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# Ion-exchange characteristics of $12CaO\cdot 7Al_2O_3$ for halide and hydroxyl ions

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## Abstract

Substitution characteristics of the halide ions $F^-$ $Cl^-$ for the $OH^-$ ions in the crystal lattice of $12CaO\cdot 7Al_2O_3$ solid solution were investigated. Single phases of composition $11CaO\cdot 7Al_2O_3\cdot CaF_2$ and $11CaO\cdot 7Al_2O_3\cdot CaCl_2$ were formed at 900 °C or above. The $OH^-$ ions in $12CaO\cdot 7Al_2O_3$ solid solution, i.e. $11CaO\cdot 7Al_2O_3\cdot Ca(OH)_2$, could be replaced wholly or partially by $F^-$ or $Cl^-$ ions from the corresponding calcium halide, forming $11CaO\cdot 7Al_2O_3\cdot Ca(OH,F)_2$ and $11CaO\cdot 7Al_2O_3\cdot Ca(OH,Cl)_2$ solid solutions above 500 °C and above 700 °C, respectively. Lattice constants of $12CaO\cdot 7Al_2O_3$ solid solution changed continuously with the proportion of $F^-$ ions or $Cl^-$ ions. The $F^-$ ions in $11CaO\cdot 7Al_2O_3\cdot CaF_2$ could be wholly or partially substituted by $Cl^-$ ions from $CaCl_2$ at 900 °C or more, forming the solid solution $11CaO\cdot 7Al_2O_3\cdot Ca(F,Cl)_2$. The $Cl^-$ ions in $11CaO\cdot 7Al_2O_3\cdot CaCl_2$ could be partially replaced $F^-$ ions from $CaF_2$ at 1000 °C or above, apparently due to slow chloride loss by evaporation.

*Keywords:* $12CaO\cdot 7Al_2O_3$; Powders-solid state reaction

## 1. Introduction

About 28 million tons of industrial waste was processed by the cement industry in Japan in 2001. It is planned to increase the amount of that in the future. It is difficult to secure the final disposal site year after year though the volume of general waste such as municipal refuse is reduced by incineration. The general waste is also expected to be used for the cement raw materials. Japan Industrial Standards (JIS R5214) of "Ecocement", which is produced with the city garbage incineration ash and the sewage sludge as a main raw material was enacted on the ground in 2002. The cement manufacturing plant has been aimed at not only recycling the earth resources effectively but also making toxic waste such as dioxin harmless. In other words, the cement industry produces materials of the social infrastructure and is also contributing to the solution of the waste problems.

However, one of the negative aspects is that the new compounds that change the property of cement are created when diversified raw materials and fuels are used. Especially, the contents of halogen, phosphorus, zinc, copper, chromium, etc., which are thought to have adverse effects on cement, in the raw materials will increase. It is also inevitable that the contents of calcium aluminates in cement clinker will increase with the use of city garbage incineration ash.

The calcium aluminates formed in ordinary Portland cement clinker is $3CaO\cdot Al_2O_3$ ($C_3A$ for short, CaO = C, $Al_2O_3$ = A). It is known that $C_3A$ is decomposed to $C_{12}A_7$ solid solution ($C_{12}A_7ss$ for short) and CaO by various halides.[1] The general formula of $C_{12}A_7$ is $Ca_{24}Al_{28}O_{64}X_2$, where X means a lattice vacancy or disordered oxygen. The compound known as $C_{12}A_7$ is not strictly anhydrous in a moist atmosphere and is able to incorporate water at the high temperature range of 950–1350 °C.[1–3] The formula of the phase was suggested as $C_{11}A_7\cdot Ca(OH)_2$ when the contents of water reached a maximum of 1.3% at 950 °C.[4–6] When the halide such as $CaF_2$ and $CaCl_2$ was added to the raw materials, $C_{11}A_7\cdot CaF_2$ and $C_{11}A_7\cdot CaCl_2$ were formed, respectively.[7,8] Although the formation process and hydration behavior of their halogenated $C_{12}A_7ss$ were investigated in the previous works,[9–14] the chemical behavior of $C_{12}A_7ss$

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including both halide ions had not been examined yet. In this report, hydroxylated-, fluorinated- and chlorinated-$C_{12}A_7$ss were prepared and the anion exchange reactions between them were investigated.

