

Chapter 4. Direct aqueous calcium sulphide carbonation

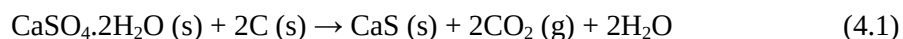
The direct aqueous reaction between solid calcium sulphide suspended in water and carbon dioxide was studied in a complete stirred tank batch reactor. In this process, calcium carbonation and the subsequent precipitation of CaCO_3 are concurrent with the CaS dissolution and the H_2S stripping reactions. The dissolution behaviour of CaS in the presence of CO_2 in the $\text{CaS-H}_2\text{O-CO}_2$ system was investigated, along with the effect of CO_2 flow-rates on the crystal structure and polymorphs of the carbonated products formed.

4.1 Introduction

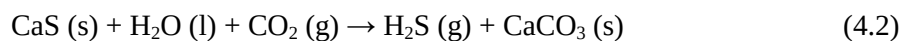
The gypsum material used here is a calcium-rich, industrial, solid residue generated in the mining industry as a result of the treatment of acid mine drainage (AMD). Acidic water is naturally generated by the weathering of sulphide minerals that are exposed to atmospheric conditions during the mining of valuable ores (Smith et al. 2013). Most of the AMD treatment systems use limestone or lime as acid neutralizing agents, which results in the production of a gypsum sludge (Kalin et al. 2006; Johnson & Hallberg 2005). Long-term storage and maintenance of the gypsum wastes present economic as well as potential environmental concerns. Not only are these gypsum stacks unsightly, but they also occupy large areas of land and require long-term expenditures for maintenance and monitoring (Tayibi et al. 2009). In the context of reducing the environmental burden and enhancing economic benefit, technologies for converting waste materials into products of commercial value are in great demand.

The recovery of sulphur and by-product CaCO_3 from waste gypsum (Figure 4.1) has been previously reported (Mbhele et al. 2009; Nengovhela et al. 2007; Kutsovskaya et al. 1996). The process involves three steps, namely, the thermal reduction of calcium sulphate to calcium sulphide (Eq. (4.1)), the production of hydrogen sulphide from the calcium sulphide (Eq. (4.2)), and subsequently, the conversion of hydrogen sulphide to elemental sulphur (Eq. (4.3)).

Thermal reduction of solid gypsum to produce a solid calcine product:



Carbonation of the calcine product to produce hydrogen sulphide and calcium carbonate:



Recovery of elemental sulphur from the hydrogen sulphide gas:

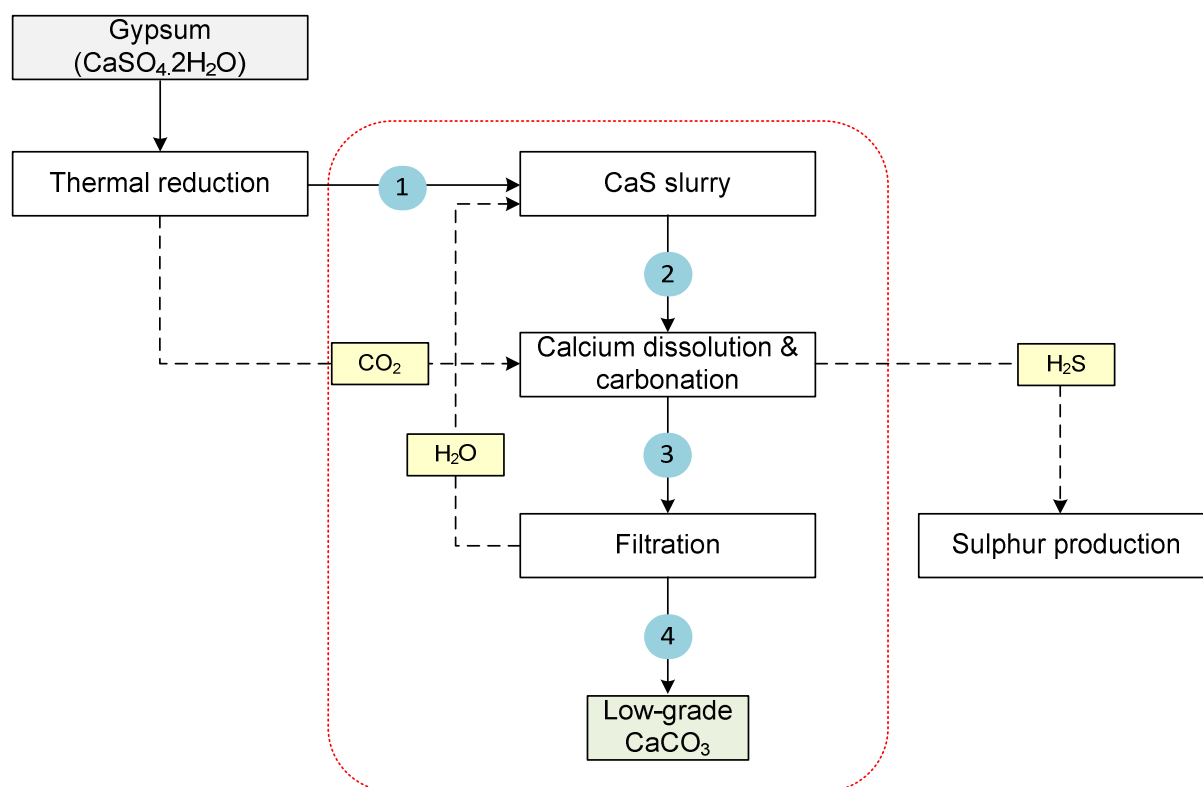
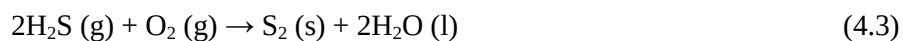


Figure 4.1 Process flow diagram for the production of CaCO₃ from waste gypsum *via* the direct aqueous CaS carbonation process route. 1) CaS solids; 2) CaS slurry; 3) low-grade CaCO₃ slurry; 4) low-grade CaCO₃ solid product

The thermal reduction of solid gypsum into calcium sulphide (CaS) has been extensively studied. It is performed in a high temperature kiln at 900-1100°C using gaseous (H₂ or CO gas; (Zhang et al. 2012; Ma et al. 2011; Kamphuis et al. 1993; Paulik et al. 1992) or solid carbon materials (Kato et al. 2012; Ruto et al. 2011; Mihara et al. 2008; Nengovhela et al. 2007) as reducing agents. The commercially available Clauss Process has become the industry standard for the recovery of elemental sulphur from H₂S gas and therefore this step was not investigated (Mark et al. 1978). This study focused only on the direct aqueous carbonation of CaS for the production of CaCO₃. Although the recovery of H₂S and CaCO₃ from CaS has been reported (Mihara et al. 2008; Nengovhela et al. 2007; Brooks & Lynn 1997; Nishev & Pelovski 1993; Biswas et al. 1976) very little information is available on the CaS dissolution behaviour and the effect of various parameters that have the potential to drive this reaction. Nengovhela et al. (2007) focussed mainly on the stripping of H₂S gas and the conversion of H₂S to elemental sulphur. Brooks and Lynn (1997) also studied the conversion of CaS into H₂S and CaCO₃ but making use of methyldiethanolamine (MDEA) as a CO₂ and H₂S solubility catalyst. The benefit of adding MDEA was not discussed in their work. Our aim was to avoid the addition of any additional chemicals. Also, neither of the above authors reported on the properties and characteristics of the formed carbonate products.

The goal of this research was to understand and to gain new insights into the direct aqueous CaS carbonation reaction pathway for the recovery of CaCO₃ from CaS. The existing and evolving dynamics in the CaS-CO₂-H₂S system were investigated by monitoring the profiles of solution conductivity, temperature, sulphide, calcium, pH as well as the chemical distribution of sulphide species between solid, liquid and gaseous phases. The influence of process parameters including the effect of stirring rate on the kinetics of the reaction and the effect of the CO₂ flow-rate on the overall reaction time and quality of the CaCO₃ products were also investigated.

4.2 Materials and Methods

Feedstock

The CaS used as the raw material was a calcine product produced from waste gypsum generated at an acid mine water neutralisation plant (see p. 33). The XRD pattern of the untreated gypsum waste demonstrated that the primary mineral phase was gypsum (CaSO₄·2H₂O; 96.9%), which co-existed with magnesite (MgCO₃; 3.1%). The calcine purity was 50.7 ± 0.85 mass% (as CaS). A photograph,

SEM images and FTIR result of the calcine sample are available in the Supplementary Information S4.1. (pp. 72-73).

Experimental procedure

The direct aqueous carbonation reactions were performed in a 3-litre Perspex stirred tank batch reactor using the experimental set-up described in Chapter 3 (p. 34 of this document). The calcine sample was dispersed in distilled water to obtain a 10 % calcine slurry concentration (300g calcine in 3ℓ distilled water). After 30 min of continuous mixing, CO₂ gas was introduced at a constant flow-rate of 2.9 ℓ CO₂/min/kg calcine into the slurry *via* the sparger. The pH, electrical conductivity and temperature of the suspension in the reactor were logged at 5 second intervals to monitor the reaction profile and kinetics. Both unfiltered and filtered samples of the CaS suspension were collected from the reactor at regular intervals. The reaction was terminated when the pH and electrical conductivity remained unchanged (constant within 1%) for 10 to 15 min. Immediately upon the completion of each experimental run, the final suspensions were removed from the reactor by vacuum filtration using 0.45μm Millipore HA membranes, washed twice with distilled water and dried at 60°C for at least 24 hours.

The effect of stirring rate on reaction kinetics, and CO₂ flow-rate on both the reaction kinetics and the CaCO₃ particle characteristics, were studied.

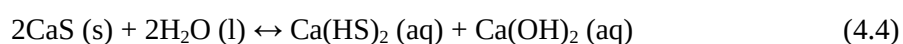
Analytical methods

Wet analytical techniques (described on pp. 38-39 of this document) were used for the analysis of the total sulphide content (unfiltered samples including both the soluble sulphide and sulphide in the solids phase) and the soluble sulphide and calcium concentrations (filtered samples using 0.45μm PALL acrodisc PSF GxF/GHP membranes (Microsep (Pty) Ltd, South Africa)).

The solid samples were characterised by XRD, ATR-FTIR, SEM and PSD. The details of these methods or techniques are described in Chapter 3 (pp. 39-42 of this document).

4.3 Results and Discussion

The overall reaction between solid CaS suspended in water and CO₂, produces solid CaCO₃ and H₂S gas according to Eq. (4.2). CaS is unstable at ambient conditions and only stable in solid, dry form under N₂ atmosphere conditions (García-Calzada et al. 2000). In aqueous solution, CaS decomposes and reacts with water to produce calcium hydrosulphide (Ca(HS)₂) and aqueous calcium hydroxide (Ca(OH)₂) (Zekker et al. 2011), according to Eq. (4.4).



CaS is a sparingly soluble salt and reported values for the solubility of CaS in water (at 25°C) varies widely, with published values ranging from 0.125 g/ℓ to 1.0 g/ℓ (Perry & Green 1984; Dean 1992; Weast 1972). The difference can be ascribed to the complicated dissolution mechanism.

Immediately upon addition of CaS to distilled water, the solution pH increased from 6.4 to 11.6 within the first minute (Figure 4.2) and stabilized at 11.7 after about 2 min of stirring. The high sulphur content (708 mmol/ℓ as S) of the solids dispersed in water and the low amount (9.9 mmol/ℓ as S) of dissolved sulphur in solution measured following a period of 30 min of dissociation prior to the addition of CO₂ confirmed the low solubility of CaS in water. The system of solid CaS in equilibrium with water, before the addition of CO₂, forms a highly alkaline solution (pH 11.7) containing soluble calcium hydrosulphide (Ca(HS)₂) and soluble calcium hydroxide (Ca(OH)₂) according to equation (4.4), as well as undissolved CaS solids.

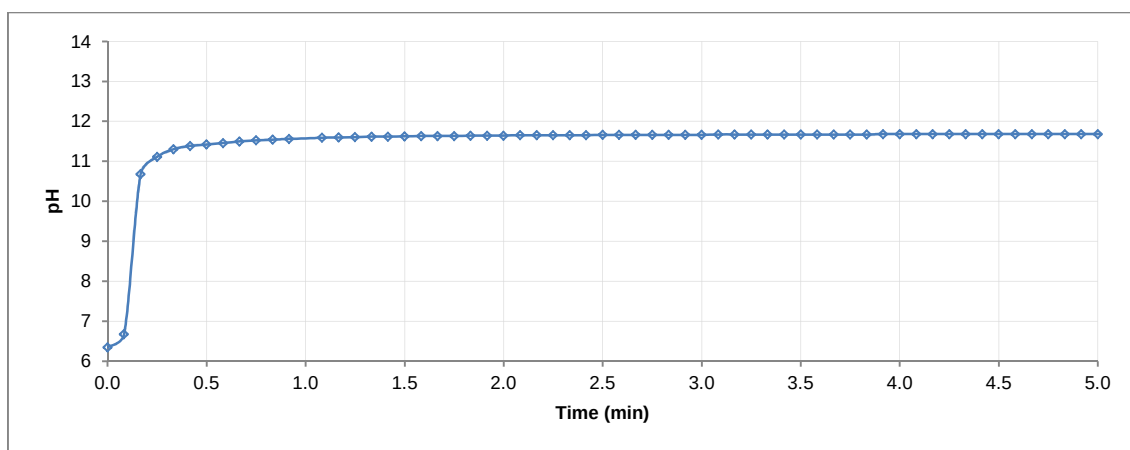


Figure 4.2 pH profile of CaS dissociation in distilled water at room temperature. (CaS slurry containing 22.7 g/l as S; initial pH: 6.4; stirring rate: 300 min⁻¹)

The dissociation of CaS in water during the decomposition process produced free/labile sulphide (S²⁻) and calcium (Ca²⁺) ions (Eq. (4.5)). The sulphide ions subsequently bound with hydrogen ions from the water molecules to form HS⁻. The HS⁻ ions again bound with water to form H₂S according to Eq. (4.6) and (4.7), and thereby generating equimolecular amounts of hydroxide ions (OH⁻) responsible for the high alkalinity of the solution.

