

Article

Ferric Hydroxide Recovery from Iron-Rich Acid Mine Water with Calcium Carbonate and a Gypsum Scale Inhibitor

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Abstract: The focus of this study was to improve the Reverse Osmosis Cooling (ROC) process by using CaCO_3 for neutralization and selective recovery of $\text{Fe}(\text{OH})_3$ at pH 3.5. By using a specific inhibitor, ferric hydroxide was recovered separately from gypsum and other metals present in mine water. Ferric hydroxide was processed to pigment, a product that is imported and used as colorant in paints and tiles. In addition to pigment recovery, aluminum hydroxide and calcium carbonate can also be recovered from mine water. The following conclusions were made: (i) the rate of gypsum crystallization, in the absence of Fe^{3+} , is influenced by the over saturation concentration in solution, the seed crystal concentration and temperature; (ii) gypsum crystallization from an over-saturated solution, in the presence of $\text{Fe}(\text{OH})_3$ sludge, required an inhibitor dosage of 100 mg/L to keep gypsum in solution for a period of 30 min; (iii) gypsum crystallization from an over-saturated solution, in the presence of both $\text{Fe}(\text{OH})_3$ sludge and CaCO_3 reactant, required a higher inhibitor dosage than 100 mg/L to keep gypsum in solution for a period of 30 min. A dosage of 200 mg/L kept gypsum in solution for the total reaction period; (iv) when only $\text{Fe}(\text{OH})_3$ is present in the slurry, gypsum inhibition is more effective when $\text{Fe}(\text{OH})_3$ sludge is allowed to settle after the initial mixing; (v) when both $\text{Fe}(\text{OH})_3$ and CaCO_3 are present in the slurry, gypsum inhibition is more effective when the inhibitor is added over a period of time (10 min) rather than applying the total dosage at time zero; (vi) $\text{Fe}(\text{OH})_3$ can be changed to yellow pigment (Goethite) by heating to 150 °C and to red pigment (Hematite) by heating to 800 °C. Pigment of nano particle size was produced; (vii) in the case of Na_2CO_3 , the TDS increased from 12,660 mg/L in the feed to 13,684 mg/L due to the replacement of metal ions (Fe^{3+} , Al^{3+} , Fe^{2+} , Mn^{2+} and Ca^{2+}) with Na^+ in solution. In the case where CaCO_3 was used for the removal of Fe^{3+} and Al^{3+} , $\text{Ca}(\text{OH})_2$ for the removal of Fe^{2+} , Mn^{2+} , and Na_2CO_3 for the removal of Ca^{2+} , the TDS dropped from 12,661 mg/L to 2288 mg/L, due to gypsum precipitation. The alkali cost in the case of calcium alkalis amounted to ZAR29.43/m³ versus ZAR48.46/m³ in the case of Na_2CO_3 .



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1. Introduction

Mining processes produce huge volumes of solid and liquid waste that must be properly managed to reduce environmental risk. Mine tailings, the by-product of mineral processing, are typically dumped as slurry in sizable impoundments or storage facilities [1–3]. Acid Mine Drainage (AMD) is difficult and expensive to treat because it contains many hazardous metals. If AMD is not adequately managed it causes significant environmental degradation, water contamination, aquatic ecosystem, and has a severe health impact on nearby communities [1,4,5]. According to South African legislation, mine water must be treated to a level suitable for drinking water, and ideally there should be zero-waste [6]. The physical and chemical stability of the acid mine waste and reservoirs is

the primary issue with regard to the management of AMD [5,7]. Furthermore, the next problem is the storage of sludge before it is collected, and the sludge must be treated to easily regulate and stabilize pollutants in it; however, this process is costly. Before treatment plants can be built, Environmental Impact Assessment (EIA) studies are required if waste is produced. By stopping the production of any waste such lengthy investigations and approval procedures can be avoided. Therefore, operations must be able to produce products that can be sold, rather than mixed sludge that must be dumped on the ground or brines in evaporation ponds. For instance, it has been reported that AMD sludge can be recycled to create adsorbents that can remove pollutants from wastewater such as rare earth elements and heavy metals [7].

Gypsum is crucial to the pre-treatment and desalination phases of the mine water treatment process. Gypsum precipitates during the pre-treatment phase when calcium alkalis are used to neutralize the metal hydroxides. Gypsum scaling of the membranes during the desalination process must be prevented by regularly washing the membranes with chemical solutions and dosing anti-scalants [8]. Calcium sulfate occurs in three different crystalline forms: calcium sulfate dihydrate (gypsum), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; calcium sulfate hemihydrate (plaster of Paris), $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; and calcium sulfate anhydrite (CaSO_4). Gypsum is the most common calcium sulfate scale found in cooling water and reverse osmosis (RO) based desalination systems, whereas $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and CaSO_4 are the most frequently formed salts in high temperature processes such as multi-stage distillation and geothermal [9,10]. The solubility of all forms of calcium sulfate changes with increasing temperature. The supersaturation level of the solution affects the force that causes crystallization [11]. Additionally, the presence of metal ions like Fe and Al and contaminants complicates the scaling problem and could render the conventional antiscalant ineffective [12].

Several experiments were performed to assess calcium sulfate scale formation and inhibition in the presence of metals at low pH [13,14]. Genesys International Limited has formulated several antiscalants specific to mining including Genmine AS34, Genmine AS45, Genmine AS26 and Genmine AS65. Genmine AS26 was developed particularly for acidic mine waters and is mainly effective at inhibiting the formation of CaSO_4 scale at low pH [14]. Investigations into the dissociation of sulfate and bi-sulfate ions at low pH levels were followed by threshold jar tests to screen water chemistries under various conditions, and finally evaluations of membrane performance and scaling inhibition using actual membrane coupons with a Flat Sheet Test rig [13]. Researchers have suggested several strategies over the past three decades for preventing the formation of scale, including the use of acids, chelants, ion exchangers, and inhibitors [15–17]. Early researchers on gypsum scaling mainly focused on the kinetics of scale formation, while later studies put the emphasis on the effects of external factors such as hydrodynamics [8,18,19].

ROC Water Technologies has developed the ROC process for treatment of mine water and continues to identify further improvements [20]. In the ROC process, acidic or neutral mine water is treated with Na_2CO_3 and/or NaOH and/or MgO in the pre-treatment stage to allow selective precipitation of metals ($\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, CaCO_3 , MnO_2 and $\text{Mg}(\text{OH})_2$ [20–22]. After pre-treatment, the sodium-rich water is passed through a membrane stage to produce drinking water and brine. The brine has a sufficient TDS concentration to allow Na_2SO_4 crystallization upon cooling. Figure 1 shows the modified process configuration of the ROC process that made provision for various improvements. These improvements could result in reduced treatment costs and recovery of valuable products from mine water.

