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FULL PAPER

Belite cement clinker from autoclaved aerated concrete waste fines with high sulfate content

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Abstract

The processing of belite cement clinker in a rotary kiln at about 1000°C in a CO_2 atmosphere is a new recycling option for Autoclaved Aerated Concrete (AAC) waste that otherwise must be landfilled. Waste fine fractions from a sorting facility enriched in sulfate due to intermixing with waste plaster have been processed. During clinkering the cement clinker phase belite (Ca_2SiO_4) besides technical ellestadite, ($Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$), or ternesite, ($Ca_5(SiO_4)_2SO_4$), are formed, depending on the addition of flux minerals. However, not all phases of the novel clinker react hydraulically. Whereas ternesite reacts with water, ellestadite forms complex solid solution series (Ca/Pb, SO_4/PO_4), which may be used as an insoluble reservoir mineral for undesirable constituents, such as phosphates and chlorides. The produced clinker has been successfully used to partially substitute OPC in AAC production in technical trials. Waste quantities and landfill costs are minimized, while at the same time, CO_2 emissions and the primary resource consumption of AAC production are reduced. Joint work with industrial companies is underway to increase technology readiness. Particularly large reduction effects on CO_2 emissions can be achieved through electrical heating of the rotary kiln.

KEYWORDS
AAC recycling, belite clinker, circular economy, reservoir minerals

1 | INTRODUCTION

One of the global sustainability goals is to ensure sustainable production and consumption patterns and to greatly reduce the demand for resources. For AAC, the concept of the circular economy pro-

vides an important solution. Through high-quality recycling, natural resources such as mineral raw materials, groundwater, and the natural environment can be used responsibly and energy-efficiently. If AAC is produced without recycling from primary raw materials, many sustainability indicators and in particular the emission of greenhouse gases

are strongly negatively influenced by the upstream chain (cement, lime) [1]. In closed-loop recycling, the secondary material is valorized within the AAC processing, which significantly reduces greenhouse gas emissions. Closed-loop recycling is common practice for production-related AAC waste. In contrast, direct recycling of AAC waste from demolition (pd-AAC) in production is only possible after pre-processing and only to a limited extent due to contamination with impurities such as gypsum, plastics, metals, and so forth [1]. One new approach is the utilization of pd-AAC as a component of a raw meal for the processing of a recycling cement clinker, which can partly substitute Portland cement in the production of AAC. The main mineral of the clinker is the mineral belite. Recycled belite clinker (RC belite clinker) is produced in a rotary kiln at below 1000°C in a CO_2-rich atmosphere. Contaminations can be incorporated into insoluble reservoir minerals. Concentrated CO_2 from the process will be used prospectively for the carbonation of construction waste. The low process temperature makes indirect electric heating possible. In this work, the production of RC belite clinker from low-sulfate and high-sulfate pd-AAC with the addition of various fluxes is investigated on a laboratory scale (muffle oven and rotary kiln), and the use of RC belite clinker in AAC production is demonstrated.

2 | MATERIALS AND METHODS

Three samples of industrial waste materials with different sulfate contents denoted as lS (low sulfate content), mS (middle sulfate content), and hS (high sulfate content) were chosen for the high-temperature experiments. All raw material samples were dried at 250°C. The samples were mixed with $CaCO_3$ (Merck) to receive a C/S ratio of 2 for the starting mixture. Since the reaction rate of sulfates depends strongly on the sample composition, the crystallinity, and the heating rate, all phases were assumed to be potentially reactive at 1000°C. Sample mixtures were prepared with and without mineralizers (2 wt.% $CaCl_2$ and 3 wt% and 5 wt.% Na_2CO_3) and were denoted lS-, mS-, hS-$CaCl_2$ and lS-, mS- and hS Na, respectively. Different quantities of Na_2CO_3 were denoted with 3Na and 5Na. Experiments in a rotary kiln were marked with RK.

