A STUDY FOR THE DEVELOPMENT AND CHARACTERIZATION OF CALCIUM ALUMINATE CEMENT (CAC)

R. Mahmood, W.A. Shah, M.P.I. Qazi and M.A. Bhatti

PCSIR Laboratories Complex, Lahore -54600, Pakistan

ABSTRACT: Calcium Aluminate Cement (CAC) with 70% Al_2O_3 is developed on Laboratory scale. It is produced by sintering at high temperature a mixture of intimately mixed aluminium trihydrate and limestone. The predominant hydraulic bonding phase is calcium aluminate CaO Al_2O_3. Pyrometric cone equivalent (refractoriness) of the cement is above SK 28 (1630°C). Hydraulic cement of such type finds application in castables and gunning mixes used at higher temperature.

INTRODUCTION

Recently the use of calcium aluminate cement [CAC] as a binder for castable refractories has increased considerably. These refractories are most frequently used in refinery and chemical process industries. Its resistance to sea water, sulphate contaminated water and weak solutions of mineral acids are outstanding. Being hydraulic setting, it gains strength after curing in a humid atmosphere. The castable refractory consisting of aggregate and aluminate cement withstands temperature upto 1800°C (Grayson, 1985). The refractoriness depends on the purity of calcium aluminate cement as well as on the nature of refractory aggregate. Calcium aluminate cement containing 70 to 90% alumina has been prepared by mixing alumina and calcium carbonate followed by sintering and fusion. The calcium aluminate is mainly formed by diffusion of CaO into Al_2O_3 (Andouze, 1961). Low purity cement can be prepared by sintering bauxite and limestone. However, the castable prepared by this method cannot be used for high temperature applications. Free lime and alumina begin to interact between 800-900°C and accelerated at 1100°C (Searle, 1959). The synthesis of CAC has also been reported by mixing calcium carbonate and alumina in stiochiometric proportion and heating for several hours (Tsueng et al, 1963).

MATERIALS AND METHODS

The raw materials (commercial grade limestone and aluminium trihydrate) used for the production of calcium aluminate cement (CAC) were analysed to ascertain their purity. Rough balance is used for weighing raw materials. Mixtures were formulated on weight basis to yield products having alumina to lime ratio of 80:20, 70:30, 65:35 (Table I.)

Table 1: Basic composition of Reactants for the Preparation of Calcium Aluminate Cement

Batch No	$Al(OH)_3$	$CaCO_3$	Al_2O_3: CaO
1	615gm	185gm	80:20
2	538gm	278gm	70:30
3	500gm	324gm	65:35

The weighed raw materials were thoroughly mixed in a locally made ball mill for 4-5 hours. The homogenized mixture was pressed into briquettes (2"x ½" x ½") by using hand press (locally made). Water was used as a binder. These briquettes were dried in an electric oven (Memmert, Germany) at 120°C and then carefully transferred manually into a prefired molochite crucible. Sintering was carried out at 1500±10°C in a gas fired drum furnace. The temperature was maintained for 5 hours.

The fused briquettes of CAC were crushed by hammering and ground in a ball mill to pass through sieve No.200 BSS, and packed in a moisture proof bag manually.

The specific gravity of the cement was determined by Kerosene displacement in pycnometer. The setting time of the cement was determined by the Vicat needle procedure (ASTM C-191-04: 2004). Pyrometric Cone Equivalent (PCE) of the calcium aluminate cement was determined by the Standard method of test (ASTM C-24-01: 2004).

For the determination of cold crushing strength of the cement 1½" cubes were cast in steel moulds. Cubes were removed from the mould after six hours and cured for 3 & 7 days respectively in water. The compressive strength of the cubes was

determined by ASTM method (ASTM C-109/C 109M-02).

The x-ray diffraction analysis was carried out on Siemens Diffractometer D-5000 to identify the phases developed during sintering. The cured sample of 70:30 Al_2O_3-CaO was viewed under Scanning Electron Microscope (SEM), Hitachi S – 2700 equipped with Energy Dispersive Analyzer (EDX).

RESULTS AND DISCUSSION

The analysis of the raw materials is given in Table 2. The results show that the raw material meets the essential requirements for the production of high temperature resistant cement i.e. low silica and iron. The presence of these impurities forms liquid phase at low temperature.