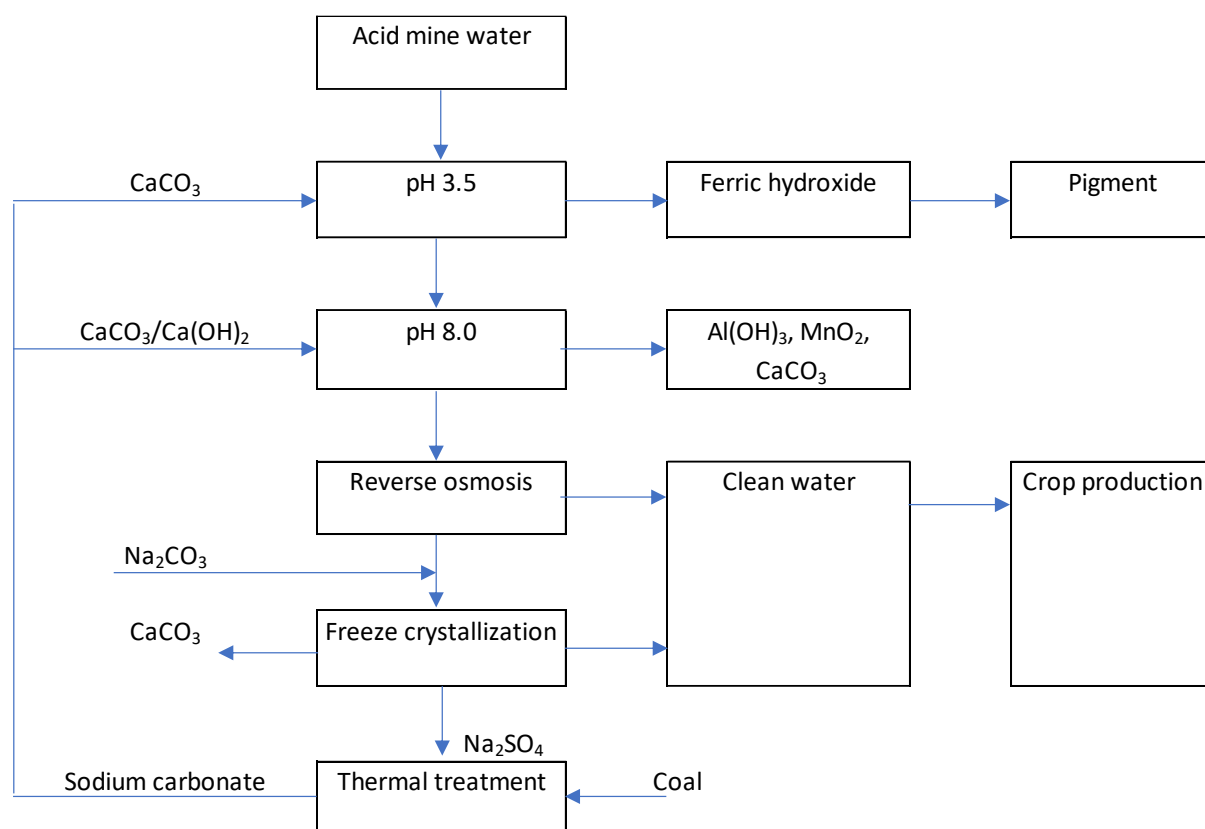


Figure 1. Ideal solution for mine water treatment.

CaCO₃ neutralization

If Na₂CO₃ can be replaced with CaCO₃ or Ca(OH)₂ for selective recovery, the alkali cost will be reduced due to its different prices: Na₂CO₃ (ZAR5 000/t) compared to the conventional alkalis: CaCO₃ (ZAR750/t) and Ca(OH)₂ (ZAR2 500/t). In order to prevent simultaneous precipitation of gypsum and metal hydroxides, an anti-scalant is used to keep gypsum in solution for the period needed for metal removal.

Pigment formation

Pigment can be recovered from the Fe(OH)₃-sludge precipitated at pH 3.5. In a wide range of applications, including energy generation and storage, catalytic transformations, and water treatment, metal oxide nanoparticles are becoming increasingly important [23,24]. The nanotechnology community is very interested in controlling size and shape since these factors are crucial in deciding how well nanoparticles work, affecting qualities like reactivity, conductivity, and magnetic behavior. Supercritical fluid nanoparticle synthesis is a reliable and simple way to meet the need to control size and form for a variety of metal oxide nanoparticles, in addition to using environmentally friendly solvents [25,26]. As reported, AMD contains higher concentrations of Fe ions that are worth recovering. Few researchers have recovered Fe from mine water for the synthesis of pigments and other industrial products [2]. The possibility of recovering iron compounds from AMD is very essential, feasible and doable given the amount of AMD produced annually [6,27,28]. Iron oxide nanoparticles (NPs) have a great adsorption capacity, are inexpensive, have improved stability, and are simple to separate, giving them potential for industrial scale wastewater treatment [29,30].

The following objectives were set for this investigation: (i) kinetics of gypsum crystallization; (ii) identify an inhibitor that will prevent gypsum crystallization in the presence of Fe(OH)₃; (iii) recovery of Fe(OH)₃ and processing to pigment (FeOOH (goethite) and

Fe_2O_3 (hematite)); and (iv) determine the feasibility when Na_2CO_3 is replaced with CaCO_3 for pigment recovery.

2. Materials and Methods

2.1. Feedstock

Neutralization (CaCO_3 (Kulu Lime, South Africa)). Acid mine water samples were collected from Emalahleni, Mpumalanga Province, South Africa. The AMD collected from the Top Dam water was rich in Fe^{3+} due to extensive exposure to oxygen over a long period in a shallow pond. Reagents of high purity were used in this study. Nitric acid, hydrochloric acid, Hydrophilic polypropylene membrane filter (0.45 μm), Anhydrous sodium sulfate, Na_2SO_4 , CaCl_2 , KMnO_4 , NaOH and NH_4 were all supplied by Sigma-Aldrich (Chemie GmbH, Germany). Table 1 shows the chemical compositions of the Top Dam water. The Top Dam had a high concentration (4500 mg/L Fe^{3+}), which made it the preferred water to treat. The Fe^{3+} had a high concentration due to evaporation and would provide a higher yield of pigment compared to other waters.

Table 1. Chemical compositions of water in the Top Dam.

	Top Dam
pH	2.3
Acidity (mg/L CaCO_3)	14,981.0
H^+ (mg/L H)	40.0
Na^+ (mg/L)	50.0
K^+ (mg/L)	30.0
Mg^{2+} (mg/L)	300.0
Ca^{2+} (mg/L)	500.0
Mn^{2+} (mg/L)	200.0
Fe^{2+} (mg/L)	400.0
Fe^{3+} (mg/L)	4500.0
t-Fe (mg/L)	5000.0
Al^{3+} (mg/L)	300.0
Si^{4+} (mg/L)	60.0
Sr^{2+} (mg/L)	0.0
Ba^{2+} (mg/L)	0.0
SO_4^{2-} (mg/L)	19,095.2
Cl^- (mg/L)	200.0
TDS (mg/L)	25,475.2
Cations (meq/L)	397.8
Anions (meq/L)	397.8

Inhibition. Solutions, over-saturated with respect to CaSO_4 , were prepared by mixing Na_2SO_4 , CaCl_2 and the inhibitor solutions. The inhibitors tested were commercial materials. The desired concentrations of the inhibitor were obtained by dilution. AMD from the Top Dam at the Khwezela Colliery site (Mpumalanga, South Africa) was the feed water.

Inhibitor B is a fully neutralized and low molecular weight polyacrylic acid. Inhibitor A is an aqueous solution of polymeric phosphates with multifunctional additives and C is an aqueous solution of phosphonates and carboxylates with multifunctional additives. $\text{Fe}(\text{OH})_3$ produced during neutralization of AMD to pH 3.5 was used for pigment studies.

