

Chapter 3. Experimental set-up and analytical methods

In this chapter the feedstock, the experimental setup and analytical methods used in the study are described in detail. The design considerations for the main reactor unit and the experimental setups for both the direct and indirect mineral carbonation process routes are presented. The methods for wet analysis and the techniques used for the particle characterization are also described.

3.1 Feedstocks

Calcium sulphide (CaS) used in this study as the starting material was a calcined product produced from waste gypsum generated at an acid mine water neutralisation plant. Two batches of CaS (May 2011 and April 2012) were prepared by thermal reduction in a pilot plant facility (Ruto et al. 2011). The conversion of the waste gypsum into CaS was performed in an electrically heated kiln at 1080°C with duff coal as the reducing agent. CaS is unstable at ambient conditions; it oxidizes in dry air and decomposes in moist air. The batch calcined samples were kept well closed in sealed plastic bags inside a container filled with nitrogen gas to insure their stability and avoid spontaneous oxidation to CaSO₄.

The CaS content of the batch 'May 2011' calcined feed material was determined by a wet analytical method (Appendix A.2.1.). The purity was 50.7 ± 0.85 mass% (as CaS). The degree of purity of the batch 'April 2012' calcined sample was initially determined by X-ray diffraction and by the wet analytical method before each experimental run. The purity was 81.7 ± 0.83 mass% (as CaS). The first batch of calcine (May 2011) was prepared under experimental conditions (gypsum fed directly into the rotary kiln) and the second batch (April 2012) after process optimisation (gypsum was first converted to bassanite at 200°C prior to thermal reduction).

Gaseous carbon dioxide (100% CO₂; Air Liquide, South Africa) was used i) to induce CaS dissolution in some of the experiments, ii) to strip hydrogen sulphide gas (H₂S) from solution and iii) to carbonate the solubilized calcium derived from CaS dissolution during all experiments.

Gaseous hydrogen sulphide (100% H₂S; Pure Gas, South Africa) was used to induce the dissolution of CaS in the two-step, indirect mineral carbonation route in an effort to increase the yield of high purity CaCO₃.

3.2 Experimental setup and equipment

CaS dissolution and the calcium carbonation/H₂S stripping reactions were performed in Perspex stirrer tank batch reactors. The experimental set-up is shown in Figure 3.1. The reactor (Figure 3.2 (a)) was equipped with four equally spaced baffles and a sparger with small diameter (< 1mm) openings for the introduction of the gas. A mechanical overhead stirrer (RW 20 digital from IKA[®]-Werke GmbH & Co. KG, Germany; Appendix A.1.3) and a Rushton turbine impeller (Figure 3.2 b)) (manufactured by Manten Engineering, South Africa) were used for mixing. A rotameter (Fisher & Porter, different models for various flow-rates; Appendix A.1.1) was used to control the gas flow-rate. The Rushton turbine impeller designed for this study had six vertical blades fixed onto a disk. This disk design ensured that most of the torque of the motor was dissipated at the tips of the agitator. All experiments were conducted at atmospheric pressure and room temperature.

The concept for the reactor unit was developed based on two main criteria. First, the reactor had to be suitable for performing precipitation experiments in a controlled and reproducible manner. Second, no H₂S gas was to escape from the reactor. In Figure 3.3, a photograph is shown of the completely mounted reactor unit and other components.

