

APPRAISAL OF ALUM SLUDGE WASTE FOR LOW-CARBON, CALCIUM ALUMINATE CEMENT PRODUCTION

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Keywords

Calcium aluminate cement (CAC); Alum sludge waste (AS); Low-carbon cement; Waste reactivity; Cementing ability.

Abstract

Calcium aluminate cement (CAC) is the most used non-Portland cement, known for its rapid hardening and high thermal resistance. The difficulty in obtaining raw materials, mainly bauxite, has resulted in the current high price of CAC. Alum sludge waste (AS) is a flocculating precipitate, high in aluminium, produced during the water purification process in drinking water treatment plants. The potential of using locally available AS, as an aluminium source, to produce CAC was investigated. This serves a dual purpose: to reduce bauxite dependence and to recycle waste. In addition, the CAC produced with AS waste would have embodied lower carbon than existing conventional cements. Cements were produced by calcining AS and lime blends, at 1:1 and 1:3 ratios, at 1100, 1200 and 1300°C. The composition and properties of the resultant cements and their hydrates were studied with mechanical tests, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The main reactive phases of the CACs were calcium aluminates such as C_3A and $C_{12}A_7$. Higher calcination temperatures result in reaction products of higher Ca/Al ratios. Hexagonal interlocking C-A-H hydrates were observed in the CAC pastes. The CAC prepared with a 1:3 (AS:lime) ratio sintered at 1300°C displayed the best performance, whereas high aluminium contents and low calcination temperatures caused flash setting and severe expansion.

1. INTRODUCTION

Calcium aluminate cement (CAC) was developed in the late nineteenth and early twentieth centuries as a response to the poor durability of Portland cement in calcium sulphate environments [1]. CAC has since become the most widely used non-Portland cement due to its exceptional ability to retain strength at high temperatures and resist extreme thermal shock [2]. Moreover, CAC is characterized by rapid hardening, reaching 80% of its ultimate strength within 24 hours of hydration [3]. As a result of these properties, CAC has gained widespread use in various fields, such as the dental materials [4], rapid repairing mortar [5], and tile adhesives [6].

Although alumina is abundant in nature, it is typically found in combination with silica, as in clay minerals. Silica is considered an impurity in CAC production because it exists as C_2AS in CAC clinkers and it is inert on hydration [7]. This phase has no contribution to strength development or hardening but makes grinding more difficult, thus silica content is controlled (<6%) [8]. Bauxite is the primary aluminium source in the manufacture of CAC [9]. However, bauxite reserves are expected to be depleted within the next twenty years, based on current proven volumes at a 5% annual growth use rate [10,11]. The difficulty of acquiring bauxite contributes to the current high cost of CAC. To meet the growing demand for CAC and reduce its cost, researchers have concentrated efforts on developing alternative sources of raw materials for CAC production. Eweis et al.[8] used aluminium sludge (AS) and aluminium slag to produce CAC and detected CA , CA_2 and CA_6 in the resultant clinker. Zhu et al.[12] used commercial alumina, light-burned magnesia and calcium carbonate to prepare CAC which generated micro $MgAl_2O_4$ spinel in the clinker.

Alum sludge waste (AS) is a flocculating precipitate produced during the water purification process in drinking water treatment plants. It is generated by the hydrolysis of alum ($Al_2(SO_4)_3$) which is used as a coagulant during the purification process, and its main component is aluminium hydroxide ($Al(OH)_3$). For a long time, the disposal of AS has not received enough attention, leading to its storage in dumps and potentially increasing the presence of heavy metals and pathogens in local soil and groundwater [13]. The recovery of AS has been reported in the literature in various applications, including Portland cement production, geopolymer addition, dye remover and heavy metal adsorbent [14].

Due to its amorphous properties, AS waste might be more reactive than other aluminium sources, which would result in a lower energy input for processing and a lower-carbon, more sustainable material. According to Lei and Pavia [15] calcined AS waste is highly pozzolanic and pyroprocessing at 800 °C is ideal, producing abundant calcium carboaluminate hydrate also known as calcium monocarboaluminate ($\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O} = \text{C}_4\text{AC H}_{11}$) in the hydrated pastes due to pozzolanic reaction and secondary hydration involving CO_3^{2-} . However, to our knowledge, using AS to produce CAC has not been reported in the literature.

