

pH Behavior of Hydrated Low-Alkalinity Cement[†]

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In the present paper, pH of the aqueous solution contacting hydrated low-alkalinity cement was measured and the chemical mechanism to maintain the moderate pH was discussed.

The low-alkalinity cement was prepared by mixing $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ containing clinker, anhydrite and blast furnace slag. Solubility of hydrated cement paste was measured to investigate the effect of blast furnace slag. The Measured pH of the liquid phase contacting hydrated cement paste was in the range of 10.4 to 12.3 after 66 weeks. The composition of the hydrated cement paste was estimated from the chemical composition of the cement. The Measured pH of the liquid phase was compared with that evaluated from the chemical composition of hydrated cement and from the solubility data of calcium silicate hydrate (C-S-H gel). It was found that the measured pH agrees well with the evaluated pH.

Keywords: low-alkalinity cement, cement, radioactive waste disposal, pH, C-S-H gel, ettringite

本研究は、低アルカリ性セメントペーストを浸漬した液相の pH 測定結果と pH 発現メカニズムについて報告している。

低アルカリ性セメントは、 $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ を含むクリンカー、セッコウと高炉スラグを混合して作製した。水和したセメントペーストの溶解度に対する高炉スラグの影響を検討した。水和セメントペーストを66週間浸漬した液相の pH は、10.4 から 12.3 であった。水和セメントペーストの水和物組成をセメントの化学組成から評価した。測定した液相の pH は、評価された水和セメントの化学組成とカルシウムシリケート水和物 (C-S-H ゲル) の溶解特性から評価した pH と比較した。測定した pH は、評価した pH の値とよく一致することが確認された。

Keywords: 低アルカリ性セメント, セメント, 放射性廃棄物処分, pH, C-S-H ゲル, エトリンガイト

1 Introduction

Cementitious materials have been used in radioactive waste disposal systems. One of the most important features of cement materials is the ability to establish high pH of the pore water. High pH (higher than 10) is beneficial because, in this condition, the solubility of many elements, especially TRU, in aqueous solution is very low [1]. In order to evaluate the long-term safety of a disposal system, it is most important to predict the migration behavior of radionuclides. The migration behavior of nuclides is greatly influenced by the chemical environmental conditions such as pH. Hence, it is necessary to understand the variation of pH of the pore water with time.

In a radioactive waste repository, the pH of the pore water in cement materials will decrease with time as the chemical constituents responsible for its maintenance are leached away. Initially the pH of the pore water in hydrated ordinary portland cement is greater than 13 due to dissolution of sodium, potassium and calcium hydroxides into the liquid phase. When sodium and potassium hydroxides have been leached out, the pH is controlled by the dissolution of calcium compounds from the hydrated cement. The solubility of the calcium hydroxide is the highest among the components of hydrated cement. However, it is difficult to keep the pH of a radioactive

waste repository high for a long term depending only the dissolution of calcium hydroxide [2]. It is necessary to develop cement capable of keeping moderate pH (at the range of 10 to 12.5) for a long term.

Recently, low-alkalinity cement has attracted attention [3], because it may maintain the moderate pH required to the low solubility of many element for a long time. Low-alkalinity cement has also been attractive because it inhibits the interaction of the leachate from the cement and the surrounding material such as bentonite.

Lea reported that final pH in the liquid phase in contacted with high alumina cements is 11.7[4]. On the other hand, Atkins et al. claimed that OH^- concentration in the leached solution from $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, which is the tentative hydrate from high alumina cement, is 23.4mM [5]. This means that equilibrium pH in the solution in contacts with high alumina cement is 12.4. Long time behavior of pH in the aqueous solution contacting hydrated cement and the mechanisms for establishing pH in high alumina cements have not been sufficiently studied. Moreover, active methods to control pH have not been suggested.

In the present paper, we measured the pH of an aqueous solution in contact with low-alkalinity cement, which mainly produces ettringite (Aft), a component that keeps the pH lower than does $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ -generating high alumina cement, and discussed the chemical mechanism for maintaining a moderate pH.