Syntheses were carried out in a muffle furnace with a lid or in a rotary tube under CO_2 flow to maintain a CO_2 atmosphere. There was no purging with CO_2 during the XRD in situ experiments up to 1000°C.

Hydrothermal experiments of the calcinated samples mixed with quartz were conducted in stainless steel high-pressure reactor BR 500 autoclaves (Berghof products+instruments, Eningen, Germany) in order to prove the suitability of the materials for AAC production and to investigate the stability of the Cl ellestadite. The resulting samples were marked with the duration of the hydrothermal treatment (6, 12, and 24 h).

XRD in situ experiments up to 1000°C were conducted on the sample with intermediate sulfate amount (P) using the Empyrean diffractometer [2] equipped with a high-temperature chamber HTK1200N (Anton Paar, Graz, Austria). Approximately 0.2 g of the sample was compressed in an aluminum oxide sample holder. After the measure-
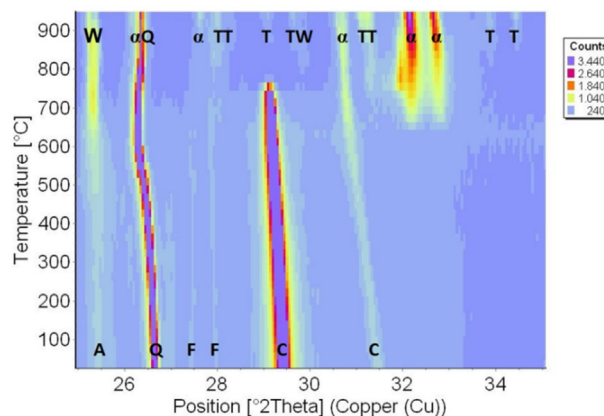

FIGURE 1 In situ XRD experiment on a mixture of AAC waste with high sulfate content and $CaCO_3$. Peak intensities are shown as a function of temperature (25°C to 950°C in 12 h). Q = quartz, C = calcite, A = anhydrite, T = ternesite, $\alpha = \alpha'$H-C_2S, W = wollastonite, F = feldspars.

ment of the starting mixture at 25°C (6°–70° 2θ in 17 min), the sample was heated at a rate of 5°C/min in steps of 25°C up to 700°C. Powder patterns were recorded every 25°C which increases the time of each temperature step to 22 min. Between 700°C and 1000°C measurements were conducted every 10°C with a heating rate of 3°C/min. Quantitative contents of the crystalline phases were determined by the Rietveld method with 20 wt.% Al_2O_3 as an external standard.

3 | BELITE CEMENT CLINKER FROM LABORATORY SCALE TO TECHNICAL TRIAL

3.1 | Formation, structure, and hydrothermal behavior of belite, ternesite, and ellestadite

The formation of RC belite clinker from fine fractions of pd-AAC with varying degrees of sulfate enrichment has been the subject of detailed studies on a laboratory scale. The main clinker phase belite or C_2S (in cement nomenclature with C = CaO, S = SiO_2, H = H_2O) replaces the mineral alite or C_3S typical for ordinary Portland cement clinker. X-ray diffraction (XRD) experiments in a high-temperature chamber (Anton Paar HTK1200N) provide the possibility to monitor the reaction kinetics and the evolution of phase contents in situ ([2], Figure 1).

