Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 35 (2009) 3381–3388

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Utilization of aluminum sludge and aluminum slag (dross) for the manufacture of calcium aluminate cement

E.M.M. Ewais [a,*], N.M. Khalil [b], M.S. Amin [c], Y.M.Z. Ahmed [a], M.A. Barakat [d]

[a] *Refarctory & Ceramic materials Lab (RCML), Central Metallurgical Research and development Institute (CMRDI), P. O. Box 87 Helwan, 11421 Cairo, Egypt*
[b] *Chemistry Department, Faculty of Science, Sebha University, Libya*
[c] *Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt*
[d] *Chemical & Electrochemical Metallurgy Laboratory, Research and development Institute (CMRDI), P.O.Box 87 Helwan 11421Cairo, Egypt*

Received 19 March 2009; received in revised form 28 April 2009; accepted 6 June 2009
Available online 7 July 2009

Abstract

Four calcium aluminate cement mixes were manufactured from aluminum sludge as a source of calcium oxide and Al_2O_3 and aluminum slag (dross) as a source of aluminum oxide with some additions of pure alumina. The mixes were composed of 35–50% aluminum sludge, 37.50–48.75% aluminum slag (dross) and 12.50–16.25% aluminum oxide. The mixed were processed then sintered at different firing temperatures up to 1500 °C or 1550 °C. The mineralogical compositions of the fired mixes investigated using X-ray diffraction indicated that the fired mixes composed of variable contents of calcium aluminate (CA), calciumdialuminate (CA_2), calciumhexaaluminate (CA_6) in addition to some content of magnesium aluminate spinel (MA). Sintering parameters (bulk density, apparent porosity and linear change) and mechanical properties (cold crushing strength) of the fired briquettes were tested at different firing temperature. Refractoriness of the cement samples manufactured at the optimum firing temperature was detected. Cementing properties (water of consistency, setting time and compressive strength as a function of curing time up to 28 days of hydration) of pasted prepared from the manufactured cement mixes at the selected optimum firing temperatures (1400 °C or 1500 °C) were also tested. Cement mixes manufactured from 45 to 50% aluminum sludge, 37.50–41.25% aluminum slag (dross) with 12.50–13.75% alumina were selected as the optimum mixes for manufacturing calcium aluminate cement since they satisfy the requirements of the international standard specifications regarding cementing and refractory properties as a result of their content of CA (the main hydraulic phase in calcium aluminate cement) and CA_2(the less hydraulic but more refractory phase). Although the recognized high refractoriness of CA_6, its formation affect badly the cementing properties of the other non-optimum mixes.

Keywords: Aluminum sludge; Aluminum dross; Calcium aluminates; Refractory cement

1. Introduction

Since its discovery at 1908 by the French scientist Paid several research works were interested with calcium aluminate cement ‘‘refractory cement’’. Calcium aluminate cement is one of special cement characterized among others with developing about 80% of its ultimate strength after only 24 h of beginning of the hydration [1]. This feature enables its use as a very rapid hardening structural material in the busy locations such as factories and military places [2]. Other applications of calcium aluminate cement include industrial flooring products (such as cast house floors), chemical resistant mortars and concretes, sewer applications, expansive grouts, floor screeds, tile adhesives, protective coatings and in building chemistry products (whereas ordinary Portland cement is combined with it to give desired setting times) [3,4]. In addition, pure calcium aluminate technology has been used to rehabilitate dam spillways and structures affected by biogenic corrosion, such as manholes and pipes [4]. However the most important feature of calcium aluminate cement is its capability to withstand high firing temperatures up to 2000 °C depending on the type of the cement and its content of impurities [5]. In the field of high temperature applications, the type of cement used is determined by the required refractoriness [1]. Calcium aluminate cement is becoming the binder of choice for refractory formulators as the properties of monolithic refractories approach, and in some

---

* Corresponding author. Tel.: +20 2 38621782; fax: +20 2 38621782.
E-mail address: dr_ewais@hotmail.com (E.M.M. Ewais).

0272-8842/$36.00 © 2009 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2009.06.008

cases surpasses, the properties of refractory bricks. The flexibility a formulator has when working with calcium aluminate cement has allowed refractory castable technology to grow from simple conventional gun mixes and castables to formulations and installation systems that have significantly enhanced the refractory formulators offer of longer lasting, lower cost refractories. Monolithic refractory technology has grown to include calcium aluminate cements in many products with enhanced properties and installation systems such as low cement, ultra low cement, low moisture, high density, self flowing, pumpable and formless (shotcrete) castables. Lafarge Company offers the full range of calcium aluminate cement, allowing the refractory formulator to benefit from formulation strategies designed to maximize the cost/benefit ratio. Lafarge manufactures seven refractory cements with alumina content (purity level) ranging from 40 to 80%. All of these cements offer the refractory formulator a high level of the calcium aluminate (CA) phase, well known for flowability and rapid strength gain [6]. Due to their outstanding characteristics, calcium aluminate cements continue to be the most important hydraulically setting cements used for bonding refractory castables (concrete) widely used in today's refractories industry, especially as lining of the furnaces used during cement, glass, aluminium, ceramics, iron and steel, and petrochemical industries [7,8]. In the traditional high temperature industry, refractory shotcretes based on pure calcium aluminate systems have been used for rehabilitating and protecting coke wharves, slag pits, drossing areas, and mill scale flumes. Each of these applications relies on the material's ability to gain strength quickly, resist heat and thermal shock, and withstand repeated mechanical abuse and abrasion. Most industrial applications of these materials have carried the additional constraint of requiring a return to service in 24 h or less, and pure calcium aluminate systems are capable of delivering over 51 MPa within 24 h [9]. The early strength development of calcium aluminate cement enables high temperature processing units to be put back on steam with minimum turnaround time, thus providing a favorable cast/performance ratio [10]. Another application for pure calcium aluminate shotcrete is in the lining of fire training structures. These cast-in-place or block-constructed buildings are used by firefighters for live-fire training purposes. Typically, large amounts of combustible materials such as wooden pallets or bales of hay are stacked and soaked with fuel oil prior to ignition. Once ablaze, temperatures exceeding 980 °C are not uncommon. To further test the integrity of the structures, firefighting trainees then quickly douse the flames with high-pressure water streams, resulting in extreme thermal shock. Conventional concretes or shotcretes are unable to withstand this type of repeated thermal abuse. Pure calcium aluminate shotcretes have proven to be a reliable means of protecting these structures and are commonly used [9].