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2 Experimental

2.1 Design and preparation of low-alkalinity cement material

The pH of pore water in the portland cement is closely related to the dissolution characteristics of hydrates which are formed by the hydration of the cement. Components of hydrated cement include AFt, gehlenite hydrate, tobermorite, hydrotalcite and calcium silicate hydrate (C-S-H gel) of a low Ca/Si mole ratio, etc. The pH of pore water in these hydrated components is relatively low [5,6]. It is known that the pH decreases with decreasing Ca/Si mole ratio especially with respect to C-S-H gel [7,8]. This suggests the possibility that the pH of pore water in hydrated cement depends on the coexistence of one of the above mentioned cement hydrates and that control of the Ca/Si mole ratio of C-S-H gel will establish the pH desired. In the present work, the combination of AFt and C-S-H gel, the latter with suitable Ca/Si mole ratio, was selected. In order to actually modulate pH conditions, properly designed clinker with admixture must be prepared.

The clinker was prepared from the mixture of technical grade chemicals (as principal raw materials were SiO_2 , Al_2O_3 , Fe_2O_3 , $\text{Ca}(\text{OH})_2$ and CaSO_4) by baking at 1570K with a small rotary kiln (0.6m inside diameter and 7m length). After pulverizing with a ball mill anhydrite was added (clinker: anhydrite ratio = 73.9: 26.1 weight). Blaine's specific surface area of clinker was about $350\text{m}^2/\text{kg}$. Blast furnace slag (BFS) was added as admixture with the mixing ratio of 0 ~ 80% (weight %). In order to control the amounts of Ca and Si in cement, BFS was added as admixture. The chemical composition of clinker, anhydrite and BFS is shown in Table 1 and the chemical composition of low-alkalinity cement is shown in Table 2.

To prepare the hydrated low-alkalinity cement, the cement paste (water : low-alkalinity cement ratio = 0.667: 1 weight) was molded into a diameter of $5.0 \times 10^{-2}\text{m}$ and length of $1.0 \times 10^{-1}\text{m}$. This hydrated cement was cured in water of 293K for 5 months and then pulverized. After this, identification of the crystalline in solid phases was carried out by X-ray diffractometry.

All chemicals were reagent grade and used without further purification.

2.2 Experimental procedure

After curing, hydrated cement samples were pulverized to particles of less than $1.2 \times 10^{-3}\text{m}$ diameter. The dissolution test was performed by sealing 10g of hydrated cement in a polyethylene container together with 50g of ion exchanged water. The dissolution test was carried out in the atmosphere and repeated for each of the pre-decided periods. The container was allowed to stand in the thermostatic chamber at 293K for a pre-decided period (4,13 and 66 weeks). After each

Table 1 Chemical composition of clinker, anhydrite and BFS

Material	Chemical composition (mol/kg)							
	Si	Al	Fe	Ca	Mg	S	Na	K
clinker	0.97	5.39	0.19	7.54	0.41	2.70	-	-
anhydrite	-	-	-	7.35	-	7.34	-	-
BFS	5.25	2.60	0.01	7.52	1.60	0.26	0.11	0.036

Table 2 Chemical composition of low-alkalinity cements

Sample No.	BFS content (%)	Chemical composition (mol/kg)					
		Si	Al	Fe	Ca	Mg	S
1	0	0.72	3.98	0.14	7.49	0.30	3.91
2	20	1.63	3.78	0.12	7.49	0.57	3.17
3	40	2.53	3.44	0.08	7.49	0.82	2.45
4	60	3.44	3.16	0.06	7.51	1.09	1.71
5	80	4.34	2.88	0.04	7.51	1.34	0.99

elapsed time, the solid phase was separated from the liquid phase by centrifuge (3500rpm,10min). The pH of the liquid phase was measured by the neutralization titration method and the chemical composition of the liquid phase was measured using ICP spectrometry. The solid phase was pulverized after drying under vacuum, and the crystalline in solid phase was identified by means of XRD.

3 Results and discussion

3.1 Identification of hydrated low-alkalinity cement

The X-ray diffraction pattern of the hydrated cement before dissolution test containing various proportion of BFS is shown in Fig.1.

