Processing of Na₂S to Na₂CO₃ and NaHS

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Abstract— Acid mine drainage (AMD), a notorious kind of pollution associated with both active and abandoned mining sites, needs to be treated with the aim of achieving net zero waste. The ROC (Reverse Osmosis/Cooling) process can be used for the treatment of AMD though neutralization with Na_2CO_3 for the removal of metals, desalination with reverse osmosis (RO), freeze-crystallization for recovering Na_2SO_4 from the RO brine, and processing of Na_2SO_4 to Na_2S. The purpose of this investigation was to identify conditions needed for the processing of Na_2S to Na_2CO_3. It was found that: (i) Na_2S can be reacted with CO_2 to form $NaHCO_3(aq)$ and $NaHS(aq)$, (ii) the latter two compounds can be separated though freeze-crystallization as $NaHCO_3$ has a lower solubility at 0°C, and (iii) $NaHCO_3$ can be converted into Na_2CO_3 though heat-treatment.

Keywords—Freeze-crystallization, $NaHCO_3$, NaHS, Na_2S

I. INTRODUCTION

Acid mine drainage (AMD) is the most significant environmental pollution problem associated with the mining industry. The high concentration of toxic metals and high levels of acidity in AMD are harmful to the vegetation, aquatic life, terrestrial wildlife, and human beings. Pyrite (FeS_2) is a major constituent of the strata being mined and large rock surfaces become exposed to air and water during mining activities [1]. Pyrite is oxidized to soluble iron complexes and sulphuric acid, catalysed by sulphur-oxidizing bacteria [2], according to the following reaction:

$$2FeS_2(s) + 7O_2(aq) + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-}(aq) + 4H^+(aq)$$
[1]
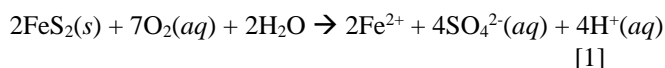
Because of its detrimental effects on the environment and public health, it is mandatory to treat acid mine drainage (AMD) with the aim to have zero waste. AMD can be treated by two methods; *viz.*, active treatment and passive treatment. Active treatment includes the use of chemical agents such as limestone ($CaCO_3$), hydrated lime ($Ca(OH)_2$), caustic soda (NaOH), soda ash (Na_2CO_3), calcium oxide (CaO), anhydrous ammonia (NH_3), magnesium hydroxide ($Mg(OH)_2$), and magnesium oxide (MgO) [3] . Passive

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treatment can be further classified into two types: conventional and emerging. Examples of conventional passive treatment are constructed wetlands and anaerobic sulphate-reducing bioreactors, while an example of an emerging passive treatment is phytoremediation [3].

The ROC (Reverse Osmosis/Cooling) process can be used for the treatment of AMD through neutralization with Na_2CO_3 for the removal of metals, desalination with reverse osmosis (RO), freeze-crystallization for recovery of Na_2SO_4 from the RO brine and processing of Na_2SO_4 to Na_2S.

In the ROC process, Na_2CO_3 is used for selective recovery of metals through a stepwise increase of the pH, resulting in the formation of Na_2SO_4, which can be recovered from the brine after the reverse osmosis and freeze-crystallization stages. It would be beneficial if the raw material, Na_2CO_3, can be recovered from the product, Na_2SO_4. Since Na_2CO_3 has a high price of R5 000/t, it would be economically beneficial if it can be processed from the product, Na_2SO_4. Mashigwana studied the direct conversion of Na_2SO_4 into Na_2CO_3 under thermal conditions and found that it was not possible, as Na_2SO_4 melted in the same temperature range as where the reduction took place, namely 860 to 920°C [4]. Van Vuuren and Maree proposed that Na_2CO_3 be produced indirectly from CaS or BaS [5]. Various researchers studied the reduction of $CaSO_4$ and $BaSO_4$ in depth without experiencing the melting problem of one of the reactants [6, 7, 8, 9, 10, 11]. Mokgohloa *at al*. studied the reduction of $CaSO_4$ and founded that Na_2CO_3 can be produced from Na_2SO_4 *via* CaS [12]. In the indirect method, $CaSO_4$ precipitates, due to its relatively low solubility, while Na_2S or NaHS remain in solution and are converted into Na_2CO_3 or $NaHCO_3$ by contacting them with CO_2. A limitation of the CaS route is, however, the partial solubility of $CaSO_4 \cdot 2H_2O$ (2 440 mg/L). The formed Na_2S is therefore contaminated with Ca^{2+}. $BaSO_4$ offers the benefit that Na_2S will be pure due to the low solubility of $BaSO_4$ (2.44 mg/L) compared to the 2 640 mg/L in the case of $CaSO_4 \cdot 2H_2O$. Less energy is also needed for the conversion of $BaSO_4$ into BaS (74 027 MJ/h) than for the conversion of $CaSO_4$ into CaS (136 165 MJ/h).

The purpose of this investigation was to identify the process steps needed for the processing of Na_2S to $NaHCO_3$ and NaHS, when Na_2S is produced *via* the BaS route.

The objectives of this investigation are as follows:

- Convert Na_2SO_4 to Na_2CO_3 *via* BaS
- Process Na_2S into $NaHCO_3$ and NaHS
- Process $NaHCO_3$ into Na_2CO_3

II. MATERIALS AND METHODS

A. Feedstock, chemicals, and reagents

High purity reagents were used throughout this work for the preparation of samples. Deionised water was used as solvent for all solutions and dilutions. The following chemicals were used: CO_2 gas (Air Liquide, South Africa), 1 M HCl, 0.1 N I_2, 0.1 N $Na_2S_3O_4$, 1M NaOH, 0.1 M Iodine solution and starch solution.