Heating of waste mixtures with $CaCO_3$ (molar C/S ratio = 2) shows the formation of low-crystalline C_2S already at 650°C with increasing content up to 1000°C. Due to the low crystallinity, the structure of α'H-C_2S cannot be identified unequivocally until temperatures around 950°C. High sulfate contents affect the C_2S formation positively. However, in sulfate-rich samples, the formation of the calcium-silicate-sulfate ternesite ($Ca_5(SiO_4)_2SO_4$) starts in parallel. The highest C_2S content of 90 wt% is found in samples with intermediate sulfate content at temperatures above 950°C. At lower temperatures high
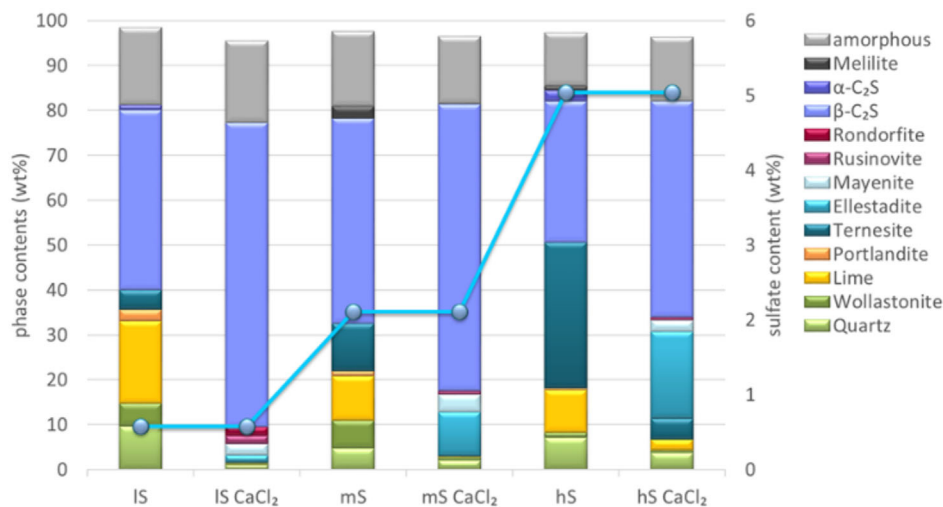
FIGURE 2 Phase contents (>1.6 wt%) of wastes of AAC calcined with $CaCO_3$ (C/S = 2) and $CaCl_2$ at 1000°C (XRD and Rietveld refinement). Sulfate contents of the raw mixtures are shown as circles (lS = low sulfate, mS = medium sulfate, hS = high sulfate sample, and $CaCl_2$ = samples with 2 wt% $CaCl_2$ addition).

contents of CaO and in low-sulfate samples also wollastonite form besides C_2S. During cooling, $\alpha'H$-C_2S transforms to β-C_2S with the transition temperature strongly affected by the cooling rate. Variation of the duration of heating from 2 to 12 h (25°C–950°C) shifts the ternesite formation temperature from 950°C to 850°C and increases the total amount of ternesite but shows hardly any impact on C_2S formation. Longer residence times at 950°C promote further growth of ternesite at the expense of C_2S. In general, ternesite has no negative impact on the cement clinker, as ternesite can be hydraulically activated with alumina. However, special attention has to be paid to the adjustment of the C/S-ratio of the raw mixture to the sulfate content of the waste material. On the one hand, the formation of ternesite instead of C_2S results in residues of quartz and wollastonite, on the other hand, an extensive increase of the C/S-ratio to 2.5 according to the formula $Ca_5(SiO_4)_2SO_4$ leads to higher ternesite contents in the product but also to lower C_2S contents besides CaO.

With increasing sample amounts (0.2 g to 100 g) in larger heating devices the demand for a mineralizing agent, such as $CaCl_2$ or Na_2CO_3 arises. Oven experiments in the temperature range between 700°C and 1200°C and subsequent analysis prove the suitability of $CaCl_2$ in the synthesis of C_2S-cement clinker ([3], Figure 2). The addition of $CaCl_2$ provokes melt formation and hence the reaction of the raw materials SiO_2 and CaO to C_2S. As the contamination of the product with soluble chlorine must be prevented, chlorine has to be immobilized by incorporation in a hardly soluble phase like chlorellestadite $(Ca_{10}(SiO_4)_3(SO_4)_3Cl_2)$.