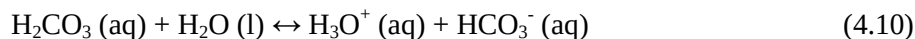
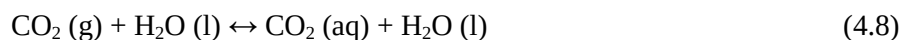


Direct aqueous carbonation of CaS

Upon addition of CO₂, after 30 min of stirring, the undissolved CaS was subjected to further aqueous dissolution, carbonation and stripping in a one-step process. CO₂ dissolved into water exists not only as dissolved CO₂ (Eq. (4.8)), but also as dissociated carbonic acid, H₂CO₃ (Eq. (4.9)). Carbonic acid is a weak acid that dissociates in two steps to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions (Eq. (4.10) and (4.11)). The sum of these concentrations in solution is the total carbonic species concentration (C_T) and is defined as:

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

The concentration of each species is described by the following series of dissociation equations:



The direct carbonation of the calcine sample suspended in water involved four primary, coexistent mechanisms in a single reactor: (i) aqueous dissolution of CO_2 gas (Eq. (4.8)-(4.11)) (ii) aqueous dissolution of CaS and other soluble mineral phases, (iii) precipitation of solid carbonates, and (iv) stripping of H_2S .

The dynamics, existing and evolving, between these four mechanisms in the $\text{CaS-CO}_2\text{-H}_2\text{S}$ system were investigated by monitoring the temporal profiles of several parameters: solution conductivity and temperature (Figures 4.3 (a) and (b), respectively), the soluble sulphide and soluble calcium species (Figure 4.4), and the solution pH and chemical distribution of sulphide species between solid, liquid and gaseous phases (Figure 4.5).

Changes in the conductivity and temperature of the solution over time exhibited similarly-shaped profiles, with both parameters having reached their maxima at 120 min of reaction time (Figure 4.3). These profiles correlated closely with the profiles found for the distribution of soluble sulphide and soluble calcium species (Figure 4.4), which also reached their maximum values at 120 min.

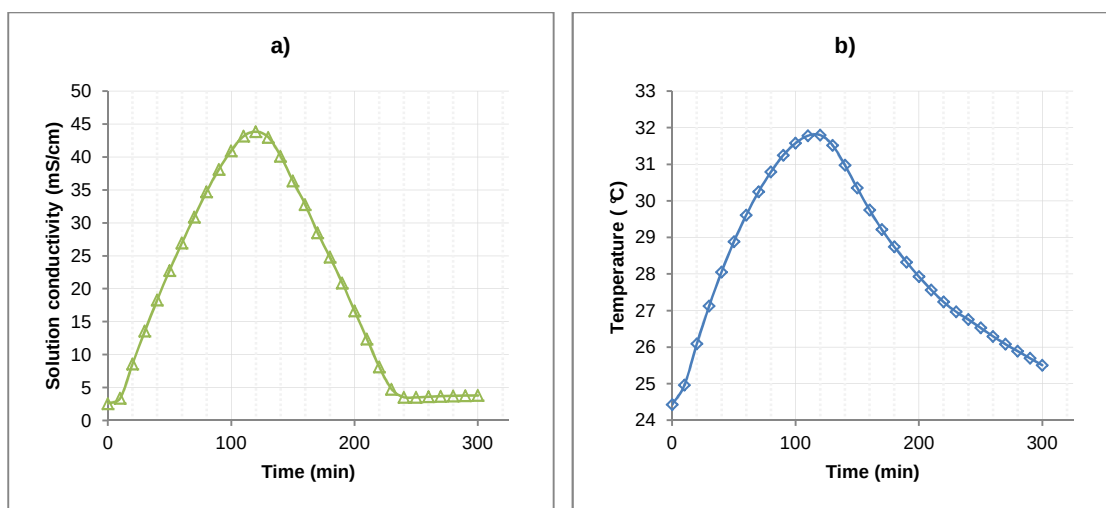


Figure 4.3 Solution conductivity (a) and temperature (b) profiles of a calcine slurry in equilibrium with distilled water upon CO_2 addition. (CaS slurry containing 22.7 g / ℓ as S; initial pH: 11.7; gas flow: 2.94 ℓ CO_2 /min/kg calcine; stirring rate: 300 min^{-1})

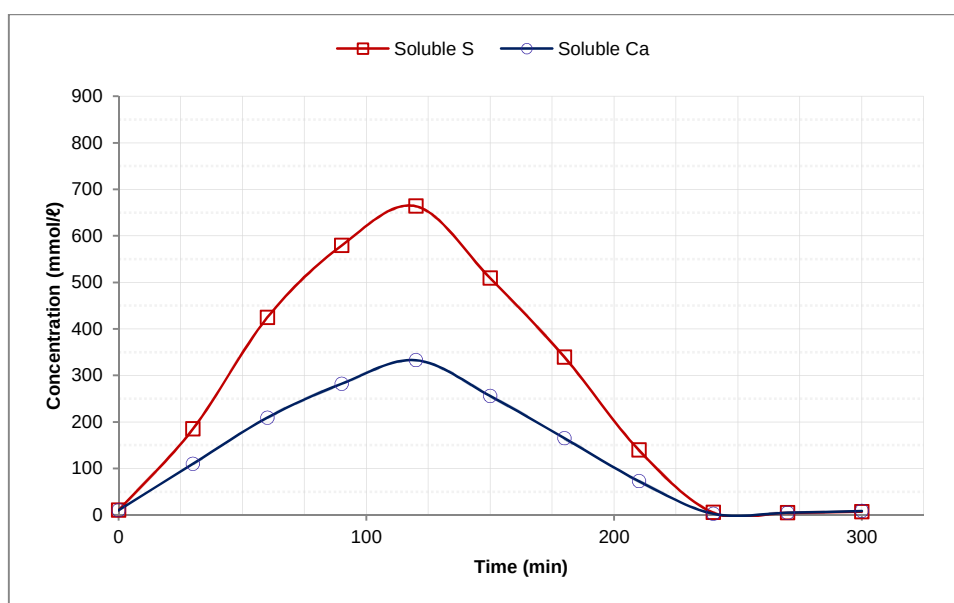


Figure 4.4 The distribution of soluble sulphide and soluble calcium concentrations with time, of a calcine slurry in equilibrium with distilled water upon CO_2 addition. (CaS slurry containing 22.7 g / ℓ as S; initial pH: 11.7; gas flow: 2.94 ℓ CO_2 /min/kg calcine; stirring rate: 300 min^{-1})

When adding CO_2 (time = 0 min), the pH initially dropped sharply from 11.7 to 9.5 within a short period of time (< 1 min), after which it continued decreasing more gradually down to approximately 6.8. The gradual drop in pH exhibited three different slopes: (1) from 1 to 125 min, (2) from 125 to

210 min, and (3) from 210 to 240 min, before stabilizing at about 6.8 from 250 min onwards (Figure 4.5).

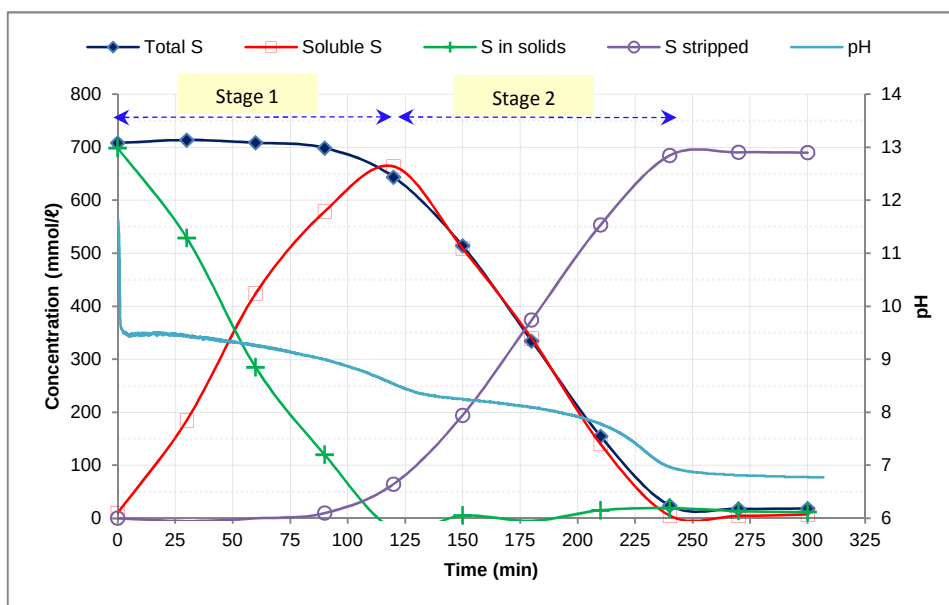
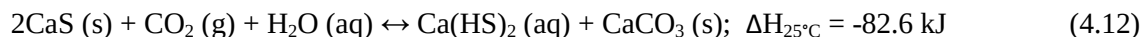


Figure 4.5. Changes in the pH and chemical distribution of sulphide species between solid, liquid and gaseous phases during direct aqueous carbonation of the calcine sample. (CaS slurry containing 22.7 g/l as S; initial pH: 11.7; gas flow: 2.94 l CO₂/min/kg calcine; stirring rate: 300 min⁻¹)

Stage 1 - CaS dissolution: During the first stage of the reaction (0 to 120 min, Figure 4.5), the total sulphur concentration in the reactor remained constant at about 708 mmol/l (as S) up to about 75 min (and pH > 9.2) followed by a slight decrease to about 660 mmol/l (as S) at time 120 min, which indicated that little S stripping had taken place. The sulphur concentration in solution increased steadily to a maximum of 684 mmol/l (as S), whilst the sulphur content in the undissolved material decreased at the same rate from about 700 mmol/l to about 5 mmol/l (as S).

From 0 to 75 min, while the pH remained above 9, no sulphide was stripped from the system. The steady increase in dissolved sulphur upon CO₂ addition, which was not observed in the absence of CO₂, indicated the greater solubility of CaS in water in the presence of dissolved CO₂. The decrease in the sulphur content in the solid phase and the increase in the sulphur content of the soluble phase during Stage 1, was due to the dissolution of solid CaS and the formation of soluble Ca(HS)₂ (Eq. (4.12)). The dissolution of solid CaS and the formation of soluble Ca(HS)₂ were also confirmed by the increase in solution conductivity from 2.57 to 43.8 mS/cm during the first 120 min

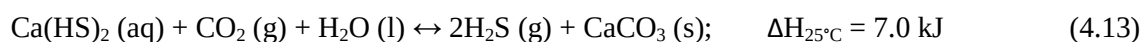
(Figure 4.3 a). Chemical analysis of the soluble sulphide and soluble calcium species with time (Figure 4.4, time = 0 to 120 min) showed that one mole of $\text{Ca}(\text{HS})_2$ was formed and 1 mole of CaCO_3 precipitated from solution for every two moles of CaS dissolved in the reactor, which was in agreement with Eq. (4.12).



Stage 2 - H_2S stripping: Stage 1 illustrated that little S stripping had taken place during the first 120 min of the reaction. During the second stage of the reaction (120 to 240 min, Figure 4.5), the total sulphur concentration in the reactor decreased steadily from about 660 mmol/l (as S) to 20 mmol/l (as S) whilst the sulphur concentration in solution also decreased from 684 mmol/l (as S) to about 5 mmol/l (as S). The sulphur content in the undissolved material remained constant, at about 20 mmol/l (as S) during this phase.

The CaS dissolution reaction occurred between the solid CaS and the dissolved CO_2 at the solid-liquid interface and was limited by how fast the CO_2 could dissolve in, and diffuse through, the solution (Eq. (4.8)-(4.11)). The precipitation of CaCO_3 at the interface most likely encapsulated the remaining CaS, preventing further reaction from taking place (Brooks & Lynn 1997). The difference in the amount of sulphur initially added (708 mmol/l as S) and the maximum sulphur in solution (684 mmol/l as S), measured during the course of the reaction, was 24 mmol/l (as S). According to Brooks and Lynn (1997), the difference could be ascribed to the encapsulation of CaS particles.

However, another mechanism is that the start of CaCO_3 precipitation and H_2S stripping, before total dissolution of CaS was reached, removed calcium and sulphur from solution, and therefore the sulphur concentration in solution never reached 708 mmol/l. The decrease in the total sulphur as well as the soluble sulphur content during Stage 2 can be attributed to the stripping of H_2S gas from solution (Eq. (4.13)). Chemical analysis of the soluble sulphide and soluble calcium species with time (Figure 4.4, time = 120 to 240 min) showed that two moles of H_2S were stripped from the reactor for every mole of calcium precipitated as CaCO_3 , which was in agreement with Eq. (4.13).