This study assesses the feasibility of manufacturing calcium aluminate cement (CAC) using local alum sludge waste (AS) as a means of lessening dependence on bauxite and recycle AS. CAC made with various AS contents at different calcination temperatures are investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The mechanical strength development of the CAC was followed for a period of one year.

2. MATERIALS AND METHODS

2.1. MATERIALS

Alum sludge (AS) collected from a drinking water treatment plant in Northern Ireland was utilized as an alternative source of aluminium to produce calcium aluminate cement (CAC). AS, which is generated as a by-product during the water purification process, undergoes a series of compression and dewatering procedures to form a black lumpy solid with high water content (approximately 82.5%). To prepare the AS for the CAC, the slurry was dried to a constant weight at 105°C and subsequently ground in a ball mill for 2 hours. The X-ray diffraction (XRD) analyses of the AS revealed that it is primarily amorphous, with traces of crystalline quartz (Figure 1). Table 1) shows that it consists mainly of Al_2O_3 , with little SiO_2 and Fe_2O_3 .

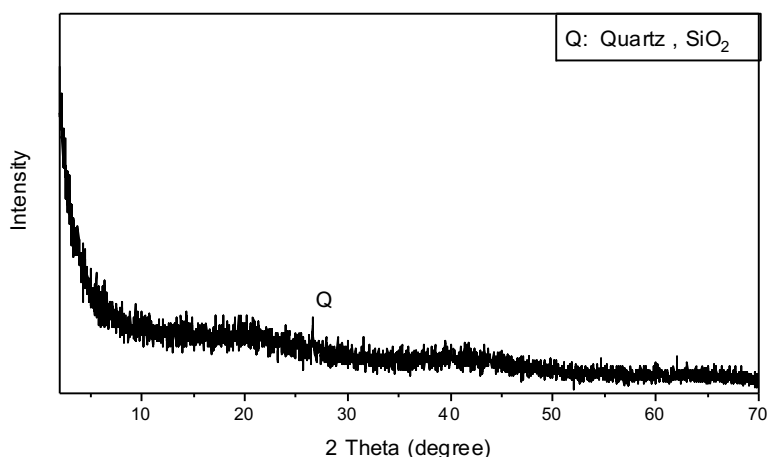


Figure 1. X-Ray Diffractogram of the raw AS.

A commercial lime (CaO) was used as a calcium source. Then ground AS was mixed with lime with ratios of 1:1 (C1A1) and 1:3 (C1A3), in a ball mill for 1h, to ensure adequate mixing. The chemical compositions of the mixtures are shown in Table 1. The ratio to CaO: Al_2O_3 is 3.53 and 1.18 for C1A1 and C1A3, respectively. The mixtures were calcined in an electrical furnace at temperatures of 1100, 1200 and 1300°C for 3 hours, and then ground in a ball mill for 1h to obtain the CAC powders.

Table 1. Chemical composition of the AS and AS/lime blends analysed by X-Ray Fluorescence and expressed as % wt by oxide.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	TiO_2	MnO	P_2O_5	SrO	BaO	LOI
AS	3.19	28.30	1.03	0.17	0.09	0.06	0.05	0.002	0.03	0.04	0.08	<0.01	0.01	66.1
C1A1	2.38	21.14	0.88	74.81	0.07	0.04	0.04	<0.01	0.03	0.06	0.06	<0.01	0.01	-
C1A3	4.74	42.09	1.53	49.93	0.13	0.09	0.07	<0.01	0.04	0.06	0.12	<0.01	0.01	-

2.2. COMPOSITION OF THE CAC AND THE RESULTANT HYDRATES

The mineral composition of the CAC generated was analysed with X-Ray Diffraction (XRD) using the powder method, by means of a Bruker D5000 apparatus from 2 to 70° 2θ. The hydration products in CAC pastes, at 7 and 28 days, were investigated with a SEM apparatus featuring an EDX attachment. The EDX technique was used for the elemental analysis of the hydrates formed. The equipment consists of a Zeiss ULTRA plus apparatus with a 20mm² Oxford Inca EDX detector. Images and composition spectrums were taken for powder and paste specimens coated with gold/palladium to avoid charging.

