

THE MECHANISMS OF ALKALI SILICA REACTION IN MORTARS IMMERSSED IN SODIUM SULPHATE AND PHOSPHATE SOLUTIONS

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ABSTRACT

The mechanism of alkali-silica reaction (ASR) in concrete induced by sodium salts released from radioactive waste materials was investigated. The expansion behavior of mortar bars immersed in sodium sulfate and sodium phosphate was compared. ASR occurred for specimens in sodium sulfate solution, but ASR did not occur for specimens immersed in sodium phosphate solution. Hydroxyl-apatite, which is a hard and dense compound, was formed in the surface layer of the specimens and therefore, no expansion was observed, regardless of solution concentration.

Keywords: ASR, sodium salts, mechanisms of expansion, radioactive waste materials, underground facilities

1. INTRODUCTION

Approximately 20% of electricity consumed in Japan is generated by nuclear power plants. For the safe disposal of the waste generated, various underground disposal facilities for short and long-lived radioactive waste materials are currently under development and/or construction. According to the guidelines, these facilities have to be built and placed at considerable deep depths, underground over 300m. Considering the severe environmental conditions at such depths and the fact that the half-life of some radionuclide are in the range of thousand years, the durability of concrete structures and human and environmental safety becomes a top concern [1].

The effects of hazardous substances supplied from external sources have been investigated through diffusivity and permeability tests. However, for those substances released from the radioactive waste materials, their type and concentration were not clearly understood [2],[3].

This research refers to a comparative study of ASR mechanisms in concrete caused by sodium sulfate and sodium phosphate solutions. Both substances are present in radioactive waste materials.

The primary research's objectives included:

- The assessment of the deleterious effect of sodium sulfate and sodium phosphate solutions in concrete.
- The characterization of the type of hydration products.

- The characterization of ASR gel formation and density of microcracks.
- Mapping of alkalis and other chemical components to assess their distribution in selected specimens.

While aiming at explaining the mechanisms of ASR in concrete immersed in sodium sulfate and sodium phosphate, the present study intends to contribute to a better understanding of the durability of concrete structures and cementitious materials.

2. EXPERIMENTS

2.1 Materials

As reactive aggregate, crushed calcined flint (CF) with the grain size ranging from 0.6mm to 2.5mm and main reactive component as cristobalite, produced from industrial raw materials in England was used. Regarding the chemical method according to JIS A1145-2007, the dissolved silica content (Sc) and the reduction in alkaline concentration (Rc) are 1063 mmol/l and 70mmol/l, respectively. Because this flint aggregate contains only crystalline α -cristobalite as the reactive mineral component, its interaction with hydroxyl ion (OH⁻) released in the pore solution enables a simple reaction process, which is useful to understand the basic ASR concept. Crushed limestone sand with 0.15mm to 5.0mm particle size was used as a non-reactive aggregate and considering the pessimum mixing ratio to this calcined flint, the mass ratio of calcined flint and crushed limestone sand was set at

Table 1 Chemical compositions of calcined flint (Wt%)

Material	Chemical Composition									
	Ig. Loss	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	CuO	SO ₃	Na ₂ O	K ₂ O	Total
CF	0.14	95.64	1.23	1.14	0.14	0.03	1.81	N/D	N/D	99.99

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25%:75%. The ordinary Portland cement (T Corporation, Ltd., density: 3.16 g/cm³, Blaine specific surface area: 3300 cm²/g) was used. The alkali content of cement was 0.42%. The chemical compositions of calcined flint aggregate are shown in Table 1.

2.2 Test Methods

The expansion test in accordance with ASTM C1620, which is the test method that promotes ASR from an external alkali source (1N NaOH solution) was applied for mortar bars immersed in sodium sulfate and sodium phosphate solutions. The mortar bars were 25mm×25mm×285mm in size, aggregate/cement ratio: 2.25 and W/C ratio: 0.48. The type and concentration of sodium salt solutions used in this experiment are shown in Table 2. The concentration of such substances in the radioactive waste materials is approximately 3.5N, therefore, a lower and upper values were selected. The sample preparation and measurements were performed under controlled room temperature of 20 °C and 60% R.H. The expansion ratio of mortar bars was measured according to the test procedures.

