Effects of Minor Components Fe_2O_3 and SiO_2 on Hydration of Compounds in a Quarternary System of $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$

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1. Introduction

A ternary system of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ has long been studied and the area containing the compounds produced in portland cement has especially been well searched with great interests. The system is, however, not so adequate as the basis of dealing with the compounds in alumina cement. This cement contains somewhat larger amount of Fe_2O_3 compared with the portland cement.

A quarternary system of $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ has to be introduced to discuss the properties of the alumina cement on the basis of the compounds in the cement. The roles of SiO_2 and Fe_2O_3 as minor components are considered to be of importance on the hydraulic properties of the alumina cement. Many researches¹⁾ have dealt with the compositions of these oxides in order to produce the cement with suitable properties. However, there have been a number of studies on the adequate compositions reporting different results from each other.

The authors have reviewed the quarternary system to look for the available domain of composition in which good hydraulic properties could be expected. Hydraulic property of each specimen was discussed in the connection with crystalline compounds produced in the specimen, and behaviors of minor components in each compound as well as their effects on the hydraulic properties were also discussed.

2. The effect of SiO_2 compound on the hydration of the alumina cement

Rapid hardening property of alumina cement depends on the hydraulic activity of the main constituent CA as well as the other calcium

aluminates. However, bauxite, one of the main raw materials, contains some amount of SiO_2 and Fe_2O_3 , so that their compounds exist in the cement in addition to calcium aluminates. Since C_2AS (gehlenite) seems to have little hydraulic property and to prevent CA from producing in the cement, the existence of this compound in large amount is not supposed to be desirable. The upper limit concentration of SiO_2 has been hitherto reported to be 6%²⁾.

2.1 Experimental

More than 70 kinds of specimens were prepared

Table 1 Relations between Chemical and Mineralogical Compositions and Mechanical Strength.

No.	Chemical composition (%)				Mineralogical composition			Compressive strength (kg/cm ²)		
	SiO_2	CaO	Fe_2O_3	Al_2O_3				1 day	7 days	28 days
1	5.0	32.3	48.5	14.2	C_4AF	C_2AS	CA	8.8		
3	"	26.6	39.9	18.5	"	CA	C_2AS	64.5		
5	"	17.1	25.7	52.2	CA_2	C_2AS	CA	13.4		
7	"	14.7	21.9	58.4	"	@A	"	10.8		
11	"	30.0	23.5	42.5	CA	C_4AF	C_2AS	229.3	299.1	324.8
12	"	23.7	19.0	52.3	CA_2	C_2AS	CA	183.6		
15	"	51.3	21.9	21.8	C_3A	$\text{C}_6\text{A}_2\text{F}$		2.0		
18	"	29.4	12.4	53.2	CA	C_2AS	CA_2	198.9		
21	"	15.6	7.6	79.8	CA_2	"	@A	119.8		
23	"	51.3	13.0	30.7	C_3A	C_4AF	C_2AS	37.4		
24	"	41.0	10.5	43.5	CA	C_{12}A_7	"	95.1		
25	"	31.1	7.9	56.0	"	C_2AS	CA_2	431.9	544.3	595.0
27	"	19.4	5.0	70.6	@A	CA_2	C_2AS	148.0		
31	"	44.0	4.7	46.3	C_{12}A_7	CA	"	96.8		
32	"	32.7	3.6	58.7	CA	C_2AS	CA_2	408.3	531.0	535.0
39	"	33.9	14.5	46.6	"	"	"	275.2	384.2	394.0
42	9.00	32.47	13.90	44.63	"	"	"	355.0	472.0	498.2
43	"	31.32	3.45	56.23	"	"	"	388.3	484.0	549.2
46	8.00	32.83	14.04	45.13	"	"	"	370.0	481.0	490.4
49	"	28.59	22.60	40.81	"	"	C_4AF	227.4	366.2	459.6
50	7.00	33.18	14.20	45.62	"	C_{12}A_7	"	142.3	163.0	172.9
51	"	32.01	3.52	57.47	"	C_2AS	CA_2	326.5	379.9	475.0
55	6.00	32.35	3.56	58.09	"	"	"	303.8	389.5	463.7
57	"	29.34	22.83	41.83	"	C_4AF	C_2AS	189.1	245.8	266.7
60	4.00	31.43	7.98	56.59	"	C_2AS	CA_2	351.2	505.2	531.6
61	"	30.31	23.24	42.45	"	C_4AF	C_2AS	176.6	208.0	218.1
62	3.00	34.61	14.81	47.58	"	"	"	297.0	492.0	493.1
63	"	33.38	3.68	59.94	"	C_2AS	CA_2	400.0	455.5	483.8
66	10.00	32.11	13.74	44.15	C_2AS	CA	"	116.4	190.0	170.6
68	"	29.46	7.49	53.05	"	"	@A	70.0	129.8	90.0
71	12.00	30.28	3.34	54.38	"	"	C_2S	210.0	237.5	258.0
73	"	28.93	17.60	41.47	"	"	"	35.0	70.0	33.8

Fig. 1 Chemical composition of specimens.
($\text{SiO}_2=5\%$)

by sintering the mixture of four oxides, the chemical compositions being shown in Fig. 1.

