

FIXATION OF CHLORIDE AND/OR FLUORIDE IONS IN MAYENITE DURING INCINERATION OF MUNICIPAL WASTE

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Introduction

In recent Japan, combustible waste has been incinerated aggressively from the viewpoint of volume reduction and public sanitation. If unburnt carbon, aromatic compounds and various chlorides are coexistent in the combustion gas, however, dioxins and dioxin-like compounds may be generated during the exhaust gas cooling. It is reasonable to suppose that the formation of dioxin is suppressed if chloride ion is fixed to the inorganic ash. Therefore, the theme of our research is about the fixation of chloride ion generated during incineration of municipal waste, waste plastics and sewage sludge. In addition, the influence of fluoride ion on a fixation behaviour of chloride ion was examined.

We chose “mayenite” corresponding to the chemical formula of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7 for short, $\text{CaO}=\text{C}$, $\text{Al}_2\text{O}_3=\text{A}$) in order to fix halide ion (see Fig. 1). It has been reported that unit cell of C_{12}A_7 is $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\text{X}_2$, and X means a lattice vacancy or disordered oxygen. The compound known as C_{12}A_7 is not strictly anhydride under normal humidity and is able to incorporate water at high temperature range of $900^\circ\text{--}1300^\circ\text{C}$.¹⁻³ A chemical composition formula having saturated water is suggested as $\text{C}_{11}\text{A}_7 \cdot \text{Ca}(\text{OH})_2$ and hydroxyl ion is exchanged with halide ion such as fluoride and chloride.⁴⁻⁷ In this study, the immobilization process of chloride ion using $\text{C}_{11}\text{A}_7 \cdot \text{Ca}(\text{OH})_2$ was investigated in detail. Moreover, halogenide-ion selectivity between chloride ion and fluoride ion was reported in this symposium.

Materials and methods

Reagents of CaCO_3 , $\text{Al}(\text{OH})_3$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and CaF_2 were used as starting material. In the synthesis of C_{12}A_7 and its analogues, each reagent was weighed out so as to give the desired stoichiometric composition, and was mixed for 30 minutes to prepare a uniform mixture. The mixture was burned at a given temperature for 4 hours in an electric furnace, and then the operation was repeated after crushing of burned product. The summary of experimental procedure is shown in Fig. 2. Compounds in the burned product were identified by powder X-ray diffractometer (XRD) using a Rigaku RAD-IIA diffractometer with a Ni-filtered $\text{Cu K}\alpha_1$ radiation. Lattice constant and a rough quantitative value were calculated from the diffraction peaks which were calibrated using silicon as the internal standard.

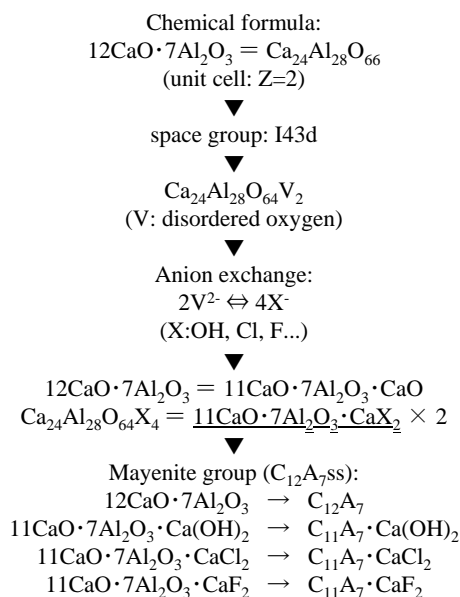


Fig. 1. What is “Mayenite” ?

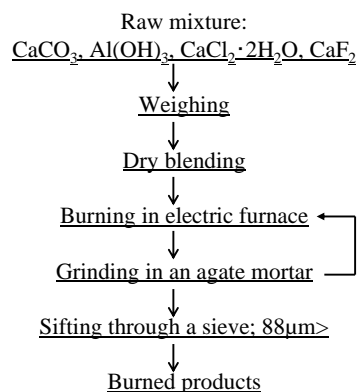


Fig. 2. Flow chart of $\text{C}_{12}\text{A}_7\text{ss}$ synthesis.

