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Conventional and potential alternative non-conventional raw materials for the production of calcium aluminates-based cements of different hydraulic activity.

Part I. SYNTHESIS.

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Abstract: Calcium aluminate cements (CACs) are well known for their rapid setting characteristics and refractory performance, owing to their significant early strength gain and excellent thermal stability. The properties of CACs vary based on their alumina content. Global demand for CACs has shown consistent growth in recent years. However, this projected rise in production is likely to intensify the demand for natural raw materials such as limestone and bauxite, thereby increasing the environmental impact-particularly due to emissions associated with limestone calcination. Numerous conventional and alternative raw materials have been identified and studied within CAC technology, owing to their multiple advantages, including cost reduction, lower carbon emissions, and enhanced sustainability. This study tackles the combined challenges of incorporating alternative raw materials and developing hydraulic binders exhibiting diverse hydration characteristics.

Keywords: calcium aluminate cement, hydration, raw materials, high-temperature processes, refractory castables

1. INTRODUCTION

The current development of engineering and technology is strongly dependent on the type and availability of binding materials, particularly those designed for specialized applications such as unshaped refractories and building materials. aluminate cement from bauxite and limestone [1-2].

Calcium aluminate cements (CACs) are a class of hydraulic binders characterized by rapid strength development, high refractory performance, and good resistance to chemical attack. They are typically synthesized from alumina- and calcium-rich raw materials, most commonly bauxite and limestone. Bauxite serves as the primary source of Al_2O_3, while limestone provides CaO upon thermal decomposition.

The production process generally involves the homogenization of raw materials followed by high-temperature treatment, during which a series of solid-state reactions and partial melting phenomena occur. These processes lead to the formation of key calcium aluminate phases, such as $CaAl_2O_4$ (CA) and $CaAl_4O_7$ (CA_2), which are primarily responsible for the hydraulic properties of CAC. The phase composition and microstructure of the final product depend strongly on factors such as the Al_2O_3/CaO ratio, impurities (e.g., SiO_2 and Fe_2O_3), and the applied thermal regime.

During synthesis, the presence of silica and iron oxides may result in the formation of secondary phases, including calcium aluminosilicates and ferrites, which can influence both the melting behavior and the mechanical performance of the cement. Therefore, careful control of raw material composition and processing conditions is essential to tailor the properties of CAC for specific applications, particularly in refractory and high-temperature environments.

In recent years, increasing attention has been paid to the use of alternative alumina sources in the production of calcium aluminate cements, driven by the limited availability and rising cost of high-grade bauxite. Among these alternatives, electrocorundum has emerged as a promising raw material due to its high Al_2O_3 content and well-defined phase composition, which can enhance the formation of desired calcium aluminate phases [3-4].

Additionally, secondary industrial by-products, such as return dusts generated during clinker production, are being explored as supplementary raw materials. These dusts often contain significant amounts of reactive oxides, including Al_2O_3, CaO, SiO_2, and Fe_2O_3, and can contribute to the formation of complex phase assemblages during high-temperature processing. Their utilization not only reduces the consumption of natural resources but also supports waste valorization and circular economy approaches.

However, the variability in chemical composition and the presence of minor impurities in such alternative materials require careful characterization and process optimization to ensure consistent phase development and desirable performance of the final cement product.

The aim of this study is to investigate the synthesis of calcium aluminate cement using alternative alumina-bearing raw materials, specifically metallurgical electrocorundum and secondary return dusts from clinker production, as substitutes for conventional bauxite. The work focuses on evaluating the influence of raw material composition on phase formation, high-temperature behavior, and the resulting phase evolution of the synthesized materials. Particular attention is given to the development of key calcium aluminate phases and the potential formation of secondary phases associated with impurity elements.

Additionally, the study seeks to assess the feasibility of utilizing industrial by-products as sustainable raw material sources, with the objective of reducing dependence on primary resources while maintaining or improving the functional properties of calcium aluminate cement.

In this work, Górka Cement company has developed and commercialized a new class of hydraulic binders utilizing alternative raw materials derived from local and recycled sources. This innovative approach not only improves application performance but also enhances process efficiency and reduces overall production costs.

2. METHODOLOGY

2.1 Materials

A commercially produced cement clinker composition and four laboratory-developed clinker compositions were created and produced using alternative raw materials. The batch compositions of the samples were as follows: *Sample 1* (as reference) was composed of bauxite and limestone; *Sample 4* was composed of metallurgical electrocorundum, limestone and return dust from GÓRKAL 40 clinker production with reduced SiO_2 content; *Sample 5* was composed of metallurgical electrocorundum, limestone and return dust from GÓRKAL 40 clinker production with increased content of SiO_2; *Sample 6* was composed of metallurgical electrocorundum, limestone and bauxite with reduced content of SiO_2; *Sample 7* was composed of metallurgical electrocorundum, limestone and bauxite with increased content of SiO_2. The samples were wet-milled to obtain suspension, thoroughly homogenized, and then dried to produce a fine powder. In the next step, the dry powder was pressed into cylindrical samples and then fired at 1350°C for 2 hours.

