

The investigation of aluminium wastes encapsulated in the individual phases of ordinary Portland cement

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ABSTRACT

There has been significant research concerning composite cements based on Ordinary Portland Cement for hazardous waste immobilisation. These works have shown that in high pH environments aluminium undergoes severe corrosion. This leads to gas evolution and expansion, resulting in a poor quality matrix for waste encapsulation. To complement work into alternative materials for waste encapsulation, this work investigates the fundamental interaction of the Ordinary Portland Cement phases with aluminium metal. These simplified systems will provide elementary information to assist in the toolbox of hazardous waste storage.

INTRODUCTION

The UK nuclear industry started in the 1950s, first with weapons production and then the opening of the first commercial power plant in 1956. In the UK there are currently 19 nuclear reactors. As of 2009 these provide 17.9% of the country's electricity supply [1]. With growing pressure on the UK Government to deal with climate change and ensure energy security new options of electricity generation, including nuclear, have to be examined. The Government recently reported that new nuclear builds can help meet environmental targets to cut CO₂ emissions [2]. However, the current fleet of nuclear power stations is entering the last years of design life, which will leave a gap in energy supply, compromising both energy security and climate change goals.

The storage and safe disposal of radioactive waste is a major issue for the nuclear industry. In addition to the legacy waste from the first reactors, new wastes have to be treated and stored to stop any loss of material to the environment.

Immobilisation of radioactive wastes is carried out to allow them to be handled and stored safely. This technique is currently carried out using composite cements [3], which are blends of Ordinary Portland Cement (OPC), blast furnace slags (BFS) and pulverised fuel ashes (PFA). The immobilised waste are collectively known as wasteforms. The composite cements have low permeability and will incorporate various waste compounds into the hydrated structure of the cements; these will stop leaching of the radionuclides into the environment.

The hardened cement makes the wasteform solid and provides strength so that is durable for long term storage.

This project aims to provide the nuclear industry with more information about the reactions and products formed in solidified waste systems. This will improve the understanding of wasteforms and act as underpinning support for waste management strategies. This project is a continuation of work carried out by the National Nuclear Laboratory, concerning the corrosion of Magnox wastes in OPC.

The issues surrounding the use of OPC systems include significant heats of hydration and the high pH environment it provides. The heat produced from the cement hydration can have several effects on the wasteform, including weakening of the structure. The high pH is important for limiting the solubility of some of the radionuclides [4]. However, metals like aluminium suffer corrosion under such conditions; this has the potential to form cracks and pores and, thus, can lead to poor quality waste forms [5;6]. The work reported here is focused on elucidating the fundamental interactions between pure cement phases and aluminium to determine whether the previously mentioned reactions can be controlled by the wasteform chemistry.

ORDINARY PORTLAND CEMENT

There are many types of cement, the most common being OPC. The main constituents of

OPC are two types of calcium silicate, small quantities of calcium aluminates and calcium alumina ferrites. These can be generalised into four major phases: tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite. The amounts of each phase are rarely the same due to the manufacturing techniques and feed materials used and thus, OPC varies significantly from place to place and time to time. The ratio of each of the phases is generalised in Table 1 [7-10].

Table 1 Ordinary Portland Cement phase names, formulae and amounts

Name	Composition	Cement Notatio <i>n</i>	Weight %
Alite	3CaO·SiO ₂	C ₃ S	55– 65
Belite	2CaO·SiO ₂	C ₂ S	15– 25
Aluminate	3CaO·Al ₂ O ₃	C ₃ A	8 – 14
Ferrite	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	C ₄ AF	8 – 12

The hydration of OPC can be seen in Figure 1, where heat from the hydration is on the y-axis and time on the x-axis.

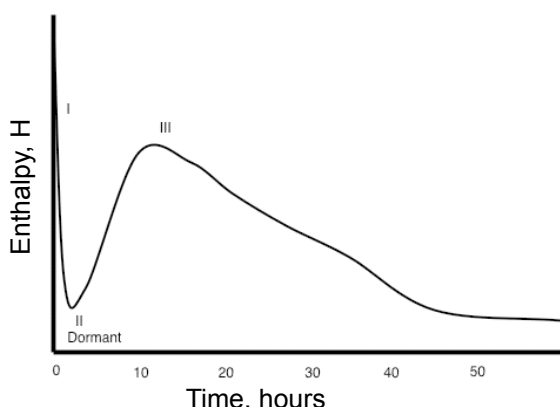


Figure 1 Hydration of OPC. The hydration reduces with time. y-axis enthalpy of hydration, x-axis time hours adapted [11]

The peaks and troughs on the graph can be attributed to the different hydration rates of each phase. Each phase will not only react at different rates, but produce different reaction products with varying properties. Of interest are the heat of reactions, the pH of the systems and the hydration product densities. The work reported here will examine the effect of hydration on a simulated wasteform. In industrial cements the inconsistency and impurities, some of which are added to the systems to engineer the properties of the cement, mean that it is difficult to see what reactions actually occur during hydration and the compounds that are formed.

