

The effect of SiO₂ additions on barium aluminate cement formation and properties

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Abstract

Barium aluminate cements have been synthesized by barium carbonate, alumina, kaolin and colloidal silica as starting materials. The effects of the source of SiO₂ and of firing temperature on phase formation and physical properties of the fired cements have been studied. Cement samples were characterized using XRD, SEM, EDX. The setting time and heat of hydration of cements were also evaluated. The barium aluminate cements were mixed in castables. Cold crushing strengths evaluated, and values compared to those obtained using calcium aluminate cement (Secar 71). Mixtures of BaCO₃ and Al₂O₃ were targeted to produce BaAl₂O₄; which had fast set time, expansive behavior and lower strength compared to samples with SiO₂ additions. SiO₂ additions, regardless of source, resulted in BaAl₂Si₂O₈ (celsian) formation. The prepared samples had short setting times and higher mechanical properties in comparison with standard calcium aluminate cement.

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1. Introduction

The progress of high temperature industrial technology in cements has resulted in substantial advances in monolithic refractories over the last decades [1]. Refractory cement products continue to be the most important hydraulically setting cement used for bonding refractory castables (concretes) because they develop high early strength after mixing [2]. Barium aluminate (BA) is a refractory material with similar hydraulic properties to calcium aluminate cements [3,4]. Refractory castables based on barium aluminate cements have the following advantages over those prepared using only calcium aluminate cement: higher refractoriness above 1850 °C, higher thermal shock resistance owing to the lower thermal expansion coefficient, lack of sensitivity towards the higher temperatures used during setting that makes them usable in hot environments without hydration problems, thermal and chemical stable, fast setting and hardening [5–7], and good protection against γ - and X-rays owing to the high density of

the BA phase [5,8]. Castables prepared with such cements therefore possess superior radiation stopping power and superior refractoriness, making them promising materials for radiation proof plasters and highly refractory castables in the steel making industry [1–3].

A few additives in the system BaO–Al₂O₃ have been made, such as rare earth elements (Eu and Dy) to improve and optimize luminescence properties [9,10], ZrO₂ to form barium aluminate–barium zirconate (BA–BZ) cements [7,11], and MgO and CaO additions to form MgAl₂O₄ and CaAl₂O₄ to improve cement strength and refractoriness [6,12]. Addition of SiO₂ to the BA system can produce several BA silicates, the most important that is formed is barium aluminium silicate (BAS), a compound called “celsian” with a chemical formula BaAl₂Si₂O₈.

Barium aluminium silicate exists primarily in three polymorphs: the monoclinic (known as monocelsian or celsian), hexagonal (known as hexacelsian) and orthorhombic phases. Below 1590 °C, monocelsian is the stable phase, and the hexacelsian polymorph is the stable phase from 1590 °C to the melting point at ~1760 °C. However, the first phase that forms during synthesis is hexacelsian, which forms first due to the sluggishness of the hexacelsian-to-celsian transformation. Hexacelsian is a metastable compound below 1590 °C, and

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Table 1
Source raw materials.

Material	BaCO ₃	Al ₂ O ₃	Colloidal silica	Kaolin	Tabular alumina	Calcium aluminate cement
Purity	98%	99.6%	40 wt% in aqueous suspension (10–20 nm particle size)	92%	99%	98%
Manufacturer (Country)	HOOKS (China)	FIBERONA (India)	Asan Ceram (Iran)	WBB (England)	ARMATIS (Germany)	LAFARGE (France)

will reversibly transform to the orthorhombic polymorph around 300 °C, causing a ~3% volume change [18].

Celsian is a highly refractory ceramic and glass–ceramic, with attractive electrical and thermal properties. General properties include a melting point of 1760 °C, and a maximum service temperature of 1590 °C [13,14]. Celsian is characterized by chemical stability, resistance to oxidation and alkali attacks; a high mechanical resistance; and has a high melting point, low dielectric constant, and low thermal expansion coefficient as a monoclinic polymorph [15–17]. Potential application for barium aluminate–celsian includes: as a ceramic matrix for high temperature composites; and as a cast protheses for biomedical applications, refractories, porcelains, glass–ceramics and electrical insulators [16,18,19].