2.3. STRENGTH, SETTING TIMES AND WATER DEMAND

The water demand of the cements fabricated was measured with the initial flow test in EN 459-2. The water content was adjusted until the sample, upon removing the mould, gave desirable workability measured as the initial flow diameter after 15 jolts. The setting time of the different CAC pastes was tested in accordance with EN 196-3:2016 using the Vicat apparatus, as a method of estimating the reactivity and the type of hydrates present.

The cements produced were used to fabricate mortar specimens to test the mechanical properties. The mixing proportions of CAC and sand are constant at 1:3. The mix proportions are presented in Table 2. All solid components (CAC and sand) were mixed for 2 minutes in a mechanical mixer. The water required, as determined with the initial flow test, was then added and mixed for a further 5 minutes. The flexural and compressive strength were measured using prismatic specimens of 160 × 40 × 40 mm, with a Zwick loading machine according to EN 196-3:2016. The mechanical behaviour of the specimens was also investigated using strength/strain curves. The fresh slurry was cast into 160×40×40 mm steel moulds and cured, wrapped in polyethene film to prevent moisture loss. The specimens were demoulded after 24 hours and stored in a curing room at 20 ± 3°C, under damp hessian to maintain humidity.

Table 2. Mix design of mortars made with the CACs

Notation	CAC		Sand	Water	w/b
C1A1 1100 °C	400	CaO:AS=1:1 calcined at 1100 °C	1200	300	0.75
C1A1 1200 °C	400	CaO:AS=1:1 calcined at 1200 °C	1200	200	0.50
C1A1 1300 °C	400	CaO:AS=1:1 calcined at 1300 °C	1200	200	0.50
C1A3 1100 °C	400	CaO:AS=1:3 calcined at 1100 °C	1200	300	0.75
C1A3 1200 °C	400	CaO:AS=1:3 calcined at 1200 °C	1200	200	0.50
C1A3 1300 °C	400	CaO:AS=1:3 calcined at 1300 °C	1200	200	0.50

3. RESULTS AND DISCUSSION

3.1. MINERAL COMPOSITION OF THE CACS

Typically, the mineral phases in commercial CAC clinkers include CA_2 , CA, $C_{12}A_7$, C_2AS , and others depending on the CaO/Al_2O_3 ratio [1]. Of these phases, CA is the primary active phase, accounting for approximately 65% of commercial CAC. CA sets in a few hours followed by rapid hardening. However, CA was not detected in the AS cements produced, likely due to the use of different raw materials than those in commercial CACs.

Figure 2 and Figure 3 show the mineral composition of the AS cements (C1A1 and C1A3). The **C1A1 cement** (CaO:AS = 1:1) produced at lower temperature (**1100°C**) consists mainly of $C_{12}A_7$ (PDF 00-009-0413) and smaller amounts of CA_2 (PDF 00-023-1037) and C_4A_3S (calcium sulfoaluminate or ye`elinite, PDF 00-016-0335). Calcium residuals are significant including CaO and $Ca(OH)_2$, indicating that not all the Ca has reacted with the Al.

$C_{12}A_7$ is one of the most important components of CACs and contribute to fast setting upon reaction with water. It is considered to be an intermediate product of the high-temperature reaction and usually occurs at lower calcination temperatures [16]. CA_2 has a low hydraulic activity, requiring 28-48 hours of hydration and lasting several weeks[17].

When increasing the calcination temperature to **1200°C**, C_4A_3S rises and, together with $C_{12}A_7$, becomes the main reactive phase, while CA_2 is no longer detected. A slight decrease in calcium residues was observed, indicating that the reaction has proceeded further.

At **1300°C**, a new phase, C_3A (PDF 00-038-1429) appears and becomes the most abundant and main reactive phase coupled to a decrease of $C_{12}A_7$ and C_4A_3S . C_3A is an important component of both Portland cement and CAC, which reacts rapidly with water and contributes to the rapid setting. Despite a decrease in calcium residues compared to the reaction products at 1200°C, significant amounts of calcium residues remain, indicating an excess of calcium in the system.