On the other hand, various analyses were carried upon test completion: the formation of ASR gel and the density of micro cracks were observed by polarizing microscope for thin section of mortar bars. Reaction products and calcium hydroxide were qualitatively evaluated by X-ray diffraction analysis (XRD) and differential scanning calorimetry (DSC). Furthermore, EPMA analysis was performed for mapping alkalis and various chemical components in selected specimens.

3. RESULTS

3.1 Expansion Ratio of Mortar Bars Immersed in Sodium Salt Solutions

The expansion behavior of mortar bars immersed in 1N and 5N sodium salt solutions is shown in Figs. 1 and 2, respectively. In both cases, specimens in sodium phosphate (NaH₂PO₄) did not expand at all, which suggests no ASR occurrence. As for sodium sulfate (Na₂SO₄), early expansion was observed and surpassed 0.4% in just 7 days. Then, the degree of expansion slightly decreased but total expansion ratio reached 0.5% over the experimental term. The magnitude order for 5N was slightly lower than 1N. However, the expected expansion ratio should be directly proportional to solution concentration. Possible reasons are not clearly understood yet and to clarify whether this experimental data is correct or not, similar experiments are currently underway.

Table 2 Type and concentration of sodium salt solutions

Concentration	Type of solution
1N (Reference)	Sodium hydroxide (NaOH)
1N and 5N	Sodium sulfate (Na ₂ SO ₄)
	Sodium phosphate (NaH ₂ PO ₄)

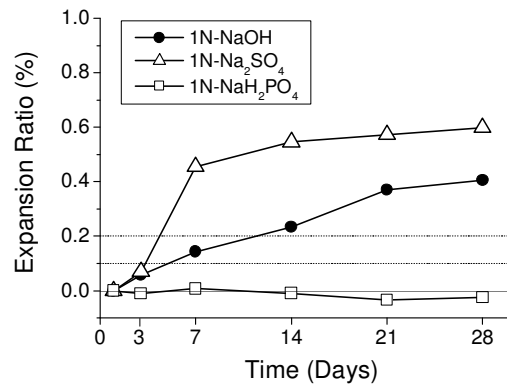


Fig.1 Expansion ratio of mortar bars immersed in 1N sodium salt solutions

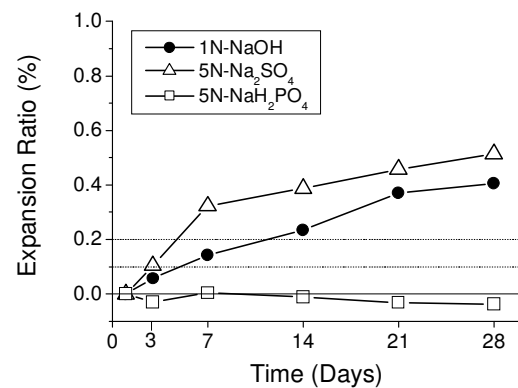


Fig.2 Expansion ratio of mortar bars immersed in 5N sodium salt solutions

3.2 Cracking in Mortar Bars Immersed in Sodium Salt Solutions

Fig. 3 shows the images of thin sections of mortar bars observed by polarizing microscope. According to the quantity of ASR gel and development of cracking, the degree of deterioration of internal microstructure is divided into four levels, as shown in the Table 3. The reaction level for mortar bars immersed in 1N and 5N sodium phosphate solutions was 1, 1N sodium hydroxide was 2, 1N and 5N sodium sulfate was 3.

Table 3 Grading standard of ASR degree of deterioration of thin section samples

Level	Cracking and state of ASR gel formation in thin layer section
1	There is no ASR reaction
2	Occurrence of minor cracks around the aggregate and formation of ASR gel
3	Development of cracking from the aggregate to cement paste phase and formation of ASR gel
4	Occurrence of large cracks and continual formation of a wide crack net, formation of ASR gel and invasion of ASR gel into air voids