A variety of processes have been developed to synthesize celsian, including traditional glass–ceramic processing, sol–gel processing, calcination of solid salt/oxide mixtures, and solid metal oxidation. Metastable hexacelsian always forms first, irrespective of the method used to produce any celsian phase. Prolonged heat treating below 1590 °C or doping with mineralizers such as Li₂O, NaF, CaO, TiO₂, MgO, SrF₂, BeO, La₂O₃, Cr₂O₃ and K₂CO₃ are commonly used to aid in the formation of monocelsian from the hexacelsian phase [18,20].

In the present work, SiO₂ from two sources (kaolin and colloidal silica) has been introduced to the BaO–Al₂O₃ mixture (pure barium aluminate cement precursor). The impact of celsian on phase formation, microstructure and cementing properties of barium aluminate cements were studied and are presented in the paper.

2. Experimental procedures

The sources of raw materials used in this study are shown in Table 1. Using these raw materials, three different compositions for study were prepared and are listed in Table 2. Sample 1 was a pure barium monoaluminate with a molar ratio of BaO:Al₂O₃ equal to 1:1, samples 2 and 3 started with the same BaO:Al₂O₃ ratios as used in sample 1 (was 1:1), but in sample 2, 20.8 wt% kaolin was added, and in sample 3, 25 wt% colloidal silica was added. These additions resulted in the SiO₂ content reaching to 10 wt% in both samples.

The starting materials for each sample were blended together, and then blended materials, colloidal silica plus water wet finely ground in an alumina ball mill for 1 h. After being dried (at 110 °C for 24 h), the prepared samples (a batch of about 20 g) were fired in air at temperatures from 900 to 1450 °C using a heating rate of 10 °C/min with a soaking time

of 2 h. The resulting sintered products were dry ground in a fused alumina ball mill to produce cement powder of suitable fineness. The particle sizes of cements were selected between sieves mesh nos. 100 and 325.

Crystalline phases present in the BA cements formed were investigated by Jeol JDX-8030 with Cu-K_α radiation X-ray diffractometer. Setting time of cements and cold crushing strength (CCS) of castables were determined according to standard test specifications (respectively ASTM C-191 and ASTM C-109). Temperature changes during mixing of the BA cement with water proportional to the heat of hydration was measured by monitoring temperature changes during mixing of 40 g cement and 40 g water in a vacuum flask. This system was used to give a rough indication of colorimetric changes.

Castables were prepared using 30 wt% of synthesized BA cement or Secar 71 (calcium aluminate cement) with 70% alumina aggregate for comparing the properties. The aggregate used was tabular alumina, with a particle size of 30 wt% below 0.5 mm and 70 wt% between 0.5 and 1.0 mm. Castables were prepared according to ASTM C-109 using 5 cm cubes and which were cured in an 80% moisture cabinet for 6 days. Secar 71 samples were prepared with conditions similar to BA samples for comparison purposes.

Scanning Electron Microscope (SEM) Cambridge S360 with energy dispersive X-ray unit (EDAX) was used to evaluate the microstructure of prepared castables.

3. Results and discussion

3.1. Phase composition of the cements

Assuming high temperature reactions have proceeded to equilibrium in fired sample compositions 1–3, phase diagrams [22,23] were used to predict the type and the amount of crystalline phases formed in the fired cements. This data is also

Table 2
Composition of starting oxides in raw materials and calculated phase composition of fired samples.

Sample	Starting oxides (wt%)			Calculated phase of fired samples (wt%)	
	BaO	Al ₂ O ₃	SiO ₂	BaAl ₂ O ₄	BaAl ₂ Si ₂ O ₈
1	60	40	–	100	–
2	59.34	30.66	10	69	31
3	40.47	49.53	10	69	31

Sample 2 = 10 wt% SiO₂ (from kaolin).

Sample 3 = 10 wt% SiO₂ (from colloidal SiO₂).