2.2 FACTSAGE 8.4 thermodynamic simulation

Thermodynamic evaluations of the sinterability of cement clinkers were performed using FactSage (version 8.4). The simulations utilized the FTmisc 8.4, FToxid 8.4, and FactPS 8.4 databases in combination with the EQUILIB module to establish equilibrium conditions. The chemical compositions of the mixtures were determined based on the data presented in Table 1. Calculations were conducted under an air pressure of 1 atm across a temperature range of 1000°C to 1700°C, with increments of 50°C. The results provided insights into the temperature-dependent evolution of the liquid phase content.

Table 1. Chemical composition of samples.

Oxides	Sample 1	Sample 4	Sample 5	Sample 6	Sample 7
SiO_2	4.79	2.99	5.02	3.36	4.26
TiO_2	2.23	0.38	0.37	0.34	0.33
Al_2O_3	53.96	51.55	51.15	50.41	50.69
Fe_2O_3	2.01	2.72	2.66	2.84	2.63
CaO	37.00	42.35	40.80	43.06	42.08

2.3 Heating Microscope Thermal Analysis (HMTA)

Laboratory-scale heating microscopy thermal analysis (HTMA) was used to examine the dimensional changes of mixtures derived from raw materials during thermal treatment. Homogenized powder mixtures were formed into cubic specimens with a height of 3 mm using a manual press. The samples were heat treated from room temperature up to 1500°C at a heating rate of 10°C/min. The measurement were carried out using Linseis L74 Heating Microscope. Sample height measurements were collected at 1°C intervals, from which shrinkage curves were derived. The relative height change (δh) was calculated according to Eq. (1).

$$\delta_h(T) = \frac{h(T)}{h_0} \times 100, \% \qquad (1)$$

where:

h_0 – initial height of the sample,

$h(T)$ – height of the sample at elevated temperature T.

2.4 Phase composition (XRD)

X-ray diffraction (XRD) patterns were recorded using the PANalytical X’Pert Pro diffractometer over a 2θ range of 15°–50°, with Cu Kα radiation (λ = 1.54060 nm) at an operating voltage of 45 kV and a step size of 0.008°. Phase identification was performed using HighScore Plus in conjunction with the ICDD PDF-2 and JCPDS databases (Powder Diffraction Files, Philadelphia, PA, USA, 1997). Prior to analysis, the castable samples were ground in a ball mill to obtain fine powders with particle sizes below 63 μm.

3. RESULTS AND DISCUSSION

3.1 FACTSAGE 8.4 thermodynamic simulation and Heating Microscope Thermal Analysis (HMTA)

The synthesis of cement clinker is a highly complex, multidimensional process, making its accurate reproduction under laboratory conditions inherently difficult. One experimental approach that approximates this process is Heating Microscope Thermal Analysis (HMTA), which is now often supplemented with thermochemical modelling. The FactSage software was used to model the quantity of the liquid phase as a function of temperature. The results of modelling are presented in Fig. 1. Figure 2 illustrates the relative change in sample height, $\delta_h(T)$, for the tested materials. Based on the results from the high-temperature microscope, it can be observed that up to 1300°C the curves follow a similar trend. However, above 1300°C, Sample 1 exhibits the highest thermal stability. As shown in Figures 1 and 2, the shrinkage curve of these samples is closely correlated with the liquid phase content determined in FactSage thermochemical calculations. This relationship is most clearly observed for the two extreme samples, 1 and 6, as well as for sample 5. In contrast, no clear correlation is found for samples 4 and 7, which may be related to the viscosity of the liquid phase. Images of the samples at 1350 °C recorded during *in situ* measurements clearly confirm shrinkage in Samples 1, 4, and 5, as well as softening in Sample 7 and melting in Sample 6 (Fig. 3).

