Immobilisation of Caesium in Magnesium Phosphate-based Blends

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ABSTRACT

Disposal of Caesium (Cs) by incorporating it into host matrices has been proved as a promising concept. Even though Portland cement (PC) based systems can be used to encapsulate low (LLW) or intermediate level waste (ILW), they are not efficient for immobilising Cs due to the very high water-solubility of Cs. Magnesium phosphate cement (MPC), a chemically bonded ceramic consists of struvite families produced by the acid based reactions between dead-burnt magnesium oxide (MgO) and phosphates (e.g., KH_2PO_4), can be a potential candidate for hosting Cs, since it has been reported that Cs can be incorporated in the K-struvite structures by substituting potassium (K) to form (K,Cs)-struvite. However, the acid-based reaction to form MPC under ambient temperature between magnesium oxide (MgO) and phosphates (e.g., KH_2PO_4) is violent and exothermic, which raises concerns about industrial application of MPC in real world. In this work, ground-granulated blast-furnace slag (GGBS) and pulverised fuel ash were used to replace MPC in order to reduce the heat released. The feasibility of MPC, as well as MPC-based blends, i.e. GGBS-MPC or PFA-MPC matrices, for immobilising Cs was assessed by their leaching behaviour at the ages of 3d, 7d and 28d. In addition, two typical PC based systems currently used in nuclear waste immobilisation, i.e., pure PC and PC-GGBS (1:9) mixes, were also produced and tested as controls. The results indicated that all the MPC mixes, including pure MPC, GGBS-MPC and PFA-MPC, demonstrated superb capability for immobilising Cs, with the immobilisation rates achieved more than 99.5% at all curing age investigated. Compared to the traditional PC and PC/GGBS mixes, the MPC mixes nearly doubled the Cs immobilisation rate, which is rather encouraging.

1.   INTRODUCTION

Recent developments in nuclear industry have heightened the need for disposal of radioactive (nuclear) wastes safely and permanently. Caesium (Cs), a radio-contaminant discharged from nuclear plants, is among the most hazardous radioactive nuclides. Disposal of radioactive nuclides by incorporating/dissolving them into host matrices to form a stable and durable solidified phase has been proved as a promising concept. However, the most-widely accepted Portland cement (PC) based matrices are inadequate for immobilising Cs due to the very high water-solubility of Cs.

Magnesium phosphate cement (MPC) is a new clinker-free binder. It is actually a chemically bonded ceramic consists of struvite families produced by the through-solution acid based reactions between dead-burnt magnesium oxide (MgO) and an acid phosphate source (e.g., KH_2PO_4). Compared to conventional PC-based materials, MPC possesses many improved characteristics such as rapid setting, high early strength, high bonding strength and better durability (e.g., chemical attack resistance and permeation resistance). These properties make MPC remarkably popular in fast-repairing concrete structures such as pavements, highways, airport runways & bridge decks. More interestingly, recent evidence suggests that MPC can be a potential candidate for accommodating Cs as Cs could be potentially incorporated into the K-struvite structures by substituting potassium (K) to form (K,Cs)-struvite (Wagh et al., 2016). However, the acid-based reaction to form MPC under ambient temperature between MgO and KH_2PO_4 is violent and exothermic, which raises concerns about industrial application of MPC in real world.

Ground-granulated blast-furnace slag (GGBS) and pulverised fuel ash (PFA) are two most-widely used supplementary cementitious materials (SCMs) worldwide. Pulverised fuel ash (PFA) is a by-product of coal combustion process, which mainly consists of amorphous SiO_2 and Al_2O_3 phases. GGBS, produced by quenching molten iron slag from the iron & steel manufacturing, also contains glassy calcium-alumino-silicates. Even though numerous studies have revealed the benefits offered by using GGBS & PFA on the properties of PC materials along with reduced carbon footprint, very little work so far is available concerning the properties of GGBS or PFA blended MPC materials. Some available work treated GGBS/PFA as an inert filler or diluent media, probably due to the pozzolanic reactivity of PFA and the latent-hydraulic nature of GGBS cannot be activated anymore in the near-neutral pH conditions of MPC matrices (Gardner et al., 2015, Covill et al., 2011). Nonetheless, our previous study showed that the replacement of GGBS & PFA caused a considerable reduction in the heat generation rate, and more importantly a lower total heat within the first 48 hours (McCague et al., 2011), which could be of great importance for encapsulating radioactive wastes at industrial scale.