Combined analysis of XRD, thermogravimetry, and x-ray fluorescence data enables the determination of the yield of CaO in the sum of the products C_2S (crystalline and amorphous) and ellestadite. The optimum temperature range for a high yield lies between 950°C and 1000°C. At lower temperatures, the formation of a carbonate-rich halogenide melt promotes the formation of spurrite at the expense of C_2S. The formation of ellestadite depends rather on the sulfate con-

tent of the sample than on the formation temperature. However, XRD in combination with Raman spectroscopy reveals a non-stoichiometric form of chlorellestadite at low temperatures [4]. Chlorine and calcium vacancies as well as partial substitution of sulfate by carbonate at temperatures between 800°C and 900°C cause the formation of a monoclinic ellestadite structure with reduced unit-cell volume.

Hence, chlorine is bound in other less crystalline and stable phases in samples with low sulfate content, and independent of the sulfate content, at low temperatures. At temperatures above 1000°C, combined combustion-ion chromatography reveals chlorine loss, particularly in low-sulfate systems where chlorine is bound in phases like $Ca_{10}(Si_2O_7)_3Cl_2$ (rusinovite), $Ca_8MgCl_2(SiO_4)_4$ (rondorfite), or $Ca_{12}(Al_{7.5}Fe_{0.5})Al_6O_{32}Cl_2$ (chlormayenite). However, temperature-dependent chlorine loss occurs also in samples with high sulfate content. Raman imaging evidences the formation of ternesite, anhydrite, and C_2S at the cost of ellestadite in C_2S-cement clinkers calcined above 1000°C. The maximum yield of CaO in C_2S and ellestadite is 83% ± 2%. This is similar in all samples synthesized at 1000°C independent of sulfate content. They differ only in the yield of C_2S in ellestadite, which makes the adaption of the sulfate content in the raw mixture to the amount of the mineralizing agent $CaCl_2$ imperative.

An even higher yield of 92%–94% could be reached for the sample with high sulfate content by the addition of 3 to 5 wt% Na_2CO_3 as mineralizing agent (Figure 3).

In addition, higher amounts of $\alpha'H$-C_2S stay stable during cooling to room temperature. Independent of the sulfate content, none of the samples calcined with Na_2CO_3 contains a significant amount of ternesite. Instead, these samples comprise a variety of minor phases. Crystalline sulfate and sodium are found in Na_2SO_3, anhydrite, and combeite.