2.2. Equipment

Neutralization and Inhibition. Batch studies were performed in 1000 mL beakers to determine the rate of neutralization. A portable pH/Electrical Conductivity (EC) meter (HACH HQ40D, Aqualytic, South Africa) was used to measure pH and EC readings of the samples during the experiments. A high temperature muffle furnace (Carbolite, type s30 fitted with 2AU ESF Eurotherm, England) was used to heat recovered Fe(III) sludge. A 4-paddle stirrer (Model 1924, Electronics, India) was used for stirring solutions.

2.3. Procedure

Neutralization. Acid mine water from the Top Dam at the Navigation mine site (Mpumalanga, South Africa) was used as feed water. Beaker studies were carried out to measure the rate of neutralization with CaCO_3 . Acid water (500 mL) was poured into beakers (1000 mL) and stirred at 250 rpm. Alkali was added at the beginning of time. Samples were taken at regular intervals (0, 10, 30, 60 and 180 min), filtered, pH recorded and analyzed for acidity, conductivity, Fe and Ca. Sludge was added to serve as a promoter of crystal growth.

Inhibition. Calcium sulfate was produced by mixing equal volumes of a 0.25 M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution and a 0.25 M Na_2SO_4 solution at room temperature. The inhibitor dosage varied between 0 and 400 mg/L. Gypsum seed crystals were added to catalyze the gypsum crystallization. The kinetics of the reactions in the absence and presence of inhibitors were monitored.

Pigment formation. A mass of 5 g $\text{Fe}(\text{OH})_3$ was placed in porcelain crucibles and subjected to various temperatures for different time periods.

2.4. Experimental

Neutralization. The effects of the following parameters were investigated over the given reaction time: Alkali dosage and temperature (25–55 °C).

Inhibition. Inhibitors A, B and C were assessed to prevent or slow down the rate of gypsum crystallization.

Pigment formation. The effects of the following parameters were investigated:

- Temperature (150 °C and 800 °C);
- Heating period (60 min).

2.5. Analytical

Standard procedures were used to collect samples at various phases, filter them through Whatman No. 1 paper, and measure their contents of Fe(II), Fe(III), pH, Ca, and alkalinity [31]. Metals were analyzed using Inductively coupled plasma-atomic emission spectroscopy (ICP-OES) (iCAP 7000 Series, ANATECH, South Africa). Fe(II) concentrations were determined by adding filtered sample (5 mL), 0.1 N H_2SO_4 (5 mL) and Zimmerman-Reinhardt (ZR) reagent (5 mL) to an Erlenmeyer flask and titrating the solution with 0.05 N KMnO_4 until pale pink [31]. Because magnesium was absent, calcium was chosen as the measure of overall total hardness. Filtered sample (5 mL), deionized water (45 mL), dilute NH_4 (5 mL) and two drops of Eriochrome Black T indicator were added to an Erlenmeyer flask (100 mL). The solution was titrated with 0.01 M EDTA to a blue endpoint. Acidity was determined by titration of sample (5 mL) to pH 8.3 using 0.1/1 N NaOH [31]. Fe, Al, Na, Ca, Ni, Mg, K and Mn were analyzed using ICP-OES. The pH/EC meters were calibrated before the start of each set of experiments and during the experiment using calibration buffers.

2.6. Characterisation of the Sludge

Morphological and elemental properties of the synthesized pigments were determined using High Resolution Field Emission Scanning Electron Microscopy (HR-FESEM) equipped with the means to perform Energy-dispersive X-ray spectroscopy (EDS). Specifically, the Auriga Cobra FIB-FESEM (Model: Sigma VP FE-SEM with Oxford EDS Sputtering System, Make: Carl Zeiss, Supplier: Carl Zeiss, USA). Particle size distribution was deter-

mined from SEM images of the particles by manually counting and delineating the particles displayed on the image. The ferrite crystallinity was determined using X-ray diffraction on a Bruker D2, 30 kV, 10 mA utilizing monochromatic $\text{CuK}\alpha$ radiation ($k = 1.54184 \text{ \AA}$) from $5\text{--}90^\circ$ (XRD Analytical Solutions and Consulting). Al_2O_3 was used in the form of corundum as a reference material for the applied standard reflection, which was pretreated at high temperature to obtain a highly crystalline with a zero full width at half maximum (FWHM). The patterns were recorded from 10° to 90° (2θ) with a scanning speed of $4^\circ/\text{min}$ at 30 kV and 10 mA. The width of the standard incident and receiving Soler slits were 2.5° and 0.5° , respectively.

2.7. OLI

In this work the behavior of metals dissolved in water under the influence of alkalis like Na_2CO_3 (Botash, Botswana) and CaCO_3 was predicted using the OLI ESP software program. The reactions were modelled using the OLI Analyzer System by running a simulated AMD sample with fictitious settings for temperature, pressure, and pH [32]. Base titrants Na_2CO_3 , CaCO_3 and MgO (Chamotte Mining, South Africa) were employed. When MgO was used to neutralize the pH to 3.5 and then Na_2CO_3 to elevate the pH to 8.6, the influence of temperature on the solubility of MgSO_4 and Na_2SO_4 was identified. The OLI Systems Chem Analyzer would display a calculated summary of the simulated outcomes once the input values were run. According to the precise qualities, this might be utilized to forecast the actual reactions to incorporate into the treatment techniques. As a result, it was applied to improve an AMD neutralization–precipitation–desalination process.

3. Results and Discussion

3.1. Kinetics of Gypsum Crystallization—No Inhibitor

Limestone (CaCO_3) and/or lime (Ca(OH)_2) are currently used by the mining industry for neutralization of acid mine drainage. CaCO_3 has the lowest cost (typically ZAR700/t) and Ca(OH)_2 has the second lowest cost (typically ZAR2 200/t). Calcium alkalis can only be utilized for selective recovery of metals if co-precipitation of gypsum can be avoided through the dosing of inhibitors. Liu and Nancollas determined the rate of gypsum crystallization and found it to be a second order reaction with respect to the over-saturation concentration of gypsum in solution. It is also related to the gypsum seed crystal concentration (Equation (1)) [15,16]. This finding was confirmed, as shown in Figure 2. Figure 3 confirmed that the reaction order is 2 with respect to the over-saturation concentration of gypsum in solution.

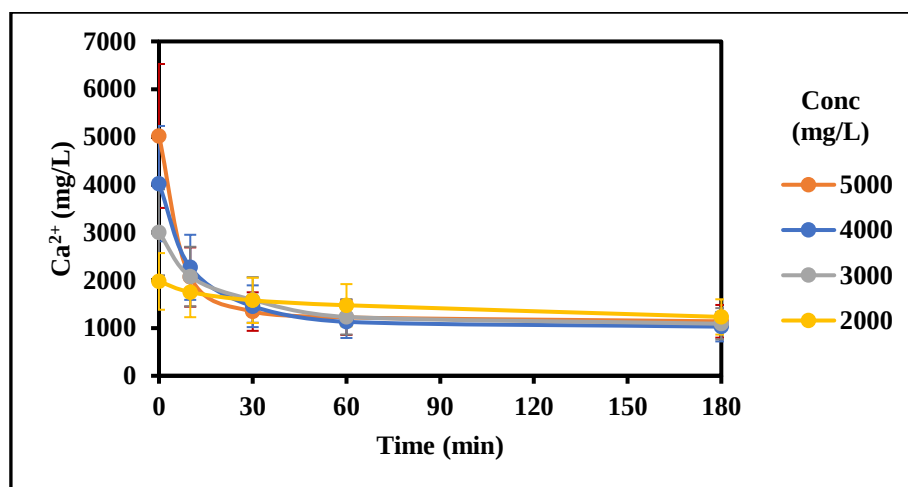


Figure 2. Effect of concentration on the rate of gypsum crystallization (2000–5000 mg/L CaSO_4 (as Ca), 5 g/L gypsum seed, 0 g/L Fe^{3+} , 0 mg/L Inh, 25°C , stirring rate: 200 rpm; Stirring time (min): 180/180).

