The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Synthesis of Alinite-Calciumchloroaluminate System Cement Using Solid State Waste

Jin-Sang Cho[1], Gi-Chun Han[1], Hyung-Seok Kim[1], Ji-Whan Ahn[1], Hwan Kim[2], Hyoung Ho Lee[2]
[1]Korea Institute of Geoscience and Mineral Resource, Daejeon,305-350, Korea
[2]Seoul National University, Seoul, 151-744, Korea

Alinite-Calciumchloroaluminate system clinker was synthesized from solid state waste. The raw materials were municipal incineration ash, sewage sludge, limestone and clay. ecocement was prepared by the mixing of synthesized clinker and optimum amount of gypsum and its hydrolysis characteristic was investigated. X-ray diffraction, conduction calorimeter and reflecting microscope were used to analyze structural and physical properties. The main phase of clinker were alinite, calcium chloroaluminate, C_2S, C_3S. From the results of hardening time, hydration reactivity of synthesized all samples was faster than that of ordinary portland cement.

1. Introduction

The processing technique and expenses of urban waste, sewage sludge and industry waste have been raised as a social problem, as the industrialization is rapidly progressing. Hence, considerable efforts have been devoted to develop safe processing and recycling techniques of such waste and sewage sludge around advanced countries.

It has been reported that the production of sewage sludge was 1.4 million ton in 1997, but only 3.5%, 45 thousand ton of total production has been used for the soil enrichment, construction materials, planting and breeding of earthworm etc., a large portion of the sludge has been reclaimed in the ground or abandoned in the sea. Furthermore, 70% of recycled sludge has been used for the compost of orchard. Especially, the reclamation of sewage sludge can cause secondary pollution during transportation because 80% of the sludge is water, then the hardening of the ground is difficult. That is why the use of the sewage sludge is avoided.

Moreover, municipal waste is rapidly increasing, and thus produced incineration ash seems to be proportionally increased.

The incineration ash produced from urban refuse contains heavy metals and harmful materials all of wich, apart from chlorines, phosphorus and zinc, are within required tolerance limits. However, the chlorine content can be as high as 10%.

Cement produced from those raw materials includes alinite cement containing calcium chlorosilicate including alinite $2C_3S \cdot CaCl_2 \cdot [Ca_{9.9}Mg_{0.8}\ _{0.3}(SiO_4)_{3.4}(AlO_4)_{0.6}O_{1.9}$ Cl, where is vacancy] and belinite $C_2S \cdot CaCl_2$ and calcium chloroaluminate $C_{11}A_7 \cdot CaCl_2$ as a hydraulic materials, and calcium chloroaluminate cement composed of calcium silicate and calcium chloroaluminate produced by substituting $C_{11}A_7 \cdot CaF_2$ of Jet Cement for $C_{11}A_7 \cdot CaCl_2$.

The composition of cement can be optimized to produce delayed hardening, low strength alinite cement and ultra-raped-hardening, high strength calcium chloroaluminate cement.

Hence, the purpose of this study is to develop manufacturing process of early-high strength cement containing Cl and main component is Alinite system ore by using the municipal waste as raw material and fuel, in order to recycle incineration ash and sewage sludge.

2. Experimental Procedures

2.1 Experimental and analysis

Law materials were mixed with proper ratio and clinker was produced by heating treatment in kantal and burnerability testing furnace, thus prepared clinker was mixed with appropriate amount of gypsum, crushed by lab mill and fabricated to cement.

In this study, different mixing ratio compared to that of the ordinary Portland cement was applied for the preparation of clinker, because new component ore is formed in this system

2.2 Raw materials

2.2.1 Municipal Incineration Ash

Fly ashes which were obtained from municipal waste incineration furnaces installed in Ilsan and Dadae area in Korea were used as raw materials and their chemical composition is shown in Table 1.

