Appendix A: **Equipment and analytic method verification and uncertainties.**

This appendix includes information on technical data regarding the equipment, instrumentation and additional analytical methods used during this study. The calibration curves for the rotameters used are available in A.1.1 and the technical data on equipment and instrumentation in A1.2 to A.1.5. Details on the analytical methods are discussed in section A.2.

A.1. Equipment

A.1.1 Rotameters and calibration curves used during the study

Fischer & Porter Model no.	Tube reference	Float	Gauge pressure (kPa)	Gas source	Range (Nℓ/min)	Calibration curve
10A6132M/B10	FP-1/8-08-G-5/81	BG-18	50	CO_2	0 - 0.45	Figure A.1.1
10A6132M/B10	FP-1/8-08-G-5/81	BG-18	200	CO_2	0 - 0.7	Figure A.1.2
10A6131M/T62	FP-1/8-08-P-3/37	CA-18	100	CO_2	0 - 1.6	Figure A.1.3
10A6132M/T62	FP-1/8-20-G-5/81	SA-18	100	CO_2	0 - 2.5	Figure A.1.4
10A6131M/T62	FP-1/8-20-P-3/37	SS-18	100	CO_2	0 - 4.0	Figure A.1.5
10A6132M/T62	FP-1/4-25-G-5/81	CD-14	100	CO_2	0 - 16	Figure A.1.6
10A6131M/T62	FP-1/8-08-P-3/37	CA-18	200	H_2S	0 - 2.5	Figure A.1.7

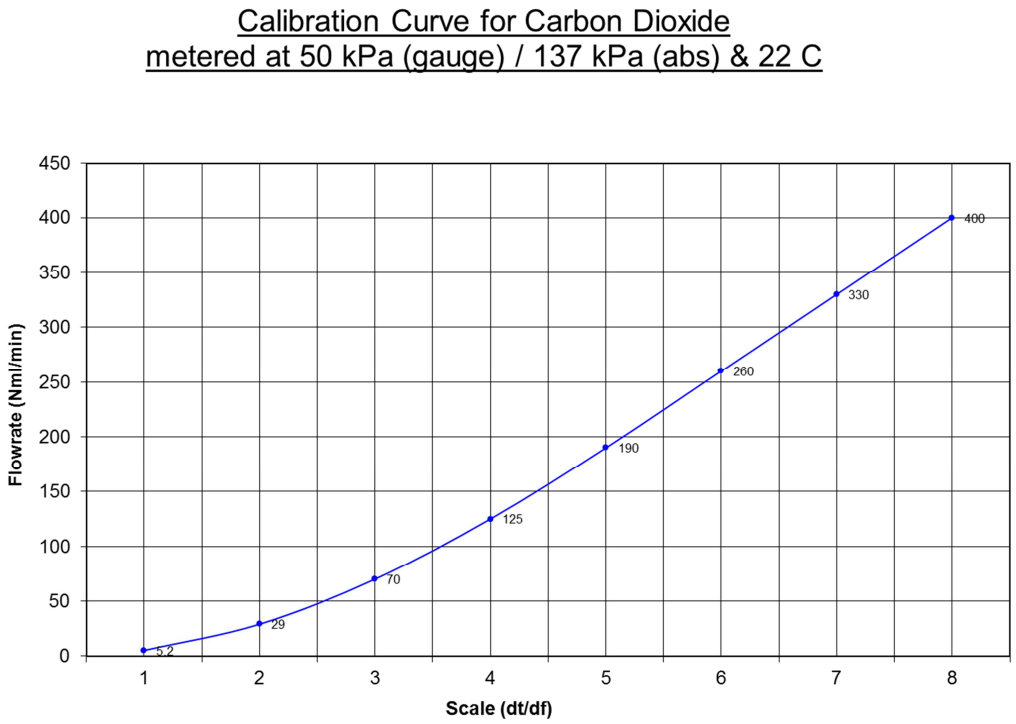

Figure A.1.1. Fisher & Porter model 10A6132M/B10; Tube FP-1/8-08-G-5/81; Float BG-18