## 2. Experimental procedures

Reagent grade $CaCO_3$, $Al(OH)_3$, $CaF_2$ and $CaCl_2 \cdot 2H_2O$ were used as starting materials. In the experiment of $C_{12}A_7$ss synthesis, they were weighed out so as to give the desired stoichiometric composition, and were mixed for 30 min to prepare a uniform mixture. The mixture was burned at a given temperature for 4 h in an electric furnace, and then the operation was repeated after crushing of burned product. The summary of the experimental procedure is shown in Fig. 1.

The phases in the burned product were identified by powder X-ray diffractometry (XRD), using a Rigaku RAD-IIA diffractometer with Ni-filtered Cu $K\alpha_1$ radiation. The rough quantitative analysis and measurement of the lattice constant were made from diffractometer traces using silicon as the internal standard.

## 3. Results and discussion

### 3.1. The effects of $CaF_2$ and/or $CaCl_2$ on the formation of $C_{12}A_7$ss

The raw mixtures were made for the compositions $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaF_2$ and $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaCl_2$ and were burned at various temperatures in air with normal humidity. Each formula corresponded to the composition for which 1 mol of CaO in $C_{12}A_7$ was wholly or partly substituted by $CaF_2$ or $CaCl_2$. The lattice constants ($a_0$) of $C_{12}A_7$ss in the case of $CaF_2$ substitution are shown in Fig. 2. The $a_0$ of $C_{12}A_7$ss decreased continuously with an increase in the amount of $CaF_2$. The shrinkage of the crystal lattice showed the formation of $C_{11}A_7 \cdot Ca(OH,F)_2$. However, the rate of change in the $a_0$ to $n$ value decreased with a decrease in burning temperature. The $a_0$ of products burned at 900 °C indicated a value close to that of $C_{11}A_7 \cdot CaF_2$.

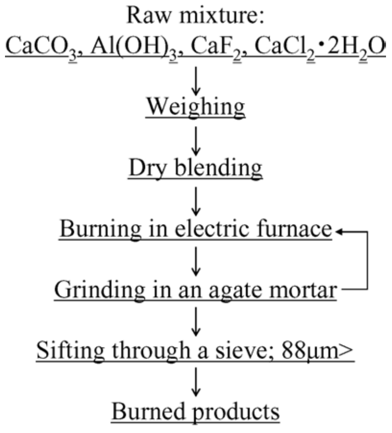

Fig. 1. Flowchart of the synthesis of $C_{12}A_7$ss.

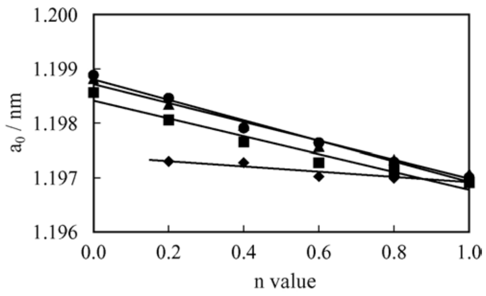

Fig. 2. Lattice constants of $C_{12}A_7$ss produced from $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaF_2$ compositions. (◆) 900 °C; (■) 1100 °C; (▲) 1300 °C; and (●) 1350 °C.

The $a_0$ in the case of $CaCl_2$ substitution are shown in Fig. 3. The $a_0$ of $C_{12}A_7$ss increased continuously with an increase in the amount of $CaCl_2$. As the result the formation of $C_{11}A_7 \cdot Ca(OH,Cl)_2$ was confirmed. As in the case of $CaF_2$ substitution, the rate of change of $a_0$ with $n$ decreased with decreasing burning temperature. The $a_0$ of products burned at 900 °C were close to that of $C_{11}A_7 \cdot CaCl_2$. The peak intensity of $C_{12}A_7$ss detected by XRD was inclined to decrease with decreasing $n$ value in both cases, and especially at the lowest temperatures used. It appears that only relative pure $C_{11}A_7 \cdot CaF_2$ or $C_{11}A_7 \cdot CaCl_2$, and not their hydroxylated solid solutions, were formed at 900 °C as $C_{12}A_7$ss. In those cases, it was also confirmed that CA and free lime were coexistent to halogenated $C_{12}A_7$ss.

