

**Cement Solidification Method For Intermediate-Level Liquid Waste
Containing Sodium Sulphate (Na_2SO_4) – 9365**

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ABSTRACT

A new cement solidification method for intermediate-level liquid waste containing large amounts of sodium sulphate (Na_2SO_4) has been developed. This method involves two safety concepts for disposal sites: reduction in the amount of sulphate ion (SO_4^{2-}) released from solidified wastes and reduction in the amount of hydrogen gas generated due to radiolysis of the water present in the solidified waste.

In order to eliminate SO_4^{2-} release from solidified wastes, two chemical reactions were important in our solidification method: (1) Barium-compounds ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, etc) were reacted with SO_4^{2-} to form BaSO_4 , and (2) using alumina cement material, SO_4^{2-} was mineralized as ettringite, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$.

Based on leaching tests, the amount of SO_4^{2-} released from the solidified forms into ion exchange water under anaerobic conditions was less than 1×10^{-3} mol/L. Thus, this method should be effective in preventing engineered concrete barrier layers from cracking.

In order to evaluate the amount of hydrogen gas generated from cement solids due to radiolysis of hydrated and non-hydrated water in the solid, gamma-ray irradiation experiments on solidified alumina cement (ALC), solidified ordinary portland cement (OPC), solidified ordinary portland cement blended with blast-furnace slag (OPC-BFS), and synthetic ettringite were performed. As a result, the generation rate of hydrogen gas from ALC was less than those from OPC and OPC-BFS and approximately equal to that from ettringite.

INTRODUCTION

Liquid waste containing large concentrations of sodium sulphate (Na_2SO_4) and radioactive nuclides is generated from elution treatment of the ion-exchanged resin used in nuclear power plants. Although cementification is a convenient method to solidify many types of radioactive waste, it has the following problems: Cracks are generated in surrounding the engineered barriers made from cementitious materials of the repository because of the low-density of the cement mineral, ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), which forms in the presence of sulphate ions. And hydrogen gas generates

from the radiolysis of water in cement solids because of the high radioactivity^{1,2}.

Lovera et al.³ have reported that U-phase (sodium-containing calcium monosulphoaluminate-like phase), ettringite, and thenardite (anhydrous sodium sulphate) form in cement samples made from 25 wt% Na₂SO₄ solution. Because thenardite dissolves easily, pre-treatment to fix sulphate ions is needed to prevent ettringite formation in the repository after disposal. Atkins et al.⁴ have reported that the sulphate ion concentration in a saturated solution is 1×10^{-3} mol/L. It is thought that this value is the upper limit of the sulphate ion concentration of the pore water in the repository.

We have reported that it is possible to decrease the sulphate ion concentration in the liquid phase by the formation of ettringite or barium sulphate before solidification and that, because ettringite is formed, it is effective to use alumina cement as a solidification material⁵. However, since alumina cement hardens rapidly, it is necessary to optimize the cement/additives composition ratio and water/cement ratio in order to use alumina cement.

In this study, a suitable composition of solidified alumina cement (ALC) for fixing sulphate ions was summarized, and the major minerals containing sulphate ions were identified. In addition, gamma-ray irradiation experiments were performed on different cements to determine the amount of hydrogen gas generated from the radiolysis of cementitious water. The hydrogen gas generated from ettringite, which is the major mineral in the ALC matrix, was measured in order to discuss the correlation between the state of water (“hydrated water” or “pore water”) in the solidified materials and the behavior of hydrogen gas generation.

EXPERIMENTAL PROCEDURES

Fixation of Sulphate Ion by Alumina Cement Materials

Effects of Alumina Cement Material

As previously reported⁵, we fixed sulphate ions by forming ettringite or barium sulphate before solidification because the sulphate ion concentration when they are dissolved is 1×10^{-3} mol/L or less. Mixing tests with a sodium sulphate solution were performed to determine the effects of the cement material on sulphate ion fixation. Table 1 shows the compositions of the cement samples.

Table 1. Compositions of cement samples for fixation of sulphate ion

Compound	Composition A	Composition B
25 wt% sodium sulphate (aq)	155 mL	183 mL
Ba(OH) ₂ ·8H ₂ O	113 g	67 g
OPC ^a	279 g	237 g
ALC ^b	0 g	36 g

^a. ordinary portland cement material.