The hydrated low-alkalinity cement which had been cured for 5 months showed qualitatively the same X-ray diffraction peak positions regardless of BFS content; its main crystalline in solid phase was AFt. It was found that the AFt diffraction intensity increased with decreasing BFS contents. In the samples with BFS content less than 40%, anhydrite ($2\theta = 31.36$) was observed. Formation of $\text{Ca}(\text{OH})_2$ ($2\theta = 34.09$) and phase transformation of AFt to monosulphate (AFm $2\theta = 9.91$) which are observed in the hydration reaction of ordinary portland cement were not observed [9]. From our previous study [10], it could be considered that the hydrated cement used in this work contained AFt, C-S-H gel, $\text{Al}(\text{OH})_3$, unhy-

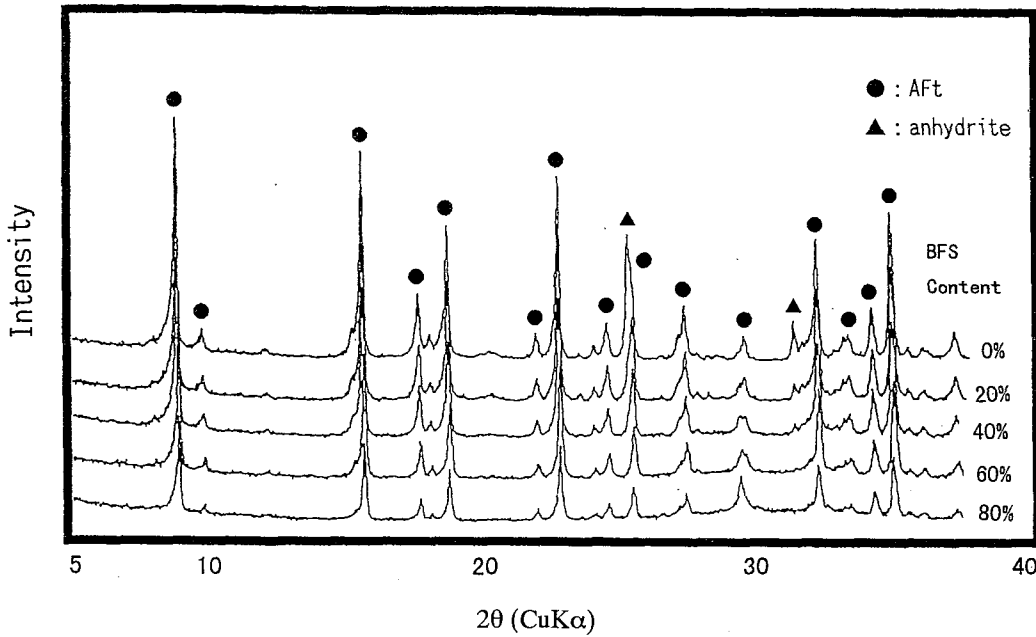


Fig.1 X-ray diffraction pattern of the hydrated low-alkalinity cement before dissolution test containing various proportion of BFS

hydrated belite ($2\theta = 31.99$), anhydrite ($2\theta = 25.44, 31.36$) and BFS. Due to the same clinker composition and the result of the X-ray diffraction test on the crystalline phase of its hydrate, the hydrated low-alkalinity cement used is considered to form the same hydrate after undergoing the same hydration process as already reported for low-alkalinity cements [10].

3.2 pH for various BFS contents and various immersion times

The measured pH of the liquid phases at immersion times of 4, 13 and 66 weeks, have been plotted on Fig.2 against the initial amount of BFS admixture. The pH after 66 weeks-immersion ranged from 10.4 (without BFS) to 12.3 (BFS content 80%).

- (1) Without BFS, the pH of the liquid phase decreases with increasing immersion time.
- (2) At 20% BFS, the liquid phase pH increases with increasing immersion time.
- (3) Beyond 60% BFS content, immersion time has no effect on the pH of the liquid phase.

