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Study on the composition and hydration of alinite and calcium chloroaluminate minerals

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Abstract

The alinites and calcium chloroaluminates are main minerals of ecocement. In this paper, the alinite and calcium chloroaluminate minerals are synthesized. Analytical reagents are mixed into the raw meals of alinite and calcium chloroaluminate that are burnt under different temperatures. Through the content of f-CaO detection and XRD analysis, we have confirmed the firing condition. Especially, the scanning electron microscope SEM-EDS analysis are used to test and analyze the composition and hydration mechanism of the minerals.

Keywords: Alinite; Calcium–silicate–hydrate; Chloride; EDS; Hydration products

1. Introduction

The cement industry, which is a large-scale industry, is a large consumer of mineral and energy resources and needs to search new minerals and energy resources. The present research mainly involves the synthesis of alinites and calcium chloroaluminates, the main minerals of alinite cement [1]. Ecocement is a new type of cement produced with recycled materials [2]. The primary raw materials are wastes such as the residue from municipal waste incinerators (ash and soot). From 1994 to 1998, Taiheiyo Cement of Japan conducted joint research and development between the public and private sectors and established the technology to produce ecocement, whose main clinker minerals are alinites and calcium chloroaluminates [3]. Taking use of incineration of urban waste and sludge as raw material for firing ecocement, because their compositions are complex, the clinker minerals are also complex. The composition and hydration mechanism of the minerals are studied by scanning electron microscope SEM-EDS especially in this paper.

2. Experiments

Pure analytical reagents $CaCO_3$, Al_2O_3, $CaCl_2$, SiO_2 and MgO are used as raw materials. Calcium chloroaluminates are synthesized according to the stoichiometry molar ratio of $C_{11}A_7CaCl_2$ (C_1) and $10.95CaO7Al_2O_31.05CaCl_2$ (C_2). The alinite is synthesized according to the chemical molar ratio of $Ca_{10}Mg_{0.8}\square_{0.2}(SiO_4)_{3.4}(AlO_4)_{0.6}O_2Cl$ (A_M) and $Ca_{11}[(Si_{0.75}Al_{0.25})O_4]_4O_2Cl$ (A_o) [4–6]. Each reagent is weighed accurately in proportion and mixed. The meals are homogenized and ground to pass a 75-μm sieve and pressed to cylinders as $\Phi 60\times 10$ mm^3. These cylinders are dried for 1 h at 100 °C, then burnt at different temperatures for 2 h. Finally, the samples are taken out to cool to room temperature and ground to 350m^2/g (Blaine). Free CaO of all clinkers is determined by the ethylene glycol method [7]. The optimal samples are mixed with water to a W/C ratio of 0.4, and the paste is put into the $2\times 2\times 2$ cm^3 moulds with vibration. These paste specimens are demoulded after being cured

Table 1
The content of f-CaO of C_1 and C_2 fired at different temperatures (%)

Temperature (°C)		1000	1100	1200	1250	1300
f-CaO	C_1	4.00	2.50	1.42	0.65	0.22
	C_2	3.87	1.90	0.71	0.24	0.00

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Table 2
The contents of f-CaO of different treating times at different temperatures (%)

Sample	Temperature (°C)	1150			1200	1250	1300
	Treating time (h)	2	4	12	2	2	2
A_O		17.67	12.76	25.43	15.95	15.86	15.80
A_M		9.14	7.33	19.00	9.00	8.36	7.64

in moist air at 20 °C for 1 day; then, the specimens are cured in water to each age for the measurement of the compressive strength.

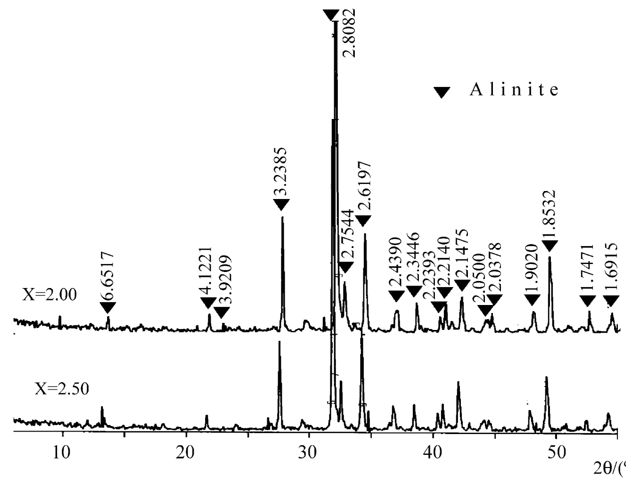

Fig. 2. XRD patterns of clinkers (A_{M5}) burnt at 1375 °C (Cu Kα).