Between 0 to 75 min, the pH remained above 9.2 and little, if any, sulphur was stripped from the system. This was explained by the hydrogen sulphide speciation diagram (Figure 4.6), which

illustrates the required pH conditions for H₂S formation. Sulphide, in the form of H₂S was stripped from solution at pH values below 9.2. The sulphide speciation diagram (Microsoft Excel 2010) was obtained by calculating the fractional composition of the sulphide species in water using the dissociation constants for hydrogen sulphides at 25 °C. The ionization of H₂S in water proceeds in two steps and the concentration of each species described by the dissociation equations (Eq. (4.14) and (4.15)). The fractional compositions were calculated from the dissociation constants ($K_1 = 9.1 \times 10^{-8}$ and $K_2 = 1.1 \times 10^{-12}$) (Perry & Green 1984) and the following two reactions:

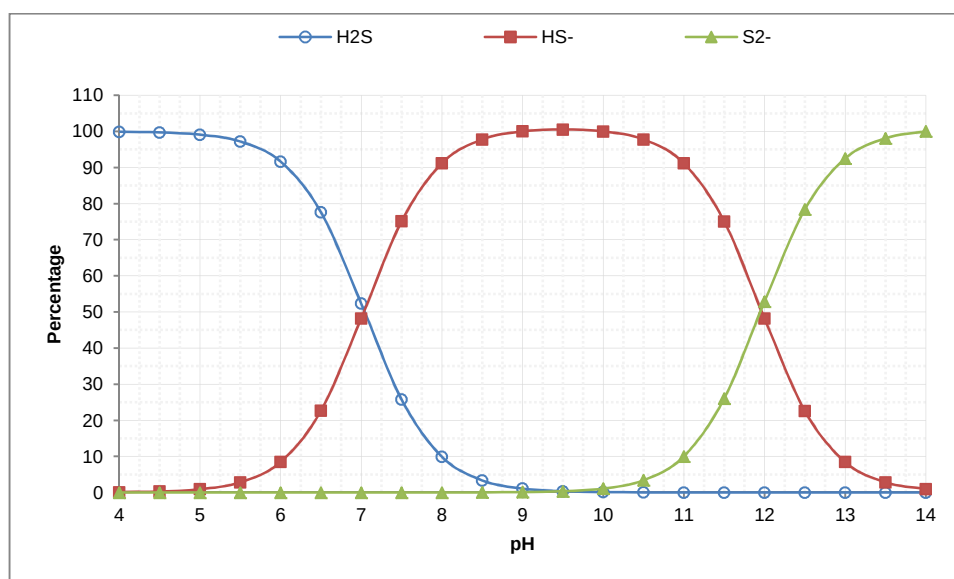
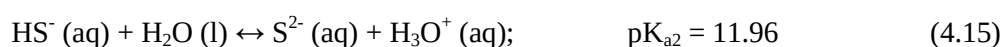
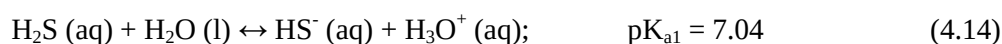


Figure 4.6 The hydrogen sulphide speciation diagram in aqueous medium

CaCO₃ dissolution: Carbonate minerals are only sparingly soluble in water but dissolve readily in strong acids (Weast 1972) at low solution pH (Supplementary Information S4.2., p. 72).

During the direct aqueous CaS carbonation reaction, the pH of the solution decreased continuously with time. After completion of the reaction, the final pH was about 6.8 (Figure 4.5). The lower pH value modifies the amount of species present in aqueous solution.

Carbonic acid (H₂CO₃) is a weak acid that dissociates in water in two steps. From the CO₂ speciation diagram (Supplementary Information S4.3., p. 73) and the two dissociation equations (Eq. (4.10) and

(4.11)), it was concluded that the major ions in the pH range 6 to 7 were HCO_3^- whilst CO_3^{2-} mainly occurred in the high pH range, at pH 10 to 11. At the final pH of 6.8, the concentration of HCO_3^- was high while the concentration of CO_3^{2-} , was low. The final carbonate product was expected to be quite stable in this solution based on reported results (Coto et al. 2012; Teir et al. 2006).

Teir et al. (2006) studied the stability of synthetic CaCO_3 in acidic solutions and reported that the stability depends mainly on the acidity of the solution. They found that the fraction of Ca dissolved in solution with initial pH of 1 was only 9 % and the fraction dissolved in solution with an initial pH greater than 2 was less than 1 %. Experimental studies and model simulation results by Coto et al. (2012) also confirmed the relative stability of CaCO_3 at pH values greater than 6.

Influence of process parameters on the direct aqueous carbonation reaction

Effect of stirring rate on reaction kinetics

Figure 4.7 shows the effect of the stirring rate on CaS dissolution and H_2S stripping reactions from the calcine slurry. During the first stage of the reaction, the electrical conductivity increased mainly as a result of CO_2 gas absorption and CaS dissolution, and decreased in the second stage as a result of H_2S gas stripping and CaCO_3 precipitation (Figure 4.7 (a)). With a stirring rate of 180 min^{-1} the reaction was complete (as indicated by levelling off of all the parameters) in approximately 390 min, while the use of a stirring rate of 300 min^{-1} and 480 min^{-1} reduced the time of completion of the reaction down to approximately 240 min and 160 min, respectively. Both the CaS dissolution and the H_2S stripping reaction kinetics were positively influenced by faster stirring rates (Figure 4.7 (a)-(f)). The linear trend conversion versus time (Figure 4.7 (e)) indicates that external mass transfer determines the solid-phase conversion rate.

The Rushton turbine is a radial flow impeller designed to provide high shear conditions required for breaking gas bubbles and thereby increasing the gas transfer rate. In systems where mass transport is the rate-determining step, it is possible to increase the reaction rate by increasing the mass transfer rate (Sardegna et al. 2004). For solid particles, the interfacial area is determined by the physical appearance of the particle and there is little benefit in increasing the stirring rate. However, for gas reactions, an increase in stirring rate generates smaller bubbles and consequently increases the interfacial area of the CO_2 gas bubbles. The increased interfacial area of the gas phase is directly related to an increase in the mass transfer rate (Martin et al. 2008). Therefore, faster reaction rates were evident, following higher stirring rates, in the direct aqueous carbonation reaction.

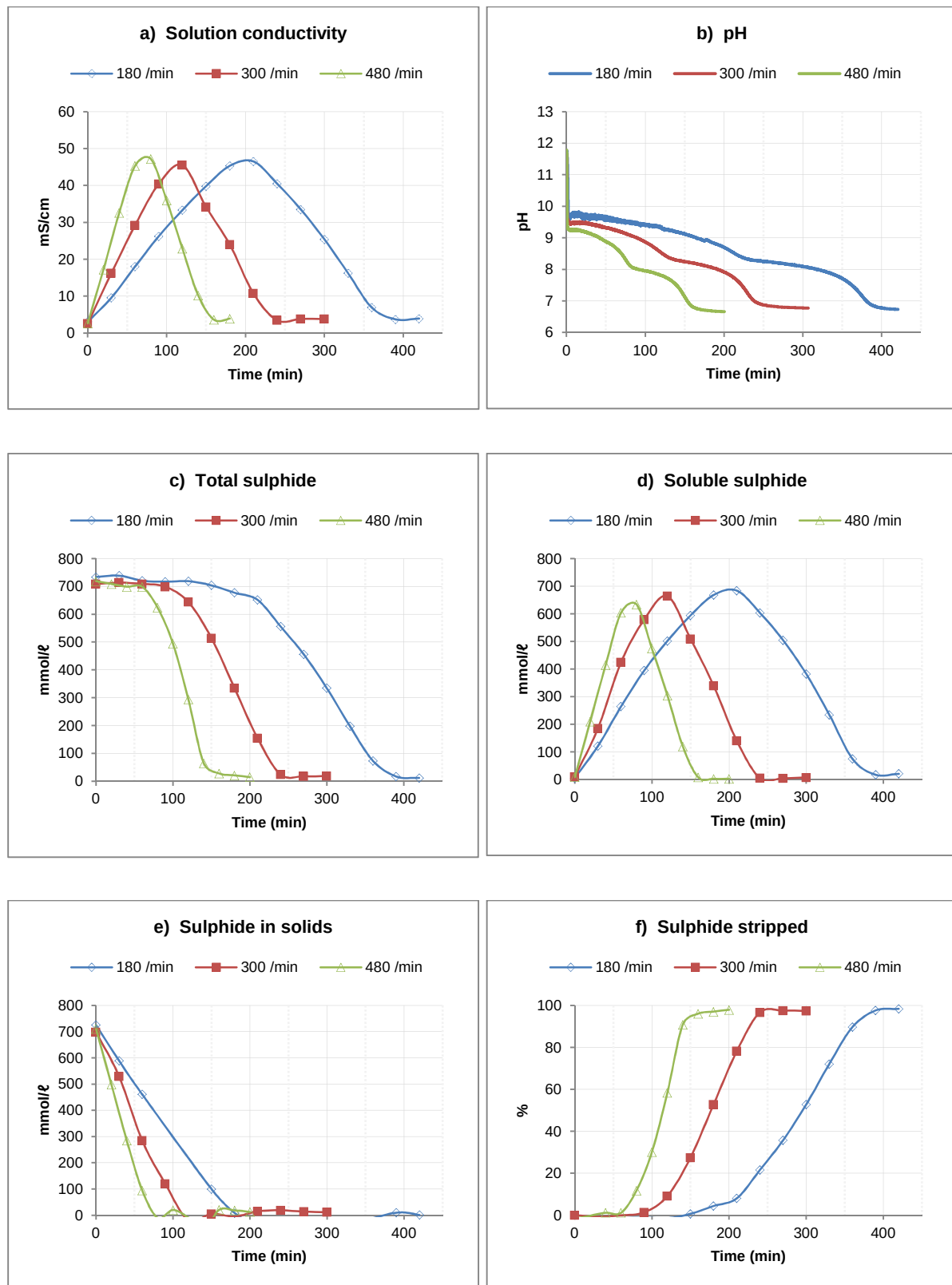


Figure 4.7 Effect of stirring rate on a) the solution conductivity, b) pH, c) total sulphide concentration, d) soluble sulphide concentration, e) sulphide in solid phase and f) sulphide stripped from solution with time. (CaS slurry containing 22.7 g / ℓ as S; initial pH: 11.7; gas flow-rate: 2.94 ℓ CO₂/min/kg calcine)

Table 4.1 presents a summary of the rate constants calculated for the different stirring rates.

Table 4.1 Rate constants in relation with the stirring rate. (CaS slurring containing 22.7g S/ℓ; initial pH: 11.7; gas flow-rate: 2.94 ℓ CO₂/min/kg calcine)

Stirring rate (min ⁻¹)	Process step	Rate constant (g/ℓ/min (as S))	Standard deviation (±)	R ²
180	CaS dissolution	0.116	0.002	0.9975
	H ₂ S stripping	-0.127	0.002	0.9972
300	CaS dissolution	0.218	0.005	0.9954
	H ₂ S stripping	-0.205	0.002	0.9993
480	CaS dissolution	0.355	0.013	0.9948
	H ₂ S stripping	-0.313	0.005	0.9985

These results showed that an increase in the stirring rate accelerated both the CaS dissolution reaction as well as the carbonation reaction.

Effect of CO₂ flow-rate on the reaction kinetics and the CaCO₃ particle characteristics

Reaction kinetics and overall reaction time: The effect of the CO₂ gas flow-rate on the temporal distribution of soluble sulphide concentrations was investigated. A summary of the calculated reaction rate constants at the various CO₂ flow-rates is presented in Table 4.2, which confirms the H₂S-stripping reaction as the rate-determining step. The rate of the overall reaction of a multistep reaction is determined by the slowest step, also known as the rate-limiting step. As shown in Figure 4.8, the reaction was complete (as indicated by the levelling off of the drop in soluble sulphide concentration) in approximately 86 min at a flow-rate of 2.53 ℓ CO₂/min/kg calcine, while at 8.80, 14.93 and 29.33 ℓ CO₂/min/kg calcine, the reactions were completed in 38, 26 and 18 min, respectively.

The dissolution of gaseous CO₂ in solution (Eq. (4.8)) is generally the first rate-limiting step in direct carbonation reactions (Jana & Bhaskarwar 2011; Uebo et al. 1992), but it can be enhanced by increasing the CO₂ flow-rate (Chen et al. 2008) when working at atmospheric pressure and thereby ensuring that carbonate ions are present in excess over Ca ions. However, a further increase of the flow-rate to more than 29.33 ℓ CO₂/min/kg calcine had little effect on the overall reaction time

(Table 4.2 and Figure 4.8). If the solubilisation of CO₂ was the limiting factor, no further improvement in CO₂ dissolution with increased flow-rates would be evident due to the solubility of CO₂, which is constant at the given conditions. For example, at 25°C and 1 atmosphere, the solubility of CO₂ is about 0.09 l CO₂ per 100 ml of water (Juvekar & Sharma 1977). When the CO₂ gas flow-rate is higher than the solubility of CO₂ gas in water, the excess CO₂ gas cannot be adsorbed and will run through the system, eventually escaping from solution in the gas phase. Although the solution used during this study was totally different from water, the interpretation remains valid.