^b. alumina cement material.

Cured and crushed cement samples were set in an atmospheric-controlled glove box filled with argon gas to prevent the effects of carbon dioxide, and ion exchange water was added in a solid/liquid ratio of 1/10. The liquid phase was sampled at 7 or 14 days after addition, and the sulphate ion concentration was measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Suitable Composition for Fixing Sulphate Ions

Since alumina cement material could be useful for sulphate ion fixation, composition studies were performed using a sodium sulphate solution with a concentration similar to actual liquid waste. Table 2 shows the composition for fixing sulphate ions by using alumina cement.

First, 0.5 equivalents of barium hydroxide octahydrate (Ba(OH)₂·8H₂O) was added as a sub-reagent before the solidification process. Second, alumina cement was selected as a mixing material for the formation of ettringite because ALC contains 3CaO·Al₂O₃·6H₂O, which is part of ettringite. In addition, because alumina cement hardens rapidly, aggregates, such as chamotte, were added as necessary.

Table 2. Suitable composition in the case of including some impurities

Compound	Content
25 wt% sodium sulphate (aq)	180 mL
(including Ni, Fe, Li, B etc in order to simulate the waste)	
Ba(OH) ₂ ·8H ₂ O	125 g
ALC ^a	45 g
Chamotte (as an aggregate)	168 g
Other additives ^b	112 g

^a. alumina cement material.

^b. Other additives, such as silica powder and/or alumina powder, and so on, were added as necessary to maintain its workability.

The mixture was poured into a plastic mold and cured for 28 days at room temperature in a water-saturated atmosphere at atmospheric pressure. The cured samples were crushed to <296 μm, and minerals were identified by using X-ray diffraction (XRD) analysis.

Evaluation of Hydrogen Gas Generation — Gamma Ray Irradiation Experiments

Specimen Preparation

In order to determine the hydrogen gas generation rate from solidified cements due to the radiolysis of water, different cement pastes were prepared (listed in Table 3). They were prepared from cement materials, chemical additives, and an aqueous sodium sulphate solution but contained no radionuclides.

Some of the ALC specimens were heated to 120 °C or 200 °C in order to change the water content by evaporating the pore water in the solidified cements.

Table 3. Cement specimens for gamma-ray irradiation experiments

Specimen type	Contents of the solid form	Desiccation ^d
OPC	120 mL water / 250 g OPC ^a	none
OPC-BFS	120 mL water / 250 g OPC-BFS ^b (ca. 45% of OPC)	none
ALC	120 ml water / 250 g materials (mixture of ALC ^c and Ba(OH) ₂ ·8H ₂ O)	desiccation rate from 0% to 90% ^e

^a. ordinary portland cement material

^b. ordinary portland cement material blended with blast-furnace slag

^c. alumina cement material

^d. Desiccation rate of specimens were controlled by adjusting the heating time.

^e. ALC desiccation rate [%]

$$= (\text{mass of water evaporated} / \text{mass of water contained in initial ALC [g]}) \times 100$$

In addition, ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O), which is the major mineral in ALC, was synthesized from the appropriate starting materials. For the irradiation experiments, two types of ettringite samples were prepared: one was “dry-ettringite”, which only had water of crystallization, and the other was “wet-ettringite”, which had excess water to simulate pore water contained in some solidified cements.

Irradiation Experiments

The specimens described in the previous section were ground into a powder, encapsulated in gas-tight glass vessels (inner bulk volume ≈ 35 mL), and set in a Co-60 irradiation apparatus at ca. 10 kGy/hour for 16 h (total dose was ca. 160 kGy). After irradiation, gas chromatography was used to determine the hydrogen gas yield per unit quantity of cement powder or per unit quantity of water.

The hydrogen gas yield was calculated as follows:

$$\begin{aligned} &\text{Hydrogen gas yield (volume (□L) of hydrogen gas/mass (g) of cement)} \\ &= \text{hydrogen gas concentration [ppm]} \times \text{vessel volume [mL]} \\ &\quad / \text{mass of cement specimen weight [g]/1000} \end{aligned} \quad (\text{eq.1})$$

$$\begin{aligned} &\text{Hydrogen gas yield (volume (□L) of hydrogen gas/ mass (g) of water)} \\ &= \text{hydrogen gas concentration [ppm]} \times \text{vessel volume [mL]} \\ &\quad / \text{water content in the specimen [g]/1000} \end{aligned} \quad (\text{eq.2})$$

RESULT AND DISCUSSION

Fixation of Sulphate Ions with Alumina Cement Materials

Leaching tests on the samples listed in Table 1 showed that the sulphate ion concentration in the liquid phase was about 9×10^{-4} mol/L for Composition A and 6×10^{-4} mol/L for Composition B. Since the amount of sulphate ion released into water was reduced by using alumina cement, we concluded that it could be used to fix sulphate ions.