B. Equipment

Figure 1 showed the experimental set-up that was used when a Na_2S solution was contacted with CO_2.
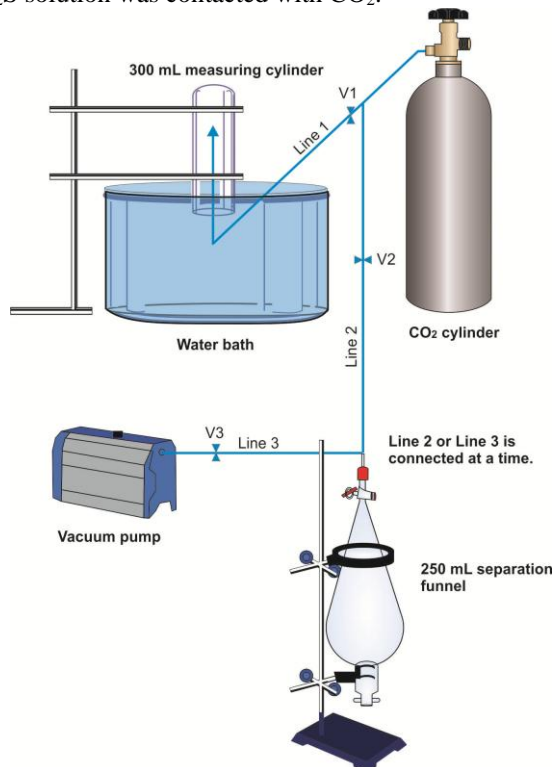

Figure 1. Schematic diagram of laboratory set-up used for monitoring the precipitation of $NaHCO_3$ when Na_2S is reacted with CO_2

C. Experimental and Procedure

OLI simulations (OLI ESP software program from OLI Systems, Inc.) were used to determine which compound will precipitate out and which compounds/elements will stay in solution after the mixing of reactant and/or cooling.
Beaker studies were carried out to convert Na_2S into $NaHCO_3$ and NaHS by reacting it with CO_2. The following procedure was followed in the experiment by using the laboratory set-up as shown in Figure 1 above.

- CO_2 was put in a 300 mL measuring cylinder, with the open end on top of a water bath *via* Line 1.
- Na_2S (0.88 g Na_2S + 4.38 g H_2O; 200 g Na_2S/L H_2O) was put in a 250 mL separation funnel
- Air was removed from the separation funnel with a vacuum pump *via* Line 3 and replaced with CO_2 stored in the 300 mL measuring cylinder *via* Line 2.

- The Na_2S and CO_2 in the separation funnel were allowed to react by shaking it for 15 min. CO_2 additions were repeated 1, 2 and 4 times to determine the effect of CO_2/Na_2S mole ratio on the completion of the reaction.
- The CO_2 in the measuring cylinder was replaced with air.
- The volume of CO_2 reacted with the Na_2S was determined by allowing the air in the measuring cylinder to flow into the 250 mL separation funnel *via* Line 2, which was partially under vacuum due to the CO_2 reaction with Na_2S. The volume of CO_2 reacted was determined by reading the volume of water that was sucked into the 300 mL measuring cylinder.
- Sulphide and alkalinity (Alk) analyses were carried out on filtered liquid samples collected from the separation funnel. Filtered samples were collected by using a 25 mL syringe with a filter tip.

D. Analysis

Sulphide was determined by standard iodometry [13] as follows: A 50 mg sample of the reduced product was weighed, dissolved and made up to 100 mL with deionized water. Then 10 mL of standard iodine solution (0.1 N) was added, followed by 50 mL of deionized water. The resulting mixture was acidified using 2 mL of 5 N HCl solution and subsequently titrated with standard (0.1 N) sodium thiosulphate using starch as indicator to a colourless end-point. The % NaS in the reduction mixture was calculated as follows:

$$\% \text{ NaS} = \frac{[\text{V(iodine: 10mL)} - \text{Titration volume}) \times 36] \times 100}{\text{Sample mass (mg)}}$$

[2]

E. OLI software simulations

The OLI System Chemical Analyser software program was used to predict the behaviour of metals dissolved in water when treated with alkalis such as MgO and NaOH [14]. OLI is an aqueous equilibrium chemistry estimator with an interactive and self-instructive interface for clarifying reactions. It has the ability to work with all kinds of common equilibrium reactions, it has a strong solution algorithm, and expressive and easily understandable displays of results, and the ability to produce results in multiple formats according to different uses. The OLI System Chemical Analyser was used to perform single point equilibrium calculations and multiple point survey calculations. The concentration of the various species in solutions or solids were calculated as a function of temperature, pressure, pH and initial concentrations. The calculations provide liquid- and solid-phase separations for a specialised model.

The OLI Analyser 9.0 System was used to simulate the reactions by running a simulated Acid Rock Drainage (ARD) sample with assumed values of temperature, pressure and pH. The base titrants used were Na_2CO_3, $MgCO_3$, $Mg(OH)_2$ and MgO. The effect of temperature on the solubility of $MgSO_4$ and Na_2SO_4 was determined to represent a scenario where MgO is used for neutralisation to pH 3.2, followed by Na_2CO_3

to raise the pH to 8.6. Once the input values are used in a calculation by the OLI Systems Chem Analyzer, a calculated summary of the simulated results appears. This could be used to predict the actual reactions that will take place under specific conditions and the final concentration of the various chemical species.

