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Interaction of strontium chloride solution with calcium aluminate phosphate (CAP) system

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ABSTRACT

Processing of contaminated water in Fukushima Daiichi Power Plant results in various aqueous secondary wastes. A significant strontium (^{90}Sr) contamination represents one of the key challenges for their management, and we have been developing a new cementing matrix based on calcium aluminate phosphate (CAP) system with reduced water content for such aqueous secondary wastes. In the present study, the interaction of CAP with $SrCl_2$ was investigated to gain insight into the capability of CAP system in Sr immobilisation. It was found that the immobilisation is possible, and the incorporation of Sr appears to be associated with the formation of insoluble phosphate salts. The obtained results also suggest that 1 kg of CAP powders can incorporate 200 g of Sr under tested condition.

1. INTRODUCTION

One of the most challenging decommissioning activities regarding the Tokyo Electric Power Company (TEPCO) Fukushima Daiichi Nuclear Power Plant is the continuous generation of contaminated water. Currently, a partially closed water circuit provides the necessary cooling to the system (Williams et al., 2015), and water is processed through the Advanced Liquid Processing System (ALPS) (Grambow et al., 2014). As a result, large amounts of contaminated aqueous secondary wastes are currently being stored on-site: 6,000 m^3 of slurries in 2,254 units in 2017 (Journeau et al., 2018).

Among the contaminants, the high concentration of strontium (^{90}Sr) resulted in a radioactivity value of 10^{17} Bq (Journeau et al., 2018), which represents a serious issue in the management of these secondary wastes. Incorporation of these wastes is challenging, in particular with conventional cement matrices based on Portland cement (PC) because of the potential hydrogen gas generation and associated risks of fire and explosions (Saji, 2014), due to the radiolysis of the water contents intrinsically present in the conventional cement matrices as pore solution and hydration products.

In order to condition these secondary wastes, we have been developing a new cement matrix based on calcium aluminate phosphate (CAP) system (Garcia-Lodeiro et al., 2018). Differing from the conventional cements, solidification of CAP system is based on acid-base reaction (Sugama et al., 1992). Since the water content is not crucial once the system is mixed, it is possible to reduce its water content by curing the system at 60-90°C without compromising the integrity of the solid products (Garcia-Lodeiro et al., 2018).

To gain further insight into the capability of CAP system as a cementing matrix for the aqueous secondary wastes contaminated with strontium, the present study investigated the interaction of a CAP system with dissolved strontium. A CAP simulant was mixed with a significant amount of water in presence of strontium ions, and the change in the concentration of key elements are examined in comparison with the system without presence of strontium ions.

2. EXPERIMENTAL

MATERIALS

Materials used in the present study are based on the previous work (Garcia-Lodeiro et al., 2018). The CAC (Secar 51, Kerneos) was used as the primary precursor of CAP, together with a reagent grade of linear metaphosphate ($(NaPO_3)_n$ 97%, Acros Organics) as a source of polyphosphate (PP). An orthophosphate ($NaH_2PO_4.2H_2O$ 99%, Acros Organics) was also added as a source of monophosphate (MP) which are usually used in CAP systems to avoid the rapid setting of CAP (Chavda et al., 2014). For the aqueous solutions of strontium ions, strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$, Alfa Aesar, 99+%) was used together with distilled water.

METHODS

Aqueous solutions used for the reactions were prepared by dissolving $SrCl_2 \cdot 6H_2O$ in distilled water at 0.1M. The CAP powders were prepared in dry state by hand-mixing Secar 51 (69 wt%), PP (27.6 wt%) and MP (3.4 wt%), based on the previous study (Garcia-Lodeiro et al., 2018).

0.3 g of premixed CAP powder was added to the 30 mL of aqueous solution placed in a plastic container while stirring at 400 rpm using a magnetic stirrer, and the system was left for reaction at room temperature for a designated period of time: 60 seconds, 1h, 2h, 4h, 8h or 24h. A separate batch was prepared for each designated period. For comparison, the exact same procedure was repeated but using only distilled water without adding $SrCl_2 \cdot 6H_2O$.