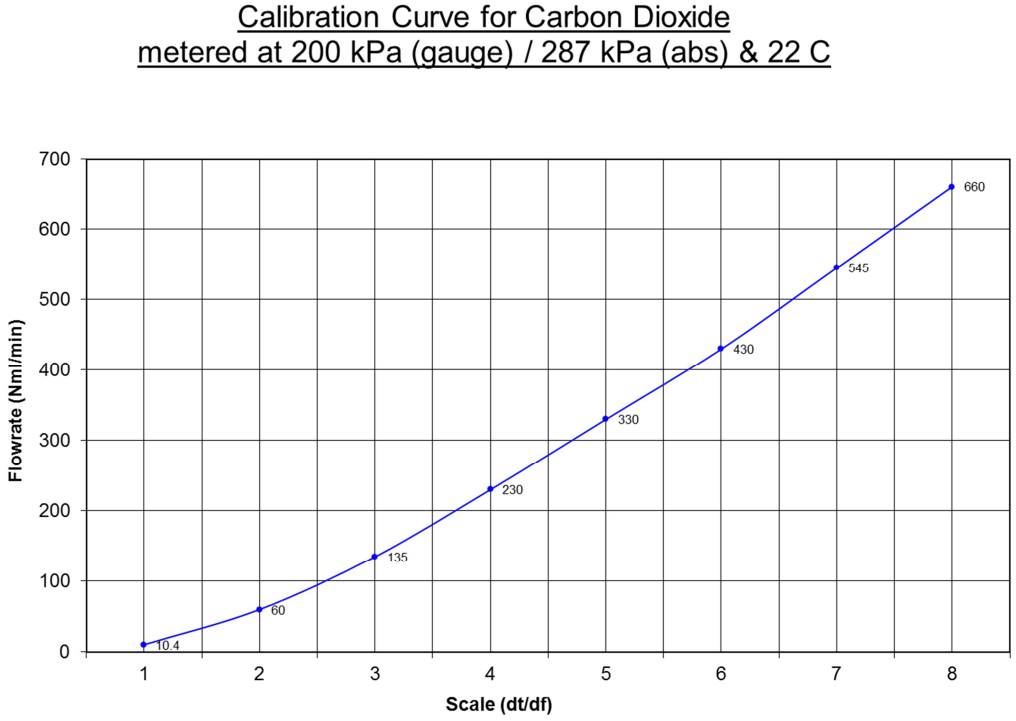

Figure A.1.2. Fisher & Porter model 10A6132M/B10; FP-1/8-08-G-5/81; BG-18

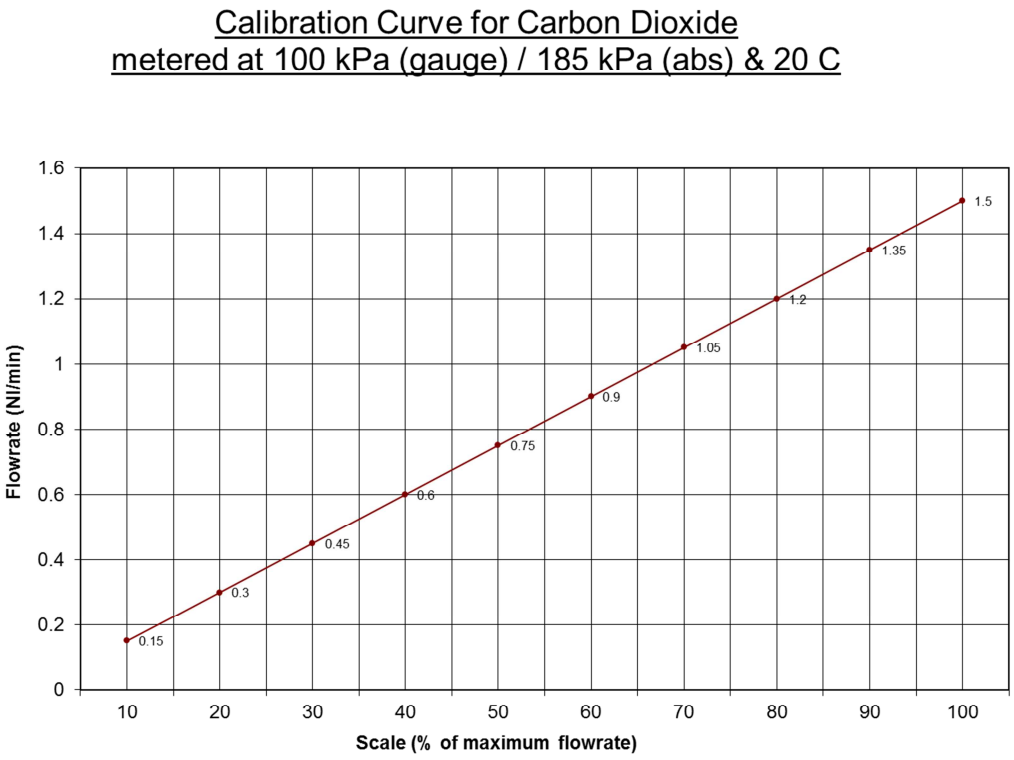

Figure A.1.3. Fisher & Porter model 10A6131M/T62; FP-1/8-08-P-3/37; CA-18

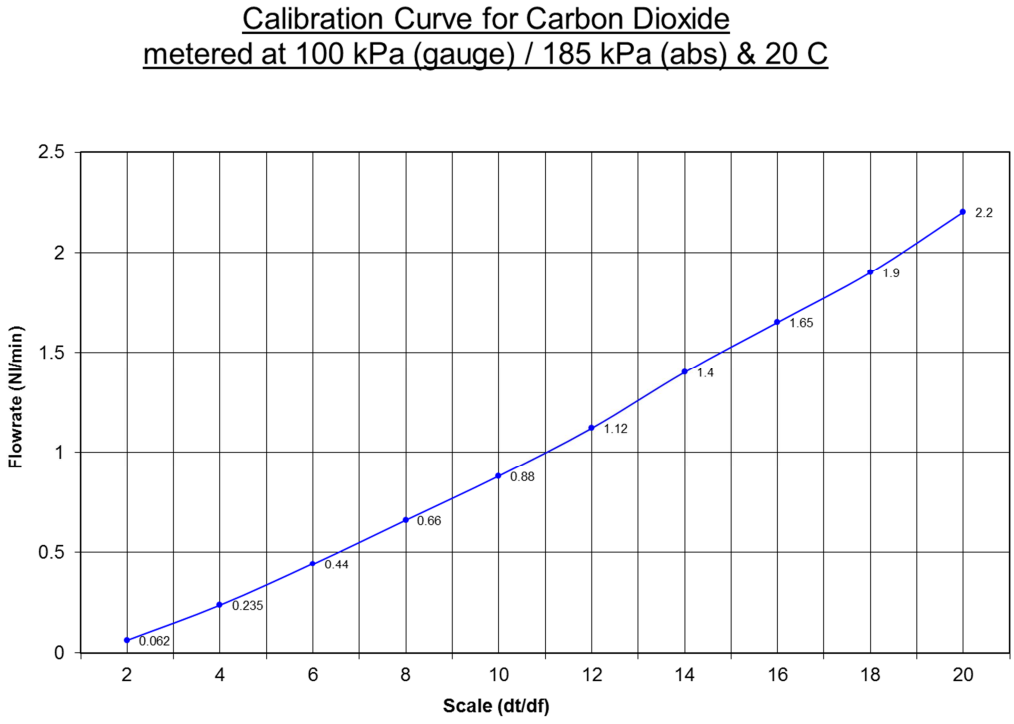

Figure A.1.4. Fisher & Porter model 10A6132M/T62; FP-1/8-20-G-5/81; SA-18

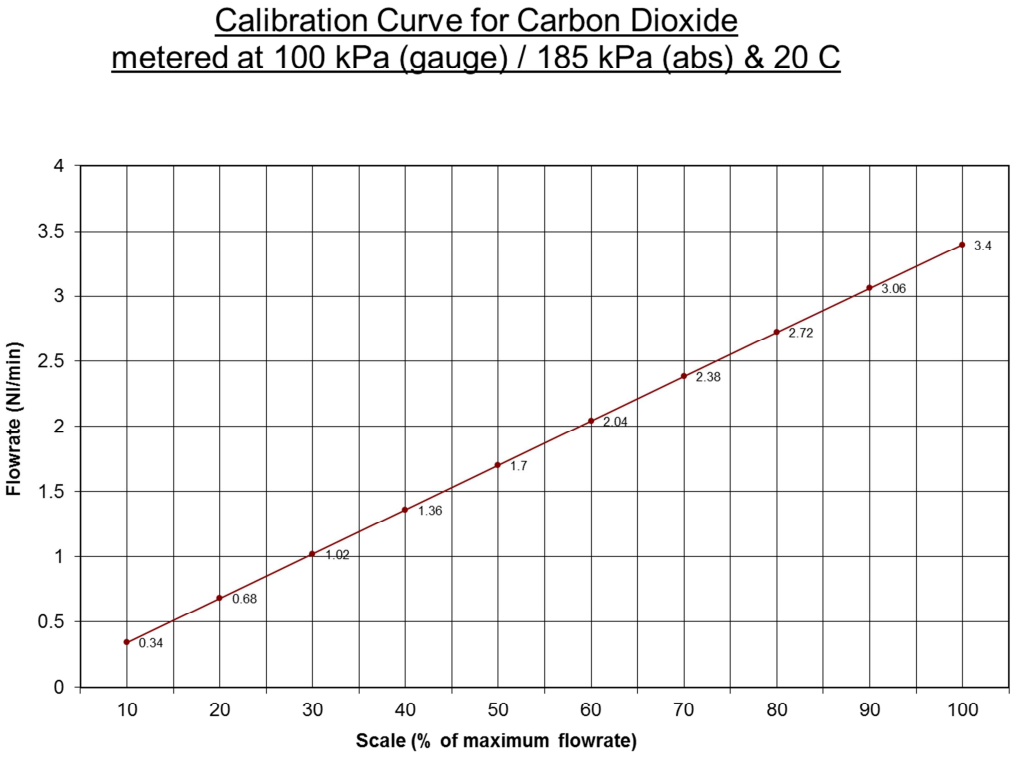

Figure A.1.5. Fisher & Porter model 10A6131M/T62; FP-1/8-20-P-3/37; SS-18