The main compositions of fly ash are Ca, Si, Al, Na and K, especially Cl is about 25%. The composition differences between two ashes are negligible, whereas Ca content was analyzed very higher in Ilsan fly ash then the Dadae's. This is attributed to the differences of dust

Table 1 Chemical Composition of fly ash (wt.%)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	Cl(ppm)	LOI
Iisan	7.10	3.15	0.91	0.77	2.21	41.86	5.47	4.60	0.11	2.16	267.005	15.04
Dadae	6.07	23.28	0.92	0.64	1.60	8.85	9.58	12.37	0.1	2.31	255.970	43.27

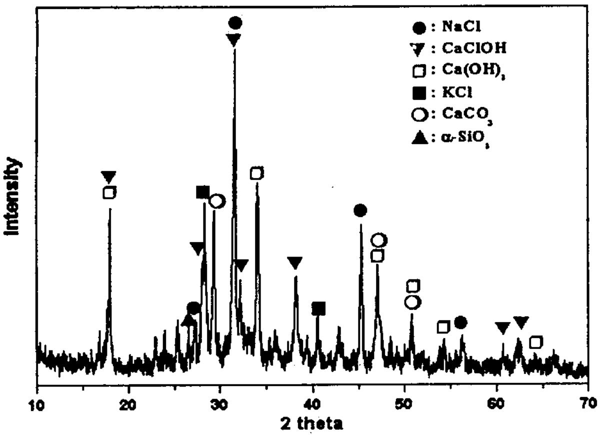

Fig. 1. XRD pattern of Ilsan fly ash.

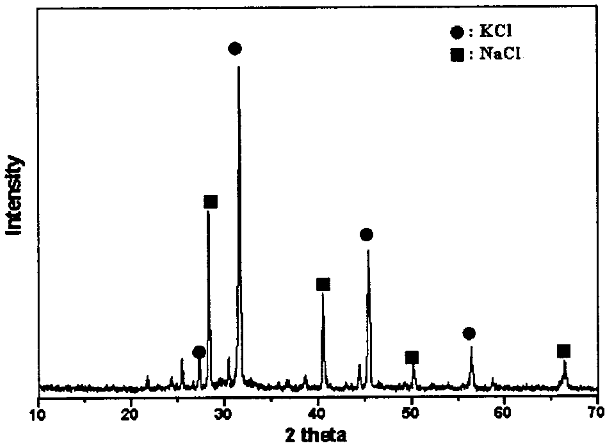

Fig. 2. XRD pattern of Dadae fly ash.

collecting system in incineration facility. In the case of the Ilsan incineration system, fly ash is collected and neutralized by semi wet method using $Ca(OH)_2$, but NaOH is used as a neutralizer in the Dadae incineration system.

As can be seen in Fig. 1 and 2, $Ca(OH)_2$, $CaCO_3$, NaCl, CaClOH and KCl with small amount of SiO_2 were main phase in the Ilsan fly ash, and only NaCl and KCl were observed in the Dadae fly ash. Consequently, dust collecting and neutralization systems are classified into two large group, NaOH and $Ca(OH)_2$ in view of neutralization system in the synthesis of Alinite system cement.

2.2.2 Swage sludge

The water content ratio of swage sludge obtained from swage disposal facility was about 80%. The sludge was firstly dried, its thermal properties were analyzed by DSC and TGA and chemical composition was evaluated by making the dried sample into ash. As can be seen in Table 2, it is believed that the sludge could partially act as a fuel in the sintering furnace, because the heat generation was recorded 2,600 kcal/kg. Also, it is certain that the weight reduction is about 53% and the exothermic reaction finishes at around 800 ℃ from the thermal analysis in Fig. 3. The sludge contains SiO_2 and Al_2O_3 over 50% in total

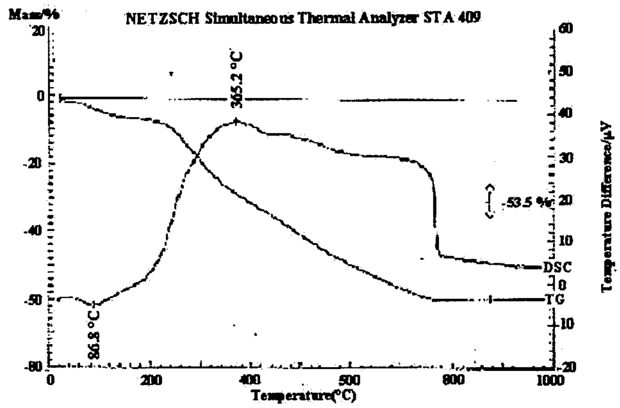

Fig. 3. Thermal analysis of swage sludge.

compositions as shown in Table 3. The heavy metals such as Pb, Cu, Zn, Cr, Mn, Hg and As in Table 4 are assumed to be solidified into clinker. Finally the sludge is suitable for the preparation of Alinite system cement due to 0.1～0.2 wt% of Cl. Furthermore, the sludge should not harmfully affect the formation of clinker, because the composition of swage sludge does not show large deviation according to a season and only small amount is used for the preparation of clinker.