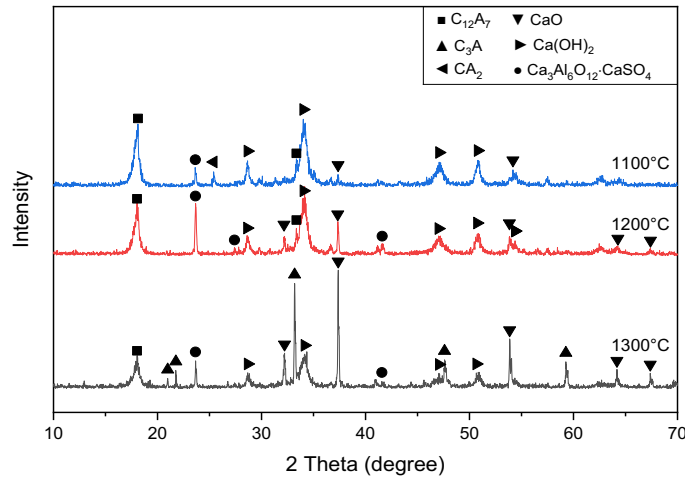


Figure 2. Mineral composition of the C1A1 cements according to the XRD analyses.

When the AS content was increased (**C1A3 cement** of CaO:AS = 1:3) similar changes in the mineral composition of the cement were observed from 1100 to 1300 °C (table 3). However, more calcium aluminate phases were detected, as well as fewer calcium residues, indicating better progress of the reaction and better proportioning in the design cement mix. This agrees with former authors as liquidus temperatures drop rapidly upon the addition of Al₂O₃ to CaO [1]. Therefore, C1A1, containing a higher proportion of CaO, requires a higher reaction temperature. In other words, under the same calcination temperature, the C1A1 cement mix will form less reactive calcium aluminates than C1A3.

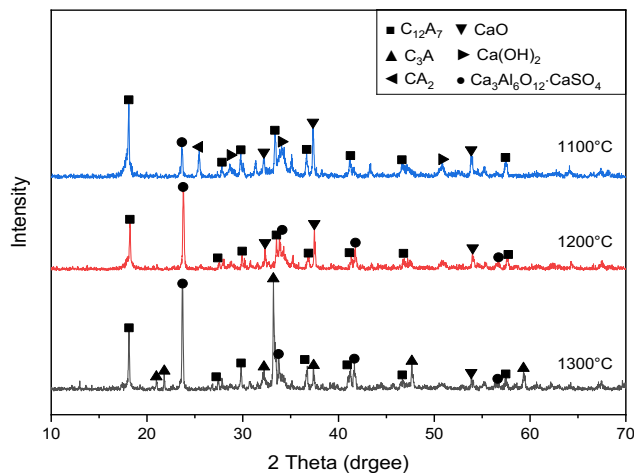


Figure 3. Mineral composition of the C1A3 cements according to the XRD analyses.

In general, increasing the calcination temperature further consumes the calcium in the reaction system, and tends to produce more abundant hydraulic phases. At the highest calcination temperatures, the aluminium binds more calcium. This is evident in the transition from CA₂ at 1100°C to C₃A at 1300°C, which leads to higher hydraulic activity.

Table 3. Summary of XRD results comparing the mineral composition of the cements.

Cement Notation	Calcination temperature	Mineral composition	
		main	subsidiary
C1A1	1100°C	C ₁₂ A ₇	CA ₂ , C ₄ A ₃ \$
	1200°C	C ₁₂ A ₇ ↓, C ₄ A ₃ \$↑	
	1300°C	C ₃ A	C ₁₂ A ₇ ↓, CA\$↓
C1A3	1100°C	C ₁₂ A ₇ ,	CA ₂ , C ₄ A ₃ \$
	1200°C	C ₄ A ₃ \$↑	C ₁₂ A ₇ ↓
	1300°C	C ₃ A, C ₄ A ₃ \$	C ₁₂ A ₇

3.2. SETTING PATTERN OF THE CAC PASTES

Figure 4 includes the initial and final setting times of pastes made with all the cements, as measured with the Vicat test. The pastes of C1A1 cement fired at 1200°C and C1A1 at 1300°C cannot be prepared due to their high reactivity and high hydration heat evolution. These pastes released a large amount of heat within five minutes of mixing with water, causing the water to evaporate and the paste to undergo significant expansion. At the end of this aggressive reaction, the paste did not harden but instead reverted to a powdery consistency.