Table 4.2 Rate constants in relation with the CO₂ flow-rate. (CaS slurry containing 22.7g S/l; initial pH: 11.7; stirring rate: 600 min⁻¹)

CO ₂ flow (l/min/kg calcine)	Process step	Reaction kinetics			Reaction time (min)	Actual yield (g/100g CaS)
		Rate constant (mmol/l/min (as S))	Standard deviation (±)	R ²		
2.53	CaS dissolution	16.08	0.43	0.9929	86	127.3 (91.7%)
	H ₂ S stripping	-13.57	0.57	0.9913		
8.80	CaS dissolution	45.57	1.58	0.9964	38	127.5 (91.9%)
	H ₂ S stripping	-21.82	4.36	0.8931		
14.93	CaS dissolution	47.87	3.06	0.9919	26	126.5 (91.2%)
	H ₂ S stripping	-30.76	2.93	0.9402		
29.33	CaS dissolution	65.12	4.16	0.9761	18	128.1 (92.3%)
	H ₂ S stripping	-38.34	1.92	0.9925		
44.00	CaS dissolution	61.81	3.65	0.9795	18	130.6 (94.1%)
	H ₂ S stripping	-36.88	2.27	0.9814		

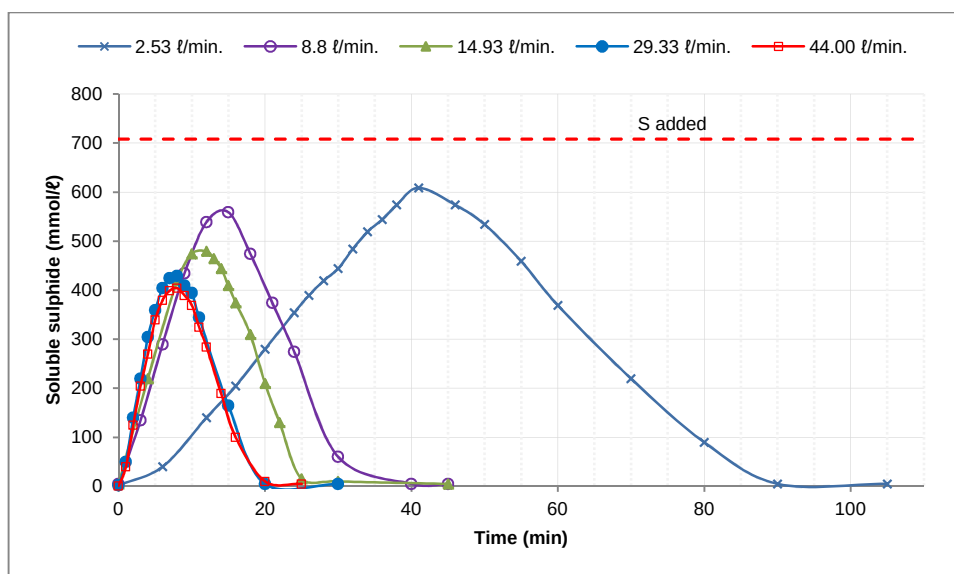


Figure 4.8 The effect of gas flow-rate (ℓ CO_2 /min/kg calcine) on the distribution of the soluble sulphide concentration with time. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

Differences were observed between the total sulphide concentrations initially added as CaS (708 mmol/ ℓ as S) and the maximum sulphide concentration measured in solution, at the various CO_2 flow-rates. The sulphur content of the solids produced at various CO_2 flow-rates were therefore estimated by SEM-EDX (Figure 4.9).

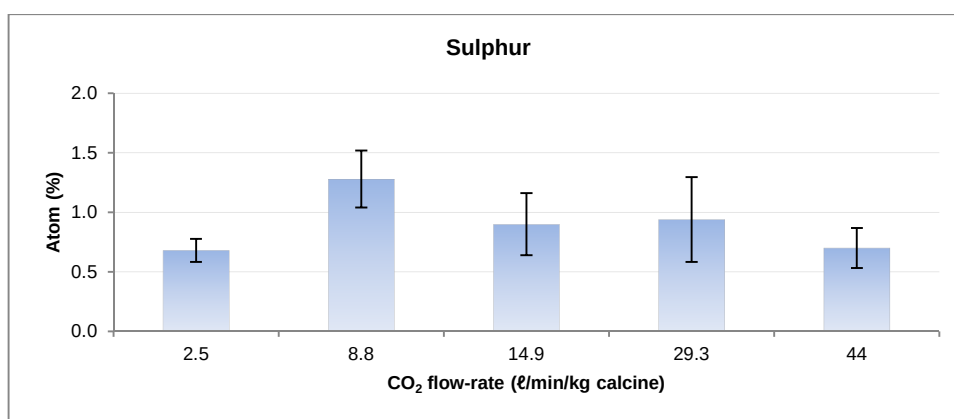


Figure 4.9 SEM-EDX analysis of the sulphur contents of the low-grade CaCO_3 products produced at various CO_2 gas flow-rates of the direct aqueous CaS carbonation process (five replicates)

The sulphur contents of all the products produced were found to be very low and less than 0.15 mass% (as S) in all the samples (Figure 4.9). The observed differences in the sulphide values initially added to the reactor and the maximum sulphide measured in solution, were therefore attributed to losses of sulphur units through the escape of H₂S gas. The full SEM-EDX elemental analysis of the products is available in the Supplementary Information S4.4.1. p. 74.

CaCO₃ characteristics

XRD, FTIR spectroscopy and SEM were employed to study the effect of CO₂ flow-rates on the crystal structure and polymorphism of the solid particles. CaCO₃ has three anhydrous crystalline forms namely calcite, aragonite and vaterite. Calcite is the most thermodynamically stable under ambient conditions and vaterite the least stable (Brecevic & Nielsen 1989). In this study, only the calcite and vaterite polymorphs precipitated, and the aragonite phase was not detected in any of the products. The formation of aragonite is generally associated with higher temperatures (> 50°C) and pressure (Liu et al. 2010) and all the experiments during this study were executed at ambient temperature and pressure.

XRD is a important tool for identification and conformation of crystalline forms. With regard to the XRD study, the phases were identified using the X'Pert Highscore plus software and the relative phase amounts (mass%) were estimated using the Rietveld method (Supplementary Information S4.4.2, p. 75). The percentages of calcite, vaterite and the other mineral phases in the samples were calculated from the XRD patterns (also presented in Figure 4.12) and the values are shown in Table 4.3. The distribution of the combined CaCO₃ phases reached 86-88 mass% (the sum of calcite and vaterite) in every sample produced, whilst the impurities (sum of all the non-CaCO₃ mineral phases) amounted to 12-14 mass% and included anhydrite, quartz, oldhamite, portlandite, apatite and fluorite. Based on their carbonate contents, the greyish products (Figure 4.10), synthesised via direct aqueous carbonation of CaS were classified as low-grade CaCO₃ products (< 90 mass% as CaCO₃, (Oates 1998)).

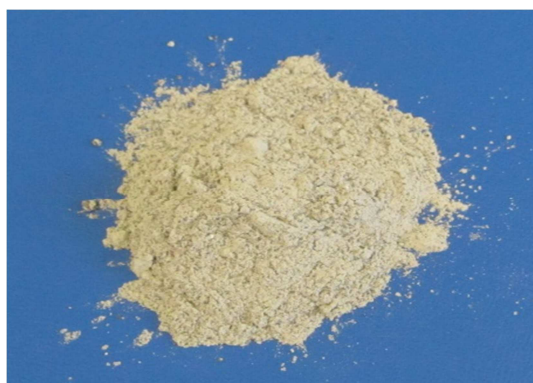


Figure 4.10 Photograph of the low-grade CaCO_3 produced in the direct aqueous CaS process

Table 4.3 Semi-quantitative XRD analysis of the low-grade CaCO_3 products generated at various CO_2 flow-rates

Mineral composition (mass%)	CO ₂ flow-rate (l CO ₂ /min/kg calcine)				
	2.5 (a)	8.8 (b)	14.9 (c)	29.3 (d)	44.0 (e)
Calcite	86.04	71.30	60.94	42.73	35.30
Anhydrite	4.49	3.44	3.15	3.10	3.63
Vaterite	1.77	15.87	25.89	43.91	50.99
Quartz	1.90	2.97	2.02	2.47	2.53
Oldhamite	0.16	0.10	0.07	0.09	0.00
Portlandite	0.14	0.41	0.51	0.68	0.78
Apatite	4.12	4.71	5.09	5.73	5.63
Fluorite	1.37	1.20	1.33	1.29	1.11

Figure 4.11 shows the XRD patterns for pure samples of the calcite and vaterite polymorphs [x]. The major peaks at $2\theta = 23.0^\circ, 29.5^\circ, 35.9^\circ, 39.3^\circ, 43.1^\circ, 47.1^\circ$ and 47.5° are characteristic of calcite, and those at $2\theta = 20.9^\circ, 24.8^\circ, 27.0^\circ, 32.7^\circ, 43.8^\circ, 49.9^\circ$ and 55.7° are characteristic of vaterite. (Calcite reference code: 00-005-0586; Vaterite reference code: 01-072-0506).

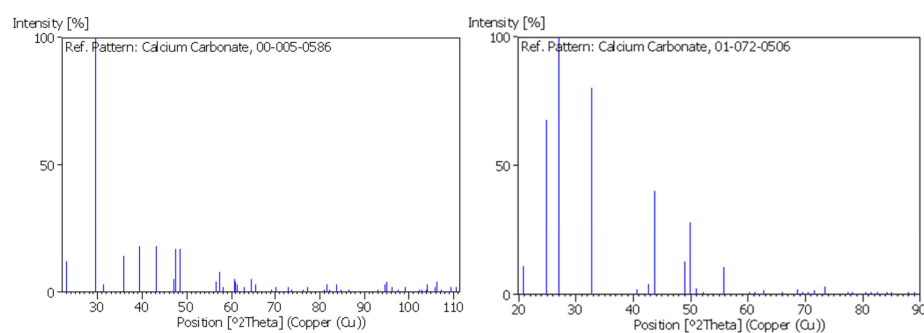


Figure 4.11 Library XRD patterns of a) calcite and b) vaterite

The XRD patterns of the samples prepared at 2.5, 8.8, 14.9, 29.3 and 44.0 ℓ CO_2 /min/kg calcine are shown in Figure 4.12 (a) to (e), respectively. In Figure 4.12 (a), peaks of the XRD spectra were consistent with the calcite crystal structure when the CaCO_3 was produced at the lowest CO_2 flow-rate (2.5 ℓ CO_2 /min/kg calcine). As shown in Figure 4.12 (b) – (e), the samples prepared at higher CO_2 flow-rates produced mixtures of calcite and vaterite. As the CO_2 flow-rate increased, some new peaks appeared that were consistent with the vaterite crystal structure (Figure 4.12 (b)–(f)). It was also noted that the intensity of the calcite peaks decreased with the increase in CO_2 flow-rate, while the intensity of the vaterite peaks increased with higher CO_2 flow-rates.

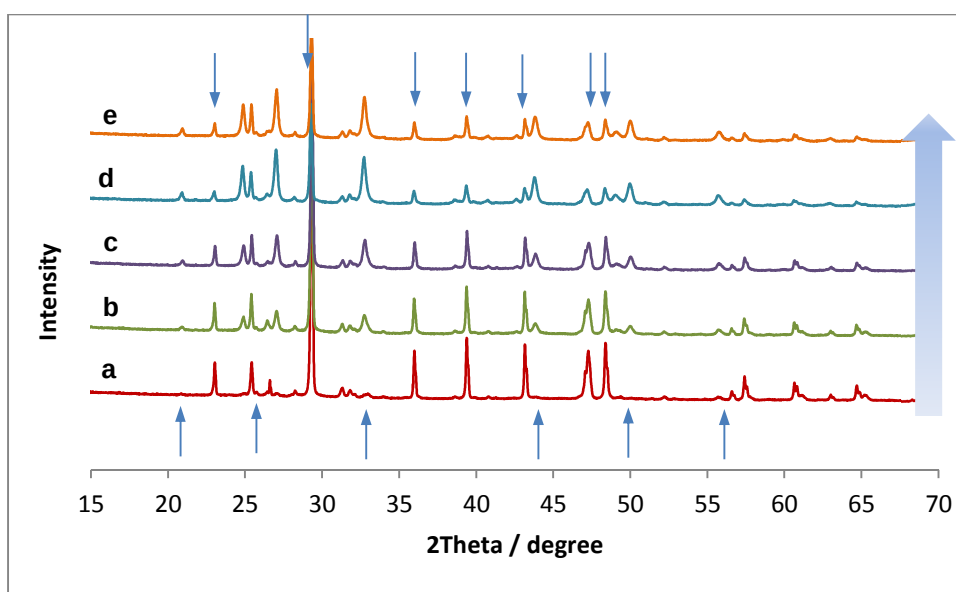


Figure 4.12 XRD patterns of low-grade CaCO_3 produced at CO_2 gas flow-rates of a) 2.5, b) 8.8, c) 14.9, d) 29.3 and e) 44.0 $\ell \text{ CO}_2/\text{min/kg calcine}$ respectively. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

The XRD results showed that at the lower CO_2 flow-rate of 2.5 $\ell \text{ CO}_2/\text{min/kg calcine}$, precipitates were mainly composed of calcite (Figure 4.12 (a)). Samples prepared at higher CO_2 flow-rates (Figure 4.12 (b)–(e)) showed the presence of binary mixtures of calcite and vaterite, with a progressive decrease in mole fraction of calcite and increase of vaterite with increased CO_2 flow-rates. The peaks corresponding to vaterite became stronger with increased CO_2 flow-rate, whilst the peak corresponding to calcite became weaker. Figure 4.13 further illustrates the interesting variation in the proportion of calcite to vaterite produced at different CO_2 flow-rates.