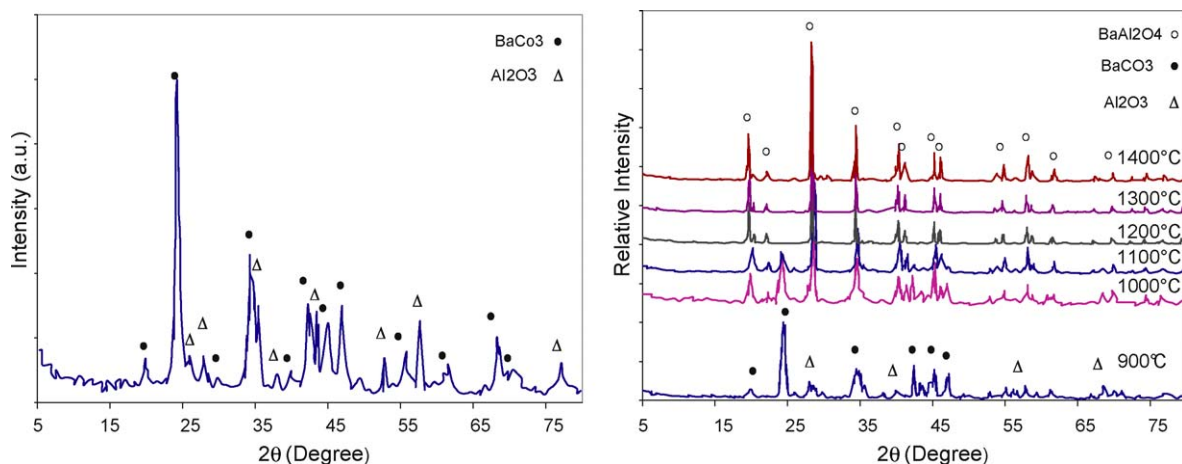


Fig. 1. XRD patterns of sample 1 in mixed state (left) and fired at different temperatures (right) for 2 h.

illustrated in Table 2, while XRD results for these samples determining actual phase compositions are shown in Figs. 1–3.

Fig. 1 illustrates the XRD patterns of sample 1 unfired (starting materials) and the results from calcination at temperatures from 900 to 1400 °C for 2 h. These patterns revealed that in the mixed starting raw mixture, peaks of BaCO₃ and Al₂O₃ are observed. After firing at 900 °C, BaAl₂O₄ was formed with small peaks of this compound observed along with BaCO₃ and Al₂O₃ in low intensity by XRD results. These results are in an agreement with the results of other researchers, and indicate that decomposition of BaCO₃ started at about 800 °C [8,9].

Increasing the firing temperature above 900 °C increased BaAl₂O₄ and decreased BaCO₃ and Al₂O₃ (according to relative intensity of XRD peaks). By 1200 °C, only BaAl₂O₄ was identified, with no peaks of the starting materials observed. At higher temperatures (1300 and 1400 °C) no other phase was produced with only BaAl₂O₄ found to exist. Using XRD data, sample 1 achieved equilibrium by 1200 °C that is in agreement with other researchers' results [8].

Figs. 2 and 3 show the XRD results for samples 2 and 3 that had SiO₂ additions from different sources. These results indicate that two phases, BaAl₂O₄ and hexacelsian (hexagonal BaAl₂Si₂O₈), were formed from the starting materials.

XRD phase analysis data agrees with the ternary phase diagram of BaO–Al₂O₃–SiO₂ [21,22]. Higher firing temperatures through 1450 °C lead to increasing BaAl₂Si₂O₈ peaks that indicate celsian formation continued at higher temperatures.

Assuming that equilibrium has been achieved at 1450 °C (the BaO–Al₂O₃–SiO₂ phase diagram indicated it), the weight ratio of BaAl₂O₄:BaAl₂Si₂O₈ would be 69:31 in samples 2 and 3 that were prepared using kaolin and colloidal silica as a SiO₂ source respectively. As expected the excess alumina from kaolin was introduced to the system, but no alumina phases such as BaO·6Al₂O₃ were detected by XRD. In previous research by other authors [23,24], it was noted that small changes in the BaO:Al₂O₃ molar ratio of 1:1 did not lead to the formation of phases other than BaAl₂O₄, when firing alumina and barium carbonate.