The remaining CAC cements set rapidly. The pastes made with C1A1 1100°C, C1A3 1200°C and C1A3 1300°C show comparable setting patterns with an initial setting time of around 16 mins and a final setting time of around 27 mins. However, considering that the w/b ratio of C1A1 1100°C was higher than other C1A3 pastes, C1A1 1100°C exhibited the fastest setting. The C1A3 1100°C paste has a prolonged setting time due to its high w/c ratio.

The calcium aluminates in the CACs ($C_{12}A_7$, C_4A_3S and C_3A) are responsible for the quick setting of the CACs pastes. This agrees with previous authors stating that $C_{12}A_7$, C_4A_3S and C_3A promote fast setting and hardening [1,18]. However, in general, the C1A1 pastes set faster than the C1A3 ones. As can be seen from Figure 2 and 3, the C1A1 cement contains more calcium residual minerals than the C1A3 cement. Previous studies indicate that reactive calcium aluminate phases dissolve in Ca^{2+} and $Al(OH)_4^-$ rich systems [19]. Upon reaching supersaturation, these ions form hydration products that trigger the setting process. Therefore, the high alkalinity and increased calcium ion concentration resulting from the calcium residue has probably promoted the setting process.

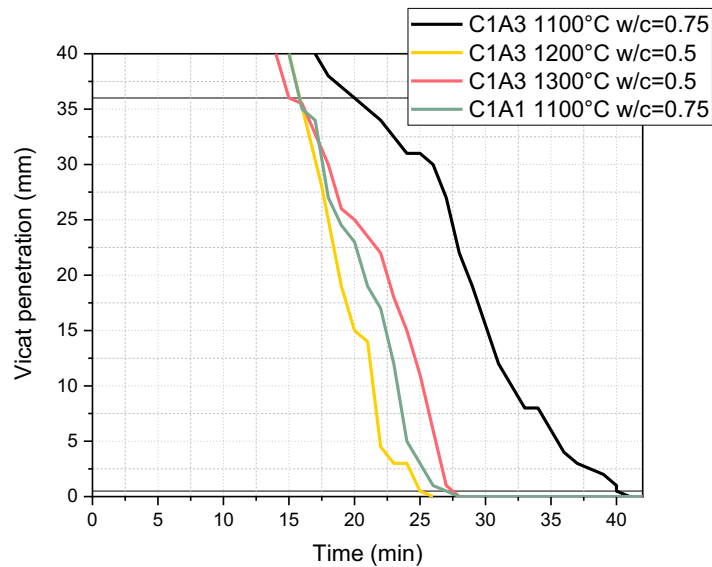


Figure 4. Setting time of CAC pastes as measured with the Vicat test.

3.3. PROPERTIES OF CAC MORTARS

As aforementioned, mortars were made with the cements sintered with the AS waste. As seen from the setting results, the C1A1 cements fired at 1200°C and 1300°C are useless due to their high reactivity and high hydration heat evolution. Furthermore, as seen from the XRD results, the increased Al of the C1A3 cements (with CaO:AS = 1:3) produced a better reaction resulting in more calcium aluminate phases and fewer calcium residues in the cement. Therefore, their strength was measured. Table 4 includes the 7-day strength of the mortars made with the C1A3 cements (CaO: AS = 1:3). At 7 days, the CACs calcined at 1100 °C and 1300 °C have similar mechanical strengths of 2.6 MPa and 1 MPa compressive and flexural strengths respectively. The CAC calcined at 1200°C has a lower compressive strength of 1.40 MPa.

Table 4. Strength of the CACs at 7 days (MPa).

	Flexural strength	Compressive strength
C1A3 1100 °C	1.00	2.61
C1A3 1200 °C	0.92	1.40
C1A3 1300 °C	0.93	2.60

The SEM micrographs of the cementing hydrates in the C1A3 (1100 °C and 1300 °C) hydrated cement pastes at 7d appear in Figure 5. The main hydration products of the C1A3 cements are calcium aluminate hydrates, C_2AH_8 , as indicated by the SEM morphologies (hexagonal plates) and the EDX analyses (Figure 6). In the C1A3 pastes, the microstructure of the hydration products varies with the calcination temperature. At 1100 °C, a matrix consisting of loose stacks of C-A-H with a diameter of approximately 1 μm was observed, while the C1A3 cement paste calcined at 1300 °C showed a denser matrix consisting of larger linked C-A-H crystals. The interlocking and bonding of these hydrates may provide a higher mechanical resistance in the longer term.