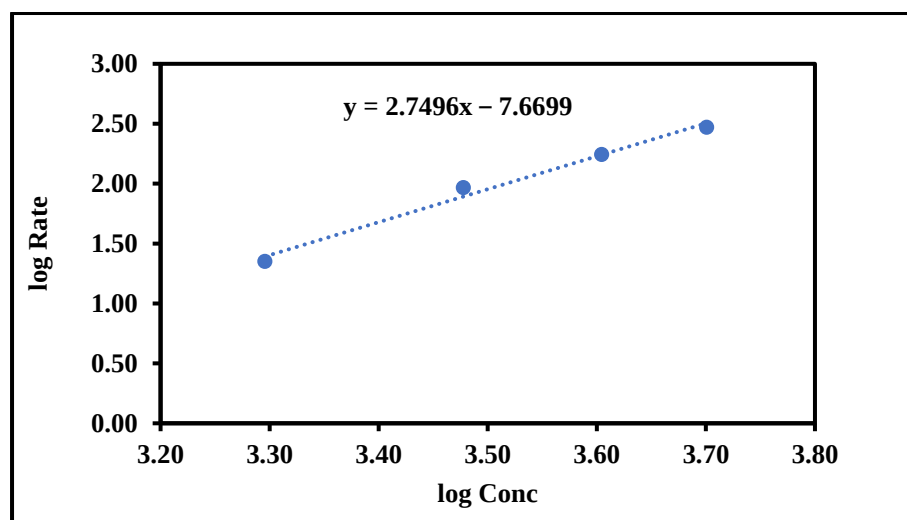


Figure 3. Determination of the reaction order.

The effects of temperature on the formation of gypsum crystals were also investigated. Figure 4 shows the effect of temperature on the reaction rate, the higher the temperature, the faster the rate of crystallization. The Arrhenius equation $\log k = \log A - E/(2.303RT)$ was used to estimate the value of the reaction rate k at other temperatures. The amounts E , R , and $\log A$ have the values 4.80 kcal/mole (activation energy), 1.987 (a constant) and 5.52 cal mole⁻¹ degree⁻¹ (gas constant), respectively (Figure 5).

$$R = k \cdot S \cdot (C - C_0)^2 \quad (1)$$

where R —rate; k —; S —Surface area; C —CaSO₄ concentration; C_0 —Equilibrium CaSO₄ concentration.

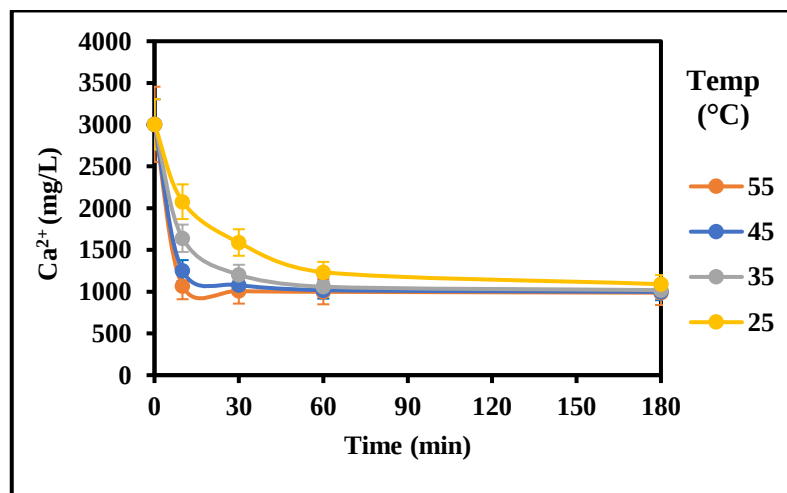


Figure 4. Effect of temperature on the rate of gypsum crystallization (3000 mg/L CaSO₄ (as Ca), 5 g/L gypsum seed, 0 g/L Fe³⁺, 0 mg/L Inh, 25–55 °C, stirring rate: 200 rpm; Stirring time (min): 180/180).

3.2. Inhibition of Gypsum Crystallization in Artificial Mine Water

The aim of this study was to recover Fe(OH)₃ in the presence of a solution that is over-saturated with respect to CaSO₄ in solution prepared artificially. A solution that is over-saturated with respect to CaSO₄ was prepared by mixing the inhibitor with solutions of Na₂SO₄ and CaCl₂. The effect of Fe(OH)₃ on the inhibition of CaSO₄ was determined by dosing FeCl₃ and the equivalent amount of NaOH. Furthermore, the inhibition of gypsum

crystallization when real mine water was neutralized with CaCO_3 was also investigated. A study by Rabizadeh (2016) [18] showed that when the pH in the reacting solution was switched from 4 to 7, the efficiency of the low molecular weight poly(acrylic acid) in preventing gypsum formation increased, while it resulted in an adverse effect on the performance of poly(acrylic acid) with higher molecular weight by forming a “net-structure” in the solution [18].

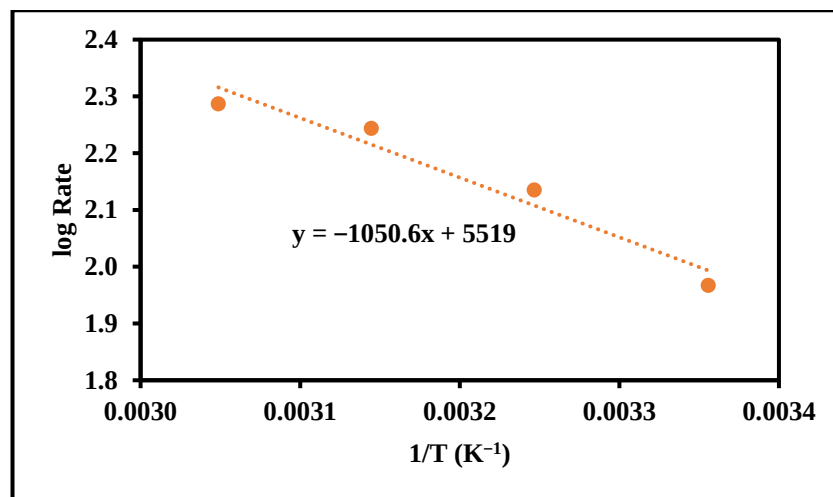


Figure 5. Determination of the activation energy.

3.2.1. Artificial Solutions

Figure 6 compares three commercially available inhibitors that were identified by Mogashane as the most promising [28]. A dosage of 100 mg/L inhibitor A kept 4000 mg/L CaSO_4 (as Ca) in solution for a period of 30 min in the presence of 4 g/L Fe^{3+} at pH 3.5 when stirred at a rate of 200 rpm for the total period. All three inhibitors were polyacrylate. The results reported by Rabizadeh (2016) [18] demonstrated the effects of 20 ppm poly(aspartic acid) (PASP) and poly(acrylic acid) (PAA) compounds on the crystallization of gypsum. The comparison showed that PAA worked better than the other anti-scalants, and it inhibited the formation of gypsum [18].