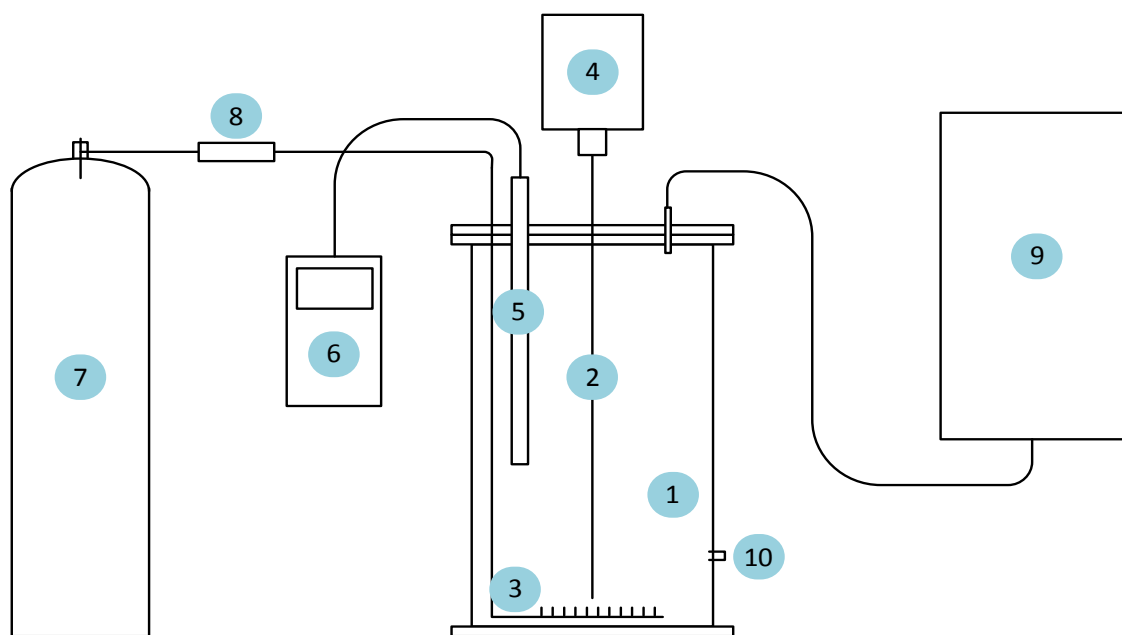


Figure 3.1 Schematic diagram of the experimental set-up used for CaS dissolution and calcium carbonation / H₂S stripping: 1) closed stirred tank reactor; 2) Rushton turbine; 3) sparger; 4) overhead stirrer; 5) pH, EC, temperature probe; 6) data logger; 7) gas cylinder (CO₂ or CO₂/N₂ or H₂S); 8) rotameter; 9) H₂S scrubber; 10) sampling port

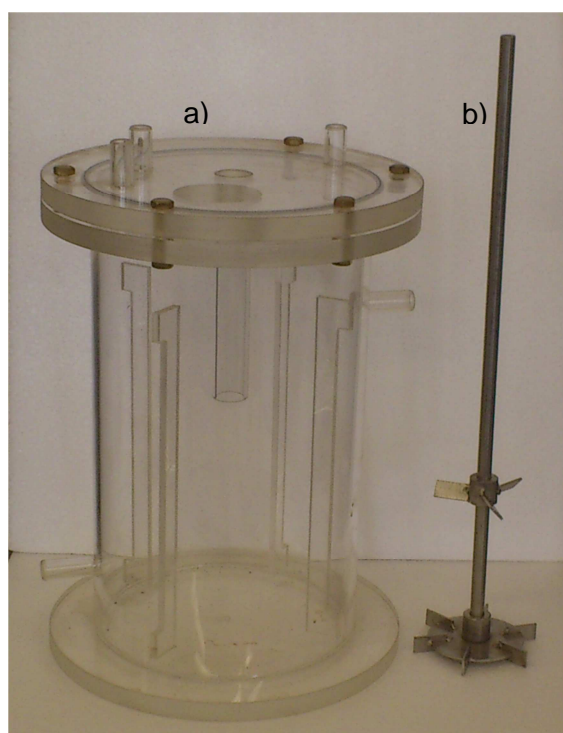


Figure 3.2 Photograph of the a) 3-litre CSTR reactor and b) Rushton turbine



Figure 3.3 Photograph of the completely assembled experimental set-up

3.3 Experimental procedure for PCC production

The degree of purity of the calcine sample, expressed as % CaS, was determined by X-ray diffraction (XRD). The calcine sample was subjected to aqueous dissolution, carbonation and stripping in either a one-step (direct) or a two-step (indirect) process. The one-step process involved the simultaneous dissolution and carbonation of CaS in a single reactor (Figure 3.4). In the two-step process, either CO₂ gas (Figure 3.5) or H₂S gas (Figure 3.6) was used to induce CaS dissolution. The characteristic of the indirect process was the adoption of two separate aqueous steps for i) the dissolution of CaS and ii) the carbonation of solubilized calcium. The advantage of this approach over the direct process is that each individual step can be optimized separately, incorporating further steps if needed. In addition, the adoption of this dual approach provided insight into the conditions at which CaCO₃ of different grades can be produced.