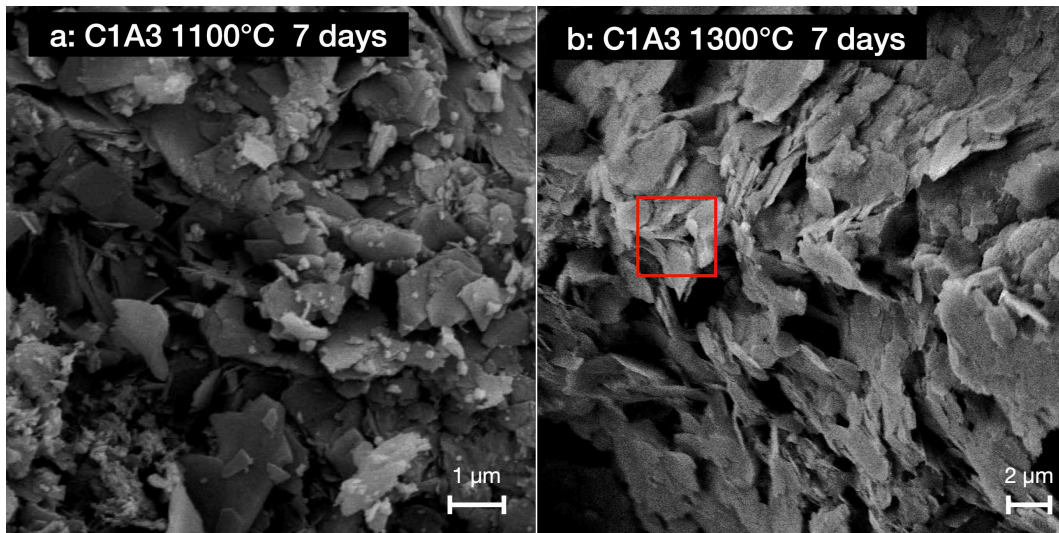


Figure 5. SEM micrographs of hydration products of C1A3 (a) 1100 °C and (b) 1300 °C at 7d.

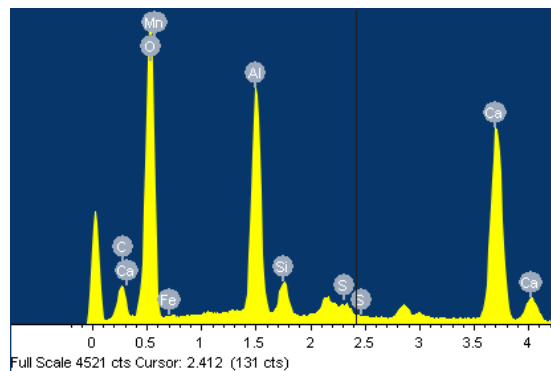


Figure 6. EDX analysis of C1A3 1300 °C in Figure 5(b).

Calcium aluminate hydrates undergo conversion over time, the metastable hexagonal phases tend to transform into stable cubic hydrates. The most stable hydrate in CAC is cubic C_3AH_6 which has a higher density than the hexagonal hydrates CAH_{10} and C_2AH_8 [1]. This can result in a significant increase in porosity thereby decreasing the mechanical strength.

Figure 7 includes the microstructure of C1A3 pastes at 28 days. In Figure 7a, a considerable amount of cubic C_3AH_6 crystals appear in lieu of the hexagonal C-A-H crystals present at 7 days (figure 5a), indicating that the conversion has taken place. In contrast, in C1A3 1300 °C, the dominant crystals remained hexagonal C-A-H, and the matrix is dense and compact indicating no obvious sign of conversion (figure 7b). The conversion causes a significant strength reduction and catastrophic failure in some of the CAC mortar specimens in the long term (1 year). This is illustrated in the macroscopic photographs of C1A3 cement mortar at 356 days (figure 8). The mortar of C1A3 cement calcined at 1100 °C underwent severe deterioration and lost the binding capacity after 12 months. On the contrary, the compressive strength of the 1300 °C C1A3 mortar increased significantly over time reaching **10.67 MPa** at one year, a significant increase compared to the strength at 7d (2.60 MPa).

