Cement and Concrete Research 40 (2010) 966–970

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Mechanical properties and micro-structures of calcium aluminate based ultra high strength cement

Etsuo Sakai *, Tomoaki Sugiyama, Tuyoshi Saito, Masaki Daimon

Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

ARTICLE INFO

Article history:
Received 30 October 2008
Accepted 6 January 2010

Keywords:
Calcium Aluminate Cement (D)
Chemically Bonded Ceramics (D)
Silica fume (D)
Hydration (A)
Microstructure (B)

ABSTRACT

This paper describes the mechanical properties and microstructure of calcium aluminate based ultra high strength cement at early age. By using silica fume, polycarboxylate based superplasticizers and a hybrid defoaming mixer, which is anon-contact mixer, cement paste with water to powder ratio of 0.1 can be cast in a mold. When the water to powder ratio is 0.1, the bending strength of hardened samples can be obtained over 30 MPa. Samples were cured at 40 or 60 °C for 7 days. At 60 °C, C_3AH_6 is mainly produced, whereas C_3AH_6 and C_2AH_8 are produced at 40 °C. The mechanical properties of hardened samples with low water to powder ratio are related to the pore volume and pore size distribution.

1. Introduction

Alumina cement is a cement whose main component is monocalcium aluminate, and compared with ordinary Portland cement (hereafter referred to as OPC) has superior early strength, fire resistance, abrasion resistance and acid resistance [1,2]. High performance concrete from calcium aluminate cements has been also reported [3]. In addition, calcium aluminate cement based ultra high strength cement has been proposed. The flexural strength of Macro-Defect-Free (MDF) cement based on high alumina cement achieves much higher values of around 150 MPa [4]. Hot pressed high strength cement with calcium aluminate cement has been also reported by Gouda and Roy [5]. But, MDF cement is a composite material of water soluble polymers and hydrated products [6]. And these materials for ultra high strength cement cannot be casted in mold.

DSP (Densified systems of homogeneously arranged ultra-fine particles) technology having a compressive strength of about 300 MPa was proposed [7], and its application to molds and other non-construction materials was investigated, but was found to be little promise. In recently year, DSP technology containing low heat Portland cement and silica fume has been used for ultra high strength concrete with design strength in excess of 100 MPa, mainly for applications such as high-rise condominium and ultra high strength fiber concrete such as Reactive Powder concrete. A problem with alumina cement is a reduction of strength and durability with time due to conversion of the hydrated products. For calcium aluminate based DSP, it has been reported that by reducing the water to powder ratio, the effect of conversion is reduced, and the strength can be maintained [8]. Calcium aluminate based DSP can be casted in mold. In recent years it has become possible to maintain workability at extremely low water to powder ratios due to the development of new high performance superplasticizers [9] in combination with ultra-fine powder. Also, in recent years mixers have been developed with excellent mixing performance using a rotating/revolving propeller-less mixing system [10,11]. Calcium aluminate based DSP with water to powder ratio of 0.1 can be casted in mold by using these methods. If the water to powder ratio is reduced by uniform mixing, and further high temperature curing is carried out to promote the formation of C_3AH_6 from the early stage of hydration, so that high strength is maintained without the conversion, use as a stable high durability material can be expected.

Therefore in this research, using the combination of a novel mixer, high performance superplasticizer, and ultra-fine powder, the properties of calcium aluminate based DSP cured at high temperature and with very low water to powder ratios were evaluated, and the microstructure of the hydrated products was investigated. This paper describes the early strength and the micro-structures of calcium aluminate based DSP cured at 40 and 60 °C for 7 days. More detail investigations for the long term durability of these materials are necessary.

2. Experimental

2.1. Materials and preparation of test specimens

Alumina cement No. 1 (hereafter referred to as AC) was used as the cement; its physical and chemical properties are shown in Table 1. Silica fume (SF) was used as the ultra-fine powder. Table 2 shows the

---

* Corresponding author. Tel.: +81357343368; fax: +81357342862.
E-mail address: esakai@ceram.titech.ac.jp (E. Sakai).

doi:10.1016/j.cemconres.2010.01.001

Table 1
Physical and chemical properties of AC.