III. RESULTS AND DISCUSSION

A. Conversion of Na_2SO_4 to Na_2S via BaS

Na_2S is the raw material in the formation of Na_2CO_3, nano $CaCO_3$ and MgO. Since direct conversion of Na_2S from Na_2SO_4 is a problem, it needs to be converted from either CaS or BaS. The reason for the difficult with the direct conversion is Na_2SO_4 melts in the same temperature range, 800°C to 900°C, where Na_2SO_4 is converted into Na_2S.

The purpose of this section is to identify which one of CaS or BaS would be the most suitable for the production of Na_2S. It is of industrial interest to convert alkali and alkaline earth metal sulphates to its carbonates. The sulphate compounds are generally produced as waste that needs to be stockpiled, while the carbonates are important raw material in industrial processes. $BaSO_4$ is mined as a raw material and converted to $BaCO_3$ to be used for glass manufacturing, brick manufacturing, oil-drilling, ceramics, photographic and chemical industries. $CaSO_4$ is produced in the fertilizer industry when H_2SO_4 is used for leaching H_3PO_4 from $Ca_5(PO_4)_3F$ (phosphate rock) and when SO_4^{2-}-rich acidic effluents are neutralized with $Ca(OH)_2$ or $CaCO_3$. Na_2SO_4 is produced when SO_4^{2-} rich acidic effluents are neutralized with Na_2CO_3 or NaOH.

If Na_2S is produced *via* the CaS route, it will contain more $CaSO_4$ than when produced *via* the BaS, due to the higher solubility of $CaSO_4$. The purpose of this section is to study the formation of Na_2S from both BaS and CaS. Error! Reference source not found. showed, through OLI simulations, that Na_2S formed stoichiometrically when BaS was reacted with Na_2SO_4, as indicated by the removal of sulphate from 1 000 mmol/L to 0.3 mmol/L. This finding was also **experimentally** confirmed (

BaS [mmol]	Na2SO4 [mmol]	BaSO4 (Barite) - Sol [mmol] (Y2)	S(+6) Aq [mmol] (Y2)
0.0	1 000.0	0.0	1 000.0
100.0	1 000.0	100.0	900.0
200.0	1 000.0	200.0	800.0
300.0	1 000.0	300.0	700.0
400.0	1 000.0	400.0	600.0
500.0	1 000.0	500.0	500.0
600.0	1 000.0	600.0	400.0
700.0	1 000.0	700.0	300.0
800.0	1 000.0	800.0	200.0

900.0	1 000.0	900.0	100.0
1 000.0	1 000.0	999.7	0.3

Temp = 25°C; pH = 12.5 to 13.1

Table). This experiment was repeated, using OLI simulations, with CaS to determine how effective SO_4^{2-} was removed from solution when precipitated as $CaSO_4$, instead of $BaSO_4$.

Parameter	Value
BaS (g)	10.00
Purity (%)	95.00
BaS (meq)	112.43
Na2SO4 (g)	8.40
H2O (mL)	200.00
Na2S (q)	4.37
Na2S (meq)	112.00
NaS production (%)	99.62

showed that in the case of CaS, sulphate was removed from only 1000 mmol/L to only 254.8 mmol/L. The difference in sulphate concentrations was due to the difference in the solubilities of $BaSO_4$ (0.0285 mg/L)) and $CaSO_4 \cdot 2H_2O$ (2 640 mg/L).

The above finding showed that the BaS route will be the preferred route for Na_2S production for applications where the presence of sulphate is a problem.

It is thus clear that the BaS-route is the preferred on for processing Na_2SO_4 to Na_2S and the downstream products.

TABLE I. Conversion of Na_2SO_4 into Na_2S *via* BaS (OLI simulation)

BaS [mmol]	Na2SO4 [mmol]	BaSO4 (Barite) - Sol [mmol] (Y2)	S(+6) Aq [mmol] (Y2)
0.0	1 000.0	0.0	1 000.0
100.0	1 000.0	100.0	900.0
200.0	1 000.0	200.0	800.0
300.0	1 000.0	300.0	700.0
400.0	1 000.0	400.0	600.0
500.0	1 000.0	500.0	500.0
600.0	1 000.0	600.0	400.0
700.0	1 000.0	700.0	300.0
800.0	1 000.0	800.0	200.0
900.0	1 000.0	900.0	100.0
1 000.0	1 000.0	999.7	0.3

Temp = 25°C; pH = 12.5 to 13.1

Table II Conversion of Na$_2$SO$_4$ into Na$_2$S *via* BaS (Experimental)

Parameter	Value
BaS (g)	10.00
Purity (%)	95.00
BaS (meq)	112.43
Na$_2$SO$_4$ (g)	8.40
H$_2$O (mL)	200.00
Na$_2$S (q)	4.37
Na$_2$S (meq)	112.00
NaS production (%)	99.62

TABLE III. Conversion of Na$_2$SO$_4$ into Na$_2$S *via* CaS (Temp = 25°C; pH = 12.5 – 12.4) (OLI simulation)

CaS [mmol]	Na2SO4 [mmol]	CaSO4·2H2O (Gypsum) [mmol] (Y2)	Ca(OH)2 (Portlandite) - Sol [mmol] (Y2)	S(+6) Aq [mmol] (Y2)
0.0	1 000.0	0.0	0.0	1 000.0
100.0	1 000.0	81.6	0.0	918.4
200.0	1 000.0	178.9	0.0	821.1
300.0	1 000.0	269.1	6.7	730.9
400.0	1 000.0	346.7	26.5	653.3
500.0	1 000.0	421.9	48.0	578.1
600.0	1 000.0	494.5	71.5	505.5
700.0	1 000.0	563.7	97.3	436.3
800.0	1 000.0	629.1	125.6	370.9
900.0	1 000.0	689.9	156.9	310.1
1 000.0	1 000.0	745.2	191.2	254.8