Hence, the current work seeks to investigate the feasibility and capability of Magnesium Phosphate Cement (MPC) blended with GGBS or PFA for immobilising Cs, by considering their leaching behaviour under the curing ages of 3d, 7d & 28d. Two typical PC based systems in nuclear immobilisation, i.e., pure PC and PC-GGBS (1:9) mixes, were also produced and tested as controls.

2. EXPERIMENTAL

2.1 Materials
MgO, a Dead Burned Magnesite (DBM) calcining at about 1750 °C with purity of 90%, was provided by Richard Baker Harrison Ltd, UK.   Monopotassium phosphate (MKP, KH_2PO_4) was from Prayon UK, and it was a food-grade MKP with specified purity > 99%. Portland cement (PC) was CEM I (in accordance with BS EN 197-1:2011) supplied by QUINN Cement. GGBS was supplied by Hanson Heidelberg Cement Group and its fineness was 450-550 m^2/kg, and PFA was from Powder Minerals Ltd and its mean particle size was around 21μm. Caesium chloride (Sigma-Aldrich UK) was used as the source of Cs ion doped into the designed mixes at 5% level.

2.2 Mixing & casting
The MPC mixes were fabricated in a High-shear mixer at MgO/KH_2PO_4 ratio of 5:1 and Boric acid dosage of 4% (wt of MgO). The replacement levels of GGBS and PFA, as well as the water/solid ratio of each mix (which was determined by trials in order to achieve an acceptable workability, i.e., mini slump value of 85 ± 5 mm) are presented in Table 1. After mixing, the pastes were cast into the moulds with dimension of 25mm x 25mm x 25mm, then sealed in plastic-bags and cured in a water-bath with controlled temperature of 40 ± 0.5 °C for 3d. After this, the cube specimens were demoulded and wrapped with water saturated hessians, which were sealed in plastic bags and stored again in the curing incubator (water-bath) until the target ages. The PC pastes were also manufactured and cured with the same regime as MPC systems.

2.3 Testing
At 3d, 7d and 28d, the paste cubes were crushed under compressive test machine for compressive strength, and selected fragments were ground for further analyses. The leaching tests were carried out with particles between 500μm and 2.36mm in accordance with BS EN 12457-1:2002, and the Cs concentration in leachate was measured by Ion Chromatography (IC, Dionex IC1100) and Cs immobilisation rate were then calculated as per BS EN 12457-1:2002.

Table 1. Summary of the mix proportions and w/s ratios

Mix		Replacement level	Water/solid ratio
M1	MPC	0	0.20
M2	MPC-Cs		
M3	PFA/MPC	50%	0.30
M4	PFA/MPC-Cs		
M5	GGBS/MPC	50%	0.30
M6	GGBS/MPC-Cs		
M7	PC	0	0.38
M8	PC-Cs		
M9	GGBS/PC	90%	0.42
M10	GGBS/PC-Cs		

3. RESULTS AND DISCUSSION

3.1 Leaching test
Table 2 reports the immobilisation rates of Cs in the five Cs-doped MPC and PC based matrices, at different curing ages of 3d, 7d and 28d respectively. Furthermore, these data were plotted against ages in Fig. 1 in order to clearly compare the Cs immobilisation rate over different mixes and ages.

Obviously, the data in Table 2 as well as in Fig. 1, is quite revealing in several ways:

i) *Different binder systems*.
It can be seen from Table 2 and Fig. 1, MPC based matrices, including the pure MPC and GGBS or PFA blended MPC materials, showed superb capabilities for immobilising Cs, with immobilisation rate reached higher than ~99.5% at all curing ages investigated. In contrast, PC systems encapsulated much reduced amount of Cs compared to MPC matrices. At 3d, the immobilisation rate of Cs for the PC and GGBS/PC systems were 62.07% and 53.36% respectively, which is only about 2/3 values of MPC matrices. Furthermore, even the highest immobilisation rate of Cs (i.e., 91.86%) possessed by the pure PC paste at 28d was still much lower than those of MPC systems. Our finding could suggest, beyond question, MPC based materials have much improved capability in terms of immobilising Cs over PC systems, which can be also clearly observed in Fig. 1.

ii) *Different mixes/Effects of SCMs*.
For the MPC systems, the replacement of MPC with GGBS or PFA slightly increased the immobilisation efficiency of Cs, which is rather encouraging. However, in terms of the PC based materials, the incorporation of GGBS caused some negative effects which reduced significantly the Cs immobilising rates. Take the values at age of 28d as an example, the substitution of GGBS for PC decreased the Cs immobilisation rate from 91.86% (pure PC) to 78.70% (GGBS/PC).

iii) *Different ages*.
As shown in Fig. 1, for the whole five mixes, there were significant positive correlations between the curing ages and the immobilisation rate of Cs. This result indicates that prolonged curing time could increase the capacity of both MPC and PC based systems for immobilising Cs.