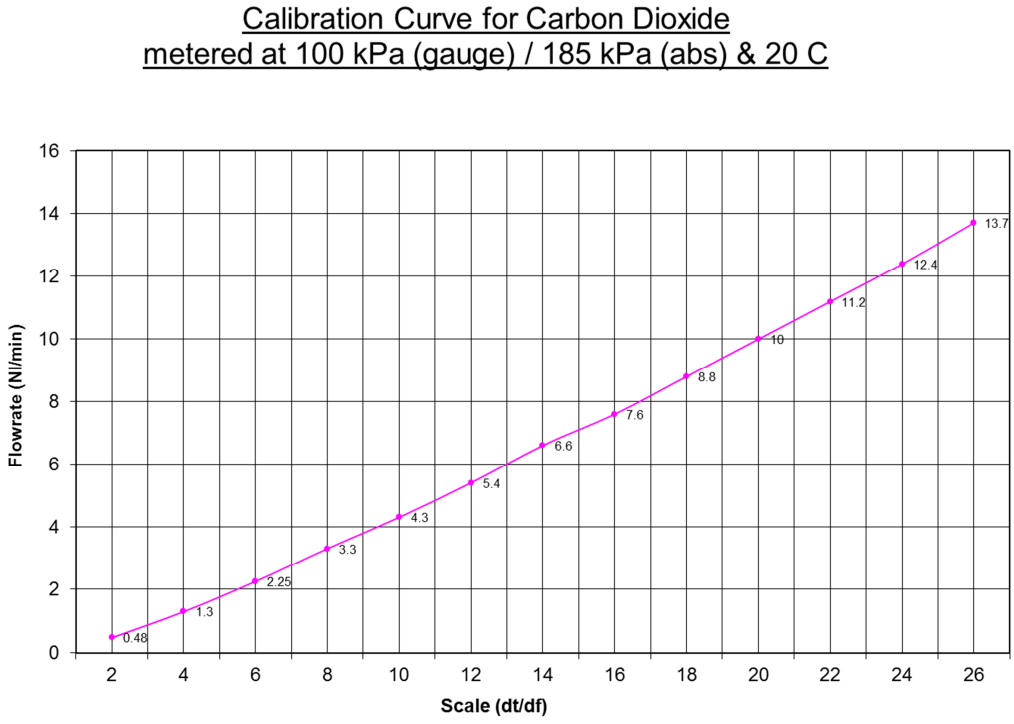

Figure A.1.6. Fisher & Porter model 10A6132M/T62; FP-1/4-25-G-5/81; CD-14

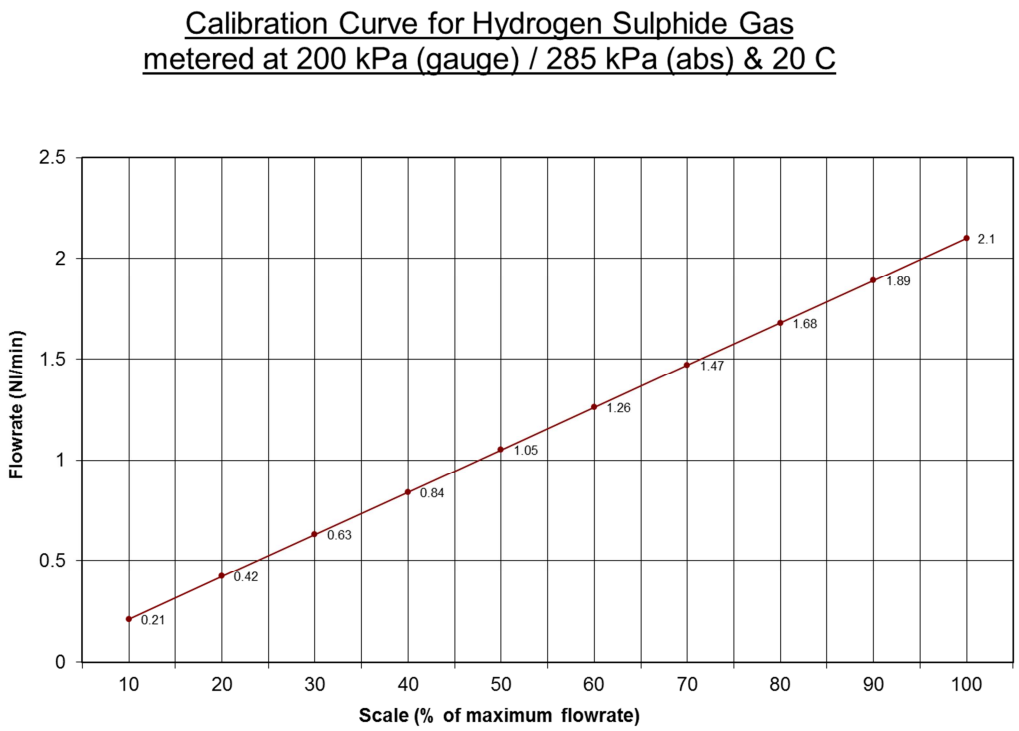

Figure A.1.7. Fisher & Porter model 10A6131M/T62; FP-1/8-08-P-3/37; CA-18

A.1.2 Multi-parameter logger

The Hanna HI 9828 multi-parameter logger, with the HI 769828/4 probe body, HI769828-1 pH/ORP sensor and HI 769828-3 EC sensor, was used to log the pH, EC and temperature for all experimental studies. The measurement type and range of the HI769828-1 pH/ORP sensor is pH (0.00 to 14.00); mV(pH) (± 600.0) and mV (± 2000.0). The measure type and range of the HI 769828-3 EC sensor is EC (0.000 to 200.000 mS/cm). The instrument has a logging memory of up to 60 000 samples with 13 measurements each and a logging interval from 1 second to 3 hours. The following set-up for the instrument was used throughout the study:

Measurement setup:

- pH; mV of pH input; ORP; D.O.; % saturation; salinity: Enabled
- Conductivity: Auto – auto ranging both uS/cm and mS/cm ranges

System set-up:

- Log interval: Logging time interval was 5 seconds.
- Reference temperature: 25°C
- Temperature coefficient: 1.90 %/°C

Calibration

- pH calibration: 3-point calibration with standard buffers at pH 4.01 (HI-5004 , pH 7.01 (HI-5007) and pH 10.01 (HI-5010)
- Conductivity calibration: Single point calibration using a standard solution with a conductivity value close to the sample being measures – 84 µS/cm (HI-7033L); 1413 µS/cm (HI-7031L); 5000 µS/cm (HI-7039L); 12880 µS/cm (HI-7030L).

Table A.1.2 Measurement specifications for the Hanna HI 9828 multi-parameter logger

	Temperature	**pH**	**Conductivity**
Range	-5.00 to 55.00°C	0.00 to 14.00 pH ± 600.0 mV	0.000 to 200.000 mS/cm
Resolution	0.01°C	0.01 pH 0.1 mV	1 µS/cm from 0 to 9999 µS/cm 0.01 mS/cm from 10.00 to 99.99 mS/cm 0.1 mS/cm from 100.0 to 400.0 mS/cm
Accuracy	± 0.15°C	± 0.02 pH ± 0.5 mV	± 1% of reading or ± 1 µS/cm whichever is greater

A.1.3 Overhead stirrer

The overhead stirrer used in the experimental setup was an IKA RW 20.n. mixer. It is suitable for liquids with a low or a high viscosity and can successfully mix up to 20 ℓ at a time (IKA Works Inc 1995). The mixing speed can be accurately adjusted between 60 min^{-1} and 2 000 min^{-1} at 50Hz AC or 72 $min^{-1}$and 2 400 min^{-1} at 60Hz AC. The power output, torque and rotational speed of the mixer were regarded as constant with a measuring fault of ± 0.5% (IKA Works Inc 1995).
The RW20 digital laboratory stirrer can be used to stir and mix liquids of low to medium viscosity with various stirring tools. It is designed for use in laboratories.

Table A.1.3 Technical data on the IKA RW 20.n. overhead mixer

Parameter	**Unit**	**Value**
Speed range: 50 Hz stage I 50 Hz stage II	min^{-1} min^{-1}	60 - 500 240 - 2000
Max. torque stirrer shaft (100 min^{-1} stage I)	Ncm	150
Permitted on-time:	%	100
Speed adjustment:		Knebelknopf (toggle)
Speed display:		LED - Display
Measurement fault:		max.±0,5% ±30 Digit
Nominal voltage:	VAC	230 ±10%
Frequency:	Hz	50
Input power:	W	72
Power output: (short term)	W	35
Power output: (constant operation)	W	20 ± 35
Overall efficiency:	%	40
Operating position:		On stand, clamping chuck, pointing down
Drive:		Rib-cooled capacitor motor with friction wheel drive and subsequent 2-stage toothed gear train
Maximum stirring: quantity - water:	ℓ	20
Ambient temperature:	°C	+5 to +40
Ambient humidity: (rel.)	%	80
Clamping chuck clamping range:	mm	0.5 - 10
Hollow shaft internal diameter:	mm	10.5
Dimensions without extension arm: (W×D×H)	mm	88 × 212 × 294
Wight with extension arm and clamping chuck:	kg	3.1

A.1.4 Magnetic stirrer

The stirrer used for mechanical agitation (Chapter 5) was an RCT basic IKAMAG® safety control magnetic stirrer. It is suitable for liquids with a low viscosity and can successfully mix up to 20 ℓ at a time (IKA Works Inc 1995). The mixing speed can be accurately adjusted between 50 min^{-1} and 1 500 min^{-1} at 50Hz AC.

Table A.1.4 Technical data on the IKAMAG RCT basic safety control magnetic stirrer

Device		
Operating voltage range	Vac	220 - 230 ± 10%
Nominal voltage	Vac	230 / 50 Hz
Frequency	Hz	50 / 60
Power consumption (+10%) max at 230 Vac	W	650
Display		Digital
Permissible duration of operation	%	100
Permissible ambient temperature	°C	+5 to +40
Permissible relative humidity	%	80
Operation at a terrestrial altitude	m	max. 2000
Dimensions (B × T × H)	mm	165 × 275 × 85
Weight	kg	2.5
Motor		
Speed range	rpm	50 - 1500
Power consumption	W	16
Setting resolution	rpm	10
Speed variation	%	±2
Stirred quantity max. (H_2O)	ℓ	20

A.1.5 Ultrasound processor

The UP400S ultrasonic processors have been developed for use in the laboratory. The ultrasonic transducers use electric excitation to generate ultrasound, which is transferred to the liquid medium via various sonotrodes. UP400S ultrasonic processors useful output power is 400 W.