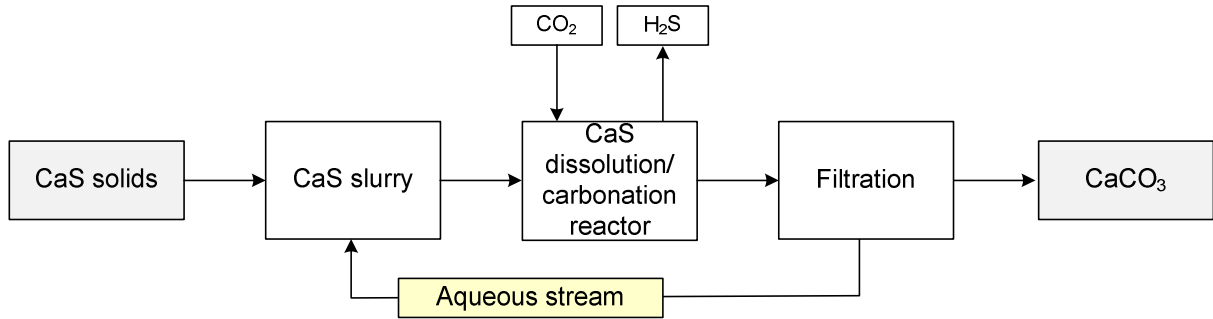


Figure 3.4 Process flow diagram for the one-step, direct aqueous mineral carbonation process

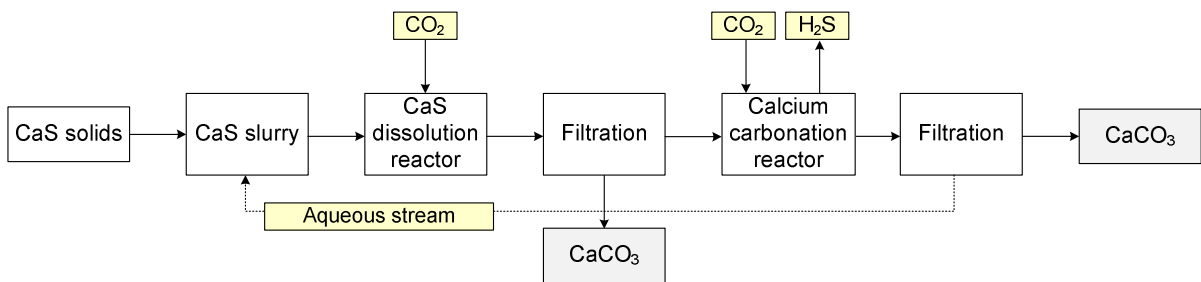


Figure 3.5 Process flow diagram for the two-step, indirect mineral carbonation using CO₂ gas for CaS dissolution

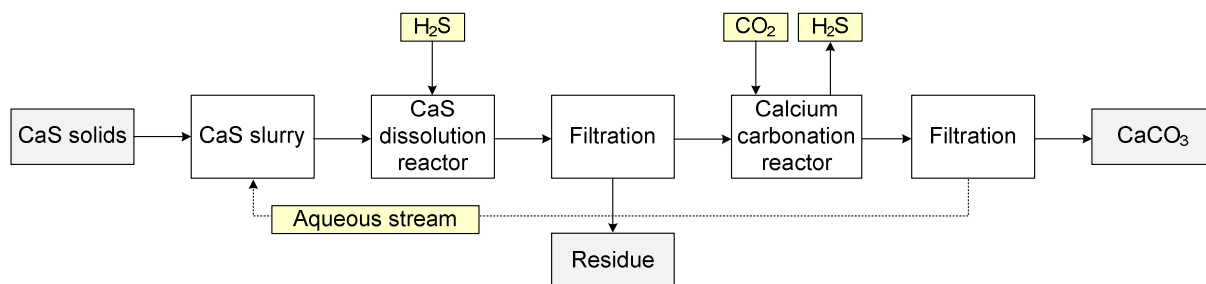


Figure 3.6 Process flow diagram for the two-step, indirect mineral carbonation using H₂S gas for CaS dissolution