Temp = 25°C; pH = 12.5 to 12.4

B. Solubilities

The production of NaHCO$_3$ and NaHS from the reactants, Na$_2$S and CO$_2$ (Eq. 3) is influenced by the solubility of the reactant, Na$_2$S and the products, NaHCO$_3$ and NaHS ( ).

$$Na_2S + 2CO_2 + 2H_2O \rightarrow 2NaHCO_3 + H_2S \qquad [3]$$

Compound	Temp	Solubility		Table No
	(°C)	mmol/L	g/L	
Na2S	25.0	2619.8	204.3	7
Na2S	80.0	6101.3	475.9	7
NaHCO3	25.0	1109.5	86.5	8

NaHCO3	0.0	640.2	49.9	9
NaHS	25.0	88203.0	4939.4	10

and

showed the behaviour of **Na₂S** added to water in steps of 1 000 mmol/L (78 g/L). Na$_2$S dissolved completely below the solubility of 2 619.8 mmol/L (204.3 g/L). At higher dosages a portion of the Na$_2$S will remain as a hydrated solid in suspension, first as Na$_2$S·9H$_2$O and then as Na$_2$S·5H$_2$O as more water is available.

shows the effect of temperature on the solubility of Na$_2$S. When 6 000 mmol (468 g) Na2S is contact with 1 kg H2O, it is observed that: (i) Na$_2$S·9H$_2$0 formed at temperatures below 40°C when the solubility is exceeded, (ii) Na$_2$S·5H$_2$0 formed at temperatures above 40°C when the solubility is exceeded, (iii) free water increased from 1 934 to 54 573 mmol as the temperature increased due to increased solubility of Na$_2$S, (iv) the solubility of Na$_2$S increase from 107.1 g/L to 475.9 g/L as the temperature increased from 0°C to 80°C

TABLE and showed the solubility of **NaHCO₃**, namely 1 109.5 mmol/L (86.5 g/L) at 25°C and 640.2 mmol/L (49.9 g/L) at 0°C respectively. showed that **NaHS** has a solubility of 88 203 mmol/L (90 000 – 1 797) or 4 939 g/L NaHS. At higher concentrations NaHS decompose into Na$_2$S and H$_2$S (Eq. 4).

$$2NaHS \rightarrow Na_2S + H_2S \qquad [4]$$

TABLE IV. Solubility of Na$_2$S, NaHCO$_3$ and NaHS (OLI)

Compound	Temp	Solubility		Table No
	(°C)	mmol/L	g/L	
Na$_2$S	25.0	2619.8	204.3	7
Na$_2$S	80.0	6101.3	475.9	7
NaHCO$_3$	25.0	1109.5	86.5	8
NaHCO$_3$	0.0	640.2	49.9	9
NaHS	25.0	88203.0	4939.4	10

TABLE V. Solubility of Na$_2$S (higher concentrations) (OLI)

Na2S [mmol]	Na2S [g/L]	S(-2) Aq [mmol] (Y2)	Na2S·9H2O [mmol] (Y2)	Na2S·5H2O [mmol] (Y2)	H2O [mmol] (Y2)
0	0	0	0	0	55 508
1 000	78	1 000	0	0	55 364
2 000	156	2 000	0	0	55 311

3 000	234	2 393	607	0	49 841
4 000	312	1 638	2 362	0	34 106
5 000	390	882	4 118	0	18 372
6 000	468	127	5 873	0	2 637
7 000	546	0	5 127	1 873	0
8 000	624	0	3 877	4 123	0
9 000	702	0	2 627	6 373	0
10 000	780	0	1 377	8 623	0

Temp = 25°C; pH = 13.1 to 15.6

TABLE VI. Solubility of Na_2S (lower concentration (OLI)

Na2S [mmol]	Na2S [g/L]	S(-2) Aq [mmol] (Y2)	Na2S·9H2O [mmol] (Y2)	Na2S·5H2O [mmol] (Y2)	H2O [mmol] (Y2)
0	0	0	0	0	55 508
300	23	300	0	0	55 425
600	47	600	0	0	55 393
900	70	900	0	0	55 371
1 200	94	1 200	0	0	55 352
1 500	117	1 500	0	0	55 336
1 800	140	1 800	0	0	55 321
2 100	164	2 100	0	0	55 307
2 400	187	2 400	0	0	55 293
2 700	211	2 620	80	0	54 562
3 000	234	2 393	607	0	49 841

Temp = 25°C; pH = 12.8 to 13.6

TABLE VII. Effect of temperature on the solubility of Na_2S (OLI)

Temperature [°C]	Na2S [mmol] (Y2)	NaS2 soluble (g)	NaS2 solubility (g/L)	Na2S.9H2O [mmol] (Y2)	Na2S·5H2O [mmol] (Y2)
0	6000	3.7	107.1	5 952.2	0.0
10	6000	5.5	143.3	5 929.2	0.0
20	6000	8.1	184.7	5 896.2	0.0
30	6000	12.2	233.4	5 843.5	0.0
40	6000	20.5	295.7	5 736.9	0.0
50	6000	301.6	376.6	0.0	2 134
60	6000	375.3	425.0	0.0	1 189