Density /g cm^{-3}	Fineness cm^{2}g^{-1}	Chemical composition/%						
		Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO
3.01	4670	0.1	3.7	55.1	0.8	3.0	36.1	0.2

Table 2
Physical and chemical properties of silica fume.

Density /g cm^{-3}	S_{BET} m^{2}g^{-1}	Chemical composition/%									
		Ig. loss	SiO_2	Fe_{23}	Al_2O_3	CaO	MgO	SO_3	TiO_2	Na_2O	K_2O
2.29	19	1.4	95.8	0.1	0.8	0.4	0.7	0.1	0.01	0.2	1.0

S_{BET} specific surface area by BET method.

physical and chemical properties. For the high performance superplasticizer [9], a high performance polycarboxylate based superplasticizer for high strength concrete ((Rheobuild SP8HU manufactured by BASF-Pozzolith Ltd.) was used.

The ratio of water to powder mass (*W*/*P*) was from 0.10 to 0.30, and the replacement ratio of SF was 10 mass% of the AC. The mixing water was added, and the paste was made in a hybrid defoaming mixer (Thinky Corporation; rotating/revolving propeller-less blending system defoaming conditioning mixer [10,11]). With this mixer, the drum holding the materials spins (at 800 rpm) while its axis revolves in an orbit (at 2000 rpm), thereby exerting an acceleration on the materials without the need for a mixing device such as a propeller as shown in Fig. 1. This type of mixer is suitable for mixing highly viscous suspensions at low water to powder ratio and the dispersion of ultra-fine particles. It uses a non-contact mixing method, with materials container that rotates and revolves at 400×*g* acceleration, that results in fast, high grade mixing with no air bubbles. The mixing water was adjusted to a predetermined concentration of high performance superplasticizer, and to limit the temperature rise when mixing, the superplasticizer was frozen in a freezer before use. The superplasticizer was adjusted considering it to be a part of the water. Dosage of superplasticizer is shown in Table 3.

In all cases it was possible to form the paste by casting, and forming was carried out by casting into 20×20×80 mm molds. Fig. 2 shows the flowing condition of fresh paste of calcium aluminate based DSP at water to powder ratio of 0.1. Calcium aluminate based DSP at water to powder ratio 0.1 can be casted in mold.

After curing in moist air at 40 °C or 60 °C for 1 day, the molds were removed, and curing in moist air was carried out at 40 °C or 60 °C for 6 days. In the following, each test specimen is indicated by their curing temperature and *W*/*P* (ex.: 40 °C–0.1).

Table 3
Dosage of superplasticizer.

Water to powder ratio	Dosage of superplasticizer/mass % of polymer to powder
0.1	0.4
0.15	0.3
0.2	0.2
0.3	0.1

3. Test method

The specimens (20×20×80 mm) were prepared. All samples were cured at 40 °C or 60 °C for 7 days. Strength tests were carried out in accordance with JIS R 5201, to obtain the compressive strength and the bending strength. For strength, the test results of three samples are averaged. The pore size distribution of the hardened specimens was measured using a mercury porosimeter, and the hydrated products were determined by powder X-ray diffraction (XRD).

The reaction ratio of CA within the alumina cement was obtained by measuring the unreacted CA by the X-ray internal standard method, using Al_2O_3 as a standard substance. The value of ignition loss was measured at 1000 °C.

Fracture cross section of hardened samples was observed by FE-SEM. Samples were prepared by frozen cutting at −170 °C and coated by carbon.