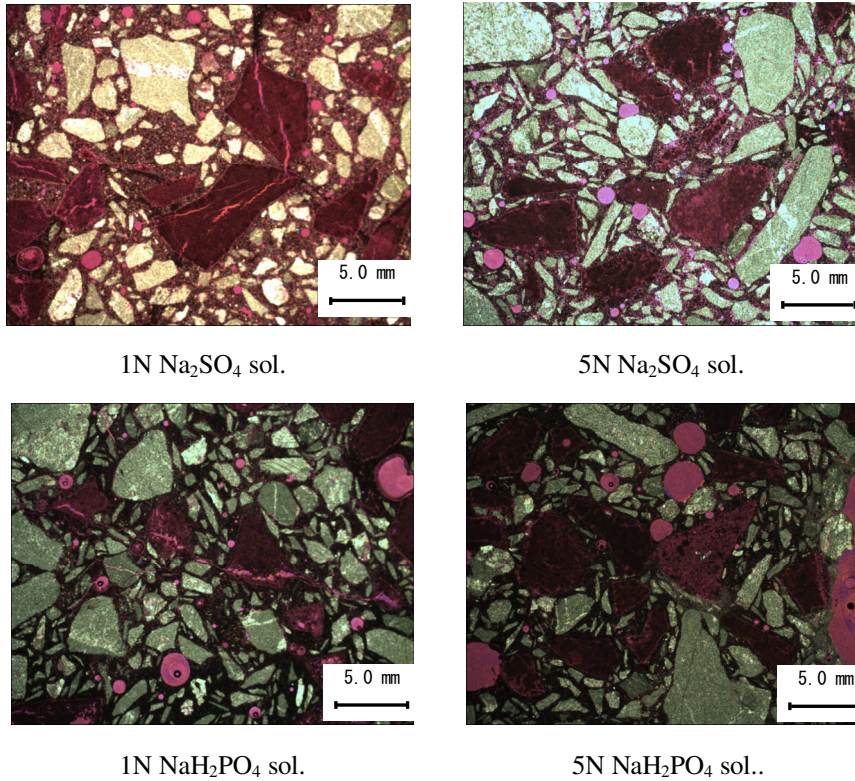


Fig.3 Polarizing microscope images for thin sections of mortar bars immersed in 1N and 5N sodium salt solutions (curing time: 28 days)

The expansion ratio of mortar bars at 0% and 0.5% corresponds to reaction level 1 and reaction level 3, respectively, which agrees with the degree of cracking observed by polarizing microscope.

3.3 Differential Scanning Calorimetry Analysis (DSC)

DSC curves of mortar bars immersed in 1N and 5N sodium salt solutions at the age of 28 days are shown in Figs. 4, 5 and 6. When immersed in sodium phosphate solutions, as shown in Figs. 4 and 6, a broad exothermic peak of calcium phosphate (CP) around 250°C is observed. At 460°C pronounced peaks of calcium hydroxide (CH) are also observed. On the other hand, for specimens immersed in sodium sulfate

solutions, as shown in Figs. 5 and 6, small endothermic peaks of ettringite (E_t) at 110°C and gypsum (G_p) at 130°C were observed. On the other end, as the result of external sodium sulfate supply, a sodium-substituted AF_t phase (U-phase), which can induce deleterious effects through its secondary formation can also be occur. The endothermic peak of calcium hydroxide (CH) was smaller than those of corresponding solutions (same concentration) of sodium phosphate. Furthermore, a considerably large endothermic peak of calcium carbonate at 800°C was observed in all samples, but it is not the result of carbonation of calcium hydroxide, it is rather something related to the mixture of limestone crushed sand which was used as non-reactive aggregate.

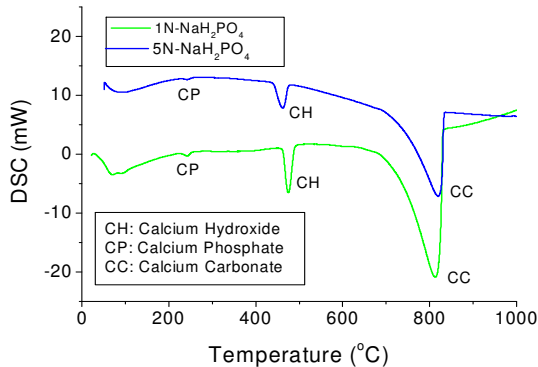


Fig.4 DSC curves of mortar bars immersed in 1N and 5N sodium phosphate solutions (curing time : 28 days)