Phase compositions of calcium aluminate cements were extensively studied [11]. Five binary phases: $3CaO{\cdot}Al_2O_3$ (C_3A), $12CaO{\cdot}7Al_2O_3$ ($C_{12}A_7$), $CaO{\cdot}Al_2O_3$(CA), $CaO{\cdot}2Al_2O_3$(CA_2), and $CaO{\cdot}6Al_2O_3$(CA_6), were reported. Liquidus temperatures drop rapidly upon addition of Al_2O_3 to CaO. Thus, $3CaO{\cdot}Al_2O_3$, melts incongruently to CaO and liquid at 1535 °C. The minimum melting compositions are the eutectics between $12CaO{\cdot}7Al_2O_3$, and either $3CaO{\cdot}Al_2O_3$, or $CaO{\cdot}Al_2O_3$; these located at 1400° and 1395 °C, respectively. Beyond the $C_{12}A_7$ eutectic with monocalcium aluminate, liquidus temperature begin to rise rapidly with increasing aluminum content. $CaO{\cdot}Al_2O_3$ incongruently to $CaO{\cdot}2Al_2O_3$ at 1608 °C; $CaO{\cdot}2Al_2O_3$ melts incongruently to $CaO{\cdot}6Al_2O_3$ at ~1790 °C, and $CaO{\cdot}6Al_2O_3$ melts incongruently to Al_2O_3 and liquid at ~1860 °C. Accordingly, normal-aluminous cement has CaO/Al_2O_3 ratios between 0.9 and 1.2. These types of cements have lower solidus and liquidus temperatures than the high alumina cements which have CaO/Al_2O_3 ratios between 1.8 and 2.5. Addition of iron to calcium aluminate system leads to formation of brownmellerite phase "C_4AF" due to preferential replacement of one set of Fe^{3+} atoms by Al^{3+} leads to Al/Fe ordering at the 1:1 mole ratio [11]. Since normal-aluminous cements contain low percentages of silica, therefore, gehlenite (C_2AS) mineral is formed as principal crystalline silica-containing phases in this type of cements. Accordingly, Alumina cements may contain CA, CA_2 C_3A, CA_6 and $C_{12}A_7$ and also corundum as well as gehlenite (C_2AS) depending on the exact CaO/Al_2O_3 ratio and on the occurring admixtures occurring. Therefore for clinkering process the knowledge of an advantageous phase composition and of the maximum firing temperature is necessary. The properties in terms of setting time, reactivity and mechanical of the cements are also correlated with phase composition.

Limestone as a source of calcium oxide and bauxite or calcined alumina is the usual starting materials used to manufacture calcium aluminate cement [10]. Sometimes due to the deficiency of these starting materials especially bauxite which present only in few countries which do an agreement with each other "as an Opec does" to control the price and production of bauxite in addition to the relatively high hardness of bauxite so it needs special processing (grinding), these requirements are reflected on the price of the manufactured calcium aluminate cement [12]. So, in recent years researchers intense their work to use alternative sources for bauxite, limestone or both for manufacturing refractory cements. M. F. Zawrah and N. M. Khalil [13] utilized calcium hydroxide byproduct wasted during preparation of ethylene gas as alternative to limestone as a source of calcium oxide together with bauxite as a source of aluminum oxide to manufacture refractory calcium aluminate cement. N. M. Khalil [14] manufactured another type of refractory cement based on barium silicate using Egyptian kaolin with barite. L. G. Girgis et. al. [15] manufactured aluminous cements containing magnesium aluminate spinel from dolomite with calcined alumina.

In Egypt huge quantities of aluminum slag (dross) and reasonable quantities of aluminum sludge are wasted during aluminum industry causing many ecological and healthy problems [16]. On the other hand, Egypt demand from refractory cement exceeds 12,000 tones per year. Therefore, the present work aims at using these two waste materials to manufacture calcium aluminate cement in a doubly valuable manner i.e. spent undesired waste materials for manufacturing highly price calcium aluminate cement.

Table 1
Chemical analysis of starting materials.