Liquid phase concentrations of the elements for low-alkalinity cements after 66 week’s immersion are listed in Table 3. The results show:

- (1) Ca, Na and K concentrations increase with increasing percentage of BFS.
- (2) Si concentration decreases with increasing percentage of BFS.
- (3) Ca concentration without addition of BFS was higher than that with BFS.
- (4) Ca concentration was higher than those of Na and K.
- (5) S concentration was found to decrease with the addition of BFS. The concentration was higher than estimated by the ion balance of Ca, Na, K, Si and Al. Moreover, good

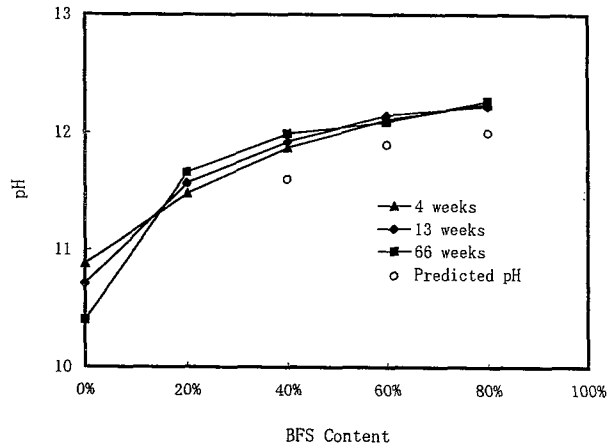


Fig.2 Dependence on BFS content of measured pH at immersion times of 4 weeks, 13 weeks and 66 weeks. The open circle represents the pH estimate based on Fujii-Kondo equilibrium data [7].

Table 3 Chemical concentration of chemical composition of the liquid phase after 66 weeks-immersion

Sample No.	BFS Content (%)	Chemical concentration (mmol/l)					
		Si	Al	Ca	Na	K	OH ⁻
1	0	0.143	ND	17.8	0.581	0.350	0.254
2	20	0.232	0.286	3.77	0.616	0.563	4.53
3	40	0.169	0.416	5.12	0.661	0.697	9.73
4	60	0.157	0.284	5.65	0.867	1.01	12.3
5	80	0.115	0.102	7.90	1.16	1.45	18.7

mass balance for S was not observed in the present experiment. Measurement of S in the liquid phase is one of the subjects to be elucidated.

The X-ray diffraction pattern of the hydrated cement after 13 weeks dissolution is shown in Fig.3 and after 66 weeks dissolution is shown in Fig.4.

It was found that AFt, which was the main crystalline in solid phase in the initial material, was also the main crystalline

in solid phase after dissolution, and the diffraction intensity increased with decreasing BFS content. The diffraction peak of anhydrite which is persistent at BFS contents below 40%, could not be observed after 13 weeks of dissolution shown in Fig.3.

By analyzing the results of XRD shown in Fig.4, it was found that AFt had not been converted to AFm for the longest immersion time. In addition $\text{Ca}(\text{OH})_2$ was not formed.