3. Results and discussion

3.1. The f-CaO of the clinkers

3.1.1. The f-CaO of calcium chloroaluminate

The contents of f-CaO of C_1 and C_2 are listed in Table 1 at different temperatures. It shows that the contents of f-CaO decrease with the improvement of firing temperature and the excessive quantity of Cl. The content of f-CaO of C_2 decreases to 0 when fired at 1300 °C for 2 h.

3.1.2. The f-CaO of alinite

At first, the raw meals are burnt at 1150 °C, but different treating time in the course of synthesizing alinite minerals. The contents of f-CaO are shown in Table 2. It shows too much f-CaO in A_O and A_M that indicates that the firing temperature is under the needed. Hence, in the extended experiments, the temperatures are selected at 1200, 1250 and 1300 °C, while the treating time is selected to be 2 h. According to Table 2, the content of f-CaO decreases with the increasing temperature.

From the above experiments, it is shown that it is difficult to get pure alinite mineral only by increasing temperature. Considering that the main reason is the evaporation of element Cl, in the extended experiments, the Cl content is improved. A_M is easier to get than A_O, and it is

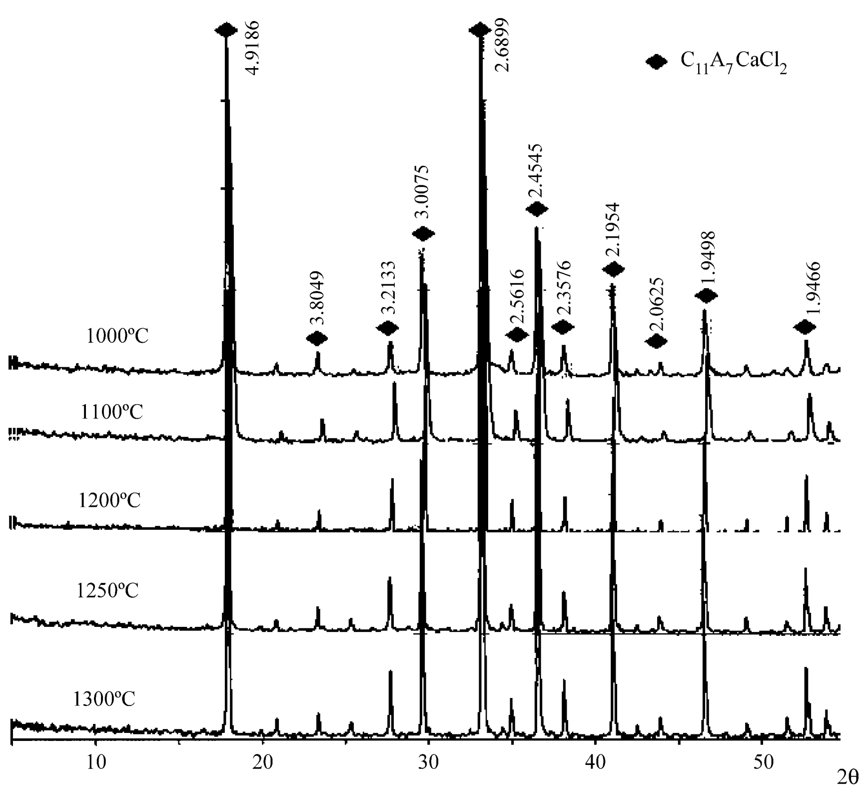

Fig. 1. XRD patterns of C_2 fired at different temperatures (Cu Kα).

said that A_O is difficult to exist because it has no Mg ion. Hence, we studied the composition of A_M only.

Based on the above experiments, considering that the f-CaO content is too high, the content of Cl and firing temperature have been improved. With the improving of Cl in A_M, naming them as A_{M1}, A_{M2}, A_{M3}, A_{M4} and A_{M5}, respectively, we selected the firing temperature as 1250, 1300, 1350 and 1375 °C and clinkering time as 2 h. The content of f-CaO (Table 3) shows that the content of f-CaO decreases with increasing firing temperature and quantity of Cl. The content of f-CaO of A_{M5} decreases down to 0 at 1375 °C.

3.2. The XRD analysis of the clinkers

The XRD patterns of C_2 under different firing temperatures are shown as Fig. 1. It is seen that the peaks of $C_{11}A_7CaCl_2$ are stronger with the increasing firing temper-