4. Results and discussion

4.1. Mechanical properties at early stage and pore structure

The relationship between bending strength and compressive strength is shown in Fig. 3. In the figure the dotted-line, proposed by Noguchi for the relationship between compressive strength and bending strength for high strength concrete using ordinary Portland cement is shown in Fig. 3 [12]. Compared with this relationship, when alumina cement is used high values of bending strength are seen, and further as the water to powder ratio is reduced, the ratio of bending to compressive strength tends to increase. In particular, for *W*/*P*=0.1, the high bending strength of about 30 MPa is indicated, regardless of curing temperature.

Fig. 4 shows the relationship between the pore volume and bending strength. At the different curing temperatures of 40 °C and 60 °C, the respective different approximate linear relationships are shown. Compressive strength and pore volume also show the same trends as for bending strength. The strength of hardened ordinary Portland cement is mainly dependent on the volume of capillary pores. But it is suggested that the strength of high strength hardened alumina cement is not simply determined by the pore volume.

Fig. 1. Revolution/rotation propeller-less blending system deforming conditioning mixer (Thinky Corp. model AR-250).

Fig. 2. Fluidity of calcium aluminate based DSP paste ($W/P = 0.1$).

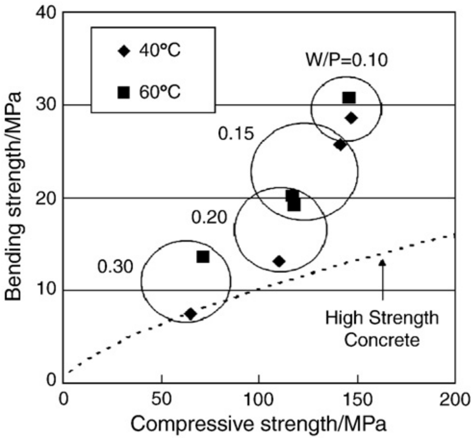


Fig. 3. Relation between the bending strength and compressive strength hardened pastes.

Fig. 5(a) shows the pore size distribution of hardened samples of 40 °C–0.10 and 60 °C–0.10, which have virtually the same bending strength of 30 MPa. The total pore volume for 60 °C–0.10 is larger than that of 40 °C–0.10, but conversely the average pore size is smaller. The strength of hardened samples is controlled by both the pore volume and pore size distribution, that is pore structure. Fig. 5(b) shows the pore size distribution of hardened samples of 40 °C–0.30 and 60 °C–0.10, which have virtually the same pore volume 0.1 ml/ml. The average pore size in the case of 60 °C–0.10 is smaller, but the strength is greater.

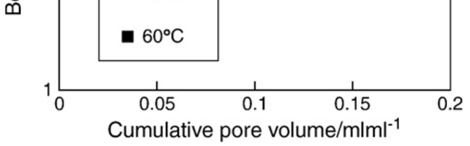


Fig.4. Relationship between the bending strength and the pore volume of hardened samples.

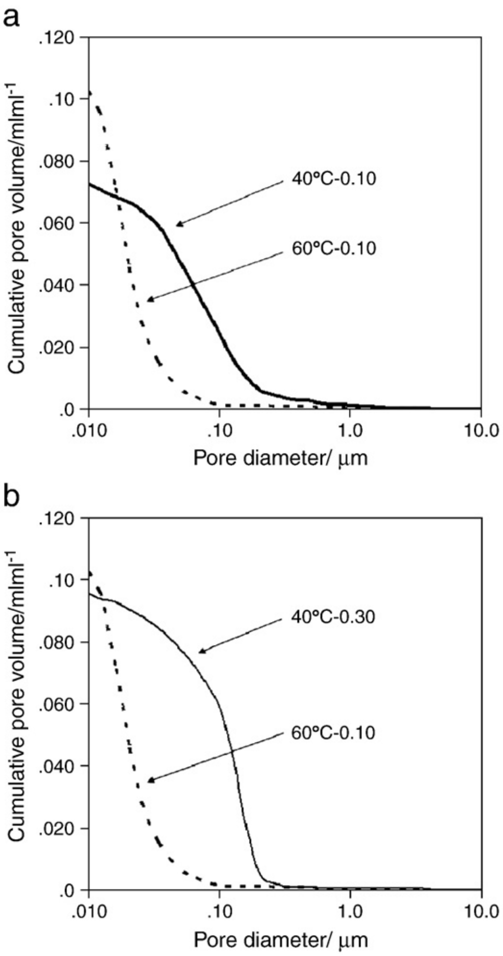


Fig.5. Pore size distribution of hardened samples.