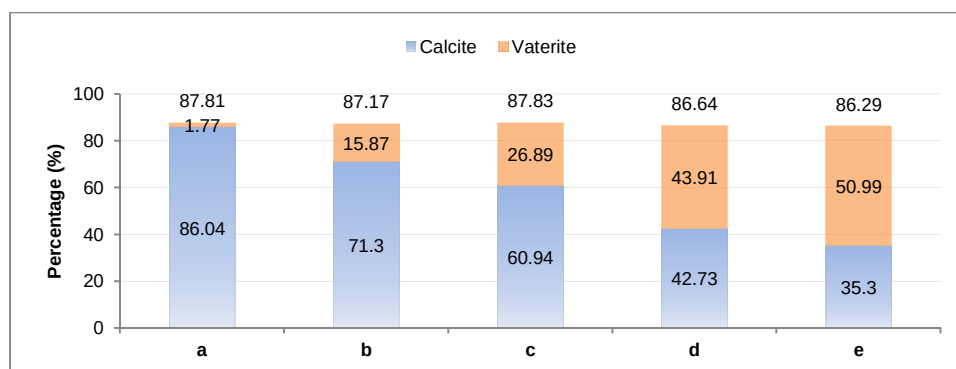


Figure 4.13 The distribution ratio of calcite and vaterite polymorphs in the low-grade CaCO_3 products produced at CO_2 gas flow-rates of a) 2.5, b) 8.8, c) 14.9, d) 29.3 and e) 44.0 $\ell \text{ CO}_2/\text{min/kg}$ calcine, respectively. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

Although the CaCO_3 content of the low-grade CaCO_3 products produced at different CO_2 flow-rates did not show major variations in the total CaCO_3 content, the distribution ratio of polymorphs (calcite and vaterite) was greatly influenced by the CO_2 flow-rate.

Along with the XRD analysis, the phase formation of the CaCO_3 products was further investigated by FTIR. The different crystal forms of CaCO_3 show different bands in FTIR spectra, due to the difference in carbonate ν_2 deformation mode (out-of-plane deformation) and carbonate ν_4 band (in-plane deformation) (Xyla & Koutsoukos 1989). The characteristic transmittance peaks centred around 745(ν_4), 874(ν_2), and 1089(ν_1) cm^{-1} corresponded to the in-plane bending, out-of-plane bending, and symmetric stretching vibration modes of CO_3^{2-} in vaterite. For calcite, ν_1 is only Raman active and ν_4 shifts to 713 cm^{-1} , although the ν_2 position was similar with that of vaterite (Socrates 2001).

FTIR spectra of CaCO_3 crystals produced at different CO_2 flow-rates are presented in Figure 4.14. As shown in Figure 4.14 (a), a single calcite phase was confirmed by the presence of the characteristic ν_2 bands at 873 cm^{-1} , ν_4 band at 713 cm^{-1} and ν_3 band at $\sim 1400 \text{ cm}^{-1}$. The introduction of higher CO_2 flow-rates resulted in the occurrence of a new peak located at 745 cm^{-1} , which is the fingerprint ν_4 deformation band of CO_3^{2-} in the vaterite form, confirming the presence of the vaterite phase. Figure 4.14 (b)-(e) shows the characteristic transmittance peaks of calcite (713 cm^{-1}) and vaterite (745 cm^{-1}), which substantiated the formation of a mixture of calcite and vaterite crystals at higher CO_2 flow-rates. It was also evident that the intensities of the peaks corresponding to vaterite and calcite became stronger and weaker, respectively, with higher CO_2 flow-rates. These results confirmed the XRD

results regarding the effect of the CO₂ flow-rates on the distribution ratio of the two CaCO₃ polymorphs. These observations were further supported by morphological studies.

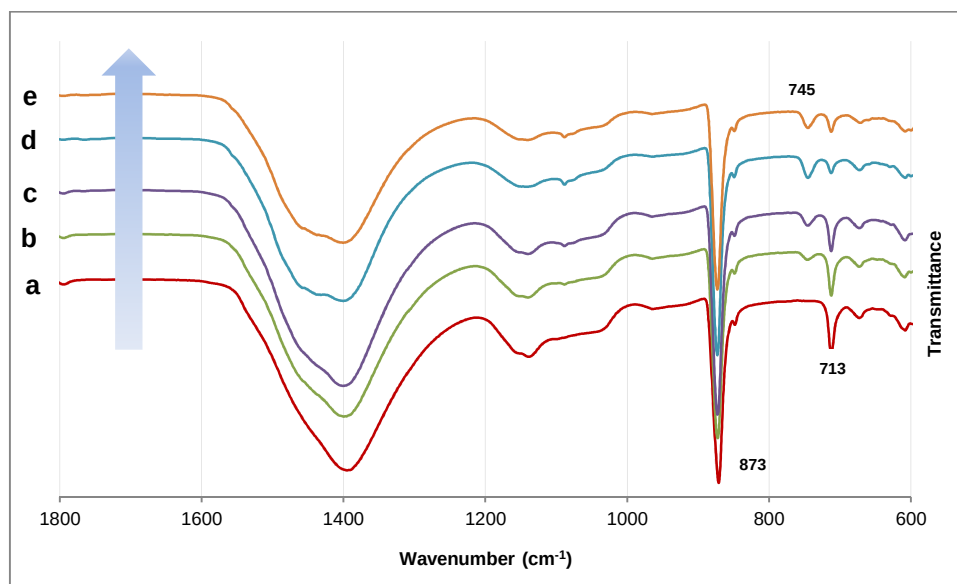


Figure 4.14 FTIR transmission spectra of low-grade CaCO₃ produced at CO₂ gas flow-rates of a) 2.5, b) 8.8, c) 14.9, d) 29.3 and e) 44.0 l CO₂/min/kg calcine, respectively. (CaS slurry containing 22.7 g/l as S; initial pH: 11.7; stirring rate: 600 min⁻¹)

As indicated by XRD and FTIR studies, only the calcite and vaterite crystals were produced during the study. The SEM images of the samples produced at different CO₂ flow-rates are presented in Figure 4.15 (a)-(e). The two prevalent CaCO₃ phases can clearly be distinguished by their characteristic morphologies. Vaterite can be recognised as the lens-shaped (Gehrke et al. 2005) and calcite as rhombohedral crystallites (Ibrahim et al. 2012). All precipitates were micron-sized lumps made up of randomly aggregated rhombohedra of calcite and lens-shaped (or ellipse-like) vaterite, depending on the CO₂ flow-rate.

The product generated at 2.5 l CO₂/min/kg calcine consisted mostly of irregular polyhedron calcite crystals (Figure 4.15 (a)). Some crystal planes of the irregular polyhedron structure were flat with smooth surfaces, while other planes were rough with a “step” structure. At higher CO₂ flow-rates, mixtures of vaterite and calcite were found, (Figures 4.15 (b)-(e)). Interpenetrated rhombohedral cubes of calcite with smooth surfaces and mixtures of ragged and sharp edges were formed at higher CO₂

flow-rates. Calcite particles aggregated to form large, irregular particles and were partly overgrown by clusters of vaterite (Figure 4.15 (b)-(e)).

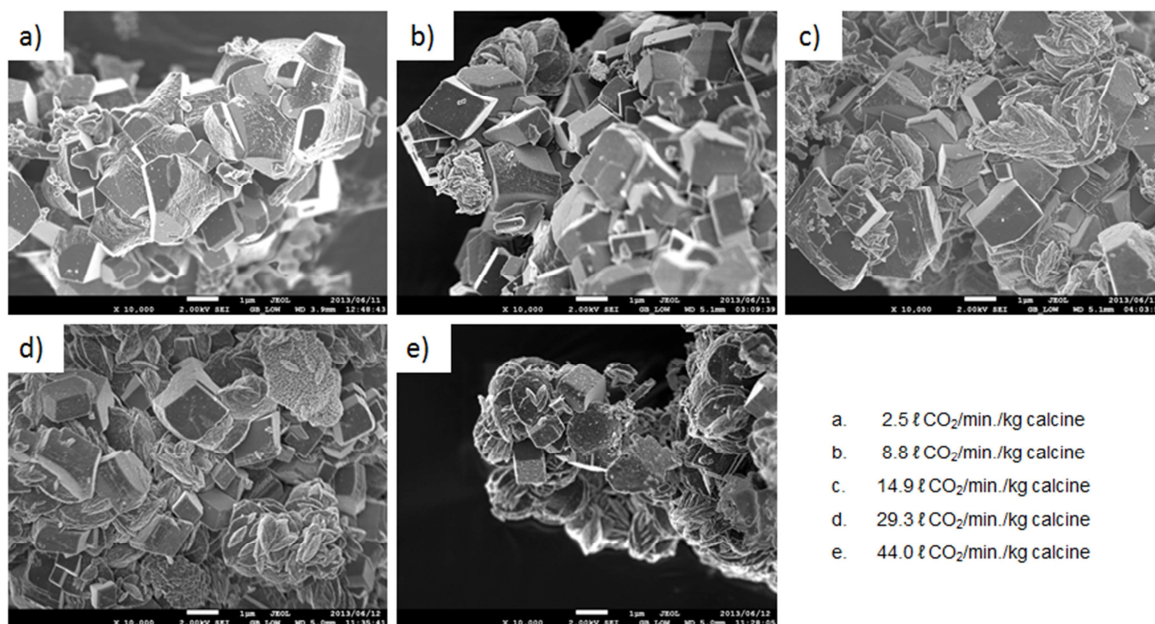


Figure 4.15 Scanning electron microscope (SEM) images at $10\,000\times$ magnification of CaCO_3 produced at different CO_2 gas flow-rates. (CaS slurry containing 22.7 g/l as S; initial pH: 11.7; stirring rate: 600 min^{-1})

Calcite usually crystallises as mono-crystalline well-faceted particles. Vaterite particles, on the other hand, are usually poly-crystalline and exhibit a spherical shape and are built up of smaller crystallites (Brecevic & Nielsen 1989). However, in this study, only lens-shape vaterite particles were formed and no classical spherical vaterite particles were identified. Figure 4.16 (a) shows a higher magnification of Figure 4.15 (c), whilst Figure 4.16 (b) reports a higher magnification of 4.15 (e) to exhibit the detail of the lens-shape vaterite crystals.

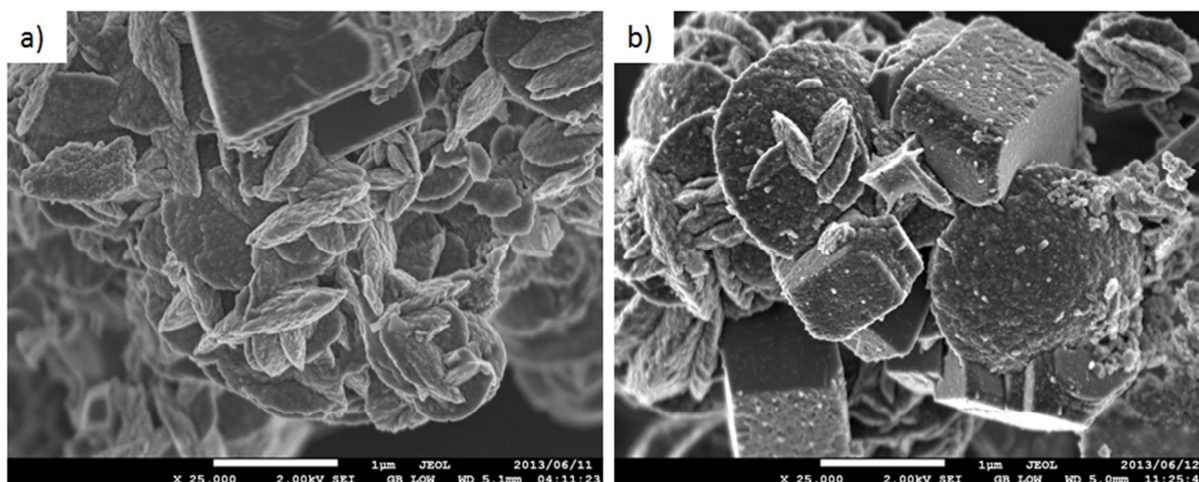


Figure 4.16 Scanning electron microscope (SEM) images at 25 000 $\times$ magnification showing the lens-shaped crystals of vaterite produced at a) 14.5 and b) 44.0 ℓ CO_2 /min/kg calcine respectively. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

The highly irregular shape of micron-sized particles produced appeared to be typical of the semi-batch process, possibly caused by multiple passages of the particle through the region of maximum supersaturation at the feed inlet.

A laser diffraction technique was used to compare the particle size characteristics of the precipitated solids (Supplementary Information S4.4.3, pp. 78-82). Figure 4.17 shows the particle size distribution versus the percentage of particle volume, and Figure 4.18, the cumulative percentage distribution of the particles produced at various CO_2 flow-rates. The actual values of the mode and median size of the products produced are given in Figure 4.19. The mode size constitutes the peak of the frequency distribution and represents the particle size most commonly found in the distribution.

The mode size of the particles produced at CO_2 flow-rates between 2.53 and 44.00 ℓ /min/kg calcine varied between 18.5 and 21.2 μm . Although these values were similar, the products produced at lower CO_2 flow-rates (2.53, 8.8 and 14.93 ℓ /min/kg calcine) also contained particles of large sizes, greater than 100 μm . All the particles produced at higher CO_2 flow-rates (29.33 and 44.00 ℓ /min/kg calcine) were less than 100 μm diameter. The larger particle sizes found at lower CO_2 flow-rates were attributed to possible particle aggregation. The median size, also known as the D50, is the particle size where 50% of the population lies above and below this diameter. The median size of the particles produced at CO_2 flow-rates between 2.53 and 44.00 ℓ /min/kg calcine varied between 16.1 and 21.3 μm .