Oxides	Chemical composition, Wt.%		
	Sludge	Aluminum slag (dross)	Aluminum oxide
SiO_2	0.89	2.77	–
Al_2O_3	17.97	87.57	99.99
TiO_2	0.018	0.13	–
Fe_2O_3	0.08	0.25	–
CaO	54.00	0.85	–
MgO	2.24	4.20	–
MnO	–	0.11	–
Na_2O	–	1.86	–
K_2O	–	0.26	–
L.O.I	24.75	–	–

2. Materials and experimental

2.1. Materials

Aluminum sludge was used a source of both CaO and Al_2O_3 in the manufacturing of refractory cement. In the Egyptian aluminum production (Alu-Misr) Co., Cairo, Egypt, reasonable quantities from the spent liquor is generated from etching the aluminum section materials by caustic soda. The addition of hydrated lime to such kind of spent materials led to precipitation of tonnage from calcium aluminate hydrate. This sludge as reported is composed of calcium aluminate hydrate, calcium carbonate and hydroxide [16].

Aluminum slag (dross) used in this study was used as a source of Al_2O_3. It is supplied by Aluminum industry, Naga Hamad, Egypt. Huge quantities from this slag are annually produced.

Calcined aluminum oxide was used in limited amounts, not exceeding 17 wt% to the previous two waste materials to increase the alumina content in the mixes and to assist the formation of different phases of calcium aluminate minerals after firing.

Chemical analysis of the starting materials was determined using Philips PW 1480 wave length dispersive X-ray fluorescence (XRF) spectrometer. The results are given in Table 1.

2.2. Experimental procedure

Five batches were prepared from different mixes of aluminum sludge, aluminum slag (dross) and alumina to give after firing calcium aluminate cements with different compositions, the starting mix compositions are given in Table 2. The method of manufacturing is based on the sintering of briquettes formed from the finely ground starting materials at 1250 °C, 1350 °C, 1400 °C and1500 °C for mixes 1, 2 and 3 and further up to 1550 °C for mix 4 [17]. At each firing temperature, sintering parameters namely; bulk density, apparent porosity and linear change, mechanical properties namely; cold crushing strength were tested according to the International standard specifications [18–21]. The refractoriness of the samples fired at the optimum firing temperatures (1400 °C or 1500 °C) were tested using Segar cone (pyrometric cone equivalent test) [22].

N.B. Each experiment in this work was carried out three times and the average of three tests was taken if the difference between two of the three values does not exceed 1.5%. However, if the difference among three values exceeded 1.5%, the experiment was repeated to overcome on the errors in experiments.

Some selected cement samples were finely ground (<100 μ) and investigated through their solid phase compositions using X-ray diffraction analysis. A Philips PW 1710 diffractometer with Ni filter and Cu kα radiation ($\lambda = 1.54$ nm) at 40 kv, 30 mA and a scanning speed of 2 min^{-1}.

The sintered briquettes were then finely ground, the specific surface area as determined by the Blain method [23] was maintained around 400 m^2/kg. The optimum water of consistency used for the preparation of cement pastes was tested using Vicat apparatus which used also to determine the initial and final setting time of the prepared cement pastes [24,25]. The cement pastes prepared using the optimum amounts of mixing water were molded in 0.0254 m × 0.0254 m × 0.0254 m steel moulds, and then kept in a humidity cupboard with a 100% relative humidity. After 24 h the hardened cement cubes were demolded, three samples were tested through their sintering parameters (bulk density and apparent porosity) and mechanical properties (cold crushing strength). The remaining hardened cubic cement samples were kept under water for further investigations at 3 h, 7 h and 28 h.

3. Results and discussion

3.1. Solid phase composition

Figs. 1–4 show the X-ray diffraction patterns of different mixes at different temperatures. After firing mixes 1 and 2 at 1250 °C, calcium monoaluminate (CA), the main hydraulic compound in calcium aluminate cement [26] with comparable amounts from two other calcium aluminates phases termed CA_2

Table 2
Composition of the mixes.

Mix no.	Green mix composition, Wt.%			Chemical composition of the fired mixes,								
	Sludge	Aluminum slag(dross)	Aluminum oxide	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Wt.%	Wt.%	MnO	Na_2O	K_2O
1	50	37.5	12.5	1.71	62.55	0.07	0.15	31.46	3.1	0.05	0.8	0.11
2	45	41.25	13.75	1.75	65.85	0.07	0.16	28.01	3.11	0.06	0.87	0.12
3	40	45	15	1.8	69.07	0.07	0.16	24.65	3.12	0.06	0.94	0.13
4	35	48.75	16.25	1.84	72.2	0.08	0.17	21.38	3.13	0.06	1	0.14

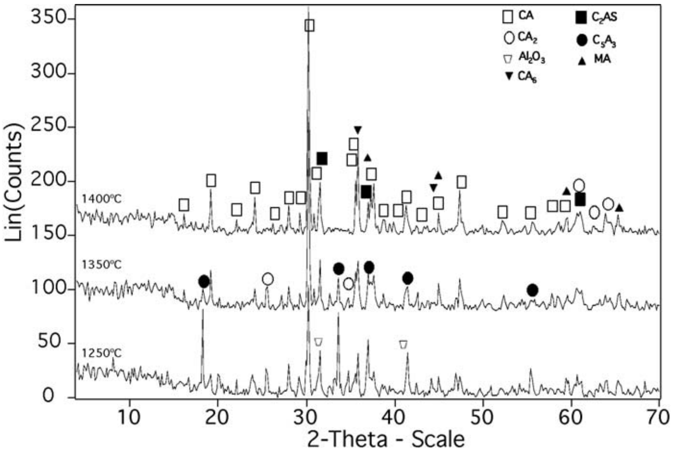

Fig. 1. X-ray patterns of mix 1.