These mixtures were heated in an electric furnace at such a temperature ranging from 1250° to 1400°C as was approximate 50°C lower than the melting temperature of each mixture. The soaking time was mostly 3 hours. After a heat treatment, each specimen was ground in an agate mortar so that the whole specimen could pass through the 350 mesh sieve. The powdered specimen was subjected to X-ray diffraction in order to check the remainder that had not yet reacted. When the specimen contained the remainder, the above treatments were repeated until the reaction was completed. The highest strength developing specimens, marked double circle, were further prepared in various amounts of SiO_2 ranging from 3 to 20%. Crystalline compounds in each prepared specimen were identified by means of X-ray diffraction, and the compressive strengths were measured at the aging times of 1 day, 7 days and 28 days.

The strength measurement was carried out for soft mortar of each specimen ($C/S=1:2$ and $W/C=60\%$) at 20°C. Six samples were prepaped of each composition to be subjected to the measurement.

2.2 Results and discussion

Crystalline compounds produced in each specimen and its compressive strength are shown in Table 1. compared with each chemical composition.

The strength distribution of 1 day cured specimen is plotted in Fig. 2, in which every specimen contained 5% of SiO_2 . The composition of specimen which developed the highest strength was included in the primary phase field of CA, and the strength decreased gradually with the increasing amount of Al_2O_3 or Fe_2O_3 , but the larger

Fig. 2 Distribution of hydraulic strength. (One-day curing, $\text{SiO}_2=5\%$) (kg/cm^2)

the amount of CaO, the more suddenly the strength fell.

It was found that CA_2 or C_4AF lowered the strength of cement only gradually, while rapid hardening compounds e.g. C_3A or C_{12}A_7 , deteriorated the strength of cement more influentially. Consequently C_{12}A_7 is not supposed to be as a desirable constituent of the alumina cement except in minor amounts.

Fig. 3 Effect of SiO_2 on hydraulic strength.

Fig. 3 shows a relation between the strength and the amount of SiO_2 in the specimens. It is derived from the experimental results that SiO_2 has no bad effect on the strength in the range of 3 to 9% with Fe_2O_3 below than 10%, but when Fe_2O_3 exceeds 10%, the strength steeply drops at 7% of SiO_2 . In the latter case C_{12}A_7 was produced in the specimen causing the sudden drop of the strength. The so-called limit concentration of SiO_2 at 6%²⁾ seems to be derived from the fact that the hydraulic strength just dropped at the compositions containing 7% of SiO_2 . However,

the specimens containing SiO_2 more than 7% developed again the high strength enough and C_{12}A_7 was not detected. Therefore it is supposed that the primary phase field of C_{12}A_7 is very close to that of CA at 7% of SiO_2 when Fe_2O_3 is present above than 10%. Since specimen containing above 10% of SiO_2 produced C_2AS rather than CA, the hydraulic strength becomes lower.

Assuming that SiO_2 forms into only C_2AS , the quantity of produced C_2AS can be calculated from ratio of SiO_2 in the composition as follows,

$$\text{C}_2\text{AS}(\%) = \frac{274 (\text{M.W. of } \text{C}_2\text{AS})}{60 (\text{M.W. of } \text{SiO}_2)} \times \text{SiO}_2(\%)$$

The quantity of produced CA can be derived if the molar ratio of CA to C_2AS in the specimen were known. To obtain the molar ratio in each specimen, pure CA and C_2AS prepared individually were mixed together at various molar ratios, then X-ray diffraction patterns were taken.

Comparing the ratio of X-ray intensity diffracted at a lattice plane of CA (022) to that of C_2AS (211) with the molar ratio of CA to C_2AS of the corresponding mixture, a calibration curve could be obtained as shown in Fig. 4.

Using the calibration curve, molar ratio of CA to

Fig. 4 CA/ C_2AS mole ratio calibration curve.

Fig. 5 Relation between hydraulic strength and quantity of CA.