With increasing Na_2CO_3 addition from 3 to 5 wt% the content of minor phases is minimized. Na_2CO_3 is expensive compared to $CaCl_2$
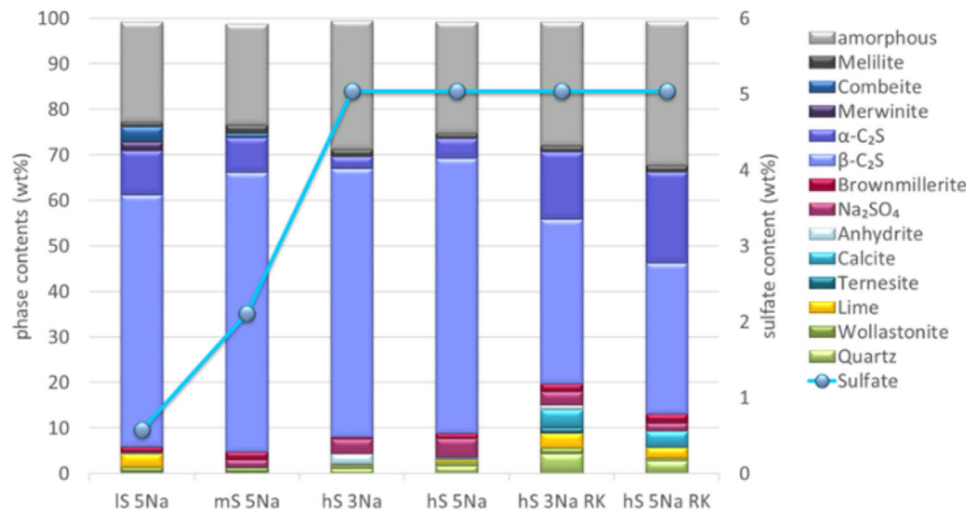
FIGURE 3 Phase contents (>1 wt%) of wastes of AAC calcined with $CaCO_3$ (C/S = 2) and Na_2CO_3 at 1000°C (XRD and Rietveld refinement). Sulfate contents of the raw mixtures are shown as circles (IS = low sulfate, mS = medium sulfate, hS = high sulfate sample, 5Na and 3Na = 5 and 3 wt% Na_3CO_3 addition, RK-synthesis in a rotary kiln).
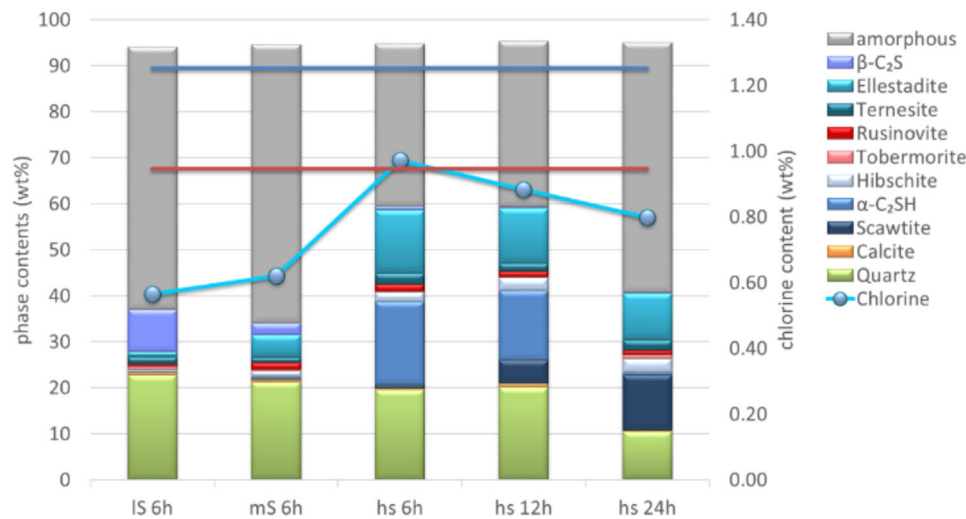

FIGURE 4 Phases assemblies (>1.5 wt%) and chlorine contents in autoclave products. The area between the red and the blue line encloses the expected chlorine content. The width is due to the hygroscopic nature of $CaCl_2$. The chlorine contents of the raw mixtures are shown as circles.

and by purging the calcined samples with water a maximum of 50% of Na_2CO_3 could be retrieved for recycling.

Hydrothermal experiments prove the stability of ellestadite during treatment for 6 h at 190°C. The amount of tobermorite is low in all samples. In the high-sulfate sample α-C_2SH forms instead. The samples with low sulfate contents lose a significant amount of chlorine during hydrothermal treatment (Figure 4). Only in the sulfate-rich sample, the chlorine content is still in the range expected. However, after a retention period of 12 and 24 h in the autoclave, successive loss of chlorine takes place also in sulfate-rich samples. In addition, such long retention times provoke the formation of minor phases like scawtite ($Ca_7(Si_3O_9)_2CO_3 \cdot 2H_2O$) and Hibschite.