70	6000	468.0	474.8	0.0	0.0
80	6000	468.0	475.9	0.0	0.0

Note Na_2S solubility (g/L) = Na_2S soluble x 55 500 / mmol H_2O; pH = 14.1 to 13.1

TABLE VIII. Solubility of $NaHCO_3$ at 25°C(OLI)

NaHCO3 [mmol]	NaHCO3 (g/L)	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	Na(+1) Aq [mmol] (Y2)	C(+4) Aq [mmol] (Y2)
0	0.0	0	0	0
300	25.2	0	300	300
600	50.4	0	600	600
900	75.6	0	900	900
1200	100.8	0	1 200	1 200
1500	126.0	196	1 304	1 304
1800	151.2	496	1 304	1 304
2100	176.4	796	1 304	1 304
2400	201.6	1 096	1 304	1 304
2700	226.8	1 396	1 304	1 304
3000	252.0	1 696	1 304	1 304

Temp = 25°C; pH = 7.95 to 7.74

TABLE IX Solubility of $NaHCO_3$ at 0°C(OLI)

NaHCO3 [mmol]	NaHCO3 (g/L)	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	Na(+1) Aq [mmol] (Y2)	C(+4) Aq [mmol] (Y2)
0	0.0	0	0	0
300	25.2	0	300	300
600	50.4	0	600	600
900	75.6	0	900	900
1200	100.8	280	920	920
1500	126.0	580	920	920
1800	151.2	880	920	920
2100	176.4	1180	920	920
2400	201.6	1480	920	920
2700	226.8	1780	920	920
3000	252.0	2080	920	920

Temp = 0°C; pH = 8.19 to 8.04

TABLE X. Solubility of NaHS (OLI)

NaHS [mmol]	pH	Na_2S - Sol [mmol] (Y2)	$S(-2)$ Aq [mmol] (Y2)	H_2S - Vap [mmol] (Y2)	HS-1 [mmol] (Y2)
0	7.0	0.0	0	0.0	0
10 000	9.7	0.0	10 000	0.0	9 994
20 000	9.9	0.0	20 000	0.0	19 998
30 000	10.3	0.0	30 000	0.2	29 999
40 000	10.6	0.0	40 000	0.1	40 000
50 000	10.9	0.0	50 000	0.0	50 000
60 000	11.3	0.0	60 000	0.0	60 000
70 000	11.6	0.0	70 000	0.0	70 000
80 000	12.1	0.0	80 000	0.0	80 000
90 000	12.5	1 796.8	86 406	1 796.8	86 406
100 000	12.5	6 796.8	86 406	6 796.8	86 406

Temp. = 25°C

C. Reaction between Na_2S and CO_2

Error! Reference source not found. showed that 10 000 mmol Na_2S (780 g Na_2S) will react with 1 L H_2O to form 1 377 mmol $Na_2S.9H_2O$ and 8 622.9 mmol $Na_2S \cdot 5H_2O$ at pH 12.2, with no free H_2O left. A reason why a portion of the Na_2S was converted to $Na_2S \cdot 5H_2O$ and not $Na_2S \cdot 9H_2O$, was due to the availability of water. Upon addition of 6 000 mmol CO_2 to pH 9.3, 2 656 mmol Na_2CO_3, $NaHCO_3 \cdot 2H_2O$ formed. By increasing the CO_2 dosage to 20 000 mmol, 18 417 mmol $NaHCO_3$ and 8 875 mmol H_2S formed (Eq. 1). The solid $NaHCO_3$ can be converted into Na_2CO_3 and H_2S to elemental sulphur.

CO_2 [mmol]	Na_2S [mmol] (Y2)	pH	$NaHCO_3$ (Nahcolite) - Sol [mmol] (Y2)	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ - Sol [mmol] (Y2)	$NaHCO_3$ - Aq [mmol] (Y2)	$Na_2S \cdot 9H_2O$ [mmol] (Y2)	$Na_2S \cdot 5H_2O$ [mmol] (Y2)	H_2S - Vap [mmol] (Y2)	H_2S - Aq [mmol] (Y2)
0	10 000	15.6	0	0	0.0	1 377	8 623	0	0.00
2 000	10 000	12.2	0	0	0.2	9	5 873	0	0.00
4 000	10 000	12.2	0	0	0.4	0	1 875	0	0.00
6 000	10 000	11.2	0	2 018	2.7	0	0	0	0.05
8 000	10 000	9.3	2 399	2 656	30.8	0	0	868	4.09

CO_2	Na_2S	pH	NaHCO3(Nahcolite)-Sol	Na2CO3·NaHCO3·2H2O-Sol	NaHCO3-Aq	Na2S·9H2O	Na2S·5H2O	H2S-Vap	H2S-Aq
10 000	10 000	9.3	9 691	0	33.8	0	0	225	4.51
12 000	10 000	9.2	11 736	0	46.0	0	0	2 151	6.80
14 000	10 000	9.0	13 747	0	64.6	0	0	4 083	10.66
16 000	10 000	8.7	15 693	0	93.6	0	0	5 999	17.33
18 000	10 000	8.4	17 417	0	135.5	0	0	7 766	27.69
20 000	10 000	8.1	18 417	0	172.0	0	0	8 875	34.80

Temp = 25°C

showed the same result as in Error! Reference source not found. except that in the case of a lower Na_2S concertation (2 500 mmol/kg H_2O and less), no $Na_2S \cdot 9H_2O$ or $Na_2S \cdot 5H_2O$ formed due to the availability of sufficient water.