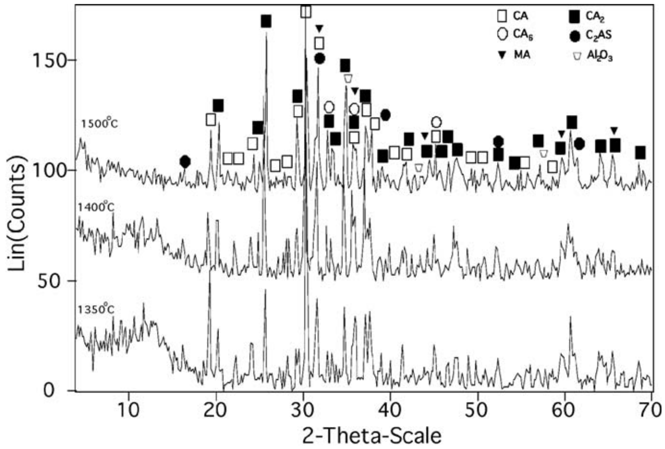

Fig. 3. X-ray patterns of mix 3.

and C_5A_3 were detected, see Figs. 1 and 2. A little amount from un-reacted alumina (Al_2O_3) and gehlenite (C_2AS) was observed. With the increase of the firing temperature up to 1350 °C, relatively small amounts from C_5A_3 with complete disappearing of alumina. On other hand, the increase of the amount of the aluminum dross in the mixtures as in mix 3 and the firing at the same temperature (1350 °C), CA as main phase and little amounts of CA_2 and C_2AS with no indication for the presence of C_5A_3 and Al_2O_3 was recorded, see Fig. 3. The further increase of the firing temperatures up to 1400 °C, the reaction among the constituents of mixes 1, 2 and 3 seems to be completed forming CA as main phase with comparable amounts of CA_2. Mix 1 is composed mainly of CA with very slight amount of CA_2. Nevertheless, in mixes 2and 3, the content of CA_2 gradually increases on the expense of CA. Mix 2 composed of comparable proportions of CA and CA_2 while mix 3 containing relatively higher content of CA_2 compared with CA. Mix 4 composed mainly of CA_2 with little content of CA, see Fig. 4. These compositions are correlated with the green (before firing) batch compositions (Table 2), as we proceed from mix composition 1 to mix composition 4 the content of aluminum sludge (the only source of CaO) decreases while the content of aluminum slag (dross) and alumina (the sources of Al_2O_3) increase leading to the increase in the more rich aluminum containing phase CA_2 on the expense of the CA. in addition, the presence of silica in the aluminum dross led to the formation of gehlenite phase. Besides CA and CA_2, some peaks characterizing magnesium aluminate spinel (MA) could be detected, its content increases as we proceed from cement mixes 1 to 4 due to the increase in aluminum slag (the source of magnesia and alumina) in the green batches. Due to the relatively lower content of magnesia in aluminum sludge (2.24%) compared with aluminum slag (4.20%) so the decrease in the aluminum sludge content in the green batches, as we proceed from mixes 1 to 4, does not affect adversely the content of MA spinel formed. As the firing temperature increases up to 1350 °C and 1400 °C (Figs. 2 and 3), no change in the proportions of the formed phases CA, CA_2 and MA spinel could be observed, this because the only change may occur at these firing temperatures is the grain growth of the formed phases [27]. After firing at 1500 °C (Fig. 4), a new assemblage of minerals could be observed. In addition to MA spinel, calcium hexaaluminate phase (CA_6) could be observed in mix 2 and increases in mix 3 reaching its maximum in mix 4. The formation in CA_6 is correlated with the increase in the Al_2O_3 content in the green batches, the absence of this phase from mix

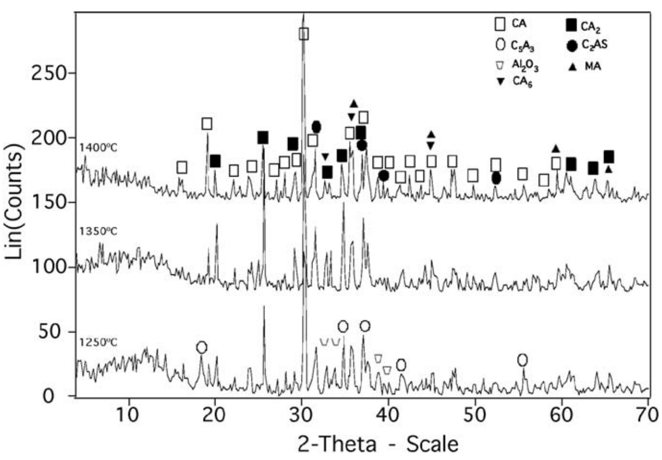

Fig. 2. X-ray patterns of mix 2.

