PFA (based as a percentage of the total powder weight including PFA) was also added and the effect on fluidity tested. This was assessed as there may be a requirement to reduce hydration temperatures of CSA cements when used for full scale encapsulation processes.

Weighed amounts of the component powders were added to chilled water (3-8°C) in a standard 3 litre Hobart mixing bowl at room temperature and subsequent mixing and testing was undertaken as outlined for MP cements. Results of the trials are shown in table VI:

Table VI. Mix results for 3 litre CSA cement studies

Component % by mass			w/s ratio	Colflow					pH	Temp (°C)	Set (hrs)	
CSA	Gypsum	PFA		0 min	30 min	60 min	90 min	120 min			initial	final
60	40		0.55	1230	1260	880	790	n.m	10.8-11.2	12-14	6	8
60	40		0.58	1360	1200	990	780	700	10.6-11	11-18	n.m	n.m
60	40		0.65	1360	1360	1250	940	900	10.5-10.9	12-15	6.5	7.5
70	30		0.60	1360	n.m	1080	1120	820	10.2-10.9	13-16	3	4
70	30		0.65	1360	1360	1330	1000	830	10.6-10.8	11-15	3	4
80	20		0.60	1360	1260	1010	770	580	10.5-10.8	10-18	n.m	n.m
80	20		0.65	1360	1360	1360	980	n.m	10.2-10.5	11-13	n.m	<24
45	30	25	0.50	1360	1080	890	770	600	9.5-10.8	11-17	n.m	n.m
45	30	25	0.60	1360	1360	1250	1120	1010	9.9-10.9	11-18	2.5	4
52.5	22.5	25	0.50	1360	1260	920	860	730	9.3-11.1	10-14	2	3
60	15	25	0.50	1360	n.m	960	800	680	9.4-11.1	9-14	n.m	n.m

n.m. = not measured
Zero bleed was measured for all mixes

Conclusions from Calcium Sulfoaluminate Cement flow Studies

The results show that all CSA cement formulations tested produced grouts of significantly higher fluidity than those obtained for the BFS/OPC reference grout, which was generally maintained over a two hour mixing period. All mixes set within 24 hours with zero bleed and displayed a short time period between initial and final set, indicating that once the main hydration reaction is initiated it goes to completion rapidly. However this process appeared not to start for a minimum of two hours after completion of mixing. Increasing water content improved fluidity as expected, whilst altering the CSA to gypsum ratios appeared to have a relatively insignificant effect on flow over the range of water contents tested, although there may be an indication of reduced flow with decreasing gypsum content in going from 70:30 to 80:20 % at 0.60 water/solids ratio. The addition of PFA produced highly fluid mixes over the CSA:gypsum ratios tested and at water contents below the theoretical value required for complete hydration and reaction of the Rockfast clinker. The temperature rise during mixing was between 2 and $8^{o}C$ and the pH of the mixes in the plastic state were around 10.5 – 11, although mixes containing PFA tended to start with a pH value below 10 and rise to approximately 11 by the end of the mix period, possibly arising from the release of silicates in solution. These values are about 2 units lower than the conventional BFS/OPC system and, as such, much closer to the pH stability range for aluminium metal waste types.

These results therefore show that by controlling sulfate and water content, CSA systems can be formulated to produce grouts of significantly higher fluidity than OPC based systems, which subsequently hydrate rapidly to give set, bleed free products over a relatively wide range of water contents. The fact that such high water contents are required to completely hydrate the CSA clinker, hence producing high fluidities, which subsequently becomes quickly bound in the cement hydrate structure could yield significant advantages in the use of this cement for waste encapsulation processes. The temperature rise during hydration for the formulations studied tended to be higher than those observed for OPC cements, although, at present, no attempt has been made to optimise formulations or powder specifications to reduce this factor.

CORROSION STUDIES INCORPORATING ALUMINIUM METAL

The processing studies have indicated that highly fluid MP and CSA grouts can be produced with pH values in the plastic state lying within, or close to, the anticipated pH stability range for aluminium metal. In order to gain an assessment of the corrosion behaviour of aluminium (and hydrogen generation rate) in both systems, 7 small scale corrosion trials have been undertaken on formulations based on, or around, those used to assess the processing characteristics of both cements. The trials were undertaken at $25^{o}C$ over a 40 day time period, using the following cement formulations:

- 60:40 wt% CSA / gypsum ratio at 0.60 w/s, denoted as CSA1
- 70:30 wt% CSA / gypsum ratio + 25 wt% PFA at 0.65 w/s, denoted as CSA2
- 70:30 wt% CSA / gypsum ratio at 0.65 w/s, denoted as CSA3
- 60:40 wt% CSA / gypsum ratio + 25 wt% PFA at 0.65 w/s, denoted as CSA4
- 1.25:1 $MgO:KH_2PO_4$ + 50 wt% PFA and 2 wt% boric acid at 0.32 w/s

- 1.5:1 MgO:KH$_2$PO$_4$ + 50 wt% PFA and 2 wt% boric acid at 0.31 w/s
- Feblab 1846 at 0.20 w/s

All mix ratios were as defined for the respective cements in the processing studies and all reagents used were as previously described.