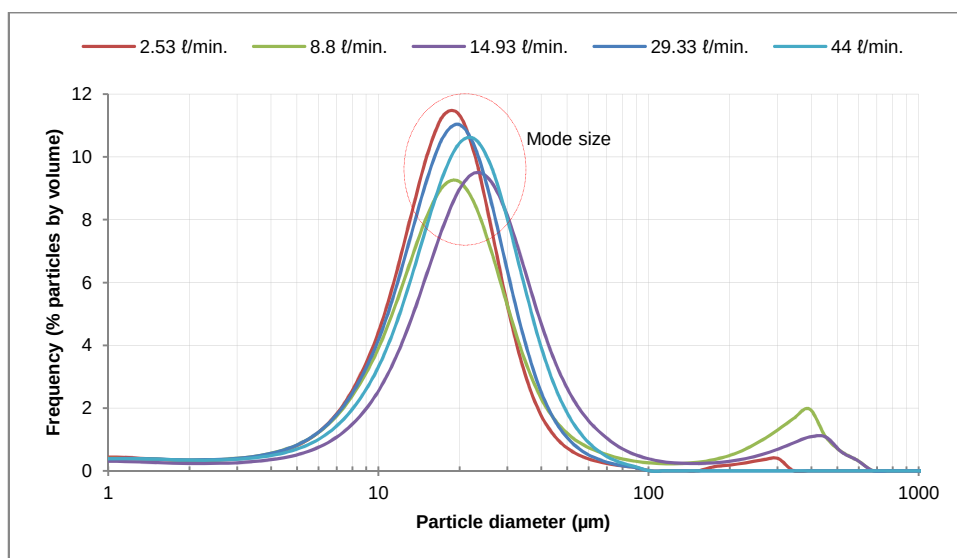


Figure 4.17 Particle size frequency distribution of the low-grade CaCO_3 produced at various CO_2 flow-rates

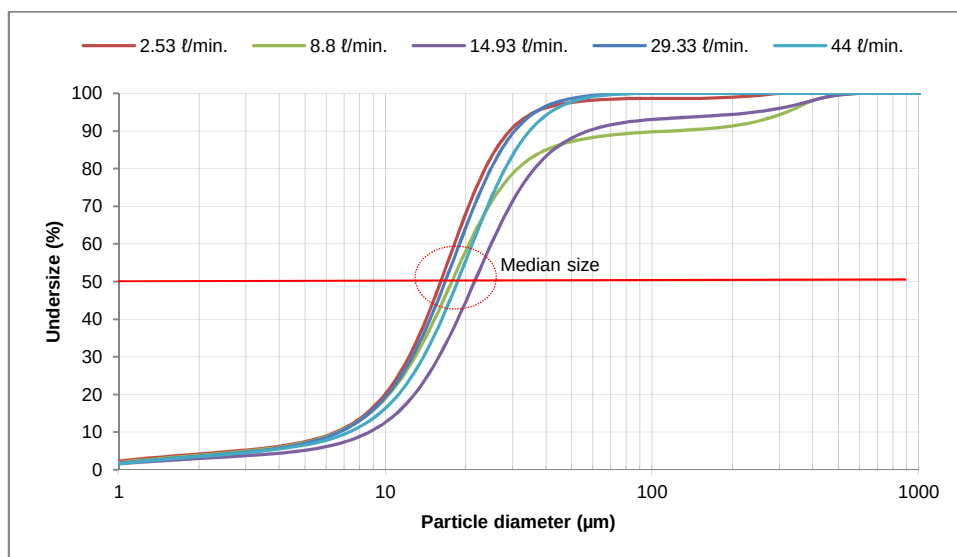


Figure 4.18 Particle size cumulative distribution of the low-grade CaCO_3 produced at various CO_2 flow-rates

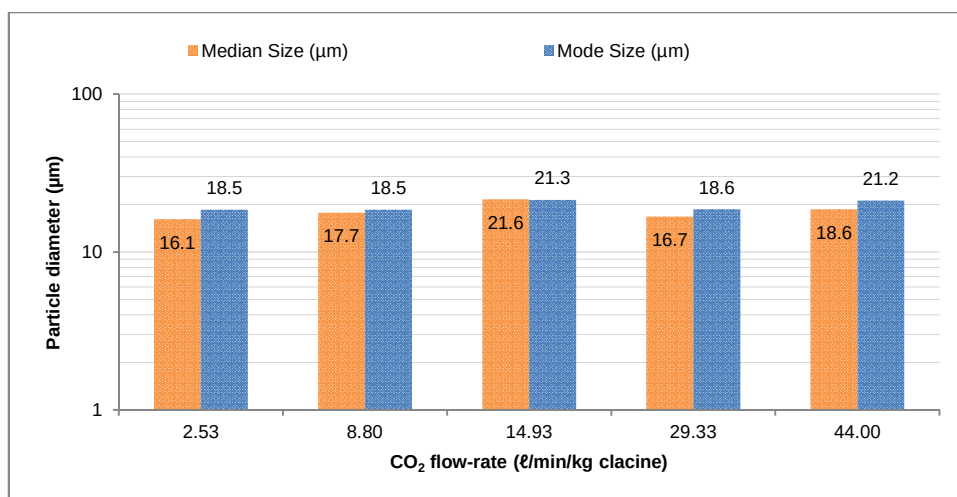


Figure 4.19 Median and mode particle sizes of the low-grade CaCO₃ produced at various CO₂ flow-rates

No significant reductions in the median and mode particle sizes upon higher carbonation reaction rates (higher CO₂ flow-rates) were observed and this result was in agreement with the results reported by Feng et al. (2007) who also found that an increase in CO₂ flow-rate did not have an influence in terms of a reduction in the CaCO₃ particle size.

4.4 Conclusions

Direct aqueous calcium sulphide carbonation, the aqueous reaction between solid CaS and CO₂, was studied. The mixing rate and CO₂ flow-rate were the studied parameters.

The kinetics of the CaS dissolution were successfully increased by increased mixing rates, including the CaCO₃ precipitation and the H₂S stripping reactions. Increasing the CO₂ flow-rate also had the advantage of speeding up the CaS dissolution, CaCO₃ precipitation and the H₂S stripping reactions. However, it affected the nature of the CaCO₃ crystals that formed. Mixtures of calcite and vaterite were produced and while the reaction was more rapid with increased CO₂ flow-rate, the proportion of vaterite to calcite also increased, most probably as a consequence of the direct effect of the CO₂ flow-rate on the solution pH and therefore on the preferential formation of one polymorph over the other, depending on the pH conditions. Increasing the CO₂ flow-rate did not appear to have a significant influence on the particle size.

The direct aqueous carbonation of CaS yielded a low-grade CaCO_3 product with very limited opportunities for useful applications (approximately 0.95 kg product, < 90 mass% as CaCO_3 for every 1 kg CaS processed). Therefore, the study continued in the development of an indirect carbonation process, with the focus of producing high-quality CaCO_3 or PCC.

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Supplementary Information to Chapter 4: The direct aqueous CaS carbonation process

Supplementary Information available regarding the direct aqueous CaS carbonation process include i) photograph, SEM images and FTIR spectrum of the CaS feed material (S4.1), ii) effect of pH on the solubility of CaCO_3 (S4.2), iii) the CO_2 speciation diagram in aqueous medium (S4.3), and iv) characteristics of the low-grade CaCO_3 products produced at various CO_2 flow-rates including SEM-EDS results, XRD results and PSA result and some low magnification SEM images and (S4.4).

S4.1. Calcine feed material characteristics



Figure S4.1.1 Photograph of the calcine feed material

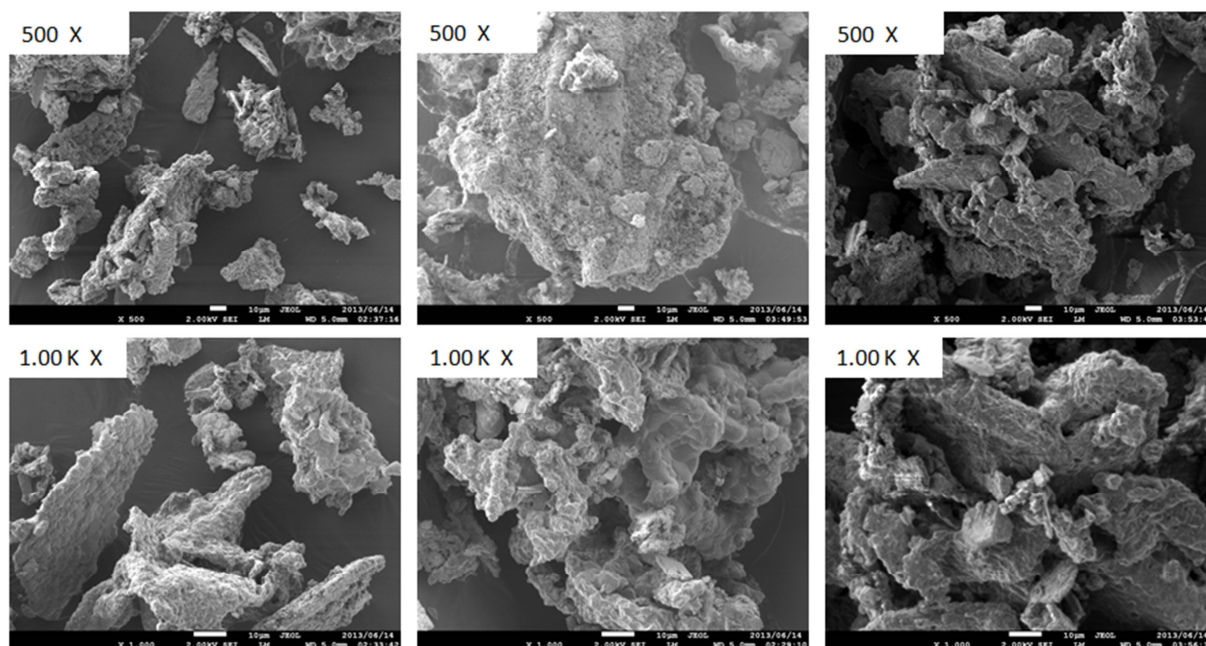


Figure S4.1.2 SEM micrograph of the calcine feed material at 500 × and 1000 × magnification

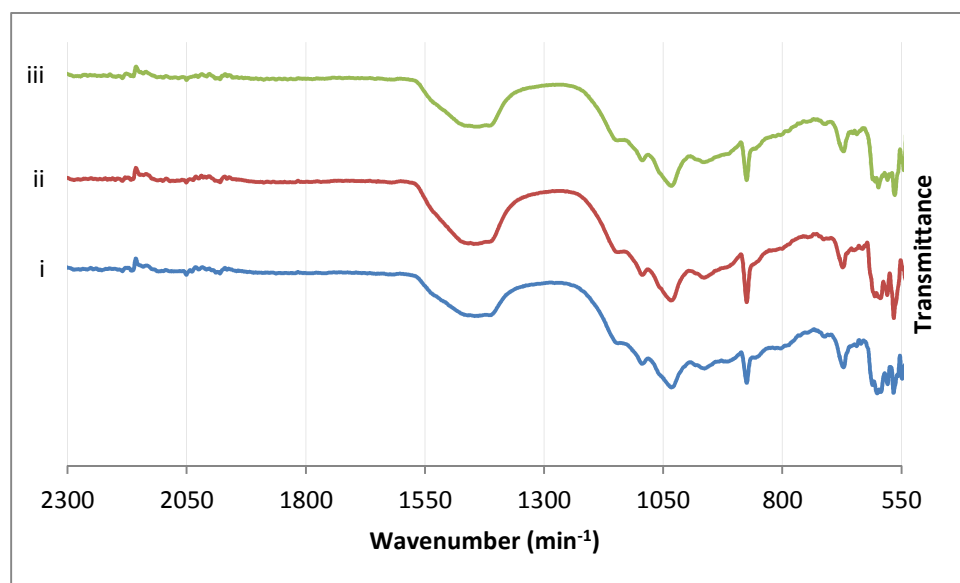
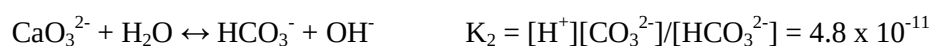


Figure S4.1.3 FTIR spectrum of the calcine feed material (triplicate)

S4.2. CaCO_3 solubility

Figure S4.2 shows the relationship between CaCO_3 solubility and pH in aqueous solution at a fixed temperature of 25°C and fixed pressure of 1 bar.

