

Thermal Processing of Sodium Sulphate to Sodium Carbonate

Lehlogonolo Mashigwana¹, Johannes Maree^{2,3}, Lizzy Monyatse⁴, Amos Adeniyi¹, and Maurice Onyango¹

Abstract— Mine water is environmentally toxic due to high metal concentrations. Strict legislation is enforced. Water of drinking quality needs to be produced and zero waste should be left at the mine site. The ROC (Reverse osmosis/Cooling) process can meet these requirements. In the ROC process, Na_2CO_3 is used in the pre-treatment stage for selective recovery of metal compounds, such as $\text{Fe}(\text{OH})_3$ at pH 3.5, followed by reverse osmosis for recovery of drinking water and brine containing 90 g/L Na_2SO_4 . In the subsequent cooling stage, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is removed through cooling, due to its low solubility of 45 g/L at 0 °C. The purpose of this investigation was to investigate the thermal conversion of the product, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, to the raw material, Na_2CO_3 . It was found that (i) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ can be converted to Na_2SO_4 though heating between 60 °C and 100 °C, (ii) Na_2SO_4 cannot be converted directly to Na_2S , as the raw material, Na_2SO_4 , melts in the same temperature region where the reduction takes place, namely above 860 °C, (iii) Na_2S can be produced via CaS (indirect method) (Pyrusim simulation studies) and (iv) Na_2S can be converted to NaHS, NaHCO_3 and Na_2CO_3 (OLI simulation studies).

Keywords— Sodium Acid mine water, sodium sulphate, sodium carbonate, Pyrusim, OLI simulations.

I. INTRODUCTION

Acid mine drainage is a serious threat to South Africa's water resources. Clean drinking water is a basic need for all citizens. Acid mine drainage may have a low pH and contain high levels of dissolved heavy metals and sulphate. Legislation ideally requiring zero liquid disposal (ZLD), which means that all water must be recovered and contaminants must be reduced to solid waste. The ROC process is a zero liquid waste disposal process where Na_2CO_3 is used for selective recovery of valuable salts in its pre-treatment stage, such as ferric hydroxide, aluminium hydroxide, CaCO_3 ; drinking water during the desalination stage and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ during the brine treatment stage. The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ has a low value due to excessive supply. The market is small and the price limited to R700/t. Value can be added to the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ by processing it via Na_2SO_4 and Na_2S to Na_2CO_3 . Na_2CO_3 is used as raw material in soap and glass manufacturing, food processing, pH-modifier, swimming pool chemical and electrolyte.

Lehlogonolo Mashigwana is an M.Eng. student at the Tshwane University of Technology, Pretoria, South Africa.

Brines from desalination processes, such as reverse osmosis (Fig. 1) can be treated with the ROC process (Reverse Osmosis/Cooling). In the pre-treatment stage of the ROC process, brine is treated with sodium carbonate to allow selective precipitation of metals, e.g. $\text{Fe}(\text{OH})_3$ at pH 3.5, $\text{Al}(\text{OH})_3$ at pH 4.5, and CaCO_3 at pH 8.0. After pre-treatment, the sodium-rich water is treated with RO to produce drinking water and brine. The brine has a concentration high enough to allow Na_2SO_4 crystallization upon cooling.

Sodium salts are used to produce water that contains the more soluble sodium sulphate instead of gypsum. This has an advantage of reducing membrane scaling. Sodium sulphate has a low solubility of 4% at 0 °C and 20% at 20 °C. The ROC process exploits this characteristic to treat the brine generated from RO by cooling it to 0 °C, thereby precipitating sodium sulphate, which in turn lowers the osmotic pressure. The lower osmotic pressure enables the use of RO, to further treat the brine in a closed loop, resulting in a zero liquid discharge process.

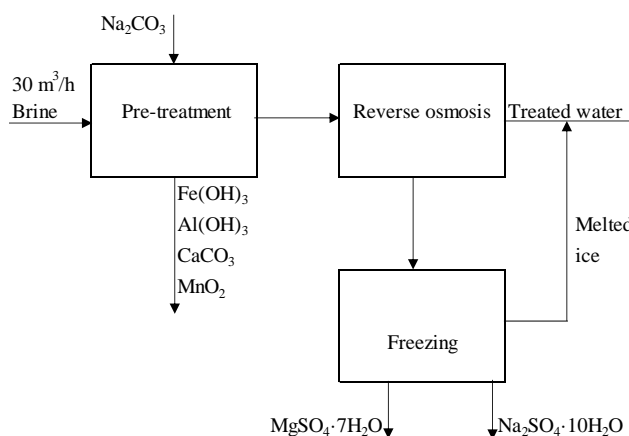


Fig. 1. Process configuration of the ROC process [1]

Calcium carbonate and H_2S is produced by reacting carbon dioxide with calcium sulphide. H_2S is converted to elemental sulphur on oxidation with SO_2 or Fe^{3+} [2]. The application of these technologies in production of elemental sulphur has been constrained by the solubility limitation of CaS. It is difficult to obtain a satisfactory reaction between carbon dioxide gas and calcium sulphide in an aqueous slurry. The main reason is the

formation of a layer of calcium carbonate on the calcium sulphide particles that slows down the reaction.

Nyman and O'Brien introduced a catalytic method which makes use of a catalyst to reduce sodium sulphate at lower temperatures [3]. **Eq. 1** shows the reaction for reducing sodium sulphate at temperatures between 700 and 1000°C.