At the end of designated reaction period, the liquid phase (>20 mL) was sampled using a syringe and membrane filter (< 0.22 µm). The pH of the liquid sample was determined using a Mettler pH/Cond bench meter SE S470-K equipped with an expert proISM probe (error = ±0.01). The probe was calibrated before each measurement using three buffer solutions at pH 4.01, 7.0 and 9.21. The liquid samples were stored in sealed plastic containers at 20^oC until analysed using Inductively coupled plasma - optical emission spectrometry (ICP-OES), performed with a Spectro-Ciros Vision Optical Emission Spectrometer. The concentration of Sr, Cl, P, Na, Al and Ca were determined simultaneously.

3. RESULTS AND DISCUSSION

EVOLUTION OF pH

The pH data for both the systems studied (with and without $SrCl_2 \cdot 6H_2O$) are presented in Figure 1.

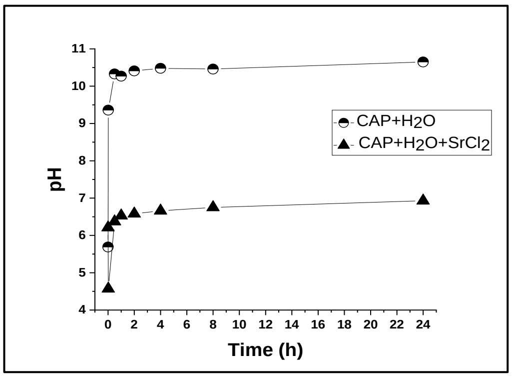

Figure 1. pH of both systems with and without $SrCl_2 \cdot 6H_2O$.

After 24 hours of reaction, pH increased in both the systems, reaching 10.65 without $SrCl_2 \cdot 6H_2O$ and 6.93 with $SrCl_2 \cdot 6H_2O$. This increase must be related to the partial dissolution of the CAC powder. The expected pH of Secar 51 in aqueous solution (10 %) is 10.5-11 (Kerneos Inc., 2016). The data obtained clearly indicates that the pH of the system is lower when $SrCl_2 \cdot 6H_2O$ was present throughout all the studied reaction times.

BEHAVIOUR OF CAP

As shown in Figure 2, the concentration of calcium and aluminium continue increasing when $SrCl_2 \cdot 6H_2O$ is not present throughout the reaction times studied, achieving final concentrations of 630 mg L^{-1} and 551 mgL^{-1}, respectively. The higher concentration of these ions suggests more dissolution of CAC clinker phases and/or relatively less precipitation of their solid reaction products. On the other hand, after 24h of mixing in presence of $SrCl_2 \cdot 6H_2O$, Ca concentration reaches only up to 75.4 $mg*L^{-1}$ and that of Al was below detection limit (<0.001 $mg*L^{-1}$), suggesting limited dissolution of CAC clinker phases and/or increased formation of their solid reaction products.

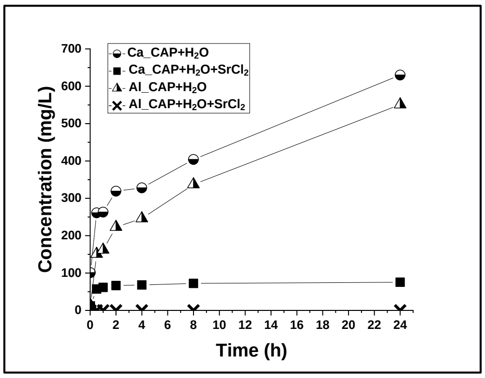

Figure 2. Concentration of Ca and Al in the systems with and without $SrCl_2 \cdot 6H_2O$.