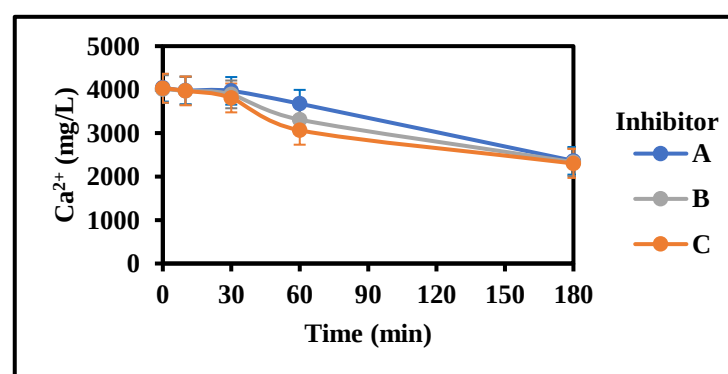


Figure 6. Comparison of various inhibitors on the rate of gypsum crystallization with initial mixing (4000 mg/L CaSO_4 (as Ca), 0 g/L gypsum seed, 4 g/L Fe^{3+} , 100 mg/L Inh, 25 °C, stirring rate: 200 rpm; Stirring time (min): 180/180; pH 3.5).

Figure 7 shows the effect of mixing time in the inhibition of gypsum. Gypsum inhibition was most effective when the solution was only stirred for the first 5 min of the total reaction period of 180 min. This can be ascribed to the settling of the $\text{Fe}(\text{OH})_3$ sludge to the bottom after mixing was stopped. The inhibitor remained in the over-saturated gypsum solution and was more effective than when in contact with suspended material on which it could absorb.

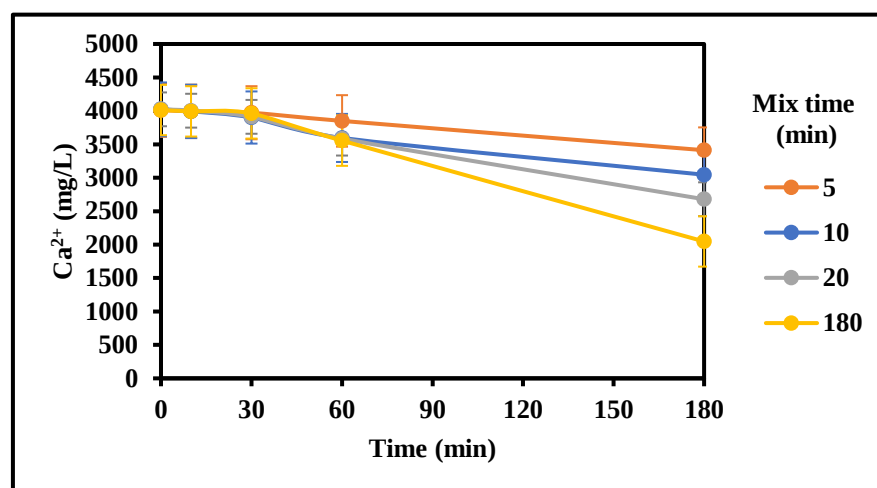


Figure 7. Effect of mixing time on the rate of gypsum crystallization with initial mixing (4000 mg/L CaSO_4 (as Ca), 0 g/L gypsum seed, 4 g/L Fe^{3+} , 0–100 mg/L Inh. A, 25 °C, stirring rate: 200 rpm; Stirring time (min): 5 to 180/180).

Figures 8 and 9 compare the effect of inhibitor A doses when stirred for the full 180 min of the reaction and only for 5 min of the reaction, respectively. As shown in Figure 7, inhibition was much more effective when the solution was stirred for only 5 min than when stirred for the full 180 min.

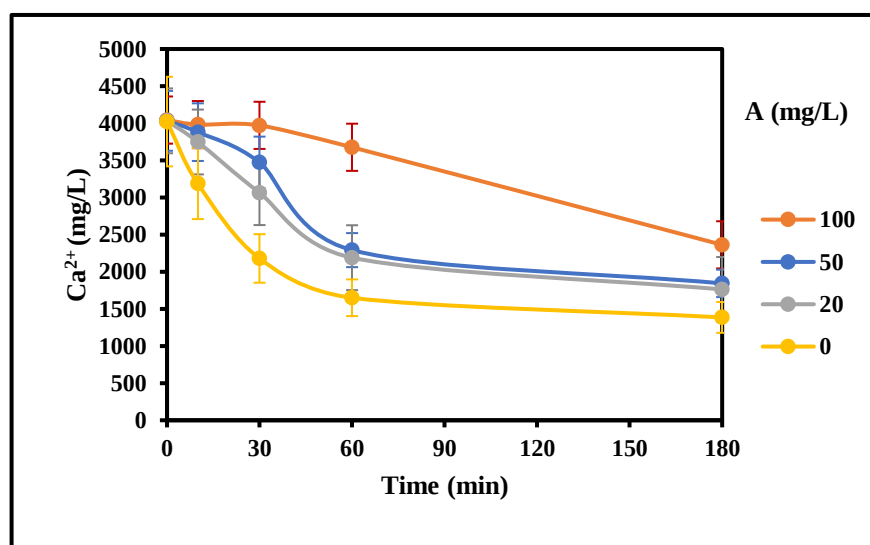


Figure 8. Effect of inhibitor A concentration on the rate of gypsum crystallization with mixing (4000 mg/L CaSO_4 (as Ca), 0 g/L gypsum seed, 4 g/L Fe^{3+} , 0–100 mg/L Inh. A, 25 °C, stirring rate: 200 rpm; Stirring time (min): 180/180).

3.2.2. Acid Mine Water

The oversaturated gypsum solution was prepared by mixing CaCl_2 and Na_2SO_4 solutions in the presence of an inhibitor. $\text{Fe}(\text{OH})_3$ sludge was produced by adding an FeCl_3 solution and NaOH to adjust the pH to 3.5. It was realized that this condition differs from the situation that will be applied in practice. In the real situation, a CaCO_3 (limestone) slurry will be dosed to an $\text{Fe}_2(\text{SO}_4)_3$ solution to raise the pH to 3.5. This differs in the sense that the inhibitor needs to inhibit gypsum crystallization, not only in the absence of any solids, or in the presence of only $\text{Fe}(\text{OH})_3$, but in the presence of both $\text{Fe}(\text{OH})_3$ and CaCO_3 solids. Figure 10 shows that when Ca^{2+} came from a solution of CaSO_4 , it remained completely in solution for 30 min. In the case where Ca^{2+} came from $\text{CaCO}_3(\text{s})$, gypsum

crystallization took place at a slow rate during the first 30 min. It was concluded that higher inhibitor doses may be needed when CaCO_3 is used for gypsum inhibition to allow selective recovery of pigment. Figures 10–12 show that gypsum crystallization could still be suppressed when CaCO_3 is dosed, but that higher inhibitor concentrations were needed.