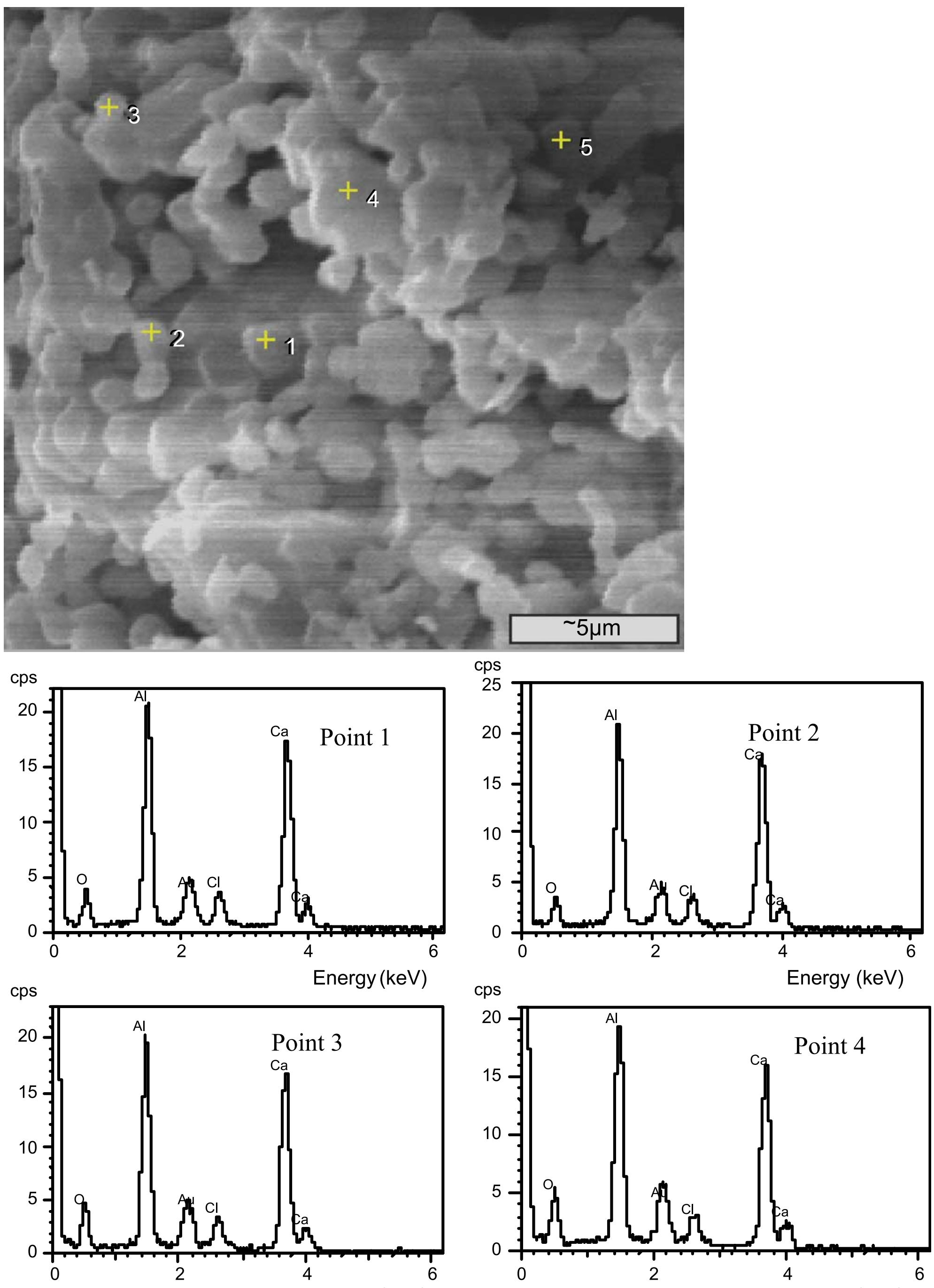

Fig. 3. The SEM photo and EDS patterns of C_2 clinkering at 1300 °C.

ature. All the peaks of C_2 belong to $C_{11}A_7 \cdot CaCl_2$ when fired at 1300 °C that shows a complete synthesis.

Fig. 2 is the XRD patterns of A_{M5}, which is burnt at 1375 °C. All the peaks belong to alinite, indicating a complete synthesis [8].

3.3. The SEM-EDS analysis of clinkers

3.3.1. The SEM-EDS analysis of calcium chloroaluminate

Using the S-2500 SEM and Oxford Link ISIS 300 XEDS, the SEM photo of C_2 that clinkering at 1300 °C are showed in Fig. 3. It appears as hexagonal, and the particle size is about 2–3 μm.

From the EDS patterns of calcium chloroaluminate mineral and from Table 4, it is seen that the average composition of calcium chloroaluminate mineral is $C_{10.82}A_{7.86}CaCl_2$.

3.3.2. The SEM-EDS analysis of alinite

Fig. 4 shows the SEM photo of alinite (A_{M5}), from which it is seen that alinite is column-shaped. From Table 5, it is seen that the average proportion is $Ca_{8.78}Mg_{1.02}(SiO_4)_{4.34}(AlO_4)_{0.77}O_{0.5}Cl$.

3.4. The analysis of hydration samples

3.4.1. The compressive strength of hydration samples

The compressive strength of the hydration samples are listed in Table 6, which shows both calcium chloroaluminate and alinite have good strength property.