The pH dependence of the solubility of CaCO_3 was calculated (MS Excel 2010) from the following equations:



The carbonate ion from the CaCO_3 dissolution take two forms, CO_3^{2-} and HCO_3^- and therefore the solubility (S) is:

$$S = [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^{2-}]$$

or $S = [\text{Ca}^{2+}] = \sqrt{K_{\text{sp}} (1 + [\text{H}^+]/K_2)}$

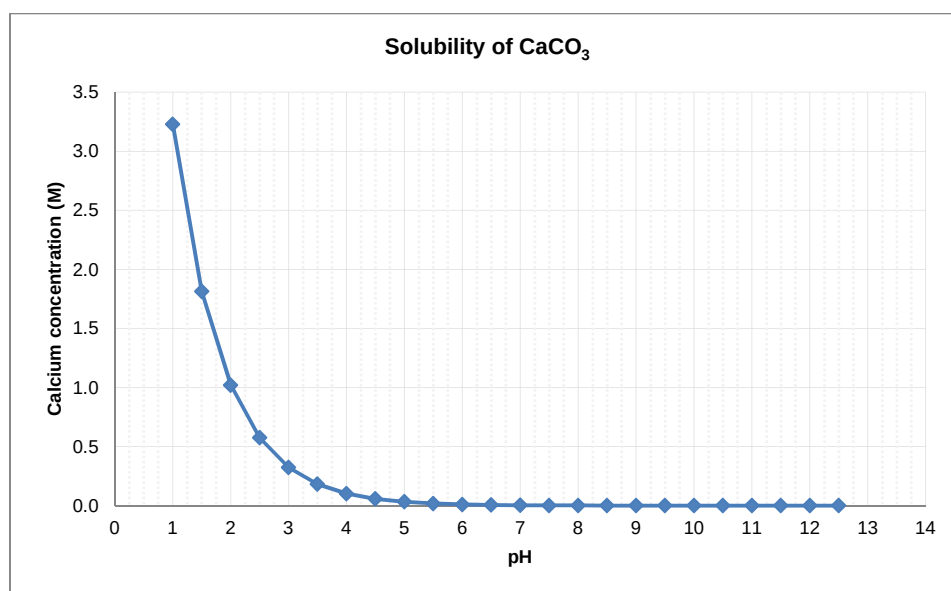


Figure S4.2 Effect of the pH on the CaCO_3 solubility at 25°C and 1 bar air pressure (MS Excel)

S4.3. Carbon dioxide speciation in aqueous medium

CO₂ dissolved into water occurs not only as dissolved CO₂ (Eq. (S4.3.1)), but also as carbonic acid, H₂CO₃ (Eq. (S4.3.2)). Carbonic acid is a weak acid that dissociates in two steps to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions (Eq. (S4.3.3) and (S4.3.4)). The CO₂ speciation diagram was obtained by calculating the fractional composition of the carbonate species in water using the dissociation constants for carbonic acid at 25°C. The concentrations of each species are described by the dissociation equations (Eq. (S4.3.3) and (S4.3.4)). The fractional composition was calculated from the dissociation constants ($K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$) (Perry & Green 1984) and the following two reactions:

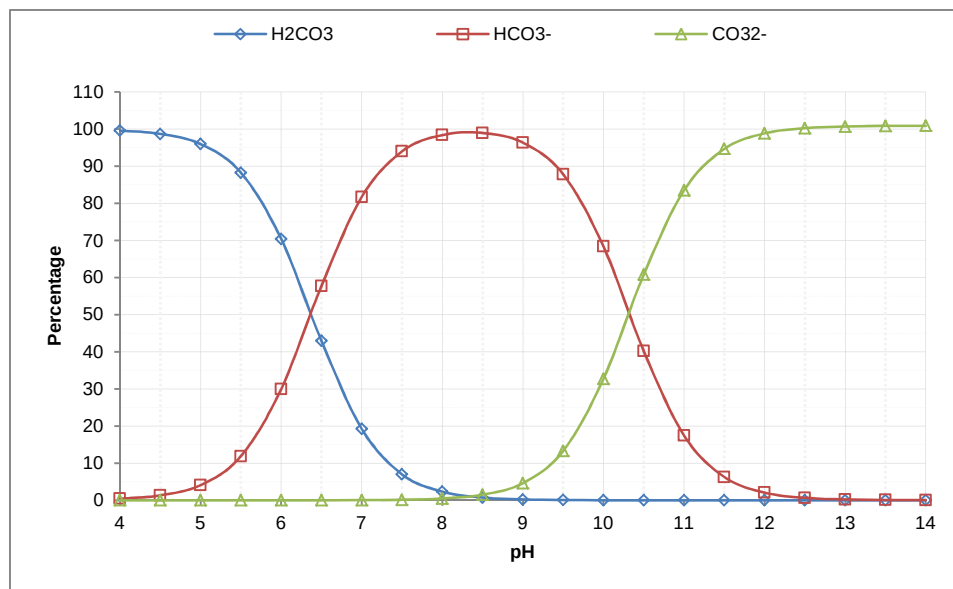
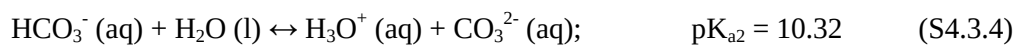
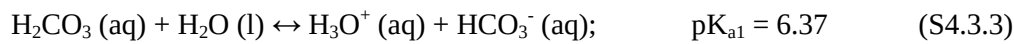


Figure S4.3 The carbon dioxide speciation diagram in aqueous medium (25°C, 1 bar)

S4.4. Characteristics of the low-grade CaCO_3 products produced via the direct aqueous CaS carbonation process

S4.4.1 SEM-EDS results

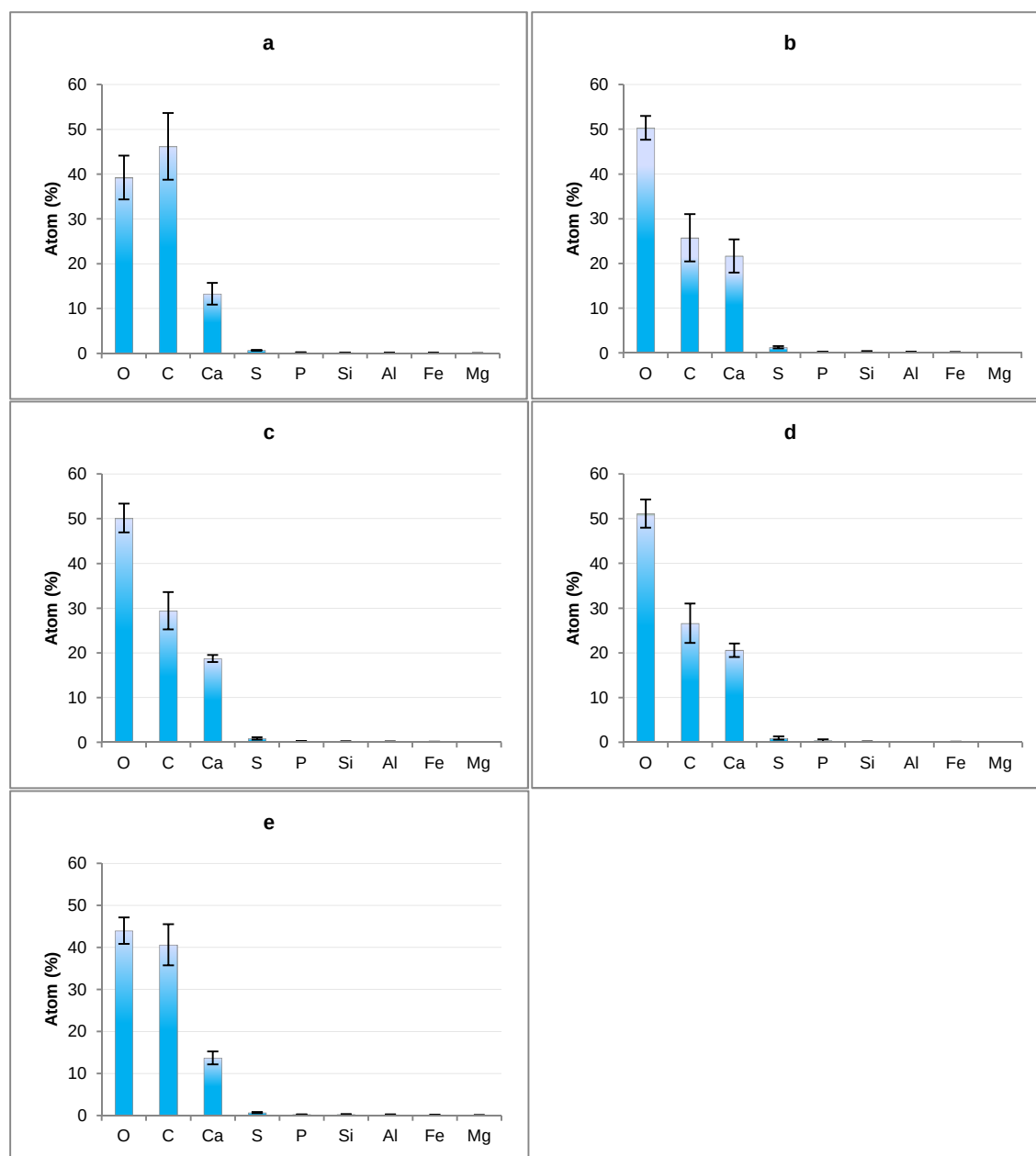


Figure S4.4.1 SEM-EDX elemental analysis of low-grade CaCO_3 produced at CO_2 gas flow-rates of a) 2.5, b) 8.8, c) 14.9, d) 29.3 and e) 44.0 l CO_2 /min/kg calcine, respectively. (CaS slurry containing 22.7 g/l as S; initial pH: 11.7; stirring rate: 600 min^{-1})

S4.4.2. XRD diffraction patterns of the low-grade CaCO_3 product from the direct aqueous carbonation process

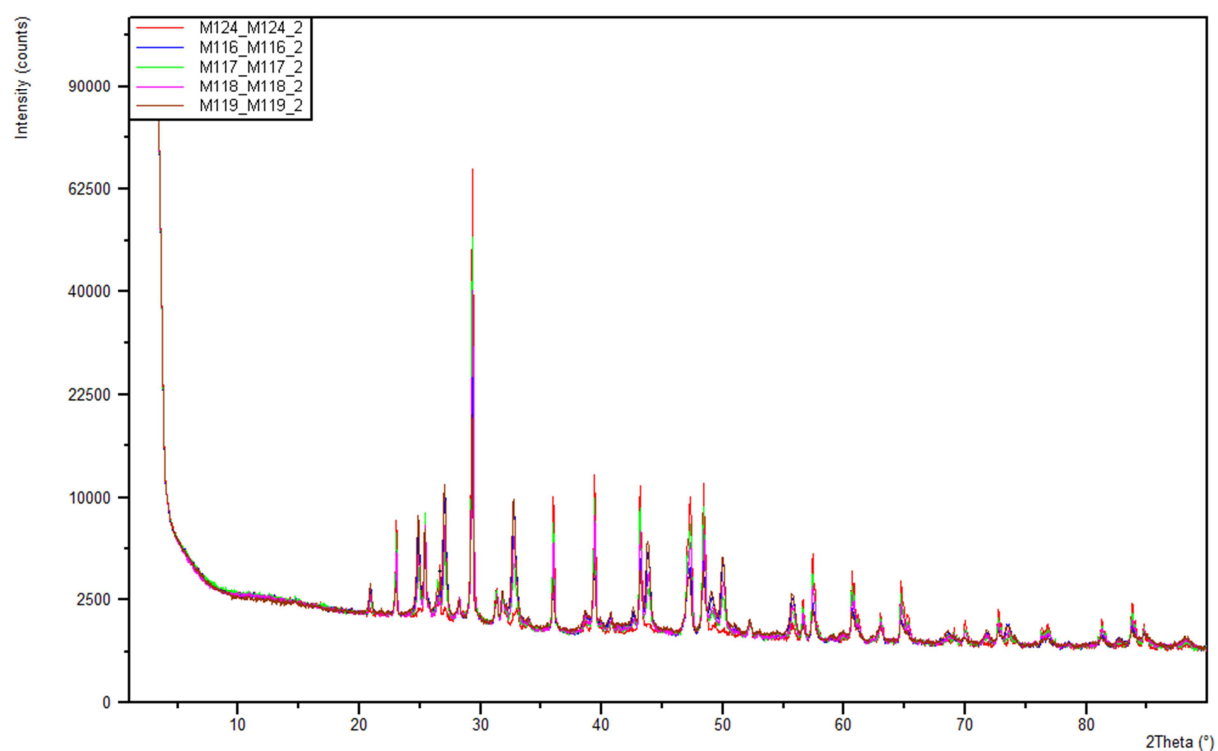


Figure S4.4.2 XRD diffraction patterns of low-grade CaCO_3 produced at CO_2 gas flow-rates of (a) 2.5, b) 8.8, c) 14.9, d) 29.3 and e) 44.0 $\ell \text{ CO}_2/\text{min/kg calcine}$, respectively. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

S4.4.3. Particle size analysis and low-magnification scanning electron microscopy images

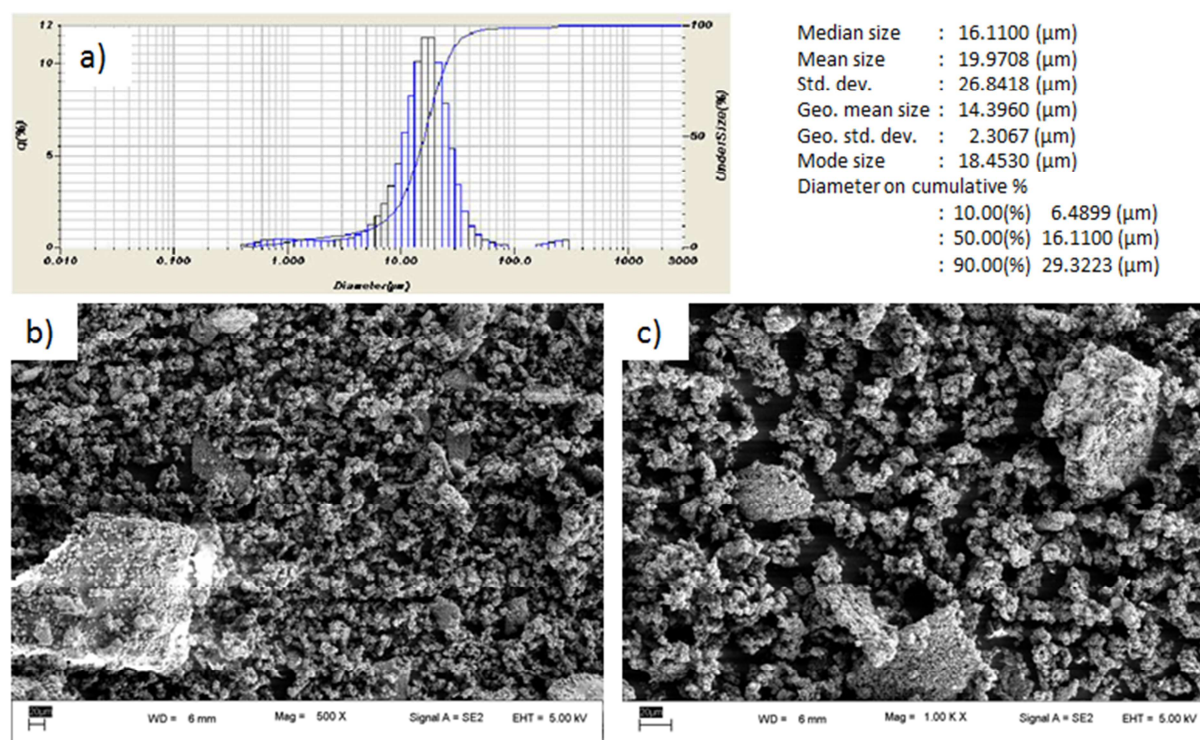


Figure S4.4.3.1 Particle size analysis a) and SEM images at b) 500 × magnification and c) 1000 × magnification of the low-grade CaCO_3 produced at 2.5 $\ell \text{ CO}_2/\text{min}/\text{kg}$ calcine flow-rate. (CaS slurry containing 22.7 g/l as S; initial pH: 11.7; stirring rate: 600 min^{-1})