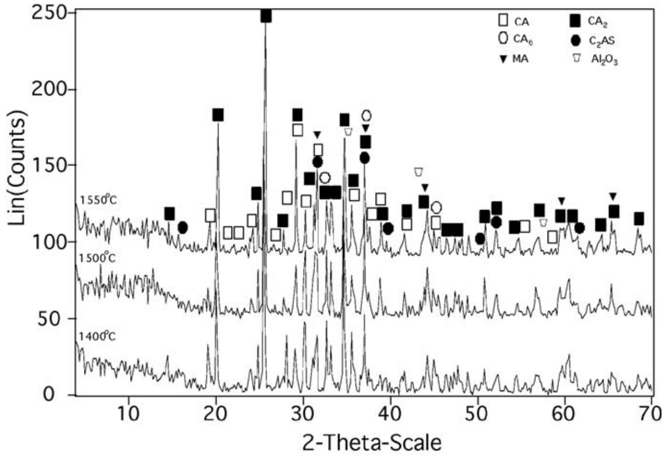

Fig. 4. X-ray patterns of mix 4.

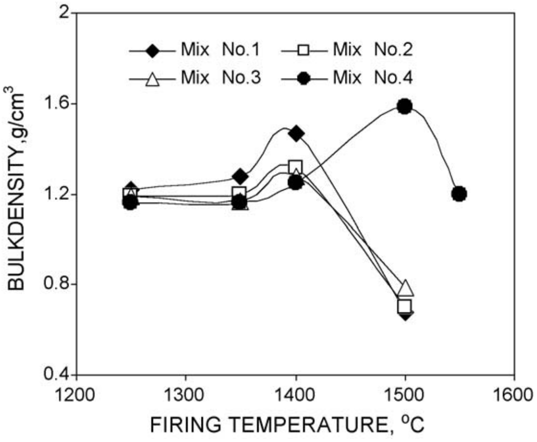

Fig. 5. Bulk density of briquettes from the fired mixes.

1 is due to the deficiency of Al_2O_3 content in its green batch since it contains the lowest proportion of Al_2O_3 sources (aluminum slag and alumina) compared with the other batches (Table 2)[28].

3.2. Densification parameters

Figs. 5–7 show the densification parameters namely; bulk density, apparent porosity and linear change of the fires mixes. Fig. 5 indicates that at 1250 °C, the four fired samples show comparable values of bulk density range between 1.18 and 1.20 with a slight increase in the order; mix $1 >$ mix $2 >$ mix $3 >$ mix 4. After firing at 1350 °C, a slight increase in bulk density values is observed compared with the bulk density values at 1250 °C, the increase is more evident with samples prepared from mix 1. After firing at 1450 °C, a pronounced increase in bulk density values is observed reaching their maxima, followed by a sharp decrease after firing at 1500 °C, except samples prepared from mix 4 in which the bulk density values reaching their maxima after firing at 1500 °C, and sharply decrease after firing at 1550 °C but still higher than those of other mixes. Fig. 6 shows an opposite behavior of apparent porosity to bulk density i.e. the percents of apparent porosity decrease with increasing firing temperature reaching their minima after firing at 1450 °C with samples of mixes 1, 2 and 3 or at 1500 °C with those of mix 4, but sharply increase after firing at 1500 °C with samples from the first three mixes or at 1550 °C with those of the fourth mix, however, being still relatively higher with the fourth mix than with the first three ones. Fig. 7 indicates that the fired samples exhibit limited linear change percents not exceed 1% reaching their minima after firing at 1400 °C with samples of mixes 1, 2 and 3 or at 1500 °C with those of mix 4. The behavior of the sintering parameters is correlated with the mineralogical composition of the manufactured samples. The slight improvement in sintering parameters of samples of mixes 1, 2 and 3 on firing up to 1400 °C is due to the grain growth of calcium aluminate and magnesium aluminate spinel crystals in addition to the formation of low contents of some glassy phases as a result of the impurities present in the starting materials (Table 1) which fill the pores and cavities in the matrix resulting in an increase in bulk density and hence a decrease in apparent porosity accompanied with a little shrinkage in diameter. As a result of high content of alumina in the green mix 4 (Table 2), calcium hexaaluminate (CA_6) is formed after firing at 1500 °C that characterized with a network structure which interlock the matrix together with magnesium aluminate spinel and corundum formed from excess alumina (matrix advantage system). This in turns leads to a noticeable improvement in sintering parameters. After firing at 1550 °C the amount of CA_6 increases causing a further stress on the matrix resulting in a loosening in the structure (relieve) and hence a noticeable decrease in sintering parameters, in case of mixes 1, 2 and 3 this occurs at 1500 °C by the action of CA or CA_2 phases [29].

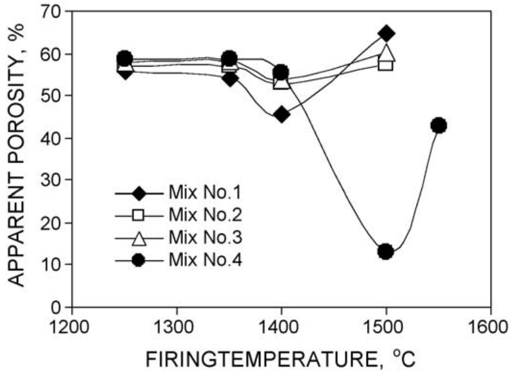

Fig. 6. Apparent porosity of briquettes from the fired mixes.

