Over View Report 1 MEXT's Nuclear Joint Research Collaboration

Development of solidification techniques with minimised water content for secondary radioactive aqueous wastes in Fukushima

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1. Introduction

The processing of the contaminated water from the TEPCO Fukushima Daiichi Nuclear Power Plant results in a large amount of secondary aqueous wastes. They contain a significant amount of water, sea salt and strontium. In order to reduce the fire risk from the hydrogen gas generation and the risk of leakage, the proposed project aims to develop a solidification technique with minimised water content for the safe storage of secondary aqueous radioactive wastes. This collaboration, led by The University of Sheffield and Japan Atomic Energy Agency, examines the following four aspects: (1) synthesis and analysis of the simulated secondary aqueous wastes; (2) development of a solidification technique with minimised water content; (3) evaluation of the effects of irradiation on the wasteform; and (4) evaluation of the long-term stability of the products.

2. Background

Processing contaminated water from the TEPCO Fukushima Daiichi Nuclear Power Plant results in a large volume of radioactive secondary aqueous wastes [1]. The evaporation facility initially used for the processing of contaminated water produced a concentrated effluent (concentrated sea water supernatant). The Advanced Liquid Processing Systems (ALPS) currently operating have been generating wastes known as iron co-precipitation slurry (iron hydroxide with organic polymer, diluted sea water supernatant) and carbonate salt slurry (calcium carbonate and magnesium hydroxide, diluted sea water and sodium carbonate supernatant). All of these secondary wastes are contaminated with ^{90}Sr.

The LLW and ILW of this type are usually homogeneously mixed and solidified using a matrix based on Portland cement for long-term storage and eventual underground disposal. However, if these secondary wastes are conditioned with a conventional cementing process, the risk of hydrogen gas generation remains due to the radiolysis of water intrinsically present in the cement matrix. The chloride ions from the sea salt may also require attention, as it may aid the $Ca(OH)_2$ dissolution in the cement matrix if it is not sufficiently bound by other phases, resulting in the reduction of the long-term integrity of the material.

The present project proposes a phosphate based cement matrix to develop a new solidification technique for these secondary wastes to restrict the generation of hydrogen gas as well as stabilising ^{90}Sr for safe storage and disposal. While conventional cements rely on the hydration of the raw materials for their solidification, phosphate cement utilises acid-base reactions between acidic phosphate solutions and basic compounds for their solidification [2]. Therefore, it is possible to reduce the water content of the system during solidification, through direct water removal by heating, once the water has initially provided sufficient flowability for handling, and thus restrict the generation of hydrogen gas from the radiolysis of the water. The phosphate minerals found in in nature are flexible in their chemical composition and able to accommodate the ions relevant to the present study. For example, the calcium phosphates in apatite family is known as a good host material for Sr, and can also retain halogens such as fluoride and chloride in the form of $(Ca,Sr)_5(PO_4)_3(F,Cl,OH)$ [3].

3. Outcomes to date

3-1. simulated secondary aqueous wastes

Simulated wastes were synthesised for the concentrated effluent, iron co-precipitation slurry and carbonate salt slurry based on the information of the wastes currently stored at TEPCO Fukushima Daiichi Nuclear Power Plant and the literature. Strontium chloride ($SrCl_2$) was introduced as a cold-tracer. The synthesis established in the present study resulted in a concentration of chloride ions by 3.4 times for the concentrated effluent. The simulated iron co-precipitation slurry and carbonate salt slurry (Fig.1) had a minor deviation in the composition and solid/liquid ratio compared with the literature information, but indicated a good agreement in average particle size and pH, confirming the reasonable properties of simulated wastes.