3.2. Setting time and heat of hydration

Table 3 shows setting times and heat of hydration of samples 1–3. As indicated in the Table 3, sample 1 had the quickest setting time. This is mainly due to pure BaAl₂O₄ phase in this cement, which is characterized by fast setting and hardening

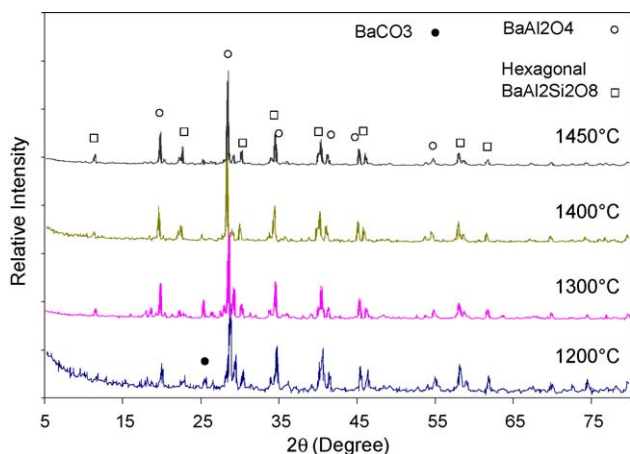


Fig. 2. XRD patterns of sample 2 fired at different temperatures for 2 h.

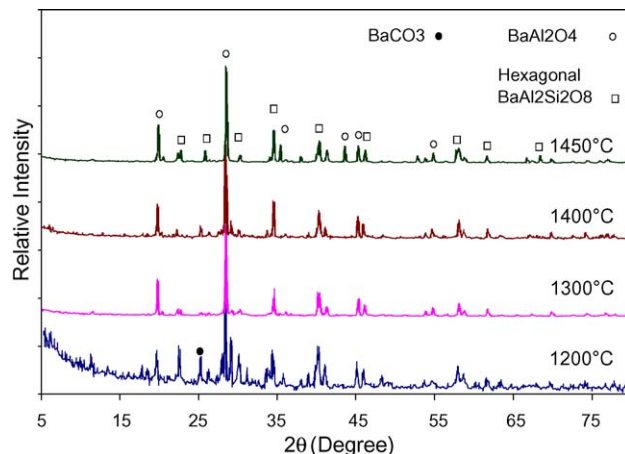


Fig. 3. XRD patterns of sample 3 fired at different temperatures for 2 h.

Table 3
Set time and temperature changes during setting of cements where mixed with 70% Al₂O₃ aggregated according to ASTM C-109.

Sample	Setting time (min)		Maximum temperature change during setting (°C)
	Initial	Final	
1	6	15	26
2	58	73	17
3	61	74	20
Secar 71	160	210	5

[1,2], Something that causes problems in preparing castables. Because of very fast setting, the concrete paste can become very thick and its workability decreases during mixing. In some applications this fast set overcomes with retarders such as gypsum [6,25]. Cement samples 2 and 3 had set times much longer than sample 1; however these setting speeds are faster than other portland and aluminous cements such as Secar 71 cement, as illustrated in Table 3. Samples 2 and 3 are fast setting cements that make them suitable for applications needing short setting times. The main difference between samples 2 and 3 and sample 1 was the presence of celsian in the cements, which may cause a slower set time because the formation of this phase causes lower BaAl₂O₄ content. The fast setting of barium aluminate cements has previously been noted in the literature by Carlson [25].

As illustrated in Table 3, there is no difference between setting times for samples 2 and 3. It is suspected that source of SiO₂ in this work (kaolin and colloidal silica) had no obvious effect on mineralogical composition and cementing properties.

The heat produced during hydration of cement is proportional to the temperature rise during mixing and setting, and can be calculated according to Eq. (1):

$$Q_{\text{tot}} = Q_c + Q_w + Q_{\text{cal}} \quad (1)$$

Q_{tot} is the total heat released during cement hydration, Q_c is the heat absorbed by cement, Q_w is the heat absorbed by water and Q_{cal} is the heat absorbed by calorimeter.