Results and discussion

Formation process of $C_{12}A_7$ ss

In binary system of $CaO-Al_2O_3$ under dry condition, C_3A , CA , CA_2 and CA_6 are present as a stable phase. So-called $C_{12}A_7$ would generate under normal humidity, however, the chemical formula saturated with water is shown as $C_{11}A_7 \cdot Ca(OH)_2$. Figure 3 showed that $C_{12}A_7$, $C_{11}A_7 \cdot CaCl_2$ and $C_{11}A_7 \cdot CaF_2$ would be a single phase at above 1350, 900 and 900°C, respectively. Halogenated $C_{12}A_7$ ss was able to generate in the presence of $CaCl_2$ and CaF_2 , the solid solution did not decompose to the other calcium aluminates. It seemed quite probable that $C_{12}A_7$ ss is able to fix various halide ions such as fluoride and chloride ion at high temperature.

Lattice constant (a_0) of $C_{12}A_7$ ss

Fig. 4 shows the change of lattice constant (a_0) of $C_{12}A_7$ ss produced by raw materials including either $CaCl_2 \cdot 2H_2O$ or CaF_2 . The mixtures were compositions of which one mole of CaO in $C_{12}A_7$ was wholly or partly substituted by either $CaCl_2$ or CaF_2 . All of their mixtures were burned at 1300°C. The a_0 of $C_{12}A_7$ ss was different depending on the kind and amount of halide ion, that is, the a_0 increased with increasing the amount of chloride ion continuously and decreased with increasing fluoride content on the other hand. The a_0 of $C_{12}A_7$ ss containing either chloride ion or fluoride ion was corresponding to the content of each halide ion, furthermore, hydroxide ion was thought to be bound to the remaining anion site.

Influence of burning temperature and amount of calcium halides on the a_0 of $C_{12}A_7$ ss

Mixtures were prepared in the composition of $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaCl_2$ and $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaF_2$, and then, they were burned at various temperatures in air with normal humidity. Each formula corresponded to the composition for which one mole of CaO in $C_{12}A_7$ was wholly or partly substituted by calcium halide.

The a_0 of $C_{12}A_7$ ss in the case of $CaCl_2$ substitution is shown in Fig. 5. The a_0 of $C_{12}A_7$ ss increased continuously with an increase in the amount of $CaCl_2$. Expansion of the crystal lattice showed a change of composition from $C_{11}A_7 \cdot Ca(OH)_2$ to $C_{11}A_7 \cdot CaCl_2$, however, rate of change in the a_0 increased with a increase in the burning temperature. The a_0 of products burned at 900°C indicated a value of $C_{11}A_7 \cdot CaCl_2$, and showed a value close to that of the $C_{11}A_7 \cdot Ca(OH)_2$ at higher