$NaHCO_3$ has a lower solubility at 0°C (640.2 mmol/L or 49.9 g/L;

) than at 25°C (1 109.5 mmol/L or 86.5 g/L;

TABLE). Therefore, it may be beneficial to separate $NaHCO_3$ from NaHS at 0°C, rather than at room temperature. Error! Reference source not found. showed that 2 119 mmol $NaHCO_3$ formed at 0°C, which is more than the 1 941 mmol $NaHCO_3$ that formed at 25°C (

CO_2 [mmol]	Na_2S [mmol] (Y2)	pH	$NaHCO_3$ (Nahcolite) - Sol [mmol] (Y2)	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ - Sol [mmol] (Y2)	$NaHCO_3$ - Aq [mmol] (Y2)	$Na_2S \cdot 9H_2O$ [mmol] (Y2)	$Na_2S \cdot 5H_2O$ [mmol] (Y2)	H_2S - Vap [mmol] (Y2)	H_2S - Aq [mmol] (Y2)
0	10 000	15.6	0	0	0.0	1 377	8 623	0	0.00
2 000	10 000	12.2	0	0	0.2	9	5 873	0	0.00
4 000	10 000	12.2	0	0	0.4	0	1 875	0	0.00
6 000	10 000	11.2	0	2 018	2.7	0	0	0	0.05
8 000	10 000	9.3	2 399	2 656	30.8	0	0	868	4.09
10 000	10 000	9.3	9 691	0	33.8	0	0	225	4.51
12 000	10 000	9.2	11 736	0	46.0	0	0	2 151	6.80
14 000	10 000	9.0	13 747	0	64.6	0	0	4 083	10.66
16 000	10 000	8.7	15 693	0	93.6	0	0	5 999	17.33
18 000	10 000	8.4	17 417	0	135.5	0	0	7 766	27.69
20 000	10 000	8.1	18 417	0	172.0	0	0	8 875	34.80

Temp = 25°C

). Due to the small benefit associated with cooling to 0°C, it is recommended that the reaction be carried out at room temperature.

The optimum concentration needs to be determined for the production of $NaHCO_3$ from Na_2S and CO_2.

CO2 [mmol]	Na2S [mmol] (Y2)	pH	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	NaHCO3 - Aq [mmol] (Y2)	HCO3-1 [mmol] (Y2)	HS-1 [mmol] (Y2)	H2S - Aq [mmol] (Y2)	S-2 [mmol] (Y2)
0	2 500	14.1	0	0	0.0	96	0.0	951.1
250	2 500	13.4	0	0	0.0	510	0.0	841.5
500	2 500	13.0	0	0	0.0	1 004	0.0	725.6
750	2 500	12.8	0	0	0.0	1 502	0.0	627.0
1 000	2 500	12.6	0	0	0.1	2 001	0.0	498.8
1 250	2 500	11.0	0	9	4.1	2 487	0.2	12.8
1 500	2 500	9.7	233	178	86.6	2 496	2.9	0.7
1 750	2 500	9.7	710	192	95.2	2 496	3.1	0.7
2 000	2 500	9.7	1 187	206	104.0	2 496	3.2	0.7
2 250	2 500	9.6	1 665	219	112.2	2 495	4.0	0.6
2 500	2 500	8.7	2 119	230	117.5	2 467	32.8	0.1

Temp = 0°C; Pressure = 1 atm

showed that showed NaHCO$_3$ (nahcolite) formed at concentration up to 10 000 mmol/kg water. At higher dosages the complex Na$_2$CO$_3$·NaHCO$_3$ formed.

TABLE XI. Reaction between 10 000 mmol Na$_2$S and CO$_2$ at 25°C (OLI simulation)

CO2 [mmol]	Na2S [mmol] (Y2)	pH	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	Na2CO3·NaHCO3·2H2O - Sol [mmol] (Y2)	NaHCO3 - Aq [mmol] (Y2)	Na2S·9H2O [mmol] (Y2)	Na2S·5H2O [mmol] (Y2)	H2S - Vap [mmol] (Y2)	H2S - Aq [mmol] (Y2)
0	10 000	15.6	0	0	0.0	1 377	8 623	0	0.00
2 000	10 000	12.2	0	0	0.2	9	5 873	0	0.00
4 000	10 000	12.2	0	0	0.4	0	1 875	0	0.00
6 000	10 000	11.2	0	2 018	2.7	0	0	0	0.05
8 000	10 000	9.3	2 399	2 656	30.8	0	0	868	4.09
10 000	10 000	9.3	9 691	0	33.8	0	0	225	4.51
12 000	10 000	9.2	11 736	0	46.0	0	0	2 151	6.80
14 000	10 000	9.0	13 747	0	64.6	0	0	4 083	10.66
16 000	10 000	8.7	15 693	0	93.6	0	0	5 999	17.33
18 000	10 000	8.4	17 417	0	135.5	0	0	7 766	27.69
20 000	10 000	8.1	18 417	0	172.0	0	0	8 875	34.80

Temp = 25°C

TABLE XII Reaction between 2 500 mmol Na$_2$S and CO$_2$ at 25°C (OLI simulation)