Table 2 Analysis of dried swage sludge

Analysis (%)							E.V (Kcal/kg) (Wet base)
T/M (Total Moisture)	F/M (Free Moisture)	I/M (Inherent Moisture)	V/M (Volatile Mat'l)	ash	F/C (Fixed Carbon)	Total sulfur (S base)	
5.4	0.32	5.08	43.22	46.16	5.54	1.3	2600

Table 3 Chemical composition of swage sludge(wt.%)

Chemical Composition									
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	LOI
45.76	19.93	8.80	7.21	2.65	2.64	0.56	1.04	11.02	0.1

Table 4 Heavy metal content in swage sludge(ppm)

Chemical Composition								
Pb	Cr	Mn	Cu	Zn	As	Cd	Kg	Cl
90.31	2.45	726.90	142.76	313.24	8.76	-	12.73	142.213

Table 5 Chemical analysis of raw materials (wt.%)

Raw materals	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Cl	LOI	K_2O	Na_2O	SO_3	P_2O_5	TiO_2	ZnO
Fly ash	9.7	4.7	1.6	13.5	3.3	21.2	0.5	14.5	14.6	7.7	3.3	2.1	3.8
Bottom ash	35.8	11.4	9.4	15.4	1.6	1.9	11.0	1.9	3.6	1.4	5.5	1.2	-
Swage sludge[1)]	46.2	20.8	9.1	4.7	1.9	-	0.6	2.6	0.9	0.6	11.9	1.0	-
Swage sludge[2)]	43.5	19.2	8.4	3.1	1.6	0.3	0.6	10.8	1.5	0.8	7.8	0.9	0.9
Lime stone	12.2	3.4	1.5	43.6	1.6	-	36.4	1.3	0.1	-	-	-	-
S/Alu`	-	71.7	-	-	-	-	27.3	-	1.0	-	-	-	-
Clay	49.4	18.9	9.2	0.4	1.2	-	17.1	2.6	0.2	0.1	0.1	0.8	-

1) Tanchun, 2) Daejeon

3. Results and Discussion

3.1 Raw materials

The main raw materials used in the preparation of clinker were municipal incineration ash and swagesludge, and limestone, siliceous and aluminous materials were added for the modification of compositions. The chemical analysis result is shown in Table 5. Incineration ash consists of fly ash and bottom ash with the ratio of 1:9. In the case of bottom ash, coarse flour like scrap of iron were filtered by 5mm mesh.

In the case of Deajeon swage disposal plant, the composition was evaluated as dry specimen, even though it varies with the producing area.

3.2 Mixing of raw materials

Table 6 shows the 6 level combination including Basic level by change of mixing ratio of incineration ash, swage sludge, limestone, S/Alu' and clay.

Firstly, basic level was performed by using fly ash and swage sludge. The combination of raw materials was designed to maximally use the waste(incineration ash and swage sludge) containing Cl then form calcium chloroaluminate($C_{11}A_7CaCl_2$). The chemical analysis results are presented in Table 7.

3.3 Burnability of clinker

Table 8 shows the content of FeO and Cl in the prepared clinker at various temperature by using kantal furnace from R/Mix in Table 7. F-CaO was excessively formed at each conditions except level 4, and all of Cl was nearly evaporated over 93~98%.

Burnability index(BI) is decided by the relative evaluation of burnability for example easy burning or hard burning of raw materials by ethylen glycol method of F-CaO in burnt sample. The burnability increased as the BI number decreased, contrary it means that the burnability decreased as the BI number increased.