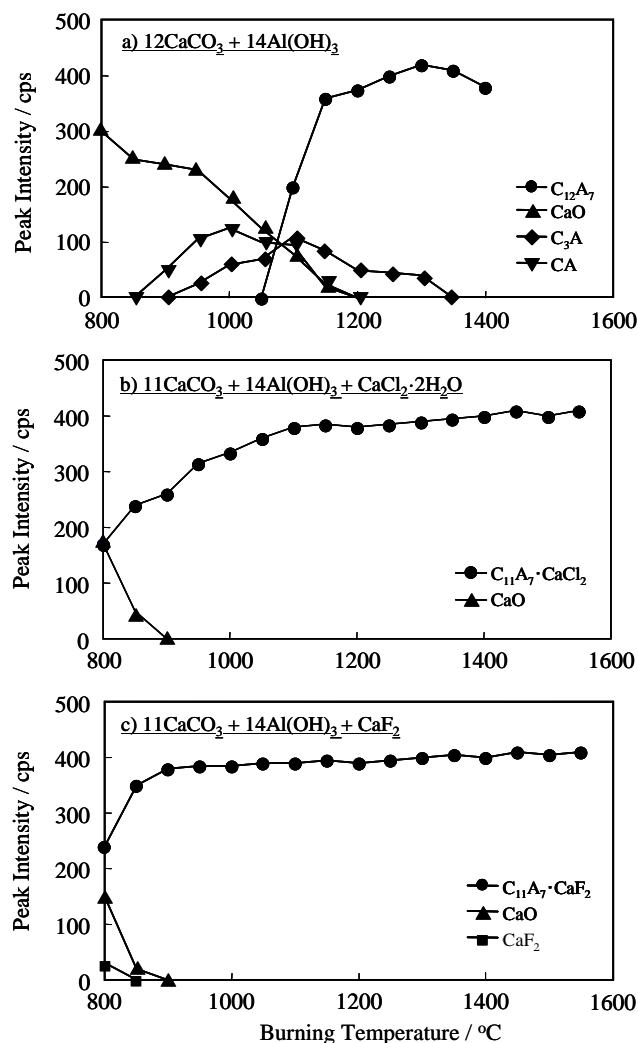


Fig. 3. Formation process of $C_{12}A_7$ ss.

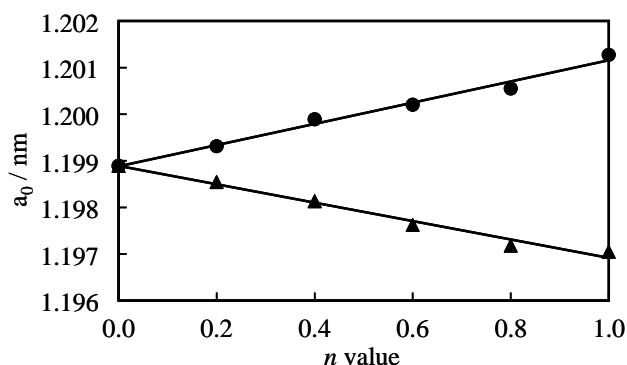


Fig. 4. Lattice constants of halogenated $C_{12}A_7$ ss burned at 1300°C. (●) $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaCl_2$ composition; (▲) $(12-n)CaO \cdot 7Al_2O_3 \cdot nCaF_2$ composition

temperature range. The case of CaF_2 substitution is shown in Fig. 6. The a_0 of $\text{C}_{12}\text{A}_7\text{ss}$ decreased continuously with an increase in the amount of CaF_2 . Shrinkage of the crystal lattice showed a change of composition from $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$ to $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$, and as a result the formation of $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH}, \text{F})_2$ was confirmed. As well as in the case of CaCl_2 substitution, change rate in the a_0 increased with a increase in burning temperature. The a_0 of products burned at 900°C were close to that of $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$.

The peak intensity of $\text{C}_{12}\text{A}_7\text{ss}$ 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 $\text{C}_{11}\text{A}_7\cdot\text{CaCl}_2$ or $\text{C}_{11}\text{A}_7\cdot\text{CaF}_2$, and not their hydroxylated solid solutions, were formed at 900°C as $\text{C}_{12}\text{A}_7\text{ss}$. In those cases, it was also confirmed that CA and free lime were coexistent to halogenated $\text{C}_{12}\text{A}_7\text{ss}$.

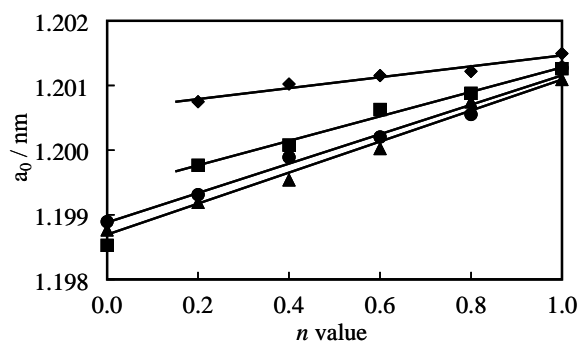


Fig. 5. Lattice constants of $\text{C}_{12}\text{A}_7\text{ss}$ produced from $(12-n)\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot n\text{CaCl}_2$ composition. (◆) 900°C , (■) 1100°C , (▲) 1300°C , and (●) 1350°C .