It has been reported that the main binding phases of CAP are amorphous phosphates (Sugama and Carciello 1995, Swift et al. 2013, Chavda et al 2014, Garcia-Lodeiro et al. 2018), and this is likely the case also for the systems studied in the present investigation. As shown in Figure 3, the trend observed in the concentration of phosphorus coincides with those for calcium and aluminium: the concentration of phosphorus becomes much lower in the system with $SrCl_2 \cdot 6H_2O$. Therefore, the difference between these systems (with or without $SrCl_2 \cdot 6H_2O$) in calcium and aluminium ion concentration must be caused mainly by the formation of reaction products, rather than the suppressed or enhanced dissolution of CAC clinkers in these systems.

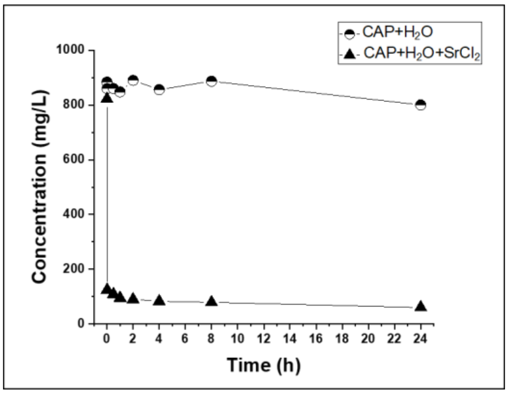

Figure 3. Concentration phosphorous in the systems with and without $SrCl_2 \cdot 6H_2O$.

Orthophosphate changes its form depending on the pH of the aqueous environment (Asadi-Eydivand et al., 2014): a significant portion can form $H_2PO_4^-$ at pH<7 whereas majority becomes HPO_4^{2-} at pH>8. Therefore, the amorphous phosphate products formed in the presence of $SrCl_2 \cdot 6H_2O$ could be different from those formed without the presence of $SrCl_2 \cdot 6H_2O$, and this may also be contributing to the different trends of the calcium and aluminium ion concentration between these two systems. Further investigation is required to elucidate this aspect.

IMMOBILISATION OF STRONTIUM

The trend observed for strontium ions was similar to that for phosphorus as shown in Figure 4, suggesting the precipitation of Sr phosphate salts.

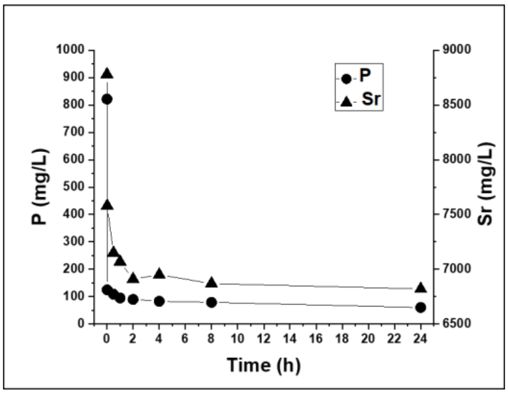

Figure 4. Phosphorous and strontium concentration in the system with $SrCl_2 \cdot 6H_2O$.

Based on the initial (C_0) and final (C) concentrations of strontium after 24 hours of reaction, the efficiency of strontium immobilisation (η %) was estimated using Equation 1.

$$\eta = \left[1 - \frac{C}{C_0}\right] \times 100 \qquad (1)$$

After 24 hours of mixing, the concentration of strontium changed from 8780 mg/L to 6820 mg/L, which corresponds to η = ~22 % immobilisation. This also indicates that 1 kg of CAP powders immobilized 200 g of strontium.

CONCLUSIONS

The presence of $SrCl_2 \cdot 6H_2O$ indicated a significant impact to the system. The pH of the solution was much lower throughout the reaction times studied when $SrCl_2 \cdot 6H_2O$ was present. The reduced concentrations of calcium, aluminium and phosphorus suggest an enhanced precipitation of the respective reaction products.

The tested amount of CAP was capable of immobilising 22 % of strontium present in the system, which corresponds to 1 kg of CAP powders immobilising 200 g of strontium.

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