Feldbaumer, et al. in their study they developed a process for the conversion of sodium sulphate to sodium carbonate [4, 5]. They also introduced finely divided sodium sulphate into a combustion chamber where sodium sulphate melted at a temperature higher than its melting point [5, 4]. The gas in the combustion chamber (carbon monoxide, hydrogen, and/or a hydrocarbon), provided the reducing atmosphere needed for the reduction of sodium sulphate to sodium sulphide [5]. The sodium sulphate, suspended in a carrier gas, was blown into the reducing part of a burner flame.

The aim of this study was to determine how the product, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, can be converted to the raw material, Na_2CO_3 , through the following reaction: (i) Processing of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to Na_2SO_4 ; (ii) Reduction of Na_2SO_4 to Na_2S , using coal as the reductant; (iii) Conversion of Na_2S to NaHCO_3 and NaHS by adding CO_2 ; concentration of the solution to allow NaHCO_3 to crystallize out due to its lower solubility.

II. MATERIAL AND METHODS

A. Feedstock, chemicals and reagents

The following chemicals were used: Sodium sulphate decahydrate produced through freeze crystallization, sodium sulphate and coal were sourced from a coal mine in Mpumalanga. Analytical grade chemicals were used. Deionized water was used for preparation of all solutions (6 M HCl, 0.1 N $\text{Na}_2\text{S}_3\text{O}_4$, 0.1 M I_2 and starch).

B. Equipment

A muffle furnace was used for thermal studies. A TGA analyser was used to investigate its thermal properties.

C. Procedure

A weighed amount of sodium sulphate decahydrate was dried at various temperatures.

Sodium sulphate and coal were mixed thoroughly, placed in a alumina ceramic boat, and heated in the muffle furnace at temperatures up to 1100°C. The reaction time for all the experiments varied between 30 and 90 minutes.

D. Experimental

Whereby the hydrated sodium sulphate was dried at an interval of 10 min while weighing the mass with temperature changes (investigated at 60°C, 80°C and 100°C).

A series of tests were conducted using Pyrosim software to determine the effect of temperature (900°C, 1100°C, 1200°C), reaction time (30min, 1hr and 24hr) and the effect of coal to sodium sulphate mole ratios (5:1, 4:1; 2:1, 1.3:1 and 1:1) on the conversion of waste dry sodium sulphate to sodium

sulphide. Pyrosim results were confirmed with laboratory studies.

E. Analytical

Sulphide was determined by standard iodometry [6] as follows: A mass of 500 mg of the reduced product was taken and made up to 100 mL with deionized water. A 10 mL aliquot was pipetted into a conical flask. Standard iodine (10 mL 0.1N) solution was added, followed by deionized water (50 mL). The combination was acidified with 1:1 HCl (2 mL) and titrated with standard (0.1N) sodium thiosulphate utilizing starch marker to a dreary end-point. The NaS was determined as follows:

$$\% \text{NaS} = \frac{[\text{V}(\text{iodine used}) - \text{Titration volume}] \times 36}{\text{Sample mass (mg)}} \times 100 \quad [2]$$

F. Pyrosim Mintek simulation

The prediction of sodium sulphate was carried out using Pyrosim Mintek model. Chemical engineering thermodynamic properties such as entropies, Gibbs free energy enthalpy change in a chemical reaction can be obtained from Pyrosim Mintek model.

The working temperature for the simulation was varied from 100°C -1200°C and working pressure factor was kept up at 1 atm for all the cycle units. The ratio of coal to gypsum and temperature were varied in order to determine the optimum ratio with the Mintek Pyrosim model. An assumption taken regarding the temperature of the matte and the exit gas temperature was that the matte stream exit temperature and the gas stream exit temperature was maintained at the same temperature. This assumption primarily affects the energy requirements and has a lesser effect on the chemistry of gypsum conversion to Na_2S .

G. OLI simulation

The OLI Analyser 9.0 System was used to simulate the reactions by running a simulated water sample with assumed values of temperature, pressure and pH. The chemicals used to determine its solubility were Na_2S , NaHCO_3 , Na_2CO_3 . Once the input values were used in a calculation in the OLI Systems Chem Analyzer, a calculated summary of the simulated results would appear. This could be used to predict the actual reactions that will take place under specific conditions and the final concentration of the various parameters. Thus, it was used to optimize a neutralization-precipitation-desalination process for acid mine drainage.

III. RESULTS AND DISCUSSION

A. Processing of sodium sulphate decahydrate to andrate

The first step in the processing of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ to Na_2CO_3 is the removal of crystal water through heating [7].

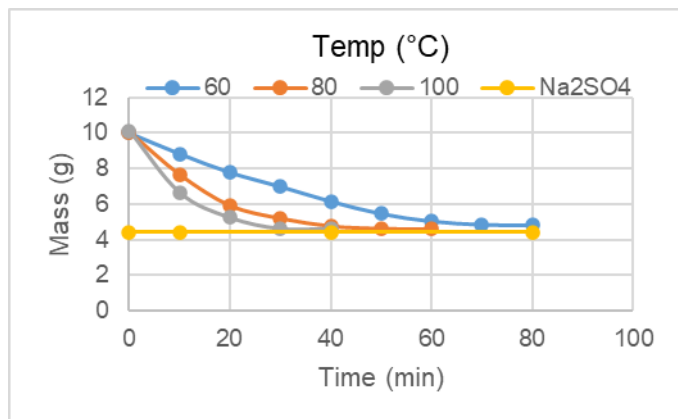


Fig. 2 shows the dehydration of sodium sulphate decahydrate at 60 °C, 80 °C and 100 °C respectively. Research studies by (Ozalp, et al., 2006) has indicated that the decomposition of sodium sulphate decahydrate begins at a temperature above 32.4 °C. At temperature above 32.4 °C, sodium sulphate decahydrate undergoes a phase transformation and starts to crystallize as it forms anhydrous sodium sulphate (**Eq.3**).