Table 2. Summary of the immobilisation rates of Cs

Mix		Immobilisation rate		
		3d	7d	28d
M2	MPC-Cs	99.51%	99.87%	99.95%
M4	PFA/MPC-Cs	99.59%	99.90%	99.93%
M6	GGBS/MPC-Cs	99.88%	99.92%	99.92%
M8	PC-Cs	62.07%	74.78%	91.86%
M10	GGBS/PC-Cs	53.36%	56.47%	78.70%

The present finding suggests the MPC based matrices can immobilise Cs efficiently, with even much improved capacity over the traditional PC base systems. Furthermore, the prolonged curing time can impose positive effect on the Cs immobilisation. Meantime, it is worthwhile to note the following issues:

i) As shown in Table 2, even at curing age of 3d, over ~99.5% (nearly 100%) of the doped Cs have already been accommodated by the three MPC mixes, including the pure MPC, GGBS/MPC and PFA/MPC pastes – nearly doubled the immobilisation rates of PC systems. This raises in the questions on the actual *waste loading capacity* of MPC matrices - as the current work employed 5% Cs dosage, it is considered appropriate that high Cs dosage should be studied in the future investigations.

ii) More broadly, detailed chemical and microstructural characterisation of these matrices needs to be carried out in order to understand the mechanisms involved in the high immobilisation rate behind the MPC matrices. In addition, the heat evolution and rheological behaviour of the MPC matrices will also need to be studied in order to justify its applicability in real plant conditions in the future.
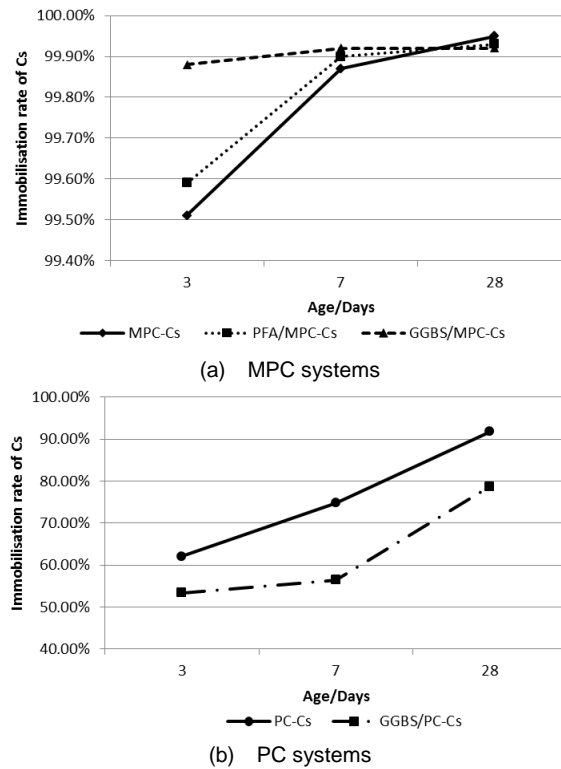
(a) MPC systems

(b) PC systems

Figure 1. Immoblilisation rates of Cs at different mixes after 3, 7 and 28 days

3.2 Compressive strength test

Compressive strengths of the Cs- doped MPC and PC pastes were also investigated in order to justify its suitability for plant application. Table 3 presents the strength results for the whole ten mixes at the ages of 3, 7 and 28d. Moreover, the strengths of different mixes were plotted against ages and shown in Fig. 2 below.

Table 3 and Fig. 2 illustrate the main characteristics of the compressive strengths of MPC and PC based matrices, as follows:

i) *Different binder systems.*

Obviously, PC based materials showed higher strength than MPC mixes, for both the mixes without or with Cs element. This phenomenon was especially apparent between the Cs-doped MPC and PC mixes, e.g., at 28d the strength of PC-Cs mix was 64.4 MPa which is even more than double the value of MPC-Cs paste (27 MPa). Nonetheless, the compressive strength of the MPC based systems can still meet the requirements of practical nuclear application.

ii) *Different mixes/Effects of SCMs or Cs*

As shown in Table 3, the replacement of MPC with GGBS or PFA reduced sharply the compressive strengths of MPC pastes. At the curing age of 28d, the strength of pure MPC mix was 39.1 MPa which was then dropped down to 11.5 MPa for PFA/MPC paste and 16.4 MPa for GGBS blends. A similar negative effect can be observed from the incorporation of Cs, i.e., the application of Cs decreased the compressive strength of all the five mixes compared to their controls.

iii) *Different ages*

As expected, there were positive correlations between the compressive strengths and curing ages for all the ten MPC and PC based materials. However, for the pure MPC mix, there was no significant grow in compressive strength from 7d to 28d.