Table 6 Mixing ratio of raw materials (wt.%)

	Municipal Incineration ash			Swage sludge	Lime stone	S/Alu`	Clay	Total
	Fly ash	Bottom ash	Total					
B.L	6.0	0.0	6.0	2	87	4	1	100
Case 1	0.6	5.4	6.0	2	92	0	0	100
Case 2	0.6	5.4	6.0	2	91	0	1	100
Case 3	0.6	5.4	6.0	6	88	0	0	100
Case 4	0.8	7.2	8.0	4	85	1	2	100
Case 5	1.0	9.0	10.0	2	88	0	0	100

B.L : Basic Level

Table 7 R/Mix mixing results (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Cl	LOI	K_2O	Na_2O	SO_3	P_2O_5	TiO_2
B.L	11.1	7.2	1.5	39.2	1.8	1.907	33.3	2.2	0.9	0.9	-	-
Case 1	12.6	4.4	1.9	42.4	1.9	0.286	34.4	1.5	0.4	0.4	-	-
Case 2	12.9	4.5	2.0	42.4	1.8	0.294	34.0	1.5	0.3	0.6	-	-
Case 3	14.0	5.5	2.2	41.1	1.9	0.284	32.8	1.5	0.5	0.6	-	-
Case 4	14.1	6.2	2.4	40.3	1.8	0.392	33.7	1.5	0.5	0.6	-	-
Case 5	13.3	4.7	2.2	1.6	1.9	0.473	33.7	1.5	0.5	0.7	-	-

Table 8 Burnability test of clinker (f-CaO : % , Cl : ppm)

	1350θC		1400θC		1450θC		1500θC		B.I
	F-CaO	Cl	F-CaO	Cl	F-CaO	Cl	F-CaO	Cl	
Case 1	12.68	0.0044	8.74	0.0045	7.40	0.0055	5.94	0.0039	125.1
Case 2	8.68	0.0050	6.80	0.0056	5.14	0.0050	4.12	0.0036	97.3
Case 3	6.71	0.0145	5.95	0.0144	4.26	0.0134	1.80	0.0119	66.6
Case 4	2.77	0.0295	2.09	0.0298	1.38	0.0298	0.65	0.0100	29.6
Case 5	8.68	0.0065	6.14	0.0059	4.88	0.0049	1.48	0.0091	66.1

In the case of level 4, the burnability was relatively good and 3 and 5 were following.

B.I = F-CaO(%) ×(1350℃ + 2 ×1450℃ + 3 ×1500℃) ×3.73/(1350℃ + 1500℃) ×1/4

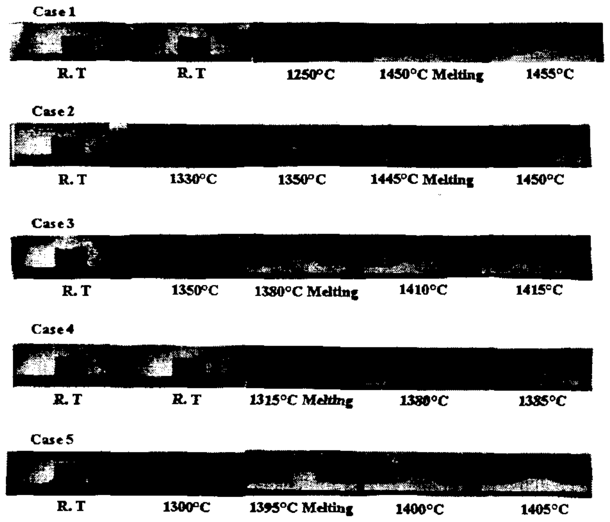

Fig. 4. High temperature micrographs.

3.4 High temperature micrograph results

Fig. 4 shows high temperature micrograph result with burning temperatures. In the case of level 4, the samples started to melt at 1,315℃ and superior burnability was found at that temperature.

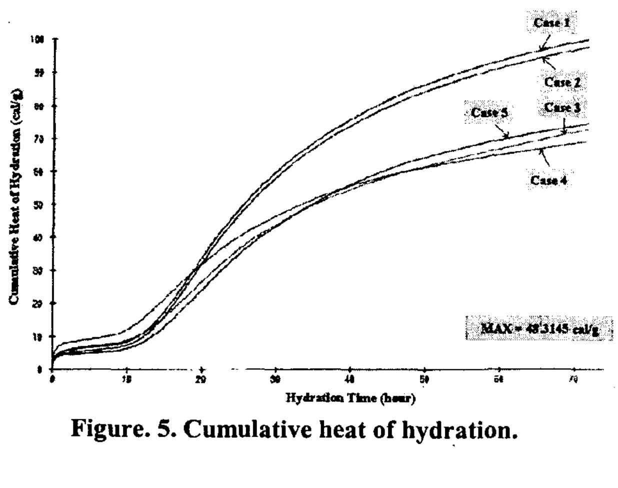

Figure. 5. Cumulative heat of hydration.