Table 2: Chemical Analysis of Raw Materials

Component/ Raw Material	Aluminium Trihydrate	Limestone
L/I	34.46%	42.03%
SiO_2	0.21%	0.95%
Al_2O_3	65.17%	0.88%
Fe_2O_3	Traces	0.09%
TiO_2	Nil	Nil
CaO	Nil	54.10%
MgO	Nil	0.10%
Alkalies	Traces	Traces

Phase diagram of the binary CaO-Al_2O_3 system (Kingery,1965) exhibits the presence of several crystalline phases in this system. Both CaO and Al_2O_3 are refractory oxides with high melting temperatures however, two eutectics are located around 1400°C with approximate 48% CaO and 43 wt % CaO compositions. The crystalline phase has been identified as $5CaO.3Al_2O_3$. Calcium aluminate as secondary phase appears when alumina percentage exceeds 50%. It becomes the major phase in 65-75 alumina regions. As calcium aluminate and to some extent calcium di-aluminate are the phases responsible for providing the desired strength to the castable, the composition mentioned in Table 1 were formulated.

Among these compositions only batch 2 (70 Al_2O_3: 30 CaO ratio) has shown cementing properties and therefore it was selected for characterization.

XRD analysis of the cement is shown in Fig.1. It shows that all the significant peaks match to the calcium aluminate phase. The cementing properties in the cement are due to this phase. SEM micrograph of the neat cement is shown in Fig. 2. The high magnification image depicts an excellent single phase. It is observed that hydrated crystals of calcium aluminate possess a fairly uniform size distribution. EDX analysis carried out on crystals present at different sample positions confirmed the uniformity of the crystalline phase. The results are shown in Fig 3.

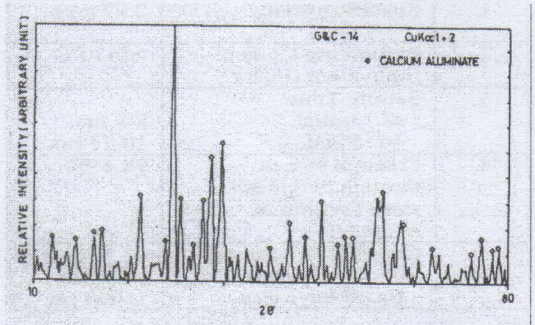

FIG.1. XRD SPECTRUM OF CALCIUM ALUMINATE CEMENT.

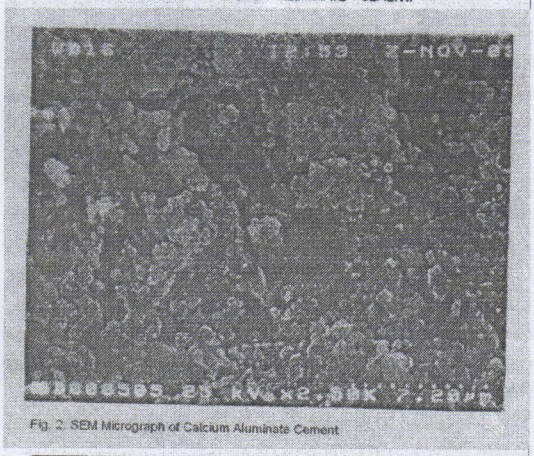

Fig. 2. SEM Micrograph of Calcium Aluminate Cement

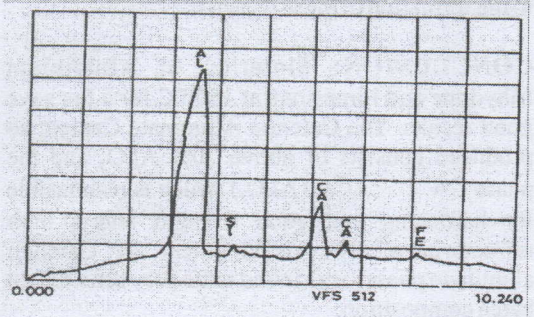

FIG. 3. EDX ANALYSIS OF CALCIUM ALUMINATE CEMENT.

It also indicates that the cement contains minor impurities of silica and iron. It can be used in castables by selecting a suitable aggregate with high temperature working range without failure. This was further confirmed when PCE of the neat cement was carried out. It was observed that there

was no cone deformation till 1630°C (SK 28). These results are enlisted in Table 3. Further increase in temperature (above 1630°C) under the prevailing conditions was not possible.

Table 3: Properties of the Calcium Aluminate Cement

Sr. No.	Test Parameter	Value determined
1.	Specific gravity	2.97 g/cc
2.	Pyrometric Cone Equivalent (PCE)	>1630°C
3.	Setting Time a) Initial b) Final	 8-9 hrs. 10-11 hrs.
4.	Fraction passes through 200 mesh sieve (Within 20 minutes) ±2	98.45%
5.	Compressive Strength a) 3-days test b) 7-days test	 8630 psi 11000 psi

The schematic presentation of hydraulic reactions is shown in Fig 4. It shows the possible dehydration reactions of calcium aluminate cement (Ningsheng et al, 2000). Hydration of both calcium aluminate and calcium di-aluminate below 21°C results in the formation of $CaAl_2O_4.10H_2O$ and $Al_2O_3.3H_2O$. Further curing gradually increases the quantity of hydrated alumina and clustering of CaO and Al_2O_3 groups. The final phase which has been reported as $Ca_3Al_2O_6$ may take several months. Compressive strength (Universal Testing Machine UH-100A, Shimadzu, Japan) of the blocks made from neat calcium aluminate cement after 3 days curing was 8630 psi which increases to 11000 psi after 7 days. The increase in strength with curing time is related to the formation of these phases.