Fig. 4 shows the change of the $a_0$ of $C_{12}A_7$ss produced from raw materials that also include mixtures of $CaF_2$ and $CaCl_2 \cdot 2H_2O$. The mixtures were the compositions of which one mole of CaO in $C_{12}A_7$ was wholly or partly substituted by $CaF_2$ and/or $CaCl_2$. All of their raw materials were burned at 1300 °C. The $a_0$ of $C_{12}A_7$ss which contained either $F^-$ ions or $Cl^-$ ions corresponded to those of Figs. 2 and 3. Open squares show the results calculated from Eq. (1) using the value indicated by closed circle and triangle. The calculations were almost equal to the measurements; therefore, the result clearly shows that the $F^-$ ions and the $Cl^-$ ions are coexistent

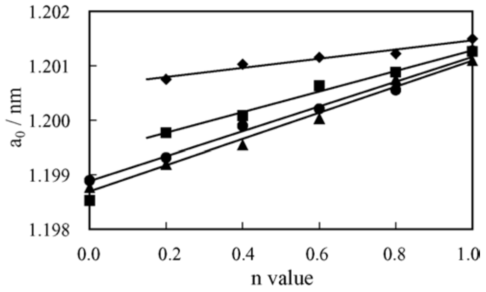

Fig. 3. Lattice constants of $C_{12}A_7$ss produced from $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaCl_2$ compositions. (◆) 900 °C; (■) 1100 °C; (▲) 1300 °C; and (●) 1350 °C.

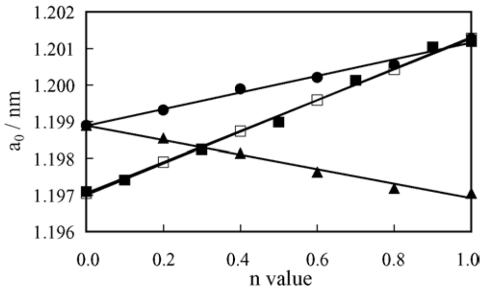

Fig. 4. Lattice constants of various halogenated $C_{12}A_7$ss burned at 1300 °C. (▲) $(12-n)CaO{\cdot}7Al_2O_3{\cdot}nCaF_2$ compositions; (●) $(12-n)CaO{\cdot}7Al_2O_3{\cdot}nCaCl_2$ compositions; (■) $11CaO{\cdot}7Al_2O_3{\cdot}(1-n)CaF_2{\cdot}nCaCl_2$ compositions; and (□) calculated values by Eq. (1).

in $C_{12}A_7$ss.

$$\begin{aligned} &L_{\mathrm{F,Cl}} = (1-n)L_{\mathrm{F}} + nL_{\mathrm{Cl}} \quad (0 \le n \le 1) \\ &L_{\mathrm{F,Cl}} : a_0 \text{ of } 11\mathrm{CaO}\cdot 7\mathrm{Al_2O_3}\cdot(1-n)\mathrm{CaF_2}\cdot n\mathrm{CaCl_2} \\ &L_{\mathrm{F}} : a_0 \text{ of } 11\mathrm{CaO}\cdot 7\mathrm{Al_2O_3}\cdot \mathrm{CaF_2} \\ &L_{\mathrm{Cl}} : a_0 \text{ of } 11\mathrm{CaO}\cdot 7\mathrm{Al_2O_3}\cdot \mathrm{CaCl_2} \end{aligned} \tag{1}$$

The influence of burning temperatures on the $a_0$ of $C_{12}A_7$ss including both $F^-$ and $Cl^-$ ions were investigated. The raw material compositions were the same as those of the closed squares in Fig. 4. There was little significant change of $a_0$ with burning temperature, as Fig. 5 indicates. It was considered that $C_{12}A_7$ss saturated with $F^-$ ions and/or $Cl^-$ ions were formed at 900 °C or above.