Throughout the one-step and the two-step processes, sub-samples of the CaS suspensions and the Ca-rich solutions were collected from the reactors at regular intervals and filtered using 0.45µm PALL acrodisc PSF GxP/GHP membranes (Microsep (Pty) Ltd, South Africa). The filtrates were analysed for their calcium and sulphide contents. Upon completion of the experiments, the final suspensions were removed from the reactor and filtered using 0.45µm Millipore HA membranes (Microsep (Pty) Ltd, South Africa); the wet solids retained on the filter (also known as the filter cakes) were dried at 60°C for 24h and characterized.

3.4 Analytical methods

Suspensions and filtrates analysis

The pH, temperature and electrical conductivity of the suspensions contained in the reactor were recorded over time throughout the dissolution/stripping/carbonation process using a Hanna HI 9828 multi-parameter logger, a HI 769828/4 probe body with a HI769828-1 pH/ORP sensor and HI 769828-3 EC sensor (Hanna Instruments, South Africa; Appendix A.1.2). Before every experimental run, pH and conductivity calibrations were performed using certified standard calibration solutions, supplied by Hanna Instruments SA.

Total sulphide concentration (sum of dissolved H_2S , HS^- and S^{2-}) of the filtrates was determined iodometrically, where an excess of added iodine was back-titrated with sodium thiosulphate. The analysis was carried out manually on filtered (for soluble sulphide) and unfiltered (for total sulphide, i.e. in both solution and solid phases) samples according to procedures 4500-S²⁻/Iodometric method described in Standard Methods (Clesceri et al. 1989). The sulphide in the solid phase and the sulphide stripped from solution were calculated by difference.

The concentration of calcium ions in solution was determined by direct complexometric titration with ethylenediamine tetraacetate (EDTA) according to the procedure 3500-Ca/EDTA titrimetric method (Clesceri et al. 1989) or by ICP-MS at an accredited laboratory (Consulting and Analytical Services, CSIR, Pretoria, South Africa).

Solids characterization (feedstock and filter cakes)

In addition to the chemical composition, the behaviour of particulate materials is often dominated by the physical properties of the particle. Some of the important physicochemical properties determined on selected solid samples during the study included: polymorphic and morphology analysis, particle size, specific surface area, pore volume, pore size, density and elemental analysis. The instrumentation/technique and the characterization facility used during the study are listed in Table 3.1.

Table 3.1 Analytical techniques used for solids characterisation

Instrumentation or technique	Particle characteristic	Characterization facility
Powder X-ray diffraction (XRD)	Crystallinity and polymorph	XRD Analytical and Consulting cc (Dr S Verryn)
Fourier transform infrared spectroscopy (FTIR)	Polymorphic form	National Centre for Nanostructured Materials (M de Beer, author)
Scanning electron microscopy (SEM)	Surface analysis (Morphology)	National centre for nanostructured materials (S Eggers and C Maepa)
Energy dispersive X-ray spectrometry (EDS) attached to SEM	Elemental analysis	National Centre for Nanostructured Materials (S Eggers)
Particle size analyser (PSA)	Particle size distribution	Consulting and Analytical Services (C Pretorius)
Brunauer-Emmett-Teller (BET)	Specific surface area, pore volume and pore size	National Centre for Nanostructured Materials (K Selatile)
Pycnometer	Bulk density	National Centre for Nanostructured Materials (Y Mnqanqeni)

Powder X-ray diffraction patterns (XRD) were obtained from a PANalytical X'Pert Pro powder diffractometer using Cu-K α radiation with X'Celerator detector. XRD patterns taken at high angles ($2\theta \approx 10 - 90^\circ$) were carried out using a step size of 0.02° and scan speed of 0.03° per second. The samples for the feed material and products were prepared using a back loading preparation method. The phases were identified using X'Pert Highscore plus software and the relative phase amounts (mass%) were estimated using the Rietveld quantitative analysis, a powerful method for determining the quantities of crystalline and amorphous components in multiphase mixtures (Hiller 2013).