CO2 [mmol]	Na2S [mmol] (Y2)	pH	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	NaHCO3 - Aq [mmol] (Y2)	HCO3-1 [mmol] (Y2)	HS-1 [mmol] (Y2)	H2S - Aq [mmol] (Y2)	S-2 [mmol] (Y2)
0	2 500	13.6	0	0	0	220	0.00	2 280
250	2 500	13.1	0	0	0	571	0.00	1 929
500	2 500	12.7	0	0	0	1 029	0.00	1 471
750	2 500	12.4	0	0	0	1 512	0.00	988.2
1 000	2 500	12.0	0	1	1	2 002	0.01	497.9
1 250	2 500	10.8	0	16	24	2 460	0.11	39.4
1 500	2 500	9.7	77	168	257	2 495	1.47	3.2
1 750	2 500	9.6	557	179	265	2 495	2.06	2.5
2 000	2 500	9.4	1 034	190	274	2 495	3.24	1.8
2 250	2 500	9.1	1 506	203	285	2 492	6.68	1.0
2 500	2 500	8.3	1 942	216	299	2 458	41.83	0.2

Temp = 25°C; Pressure = 1 atm

TABLE XIII Reaction between 2 500 mmol Na$_2$S and CO$_2$ at 0°C (OLI simulation)

CO2 [mmol]	Na2S [mmol] (Y2)	pH	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	NaHCO3 - Aq [mmol] (Y2)	HCO3-1 [mmol] (Y2)	HS-1 [mmol] (Y2)	H2S - Aq [mmol] (Y2)	S-2 [mmol] (Y2)
0	2 500	14.1	0	0	0.0	96	0.0	951.1
250	2 500	13.4	0	0	0.0	510	0.0	841.5
500	2 500	13.0	0	0	0.0	1 004	0.0	725.6
750	2 500	12.8	0	0	0.0	1 502	0.0	627.0
1 000	2 500	12.6	0	0	0.1	2 001	0.0	498.8
1 250	2 500	11.0	0	9	4.1	2 487	0.2	12.8
1 500	2 500	9.7	233	178	86.6	2 496	2.9	0.7
1 750	2 500	9.7	710	192	95.2	2 496	3.1	0.7
2 000	2 500	9.7	1 187	206	104.0	2 496	3.2	0.7
2 250	2 500	9.6	1 665	219	112.2	2 495	4.0	0.6

| 2 500 | 2 500 | 8.7 | 2 119 | 230 | 117.5 | 2 467 | 32.8 | 0.1 |

Temp = 0°C; Pressure = 1 atm

TABLE XIV Reaction between 0 to 20 000 mmol Na_2S and 0 to 20 000 mmol CO_2 at 25°C (OLI simulation)

CO2 [mmol]	Na2S [mmol] (Y2)	pH	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	Na2CO3·NaHCO3·2H2O - Sol [mmol] (Y2)	H2S - Vap [mmol] (Y2)	CO2 - Vap [mmol] (Y2)	S(-2) Aq [mmol] (Y2)
0	0	7.0	0	0	0	0.00	0
2 000	2 000	8.3	1 358	0	0	0.00	2 000
4 000	4 000	8.6	3 599	0	29	0.48	3 971
6 000	6 000	8.8	5 697	0	80	0.39	5 920
8 000	8 000	9.1	7 722	0	142	0.26	7 858
10 000	10 000	9.3	9 691	0	225	0.17	9 775
12 000	12 000	9.3	3 210	4 274	4 446	3.31	7 554
14 000	14 000	9.5	0	6 903	7 059	2.71	6 941
16 000	16 000	9.8	0	7 896	8 091	0.92	7 909
18 000	18 000	10.1	0	8 851	9 143	0.36	8 857
20 000	20 000	10.5	0	9 706	10 291	0.20	9 709

Temp = 25°C; Pressure = 1 atm

D. Separation of $NaHCO_3$ and $NaHS$

$NaHCO_3$ can be recovered from a $NaHCO_3/NaHS$ solution by using the solubility differences (Error! Reference source not found.).

showed the removal of $NaHCO_3$ after the 200 g/L Na_2S (30 g/150 mL) was reacted with the equivalent CO_2 (8.62 L CO_2/30 g Na_2S).

OLI simulations showed that 200 g/L Na_2S can dissolve in water at 25°C. An experiment was planned to confirm that sulphide will remain in solution when contacted with CO_2.

showed the experimental results when a 50 mL Na_2S solution was contacted with 250 mL CO_2 (at STP), where the CO_2/Na_2S mole ratios varied between 5 and 0.5. It was noted that the sulphide in solution as measured with the iodine method corresponded closely with the Na_2S that was prepared, as expected from Eq. 5.

$$Na_2S + CO_2 + H_2O \rightarrow NaHS + NaHCO_3 \qquad [5]$$
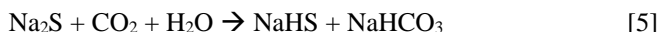
The results above obtained from OLI simulations, and confirmed experimentally showed that N_2S has a high solubility of 204.3 g/L (Error! Reference source not found.) and that it can be determined through sulphide analyses (as Na_2S) (Eq 6) or Alkalinity analyses (as Na_2S) (Eq 7).

$$Na_2S \ (mg/L) = \frac{eq. \ mass \ of \ Na_2S \ x \ (V_{I2} \ x \ N_{I2} - V_{S2O3} \ x \ N_{S2O3}) \ x \ 1000}{Sample \ Vol} \qquad [6]$$

$= 78 / 2$ x $(10$ x $0.096 - 4.6$ x $0.1)$ x $1000 / 0.1$

$$Na_2S \ (mg/L) = \frac{eq. \ mas \ of \ Na_2S \ x \ V_{HCl} \ x \ N_{HCl} \ x \ 1000}{Sample \ Vol} \qquad [7]$$