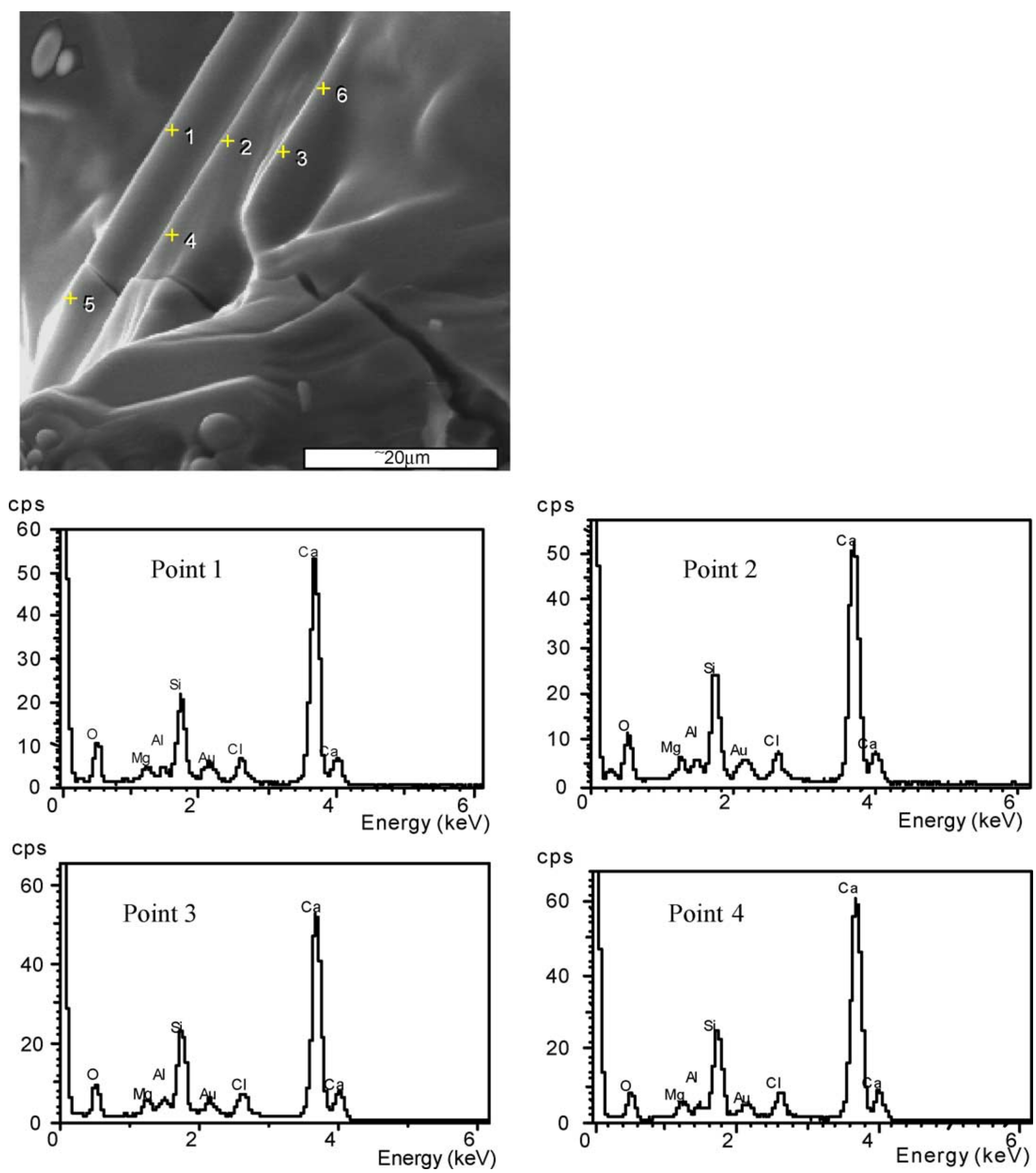

Fig. 4. The SEM photo and EDS patterns of alinite mineral (A_{M5}).