Table 3. Summary of the compressive strengths

Mix		Compressive strength/MPa		
		3d	**7d**	**28d**
M1	MPC	34.8	39.0	39.1
M2	MPC-Cs	2.0	26.2	27.0
M3	PFA/MPC	8.0	10.5	11.5
M4	PFA/MPC-Cs	2.5	3.8	5.3
M5	GGBS/MPC	2.0	5.8	16.4
M6	GGBS/MPC-Cs	1.3	2.1	3.8

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M7	PC	56.0	57.9	78.1
M8	PC-Cs	42.8	48.6	64.4
M9	GGBS/PC	14.1	19.8	23.2
M10	GGBS/PC-Cs	11.5	14.3	19.2

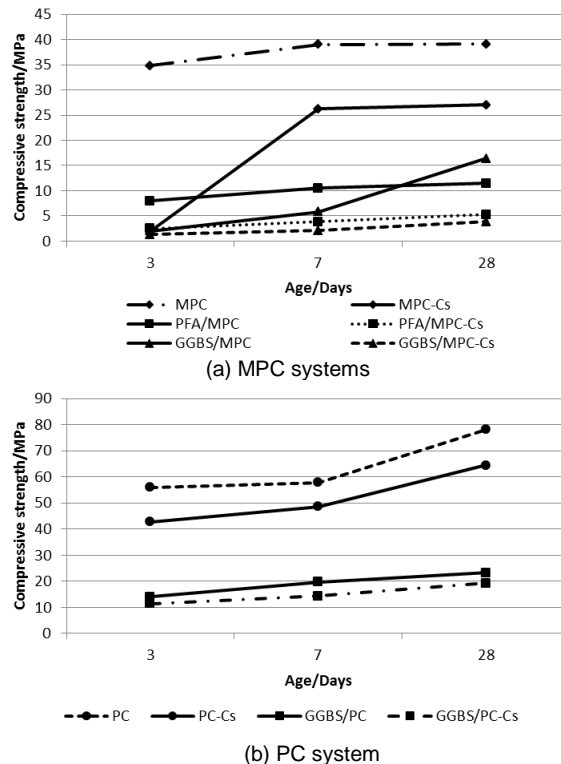
(a) MPC systems

(b) PC system

Figure 2. Compressive strengths of different mixes after 3, 7 and 28 days

4. CONCLUSIONS

The current work investigated the capacity of MPC, as well as MPC-based blends, i.e. GGBS-MPC or PFA-MPC matrices, for immobilising Cs, by assessing their leaching behaviour at the ages of 3d, 7d and 28d. The compressive strength was also evaluated. The finding obtained so far confirmed that MPC-based blends could be potential matrices for immobilising Cs. However, the exact mechanisms behind the high immobilisation rate offered by MPC, the roles of GGBS and PFA along with the actual loading capacity of MPC matrices in terms of Cs, are still unclear, which are worthwhile to be further explored.

ACKNOWLEDGEMENTS

REFERENCES

Covill, A., Hyatt, N., Hill, J. & Collier, N. 2011. Development of magnesium phosphate cements for encapsulation of radioactive waste. *Advances in Applied Ceramics,* 110**,** 151-156.

Gardner, L.J., Bernal, S.A., Walling, S.A., Corkhill, C.L., Provis, J.L. & Hyatt, N.C. 2015. Characterisation of magnesium potassium phosphate cements blended with fly ash and ground granulated blast furnace slag. *Cement and Concrete Research,* 74**,** 78-87.

Mccague, C., Wang, L. & Bai, Y. Magnesium Phosphate Cement as a Potential Alternative for Encapsulation of Nuclear Wastes Containing Aluminium. 2011. Novel Developments and Innovation in Cementitious Materials, 31st Cement and Concrete Science Conference, London, UK.

Wagh, A.S., Sayenko, S., Shkuropatenko, V., Tarasov, R., Dykiy, M., Svitlychniy, Y., Virych, V. & Ulybkina, E. 2016. Experimental study on cesium immobilization in struvite structures. *Journal of hazardous materials,* 302**,** 241-249.