$= 78 / 2$ x 5 x 1 x $1000 / 1$

TABLE XV Sulphide in solution after Na_2S has reacted with CO_2 (experimental)

Na2S prepared	Na2S prepared	Na2S	CO2/Na2S ratio	Volume	pH	Sulphide measured
mg Na2S/ 50 mL	g Na2S/L	meq/50mL		mL		mg Na2S/50mL
174	3.5	4.5	5.0	50	12.1	166
435	8.7	11.2	2.0	50	12.0	410
871	17.4	22.3	1.0	50	11.5	819
1 741	34.8	44.6	0.5	50	11.4	1 716

CO_2 volume = 250 mL

Error! Reference source not found. also showed that: (i) the Na_2S concentration, determined with both the sulphide and the alkalinity methods, to be 195 g/L (as Na_2S), which corresponded closely with the nominal concentration of the prepared solution, i.e., 200 g/L (as Na_2S), (ii) Sulphide remained in solution, as expected from Eq 5. It is only converted from S^{2-} to HS^-, and (iii) $NaHCO_3$ precipitated according to Eq. 5 when Na_2S reacts with CO_2, as indicated by the reduction of Alk from 136 500 mg/L (as Na_2S) at a CO_2/Na_2S mole ratio of 1, to 113 100 (as Na_2S) at a CO_2/Na_2S mole ratio of 4. The reason for why the Alk was not already lower at a ratio of 1 can be ascribed to incomplete mixing between the large volume of CO_2 needed (250 mL) and the small volume of the concentrated Na_2S solution (4.3 mL of a 200 g/L Na_2S solution). This challenge was overcome by bubbling CO_2 through a 100 mL solution of 200 g/L Na_2S.

showed how the pH dropped from 13.1 to 8.2 as CO_2 was added, the Na_2S concentration remained constant around 195 975 mg/L Na_2S, as S^{2-} was converted to HS^- and Alk decreased by 50% as $NaHCO_3$ precipitated (from 198 900 to 93 600), according to Eq. 5.

TABLE XVI Effect of CO_2 addition to a Na_2S solution of 200 g/L Na_2S (Experimental)

Reactants	Mass (g)	CO2/Na2S mole ratio			
		Feed	1.00	2.00	4.00
Na2S (g)	200	0.88	0.88	0.88	0.88
H2O (g)	1 000	4.38	4.38	4.38	4.38
CO2 (g)	113	0.49	0.49	0.99	1.97
CO2 (mL)		251.3	251.3	502.6	1 005
Parameters					

| pH		13.1	10.6	9.5	8.7
Sulphide (mg/L Na₂S)		195 000	206 700	198 900	187 200
Alkaliniity (mg/L Na₂S)		195 000	136 500	120 900	113 100

Temp = 25°C

TABLE XVII NaHCO₃ precipitation when CO₂ is bubbled through a 200 g/L Na₂S solution (100 mL) (Experimental)

Time	pH	S²⁻	Alk
min		mg/L Na₂S	mg/L Na₂S
0	13.1	198 900	198 900
5	12.1	202 800	167 700
10	11.1	191 100	159 900
15	10.0	200 850	140 400
20	9.1	195 000	117 000
21	8.2	187 200	93 600
Average		195 975	

E. Na₂CO₃ from NaHCO₃

showed the conversion of NaHCO₃ to Na₂CO₃. It is noted that the double salt, Na₂CO₃·NaHCO₃·2H₂O, formed (Eq. 8).

$$3NaHCO_3 + H_2O \rightarrow Na_2CO_3 \cdot NaHCO_3 + CO_2 + 2H_2O \quad [8]$$
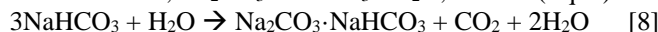
TABLE XVIII Conversion of NaHCO₃ to Na₂CO₃·NaHCO₃ (OLI simulation).

NaHCO3 [mmol] (Y2)	H2O [mmol]	NaHCO3 (Nahcolite) - Sol [mmol] (Y2)	Na2CO3·NaHCO3·2H2O - Sol [mmol] (Y2)	Na(+1) Aq [mmol] (Y2)	H2O - Vap [mmol] (Y2)	CO2 - Vap [mmol] (Y2)
500	55 500	0	0.0	500	29 279	204
500	50 505	0	0.0	500	28 118	206
500	45 510	0	0.0	500	26 750	209
500	40 515	0	0.0	500	25 143	212
500	35 520	0	0.0	500	23 263	214
500	30 525	0	0.0	500	21 082	217
500	25 530	0	0.0	500	18 589	219
500	20 535	0	0.0	500	15 810	221
500	15 540	0	31.5	406	13 006	211
500	10 545	0	163.4	10	10 321	168

Temp = 100°C; pH = 9.46

IV. CONCLUSIONS

It was found that: (i) The production Na₂S via BaS is preferred above Na₂S via CaS due to less CaSO4 left in solution, (ii) Na₂S can be reacted with CO₂ to form NaHCO₃(*aq*) and NaHS(*aq*), (iii) the latter two compounds can be separated through freeze-crystallization, as NaHCO₃ has a lower solubility at 0°C, and (iv) NaHCO₃ can be converted into Na₂CO₃ though heating via Na₂CO₃·NaHCO₃·2H₂O.

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- Mokgohloa, C.P., Thomas, M.S., Mokgalaka, N.S. and Ambushe, A.A., 2020. Speciation of chromium in river sediments by graphite furnace-atomic absorption spectrometry after microwave-assisted extraction. International Journal of Environmental Analytical Chemistry, pp.1-15.

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