From these results, it is considered that in determining the strength of high strength cement made by using alumina cement, it is also necessary to take into consideration the pore size distribution compared with the case of normal water cement ratio [13], in addition to the relationship to pore volume as typified by Ryshkewitch's equation. It is considered that this is due to the effect of the particle packing and the hydrated products.

4.2. Hydrated products

Table 4 summarizes the hydrated products determined by XRD for 40 °C–0.10, 40 °C–0.30, and 60 °C–0.10. At 40 °C, in all cases C_2AH_8

Table 4
Products for alumina cement–silica fume at low water to powder ratio.

Samples	Products
40 °C–0.3	Unreacted CA, C_3AH_6,AH_3,C_2AH_8,C_2ASH_8
40 °C–0.1	Unreacted CA, C_2AH_8, C_3AH_6, AH_3
60 °C–0.1	Unreacted CA, C_3AH_6, AH_3

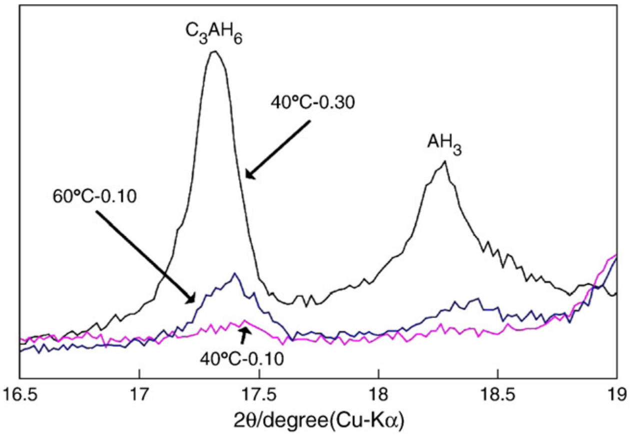


Fig. 6. XRD patterns of hydrated samples.

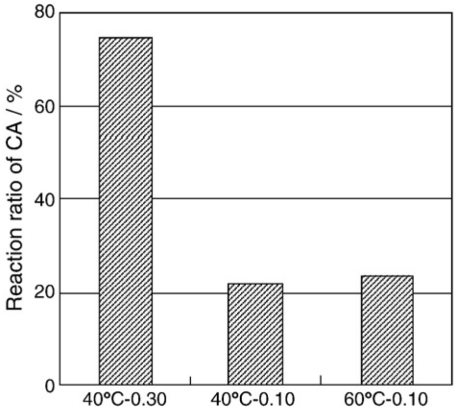


Fig. 7. Reaction ratio of CA.

was formed. Also, when *W*/*P* was 0.3, in addition C_2ASH_8 was formed. It is thought that C_2ASH_8 is formed by hydration of C_2AS in the alumina cement and reaction of the silica fume. It is considered that when the water to powder ratio is small, such as 0.1, almost none of the C_2AS is hydrated, so a peak for the C_2ASH_8 product does not clearly appear. Also, in all cases C_3AH_6 and AH_3 are formed. At 60 °C, only C_3AH_6 and AH_3 are formed. In each case the formation of CAH_{10} could not be confirmed.