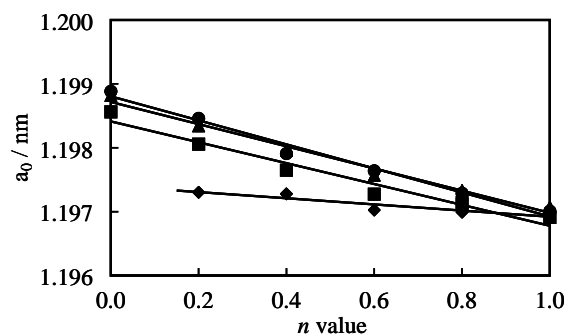


Fig. 6. Lattice constants of $\text{C}_{12}\text{A}_7\text{ss}$ produced from $(12-n)\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot n\text{CaF}_2$ composition. (◆) 900°C , (■) 1100°C , (▲) 1300°C , and (●) 1350°C .

The a_0 of $\text{C}_{12}\text{A}_7\text{ss}$ generated from the raw material containing both calcium fluoride and calcium chloride

Fig. 7 shows the a_0 of $\text{C}_{12}\text{A}_7\text{ss}$ generated from the mixtures, which contained both calcium fluoride and calcium chloride. The raw material was prepared with the composition of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot \text{CaCl}_2\cdot \text{CaF}_2$, of which the total amount of halides exceeded the solubility to C_{12}A_7 . A gradual decrease of the a_0 with an increasing of burning temperature meant the elimination of chlorine 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 chloride ion in crystal lattice of $\text{C}_{12}\text{A}_7\text{ss}$. This result proved clearly that $\text{C}_{11}\text{A}_7\cdot\text{CaCl}_2$ was preferentially formed when calcium fluoride coexisted with calcium chloride.

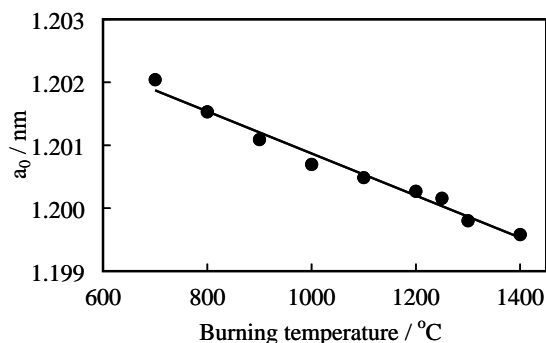


Fig. 7. Influence of burning temperature on the lattice constants of $\text{C}_{12}\text{A}_7\text{ss}$ with burning temperature. Mixing ratio of $\text{CaCO}_3\cdot\text{Al}(\text{OH})_3\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}\cdot\text{CaF}_2$ is 12:14:1:1 in mole.

Ion-exchange reaction between $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$ and various calcium halides

Ion-exchange reaction, in other words, anion-substitution reaction between $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$ and various calcium halides were examined. The compound $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$ was synthesized by burning at 1350°C in atmosphere with normal humidity. Then, mixtures of $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$ with $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ and/or CaF_2 were burned. The mixing ratio of $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$:calcium halide was 1:1 by mole. The change of the a_0 of $\text{C}_{12}\text{A}_7\text{ss}$ with burning temperature are shown in Fig. 8. In the case of $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ addition, hydroxyl ion in $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$ was exchanged for chloride ion at 1000°C or more. On the other hand, the substitution reaction between hydroxyl ion and fluoride ion occurred at 500°C by the addition of CaF_2 . When both CaF_2 and $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ were added to $\text{C}_{11}\text{A}_7\cdot\text{Ca}(\text{OH})_2$, the exchange for fluoride ion and for chloride ion 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. The slow decreases in a_0 value observed for the chlorinated phase at temperatures of above $1000^\circ C$ 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.⁶