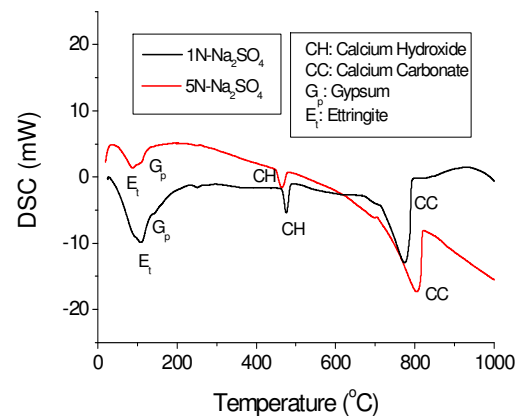


Fig.5 DSC curves of mortar bars immersed in 1N and 5N sodium sulfate solutions (curing time : 28 days)

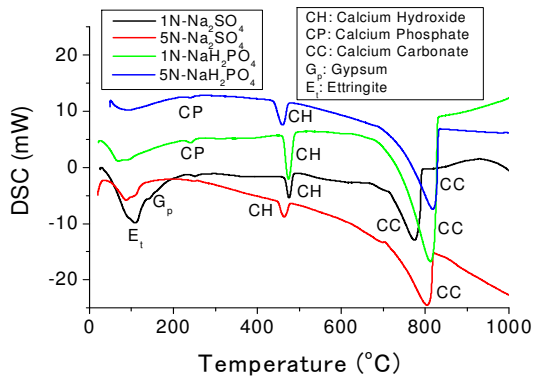


Fig. 6 DSC curves of mortar bars immersed in 1N and 5N sodium sulfate and sodium phosphate solutions (curing time: 28 days)

3.4 X-ray Diffraction Analysis

The X-ray diffraction diagram of specimens immersed in 1N and 5N sodium sulfate and sodium phosphate at the age of 28 days are shown in Figs. 7, 8 and 9. In specimens immersed in sodium sulfate solution, as shown in Figs. 7 and 8, ettringite (E_t) peaks were observed at 8.9° , 15.8° and 22.9° . As for specimens in sodium phosphate, shown in Figs. 7 and 9, such peaks are not clear. Di-hydrated gypsum (G_p) peaks were detected at 11.7° in those of sodium sulfate solution and calcium phosphate peaks were observed at 22.2° in specimens immersed in sodium phosphate. Sharp peaks of calcium hydroxide at 18.1° and 34.1° were observed in all specimens. The same was also noted for calcium carbonate peaks at 29.3° and 39.3° . These results are in agreement with those obtained by Differential Scanning Calorimetry analysis, since similar crystalline phases were observed in both analysis.

3.5 EPMA Analysis

In order to further understand the non occurrence of ASR in specimens immersed in sodium phosphate, electron probe microscope analysis (EPMA) of thin sections was conducted for both, 1N and 5N samples. The mapping imagery of silica (Si), sodium (Na) and phosphorous (P) in the cross-section of specimens immersed in 1N and 5N solutions is shown in Fig. 10. EPMA results revealed that, while the silica (Si) content is high and although low, sodium (Na) is fairly distributed across the sample, alkali atmosphere is not generated, thereby no ASR occurrence was observed. It is also noted that the concentration of phosphorous (P) is higher along the boundary area. This fact may be associated with the formation of calcium phosphate, which is a very hard, dense and relatively insoluble substance. Evidence of this occurrence is the rigidity of the specimens immersed in sodium phosphate solutions, after the completion of the expansion test: in the process of preparing the samples for the various analysis, it was very difficult to break, cut or grind the specimens. A very hard surface layer of more than 5mm was formed around the specimens.

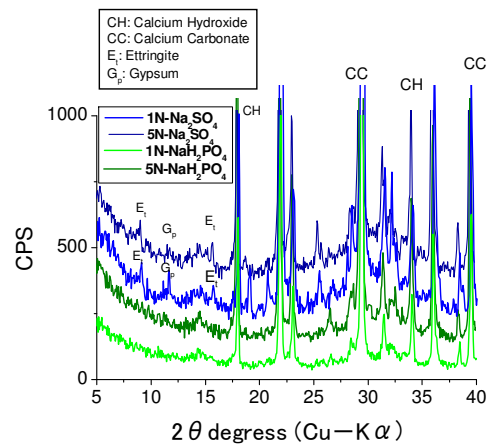


Fig.7 XRD curves of mortar bars immersed in 1N and 5N sodium sulfate and sodium phosphate solutions (curing time: 28 days)