Despite their high efficiency, the ultrasonic processors do not have to be artificially cooled and are suitable for continuous operation. The amplitude of the oscillatory system can be adjusted between 20 % and 100 %; the set value remains constant under all operating conditions.

The sonotrodes are power-adjusted and can therefore be run without amplitude limitation.

Table A.1.5 Technical data on the Hielscher UP400S ultrasound processor

Technical specification	
Ultrasonic processor	UP400S
Efficiency	> 90%
Working frequency	24 kHz
Control range	± 1 kHz
Output control	20% …100%
Pulse-pulse mode factor	10% …100% per second
Electrical data	
Usable/nominal output	400 W (in aqueous media with sonotrode H22 300 W)
Maximum energy density	12 … 600 W/cm^2 depending on sonotrode
Maximum amplitude	12 … 260 µm depending on sonotrode
Permissible ambient conditions	
Temperature range	+5 …+40°C
Relative air humidity	10 …90 %, on-condensing
Device parameters	
Dimensions (l × w × h)	300 mm × 210 mm × 100 mm
Mass	Approx. 3.8 kg

A.2. Analytical methods

A.2.1 Calcium sulphide purity determination

Method: A 20 to 35 mg finely ground calcine feed sample was placed in an Erlenmeyer flask, and 50.00 mℓ distilled water was added using a Grade A pipette. 10.00 mℓ of 0.10 N Iodine (Titrisol, Merck) was added using a Grade A pipette. Three drops of concentrated HCl were added to the calcine slurry/I_2 mixture and stirred on a magnetic stirrer to dissolve the calcine in the acid solution. The contents were titrated with standard 0.1 N $Na_2S_2O_3$ solution (x ml) to close to end point (colour change from blue-black to straw) where after two drops of soluble starch solution were added. The titration was continued to the colourless end point.

Calculation: Excel spread sheet example

	C	D	E
20			
21			
22	Sample #	**M770.1**	**M770.2**
23	Calcine (mg)	20.7	21.8
24	Calcine (g)	=+D23/1000	=+E23/1000
25	H_2O (mL)	50	=+D25
26			
27	Vol (ml)	=+D25	=+E25
28	Sample (g as CaS)	=+D24	=+E24
29	Sample (mg as CaS)	=+D28*1000	=+E28*1000
30			
31	CaS (g/mol)	=32.066+40.078	=32.066+40.078
32	S (g/mol)	32.066	32.066
33			
34	I_2 (N)	=+G18	=+D34
35	I_2 (ml)	10	10
36	$Na_2S_2O_3$ (N)	0.1	0.1
37	$Na_2S_2O_3$ (ml)	5.3	5.15
38	mg/l as S^{2-}	=+((D34*D35)-(D36*D37))*16000/D27	=+((E34*E35)-(E36*E37))*16000/E27
39	mg/l as CaS	=+D38*D31/D32	=+E38*E31/E32
40	g as CaS	=D39*D27/1000	=E39*E27/1000
41			
42	%	=D40/D29*100	=E40/E29*100
43			
44	Avg Purity	**=AVERAGE(D42:H42)**	
45	Std dev	=STDEV(D42:H42)	

A.2.2 Calcium carbonate content determination

Method: A ~ 0.500 g sample was placed in an Erlenmeyer flask, and 50.00 mℓ of standard 0.250 M HCl was added using a Grade A pipette. The mixture was stirred for 30 min (magnetic stirrer) until all the $CaCO_3$ had dissolved (no more bubbles of CO_2 being evolved). The unreacted acid in the flask was titrated to pH = 7 with standard 0.100 M NaOH. Titration value (28.09 mℓ) was used to calculate the mass% $CaCO_3$ of the sample.

Reaction: $CaCO_3$ (s) + 2 HCl (aq) → $CaCl_2$ (aq) + H_2O (l) + CO_2 (g)

Calculation:

- Calculate moles of HCl added:
  50.00 mℓ HCl × 1ℓ/1000 mℓ × 0.250 mol HCl / ℓ
  = 1.25×10^{-2} mol HCl added
- Calculate moles of unreacted HCl:
  28.09 mℓ NaOH × 1 ℓ/1000 mℓ × 0.100 mol NaOH / ℓ × 1 mol HCl / 1 mol NaOH
  = 2.92×10^{-3} mol HCl unreacted
- Calculate moles of $CaCO_3$:
  $(1.25 \times 10^{-2} - 2.92 \times 10^{-3}) \times 1$ mol $CaCO_3$ / 2 mol HCl = 4.79×10^{-3} mol $CaCO_3$
- Calculate mass percent $CaCO_3$:
  4.79×10^{-3} mol $CaCO_3 \times (100.09$ g $CaCO_3$ / 1 mol $CaCO_3) / 0.500$ g sample × 100
  = 95.1 mass% $CaCO_3$

  Notes: Standardized reagents for HCl and NaOH supplied as Titrisol (Merck)

Appendix B: **Matrix of experiments and experimental data**

Lists of experiments including the experimental conditions carried out during the study on i) the direct aqueous CaS carbonation reaction (B.1), ii) the indirect CaS carbonation process using CO_2 gas for CaS dissolution (B.2) and the indirect CaS carbonation process using H_2S gas for CaS dissolution (B.3)

B.1. Direct aqueous CaS carbonation: Matrix of experiments

Table B.1.1. Matrix for the CaS dissolution and carbonation experiments in a single reactor.

