



ISSN: 2350-0328

International Journal of Advanced Research in Science,
Engineering and Technology

Vol. 11, Issue 2, February 2024

Development of Calcium Aluminate Refractory Cement from Recycled Calcium Carbide Waste and Commercial Grade Alumina

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ABSTRACT: Calcium carbide waste was used as a source of CaO for the production of calcium aluminate cement. The processed waste was combined in stoichiometric proportions to produce a CA-rich batch and a CA₂-rich batch. The two batches were sintered in a porcelain crucible at a temperature of 1300°C in a gas kiln. The sintered pellets were then combined in the ratio of 61%:38%, CA:CA₂ and milled to a fine cement powder. The resulting cement paste was cast into cubes using a water to cement ratio of 0.5, the compressive strength of the cubes were determined both at room temperature and after heat treatment at 1000°C. The initial and final setting times of the cement paste were also determined using a Vicat apparatus. The pyrometric cone equivalent of the cement paste was also determined, using Orton cones, as well as the specific surface area and density of the cement. The compressive strength of the cement paste was 38.6N/mm² at room temperature and 31.4 N/mm² after heat treatment at 1000°C. The specific area of the cement 4100g/cm² and density was 3.16g/cm³. The pyrometric cone equivalent of the cement paste was 1390°C (cone 13). The initial setting time of the cement paste was 88 minutes and the final setting time was 105 minutes. The x-ray fluorescence spectroscopy of the cement powder revealed the presence of 52.30% of Al₂O₃, 34.94% CaO and low amounts of alkali metal oxides, (K₂O and Na₂O) below 1%. The x-ray result indicate that the produced calcium aluminate cement is of intermediate quality. The results from this research work indicates that calcium carbide waste can be utilized as a source of CaO for the production of calcium aluminate cements. The procedure used in this research work is suitable for small scale production of calcium aluminate cements and for research purposes. Further efforts is recommended to quantify the various cement phases present in the cement powder. This will improve the understanding of the technical behavior of the cement and ways to improve it.

KEYWORDS: calcium aluminate, refractory, compressive strength, setting time, specific surface, cement phase.

I. INTRODUCTION

Refractory cements are special cements used in high temperature applications. More common ordinary Portland cement remain stable only up to about 300°C and disintegrates completely at about 500-600°C, (Lubloy, 2021). Thus they cannot be used in the installation of refractory linings for kilns and furnaces, where service temperatures can reach up to 1200°C and upwards.

Refractory cements must necessarily possess high melting temperature greater than 1500°C coupled with excellent resistance to molten metal, ferruginous slag and flue gases (Titiladunayo et al. 2011), (Gosin et al. 2010). The material of choice for such applications is calcium-aluminate cement. They contain **lime-alumina compounds as the core reactive phases.**

Calcium aluminate cements are manufactured from a mixture of calcium bearing materials, (that supply CaO) and aluminum bearing material, (that supply Al₂O₃). Calcium carbide waste consists chiefly of slake lime, Ca(OH)₂ as well as other caustic solid substances and perhaps some heavy metal impurities. Slake lime decomposes upon heating to yield CaO.



The American Concrete Institute defines hydraulic cements as inorganic materials that have the ability to react with water under ambient conditions to form a hardened and water-resistant product. The most common cements are those based on calcium silicates, such as the Portland cements. They are **based mainly on lime-silica mineral phases and are often used in the construction industry.**

On the other hand, calcium aluminate cements (CAC), another category of hydraulic cements have lime-alumina compounds as the core reactive phases. They consist predominantly of hydraulic calcium aluminates, (Hewlett, 1998). Calcium-aluminate cements are primarily used for high heat refractory applications. Other uses include moderate acid-resistant applications, high-early-strength and quick-setting mixtures, and as part of the expansive component in some shrinkage-compensating cements, (ACI, 2009).

These cements are typically designed to gain strength much faster than ordinary portland cements and predominately consist of calcium aluminate that can produce large amounts of heat during the first 24 hours. The cement phase ratios (CA or CA₂) are proportioned according to the intended application performance characteristics.

Calcium-aluminate cements are typically obtained by pulverizing a solidified melt or clinker that consists predominantly of hydraulic calcium aluminates formed from proportioned mixtures of aluminous and calcareous materials. The calcareous material supply calcium oxide, typically from limestone or some other source, while the aluminum bearing material could be bauxite, or refined alumina, (Taylor, 1990).