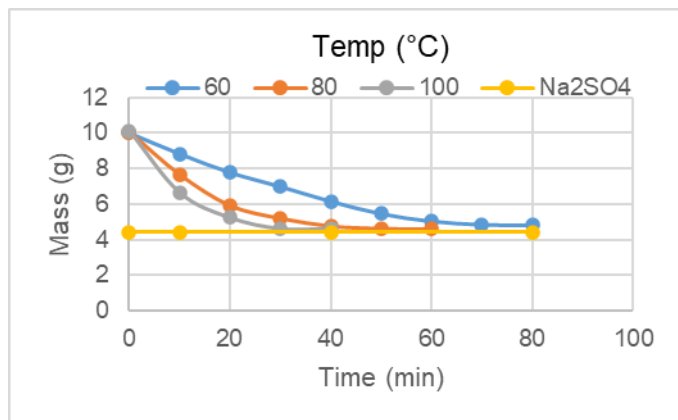
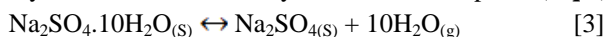


Fig. 2. Dehydration of Sodium Sulphate Decahydrate at 100 °C

B. Na_2SO_4 reduction

Fig. 3 shows the TGA (Thermogravimetric analysis) mass loss when Na_2SO_4 is reacted with carbon. The mass loss between 820 to 920 °C can be ascribed to the conversion of Na_2SO_4 with a mol mass of 136g to Na_2S with a mol mass of 72g.

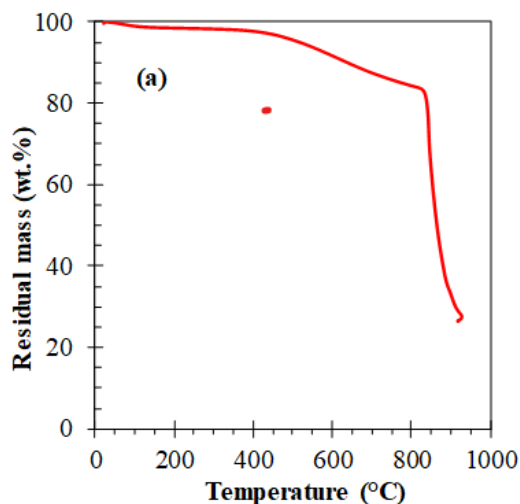
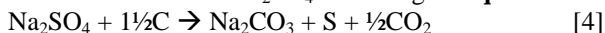


Fig. 3. TGA curve

1) Pyrosim predictions

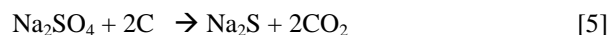
Na_2CO_3 is the preferred raw material in the ROC process. It is therefore ideal if Na_2CO_3 can be recovered directly from the thermal treatment of Na_2SO_4 according to **Eq 4**.



Pyrosim simulations showed that Na_2CO_3 is the main product at a temperature of 350 °C and with a C/ Na_2SO_4 mole ratio greater than 1.5 (**Table**, Run 5). At a Carbon to Na_2SO_4 mole ratio of 2.66, 75.2% of the Na_2SO_4 was converted to Na_2CO_3 , 29.8% to S and 4.9% remained as Na_2SO_4 . By varying the temperature, it was noticed that 350 °C is the optimum temperature for Na_2CO_3 production. From the thermodynamic viewpoint, the Na_2CO_3 route looks attractive due to the low temperature that is needed. With thermodynamics the end products can be predicted but not the reaction rate. Laboratory studies showed that the reaction is extremely slow.

At temperatures above 500°C, Na_2S is the main product (

Table, Runs 9 to 19). At a C/ Na_2SO_4 mole ratio of 2.22 and a temperature of 500 and higher, 77.8% and more of the Na_2SO_4 is converted to Na_2S and 13.4 and less to Na_2CO_3 . The C/ Na_2SO_4 mole ratio determines the ratio of Na_2S to S in the product. At a temperature of 1000 °C and mole ratio of 2.22, 99.6% of the Na_2SO_4 was converted to Na_2S , compared to 80.7% Na_2S and 18.2% S where the ratio was 5.33 (**Table**, Runs 20 and 21). **Eq. 5** shows the reaction for Na_2S production.



2) Muffle furnace studies

The aim of this section was to determine the effect of various parameters on the kinetics of Na_2SO_4 reduction with activated carbon. **Fig. 4** shows the product when 10 g Na_2SO_4 was reacted with 4 g activated carbon. This represented a C/ Na_2SO_4 mole ratio of 4.26. Na_2SO_4 was not converted to Na_2S , instead a hard melted product was produced. From literature, it was learned to be melted Na_2SO_4 [8].



Fig. 4. Photo of melted Na_2SO_4 when heated to 1000 °C

The reason sodium sulphate is not reduced directly with carbon is because sodium sulphate has a relatively low melting point of 890°C. When sodium sulphate is directly reduced with carbon at elevated temperatures, an intermediate molten phase is formed that is difficult to contain and which is very corrosive [9]. They recommended a maximum operating temperature of 630°C. Roberts studied the reduction of Na_2SO_4 with carbon monoxide at 900°C. He found that both ceramic and platinum boats reacted with the Na_2S [8]. It will be difficult to find a suitable material for construction for Na_2SO_4 reduction at elevated temperatures. Feldbaumer et al. developed an apparatus for the reduction of sodium sulphate to sodium sulphide include that fed sodium sulphate into a combustion chamber. In this design the sodium sulphate was exposed to a reducing atmosphere while at the same time being exposed also to high temperature above the melting point of sodium sulphide [5]. This system needed special procedure to deal with the off gas.