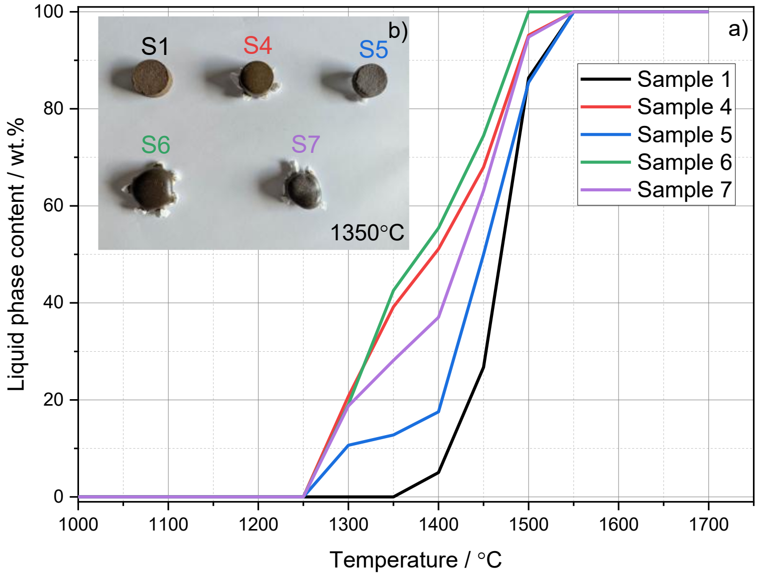


Fig. 1. Liquid phase content of the individual samples as a function of temperature, calculated by the FactSage software, additionally pictures of the samples after heat-treatment at 1350°C.

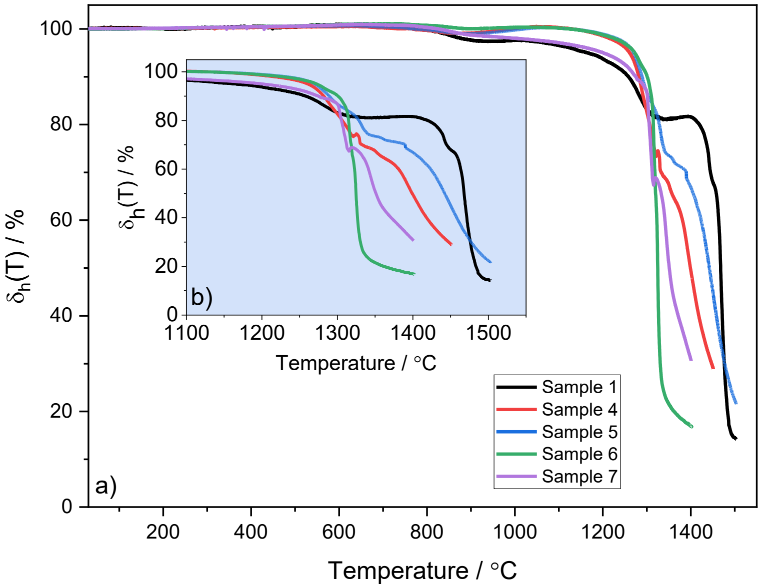


Fig. 2. Relative change in height $\delta_h(T)$ of the tested samples during heating.

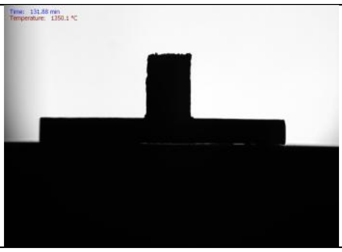
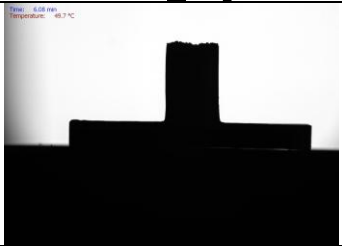
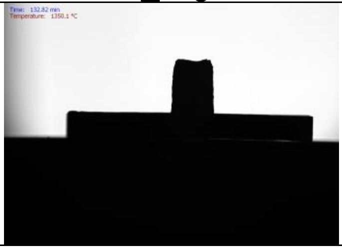
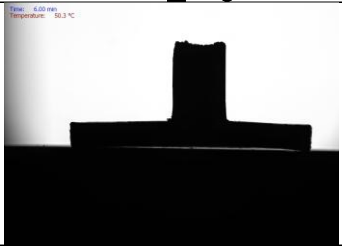
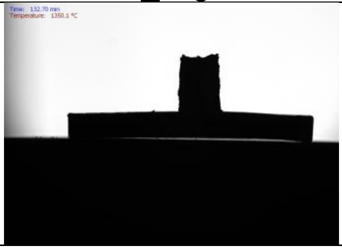
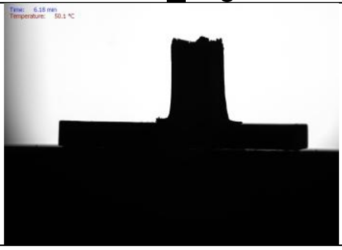
Sample 1		
	cam0_img0	cam0_img7611
Sample 4		
	cam0_img0	cam0_img7603
Sample 5		
	cam0_img0	cam0_img7601
Sample 6		
	cam0_img0	cam0_img7600
Sample 7		
	cam0_img0	cam0_img7599

Fig. 3. Images of the samples at 1350°C (right) recorded during *in situ* measurements. On the left-hand side, the sample is shown at room temperature.