C_2AS was derived from the ratio of diffracted X-ray intensity of CA to that of C_2AS in each specimen. Consequently the quantity of produced CA was calculated as follows,

$$\text{CA}(\%) = \text{C}_2\text{AS}(\%) \times \text{molar ratio of CA/C}_2\text{AS} \times \frac{158 (\text{M.W. of CA})}{274 (\text{M.W. of } \text{C}_2\text{AS})}$$

Fig. 5 shows the relation between the hydraulic strength and the quantity of CA in the specimen.

The specimens in which CA was produced in the amount lower than 25% could not develop the suitable strength either in the early stage or in the long ages. It is shown that the strength rises with the increasing quantity of CA until the quantity reaches 40%, above which the strength becomes nearly constant. Therefore it should be noted that the cement has to contain CA in amount above 40% and SiO_2 less than 9% in order to develop the high strength enough for practical use.

3. The behavior of iron oxide in the quaternary system

Any compounds containing ferrous or ferric ions could not be detected by X-ray diffraction in the specimens in which a large amount of CA or CA_2 was produced, even if the specimens contained up to approximate 15% of Fe_2O_3 in their chemical composition. It has been reported that CA and C_{12}A_7 take ferric oxide into solid solution³⁾. In this work, the authors have studied the exact state of solid solution of CA and CA_2 with ferric oxide as well as the effect of iron in CA on the hydraulic property of the cement.

3.1 Experimental

The specimens were prepared through the following procedure; some amount of Fe_2O_3 ranging 0 to 30% was added into the mixture of CaO and Al_2O_3 the composition of which just corresponded to CA or CA_2 in stoichiometry, and each mixture was sintered at 1350°C for 4 hours or at 1500°C for 4 hours in the case of CA or CA_2 , respectively. Interplanar spacing of CA or CA_2 of each prepared specimen was calculated from X-ray diffraction pattern using Si as an internal standard.

3.2 Results and discussion

Interplanar spacing of CA lattice in each specimen became larger than pure CA, and CA_2 lattice is also expanded by addition of Fe_2O_3 as shown in Fig. 6. Since ionic radii of Fe^{3+} and Al^{3+} are 0.60 Å and 0.50 Å, respectively, it is presumed that a crystal lattice of CA or CA_2 expands owing to the distortion occurring in the atomic order, when Fe^{3+} ions take the places of regular sites of Al^{3+} ions in the lattice. Therefore both CA and CA_2 are considered to form

Fig. 6 Changes in interplanar spacings as functions of added amounts of Fe_2O_3 .

solid solutions in which Al^{3+} ions are substituted for Fe^{3+} ions in the lattices, the limit of substitution being 4.76% in CA and 15.0% in CA_2 , respectively. In Fig. 7, X-ray diffraction patterns showed that only CA was produced by adding Fe_2O_3 less than 4.76%, while CA and CA_2 were produced in the case of higher content of Fe_2O_3 , and no stoichiometric compound of Fe_2O_3 was produced in any case. Similarly, addition of Fe_2O_3 over the limit concentration lead to production of CA_6 besides CA_2 as shown in Fig. 8. From these facts it is considered that in a system of CaO, Al_2O_3 and Fe_2O_3 , Fe_2O_3 reacts with CaO taking the place of Al_2O_3 and remaining Al_2O_3 forms the compounds with higher ratios of Al_2O_3 to CaO, i.e., from CA to CA_2 and then to CA_6 , with the increasing amount of Fe_2O_3 . The molecular formula of CA containing Fe_2O_3 is considered to be $\text{Ca}(\text{Al}_x, \text{Fe}_y)_2\text{O}_4$ exactly. In the study of commercial alumina cement, Dayal⁴⁾ reported that CA had taken Fe_2O_3 into solid solution up to the limit concentration, 4.8%, which has approximately corresponded with the value obtained in this work. Jeanne⁵⁾ also examined the commercial cement by means of electron microscope and reported that Fe_2O_3 had formed solid solution with C_2AS or C_{12}A_7 besides CA and CA_2 .

Fig. 9 shows the hydraulic strength of CA bearing Fe_2O_3 at various amounts. CA containing

Fig. 7 X-ray diffraction patterns of CA with various amounts of Fe_2O_3 . Fig. 8 X-ray diffraction patterns of CA_2 with various amounts of Fe_2O_3 .

Fig. 9 Effect of Fe_2O_3 on the hydraulic strength of CA.