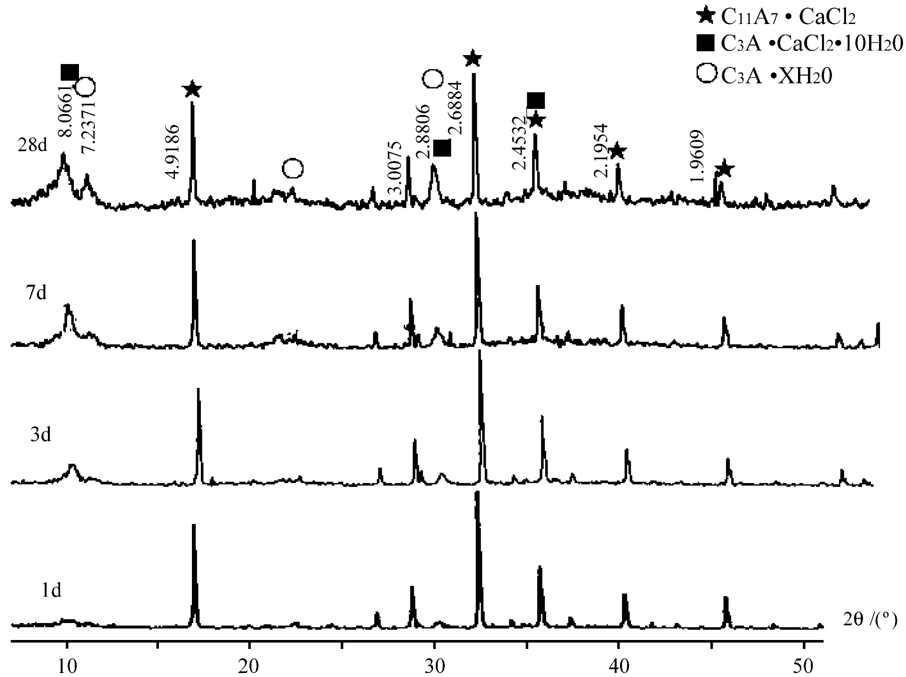

Fig. 5. XRD patterns of calcium chloroaluminate hydrated samples (Cu Kα).

3.4.2. The XRD analysis of hydrated samples

From Fig. 5, it is seen that the hydrated products of calcium chloroaluminate are mainly $C_3ACaCl_210H_2O$, C_3AxH_2O and $Al_5Cl_3(OH)_{12}{\cdot}7.5H_2O$.

The XRD patterns of hydrated samples of alinite at different curing ages (Fig. 6) show that the hydrated products of alinite are mainly $Ca_5Al_2(OH)_4Si_3O_{12}$, $Ca_3Al_2(SiO_4)_{1.25}(OH)_7$ and $Ca(OH)_2$.

3.4.3. The SEM-EDS analysis of hydrated samples

The SEM photos of C_2 clinkering at 1300 °C at different ages are analyzed (Fig. 7).

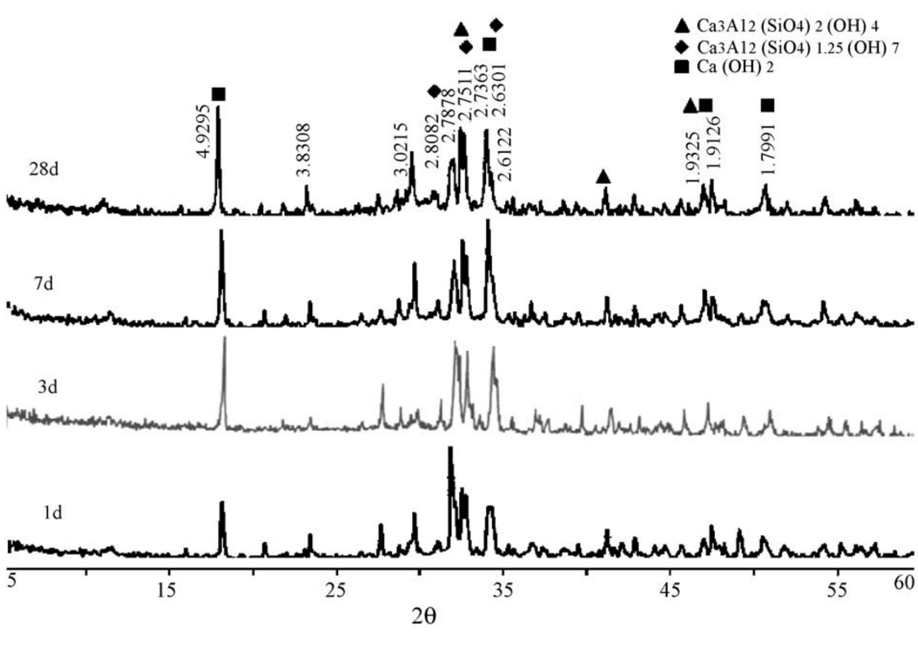

Fig. 6. XRD patterns of alinite hydrated samples (Cu Kα).