At a constant pressure

$$Q = C_p \Delta T \quad (2)$$

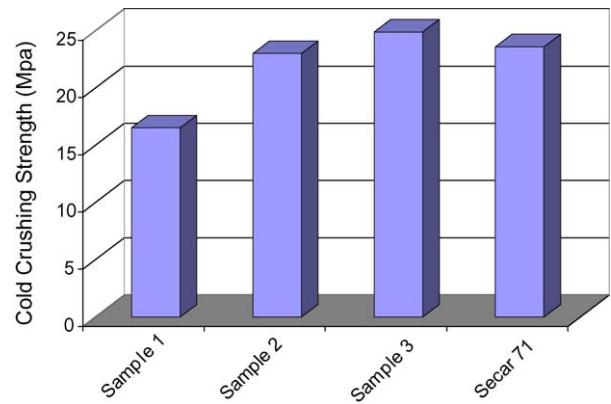


Fig. 4. Cold crushing strength of prepared samples after drying at 110 °C for 24 h.

Therefore, combining Eqs. (1) and (2);

$$Q_{\text{tot}} = (C_p^c + C_p^w + C_p^{\text{cal}}) \Delta T \quad (3)$$

Using Eq. (3) and assuming thermal equilibrium has been achieved; Q_{tot} would be proportioned to the ΔT . Table 3 illustrates the maximum temperature changes (ΔT) during setting, which would be proportional to the heat of hydration of cements. As shown in this table, cement no. 1 produces the highest heat, mainly because of the amount of its cementitious phase. Heat of hydration of samples 2 and 3 are lower than of sample 1 because of the formation of celsian, and therefore, a lower quantity of cementitious phase.

3.3. Cold crushing strength

Cold crushing strengths of prepared castables 1–3 after drying are given in Fig. 4. For reference purposes, one sample, Secar 71, was prepared, using this as standard aluminous cement. As the figure shows, the CCS of castables prepared with synthesized cements was in the range of the aluminous cement. The lower CCS of sample 1 versus samples 2, 3, and Secar 71 is may be due to expansion that occurs during setting of this cement or the early set of the sample that may have started during mixing. This expansion was about 1% (as measured), and lead to micro-cracking of the concrete (Fig. 5).

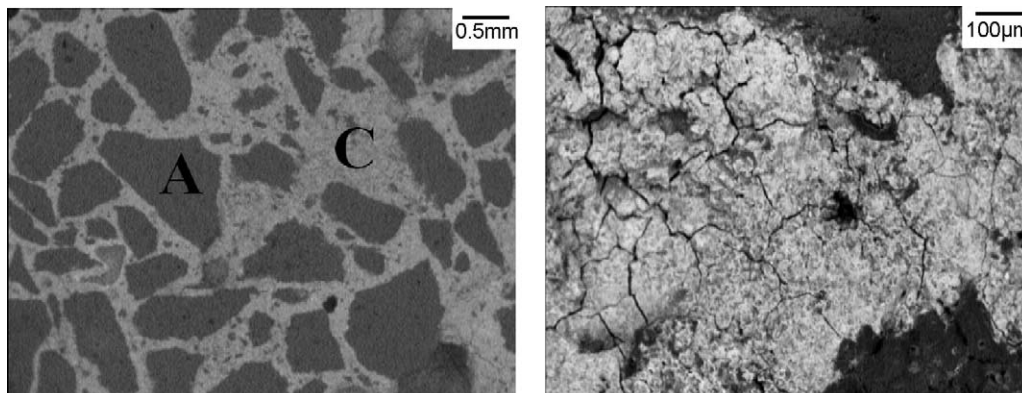


Fig. 5. SEM micrographs of sample 1 after drying at 110 °C for 24 h in two magnifications. A: alumina aggregates, C: hydrated barium aluminate cement.

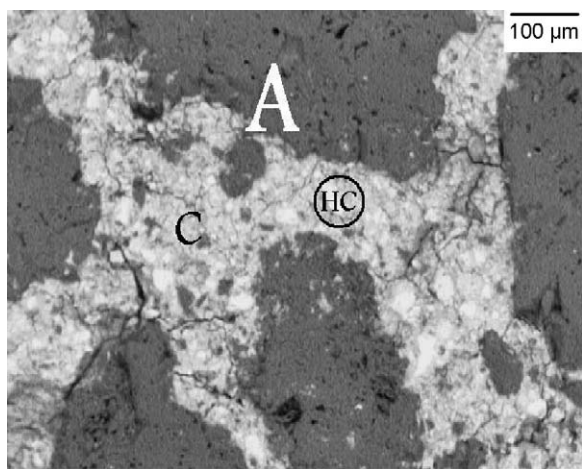


Fig. 6. SEM micrograph of sample 2 after drying at 110 °C for 24 h. A: alumina aggregates, C: hydrated barium aluminate cement, HC: hexacelsian particles.