Using the conditions listed in Table 2, an aqueous sodium sulphate solution, prepared to simulate actual liquid waste samples, was solidified. Fig. 1 shows an X-ray diffraction pattern for this sample. In the XRD pattern, barium sulphate (BaSO_4) and ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) were clearly identified.

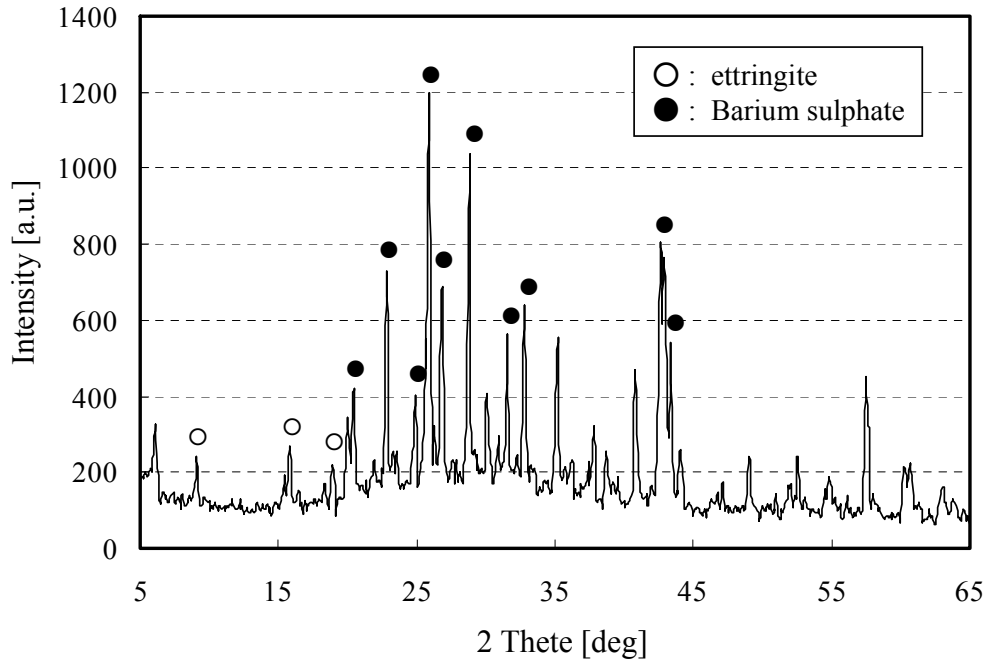
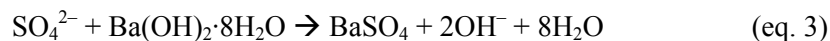


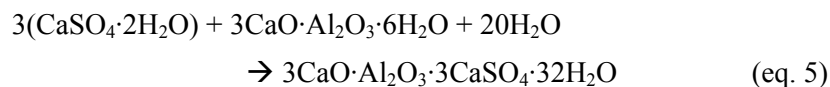
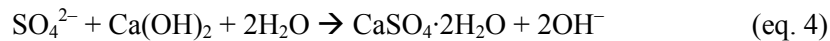
Fig. 1. X-ray diffraction analysis for the solidified alumina cement.

Barium sulphate and ettringite were formed via the following reaction pathway:

<Barium sulphate>



<ettringite>



Since the solubility of barium sulphate is 9.6×10^{-6} mol/L (2.23×10^{-3} g/L at 25 °C ⁶) and that of ettringite is 1×10^{-3} mol/L ⁷, we attributed the sulphate ion concentration measured in this leaching tests to the solubility of ettringite. Thus, since the sulphate ions formed BaSO₄ and ettringite in the solid waste, this method should be useful in preventing engineered concrete barriers from cracking.