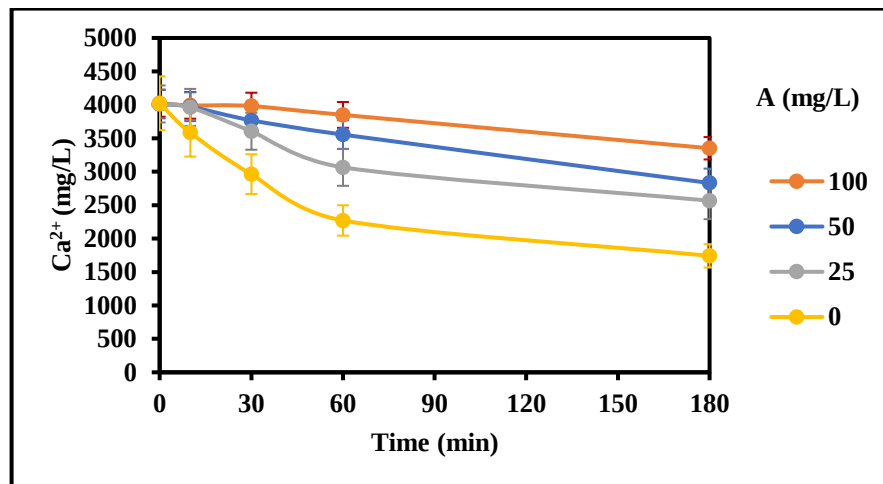


Figure 9. Effect of inhibitor A concentration on the rate of gypsum crystallization with initial mixing (4000 mg/L CaSO_4 (as Ca), 0 g/L gypsum seed, 4 g/L Fe^{3+} , 0–100 mg/L Inh. A, 25 °C, stirring rate: 200 rpm; Stirring time (min): 5/180).

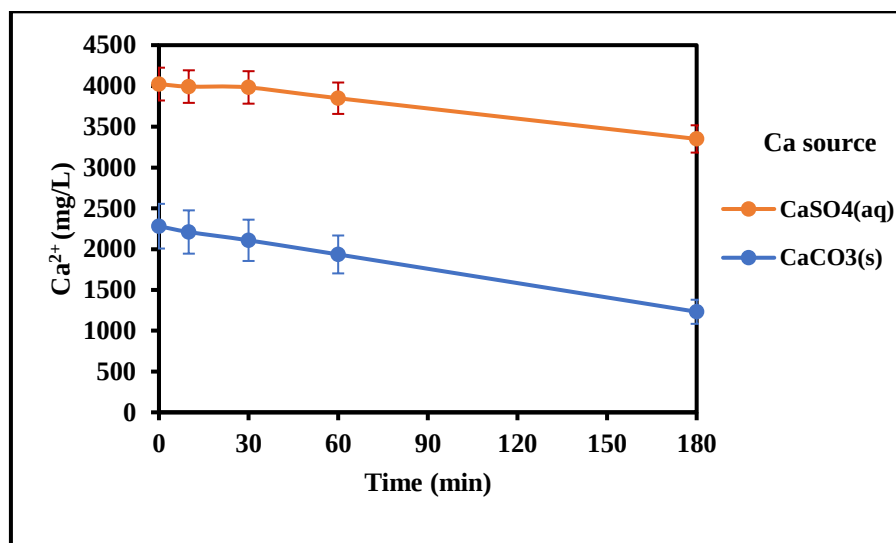


Figure 10. Effect of CaCO_3 addition period on gypsum inhibition (Top Dam water, 15 g/L Acidity, 4 g/L Fe^{3+} , 22 g/L CaCO_3 , 0 g/L gypsum seed, 100 mg/L Inh. A, 25 °C, stirring rate: 200 rpm; Stirring time (min): 180/180; CaCO_3 addition: Time 0 to 10 min).

Figure 10 compares the inhibition of gypsum crystallization when Ca originated from solution (when CaSO_4 and CaCl_2 was mixed) and when added as a solid to neutralize Fe^{3+} and H^+ in solution. The Ca^{2+} in the artificial mine water was higher than in the actual mine water due to different Fe^{3+} concentrations, namely 3220 mg/L Fe^{3+} and 503 mg/L Fe^{2+} in the artificial mine water and 2560 mg/L Fe^{3+} and 251 mg/L Fe^{2+} in the actual mine water. In the artificial mine water no gypsum crystallization took place during the first 30 min, while in the presence of $\text{CaCO}_3(\text{s})$ some crystallization was noticed. This indicated that CaCO_3 as a solid absorbs a portion of the inhibitor and requires a higher inhibitor dosage.

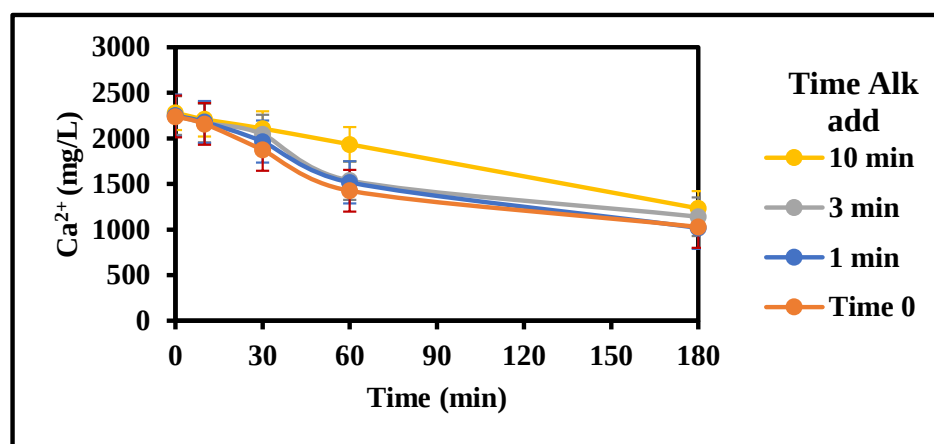


Figure 11. Effect of inhibitor concentration gypsum inhibition (Top Dam water, 15 g/L Acidity, 4 g/L Fe^{3+} , 22 g/L CaCO_3 , 0 g/L gypsum seed, 100, 200, 400 mg/L Inh A, 25 °C, stirring rate: 200 rpm; Stirring time (min): 180/180; CaCO_3 addition period: 10 min).

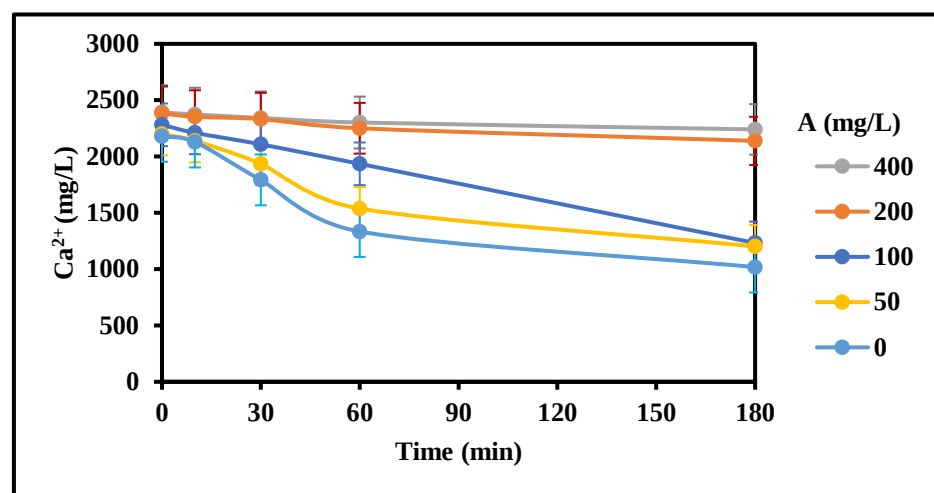


Figure 12. Effect of CaCO_3 solids on the efficiency of inhibition of gypsum crystallization (see Table 2 for metal concentrations).