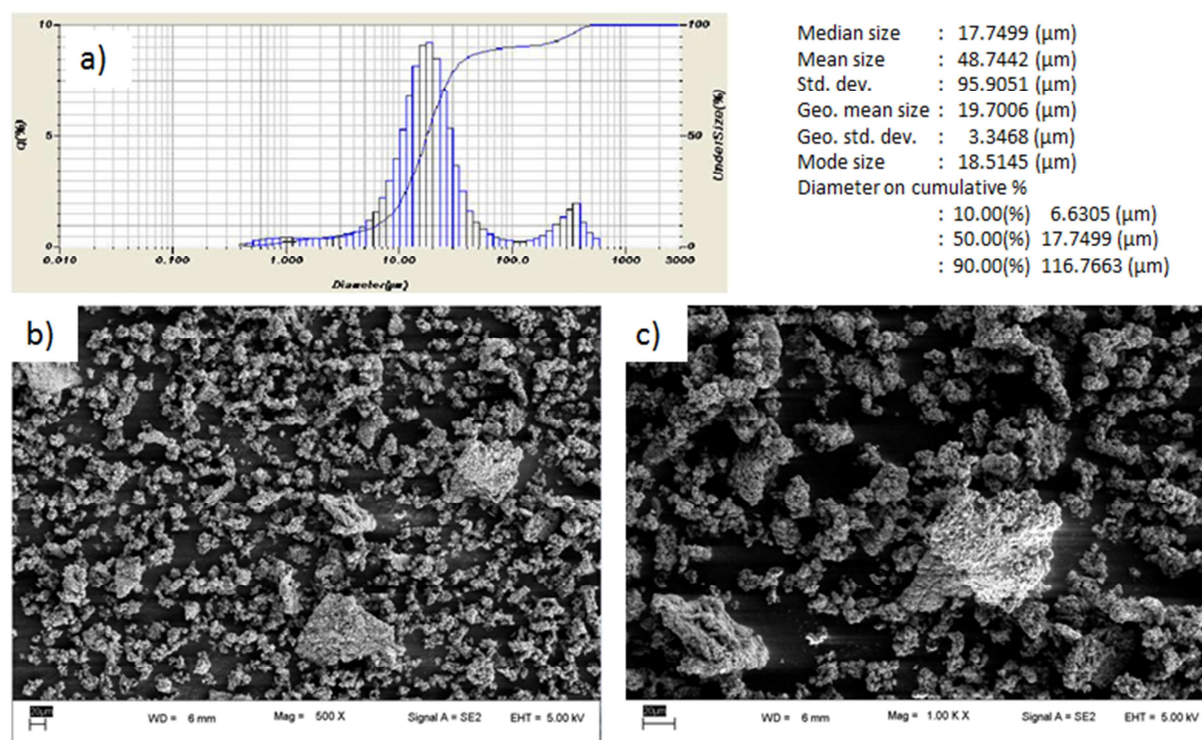


Figure S4.4.3.2 Particle size analysis a) and SEM images at b) 500 × magnification and c) 1000 × magnification of the low-grade CaCO_3 produced at 8.8 $\ell \text{ CO}_2/\text{min}/\text{kg}$ calcine flow-rate. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

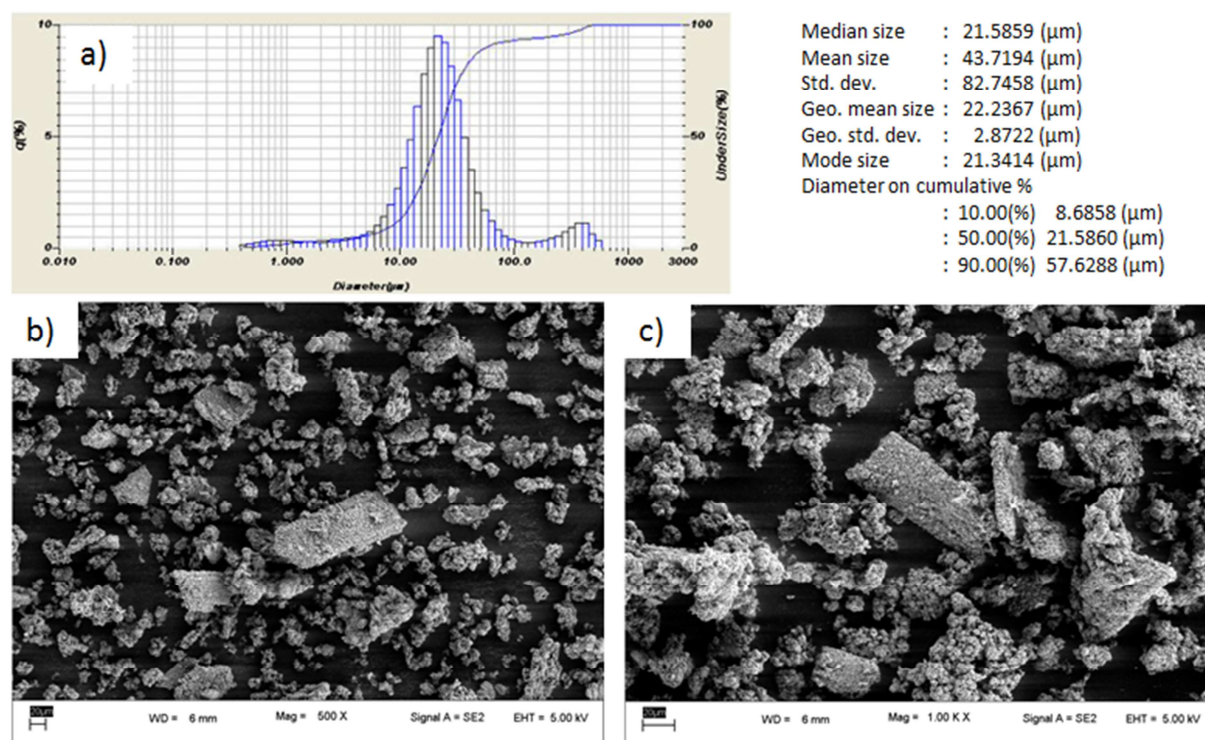


Figure S4.4.3.3 Particle size analysis a) and SEM images at b) 500 $\times$ magnification and c) 1000 $\times$ magnification of the low-grade CaCO_3 produced at 14.9 ℓ $\text{CO}_2/\text{min}/\text{kg}$ calcine flow-rate. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

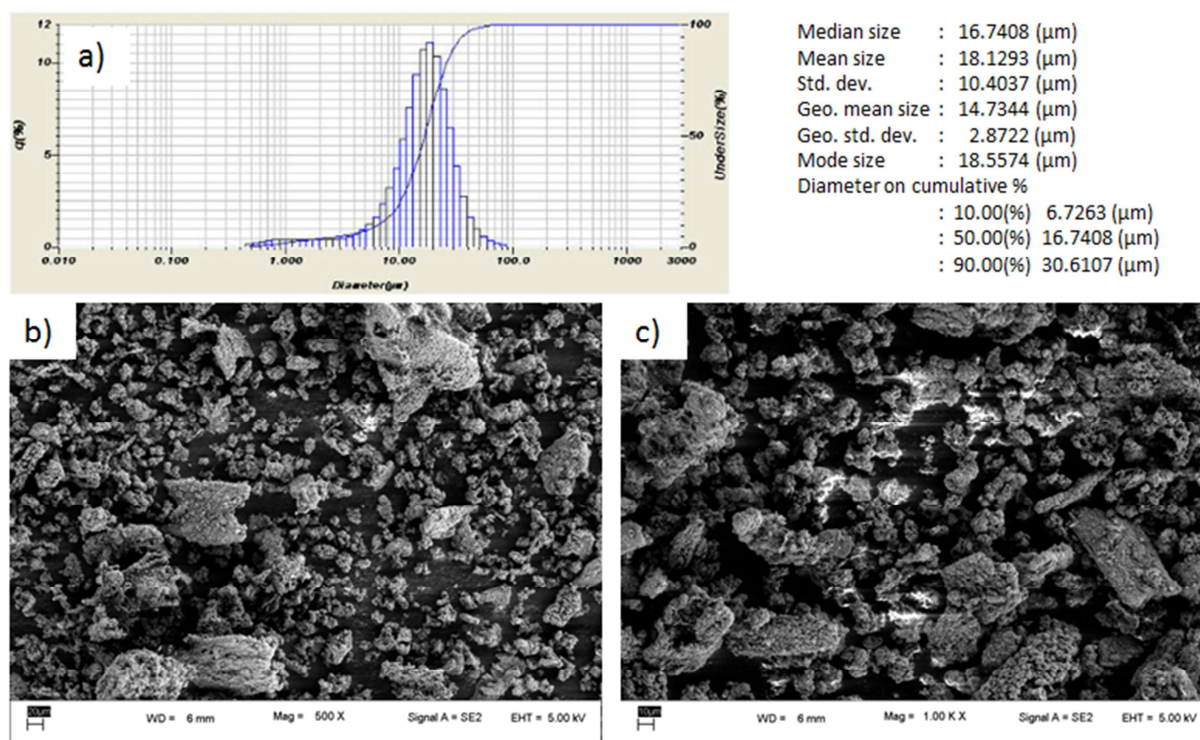


Figure S4.4.3.4 Particle size analysis a) and SEM images at b) 500 $\times$ magnification and c) 1000 $\times$ magnification of the low-grade CaCO_3 produced at 29.3 $\ell \text{ CO}_2/\text{min}/\text{kg}$ calcine flow-rate. (CaS slurry containing 22.7 g/ ℓ as S; initial pH: 11.7; stirring rate: 600 min^{-1})

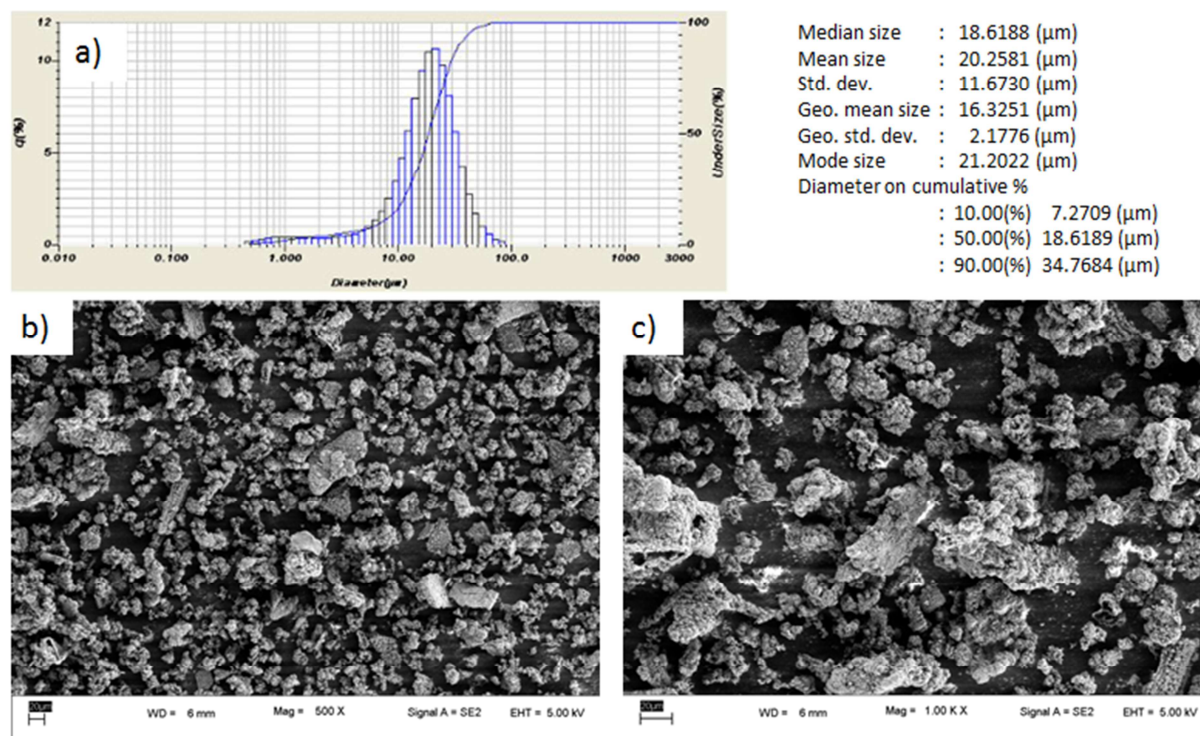


Figure S4.4.3.5 Particle size analysis a) and SEM images at b) 500 × magnification and c) 1000 × magnification of the low-grade CaCO_3 produced at 44.0 $\ell \text{ CO}_2/\text{min}/\text{kg}$ calcine flow-rate. (CaS slurry containing 22.7 g/l as S; initial pH: 11.7; stirring rate: 600 min^{-1})