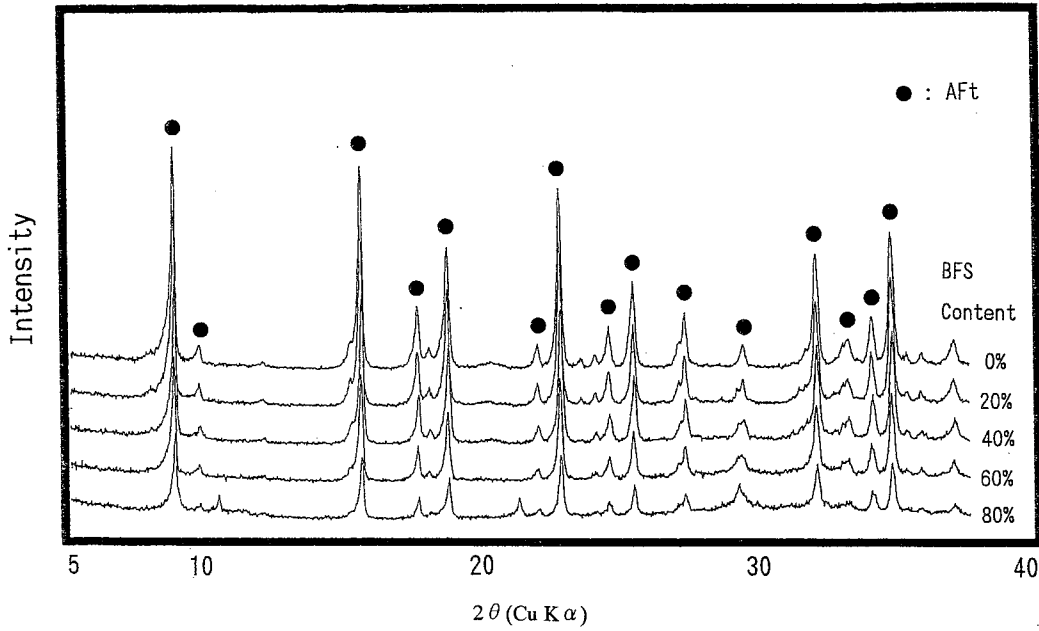


Fig.3 X-ray diffraction pattern of the hydrated low-alkalinity cement after the 13 week dissolution test

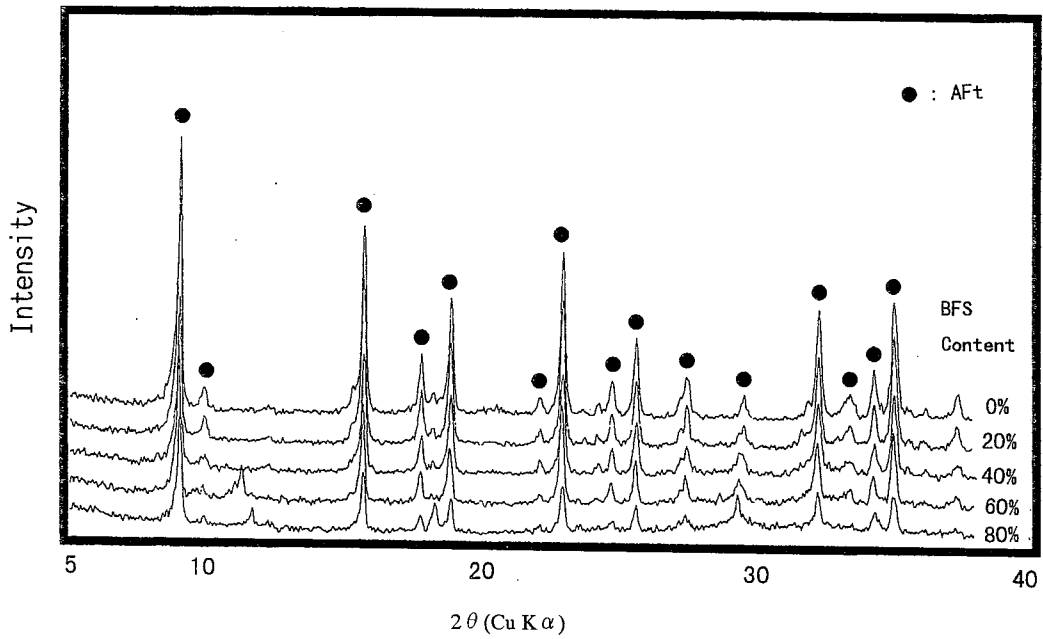


Fig.4 X-ray diffraction pattern of the hydrated low-alkalinity cement after the 66 week dissolution test

3.3 Discussion on experimental results

In the present work, the main components like $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$, belite ($2\text{CaO} \cdot \text{SiO}_2$), ferrite (mainly $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) and anhydrite were supplied from clinker [10]. In order to control the amounts of Ca and Si, BFS was added as admixture.

When sufficient water for the hydration reaction is supplied, the following hydrate products form, successively [10]:

- (1) $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$ (AFt) is generated as long as Ca, Al and S exist.
- (2) CaSO_4 is generated in the case that sulfate is still present, but no Al.
- (3) $\text{Al}(\text{OH})_3$ is generated in the case that Al remains after sulfate is consumed.
- (4) The remaining Ca reacts with Si and generates C-S-H gel. The upper limit of the Ca/Si mole ratio of C-S-H gel is 1.8.
- (5) And remaining Ca generates $\text{Ca}(\text{OH})_2$

The expected composition of hydrated low-alkalinity cements for the various amount of BFS (admixture) were calculated stoichiometrically based on the above mentioned assumptions (1) to (5). The calculated results are shown in Table 4.