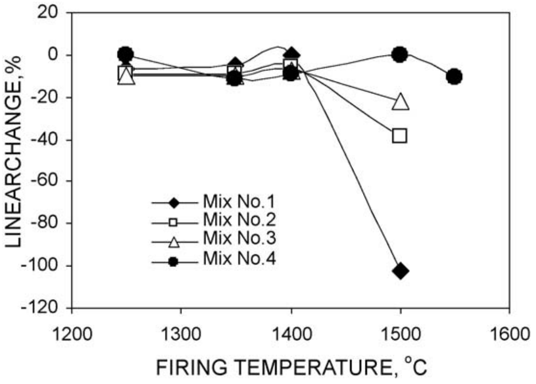

Fig. 7. Linear change of briquettes from the fired mixes.

3.3. Mechanical properties of the fired samples

Fig. 8 shows that samples of the mixes fired at 1250 °C exhibits comparable values of compressive strength, slightly increase after firing at 1350 °C reaching their maxima after firing at 1400 °C for samples of mixes 1, 2 and 3 or 1500 °C of those of mix 4. But decrease after firing at 1500 °C for samples of mixes 1, 2 and 3 or 1550 °C for those of mix 4.This behavior is parallel to the bulk density one, as the bulk density increases, the pores and cavities are being closed leading to a compact microstructure and hence an improved compressive strength. The formation of CA_6 network is responsible for the recognized

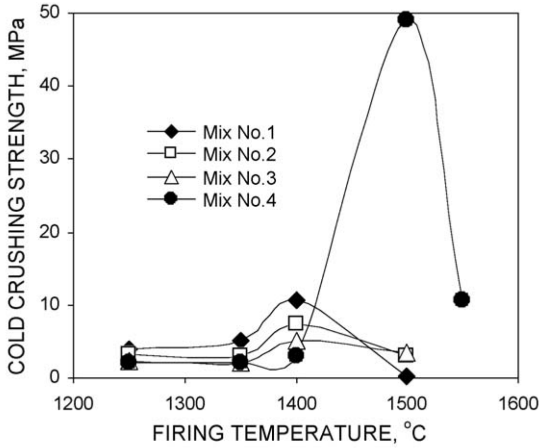

Fig. 8. Compressive strength of briquettes from the fired mixes.

improvement in mechanical properties of mix 4 at 1550 °C [30].

3.4. Refractoriness

Table 3 indicates that the refractoriness of the fired samples (1400 °C) increase in the following sequence; samples of mix 4 > mix 3 > mix 2 > mix1. This behavior is correlated with the increase in the alumina Al_2O_3 (m.p.: 2050 °C) content in the green mixes especially in mix 4 and to less extent in mix 3 which results in the formation of the highly refractory system CA_6 (m.p.: > 1700 °C) + MA (2135 °C) + corundum (2050 °C), see the ternary diagrams of Al_2O_3–CaO–MgO and Al_2O_3–CaO–SiO_2 [31] in Fig. 9. The relatively lower refractoriness of samples of mix 1 is correlated with the relatively lower refractoriness of its main component CA (1600 °C), the refractoriness slightly improved in mix 2 due to the formation of CA_2 with relatively higher refractoriness (1750 °C) compared with CA. The presence of limited contents of impurities in aluminum sludge and aluminium slag (dross) results in the formation of limited amounts of some glassy phases which affect adversely the refractoriness of samples of mixes 1 and 2, the increase in alumina content on the expense of aluminium sludge in the green mixes 3 and 4 results in relatively lower contents of glassy phases and hence improved refractoriness [32].

Table 3
Refractoriness of samples of the fired mixes.

Mix no.	Fusion point, °C (Segar cone no.)
1	1580–1595 (26–27)
2	1635–1650(29–30)
3	>1700 (>33)
4	>1700 (>33)

3.5. Cementing properties

Based on the above results, 1400 °C (firing temperature) was selected as the optimum for manufacturing cements of mixes 1, 2 and 3 while 1500 °C was the optimum for manufacturing cement from mix 4. Cementing properties of the manufactured cements namely; water of consistency, setting time as well as compressive strength at different curing times (1, 3, 7 and 28 days) were tested.

3.5.1. Water of consistency

Table 4 indicates that the prepared cement mixes consume 24–31.5% of mixing water to obtain workable cement pastes. The contents of mixing water is the largest with cement mix 1 which composed mainly of the main hydraulic phase (CA) in calcium aluminate cement while cement mix 2 consumed