Figure 11 shows the effect of time (immediately, or over 1, 3 and 10 min) in which CaCO_3 is added to actual acid mine water. When CaCO_3 was added over a 10 min period it was noticed that gypsum remained for a longer time in solution than when added over shorter periods. This can be ascribed to the rapid dissolution of CaCO_3 at low pH values, leaving less solid CaCO_3 in suspension that could absorb the inhibitor. This conclusion needs to be confirmed with more experiments.

Figure 12 shows that 200 mg/L Inhibitor A keeps gypsum in solution for more than 180 min when actual mine water containing 4 g/L Fe^{3+} is neutralized with CaCO_3 . This is in line with the study of Fazel et al. (2019) who investigated calcium sulfate scale formation in acidic pH and in the presence of a variety of soluble metals. The study revealed that Inhibitor A was able to prevent scale formation at low pH, especially for AMD waters, and gave near 100% inhibition [13].

3.3. Pigment Formation

$\text{Fe}(\text{OH})_3$ produced during neutralization of mine water with CaCO_3 can be changed to yellow pigment (Goethite) by heating to 150 °C, and to red pigment (Hematite) by heating to 800 °C (Figure 13). Mogashane et al. (2022) investigated the effect of temperature on the color when $\text{Fe}(\text{OH})_3$ produced during neutralization of AMD with Na_2CO_3 is heated. Their study showed that temperature has a dominant influence on the color [28]. Figure 13

shows the effect of temperature on the color when $\text{Fe}(\text{OH})_3$ is heated. It indicates that temperature has a dominant influence on the color. Figure 13 shows examples of goethite and hematite that were produced from acid mine-water.

Table 2. Metals concentrations in Figure 3.

Parameter	Unit	Artificial Mine Water	Actual Mine Water
Fe^{3+}	mg/L	3220	2569
Fe^{2+}	mg/L	503	251
Ca^{2+} after Fe^{3+} removal	mg/L	5000	3460
AS26 inhibitor	mg/L	100	100
Prepared from		CaSO_4 and FeCl_3	Mine water and CaCO_3
Stirring rate	rpm	200	200
Stirring time	min	180/180	180/180
Temperature	$^{\circ}\text{C}$	25	25

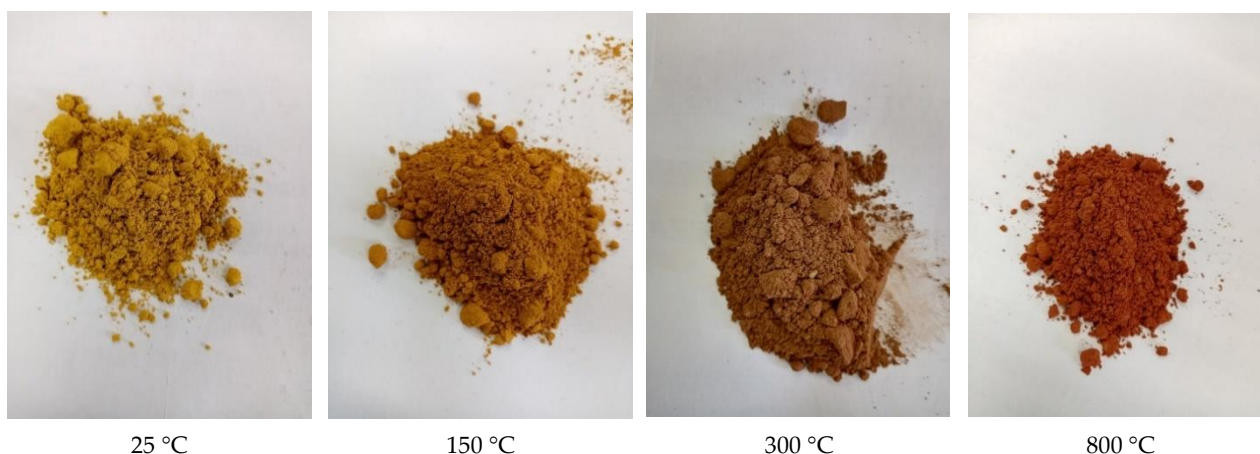


Figure 13. Pigments produced from iron-rich mine water using CaCO_3 for neutralization.

The XRD analysis was employed to assess the crystallite sizes and phase structures of Goethite Nanoparticles (GNPs) and Hematite Nanoparticles (HNPs). Particles are classified as nanoparticles if their size is smaller than 100 nm. The $\text{Fe}(\text{OH})_3$ was recovered by adjusting the coal leachate with CaCO_3 to pH 3.5. As shown in Figure 14, after separation of the $\text{Fe}(\text{OH})_3$ from the water the $\text{Fe}(\text{OH})_3$ -sludge was dried and heated to different temperatures. Goethite (yellow) was produced at 150 $^{\circ}\text{C}$ and hematite (red, 4B) at 800 $^{\circ}\text{C}$. The XRD pattern showed that the synthesized product contained iron oxide nanoparticles both in crystalline and in amorphous state. The black line (not marked) represents the XRD for Sample 1B at 25 $^{\circ}\text{C}$ possessing the intense reflection around 11 $^{\circ}$, 22 $^{\circ}$ and 30 $^{\circ}$ 2theta due to the presence of the diffractogram shows the reflections of $\text{Al}(\text{OH})_3$ (JCPDS#70-2038), $\text{Ca}(\text{OH})_2$ (JCPDS#01-073-5492) and CaCO_3 (JCPDS#47-1743) [19], respectively. This advocates that the Sample 1B contains layered double hydroxides that may have formed with interlayer carbonate and sulfate anions even in this slightly acidic environment, which was in agreement with the observation from EDS. The sample was not converted to goethite. Furthermore, the XRD pattern (Figure 14) obtained after heating samples at different temperatures revealed that goethite (2B) is completely transformed to hematite (4B). The blue line (300 $^{\circ}\text{C}$) corresponding with goethite is shown by the red line in Figure 14. The diffraction peaks of HNPs (4B) are well defined, indicating that the crystalline nature of the prepared hematite products represents a practical route to prepare $\alpha\text{-Fe}_2\text{O}_3$ of high purity. The formed XRD patterns correspond to the characteristic $\alpha\text{-Fe}_2\text{O}_3$ pattern reported for hematite in literature [33]. However, the XRD pattern of hematite showed lower intensity

as compared to the one reported in the literature [33], due to the presence of impurities. This shows that HNPs were successfully recovered in a crystalline state and these results were found to be in good agreement with the previously reported values [33,34].

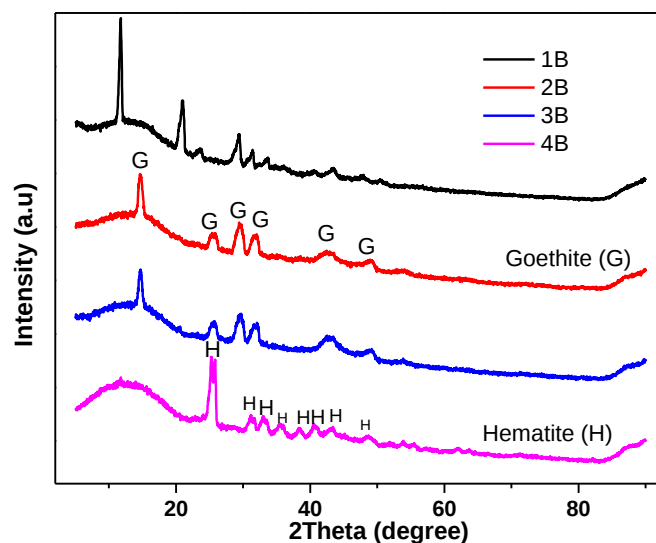


Figure 14. XRD patterns of Nanoparticles (NPs) samples produced from AMD. Notes: 1B = (25 °C-CaCO₃ as alkali); 2B = Goethite (150 °C-CaCO₃ as alkali); 3B = Goethite (300 °C-CaCO₃ as alkali); 4B = Hematite (800 °C-CaCO₃ as alkali).