Since one mole-AFt can fix 6 moles of calcium, the consumption of Ca can increase with the amount of AFt formed through the hydration process. This causes a low absolute amount of Ca in C-S-H gel, resulting in a decreased Ca/Si mole ratio. Thus, it can be expected that the pH decreases with decreasing the Ca/Si mole ratio of C-S-H gel.

The pH of the liquid phase where AFt coexists with C-S-H gel of various Ca/Si mole ratios (0.9 to 1.7) has been calculated by Atkins et al. [11]. The pH of the liquid phase where AFt coexists with C-S-H gel is almost equal to the pH from the solubility data of C-S-H gel measured by Fujii and Kondo [7]. Also, the pH increase as the value of Ca/Si mole ratio increase. Therefore, we assumed that the pH of the liquid phase where AFt coexists with C-S-H gel is equal to the pH of C-S-H gel. By taking into account the above hypothesis, Atkins' results and this assumption, we estimated the pH of hydrated low-alkalinity cement. The estimated pH of the hydrated low-alkalinity cement whose BFS content was 40 to 80% (calculated Ca/Si mole ratio is 1.02 to 1.27) based on the solubility data by Fujii and Kondo are summarized in Table 4. These estimated pH agree well with the measured pH, as shown in Fig.2. For the hydrated low-alkalinity cement with BFS content of 0 and 20 %, we could not estimate pH. The Atkins' work is not validity for this level of BFS content because few solubility data are available. It is important to be able to predict reliably the pH for low-alkalinity cement with low BFS content. We intend to study the dissolution behavior of low BFS content cement in detail in the near future.

In order to develop low-alkalinity cement, to lower the pH

of liquid phase, the validity of the following hypothesis, based on our preliminary experiment and work by several other researchers, was investigated:

- (1) The pH of the liquid phase in the hydrated cement is kept low when AFt exists stably and in a large quantity [5,6,10,11].
- (2) In case AFm exists stably in the hydrated cement and in a large quantity, the pH of the liquid phase become high [5,6].
- (3) The most important and dominant factor to control the variation in the pH of the liquid phase is the dissolution of C-S-H gel and the existence of AFt coexists with C-S-H gel of low Ca/Si mole ratios existing in the hydrated cement [6,10,11].

Table 4 Expected hydrated low-alkalinity cement composition and pH values

Composition of Hydrated cements	(mol/kg)				
	BFS content (%)				
	0	20	40	60	80
AFt	1.25	1.06	0.82	0.57	0.33
CaSO_4	0	0	0	0	0
$\text{Al}(\text{OH})_3$	1.48	1.66	1.80	2.02	2.20
C-S-H (Ca/Si)	0	1.63 (0.69)	2.53 (1.02)	3.44 (1.19)	4.34 (1.27)
$\text{Ca}(\text{OH})_2$	0	0	0	0	0
pH*	-	-	11.6	11.9	12.0

*: Predicted based on Fujii-Kondo equilibrium data [7].

Table 5 Comparison of observed and theoretically calculated Ca concentration in the liquid phase after 66 weeks immersion

Sample No.	BFS Content (%)	Ca concentration (mmol)		
		Observed	Theoretical	
			C-S-H ¹	AFt ²
1	0	17.8	15.1 ³	2.67
2	20	3.77	-	2.67
3	40	5.12	2.66	2.67
4	60	5.65	4.38	2.67
5	80	7.90	5.19	2.67

1*: Ca concentration predicted based on Fujii-Kondo's solubility data [7]

2*: solubility of AFt [5]

3*: solubility of anhydrite

As explained in section 3.2, Ca concentration in the liquid phase in contact with low-alkalinity cement containing BFS was found to increase with increase of BFS amount: 3.77 mM for 20% BFS and 7.90 mM for 80% BFS as shown in Fig.2. Comparison of observed Ca concentration with theoretically calculated Ca concentration in the liquid phase after 66 weeks-immersion is shown in Table 5. Ca concentration for 40% to 80% BFS agreed with the concentration evaluated by interpolation from C-S-H gel dissolution data reported by Fujii and Kondo [7]. Thus, evaluated Ca concentration was 2.66 mM for 40% BFS, 4.38 mM for 60% BFS and 5.19 mM for 80% BFS.