3.2 Phase composition (XRD)

A XRD-based phase-composition analysis of (Fig. 4) shows the presence of $CaAl_2O_4$ (CA) and $Ca_2Al_2SiO_7$ (C_2AS) in Sample 1; $CaAl_2O_4$ (CA), $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), $Ca_2Al_2SiO_7$ (C_2AS), Ca_2SiO_4 (C_2S) and $CaAl_{0.5}Fe_{0.5}O_{2.5}$ (C_4AF) in Samples 4, 6 and 7; $CaAl_2O_4$ (CA), $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), $Ca_2Al_2SiO_7$ (C_2AS) and Ca_2SiO_4 (C_2S) in Sample 5.

The results indicate a clear variation in phase assemblage depending on the sample composition, particularly with respect to the presence of iron-bearing phases. The occurrence of C_4AF in Samples 4, 6, and 7 suggests the incorporation of Fe into the crystal structure, which may significantly influence the high-temperature behavior of these materials, including their melting and softening characteristics. In contrast, the absence of this phase in Samples 1 and 5 points to a comparatively simpler phase composition.

Furthermore, the coexistence of calcium aluminate (CA, $C_{12}A_7$) and calcium aluminosilicate (C_2AS) phases across most samples indicates partial interaction between alumina- and silica-rich components. The presence of C_2S in selected samples (4, 5, 6, and 7) may also contribute to the formation of a liquid phase at elevated temperatures, thereby affecting densification, shrinkage, and viscosity during thermal treatment.

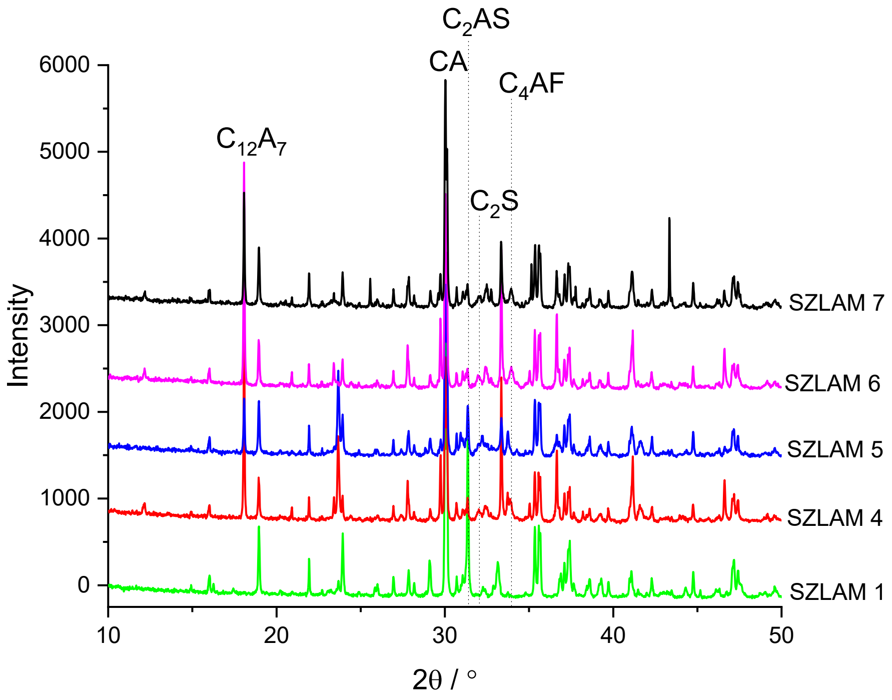


Fig. 4. X-ray diffraction patterns of the samples.

Conclusions

The results of this study demonstrate that the unique raw material composition has a significant influence on the phase assemblage of the investigated materials. Variations in the proportions and types of alumina- and calcium-bearing components, as well as the presence of minor constituents such as iron and silica, lead to noticeable differences in the formation and stability of crystalline phases. In particular, the use of alternative alumina sources and secondary raw materials promotes the development of complex phase systems, including calcium aluminate, calcium aluminosilicate, and ferrite phases.

These findings confirm that the specific chemical and mineralogical characteristics of the starting materials play a decisive role in determining the final phase composition, and consequently the high-temperature behavior and potential performance of the synthesized products.

Importantly, the application of secondary raw materials enabled a reduction in the firing temperature required for material synthesis. This effect is attributed to the presence of admixtures, which promote earlier liquid-phase formation and enhance solid-state diffusion processes during thermal treatment. As a result, densification and phase formation occur at lower temperatures compared to compositions based solely on conventional raw materials.

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