Hydrogen gas generation from cement solidified forms

Prior to irradiation experiments, the cement specimens listed in Table 3 were mixed and cured under ambient conditions for approximately one month, and gamma-ray irradiation experiments were performed under the conditions outlined in the EXPERIMENTAL PROCEDURES. Hydrogen gas accumulated in the head space of the glass vessels containing the cements. Hydrogen generation occurred due to radiolysis of the water contained in the cement powder.

Fig. 2 shows the hydrogen gas yield from OPC, OPC-BFS, and ALC (not heated). The rate of hydrogen gas generation from ALC was lower than those from OPC and OPC-BFS.

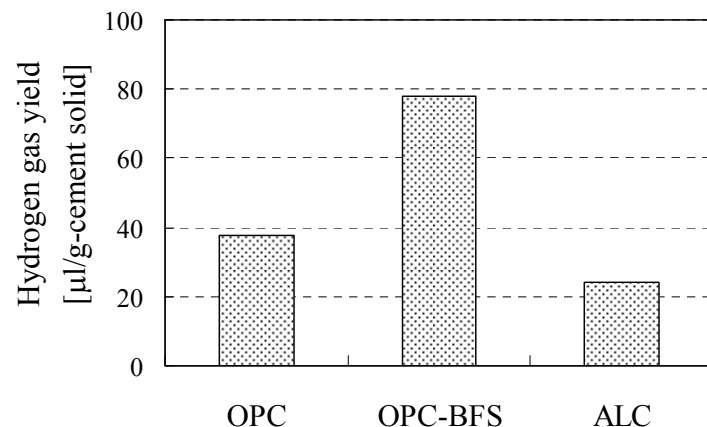


Fig. 2. Hydrogen gas yield of OPC, OPC-BFS, and ALC (total dose \approx 160 kGy).

Fig. 3 shows the correlation between the hydrogen gas yield per unit quantity of cement powder and the ALC desiccation rate. The results indicated that hydrogen gas generation depended on the ALC desiccation rate. Thus, in order to reduce the hydrogen gas generation due to radiolysis of water, it is effective to use alumina cement as a solidification material and to control the volume of cementitious water.

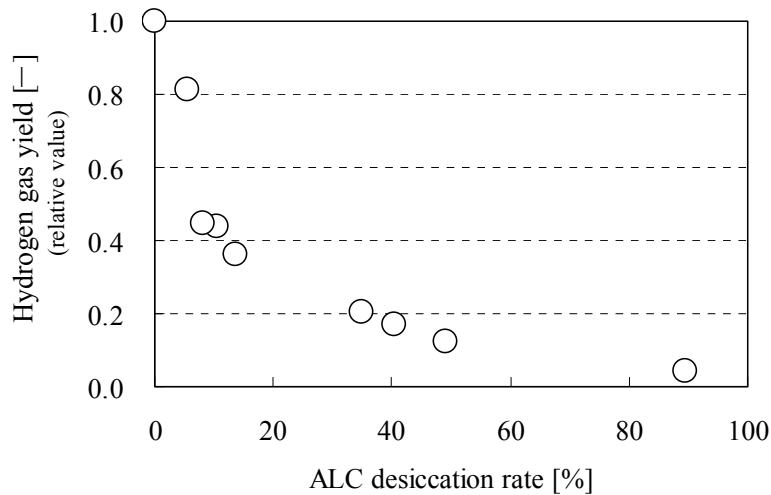


Fig. 3. Correlation between the hydrogen gas yield per unit quantity of cement powder and ALC desiccation rate (total dose \approx 160 kGy).

In addition, Fig. 3 shows that the hydrogen gas generation behavior may depend on the ALC desiccation rate. Hydrogen gas generation decreased rapidly with an increase in the ALC desiccation rate, but at desiccation rates above 20%, the decrease was not as steep.

When the ALC desiccation rate is less than 20%, the excess water in ALC should mainly be “pore water”. On the other hand, when the desiccation rate is greater than 20%, hydrated water should be dominant in cement because almost pore water should be removed by evaporation. Since ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$), which has a hydrated water content of about 46 wt%, is the major mineral in solidified ALC, a significant proportion of water in desiccated cement should come from ettringite. Therefore, the hydrogen gas generation behavior is thought to vary according to the state of the water, i.e., pore water or hydrated water.