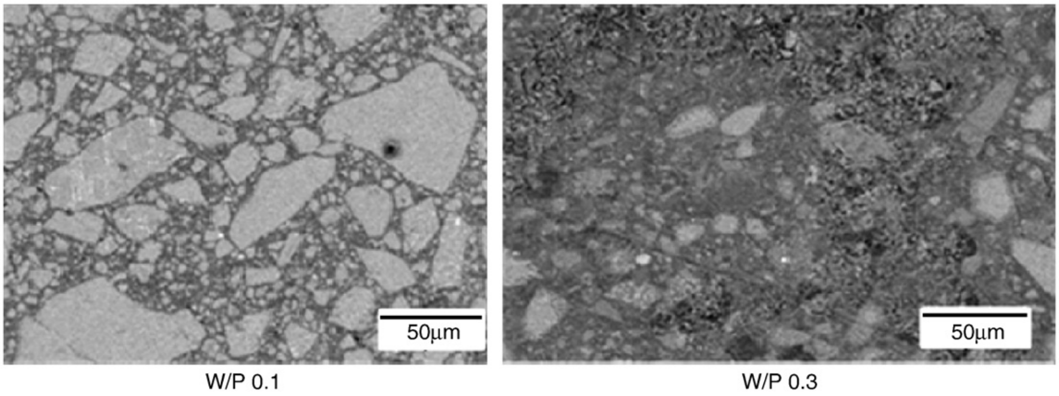
However, as shown in Fig. 6, when *W*/*P* is 0.1, the peaks for these products are significantly smaller compared with the case where *W*/*P* is 0.3. These results are related to the CA reaction ratios. Fig. 7 shows the reaction ratios for CA for each test specimen. Fig. 8 shows the backscattered electron image (BEI) of polished surface of samples cured at 60 °C. When *W*/*P* is 0.3, the CA reaction ratio is 75% and hydrated products are formed. However, when *W*/*P* is 0.1 the CA reaction ratio is about 20% for curing at both 40 °C and 60 °C, so a large amount of unreacted cement remains, and the quantity of products formed is very small as shown in Fig. 8. A large amount of unreacted cement was densely packed in this ultra high strength cement.

It is inferred that the microstructure and phase composition of hardened samples greatly differs depending on the water to powder ratio and the curing temperature. With water to powder ratio of 0.1, the powder binds together extremely closely, in a structure that is close to the densest possible filling. Only a very small amount of reaction occurs, so a large quantity of unreacted cement remains. At 40 °C, C_3AH_6, AH_3 in gel form, as well as plate-like crystals such as C_2AH_8 and C_2ASH_8 are formed. At 60 °C, polyhedral C_3AH_6 and AH_3 are formed. Small crystals of C_3AH_6 and AH_3, form within the voids between the densely packed unreacted cement particles, producing an elaborate structure. In contrast, at 40 °C, in addition to C_3AH_6 and AH_3 in gel form, plate-like crystals are also formed, so the pores are larger than for 40 °C.

Fig. 9 shows the SEM photographs of hardened cured at 60 °C. The samples cured at 40 °C followed the same tendency. The microstructure of the hardened sample is dense, showing densely packed unreacted cement particles covered by dense hydrates. Gel phase hydrates and gibbsite of columnar grain structure were observed. In addition, spherical particles of silica fume remained. More detailed investigations, into the reaction of silica fume are necessary.

5. Conclusions

By combination of ultra-fine particles, high performance superplasticizer and the hybrid defoaming mixer, the alumina cement paste for *W*/*P* = 0.1 can be casted in molds. For *W*/*P* = 0.1 of samples cured at 40 and 60 °C for 7 days, the high bending strength of about 30 MPa is indicated, regardless of curing temperature. But the pore size distribution of hardened samples is influenced by curing temperature, because the hydrates are changed. At 40 °C, C_3AH_6, AH_3 in gel form, as well as plate-like crystals such as C_2AH_8 and C_2ASH_8 are formed. At 60 °C, polyhedral C_3AH_6 and AH_3 are formed. The strength of high strength cement with alumina cement is related to the pore volume and pore size distribution. When *W*/*P* is 0.1 the reaction ratio of CA is about 20% for curing at 40 and 60 °C. Therefore, a large amount of unreacted cement was densely packed in this ultra high strength cement.