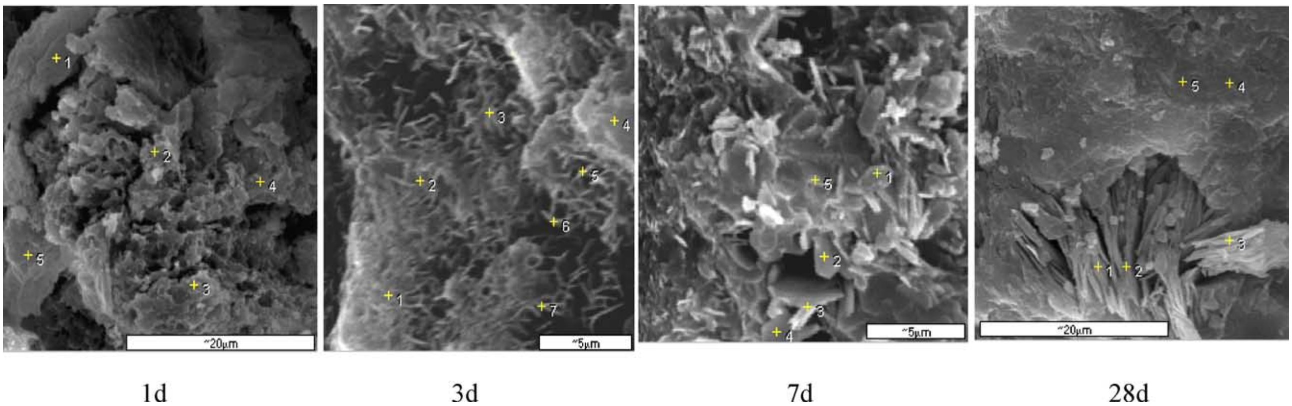

Fig. 7. SEM photos of calcium chloroaluminate hydrated samples (C2 clinkering at 1300 °C).

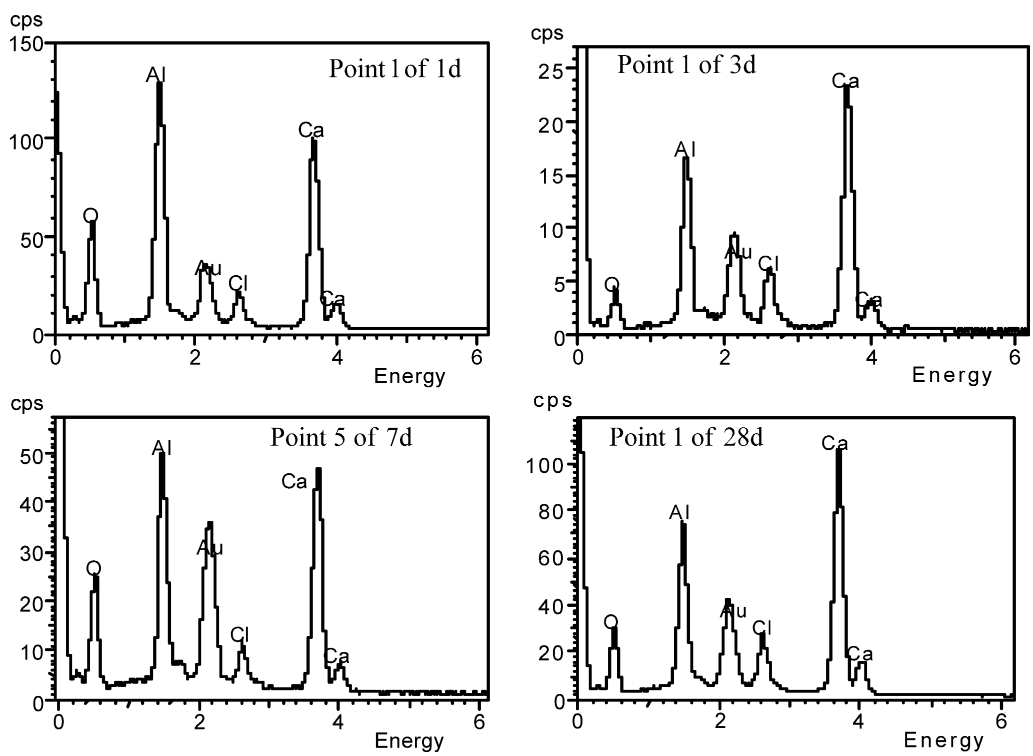

Fig. 8. EDS patterns of calcium chloroaluminate hydrated samples.

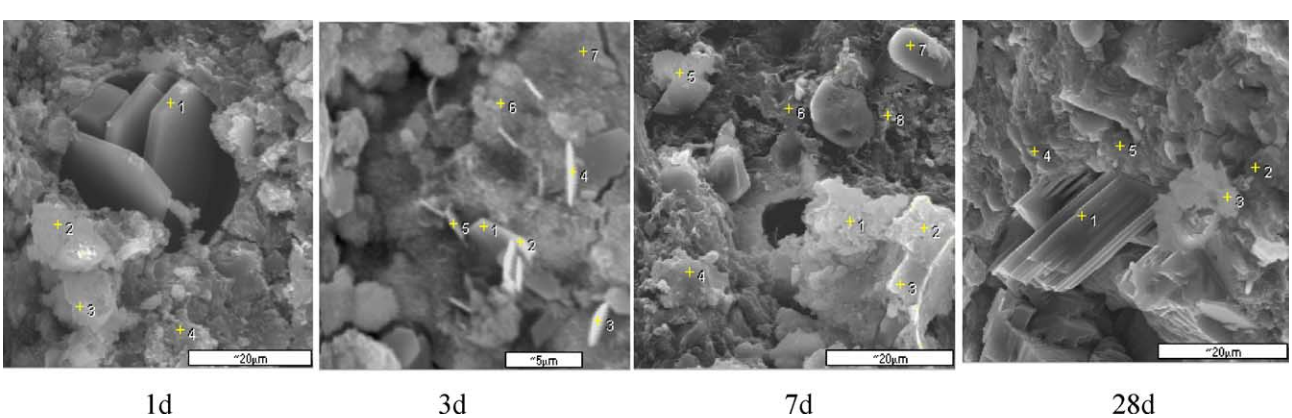

Fig. 9. SEM photos of hydrated samples of alinite (A_{M5}).