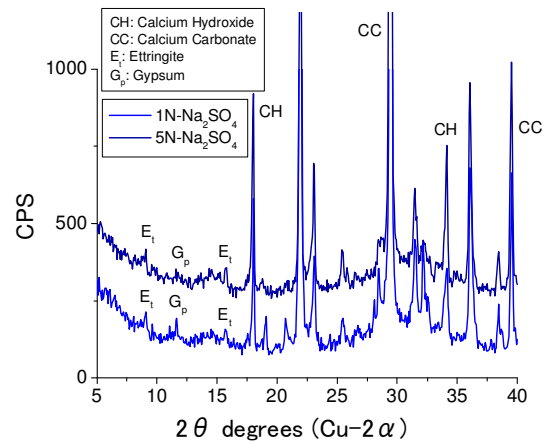


Fig.8 XRD curves of mortar bars immersed in 1N and 5N sodium sulfate solutions (curing time: 28 days)

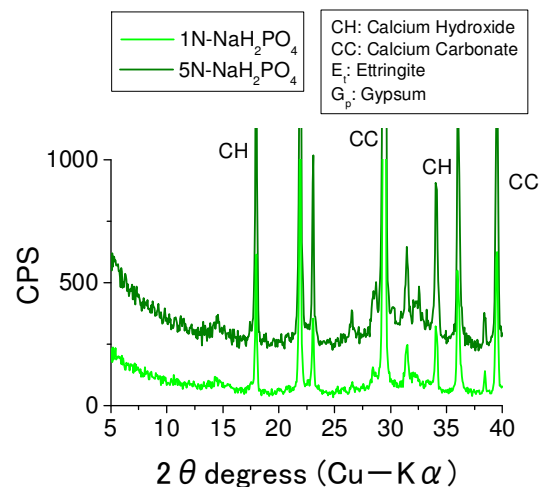


Fig.9 XRD curves of mortar bars immersed in 1N and 5N sodium phosphate solutions (curing time:28 days)