Ca concentration without addition of BFS was found to agree with the Ca solubility (15.1 mM) from anhydrite. This generates the possibility of anhydrite residue, although the XRD results did not show peaks from anhydrite.

Na and K concentration in the liquid phase increased with BFS amount. This could be attributable to the dissolution of Na and K, which were included in BFS during the hydration process.

It was found that AFt was the main crystalline in solid phase in the hydrated cement. The XRD intensity of AFt increased with decreasing amounts of admixture (BFS) added at the initiation of the hydration process. Theoretically calculated AFt amounts in the hydrated cement increased with the decrease of the BFS (admixture) amount. This tendency is the same as the experimental result depicted in Fig. 1.

Reviewing the overall experimental results, it can be said that the material design method for low-alkalinity cement, which was described in Section 2.1. of this paper, is adequate.

4 Summary and Conclusions

In the present work, we investigated the solid phase of low-alkalinity cement and its dissolution behavior. The following conclusions can be derived:

- (1) According to the XRD patterns, AFt was found to be the main crystalline in solid phase at any composition and at any immersion period.
- (2) Based on the solubility data of C-S-H gel by Fujii and Kondo, dependence of the pH for low-alkalinity cement on BFS contents above 40% was estimated theoretically. It was found that theoretically predicted pH agreed with the experimental results.
- (3) Since the Ca/Si mole ratios in C-S-H gel can be controlled by added amounts of BFS, and the increase in Ca/Si mole ratios leads to higher pH and Ca concentration in the liquid phase.
- (4) The pH of the liquid phase in contact with hydrated cement with less than a 40% BFS content and the dissolution behavior of the hydrate remain to be investigated. It is especially important to reveal the dissolution behavior of the system where AFt coexists with C-S-H gel of low Ca/Si mole ratios, because it may affect the long-term leaching process of the low-alkalinity cement containing $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ studied in the present work.

Acknowledgment

The authors would like to acknowledge and thank Mr. D. Sugiyama and Mr. Y. Fukaya, for valuable comments in hydration reaction for low-alkalinity cement and Mr. M. Shibata for the laboratory measurements.

References

- [1] Ewart, F. T. et al.: The solubility of actinides in a cementitious near-field environment, *Waste Management* **12**, 241-252 (1992).
- [2] Atkinson, A.: The time dependence of pH within a repository for radioactive waste disposal, AERE R 11777, United Kingdom Atomic Energy Authority (1985).
- [3] Mihara, M. et al: Experimental and modelling studies on the interaction between cement paste with silica fume and distilled water, *Radioactive Waste Research* **3** No.2, 71-79 (1997).
- [4] Lea, F. M.: The chemistry of cement and concrete, Edward Arnold Ltd., UK, 502-506(1970) SUN 713122773.
- [5] Atkins, M. et al.: Solubility properties of ternary and quaternary compounds in the CaO-Al₂O₃-SO₃-H₂O System. *Cement and Concrete Research* **21**, 991-998 (1991).
- [6] Atkins, M. Glasser, F. P., Kindness, A.: Cement hydrate phases: Solubility at 25 °C. *Cement and Concrete Research* **22**, 241-246 (1992).
- [7] Fujii, K., Kondo, W.: Estimation of thermochemical data for calcium silicate hydrate (C-S-H gel). *Journal of the American Ceramic Society* **66**, C-220-C-221 (1983).
- [8] Greenberg, S. A., Chang, T. N.: Investigation of the colloidal hydrated calcium silicates. II. solubility relationships in the calcium oxide-silica-water system at 25 °C. *The Journal of Physical Chemistry* **69**, 182-188 (1965).
- [9] Arai, Y.: Cemento no Zairyou Kagaku, 2nd revision, Dainihon Tosho, pp.131-137 (1991) (in Japanese).
- [10] Takuma, Y. et al.: Hydration and pH behavior of the cement prepared from the mixture of haunite-containing clinker, anhydrite and blastfurnace slag. *Journal of the Ceramic Society of Japan* **104**, 1040-1047 (1996).
- [11] Atkins, M. et al.: A thermodynamic model for blended cements. *Cement and Concrete Research* **22**, 497-502 (1992).