3.2 | Synthesis of belite-cement clinker in a rotary kiln

Belite-cement clinkers processed in a rotary kiln at about 1000°C in a CO_2 atmosphere (600-800 g) follow the trends observed in the small-scale experiments (Figure 5). High C_2S contents form in mixtures with 2 wt% sulfate, whereas at higher sulfate contents large amounts of ternesite or ellestadite form, dependent on whether $CaCl_2$ mineralizer is added. In the samples with $CaCl_2$ addition, the chlorine contents are between 1.15 and 1.29 which evidences that there is no chlorine loss during calcination. The positive effect of the mineralizing agent on the consumption of raw materials and the formation of products is also visible. In addition, the synthesis in the rotary kiln promotes
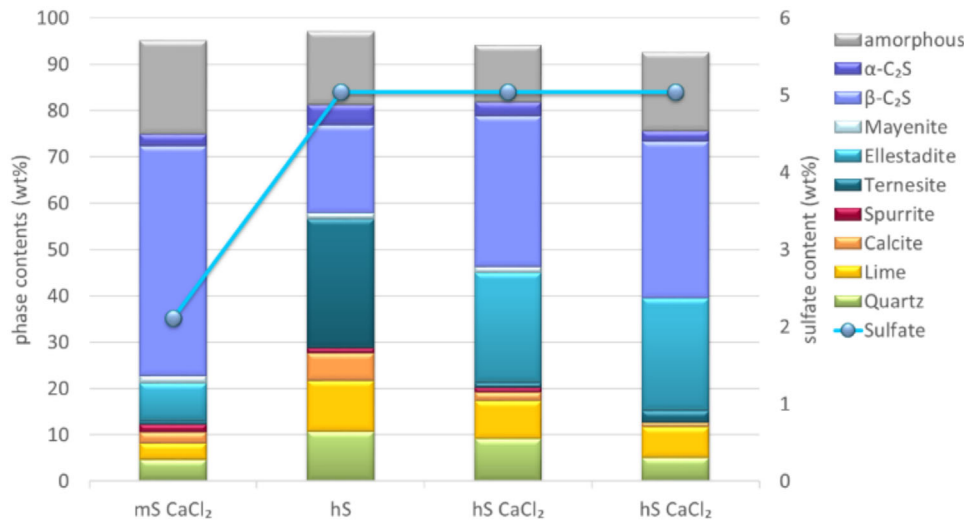
FIGURE 5 Phase contents (>1.6 wt%, XRD and Rietveld refinement) and sulfate content of wastes from AAC treated with $CaCO_3$ (C/S = 2) in a rotary kiln.

the room temperature stability of $\alpha'H$-C_2S which is expected to have a higher hydraulic reactivity compared to β-C_2S [5]. However, the overall amount of C_2S is smaller than in samples synthesized in the laboratory oven and the residuals in raw materials are higher. This manifests in the yield of CaO in C_2S and ellestadite that is 0.72 and 0.77 in high-sulfate samples calcined in two runs in the rotary kiln. Comparison to the samples calcined with 2 and 5 wt% Na_2CO_3 reveals slightly higher yields of 0.79 and 0.82 (Figure 3). However, these values are also below the ones determined for the experiments in the laboratory oven.

3.3 | Technical trial: Application of belite-cement clinker in AAC production

In joint work with the industrial partner Xella, it was demonstrated that clinkers produced from different qualities of post-demolition AAC can replace up to 50% of the cement used in AAC production. Although the replacement impairs early strength development (−50%), the final strength is not affected by binder replacement. This is consistent with the mineral phase composition after hydrothermal treatment. All AACs contain 10%–13% quartz, 36%–39% 11 Å tobermorite, and 27%–30% amorphous material. Final product strength and mineral phase composition are not affected by the mineralizing agent used in the calcination process ($CaCl_2$ or Na_2CO_3). The loss in early strength can be compensated by the addition of 2% accelerator X-Seed 100 (BASF) though this has a negative impact on the final strength. In a technical trial on an industrial scale, RC belite clinker from a 1.5 t test firing was used to replace 25% of cement in AAC production.

4 | OUTLOOK

It has been demonstrated that the production of RC belite clinker from pd-AAC samples contaminated to different degrees with sulfate is pos-

sible by individual adjustment of the mineralizing agent or the raw meal composition. However, the yield of the desired hydraulically reactive clinker phases decreases with the degree of pd-AAC contamination. Sulfates and chlorides are structurally incorporated into the reservoir mineral ellestadite (tech.). When Portland cement is substituted by RC belite clinker in the AAC manufacturing process, ellestadite remains stable. In technical trials, 25% of Portland cement was substituted. A small pilot plant for the production of RC belite clinker is currently under construction. The use of a chloride-containing RC belite clinker in other applications is only possible in individual cases due to technical standards.

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