The problem of a melted compound was not experienced in the thermal processing of CaSO_4 to CaS and BaSO_4 to BaS [10, 11, 12]. **Table** shows that Na_2SO_4 has a melting point of 884 °C which is in the temperature range where Na_2SO_4 is converted to Na_2S , unlike CaSO_4 , which melts at 1469°C and BaSO_4 at 1580°C.

An ideal solution may be the new process that was developed by van Vuuren and Maree [13]. In this process, CaS is reacted with Na_2SO_4 in solution to form Na_2S . A provisional patent was filed for this development. This development will offer the following additional benefits: The reduction of CaSO_4 to CaS is known and do not offer any challenges; Rare earth metals can be recovered from gypsum from the fertilizer industry, nano CaCO_3 can be recovered as a by-product as well as S , Na_2S and NaSH . Mokgohloa *et al.* studied this reaction and showed that Na_2S can be produced by reacting Na_2SO_4 with CaS [14].

TABLE I
MELTING POINTS OF VARIOUS METAL COMPOUNDS

Compound	Melting Point (°C)	Solubility (g/L)
Na_2SO_4	884; 1170	281
K_2SO_4	1069	120

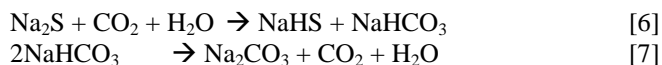
MgSO_4	1137	357
CaSO_4	1460	2.05
BaSO_4	1580	0.00312
Na_2S	950; 1170	
K_2S	840	
CaS	2525	
BaS	2235	

TABLE II
MELTING POINTS OF VARIOUS METAL COMPOUNDS

Compound	Melting Point (°C)	Solubility (g/L)
Na_2SO_4	884; 1170	281
K_2SO_4	1069	120
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CaSO_4	1460	2.05
BaSO_4	1580	0.00312
Na_2S	950; 1170	
K_2S	840	
CaS	2525	
BaS	2235	

C. Processing of sodium sulphide to sodium carbonate

The aim of this investigation is to convert the product from the thermal stage, Na_2S , to Na_2CO_3 , the raw material for the ROC process. It was proposed by Maree (Pers. comm, 2020) that freeze crystallization be evaluated for the processing of Na_2S to NaHCO_3 and NaHS (**Eq. 6**) by removing water through freeze crystallization. NaHCO_3 is separated from NaHS through cooling and or removal of water through freeze crystallization as it has a much lower solubility. The NaHCO_3 is converted to Na_2CO_3 through heating to 40°C (**Eq. 7**). **Fig. 5** shows the process configuration for the conversion of Na_2S to Na_2CO_3 and NaHS . This process has the potential to reduce the cost of Na_2CO_3 from the current purchase price of R5 000/t to less than R2 000/t.



a) Sulphide species

Fig. 5 shows the sulphide species (S^{2-} , HS^- , $\text{H}_2\text{S}(\text{aq})$, $\text{H}_2\text{S}(\text{g})$) as a function of pH when 100 mmol Na_2S is titrated with HCl . It shows the dominant specie in solution and in gas phase over the pH range 12 to 3 due to equilibrium reactions in **Eq. 8** to **Eq. 9**.



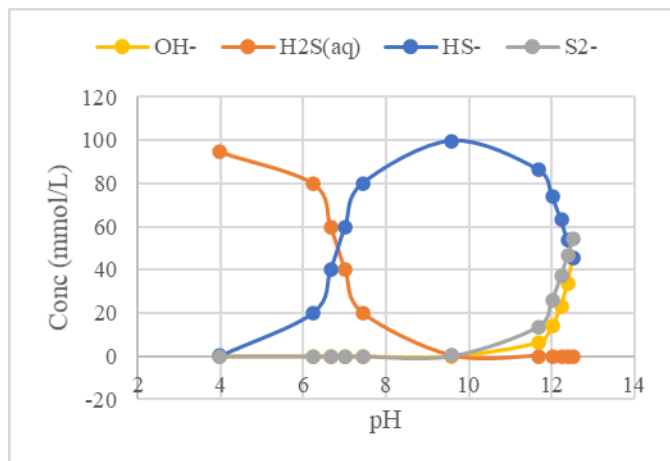


Fig. 5. Sulphide species in solution as a function of pH

b) Solubilities

• Na₂S

OLI software was used to calculate the solubility of Na₂S by increasing the dosage with increments of 300 mmol in 1 L (55 508 mmol) of water [15]. When 3 000 mmol Na₂S is dissolved in water, it was calculated that 2665 mmol Na₂S dissolved in 1 L of water (1 L ≡ 55 508 mmol H₂O) or 207.9 g Na₂S/L (Table). The fraction that did not dissolve remain as a solid, Na₂S·9H₂O (Eq. 11). The following species were also shown: Na⁺ and S²⁻ in solution and free H₂O left after crystal water was linked to Na₂S(aq) or Na₂S·9H₂O(s).



• NaHCO₃

OLI software was used to calculate the solubility of NaHCO₃ (Nahcolite) by increasing the dosage with increments of 200 mmol in 1 L (55 508 mmol) of water [15]. When 2 000 mmol NaHCO₃ is dissolved in water, it was noticed that 1 305 mmol NaHCO₃ dissolved in 1 L of water (1 L ≡ 55 508 mmol H₂O) or 109.6 g NaHCO₃/L (Table). The fraction that did not dissolve remain as a solid did not contain crystal water, as the case was with Na₂S·9H₂O.