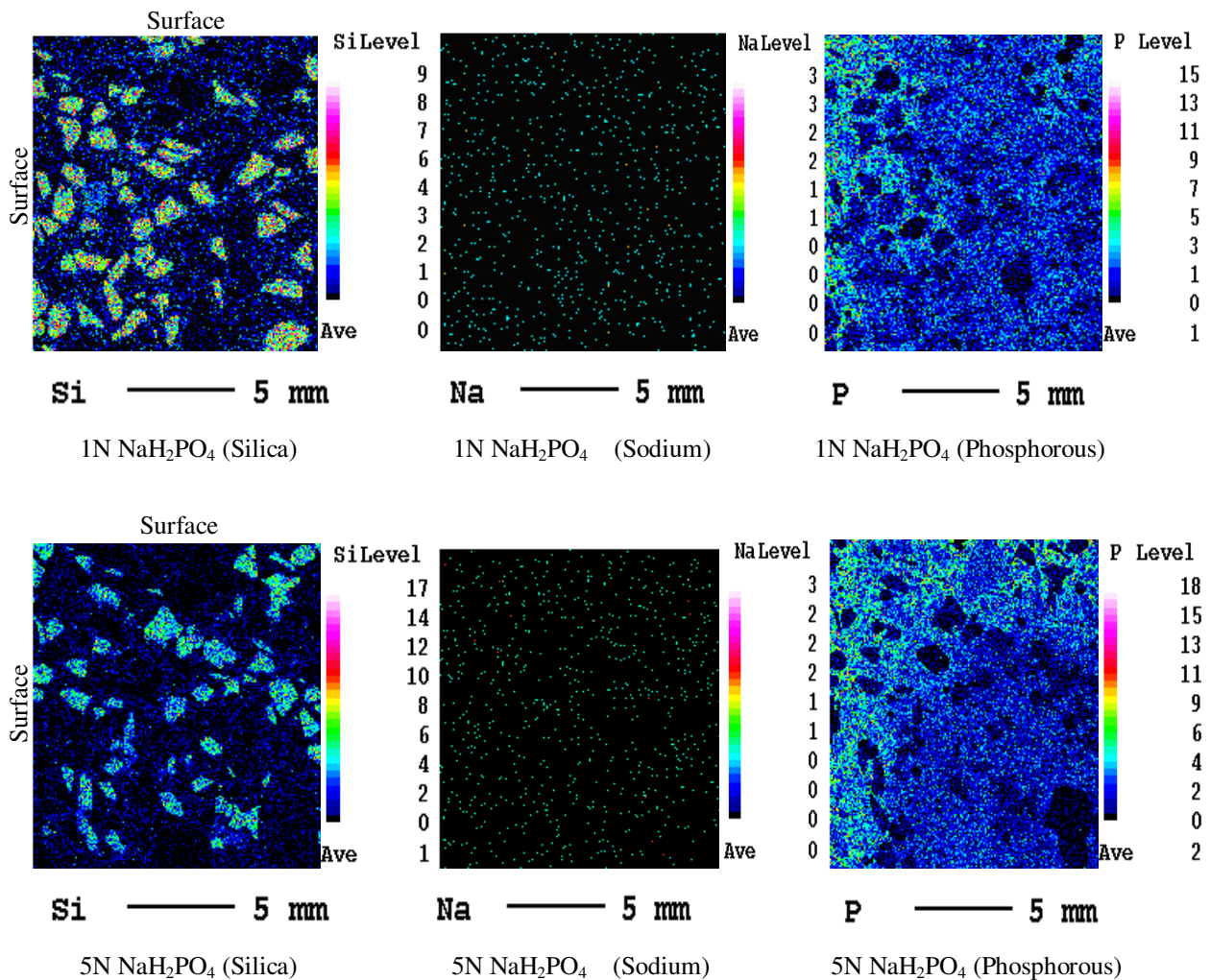


Fig.10 Mapping imagery of silica, sodium and phosphorous of mortar bars immersed in 1N and 5N sodium phosphate solutions obtained by EPMA analysis (curing time : 28 days)

4. DISCUSSION

4.1 Expansion Ratio of Mortar Bars Immersed in Sodium Salt Solutions

In the case of specimens immersed in sodium sulfate solutions, it is considered that ASR-related expansion occurs due to the interactive reaction between the alkaline salt, which contains sodium ions, and unhydrated C₃A phase and other aluminates in the mortar. On the other hand, the interaction between the dissociated sodium ion (Na⁺) and calcium hydroxide (Ca(OH)₂) contributes to the rising of concentration of alkali hydroxide (NaOH) concentration in the pore solution as high as the pH level of 14 [5]. As per specimens immersed in sodium phosphate, no expansion and no ASR was observed. Various factors maybe associated with this phenomenon. Phosphate ion is strongly electronegative and prone to attract any cation. Therefore, it will compete with silica gel for the alkalis. Because sodium (Na⁺) forms mostly soluble salts, phosphate ion will strongly react with calcium hydroxide (CH) and form hydroxy-apatite (Ca₁₀(PO₄)₆(OH)₂) which is a hard and relatively insoluble substance. According to a study conducted by

Hudec P. *et al*, sodium phosphate could be also effective in preventing ASR expansion [6].

4.2 Cracking in Mortar Bars Immersed in Sodium Salt Solutions

In the images obtained by means of polarizing microscope, there are no cracks in those specimens immersed in sodium phosphate solutions, as shown in Fig. 3. According to Yamato *et al* [5], in the case of specimens immersed in sodium sulfate, microcracking generation is accelerated when alkaline solution easily penetrates into the flint particle itself, due to its porosity and microcracks. Therefore, from the early stage of immersion, when alkali hydroxide solution interacts with the reactive component of the particle, ASR occurs altogether. After that, the quantity of ASR gel formed increases, and ASR gel keeps expanding out the cement paste phase through micro cracks developed around the boundary of the particles and other aggregates.

4.3 Differential Scanning Calorimetry Analysis

In the specimens immersed in sodium phosphate, the peak at 250 °C corresponds to the liberation of two-hydroxyl groups, which confirm their presence

along with calcium phosphate (CP) in the form of hydroxyl-apatite. Hydroxyl-apatite has 40% of calcium and 18.5% of phosphorous in composition, with hexagonal ion crystals. On the other hand, in the specimens immersed in sodium sulfate solutions, the gypsum peak is due to loss of approximately 75% of its hydrate water, which prompts the formation of hemihydrate [7]. In addition, CH peaks significantly decreased, indicating that calcium hydroxide was consumed by ASR to a large extent [4],[5]. The reduction of CH was pronounced for specimens immersed in 5N solution, which indicates that ASR is promoted in the case of high concentrated solutions.