Table 1. below shows the cement chemistry nomenclature adapted from Taylor, (1990).

Table 1. Cement Chemistry Nomenclature. (Adapted from Taylor, 1990).

Symbol	Oxide species
A	Al ₂ O ₃ Alumina
C	CaO Lime
S	SiO ₂ Silica

The main active constituent of calcium aluminate cements is monocalcium aluminate (CaAl₂O₄, CaO · Al₂O₃, or CA in the [cement chemist notation](#)). They also usually contain other [calcium aluminates](#), such as CA₂, C₃A, CA₆ as well as a number of less reactive phases deriving from impurities in the raw materials. According to XU et al. (2014), a wide range of compositions is encountered practically, depending on the application and the purity or grade of raw materials used.

Rankin and Wright (1915) demonstrated the presence of five calcium aluminate compounds in the lime-alumina phase diagram, namely CA, CA₂, C₃A, CA₆, and C₁₂A₇. The reactivity of calcium aluminates generally increases with the lime content, making C₃A the most reactive among all these compounds.

The reason is that compounds with higher lime content exhibit relatively faster dissolution re-crystallization reactions. However, alumina content is directly proportional to the refractory nature of the calcium aluminate compound, (Stinnesen et al. nd). Hart (1990) described three categories of classification for calcium aluminate cements.

The low purity CACs contains 39 to 50% Al₂O₃, with specific gravity and refractoriness corresponding to a range of 3.05 to 3.25g/cm³ and 1350°C, respectively. The intermediate purity CACs contains 50 to 70% Al₂ O₃, with specific gravity and refractoriness corresponding to a range of 2.95 to 3.10g/cm³ and 1410 to 1450°C, respectively. The high purity CACs contains 70 to 90% Al₂O₃, with specific gravity and refractoriness corresponding to a range of 3.00 to 3.30g/cm³ and 1760°C, respectively, (Hart, 1990).

Two major methods are available for the manufacture of calcium aluminate cement on an industrial level. The first method is by fusion, which involves liquefying a raw feedstock of bauxite and limestone together, in a reverberatory furnace, where temperatures could range between 1315 and 1425°C, (Lee et al. 2001). In the second method, high-purity limestone and high-purity alumina are sintered together in a rotary kiln. The kiln produces a relatively purer grade of cement, namely the HAC. The resulting clinker is then ground in a ball mill to the required fineness.



The effect of impurities, particularly SiO_2 , TiO_2 and Fe_2O_3 can have a marked influence on the amount and ratio of these phases and can in turn lead to inconsistency in the cement properties. This is because these impurities react preferentially with the calcia and alumina, producing generally non hydratable compounds, such as calcium titanate, calcium aluminoferrites and calcium aluminosilicates, thus reducing the amount of available calcium aluminate for proper cement hydration and affecting setting time and strength development.

Pereira et al. (2017) stated that differences in the final product are caused by different chemical and mineralogical compositions of the raw materials and their size distribution in addition to the sintering and fusion conditions, such as the furnace atmosphere and the heating/cooling rate. For example, a reducing atmosphere of the furnace will mainly affect the clinker color, due to the reduction of Fe_2O_3 to FeO and a very fast cooling rate reduces the initial compressive strength, due to the lower crystallinity of the CAC. On the other hand, a slow cooling rate will usually lead to a shorter setting time of the CAC.

At sub industrial scales, the concerns about the purity of feed stock could be offset by the cost benefits of using cheaper raw materials that could reduce the final cost of the product. In a developing economy like Nigeria, high cost of importation could be a limiting factor. Using recycled calcium carbide waste as a lime source could lower the overall cost of refractory calcium aluminate cements, especially for small scale applications.

Calcium carbide reacts with water to produce acetylene and calcium hydroxide according to the equation $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$, (Greenwood et al. 1997). This reaction is the basis for the production of acetylene gas used in oxy-acetylene welding. The waste by product consists mainly of $\text{Ca}(\text{OH})_2$ (slake lime) and caustic solid substances and are white in appearance when pure, (Joel et al 2014).