Exp #	Reactor	Volume (mℓ)	Slurry (%)	CO_2 flow (ℓ/min)	CO_2 flow (ℓ /min/kg calcine)	Stirring (min^{-1})	Solid name	Actual yield (g)
Exp 6	3 ℓ CSTR	3000	5% CaS	1.700	11.3	400	-	
Exp 27	1 ℓ CSTR	700	4% CaS	0.440	15.7	745	M27	31.58
Exp 28	1 ℓ CSTR	700	4% CaS	1.120	40.0	745	M28	32.37
Exp 29	1 ℓ CSTR	700	4% CaS	1.900	67.9	745	M29	32.04
Exp 30	1 ℓ CSTR	700	4% CaS	1.120	40.0	1020	M30	32.13
Exp 31	1 ℓ CSTR	700	4% CaS	1.120	40.0	430	M31	32.13
Exp 32	1 ℓ CSTR	700	4% CaS	0.500	17.9	714	M32	31.71
Exp 78	3 ℓ CSTR	3000	5% CaS	0.440	2.9	580	M78	158.94
Exp 83	3 ℓ CSTR	3000	5% CaS	1.900	12.7	580	M83	168.30
Exp 110	3 ℓ CSTR	3000	7.5% CaS	2.200	9.8	500	M110	247.31
Exp 112	3 ℓ CSTR	3000	7.5% CaS	0.660	2.9	500	M112	247.06
Exp 116	1 ℓ CSTR	750	10 % CaS	3.300	44.0	500	M116	72.68
Exp 117	1 ℓ CSTR	750	10 % CaS	0.660	8.8	500	M117	70.95
Exp 118	1 ℓ CSTR	750	10 % CaS	1.120	14.9	500	M118	70.41
Exp 119	1 ℓ CSTR	750	10 % CaS	2.200	29.3	500	M119	71.30
Exp 124	1 ℓ CSTR	750	10 % CaS	0.190	2.5	500	M124	70.83

B.2. Indirect CaS carbonation using CO_2 gas for CaS dissolution: Matrix of experiments

Table B.2.1 Matrix for the CaS dissolution using CO_2 gas experiments

Exp #	Reactor	Volume (mℓ)	Slurry (%)	CO_2 flow (ℓ/min)	CO_2 flow (ℓ /min/kg calcine)	Stirring (min^{-1})	Solid name	Actual yield (g)
Exp 33	1 ℓ CSTR	700	4% CaS	1.12	40.0	1020	M33	27.64
Exp 35	1 ℓ CSTR	700	4% CaS	0.44	15.7	1045	M35	22.61
Exp 53	1 ℓ CSTR	700	4% CaS	1.40	50.0	1000	M53	27.17
Exp 81	3 ℓ CSTR	3 000	5% CaS	0.44	2.90	580	M81	127.88
Exp 84	3 ℓ CSTR	3 000	5% CaS	1.90	12.7	580	M84	137.33

Table B.2.2 Matrix for the $Ca(HS)_2$ carbonation experiments (following CaS dissolution using CO_2 gas)

Exp #	Reactor	Volume (mℓ)	CO_2 flow (ℓ/min)	Stirring (min^{-1})	Solid name	Actual yield (g)
Exp 34	1 ℓ CSTR	700	1.12	1050	M34	3.81
Exp 36	1 ℓ CSTR	700	0.44	1045	M36	4.83
Exp 54	1 ℓ CSTR	700	1.40	1000	M54	3.83
Exp 82	3 ℓ CSTR	3 000	0.44	580	M82	38.98
Exp 85	3 ℓ CSTR	3 000	1.90	580	M85	31.82

B.3. Indirect CaS carbonation using H_2S gas for CaS dissolution: Matrix of experiments