Procedure

Each of the 7 trials was undertaken in a 12.5 litre stainless steel reaction vessel has shown in fig. 1.

Fig. 1. Stainless steel reaction vessel with pressure transducer, thermometer & heating jacket

Each vessel was loaded with 54 aluminium coupons (dimensions 90mm x 50mm x 1mm) of grade 1050 to give a total surface area of 0.5m,^{2} the coupons being twisted prior to placement to avoid obscuration of metal surfaces. Each encapsulant was then mixed in a standard 25 litre Hobart mixer for 20 minutes prior to pouring over the aluminium coupons to leave an ullage volume of approximately 3 – 3.5 litres. Samples of each encapsulant were taken to obtain set

density data, which allowed accurate calculation of the ullage volume in each vessel when combined with knowledge of the reactor vessel internal volume, S.G. and weight of aluminium and weight of each encapsulant added. After fitting the lid, the vessels were gas leak tested and then transferred to a cure facility at 25^oC and wrapped in individual heating jackets set at this temperature to ensure good temperature control.

The corrosion rate was then monitored by measuring the increase in pressure as a result of the corrosion reaction, and temperature of the ullage volume, over time and applying the gas law to calculate the number of moles of gas (n) present in that volume, at the particular temperature measured:

$$PV = nRT \hspace{5cm} (Eq.7)$$
Where
P= measured pressure, V=ullage volume, R=gas constant, T=ullage temperature

The number of moles of gas generated can also be converted into weight of aluminium corroded, based on the reaction:
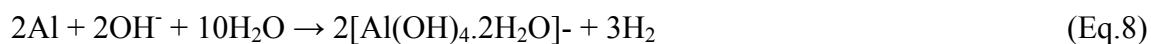
$$2Al + 2OH^- + 10H_2O \rightarrow 2[Al(OH)_4.2H_2O]- + 3H_2 \hspace{2cm} (Eq.8)$$
Using this principle, either the number of moles or litres of hydrogen evolved or weight of aluminium metal corroded can be plotted against time. The data can therefore be expressed as grams metal corroded per m^2 per day $(g/m^2/day)$ or as litres of hydrogen evolved per m^2 per hour $(l/hr/m^2)$.

Results of Corrosion Studies

The results of the aluminium corrosion trials for the CSA cement formulations are shown in table VII, alongside previously recorded data for a BFS/OPC grout for purpose of comparison:

Table VII. Aluminium corrosion rates in CSA cement formulations

Trial	Peak Rate first 24 hours $g/m^2/day$	Peak Rate first 24 hours $l/hr/m^2$	Rate at 24 hours $g/m^2/day$	Rate at 24 hours $l/hr/m^2$	Rate at 4 days $g/m^2/day$	Rate at 4 days $l/hr/m^2$	Rate at 40 days $g/m^2/day$	Rate at 40 days $l/hr/m^2$
CSA 1	3.9	0.22	0.18	0.010	0.003	0.0002		n.d
CSA 2	5.3	0.30	0.26	0.015	0.146	0.008	0.049	0.0028
CSA 3	1.8	0.1	0.17	0.01	0.040	0.0023		n.d
CSA 4	6.6	0.37	0.13	0.008	0.035	0.002		n.d
9:1 BFS/OPC, 0.33 w/s*	**96.5**	**5.8**	**13.5**	**0.81**	**1.66**	**0.1**	**n.m.**	

* Trial undertaken at 40^oC
n.m = not measured, n.d = no pressure increase detected

Results of the measured corrosion rates in MP cements are shown in table VIII.

Table VIII. Aluminium corrosion rates in MP cement formulations

Trial	Peak Rate first 24 hours $g/m^2/day$	Peak Rate first 24 hours $l/hr/m^2$	Rate at 24 hours $g/m^2/day$	Rate at 24 hours $l/hr/m^2$	Rate at 4 days $g/m^2/day$	Rate at 4 days $l/hr/m^2$	Rate at 40 days $g/m^2/day$	Rate at 40 days $l/hr/m^2$
Feblab 1846	0.32	0.02	0.32	0.02		n.d		n.d
Mg:PO$_4$ 1.25:1	0.55	0.03	0.50	0.03	0.01	0.0006	0.	n.d
Mg:PO$_4$ 1.5:1	0.82	0.05	0.47	0.03	0.004	0.0003		n.d
9:1 BFS/OPC, 0.33 w/s*	**96.5**	**5.8**	**13.5**	**0.81**	**1.66**	**0.1**	**n.m.**	

* Trial undertaken at 40°C
n.m = not measured, n.d = no pressure increase detected

These preliminary studies therefore show that aluminium corrosion rates in both cement systems are significantly reduced in comparison to OPC based grouts, even allowing for the fact that the experiments were conducted at a lower temperature than previous studies using BFS/OPC cements.