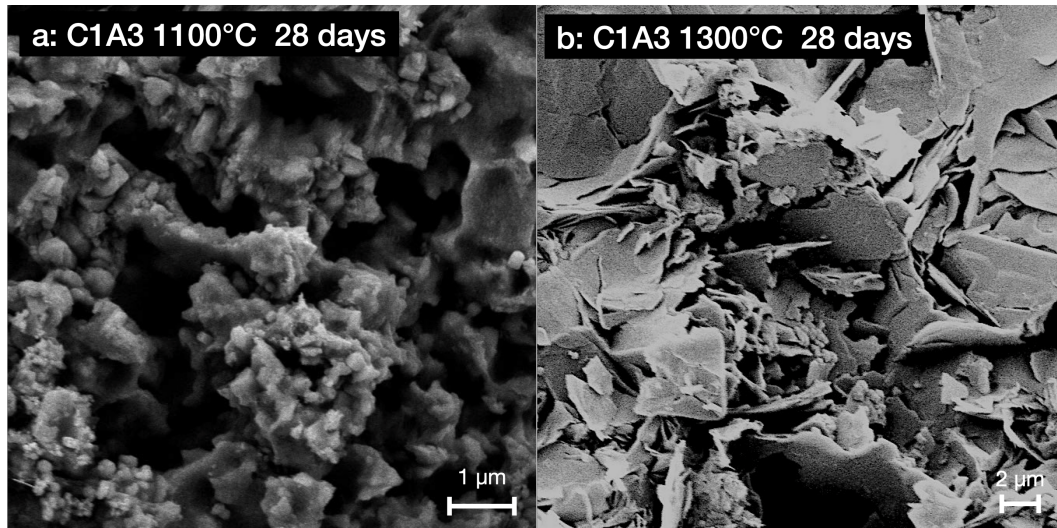


Figure 7. SEM micrographs of hydration products of C1A3 (a) 1100 °C and (b) 1300 °C at 28d.

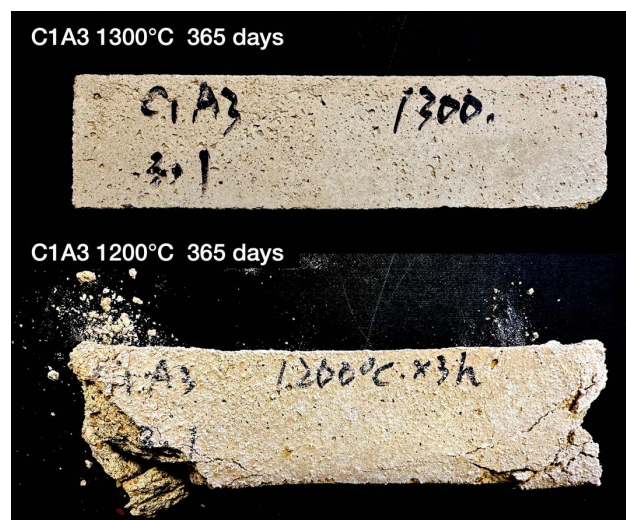


Figure 8. C1A3 mortars cured in ambient conditions at 365 days.

4. CONCLUSION

This paper investigated the potential to utilize alum sludge waste, as an aluminium source, to produce calcium aluminium cement. Reactive phases C_3A , $C_{12}A_7$, C_4A_3S and CA_2 were detected in the resulting cement. Increasing the Al content and calcination temperature facilitated the reaction between Al and Ca to produce reactive calcium aluminate compounds. The resulting cement is mainly composed of C_3A , C_4A_3S and a small amount of $C_{12}A_7$. The pastes made with this cement demonstrated a rapid setting pattern and yielded strength ranging from ~ 3 (7 days) to ~ 11 MPa (1 year). Interlocking hexagonal C-A-H crystals were observed in the resulting CAC matrix. However, over time, the conversion of metastable hexagonal C-A-H crystals into their stable cubic polymorphs increased porosity and lowered strength. A one year-long, follow-up study has shown that the CAC produced at 1300°C is stable in ambient conditions and reached a significant strength (11 MPa) after one year of curing. Therefore, alum sludge: CaO ratio at 3:1 and calcination at 1300°C are selected as the optimum production procedure. This paper provided an economical and low-carbon approach to the production of CAC, whilst also being an effective method of recycling and adding value to AS waste.

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