3.5 Minute hydrolysis heat

Minute hydrolysis heat reactions of synthesized clinkers were presented in Table 9. The most rapid hardening was found at level 4, and overall hydrolysis heat was lowest.

Table 9 Hydrolysis heat

	Peak		Result
	Cal/g/h	Min	Cal/g
Case 1	8.12705	6.5	48.3149
Case 2	7.94107	6	47.2064
Case 3	7.31809	6	35.3642
Case 4	13.4971	4.5	33.5187
Case 5	7.02895	6.5	36.1652

3.6 Properties of synthezied clinker

Table 10 shows the hardening time of 10 g of clinker with 30 % water as functions of mixing ratio and burning temperature, in order to decide proper gypsum content for the synthesis of ecocement. As a result, well burnt level 4 shows most rapid hardening, other samples show more rapid hardening characteristic than OPC

It was found that Alinite and $C_{11}A_7CaCl_2$ were found at every level as shown in XRD result of Fig. 6.

The main peak of Alinite is 2.80(theta=31.9) which is similar to 2.87 of C_3S, and it was revealed that the phase is presented in the burnt clinker. However, from XRF result, the content is negligible.

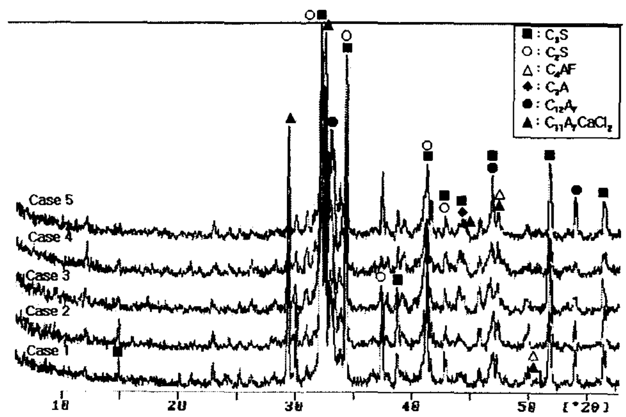

Fig. 6. XRD patterns of clinkers.

Table 10 Hardening test

Sample	Clinker(g)	W/S(%)	Hardening Time(min)
OPC	10	30	56
Case 1			38
Case 2			39
Case 3			25
Case 4			10
Case 5			48

4. Conclusion

In this study, feasibility was tried to recycle sewage sludge and minicipal incineration ash for the raw material of cement, and the results are as follows;

(1) It is necessary to adopt proper application, because the properties of incineration ash are different according to each dust collecting system, then sufficient data about each sludge according to season and area is essential to utilize them.

(2) Calcium chloroaluminate was synthesized by burning of waste(incineration ash and swage sludge) with large amount of Cl at 1,350～1,500℃. The mixing ratio was incineration ash : 6～10, swage sludge : 2～6, limestone : 85～92 and clay : 0～2. It was found that 93～98 % of Cl was evaporated and burnability was poor. The cement prepared by using of synthesized clinker and gypsum shows more rapid harding characteristic than OPC, and it is believed that this is attributed to the formation of Alinite ore.

References

[1] K.. Sekino, 1997.Inorganic Materials, Vol. 4, Sep. 483-490.

[2] H. Obana, 1996. Cement ⓖConcrete, No. 594, Aug. 153-155

[3] Y. Ono. et. al, 1995. Cement ⓖConcrete, No. 586, Dec 1-8

[4] C. Ftikos and D. Kiatos, 1994. Cement and Concrete Research., Vol. 24, 49-54

[5] R. Kikuchi, 2001. Resources, Conservation and Recycling, 31, 137-147

[6] H. Uchikawa and H. Obana, 1995. World Cement, Vol 26(11), 33-40

[7] T. Maruta, H. Ohmori, M. Moriya, K. Uchida and H. Isoda, 1997. Inorganic Materials, Vol. 4, Mar, 152-155

[8] H. Ohmori, T. Maruta, M. Moriya and H. Isoda, 1997, Inorganic Materials, Vol. 4, Mar. 119-125

[9] A. Gadayev and B. Kodess, 1999. Cement and Concrete Research, 29, 187-191