In trials conducted on CSA cements, some initial corrosion was detected in the first 24 hours, although the technique employed can lead to errors in measurement during this period as a result of changing ullage volumes and temperature fluctuations as the grout hydrates. Following this initial period, rates subsequently fell to very low levels with, in the case of CSA1, 3 and 4 formulations, little corrosion detected after 4 days. The trial incorporating the CSA 2 formulation did exhibit the highest degree of corrosion of all alternative cement systems tested, however the rate in this trial was still significantly lower than the reference grout system. The results obtained for the CSA systems are not unexpected, in that the formulations contain a relatively high amount of mix water at an initial pH of ~11, outside the known stability range of aluminium [1], and therefore some initial corrosion is to be expected. Subsequently, the binding of a large amount of water into the ettringite structure is likely to lead to self-dessication of the system, lowering the internal humidity and hence reducing ongoing corrosion. In addition, unlike OPC cements, calcium hydroxide is not a hydration product of CSA cement (equations 5 and 6) and so the pore solution pH is lower than in the OPC system, which may result in the metal becoming protected by an aluminium hydroxide layer with a concomitant expected reduction in corrosion rate. Further studies will be required to confirm this hypothesis.

In terms of comparing the extent of corrosion obtained in each CSA system over the first 40 days, the lowest was observed in CSA 1, which also had the lowest water and highest sulphate content of the systems studied, and therefore would be expected to have both the lowest amount of water available to support corrosion and also the potential to form a greater proportion of ettringite as the principal hydration product, binding a greater quantity of water chemically within the hydrate structure. Although the data reported covers only 40 days, these samples have subsequently exhibited very little gas evolution indicating that the very low corrosion rates have been maintained. At present, it is unclear whether it is the low internal relative humidity or

lowered pH (or combination of both) that is leading to the observed reduced rates, and the role of sulfate in the corrosion mechanism also requires investigation. However, these observations are very encouraging, consistent with other work [6], and warrant further study.

The results of the corrosion trials for MP cements also indicate that little corrosion had taken place over the duration of the test period. As described for the CSA trials, there are potential errors in the measurement of the initial peak corrosion rate using the pressure transducer technique, but each of the vessels required very little venting over the test period suggesting that aluminium corrosion within this system was highly limited. This again could be anticipated from the much lower internal pore solution pH of each system, combined with the hydration products formed binding a significant proportion of the associated mix water. As in the case of CSA cements, further studies will be required to elucidate the corrosion mechanism and hence assess the contribution of these factors to the low corrosion rates observed. In addition further work will also be required to assess the corrosion behaviour of other reactive metals in these cements, and assess if the higher water binding capability can reduce their corrosion rates.

CONCLUSIONS

Calcium sulfoaluminate and magnesium phosphate cements are relatively new cement systems that offer a different hydration chemistry to conventional OPC cements. The internal pore solution of both cements is low and the main hydration products, ettringite or struvite (or analogue) bind a significant proportion of the mix water. These properties make them potential candidates for the immobilisation of intermediate level wastes containing reactive metals.

The preliminary results from this study have shown that:
- Grouts can be produced for both cement systems over a range of water contents and reactant ratios in which fluidities are significantly above those achieved for OPC based cements.
- CSA cements, despite high initial w/s ratios, produced cements with zero bleed as ettringite formation rapidly binds water.
- MP cements are formulated at lower w/s ratios producing cements with zero bleed.
- The pore solution pH of both cements are significantly lower than conventional OPC cements being in the range 10-11 for CSA and 5-7 for MP cements
- The corrosion of aluminium metal in both systems over a 40 day curing period is markedly reduced in comparison to the BFS/OPC system.

However studies on these cements are in their preliminary stages and significant further work is required before they can be utilised for ILW encapsulation. These studies should include:
- Long term aluminium corrosion behaviour monitoring to elucidate a corrosion mechanism, which may also explain the corrosion behaviour of other reactive metals.
- Assessment of corrosion rate behaviour when encapsulating magnox and uranium metal.
- Better understanding of hydration chemistry, phase formation and the durability of these phases over time and differing temperature regimes.
- Optimisation of formulations and definition of powder specifications.

- Understanding the incorporation mechanism of wastes and the long term stability of both systems with waste ions immobilised.
- Trials to assess the practical applications at large scale.

ACKNOWLEDGEMENT

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