• NaHS

OLI software was used to calculate the solubility of NaHS by increasing the dosage with increments of 10 000 mmol in 1 L (55 508 mmol) of water [15]. When 100 000 mmol Na₂S is dissolved in water, it was noticed that 86 406 mmol NaHS dissolved in 1 L of water (1 L ≡ 55 508 mmol H₂O) or 4 839 g NaHS/L (Table). The fraction that did not dissolve remain as a solid, Na₂S. The following species were also shown: Na⁺ and S²⁻ in solution. No crystal water was formed, as indicated by the constant value of H₂O (55 508 mmol) for different dosages. When the solubility of NaHS is exceeded, it decomposes to form Na₂S(s) and H₂S(g) (Eq. 12).



c) NaHCO₃ production

NaHCO₃ formed when Na₂S reacted with CO₂ and H₂O (Eq. 13 to Eq. 15). The two products can be separated due to

the low solubility of NaHCO₃ (109.6 g/L) compared to the high solubility of NaHS (4 839 g/L).

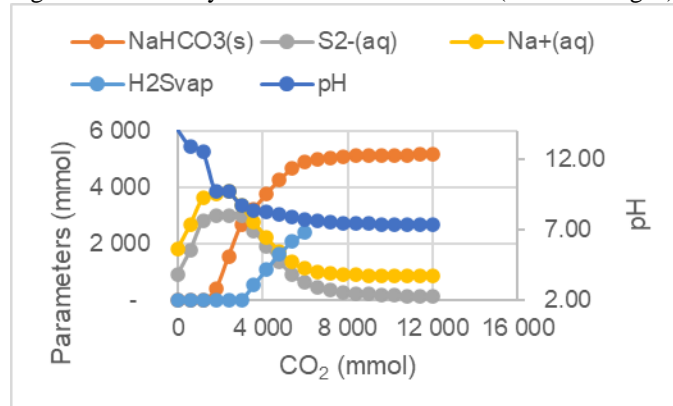


Fig. 6 shows the effect when 12 000 mmol CO₂ was added in increments of 1 200 mmol to 3 000 mmol Na₂S in 1 L water. The following observations were made:

With a CO₂ dosage of 0 to 1 500 mmol the pH dropped from 14 to 10 as 3000 mmol Na₂S dissolved to produce 3000 mmol S²⁻(aq) and 6000 Na⁺(aq) (Phase 1) (Eq. 13).

A further CO₂ dosage from 1 500 to 3 000 mmol resulted in the precipitation of 3 000 mmol NaHCO₃ (Phase 2). S²⁻ remained constant at 3 000 mmol as all the S²⁻ dissolved during Phase 2 (Eq. 14).

A further CO₂ dosage from 3000 to 6000 mmol (Phase 3) resulted in the precipitation of a further 3 000 mmol NaHCO₃ and the stripping of 3 000 mmol H₂S due to excess CO₂ (Eq. 15).

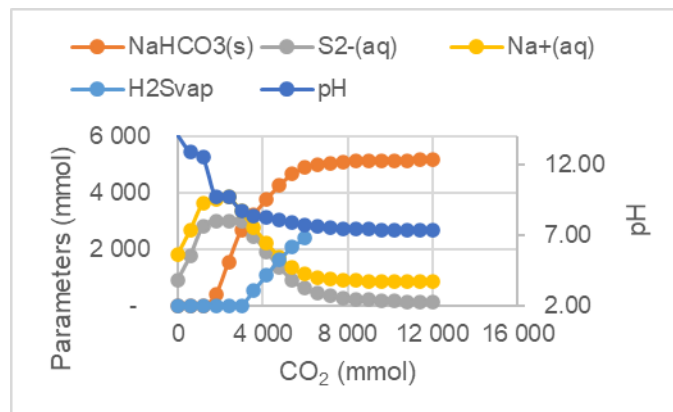
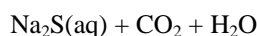
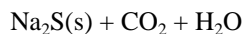


Fig. 6. Behaviour of various parameters when CO₂ is added stepwise to Na₂S(aq) (OLI, 2015)

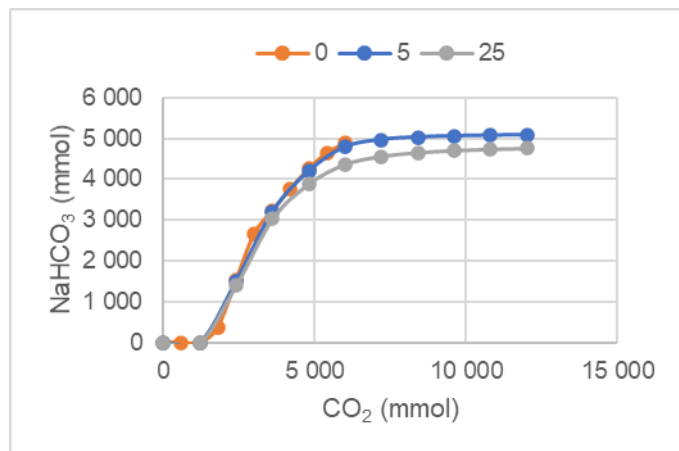


Fig. 7 shows the effect of temperature on the concentrations of $\text{NaHCO}_3(\text{s})$ that formed when 3 000 mmol of Na_2S was added to 1L of water. There was a slight increase with lower temperatures.