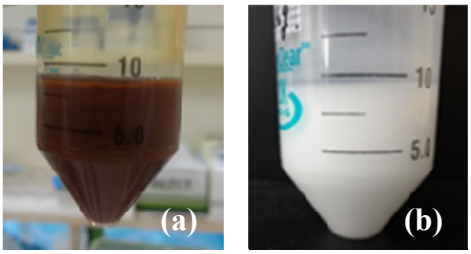

Fig.1 Simulated iron co-precipitation slurry (a) and carbonate salt slurry (b) [4]

3-2. Solidification with minimised water content

Calcium aluminate cement (CAC) and a mixture of sodium phosphates ($Na(PO_3)_n$ and NaH_2PO_4) were used to produce phosphate cement through acid-base reaction, and the effects of water reduction during the curing of phosphate cement system were studied at 35-180ºC for 28 days. Cement pastes were prepared with a water/cement ratio of 0.35, a polyphosphate/cement ratio of 0.4 and a monophosphate/cement ratio of 0.05. Curing at a higher temperature but below 100ºC indicated the favourable outcomes. By curing at 95ºC, it was possible to reduce the water content by 50% in 7 days and 60% in 28 days, as well as reducing the significant cracks commonly observed in the materials cured at lower temperatures (Fig.2). Formation of hydroxyapatite was also detected in the products cured at temperatures ≥ 60ºC.

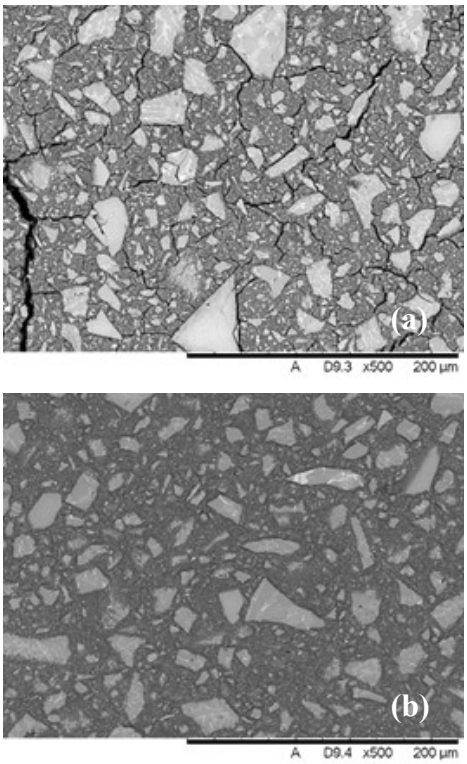

Fig.2 BSE images of phosphate cements: (a) cured at 35ºC and (b) 95ºC [5]

3-3. Effects of irradiation

Effects of irradiation was investigated using ^{60}Co-γ radiation at 40 Gy/h for 7 days (168 hours) [6]. The effects were evaluated based on the amount of H_2 gas, represented by the value $G_\gamma(H_2) = (n_{H2} \times N_A \times 1.6\times10^{-17}) / (R_\gamma \times W)$ where n_{H2} is amount of H_2 (mol), N_A is Avogadro's number (molecules/mol), R_γ is the irradiation (kGy = J/g) and W is the sample weight (g). The unit of 1.6×10^{-17} is (J/100eV). The irradiation during the curing process at 90ºC indicated a gradual decrease in $G_\gamma(H_2)$ in the phosphate cement system, corresponding to the reduction of water content. The $G_\gamma(H_2)$ was also smaller for the samples cured at higher temperatures, confirming a positive effect of reduced water content at higher temperatures. The gamma irradiation did not cause negative impact on the properties of the products both with and without simulated wastes.

3-4. Long-term stability

Phase stability and chemical durability of phosphate cement systems were investigated using leaching tests. Phosphate systems containing simulated secondary wastes were prepared curing at 35 and 90ºC for 7 days. Leaching test was conducted in accordance with ASI/ANS procedure for up to 90 days [2]. CAC without phosphates was also prepared as a reference system. The effect of curing temperature and reduction in water content was small for CAC, both 35 and 90ºC curing resulted in a similar level of leaching results and materials properties. The effects of high

temperature curing and reduction of water content was significant in phosphate system. Leaching of Sr and Ca were reduced, along with that of P, suggesting that they are forming solid phosphate products. Phosphate system indicated a clear ability to immobilise Sr, especially when cured at elevated temperatures.

4. Acknowledgement

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