W/P 0.1

W/P 0.3

Fig. 8. Backscattered electron image (BEI) of polished surface of samples cured at 60 °C.

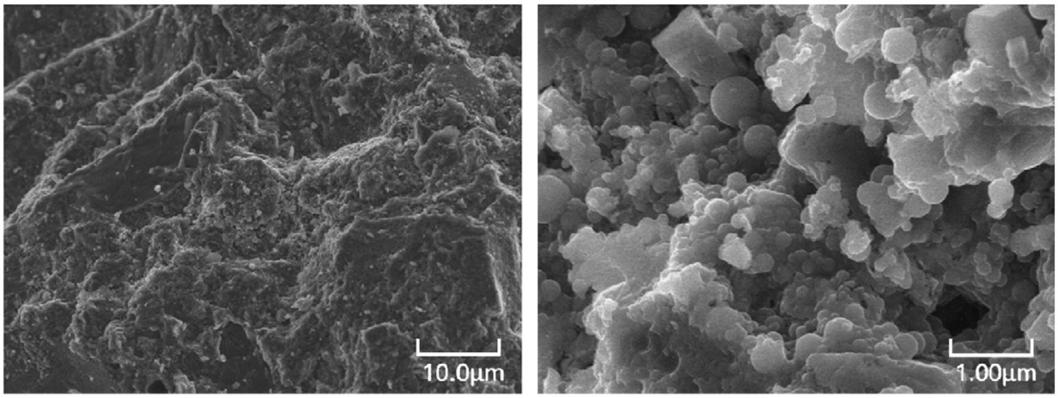


Fig. 9. SEM photographs of hardened sample cured at 60 °C.

References

[1] G. Midgley, High alumina cement in construction — A future based on experience, Calcium aluminate Cements, E. & F.N. Spon, London, 1990, pp. 1–13.

[2] C.H. Fentiman, R.J. Mangabhai, K.L. Scrivener (Eds.), Proc. of the centenary conference 2008, Calcium Aluminate Cement, IHS BRE Press, 2008.

[3] K.L. Scrivener, J.L. Cabiron, R. Letourneux, High-performance concretes from calcium aluminate cements, Cement Concr Res. 29 (1999) 1215–1223.

[4] J.D. Birchall, A.J. Howard, K. Kendall, Flexyral strength and porosity of cements, Nature 289 (1981) 388–390.

[5] G.R. Gouda, D.M. Roy, Properties of hot-pressed calcium aluminate cements, Cement Concr Res 5 (1975) 551–564.

[6] W. Sinclair, G.W. Groves, The microstructure of high strength cement pastes, Mat Res Symp Proc 42 (1985) 31–37.

[7] H.H. Bache, Cementitious Composite materials, Japanese published examined application 60-59182(WO80/00959)(Claimed priority 1978).

[8] I. Mino, E. Sakai, Engineering Concrete, Proc.MRS Int'l Meeting on Advanced cements and chemically bonded ceramics, 1989, pp. 247–254.

[9] E. Sakai, A. Ishida, A. Ohta, New trends in the development of chemical admixtures in Japan, J Adv Concr Tech 4 (2) (2006) 211–223.

[10] http://www.thinkey.co.jp/english/w-rentaro_e.html.

[11] E. Sakai, Y. Kakinuma, K. Yamamoto, M. Daimon, Relation between the shape of silica fume and the fluidity of cement paste at low water to powder ratio, J Adv Concr Tech 7 (1) (2009) 13–20.

[12] T. Noguchi, F. Tomosawa, Relationship between compressive strength and various mechanical properties of high strength concrete, J Struct Construct Engr Trans AIJ (1995) 11–16.

[13] T. Matusinovic, J. Sipusic, N. Vrbos, Porosity-strength relation in calcium aluminate cement pastes, Cement Concr Res 33 (2003) 1801–1806.