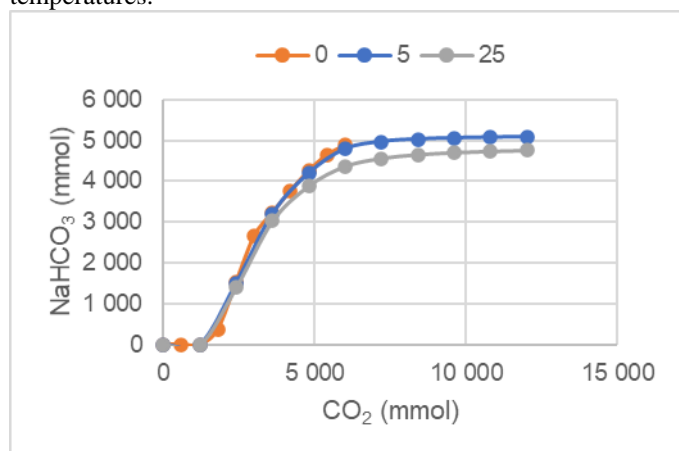
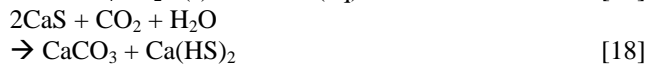
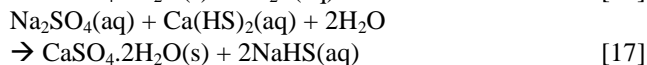
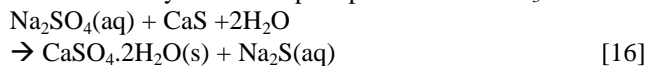


Fig. 7. Effect of temperature ($^{\circ}\text{C}$) on the formation of NaHCO_3 [15]

This investigation used OLI software to identify conditions needed for the conversion of Na_2S to NaHCO_3 and NaHS . Laboratory studies by Mokgohloa *et al.* were used to confirm that Na_2SO_4 can be converted to Na_2S by reacting to it with CaS (Eq. 16) or $\text{Ca}(\text{HS})_2$ (Eq. 17) (Mokgohloa, *et al.*, 2021). $\text{Ca}(\text{HS})_2$ it was produced by reacting CaS with CO_2 according to Eq. 18. CO_2 was added during the course of the experiment to control the pH at 7.9. This resulted in the removal of 50% of the alkalinity due to the precipitation of CaCO_3 .



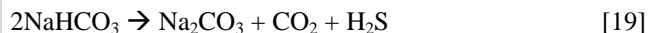
d) Up concentration of NaHS

After removal of NaHCO_3 as a solid, NaHS remained in solution. NaHS is a valuable product as it is used as a flotation agent in the mining industry and for hair removal in the tanning industry. After removal of NaHCO_3 with CO_2 addition, the NaHS has a concentration of 188 g/L (3.37 mol/L). This solution can be up-concentrated to be sold as a commercial product.

Fig. 8 shows that when 1 L of water (55 508 mmol) is reduced to 150 mL (8 117 mmol), the NaHS concentration in solution increased from 188 g/L to 1 180 g/L (21.1 mol/L). $\text{NaHCO}_3(\text{s})$ would have increased to the same extent if not removed as a solid prior to water removal through freeze crystallization.

e) Na_2CO_3 production

The sodium hydrogen carbonate is heated in rotating ovens at 450 K so that it decomposes to sodium carbonate, water and carbon dioxide:



IV. CONCLUSIONS

The following conclusions were made: (i) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ can be converted to Na_2SO_4 though heating between 60°C and 100°C , (ii) Na_2SO_4 cannot be converted directly to Na_2S , as the raw material, Na_2SO_4 , melts in the same temperature region where the reduction takes place, namely above 860°C , (iii) Na_2S can be produced via CaS (indirect method) (PyruSim simulation studies) and (iv) Na_2S can be converted to NaHS , NaHCO_3 and Na_2CO_3 (OLI simulation studies).

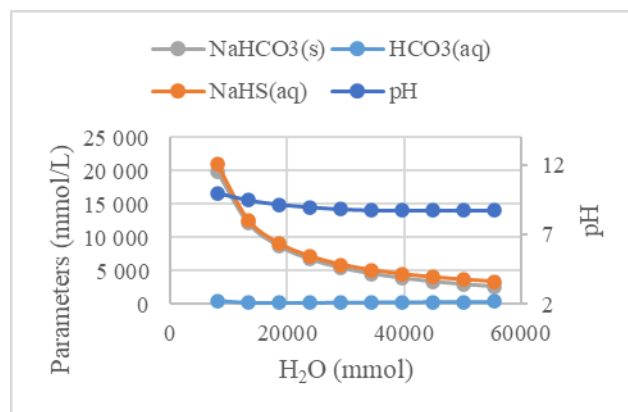


Fig. 8. Up-concentration of NaHS through freeze crystallization

REFERENCES

- [1] S. L. Letjiane, J. P. Maree, M. S. Onyango and A. Adeniyi, "Pre-treatment of coal dump leachate with MgO for pigment recovery," in *IMWA 2019 Conference - Mine Water: Technological and Ecological Challenge*, Perm, Russia, 2019.
- [2] R. N. Nengovhela, C. A. Strydom, J. P. Maree, S. Oosthuizen and D. J. Theron, "Recovery of sulphur and calcium carbonate from waste gypsum," *Water SA*, vol. 33, no. 5, pp. 741-748, 2007. <https://doi.org/10.4314/wsa.v33i5.184097>
- [3] C. J. N. T. D. O'Brien, "Catalytic method of reducing sodium sulphate," *ACS Publications*, vol. 8, no. 39, p. 1019-1021, 1947. <https://doi.org/10.1021/ie50452a019>
- [4] E. Feldbaumer, L. H. and A. Sandri, "reduction of sodium sulphate to sodium sulfide," *US patent*, 1977.
- [5] E. Feldbaumer, H. Loquenz and A. Sandri, "Reduction of sodium sulphate to sodium sulphide". USA Patent 4,198,385, 15 April 1980.
- [6] APHA, Standard methods for the examination of water and wastewater, 12th ed, Washington, DC: American Public health Association., 2012.
- [7] B. Ozalp, S. Tarhan, A. Seyrankaya and E. Kaya, "Alternative Drying of Sodium Sulfate Decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) with Microwave Energy.," *Istanbul: Proceeding of XXIII International Mineral Processing Congress*, 2006.