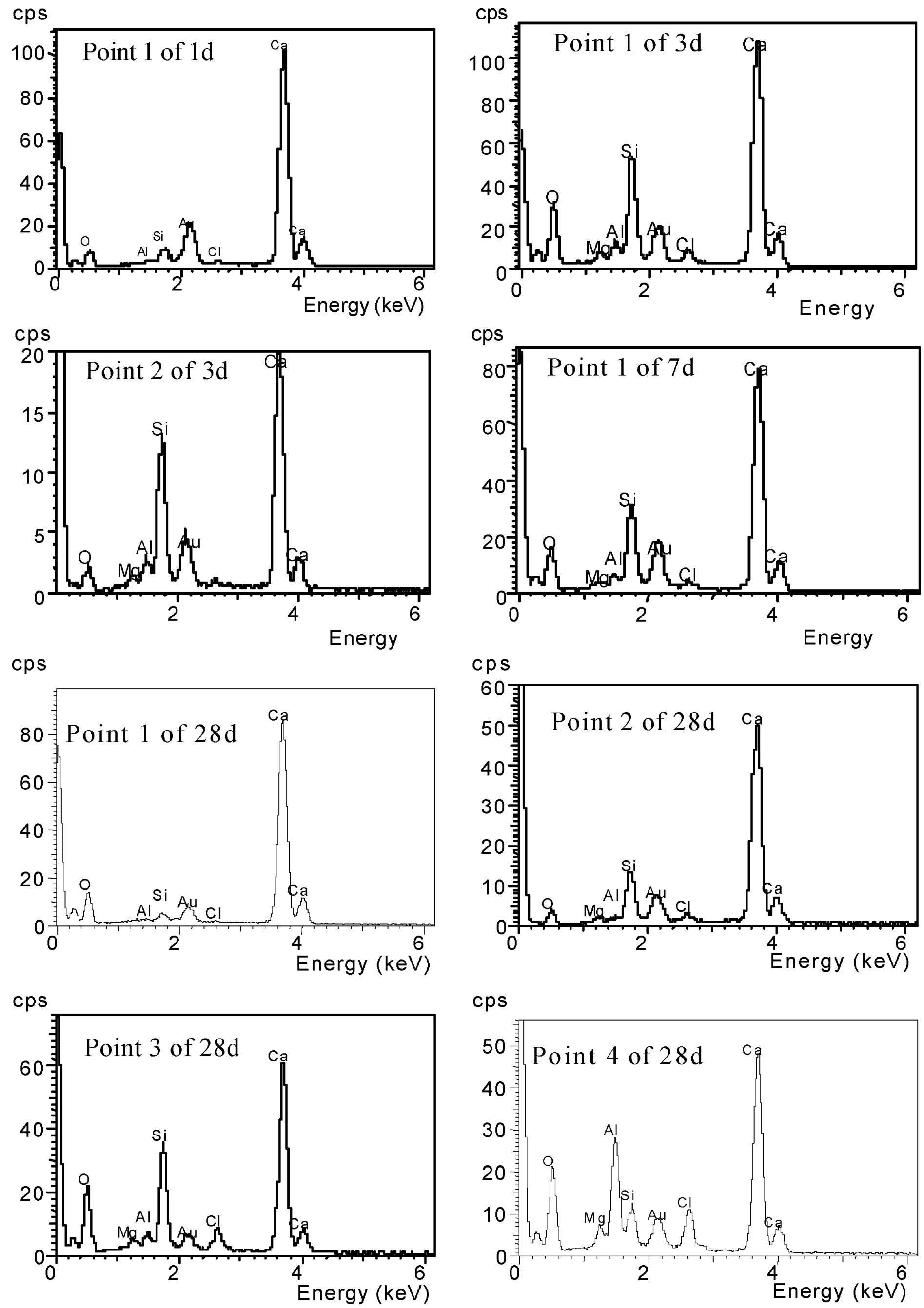

Fig. 10. XEDS patterns of hydrated samples of alinite mineral (A_{M5}).