In samples 2 and 3, expansion was small, and therefore the amounts of cracks were fewer and smaller in size (show in the backscatter SEM micrographs of Figs. 6 and 7 versus Fig. 5). Expansion of BA cements during hydration, and hence cracking of them also reported by Carlson [25].

3.4. Microstructure of the castables

The backscattered (BSE) SEM images for hydrated concrete samples after drying are shown in Figs. 5–7. As indicated in the SEM images in all samples, some cracks and pores were present. Using EDX the dark regions, Figs. 5–7 were identified as alumina aggregates (A), and the brighter regions were hydrated cement phases (C). In sample 1 (Fig. 5), the brighter region was a single phase, hydrated BaAl_2O_4 ; but in other images these regions, it consisted of two phases, BaAl_2O_4 and $\text{BaAl}_2\text{Si}_2\text{O}_8$. Using EDX analyses and XRD results, the brightest phase (HC) in Figs. 6 and 7 was identified as $\text{BaAl}_2\text{Si}_2\text{O}_8$, and the lighter phase (C) as hydrated BaAl_2O_4 . The difference between sample 2 containing celsian in cement prepared using kaolin (Fig. 6) and sample 3 prepared using colloidal silica (Fig. 7) was that colloidal silica produced a finer

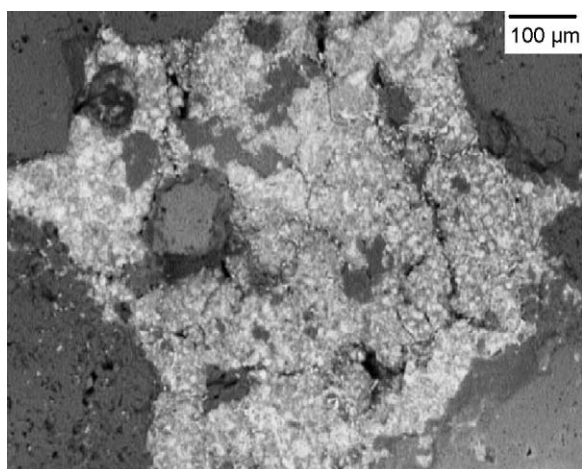


Fig. 7. SEM micrograph of sample 3 after drying at 110 °C for 24 h.

and more homogeneously distributed $\text{BaAl}_2\text{Si}_2\text{O}_8$ phase. This fineness and homogeneity was probably due to the fineness of the nano-sized colloidal silica (10–20 nm) and its higher reactivity. The slightly higher CCS in sample 3 in comparison with sample 2 (Fig. 4) was also probably due to the fineness and homogeneity created by the colloidal silica. As mentioned, in all samples some micro-cracks were observed, which may be due to the expansion on setting of the cements. As noted in samples 2 and 3 containing celsian, the amount of cracks are lower and smaller than in sample 1, where celsian was not present. The existence of celsian and decreasing the amount of BaAl_2O_4 phase resulted in slower setting and less expansion of the cement, and hence less cracking in the castables and better mechanical properties.

4. Conclusion

In this study barium aluminate cements were made with and without 10 wt% SiO_2 from either kaolin or colloidal silica, and then crystalline phases development between 900 and 1450 °C evaluated. Also cold crushing strength after drying, setting time and SEM microstructure investigations were done and the following results were observed.

1. Addition of 10 wt% SiO_2 using kaolin or colloidal silica to a BaAl_2O_4 composition leads to the formation of a barium aluminate–celsian composite cement.
2. Colloidal silica produced a more homogenous and finer microstructure in the composite cements than kaolin, with higher mechanical strength.
3. Pure barium aluminate cement has a very short setting time that caused a short set time during concrete mixing that was the shortest of all samples evaluated.
4. Addition of SiO_2 regardless of the SiO_2 source increased the set time of the barium aluminate and improved its workability.
5. The homogenous dispersion of fine celsian phase formed from colloidal silica can inhibit crack propagation in the castable and improve its mechanical properties.

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