CONCLUSION: Sintering of Aluminium trihydrate and Limestone at 1500°C for 5 hrs gave good results. The Calcium Aluminate Cement so produced consists of above 70% Al_2O_3 and the phase CA ($CaO\ Al_2O_3$) which is responsible for hardening and good strength and a high refractoriness. The development of Calcium aluminate phases was found to be very sensitive to batch composition.

REFERENCES

Andouze B., Solid State Reaction between Lime and Alumina Silicates Ind. 26, p. 179-90 (1961).

ASTM Standards, Standard test method for compressive strength of hydraulic cement mortars Designation C-109/C 109M-02 (2004).

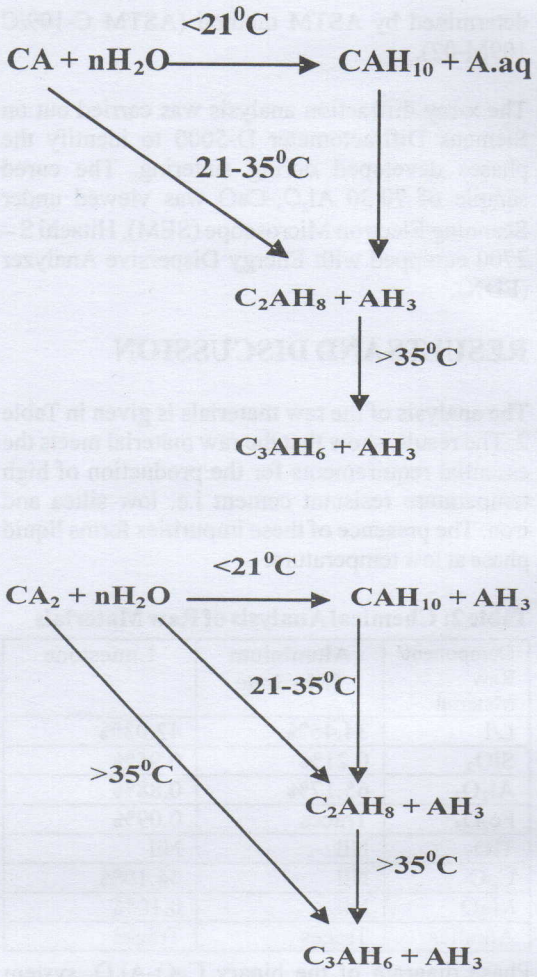

Fig 4: Hydration reaction of Calcium Aluminate Cement

ASTM Standards, Standard test method for pyrometric cone equivalent (PCE) of fire clay and high alumina refractory materials Designation C-24-01 (2004).

ASTM Standards, Standard test method for time of setting of Hydraulic Cement by Vicat needle Designation C-191-04 (2004).

Cong X. and R.Kirkpatrick, Hydration of Calcium Aluminate Cements: A Solid State NMR Study J.Amer.Cer.Soc., 76: 409-416 (1993).

Gan S. and Y.Weidong, Synthetic raw materials for Refractories in China, Proceedings "3rd International Workshop on Technology and Development of Refractories, Luoyang China, p. 63-73 (2000).

Grayson M., Encyclopedia of Glass, Ceramics and Cement John Wiley and Sons, Inc. New York, p. 228 (1985).

Kingery W.D., Introduction to Ceramics John Wiley & Sons, Inc. New York, p. 260 (1965).

Ningsheng Z., L. Zaigeng, Z. Sanhua and B. Zhenyong , Bonding Modes and Development in Bonding System of monolithic Refractories Proceedings The 3rd International Workshop on Technology and Development" Luoyang China, p. 21-42 (2000).

Searle A.B. and R.W. Grimshaw , The Chemistry and Physics of Clays and other Ceramic Materials Ernest Benn Ltd.,London, p. 570 (1959).

Tseung A.C.C. and T.G. Carrruthers , Refractory Concretes based on pure Calcium Aluminate Cement Trans. Brit. Cer. Soc., p. 305-320 (1963).

Wygant J.F. and M.S. Crowley, Designing monolithic refractory vessel liningsAmer. Cer.Soc.Bull., 43: 173-181 (1964).