Hydrogen gas generation from ettringite

In order to confirm that the hydrogen gas behavior depends on the state of water, gamma-ray irradiation experiments were carried out on two types of ettringite. Prior to the irradiation experiments, ettringite samples were synthesized based on the method reported by Daimon et al.⁸. As described in the EXPERIMENTAL PROCEDURES, dry-ettringite had only hydrated water and wet-ettringite had excess water to simulate pore water. For the irradiation experiments, \sim 9 g of dry-ettringite was prepared so that the water content was \sim 4.1 g. The water content of wet-ettringite, adjusted by dropping water (1g) onto 9 g dry-ettringite, was about 5.1 g (= hydrated water (4.1 g) + added water (1 g)).

Fig. 4 shows the hydrogen gas yield per unit quantity of water of dry-ettringite, wet-ettringite, and heated ALC.

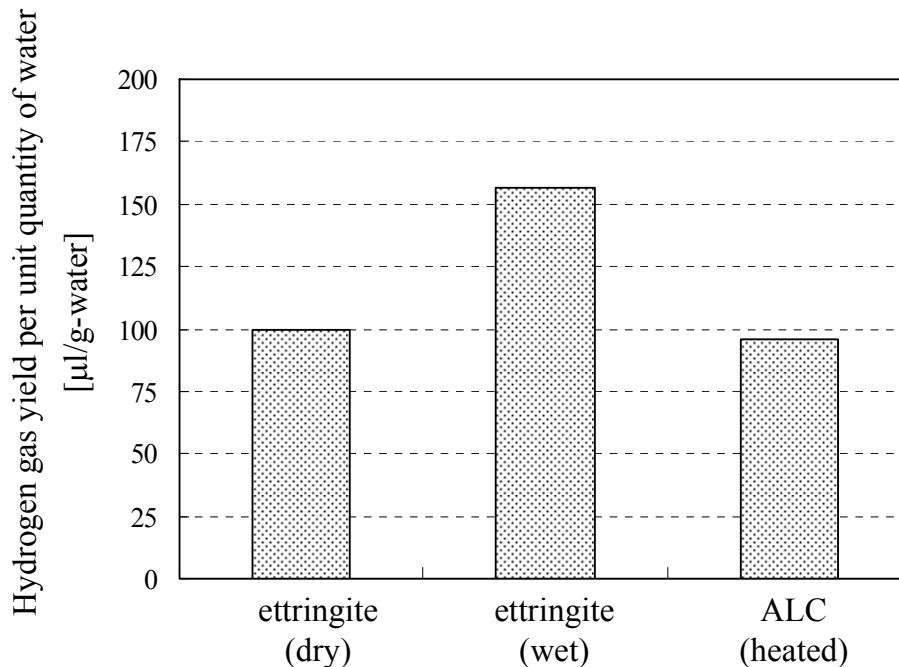


Fig. 4. Hydrogen gas yield of dry-ettringite, wet-ettringite, and heated ALC (total dose ≈ 160 kGy).

The hydrogen yield of dry-ettringite and wet-ettringite were different. Thus, it is thought that hydrogen gas yield (per unit quantity of water) is affected by the state of water. In addition, pore water contributes more to hydrogen gas generation than hydrated water does.

Fig. 4 also shows a comparison of the hydrogen gas yield (per unit quantity of water) from ettringite and heated ALC. Since hydrogen gas generation from heated ALC was approximately equal to that from dry-ettringite, the state of water in heated ALC may be similar to that in dry-ettringite. From these findings, hydrogen gas generation from cements can be reduced effectively by using an alumina cement material.

CONCLUSION

In this study, for the purpose of developing a new cement solidification method for intermediate-level liquid waste containing large amounts of sodium sulphate (Na_2SO_4), suitable mixing conditions were studied. It was found that by using $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ as a sub-reagent and alumina cement material as a mixing substance, it is possible to eliminate the release of sulphate ions from solidified wastes. In addition, Co-60 gamma-ray irradiation experiments were performed on cementitious solids and ettringite to evaluate the hydrogen gas generation behavior. It was found that the hydrogen gas yield depended on the ALC desiccation rate. In other words, hydrogen gas generation was reduced by ALC drying. In

addition, the hydrogen gas yield was affected by the state of water in the solid, meaning pore water contributes to hydrogen gas generation more than hydrated water does.

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