Fig. 6 shows the $a_0$ of $C_{12}A_7$ss generated from the mixtures, which contained the halide in excess. The raw material was prepared with the composition of $12CaO{\cdot}7Al_2O_3{\cdot}CaF_2{\cdot}CaCl_2$, of which the total amount of halides exceeded the solubility to $C_{12}A_7$. The gradual decrease of the $a_0$ with an increase of burning temperature meant the dechlorination from the raw mixture. It was considered that the change of the $a_0$ from 1.200 to 1.202 nm showed the existence of the $Cl^-$ ions in crystal lattice of $C_{12}A_7$ss. This result proved clearly that $C_{11}A_7{\cdot}CaCl_2$ was preferentially formed when $CaCl_2$ coexisted with $CaF_2$.

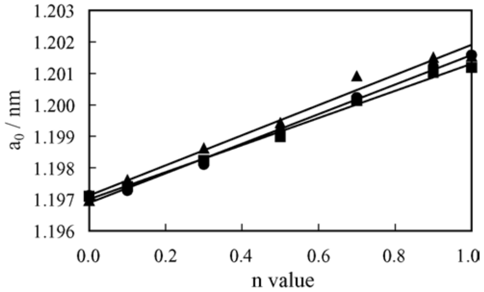

Fig. 5. Influence of burning temperature on the lattice constants of $C_{12}A_7$ss produced from $11CaO{\cdot}7Al_2O_3{\cdot}(1-n)CaF_2{\cdot}nCaCl_2$ compositions. (▲) 900 °C; (●) 1100 °C; and (■) 1300 °C.

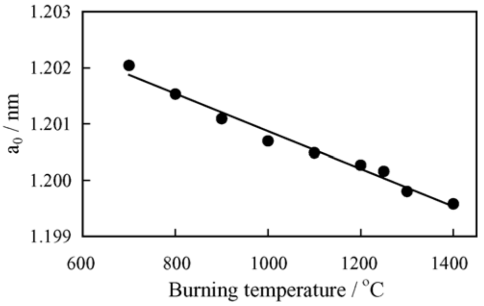

Fig. 6. Influence of burning temperature on the lattice constants of $C_{12}A_7$ss with burning temperature. Mixing ratio of $CaCO_3:Al(OH)_3:CaF_2:CaCl_2{\cdot}2H_2O$ is 12:14:1:1 in mole.

### 3.2. Ion-exchange reaction between $C_{11}A_7{\cdot}Ca(OH)_2$ and various calcium halides

Ion-exchange reaction, in other words anion-substitution reaction, between $C_{11}A_7{\cdot}Ca(OH)_2$ and various calcium halides were examined. The compound $C_{11}A_7{\cdot}Ca(OH)_2$ was synthesized by burning at 1350 °C in atmosphere with normal humidity. Then, mixtures of $C_{11}A_7{\cdot}Ca(OH)_2$ with $CaF_2$ and/or $CaCl_2{\cdot}2H_2O$ were prepared and burned. The mixing ratio of calcium-halide:$C_{11}A_7{\cdot}Ca(OH)_2$ was 1:1 by mole.

The changes of the $a_0$ of $C_{12}A_7$ss with burning temperature are shown in Fig. 7. In the case of $CaCl_2{\cdot}2H_2O$ addition, the $OH^-$ ions in $C_{11}A_7{\cdot}Ca(OH)_2$ were exchanged for the $Cl^-$ ions at 1000 °C or more. On the other hand, the substitution reaction between the $OH^-$ ions and the $F^-$ ions occurred at 500 °C by the addition of $CaF_2$. When both $CaF_2$ and $CaCl_2{\cdot}2H_2O$ were added to $C_{11}A_7{\cdot}Ca(OH)_2$, the exchange for the $F^-$ ions and for the $Cl^-$ ions were observed in the temperature range of 800 °C or less and at 900 °C or more, respectively. In addition, calcium oxide was simultaneously formed, when $C_{11}A_7{\cdot}Ca(OH)_2$ was heated with various calcium halides and ion exchange occurred to form halogenated $C_{12}A_7$ss. The slow decreases in $a_o$ value observed for the chlorinated phase at temperatures of 1000 °C and above were assumed to be due to the loss of chloride by evaporation. These results agreed with our previous work, which has reported on a chemical analysis of the product for chloride.[7]