Slake lime decomposes upon heating to give steam and calcium oxide according to the equation $\text{Ca}(\text{OH})_2 = \text{CaO} + \text{H}_2\text{O}$. Osonwa et al. (2021) suggested that the risks posed by indiscriminate dumping of calcium carbide waste, such as contamination risks for surface and ground water, could be mitigated by recycling the waste into more useful and harmless products.

Two major techniques are used to compare and evaluate the quality of calcium aluminate cements, namely setting time and heat evolution characteristics. According to IS 4031 (1988), Initial setting time is regarded as the time elapsed between the moments that water is added to the cement, to the time that the paste starts losing its plasticity.

The final setting time is the time elapsed between the moment the water is added to the cement, and the time when the paste has completely lost its plasticity and has attained sufficient firmness to resist certain definite pressure. The setting times of cement gives an indication of how long the cement will remain workable when used in a concrete or mortar mix.

Another technique involves the measurement of heat development in a newly cast mortar to study the evolution of heat from the reactions of the cement during setting and hardening. Two points on the curve of heat evolution vs. time are particularly important. Exo-Start is the time at which the temperature of the test castable begins to rise, and corresponds to the end of workability, Exo-Max is the time of maximum temperature rise, and corresponds with hardening, to the point of developing sufficient strength for demolding, (Fentiman et al. 1985).

In comparison to portland cement, calcium aluminate cements (CAC) show relatively slow setting but rapid hardening characteristics, (Ukrainczyk et al. 2010). The initial and final setting times for ordinary Portland cement are about 45 minutes and 375 minutes respectively, (Amathieu et al. 2001). Initial setting time for Calcium Aluminate Cement paste is generally similar to that of OPC, but the time between initial set and final set is rapid. Final setting for CAC paste at 20 °C occurs around four hours, (Adams et al. 2014).

II. DESCRIPTION OF STUDY AREA

Sample preparation of the calcium carbide waste was done at the ceramic workshop of the department of Ceramic and Glass Technology, Akanu Ibiam Federal Polytechnic Unwana. Mixing, milling and pelletizing operations, as well as firing operations and refractoriness tests were also done in the ceramic workshop. Compressive strength test of the mortar



cubes, as well as setting time tests, were done at the concrete testing laboratory of the department of civil engineering, while specific surface tests were done at the National Geological Institute Kaduna, Nigeria.

III. MATERIALS AND METHODOLOGY

The calcium carbide waste used for this research was obtained from a dump site near a mechanic garage at Afikpo, Ebonyi state of Nigeria. The calcium carbide waste was soaked in ample water in a clear transparent bucket. The sample was vigorously stirred with a wooden stirrer and bubbles of gas from unreacted carbide were continuously released as the sample was stirred. Excess water was decanted as well as some organic and soluble impurities which floated at the top of the bucket.

The sample was allowed to soak for seven days, with the excess water decanted daily and refilled with fresh distilled water until no more bubbles were released from the sample. The excess water was finally decanted and the wet sample was spread out on a drying mat and allowed to dry in open air for seven days.

The calcium carbide waste was then heat treated at 1000°C in a kiln, to get rid of any hydroxides and volatile impurities. After cooling the calcium carbide waste was mixed with commercial grade alumina. Two batches were mixed, according to the desired C:A ratio in the reaction products. Batch A contained 1:1, while batch B contained 1:2 calcium carbide waste and commercial grade alumina.

Each batch was ground together in a ball mill for 8 hours to enhance mixing and homogenization and later transferred to a pin mixer, where the mixing of the composition continued. Suitable amounts of prepared liquid starch was added, as binder. The homogenized mixture was later transferred to a disc pelletized, where suitably sized agglomerated pellets were formed.

The pelletized samples of each batch were then transferred to porcelain crucibles and heat treated in a gas kiln at a temperature of 1300°C. After cooling, the sintered pellets from the two batches were mixed in the proportion 61% : 38%, CA:CA2, to replicate the proportions reported for some commercial brands by Lourenço et al. (2013). The mixture of pellets milled again for several hours to reduce the particle size to a very fine powder and to aid mixing. The resulting powder was then sieved using mesh 200 sieve (74 microns).

The resulting calcium aluminate cement was then prepared into a paste with water to cement ratio of 0.5 and cast into a cube of 15cm x15cm x 15cm, using a wooden mold. The cast cubes were cured for 28 days in open air and later tested to determine their compressive strength. The average of three tests was reported. Some of the cast cubic specimens were then heat treated in a kiln to a temperature of 1000°C. After cooling, they were also tested to determine the compressive strength of the heat treated cubes. The average of three tests was reported.