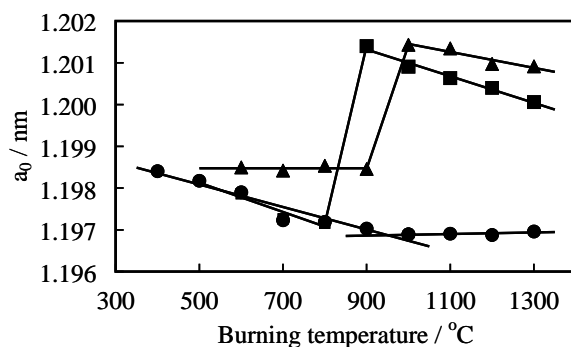


Fig. 8. Influence of burning temperature on anion substitution between $C_{11}A_7 \cdot Ca(OH)_2$ and various halides. (▲) added $CaCl_2 \cdot 2H_2O$, (●) added CaF_2 , and (■) added both $CaCl_2 \cdot 2H_2O$ and CaF_2 .

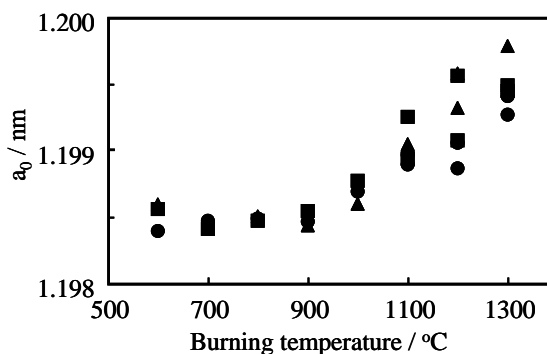


Fig. 9. Lattice constants of $C_{12}A_7$ ss produced from $C_{11}A_7 \cdot Ca(OH)_2$ mixed with n mol of $NaCl$. (●) $n=1$, (▲) $n=2$, (■) $n=3$

Ion-exchange reaction between $C_{11}A_7 \cdot Ca(OH)_2$ and sodium chloride

It was inferred that residual ash included much kinds of chloride because various wastes were incinerated. Figure 9 shows the a_0 of $C_{12}A_7$ ss generated from the mixtures of $C_{11}A_7 \cdot Ca(OH)_2$ and $NaCl$. It was confirmed that chlorine was fixed because the a_0 of $C_{12}A_7$ ss was increased at the temperature of $1000^\circ C$ or more. The lattice of $C_{12}A_7$ ss expanded with increasing the amount of chloride at the higher temperature region though there were slight variations.

Conclusions

- 1) Single phases of $C_{11}A_7 \cdot Ca(OH)_2$, $C_{11}A_7 \cdot CaCl_2$ and $C_{11}A_7 \cdot CaF_2$ formed at 1350 , 900 and $900^\circ C$ or more, respectively. The a_0 of $C_{12}A_7$ ss decreased continuously with a decrease in a content of chloride ion with an increase in a content of fluoride ion. When both calcium chloride and calcium fluoride were included in raw materials, $C_{11}A_7 \cdot CaCl_2$ was preferentially generated.
- 2) Hydroxyl ion in $C_{11}A_7 \cdot Ca(OH)_2$ could easily be replaced by either fluoride or chloride ion by heating it with calcium halide. Substitution of fluoride ion began at $500^\circ C$; that of chloride ion began at $1000^\circ C$.
- 3) Anion exchange between hydroxyl ion in $C_{11}A_7 \cdot Ca(OH)_2$ and chloride ion of sodium chloride occurred at above $1000^\circ C$.

From the above results, $C_{11}A_7 \cdot Ca(OH)_2$ was found to be a promising material for fixing the chloride ion in the high-temperature range. Therefore, it is expected that the generation of dioxins and dioxin-like compounds would be suppressed by the immobilization of chloride ion. Because chloride ion was absorbed into $C_{11}A_7 \cdot Ca(OH)_2$ in preference to fluoride ion, fluoride ion did not interfere with the fixation of chloride ion.

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