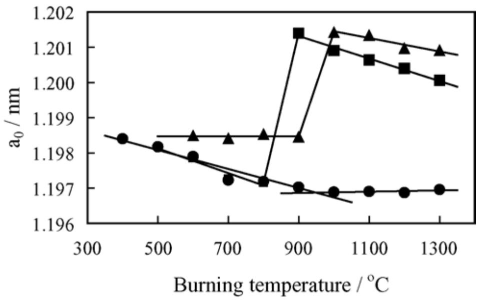

Fig. 7. Influence of burning temperature on anion substitution between $C_{11}A_7{\cdot}Ca(OH)_2$ and various halides. (●) added $CaF_2$; (▲) added $CaCl_2{\cdot}2H_2O$; and (■) added $CaF_2$ and $CaCl_2{\cdot}2H_2O$.

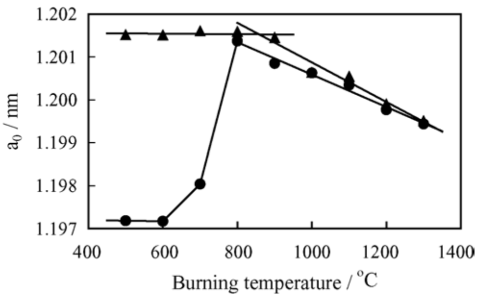

Fig. 8. Influence of burning temperature on anion substitution between $C_{12}A_7$ss and halides. (●) $C_{11}A_7 \cdot CaF_2$ with $CaCl_2 \cdot 2H_2O$; and (▲) $C_{11}A_7 \cdot CaCl_2$ with $CaF_2$.

### 3.3. *Substitution reaction of the halide ions in $C_{11}A_7 \cdot CaF_2$ and in $C_{11}A_7 \cdot CaCl_2$*

Substitution reaction of the halide ions between halogenated $C_{12}A_7$ss and the calcium halide were examined. Single phases of $C_{11}A_7 \cdot CaF_2$ and $C_{11}A_7 \cdot CaCl_2$ were synthesized at 900 °C, and then were mixed with $CaCl_2 \cdot 2H_2O$ and $CaF_2$, respectively. The mixing ratio of halide:$C_{12}A_7$ss was 1:1 by mole. The $a_0$ of $C_{12}A_7$ss in the mixtures, which were burned at various temperatures are shown in Fig. 8. The exchange between the $F^-$ ions in $C_{11}A_7 \cdot CaF_2$ and the $Cl^-$ ions of $CaCl_2 \cdot 2H_2O$ was clearly affirmed because of a sudden increase in the $a_0$ at 700 °C or more. Besides, a decrease of the $a_0$ caused by the dechlorination from $C_{12}A_7$ss or by the vaporization of $CaCl_2$ in raw mixture was also observed in the temperature range of 900 °C or more.

On the reaction of $C_{11}A_7 \cdot CaCl_2$ and $CaF_2$, it is unclear whether the decrease of the $a_0$ at 900 °C or more was caused simply by dechlorination or also by the incorporation of $F^-$ ions. Moreover, it seemed unreasonable to conclude that a solid solution with both occurred at 900 °C because the $a_0$ of both cases were roughly identical at this temperature. This point will be examined in detail in Fig. 10.

The formation of the solid solution in $C_{11}A_7 \cdot CaF_2$–$C_{11}A_7 \cdot CaCl_2$ system, that is $C_{11}A_7 \cdot Ca(F,Cl)_2$, was examined. The $a_0$ of $C_{12}A_7$ss which were formed from the mixtures of $C_{11}A_7 \cdot CaF_2$ and $CaCl_2 \cdot 2H_2O$ are shown in Fig. 9. The *n* value indicates the mole ratio of $CaCl_2 \cdot 2H_2O$ to $C_{11}A_7 \cdot CaF_2$. The $F^-$ ions in $C_{11}A_7 \cdot CaF_2$ were able to be continuously exchanged for the $Cl^-$ ions. As a result $C_{11}A_7 \cdot Ca(F,Cl)_2$ was formed from 900° to 1100 °C. The decrease of the $a_0$ clearly showed that dechlorination occurred at 1300 °C or more.