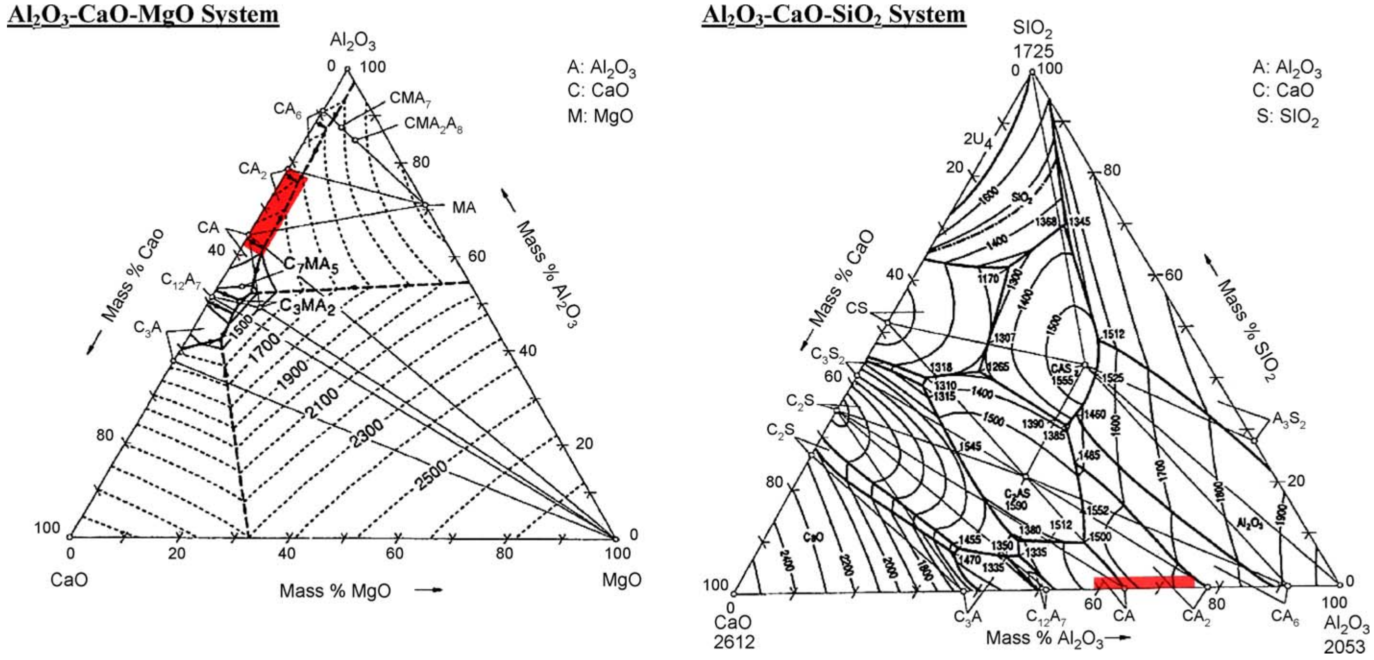

Fig. 9. Positions of the investigated mixes (highlighted area) in the ternary diagrams of Al_2O_3–CaO–MgO and Al_2O_3–CaO–SiO_2. [31].

Table 4
Water of consistency of the manufactured mixes.

Mix. No.	Water of consistency (%)
1	31.5
2	27.5
3	25
4	24

relatively lower content of mixing water due to the presence of some content of the less hydraulic CA_2 together with CA, cement mix 3 consumes relatively lower contents of mixing water compared with cement mixes 1 and 2 due its relatively higher content of CA_2, while cement mix 4 consumes the lowest content of water since it composed mainly of the non-hydraulic CA_6 and corundum phases.

3.5.2. Setting time

Table 5 indicates that the initial and final setting time increase according to the following sequence; cement mix 4 > cement mix 3 > cement mix 2 > cement mix 1. The shortest setting time given with cement mix 1 is due to its relatively higher content of CA (the main hydraulic compound of calcium aluminate cement) characterized with relatively fast setting time[33]. As we proceed to cement mix 2 and 3 the content of the less hydraulic CA_2 (characterized with relatively longer setting time) increases on the expense of CA leading to delay relatively longer setting time. Cement mix 4 exhibits the longest setting time because it composed mainly of the non-hydraulic CA_6 and corundum phases [17].

3.5.3. Mechanical properties of the hardened cements

Fig. 10 shows the compressive strength values of the hydrated cement pastes after 1, 3, 7 and 28 days of hydration. The figure shows that only cement mixes 1 and 2 exhibits considerable values of compressive strength at different ages of hydration (satisfy the requirements of the international standard specifications). Cement mix 3 shows relatively lower values of compressive strength compared with cement mixes 1 and 2 while cement mix 4 exhibits the lowest compressive strength values. This mechanical behavior is correlated with the mineralogical compositions of the manufactured cement mixes. Cement mix 1 composed mainly of CA, the main hydraulic product of calcium aluminate cement; it is responsible for the rapid hardening of calcium aluminate cement [3,17]. Cement mixes 2 and 3 exhibit relatively lower compressive strength values due to the presence of CA_2 (reacts slowly with water) which predominates in cement mix 3. Cement mix 4 exhibits the lowest values of compressive strength among the investigated cement mixes due its very low content of the CA and its relatively higher content of the non-hydraulic CA_6, MA and corundum.

Table 5
Setting time of the manufactured cement mixes.

Cement mix no.	Setting time, Minutes	
	Initial	Final
1	140	320
2	220	350
3	380	430
4	440	520

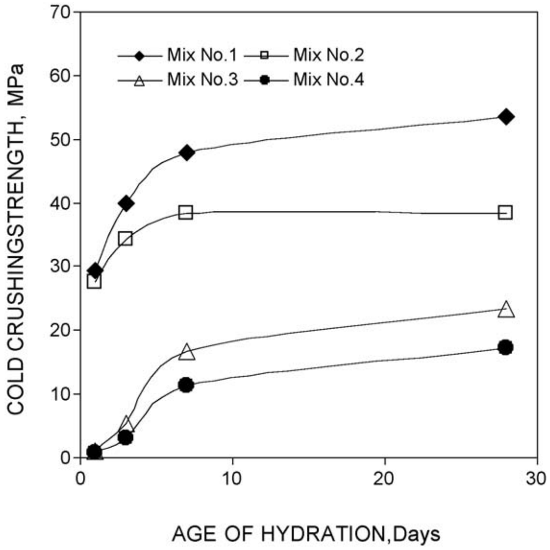

Fig. 10. Compressive strength of the hydrated samples made from manufactured cement.