- [8] W. F. Roberts, "The high temperature reactions between sodium sulphate and carbon monoxide," Oklahoma Agricultural and Mechanical College, Oklahoma, 1947.
- [9] C. J. Nyman and O'Brien, "Catalytic reduction of sodium sulphate," *Ind. Eng. Chem.*, vol. 39, no. 8, pp. 1019-1021, 1947.
<https://doi.org/10.1021/ie50452a019>
- [10] S. Ruto, J. P. Maree, C. M. Zvinowanda, A. Kolesnikov and W. Louw, "Thermal studies on barium sulphate in a pilot scale, rotary kiln," Sheraton Santiago Hotel & Convention Center, Chile, 10 - 12 April, 2011.
- [11] S. Ruto, J. P. Maree, C. M. Zvinowanda, A. V. Kolesnikov and W. J. Louw, "Thermal studies on gypsum in a pilot-scale, rotary kiln," Ingwenyama Conference & Sport Resort, White River, 15 – 17 February, 2011.
- [12] R. K. Tewo, J. P. Maree, S. Ruto, H. L. Rutto and L. K. Koech, "Reduction Process and its Validation using the Mintek Pyrosim Model," *Chemical Engineering*, no. Communications, DOI: 10.1080/00986445.2017.1365064, 2017.
- [13] D. S. van Vuuren and J. P. Maree, "Production of sodium carbonate from sodium sulphate". South Africa Patent 2020/07178, 18 November 2020.
- [14] C. P. Mokgohloa, J. P. Maree, D. S. van Vuuren, K. D. Modibane and M. M. M. Mujuru, "Recovery of Na₂CO₃ and nano CaCO₃ from Na₂SO₄ and CaSO₄ wastes," in *Nano Technology*, New York, Wiley Scrivener, 2021, pp. 1-2.
- [15] OLI, "[http://www.olisystems.com/.](http://www.olisystems.com/)," 23 11 2015. [Online]. [Accessed 2015].

TABLE III. THERMAL PRODUCTION OF Na₂CO₃

No	Conversion (%)						Input data								Matte (% mass)						
Run No	Sum	Na ₂ CO ₃	Na ₂ S	Na ₂ SO ₄	S	C/Na ₂ SO ₄	Temp	Na ₂ SO ₄	Na ₂ SO ₄	Coal	Coal	H ₂ O	Volatiles	NaO	Na ₂ CO ₃	Na ₂ S	Na ₂ SO ₄	S	C	Total	
	%	%	%	%	%		°C	%	kg/h	kg/h	%	%	%	%	%	%	%	%	%	%	
Effect of coal ratio: Na ₂ SO ₄ ; Temp = 350°C																					
1	100.0	20.4	0.0	73.8	5.8	0.44	350	100	100	5	75	5.4	19.6		20.39	0.00	73.62	5.75	0.24	100.00	
2	100.0	39.4	0.0	49.6	11.0	0.89	350	100	100	10	75	5.4	19.6		39.09	0.01	49.19	10.91	0.80	100.00	
3	100.0	66.7	0.0	15.1	18.2	1.78	350	100	100	20	75	5.4	19.6		64.11	0.05	14.52	17.52	3.81	100.00	
4	100.0	67.4	0.1	14.5	18.1	2.22	350	100	100	25	75	5.4	19.6		67.70	0.06	14.52	18.17	6.49	106.94	
5	100.0	75.2	0.1	4.9	19.8	2.66	350	100	100	30	75	5.4	19.6		68.10	0.06	4.47	17.91	9.46	100.00	
6	100.0	77.9	0.1	2.5	19.6	3.55	350	100	100	40	75	5.4	19.6		65.98	0.06	2.08	16.57	15.31	100.00	
7	100.0	79.4	0.1	1.5	19.0	4.44	350	100	100	50	75	5.4	19.6		63.00	0.05	1.21	15.07	20.67	100.00	
8	100.0	80.6	0.1	1.1	18.3	5.33	350	100	100	60	75	5.4	19.6		60.02	0.04	0.79	13.64	25.52	100.00	