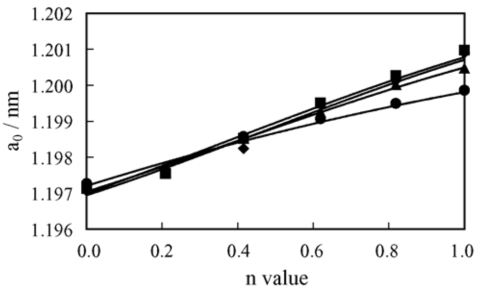

Fig. 9. Lattice constants of $C_{12}A_7$ss produced from $C_{11}A_7 \cdot CaF_2$ mixed with $nCaCl_2 \cdot 2H_2O$. (♦) 900 °C; (■) 1000 °C; (▲) 1100 °C; and (●) 1300 °C.

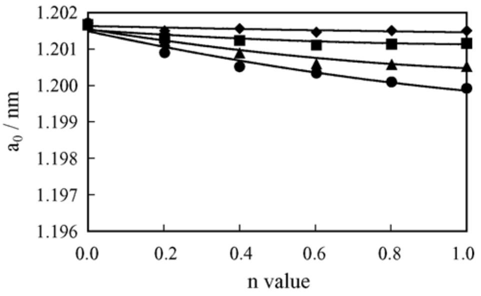

Fig. 10. Lattice constants of $C_{12}A_7$ss produced from $C_{11}A_7 \cdot CaCl_2$ mixed with $nCaF_2$. (♦) 900 °C; (■) 1000 °C; (▲) 1100 °C; and (●) 1300 °C.

The $a_0$ values of $C_{12}A_7$ss formed from mixtures of $C_{11}A_7 \cdot CaCl_2$ and $CaF_2$ are shown in Fig. 10. The *n* value means the mole ratio of $CaF_2$–$C_{11}A_7 \cdot CaCl_2$. The value of $a_0$ decreased a little with an increase in burning temperature and with an increase in the amount of $CaF_2$. An important point to emphasize is the latter. It means clearly that the $Cl^-$ ions in $C_{11}A_7 \cdot CaCl_2$ were exchanged for the $F^-$ ions at 1000 °C or more because of dechlorination, without which the substitution of $F^-$ for $Cl^-$ is thought to be unaffected by the amount of fluoride added. Therefore, a decrease in the $a_0$ value showed not only the dechlorination but also the fluorination has simultaneously occurred. However, not all $Cl^-$ ions were substituted by $F^-$ ions.

## 4. Conclusions

Both $C_{11}A_7 \cdot CaF_2$ and $C_{11}A_7 \cdot CaCl_2$ formed at 900 °C or above in preference to the hydroxyl-substituted phase. The $a_0$ of $C_{12}A_7$ss decreased continuously with an increase in its content of fluoride ions or with a decrease in its content of chloride ions. When $CaF_2$ and $CaCl_2$ were both included in the raw materials, $C_{11}A_7 \cdot CaCl_2$ was preferentially generated.

The $OH^-$ ions in $C_{11}A_7 \cdot Ca(OH)_2$ could easily be replaced by either fluoride or chloride ions by heating it with the calcium halide. The substitution of fluoride ions began at 500 °C; that of chloride ions began at 700 °C. The fluoride ions in $C_{11}A_7 \cdot CaF_2$ could also be replaced by chloride ions of $CaCl_2$ at 700 °C or above. On the other hand, the replacement of chloride ions in $C_{11}A_7 \cdot CaCl_2$ by fluoride ions from $CaF_2$ was observed at above 1000 °C, but was assumed to be caused by slow volatilization of chloride, which increased with increasing temperature.

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