For the pure cement phases that this project will investigate, hydration will be carried out using deionised water. This simplified cement system will then be assessed to investigate interactions that the individual phases have with waste systems,

specifically aluminium, present in the rod casings from Magnox reactors.

The hydration of cement produces very alkaline solutions, of approximately pH13 [5]. Over time these form the crystalline structures that give the cements their compressive strength. The reactions 1 – 4 are shown below in cement chemistry notation where, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃ and H represents H₂O [[11]]. The major products of the hydration reactions are calcium-silicate-hydrates (CSH), calcium hydroxide (CH) and heat.

- $2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$ (1)
- $2C_2S + 4H \rightarrow C_3S_2H_3 + CH$ (2)
- $C_3A + 6H \rightarrow C_3S_2H_3$ (3)
- $C_4AF + 6H \rightarrow C_3S_2H_3$ (4)

The investigation carried out in this project will assess how the hydration properties of each of the phases effect the corrosion of the encapsulated aluminium.

CORROSION OF ALUMINIUM

Due to the high pH of hydrated OPC the aluminium metal present is susceptible to corrosion. Under these conditions the oxide layers that have formed on the surface of the aluminium metal will dissolve and the metal underneath will be exposed. This will then undergo further corrosion. The theoretical Pourbaix diagram (Figure 2) shows the redox potential of aluminium compounds against pH. Under standard conditions the passive layer that protects the aluminium from corrosion is dissolved above pH 8.5. In OPC systems the pH will be 13, so unhindered corrosion of the aluminium can occur, which presents a significant issue.

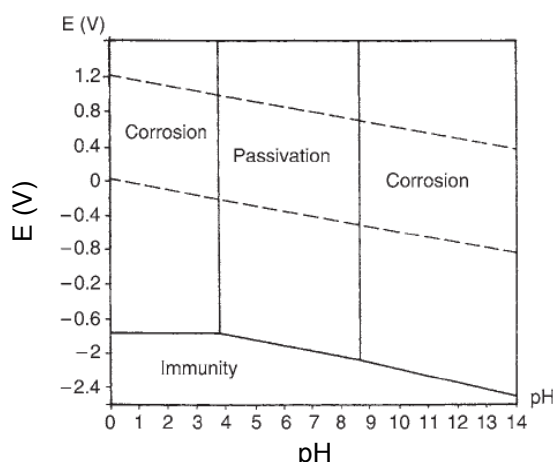
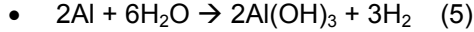


Figure 2 Simplified Pourbaix diagram of aluminium in water [12]

In the high pH environment of hydrated OPC, the aluminium metal reacts with the water present in the system to produce hydrogen gas and aluminium hydroxide. The overall reaction for

aluminium corrosion can be described by Equation 5 [12]:



One issue the corrosion of the aluminium metal presents is that the density of aluminium hydroxide is less than that of the pure metal (Table 2), so the corrosion causes expansion within the wasteforms. To add to this problem the hydrogen gas causes pores to form in the matrix, which allows further corrosion products to grow and cause further degradation to the structure.

Table 2 Density change values [13]

Material	Density kg m^{-3}
Al	2698
Al(OH) ₃	2420

Due to the lower density of aluminium hydroxide in comparison to aluminium, there is an increase in volume per mole of 222% when corrosion occurs.

EXPERIMENTAL METHODS

This project has two main stages, phase synthesis and aluminium analysis. The interaction of the pure phases with aluminium will be investigated using two methods. First, the investigation of the rate of hydrogen gas evolution over time for each phase. Second, the investigation of the reaction products over time.

CEMENT PHASE PRODUCTION

The production of pure phases will require high temperature sintering methods and XRD analysis to ensure the composition of the phase. Following the production of sufficient material, the encapsulation of aluminium will be undertaken.

The production of each phase requires mixing of the reactants according to the desired stoichiometry. The reactant materials will be compacted together with small quantities of doping agents to obtain the different crystal structures of each phase that are present in industrial cements. In industrial processes the phases' crystal structures are stabilised by foreign ions, that are either added to the system or are already present in the reactants themselves. However, due to the requirement for purity in this work, the doping agents will be added in known quantities and their effects examined. The agents used to stabilise pure phases are described below in Table 3.