4. Conclusion

Calcium aluminate cement mixes could be prepared in a doubly valuable manner using the paltry price aluminium sludge and aluminum slag (dross) wastes as sources of CaO and Al_2O_3, respectively with some additions of alumina to manufacture valuable calcium aluminate cement. Cement mixes prepared from 45 to 50% aluminum sludge, 37.5–41.25% aluminum slag and 12.5–13.75% alumina, are selected as the optimum cement mixes since they satisfy the requirements of the international standard specifications.

References

[1] R. G. Mangabhai, Calcium aluminate Cement, (1980), Cambridge, Spon.
[2] N. M. Khalil, Preparation and characterization of highly pure calcium and barium aluminate refractory cements and their applications, Ph. D thesis, Menoufia University, Egypt. (1997).
[3] M.M. Radwan, N.M. Khalil, Calcium aluminate cement/slag composite, Ind. Ceram. 21 (3) (2001) 151–158.
[4] F. M. Lea, The chemistry of cement and concrete, Edn. Edward Arnold, London (1998).
[5] L.G. Girgis, S.A.S. El-hemaly, N.M. Khalil, Preparation and characterization of some aluminous cement compositions, Tile Brick Int. 16 (4) (2000) 250–256.
[6] C.M. George, The hydration kinetics of refractory aluminous cements and their influence on concrete properties, J. Br. Ceram. Soc. 79 (1980) 82–90.
[7] A.N. Scian, E. Pereira, Mechanochemical activation of high alumina cements—hydration and thermomechanic behaviour, Cement Concrete Res. 24 (1994) 937–947.
[8] M. Neville-Adam, A new look at high alumina cement, Concrete Int. 20 (8) (1998) 51–55.

[9] M. W. Fitzgerald, J. Talley and C. W. Alt, Calcium aluminate technology and its application, Shotcrete, summer (2002).

[10] T.D. Robson, Aluminous refractory castables, Academic Press, London, 1964.

[11] A. M. Alper, Phase diagrams–Materials science and technology, Volume II: The use of phase diagrams in metal, refractory, ceramic, and cement technology, pp. 149–161, Academic press, NY, San Francisco, London, A subsidiary of Harcourt Brace Jovanovich, Publishers, (1970).

[12] H. A. Othman, Extraction of Al_2O_3 from some south Libyan clays, M.Sc. thesis, Sebha University, Libya, (2007).

[13] M.F. Zawrah, N.M. Khalil, Utilization of Egyptian industrial waste material in manufacturing of refractory cement, J. Br. Ceram. Soc. 101 (5) (2002) 225–228.

[14] N.M. Khalil, Refractory barium silicate cement from Egyptian barite and fumed silica waste materials, Refract. Eng. 11 (2001) 22–25.

[15] N.M. Khalil, S.A. El-Hemaly, L.G. Girgis, Aluminous cements containing MA spinel from Egyptian dolomite, Ceram. Int. 27 (2001) 865–873.

[16] M.A. Barkat, S.M. Elsheikh, F.A. Farghaly, J. Separ. Purif. Technol. 46 (2005) 214–218.

[17] N. M. Khalil, Study of some calcium aluminate refractory cements, M.Sc. thesis, Menoufia University, Egypt, (1994).

[18] DIN 51056.

[19] DIN 51067.

[20] ASTM C113-02 (2008).

[21] DIN 51063.

[22] DIN 51057.

[23] ASTM C204-07).

[24] ASTM C187-86.

[25] ASTM C191-92.

[26] K.M. Parker, J.H. Sharp, Refractory calcium aluminate cements, Trans. J. Br. Ceram. Soc. 81 (2) (1982) 35–42.

[27] M.R. Nilforaushan, Proc. 44th International Colloqium on Refractories Refractories in Stealmaking, Aachen Germany September, (2001), p. 160.

[28] H. Pollmann, Proceedings of International Conference on Calcium Aluminate Cements, Heriot-Watt University, Edinburgh, UK, July, 2001.

[29] N.M. Khalil, M.F. Zawrah, Self-forming mullite containing refractory barium silicate cement, Trans. J. Br. Ceram. Soc. 103 (4) (2004) 1–4.

[30] K. M. Parker and J. H. Sharp, Solid State Chemistry, Bratislave, 6–12 July (1996).

[31] Slag Atlas, 2nd edition. Edited by the Verein Deutsche Eisenhüttenleute (VDEh). Verlag Stahleisen GmbH, Düsseldorf (1995) pp. 104–105.

[32] J. White, High Temperature Oxides, Endn Alper, M. A. Academic Press, New York, (1970) P. 77.

[33] J. E Kopanda, G. MacZura, Production Processes, Properties and Applications for Calcium Aluminate Cements, Alumina Chemicals Science and Technology handbook, ed. LeRoy D. Hart, American Ceramic Society (1990) pp 171–181.