Fe_2O_3 below the limit concentration developed remarkably high strength in comparison with pure CA at early stage, but the strength has again become lower with the increasing amount of Fe_2O_3 over the concentration of 4.76%. However, the strength developed during long ages was rather high even if the content of Fe_2O_3 increased up to about 10%. These phenomena seem to be explained as follows. The CA lattice expands owing to the substitution of Fe^{3+} for Al^{3+} in CA until the limit of substitution is reached, and the stability of the lattice becomes lower compared with the case of pure CA without any substitutional disorder. Therefore the hydraulic activity of CA is also increased with addition of Fe_2O_3 , and then CA bearing some amount of iron develops higher strength than that in pure CA. On the other hand, the reason why the high strength was kept during long ages at the content of Fe_2O_3 up to 10% is considered as follows. CA_2 is produced besides CA when the amount of Fe_2O_3 exceeds the limit as shown in Fig. 7, and the quantity of produced CA decreases with the increasing amount of CA_2 , so that the strength at early stage, e.g. at 1 day, becomes lower with the amount of Fe_2O_3 , but the strength at later stage does not fall steeply under the presence of Fe_2O_3 within 10% because of the hydration of CA_2 starting at later stage. When the amount of Fe_2O_3 becomes above 10%, the ratio of CA to CA_2 further decreases, then the hydration of CA_2 could hardly proceed because of too little amount of co-existing

CA that has been reported to accelerate the hydration of CA_2 ⁶⁾. This is the reason why either the early developed strength or that in long age is lowered if the specimen contains too much amount of Fe_2O_3 .

4. Summary

The roles of SiO_2 and Fe_2O_3 in the alumina cement were investigated and the following conclusions were obtained.

(1) SiO_2 is an undesirable component for the alumina cement, and the limit of concentration of this is 9%.

(2) Both CA and CA_2 take ferric oxide into them forming solid solution, and the maximum amounts of Fe_2O_3 are 4.76% in CA and 15.0% in CA_2 , respectively. CA bearing Fe_2O_3 up to the limit concentration (4.7%) develops higher early strength than that developed by pure CA, and addition of Fe_2O_3 up to 10% makes the strength higher at later stages.

In the quaternary system of $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ the composition range of each oxide to obtain suitable hydraulic properties is as follows; CaO : 25~40%, Al_2O_3 : 55~75%, SiO_2 should not exceed 9%, and it is desirable to contain a little amount of Fe_2O_3 in the cement, not exceeding 20%.

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4 成分 $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$ 系内化合物の水硬性に対する Fe_2O_3 および SiO_2 の影響

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上記4成分系において、アルミナ・セメントとして良好な水硬性を期待できる組成範囲を再検討することを最終目的として、特に従来、その影響が水硬性に対して重大であると考えられている成分 SiO_2 および Fe_2O_3 の役割ないし挙動について検討した。

所定の組成に調合し、焼成法により合成した試料の水硬強度を測定し、試料中に生成した化合物の種類および量と対比して、各試料の水硬性を論じ、さらに SiO_2 , Fe_2O_3 が水硬性に対して与える影響を明らかにした。 SiO_2 は、アルミナ・セメントの主成分である化合物 CA の生成に対して好ましくない成分であり、組成に含み得る量に関して、従来6%が限界であるという説が支持されていたが、本研究の結果より限界値が9%に達するこ

とを確かめた。同時に鉄分の量によっては SiO_2 7% 近傍に低強度を示す組成の存在することを見出し、その理由を考察した。

一方 Fe_2O_3 は CA および CA_2 と、 Fe^{3+} イオンと Al^{3+} イオンとが置換した固溶体を形成することを示唆する結果を得た。固溶の限界値は、CA に対して 4.76%, CA_2 に対して 15.0% であった。

固溶限界以下の鉄の存在は、却って CA の水硬性を上昇させ、さらに、4.76% を越えると初期強度は若干低下するが、10% までの鉄は、長期強度の発現に対して、有効な働きをすることを見出した。

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CaO と単結晶 Al_2O_3 の高温反応

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Solid State Reactions between CaO and a Single Crystal of Al_2O_3

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Reflection microscopy, electron probe X-ray microanalysis and single crystal X-ray diffraction were used to analyse the reaction between CaO and a single crystal of Al_2O_3 at high temperatures. A single crystal of $\alpha\text{-Al}_2\text{O}_3$ was embedded in CaO powder and heated in the temperature range 1200° to 1500°C. The polished cross sections of the specimens were investigated by the methods above mentioned. The following results were obtained.

1) Calcium aluminate layer appeared on the surface of a single crystal of Al_2O_3 . More than two or three phases usually consisted in the layer, and only one phase was rarely obtained. They were determined as C_3A , C_{12}A_7 , CA, CA_2 and CA_3 by the electron probe X-ray microanalysis.

2) Among these phases, C_{12}A_7 of more than 1 mm was especially easily obtained and it showed a single crystal X-ray pattern. By firing at 1390°C for 36 hours and slow cooling, a single crystal of C_3A of more than 100 μ was obtained.

3) Inert marker experiment showed that the process was not counter-diffusion of Ca