4.4 Durability Considerations

The various analysis conducted in this research have explained the mechanisms of ASR in concrete caused by sodium sulfate solution. Although not harmful and even enabling the formation of a dense structure in the early stages, the long-term effects of phosphates in concrete should be further investigated. According to Nonat et al., when phosphates are added to tricalcium silicate (C₃S), the increasing adsorption of phosphorous ion slows down the dissolution of C₃S [8]. According to Nurse, cited by Nawa et al. [9], excessive phosphates tend to reduce the concrete strength in the long term.

5. CONCLUSIONS

The expansion behavior of mortar bars immersed in sodium sulfate and sodium phosphate solutions have been investigated. From the various analysis conducted, the following conclusions are drawn:

- (1) ASR occurred for specimens immersed in sodium sulfate solution. The expansion of mortar bars mostly occurred in the first 7 days of experiments and slowed down afterwards.
- (2) ASR did not occur for specimens immersed in sodium phosphate solution. Hydroxy-apatite, which is a hard and dense compound was formed in the surface layer of the specimens and no expansion was observed, regardless of solution concentration.
- (3) Cracking was observed in specimens immersed in sodium sulfate and a deterioration level 3 was confirmed. No cracking was observed in the case of specimens immersed in sodium phosphate solution, thereby, deterioration level 1 was confirmed.
- (4) The expansion ratio of mortar bars varied depending on the type of sodium salts penetrating from the external source. Therefore, in 1N concentration conditions, the following sequence of increasing expansion ratio was observed: sodium phosphate << sodium hydroxide < sodium

sulfate.

- (5) There was a plain agreement among the results of the various analysis conducted
- (6) Although not harmful in the early stages, the long-term effects of phosphates in concrete should be further investigated, for assurance of the durability of radioactive waste facilities.

REFERENCES

- [1] K. Kamei et al.: TRU Waste Disposal: Research and Development of Disposal Technology, 2007 Annual Report, Japanese Atomic Energy Agency-Research and Development Directorate, 2008 (in Japanese).
- [2] M. Mihara, K. Torii: Research on the Porosity of Low Alkali Hardened Cement Paste and the Apparent Diffusion Coefficient of Chloride Ion, 2009 Annual Report, Japanese Atomic Energy Agency-Research and Development Directorate, 2009 (in Japanese).
- [3] K. Haga et al: The Deterioration of Leaching Hardened Cement Paste by Water Flow Test with Centrifugal Force Method, Journal of the Japan Atomic Energy Society, Vol.1, No.1, 2002, pp.20-29 (in Japanese).
- [4] S. Diamond et al.: Chemical Aspects of Severe ASR Induced by Potassium Acetate Airfield Pavement De-Icer Solution, Proceedings of Marc-Andre Berube Symposium on Alkali-Aggregate Reactivity in Concrete, 2006, pp.261-279.
- [5] H. Yamato, T. Liu, T. Omura, K. Torii: Mechanisms of ASR Deterioration Caused by Alkaline Salt Solution at High Concentration, Cement Science and Concrete Technology, No.63, 2009, pp.393-399 (in Japanese).
- [6] Hudec, P., Banahene, N., "Chemical Treatments and Additives for Controlling Alkali Reactivity", Cement & Concrete Composites, No 15, 1993, pp. 21-26
- [7] Ramachandran, V.S., Paroli, R.M., Beaudoin, J.J., Delgado, A.H., "Handbook of Thermal Analysis of Construction Materials", Construction Materials Science and Technology Series, 2002
- [8] Benard, P., Garrault, S., Nonat, A., Cau-dit-Coumes, C., "Influence of Orthophosphate Ions on the Dissolution of Tricalcium Silicate", Cement and Concrete Research, Vol.38(10), pp.1137-1141, 2008
- [9] Nawa, T., Kurumisawa, K., "Sustainable Development in Construction", Proceedings of the 2nd International Conference on Durability of Concrete Structures-ICDCS2010, pp.211-217, 2010