TABLE IV. THERMAL PRODUCTION OF Na₂S

No	Conversion (%)						Input data								Matte (% mass)							Matte (kg/h)					
Run No	Sum	Na ₂ CO ₃	Na ₂ S	Na ₂ SO ₄	S	C/Na ₂ SO ₄	Temp	Na ₂ SO ₄	Na ₂ SO ₄	Coal	Coal	H ₂ O	Volatiles	NaO	Na ₂ CO ₃	Na ₂ S	Na ₂ SO ₄	S	C	Total	Na ₂ CO ₃	Na ₂ S	Na ₂ SO ₄	S	C	Total	
	%	%	%	%	%		°C	%	kg/h	kg/h	%	%	%	%	%	%	%	%	%	%	%	kg/h	kg/h	kg/h	kg/h	kg/h	kg/h
Effect of temperature; C/Na ₂ SO ₄ ratio = 2.22																											
9	100.0	11.0	0.0	86.6	2.4	2.22	100.0	100.0	100.0	25.0	75.0	5.4	19.6		9.4	0.0	74.0	2.1	14.5	100.0	8.2	0.0	64.6	1.8	12.7	87.3	
10	100.0	43.4	0.0	45.7	10.9	2.22	200.0	100.0	100.0	25.0	75.0	5.4	19.6		38.9	0.0	40.9	9.8	10.5	100.0	32.4	0.0	34.1	8.1	8.7	83.4	
11	100.0	67.2	0.0	14.9	17.9	2.22	300.0	100.0	100.0	25.0	75.0	5.4	19.6		62.3	0.0	13.8	16.6	7.2	100.0	50.2	0.0	11.1	13.4	5.8	80.4	
12	100.0	72.4	0.1	8.1	19.4	2.22	350.0	100.0	100.0	25.0	75.0	5.4	19.6		67.7	0.1	7.6	18.2	6.5	100.0	54.0	0.0	6.0	14.5	5.2	79.8	
13	100.0	74.9	0.6	4.3	20.2	2.22	400.0	100.0	100.0	25.0	75.0	5.4	19.6		70.4	0.5	4.0	19.0	6.1	100.0	55.9	0.4	3.2	15.1	4.8	79.5	
14	100.0	13.4	77.8	8.8	0.0	2.22	500.0	100.0	100.0	25.0	75.0	5.4	19.6		12.8	74.7	8.4	0.0	4.0	100.0	10.0	58.1	6.6	0.0	3.1	77.8	
15	100.0	13.8	85.4	0.8	0.0	2.22	600.0	100.0	100.0	25.0	75.0	5.4	19.6		13.5	83.8	0.8	0.0	1.9	100.0	10.3	63.8	0.6	0.0	1.4	76.1	
16	100.0	13.2	86.4	0.4	0.0	2.22	700.0	100.0	100.0	25.0	75.0	5.4	19.6		13.1	85.9	0.4	0.0	0.5	100.0	9.9	64.5	0.3	0.0	0.4	75.1	
17	100.0	11.6	87.4	1.0	0.0	2.22	800.0	100.0	100.0	25.0	75.0	5.4	19.6		11.5	87.2	1.0	0.0	0.1	99.9	8.6	65.3	0.7	0.0	0.2	74.8	
18	100.0	9.6	87.8	2.6	0.0	2.22	900.0	100.0	100.0	25.0	75.0	5.4	19.6		9.6	87.6	2.6	0.0	0.0	99.8	7.2	65.5	1.9	0.0	0.2	74.8	
19	100.0	0.4	99.6	0.0	0.0	2.22	1000.0	100.0	100.0	25.0	75.0	5.4	19.6		0.4	99.6	0.0	0.0	0.0	100.0	0.3	74.4	0.0	0.0	0.0	74.7	
Effect of C/Na ₂ SO ₄ ratio; Temp = 1000°C																											
20	100.0	0.4	99.6	0.0	0.0	2.22	1000.0	100.0	100.0	25.0	75.0	5.4	19.6		0.4	99.6	0.0	0.0	0.0	100.0	0.3	74.4	0.0	0.0	0.0	0.0	74.7
21	100.0	80.7	0.8	0.3	18.2	5.33	1000.0	100.0	100.0	60.0	75.0	5.4	19.6		56.5	0.6	0.2	12.7	29.7	99.7	60.2	0.6	0.2	13.6	32.0	106.6	

TABLE V. SOLUBILITY OF Na_2S [15]

Na_2S [mmol]	pH	Temperature [$^{\circ}\text{C}$]	$\text{S}(-2)_{\text{Aq}}$ [mmol]	$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ [mmol]	$\text{Na}(+1)_{\text{Aq}}$ [mmol]	H_2O [mmol]	Na_2S [mmol/L]	Na_2S [g/L]
1800	13.36	25	1800	0	3 600	55 321		
2100	13.45	25	2100	0	4 200	55 307		
2400	13.54	25	2400	0	4 800	55 293		
2700	13.61	25	2620	80.32	5 239	54 562	2 665	207.9
3000	13.61	25	2393	606.96	4 786	49 841	2 665	207.9

TABLE VI. SOLUBILITY OF NaHCO_3

NaHCO_3 [mmol]	pH	Temperature [$^{\circ}\text{C}$]	NaHCO_3 (Nahcolite) - Sol [mmol]	$\text{Na}(+1)_{\text{Aq}}$ [mmol]	H_2O [mmol]	$\text{C}(+4)_{\text{Aq}}$ [mmol]
1200	7.75	25	-	1200.0	55 508	1200
1400	7.74	25	95.5	1304.5	55 508	1304
1600	7.74	25	295.5	1304.5	55 508	1304
1800	7.74	25	495.5	1304.5	55 508	1304
2000	7.74	25	695.5	1304.5	55 508	1304

TABLE VII. SOLUBILITY OF NaHS

NaHS [mmol]	pH	Temperature [$^{\circ}\text{C}$]	$\text{S}(-2)_{\text{Aq}}$ [mmol]	$\text{Na}_2\text{S} - \text{Sol}$ [mmol]	$\text{Na}(+1)_{\text{Aq}}$ [mmol]	$\text{H}_2\text{S} - \text{Vap}$ [mmol]	H_2O [mmol]
70 000	11.63	25	70 000	-	70 000	0	55 508
80 000	12.11	25	80 000	-	80 000	0	55 508
90 000	12.49	25	86 406	1 797	86 406	1 797	55 508
100 000	12.49	25	86 406	6 797	86 406	6 797	55 508