Setting time of the produced calcium aluminate cement paste was determined using vicat needle according to the method described in literature. The cement paste as also used to produce pyrometric cone samples of similar dimensions and tilt as Orton cones. The pyrometric cone equivalent of the produced cones were then determined by firing them alongside Orton cones.

The specific surface area of the cement sample was also determined using a Blain apparatus, according to ASTM C204-00 Volume: 04.01, described by Mantellato et al. (2015). The oxide composition of the cement was also determined using x-ray fluorescence spectroscopy.

IV. RESULTS AND DISCUSSION

Table 4.1. Oxide composition of the cement as determined by x-ray fluorescence spectroscopy, while table 4.2 shows the results of other parameters tested for the cement mortar.

Table 4.1. Oxide composition of the cement as determined by x-ray fluorescence.

Oxide	Al ₂ O ₃	CaO	SiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	TiO ₂	Nb ₂ O ₅	Ag ₂ O	Y ₂ O ₃
Composition	52.30	34.94	2.53	1.96	0.09	0.12	1.26	1.06	2.27	2.31	1.84

Table 4.2. Results of various parameters tested from the cement mortar.

Parameter	Compressive Strength (25°C) N/mm ²	Compressive Strength (1000°C) N/mm ²	Initial Setting Time (Minute)	Final Setting Time (Minute)	Specific Surface Area (g/cm ²)	Refractoriness (°C)	Density (g/cm ³)
Value	38.6	31.4	88	105	4100	1390°C	3.16

The results of the x-ray fluorescence spectroscopy shows that the produced calcium aluminate cement is of intermediate quality, with Al₂O₃ content of 51% and density of 3.16g/cm³. Also the low concentrations of alkali metal oxides K₂O and Na₂O, as well as alkaline earth metal oxide MgO imparted positively on the refractory properties of the cement.

The production of CA-rich and CA₂-rich batches separately and their subsequent stoichiometric combination was done with the expectation to maintain desirable proportions of these phases in the final cement powder. This expectation appears to have been realized going by the impressive compressive strength of the cement mortar, both at room temperature and after heat treatment at 1000°C. Lea (1970) stated that the CA phase is the main phase responsible for the high compressive strength of calcium aluminate cements.

The compressive strength of the CA₂ phase is relatively lower than that of the CA phase, but because of its low thermal expansion coefficient, ($4.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, from 20 to 1400°C), it contributes immensely to the refractoriness of the calcium aluminate cement when present in the right proportions. The pyrometric cone equivalent of the cement paste obtained in this research work (1390°C), suggests that the proportion of CA₂ phase in the cement is within the suitable range of about 25wt%.

Although the amounts of the various cement phases were not quantified by x-ray diffraction technique in the present work, the reactivity of the cement suggests a reasonable presence of some less reactive cement phases, such as mayenite (C₁₂A₇), gehlenite (C₂AS) which could impact somewhat negatively on setting time behavior of the cement. However, the formation of C₂AS is limited when SiO₂ is below 5wt% as reported by Robson (1962). Another factor that could have affected the setting time recorded is the specific surface as commercial cements are ground to much finer sizes than were used in this research work.

V. CONCLUSION AND RECOMMENDATIONS

From the results discussed above, it is evident that calcium carbide waste can serve suitably as a source of CaO for the production of calcium aluminate cements. Low amounts of alkali metal oxides and silica in the waste are beneficial for good compressive strength development and refractoriness.

Calcium aluminate cements produced using this source of CaO would have desirable technical performance comparable to some commercial grade samples. The cheaper source of CaO could lower the overall cost of the calcium aluminate cement. The method of production used in this research work can be adapted for small scale production of calcium aluminate cements in the absence of functional rotary kilns and for research purposes.

Further efforts are recommended to evaluate the quantities of the various cement phases present in products produced via this method. This will help to deepen the understanding of the technical behavior of the cement and ways for further improvement.



ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 11, Issue 2, February 2024

VI. ACKNOWLEDGEMENTS

Authors are grateful to Tertiary Education Trust Fund Nigeria, for sponsoring this research.



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