From Fig. 8 and Table 7 (C_2 clinkering at 1300 °C), we can see some crystal that Point 1 of 1 d is $C_{13.33}A_{7.16}CaCl_2 \cdot 9H_2O$, Point 1 of 3 d is $C_{11.17}A_{5.97}CaCl_29.95H_2O$, Point 5 of 7 d is $C_{9.25}A_{5.92}CaCl_29.88H_2O$, Point 1 of 28 d is $C_{5.09}A_{3.59}CaCl_210.26H_2O$ and Point 4 of 28 days is $C_{11.46}A_{10}CaCl_216H_2O$.

Table 3
The content of f-CaO of clinkers burnt at different temperatures (%)

Temperature (°C)	A_{M1}	A_{M2}	A_{M3}	A_{M4}	A_{M5}
1250	7.25	6.45	5.54	3.51	2.91
1300	4.24	3.10	2.20	1.55	1.24
1350	3.96	2.80	1.54	1.04	0.83
1375	3.00	2.32	1.02	0.52	0.00

Table 4
Atomic proportion of points in Fig. 3

Element	1	2	3	4	5	Average	Theoretic
Al	24.77	24.09	24.43	24.91	22.80	24.20	23.33
Cl	3.07	3.16	2.87	3.07	3.25	3.08	3.33
Ca	17.50	18.31	18.03	17.33	19.87	18.21	20.00
O	54.66	54.44	54.67	54.69	54.08	54.51	53.33
Total	100.00	100.00	100.00	100.00	100.00	100.00	99.99

Table 5
Atomic proportion of points in Fig. 4

Element	1	2	3	4	5	Average	Theoretic
Mg	2.67	3.19	3.21	2.45	2.90	2.88	2.35
Al	2.07	2.41	2.29	1.92	2.22	2.18	1.76
Si	12.11	12.41	11.87	12.04	12.59	12.20	10.00
Cl	2.85	2.70	2.83	3.10	2.57	2.81	2.94
Ca	25.16	23.84	24.71	25.53	24.17	24.68	29.41
O	55.15	55.45	55.09	54.95	55.56	55.24	52.94
Total	100.00	100.00	100.00	100.00	100.00	99.99	99.40

Table 6
The compressive strength of the minerals (W/C = 0.4)

Sample	Compressive strength (MPa)			
	1 d	3 d	7 d	28 d
C_1	28.8	38.4	47.0	57.7
C_2	37.0	45.4	50.0	65.7
Alinite	26.1	41.0	52.5	67.6

From the SEM photos (Fig. 9) of different hydration ages of alinite, it is seen that $Ca(OH)_2$ in 1-d hydrated samples coexist with the C-S-H gel. Fig. 10 and Table 8 shows that there are $Ca(OH)_2$ in 3d, 7d and 28d hydrated samples, some Ca_5Al_2 $(SiO_4)_3(OH)_4$, $Ca_3Al_2(SiO_4)_{1.25}(OH)_7$ and C-S-H in 3-, 7- and 28-day samples.

4. Conclusions

1. The optimal condition of calcium chloroaluminates is at the firing temperature of 1300 °C for 2 h alinite synthesized at 1375 °C for 2 h.
2. The alinite and calcium chloroaluminate mineral have good compressive strength property.
3. The hydrated products of $C_{11}A_7CaCl_2$ are mainly hydrated calcium chloroaluminates.
4. The hydration rate of alinite is quick. The hydrated products of alinite are mainly $Ca(OH)_2$, Ca_5Al_2 $(SiO_4)_3$ $(OH)_4$, $Ca_3Al_2(SiO_4)_{1.25}(OH)_7$ and C-S-H.

Acknowledgements

This work was financed by the Natural Science Foundation of Shandong Province (012120109).

Table 7
Atomic proportion of points in Fig. 7

Atomic	Point 1 of 1 day	Point 1 of 3 days	Point 5 of 7 days	Point 1 of 28 days	Point 4 of 28 days
Al	23.50	21.25	22.72	19.12	25.99
Cl	3.27	3.56	3.84	5.31	2.6
Ca	18.99	21.66	19.68	23.45	16.2
O	54.24	53.53	53.76	52.12	55.19
Total	100.00	100.00	100.00	100.00	100.00

Table 8
Atomic proportion of points in Fig. 10

	Point 1 of 1 d	Point 1 of 3 d	Point 2 of 3 d	Point 1 of 7 d	Point 1 of 28 d	Point 2 of 28 d	Point 3 of 28 d	Point 4 of 28 d
Mg	–	1.85	1.69	0.10	–	1.37	1.70	3.05
Al	0.34	2.82	3.05	0.33	0.20	0.93	1.92	13.44
Si	3.93	13.60	14.46	3.95	2.26	9.76	12.60	5.77
Cl	0.78	1.36	1.30	0.75	0.3	1.29	1.50	4.19
Ca	43.29	23.54	22.17	43.32	46.19	32.17	26.25	19.39
O	51.66	56.83	57.34	51.55	51.00	54.47	56.03	54.15
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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