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used to measure the lattice vibrations of the CaCO₃ products. The infrared spectra were recorded at room temperature with a Perkin-Elmer Spectrum 100 Fourier Transform Infrared Spectrometer (FTIR) equipped with a Perkin-Elmer Precisely Universal Attenuated Total Reflectance (ATR) sampling accessory equipped with a diamond crystal. The Perkin-Elmer Spectrum 100 FTIR is an optical system that gives data collection over the total range of 7800 to 370 cm⁻¹ with a best resolution of 0.5 cm⁻¹ with a mid-infrared detector as standard (DTGS, deuterated triglycine sulphate). The instrument was connected to a PC which utilized Spectrum software to control the instrument and to record the spectra.

The powdered sample was placed on the crystal and a force was applied to ensure proper contact between the sample and the crystal. The spectral study was extended over the range 4000–400 cm⁻¹,

with a resolution of 4 cm^{-1} and 32 accumulations. The spectra were analysed using the Spectrum 100 software (Perkin Elmer).

High-vacuum scanning electron micrographs (SEM images) were collected using a JEOL JSM7500 microscope to obtain information on morphologies and size distribution of the solid materials. Samples were dispersed on carbon tape and sputter-coated with a thin, conductive layer of gold using an Emitech K950X sputter coater. The acceleration voltage was 2.00 kV.

Energy Dispersive X-Ray Analysis (EDX), also referred to as EDS, is an x-ray technique used to identify the elemental composition of materials. The EDX system used was attached to an SEM instrument (FIB-SEM, Auriga from Carl Zeiss) where the imaging capability of the microscope identified the specimen of interest. EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. X-ray intensities are measured by counting photons and the precision obtainable is limited by statistical error. For major elements it is usually not difficult to obtain a precision (defined as 2σ) of better than $\pm 1\%$ (relative), but the overall analytical accuracy is commonly nearer to 2%, owing to factors such as uncertainties in the composition of the standards and errors in the various corrections that need to be applied to the raw data.

The particle size analysis was carried out using a Horiba LA-950 particle size analyser with a detection range of 0.01 to 3000 μm . The Horiba LA-950 particle size analyser uses the laser diffraction method to measure size distributions. In the laser diffraction (LD) method, the detection and analysis of the angular distribution of dispersed light produced by a laser beam passing through a dilute dispersion of particles is directly related to their size. The Mie scattering theory used allows the conversion from the distribution of intensity (scattered light energy) to volume measurements to be carried out.

The most common technique to determine the specific surface area and pore volume of solid particles is the Brunauer-Emmett-Teller method (BET). A Tristar II 3020 BET from Micromeritics was employed to determine the specific surface areas and the pore volumes by using nitrogen adsorption at the liquid nitrogen temperature (-196°C or 77K). The absolute pressure measurement range for the instrument is 0 to 50 mmHg with a resolution within 0.05 mm Hg, an accuracy within 0.5% and linearity within 0.25% of full scale. Surface areas as low as $0.01 \text{ m}^2/\text{g}$, total surface area of 0.1 m^2 and a pore volume from $4 \times 10^{-6} \text{ cm}^3/\text{g}$ can be measured with the standard nitrogen system. Prior to analysis, the samples were preconditioned to remove the humidity adsorbed to the particle surfaces. This de-gassing procedure was accomplished by applying elevated temperatures (120°C for 20 hours) to the samples in conjunction with vacuum in the Micromeritics VacPrep 061 sample preparation device.

The pore size was estimated by the BJH (Barrett, Joyner, Halenda) equation and statistical thickness (t-plot) equation. The BJH equation is the modified Kelvin equation and predicts the pressure at which the adsorptive spontaneously condenses (and evaporates) in a cylindrical pore of a given size.

The densities of the samples were measured by a helium gas pycnometer (AccuPyc II 1340) from Micromeritics at room temperature (24°C). This analytical technique uses a gas displacement method to measure the volume accurately. Instrument analysis reproducibility is typically within $\pm 0.01\%$ of the nominal full-scale cell chamber volume, with accuracy within 0.03% of reading, plus 0.03% of sample capacity. Helium gas was used as the displacement medium for this study. The sample was sealed in a compartment of known volume, the helium gas admitted and then expanded into another precision internal volume. The measured pressures before and after expansion were used to compute the sample volume. This volume was divided into the sample mass to yield the gas displacement density.

References

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