To obtain the correct phase the reactants must be heated to very high temperatures, e.g. C₃S requires sintering at 1600 °C for three hours [14;15]. These temperatures are established from the thermodynamic phase diagrams of binary and tertiary systems of the reactants. Transitions from the differing phases in the systems are at set

temperatures. The high temperature sintering of the reactant powders is carried out to ensure the correct phase is produced. The phases require the freezing of their crystal structures that are stable at the higher temperatures, which is achieved via quenching.

Table 3 Phase crystal structures and Doping agents [14]

Phase	Crystal form	Additives	Weight Percent, wt. %
C ₃ S	Triclinic	-	-
C ₃ S	Monoclinic	Al ₂ O ₃ /MgO	1.8
C ₂ S	Monoclinic	H ₃ BO ₃	0.4
C ₃ A	Cubic	-	-
C ₃ A	Orthorhombi	NaNO ₃	9.86
	c		
C ₄ AF	-	-	-

To assess the composition of the samples and the purity of the phase, powder x-ray diffraction (XRD) will be used. XRD will readily identify the phases present. To increase the purity of the samples, regrinding and sintering at desired temperatures will be necessary.

H₂ EVOLUTION

The corrosion of aluminium in water yields hydrogen gas; this can be used to assess the effect that the individual phases have on the rate of corrosion. The oxidation of the aluminium metals results in reduction of hydrogen ions to form hydrogen gas. The experimental setup can be seen in Figure 3. This method requires the hydration of each phase under a head of water to allow hydrogen gas produced from the corrosion reactions to be measured by displacement of the water. Hence, this will give an idea of hydrogen evolution rates for known amounts of aluminium per volume of cement. The container and rod will be cylindrical so that there is a constant interaction surface area.

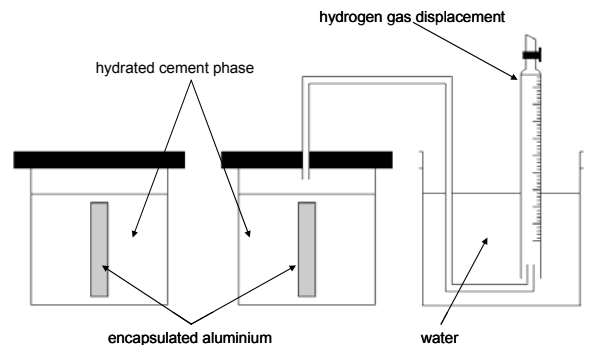


Figure 3 Left; simulated encapsulation of aluminium waste, Right; hydrogen displacement setup

PHASE ENCAPSULATION

To fully examine the effect that the hydration of each phase has on the aluminium, several rods will be encapsulated in each phase (Figure 3). These

will then be individually examined at certain time periods to see the extent of corrosion. The amount of water added will have a significant effect on the hydrated system; in particular the strength, porosity and workability of the cement. In cases where there is insufficient water, there will not be full hydration and excess water can lead to poor wastefoms. This work will look at water/solid ratios between the stoichiometric water requirement of around 25 – 33 wt.%. This is similar to ratios used for OPC-composite systems that have been examined by other work [16]. Additional work needs to be carried out to investigate the effect that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Calcium sulphate dihydrate) has on the more reactive phases, specifically aluminate. In industrial clinkers gypsum is added to avoid flash set, which causes poor strength and a lot of heat and thus, undesirable wastefoms. Adding gypsum to reduce the rate of the hydration reaction will also introduce sulphur into the system and complicate further the reactions that will occur.

The extent of corrosion will require characterisation of the waste form, the compounds present, porosity, pH and visible effects. XRD can be used to identify the hydration products and corrosion products; this can be undertaken quantitatively to look at the amount of compounds present in the samples. Scanning Electron Microscopy (SEM) can look at the surface interactions and examine the system at a micron scale. This can be used to assess the growth of corrosion products and the extent of penetration of the aluminium. Along with SEM, the use of Energy Dispersive X-ray Spectroscopy (EDS) can be used to identify the atoms present. Measurement of sample porosity can be carried out using adsorption techniques. The pH of the samples can be established by breaking up the samples into deionised water, and then using a pH probe.

CONCLUSION

Magnox-based waste encapsulated in Ordinary Portland Cement systems have been widely investigated. This work looks to simplify the cement system and to trace the reactions and the products formed. The systematic evaluation of the aluminium in each of the phases will build up a picture of the fundamental reactions that occur within encapsulated waste forms.

The use of individual cement phases will allow for a detailed assessment of the hydration and subsequent reactions of each phase with the aluminium metal. The products formed can be analysed and the reactions deduced. Comparison with work carried out using OPC, composite OPC and alternative cements to examine trends and patterns will point to a better understanding of the physicochemical aspects of waste material encapsulation.

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