Table B.3.1 Matrix for the CaS dissolution using H_2S gas experiments

Exp #	Reactor	Volume (mℓ)	Slurry (%)	H_2S flow (ℓ/min)	H_2S flow (ℓ /min/kg calcine)	Stirring (min^{-1})	Solid name	Actual yield (g)
Exp 7	3 ℓ CSTR	3 000	2% CaS	0.63	10.5	500	M7	
Exp 15	3 ℓ CSTR	3 000	4% CaS	0.63	5.3	720	M15	
Exp 21	3 ℓ CSTR	3 000	8% CaS	0.63	2.6	720	M21	
Exp 37	1 ℓ CSTR	800	4% CaS	1.89	59.1	900	M37	8.80
Exp 38	1 ℓ CSTR	800	4% CaS	1.26	39.4	900	M38	7.45
Exp 39	1 ℓ CSTR	800	4% CaS	1.26	39.4	900	M39	10.92
Exp 40	1 ℓ CSTR	800	4% CaS	0.63	19.7	900	M40	8.01
Exp 41	1 ℓ CSTR	800	2% CaS	0.63	19.7	900	M41	10.08
Exp 42	1 ℓ CSTR	800	2% CaS	0.63	19.7	900	M42	10.10
Exp 48	3 ℓ CSTR	3 000	16% CaS	1.89	4.1	700	M48	188.88
Exp 66	3 ℓ CSTR	3 000	3% CaS	0.94	10.4	700	M66	31.08
Exp 68	3 ℓ CSTR	3 000	4% CaS	0.94	7.8	700	M68	45.43
Exp 91	3 ℓ CSTR	3 000	5% CaS	1.88	12.5	700	M91	62.47
Exp 92	3 ℓ CSTR	3 000	5% CaS	0.68	6.4	700	M92	64.38
Exp 93	3 ℓ CSTR	3 000	5% CaS	1.26	8.4	700	M93	67.28

Table B.3.2 Matrix for the $Ca(HS)_2$ carbonation experiments (following CaS dissolution using H_2S gas) – mechanical stirring

Exp #	Reactor	Volume (mℓ)	Initial calcium (mmol/ℓ)	CO_2 flow (ℓ/min)		Stirring (min^{-1})	Solid name	Actual yield (g)
Exp 11	1 ℓ CSTR	700	228	0.26		750	M11	8.25
Exp 12	1 ℓ CSTR	700	227	0.33		740	M12	9.08
Exp 13	1 ℓ CSTR	700	228	0.54		740	M13	9.20
Exp 14	0.5 ℓ beaker	300	233	0.54		690 (Mag)	M14	4.14
Exp 16	1 ℓ CSTR	700	456	0.33		740	M16	20.28
Exp 18	1 ℓ CSTR	700	452	0.54		740	M18	15.56
Exp 19	1 ℓ CSTR	700	455	0.26		740	M19	19.26
Exp 20	1 ℓ CSTR	690	446	0.66		740	M20	18.56
Exp 22	1 ℓ CSTR	700	858	0.54		735	M22	33.08
Exp 23	1 ℓ CSTR	700	891	0.66		740	M23	40.23
Exp 24	1 ℓ CSTR	700	898	0.19		740	M24	35.09
Exp 25	1 ℓ CSTR	690	883	0.33		735	M25	41.66
Exp 43	1 ℓ CSTR	750	439	0.66		770	M43	16.94
Exp 44	1 ℓ CSTR	750	446	1.65		775	M44	16.90
Exp 45	1 ℓ CSTR	750	456	2.20		770	M45	17.56
Exp 46	1 ℓ CSTR	750	499	1.65		305	M46	17.55
Exp 47	1 ℓ CSTR	750	452	1.65		1115	M47	16.59
Exp 49	1 ℓ CSTR	700	1769	2.20		905	M49	78.65
Exp 50	1 ℓ CSTR	700	1821	5.40		914	M50	78.82
Exp 52	1 ℓ CSTR	700	1723	2.20		922	M52	77.33
Exp 67	4.5 ℓ Column	4 500	?	1.90		none	M67	64.16
Exp 69	3 ℓ CSTR	3 000	462	1.12		700	M69	70.63

Table B.3.3 Matrix for the $Ca(HS)_2$ carbonation experiments (following CaS dissolution using H_2S gas) – effect of ultrasound irradiation

Exp #	Reactor	Volume (mℓ)	Initial calcium (mmol/ℓ)	CO_2 flow (ℓ/min)	Ultrasound mixing		Stirring (min^{-1})	Solid name	Actual yield (g)
					Cycle	Amplitude (%)			
Exp 95	1 ℓ	750	573	1.62	-	-	730	M 95	22.79
Exp 96	1 ℓ	750	593	1.62	0.5	55	730	M 96	22.83
Exp 97	1 ℓ	750	575	1.62	1	55	730	M 97	22.68
Exp 98	1 ℓ	750	618	1.62	1	55	-	M 98	22.96
Exp 99	1 ℓ	750	568	1.62	1	90	-	M 99	22.66
Exp 100	1 ℓ	750	565	0.36	1	90	-	M 100	23.27
Exp 101	1 ℓ	750	571	0.90	-	-	730	M 101	22.46
Exp 102	1 ℓ	750	566	0.90	1	90	-	M 102	23.39
Exp 103	1 ℓ	750	615	0.36	-	-	730	M 103	23.39
Exp 104	1 ℓ	750	560	0.00	1	90	-	-	-
Exp 106	1 ℓ	750	560	$NaHCO_3$	1	90	730	M 106	16.88