The XRD pattern of the goethite nanoparticles (GNPs) (2B) sample was also evaluated as shown in Figure 14. The diffraction peaks are slightly broad, indicating a smaller crystal size. Its XRD patterns contain all the major peaks referring to JCPDS card No. 29-0713 [35], thus representing the formation of α -FeOOH. The diffraction peaks and lattice parameters of the GNPs in this study were found to be in good agreement with those reported in the literature [33,35]. The XRD results showing low in the α -FeOOH were contaminated with Ca, coming from the CaCO₃, S and Al³⁺, coming from the SO₄²⁻ and Al³⁺ in the mine water.

The average crystallite sizes of the samples (1B, 3B), Hematite (4B) and Goethite (2B) were calculated using the Debye–Scherrer formula (Equation (2)) [36]:

$$D = 0.9\lambda / \beta \cos\theta \quad (2)$$

where β is the full-width at half-maximum (FWHM) measured in radians, λ is the X-ray wavelength of Cu-K α radiation (1.5406 Å), and θ is Bragg's angle. The crystallite sizes (Table 3) were found to be 11.9 nm, 7.02 nm, 7.27 nm and 8.07 nm for samples 1B, 2B, 3B and 4B, respectively. The HNPs showed to have large particle size as compared to Goethite nanoparticles owing to the improved density of active centers for nucleation in the prepared nano-product. The findings revealed that nano-pigments can be produced from Fe(OH)₃ that is recovered in the pre-treatment stage of the ROC process. With CaCO₃ as alkali, Fe(OH)₃ crystals with a smaller crystallite size are recovered due to a fast reaction rate [28].

Table 3. Particle size parameters for Goethite and Hematite nanoparticles.

	Temperature (°C)	FWHM (2 θ)	B = FWHM*PI/180°	Average Crystallite Size D (nm) = 0.9 λ / β Cos θ	d-Spacing (Å) = λ /2sin(θ)
1B	25	0.74	0.00654	11.9	4.25
2B	150	0.73	0.00637	7.02	3.02
3B	300	4.50	0.0393	7.27	2.81
4B	800	7.47	0.0652	8.07	3.51

In addition, using XRD data analysis, Bragg's law (Equation (3)), the interplanar spacing d_{hkl} was also calculated for the as-synthesized HNPs and GNPs

$$\Lambda = 2d\sin(\theta) \quad (3)$$

where λ is the wavelength of the X-ray beam (1.5406 Å), d is the interplanar d spacing, and θ is the diffraction angle. The d spacing values for $\text{Fe}(\text{OH})_3$ (1B, at 2θ angle of 20.9°), Goethite (2B, at 2θ angle of 36.8°), Goethite (3B, at 2θ angle of 31.8°) and Hematite (4B, at 2θ angle of 25.4°) are given in Table 3 and found to be 2.81 Å and 3.02 Å for Goethite nanoparticles and 3.51 Å for Hematite nanoparticles.

Figure 15 shows the SEM images and their average particle size distribution histogram of Nanoparticles samples produced from AMD. It also reveals the presence of spherical particles, which are distributed across the surface of the material. The morphological properties further demonstrated that the surface properties of the samples are homogeneous, hence confirming that a high-grade material was synthesized. A particle size distribution histogram of the material indicated that Goethite (2B) and Hematite 4B had the average particle size of 1.96 μm and 1.45 μm , respectively. Moreover, it was clear that the morphological properties of the samples were the same at different magnifications. The results obtained from this study substantiated the EDS results in terms of purity and homogeneity.

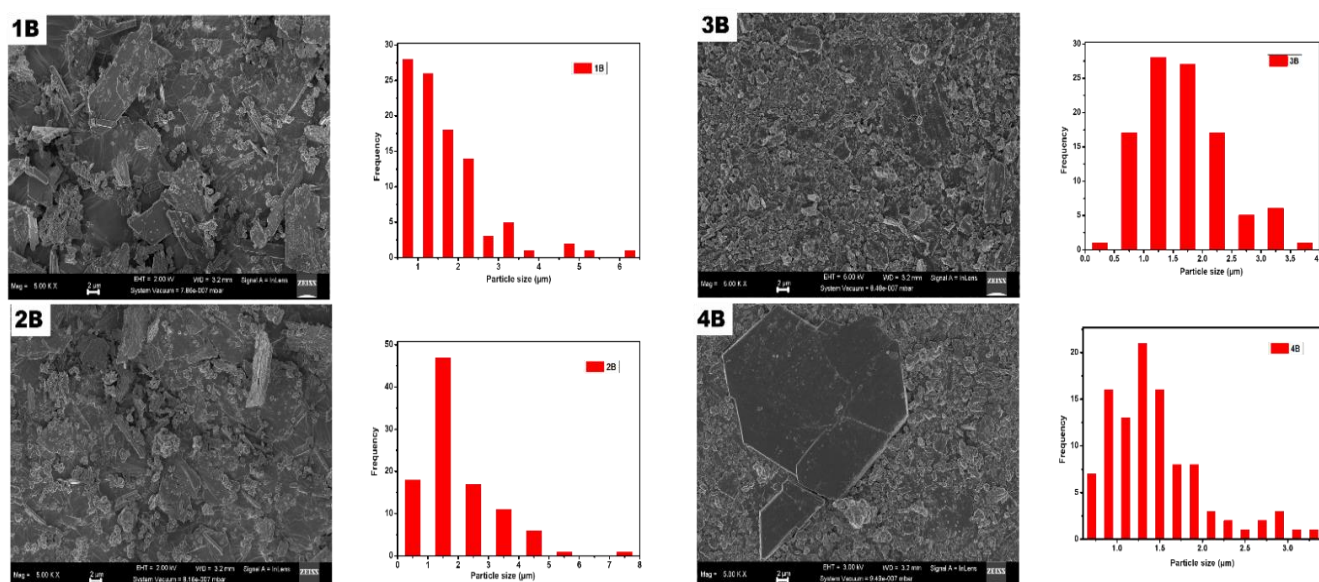


Figure 15. Scanning electron microscope (SEM) pictures and their particle size distribution histogram of Nanoparticles samples produced from AMD.

Figure 16 shows the mapping of the elemental composition of the samples (1B, 3B), Hematite (4B) and Goethite (2B). The synthesized pigments were found to be enriched with Fe and O as principal elements. Moreover, traces of other elements (Ca, C, Al, S, Si and Mn) were present. The results obtained show that the synthesized samples 1B, 2B, 3B and 4B consisted of 55.8%, 53.1%, 49.8% and 43.4%, respectively, of Fe-O mineral. This demonstrated that goethite and hematite nanoparticles were produced. However, significant levels of sulfate were found in all the samples; this was likely the result of oxyhydrosulfates that formed during the precipitation of Fe-O minerals. CaCO_3 alkali was added to AMD when preparing these samples. The results attained confirmed that the synthesized pigments were rich in Fe-O constituents. The XRD results showed that the $\alpha\text{-FeOOH}$ was contaminated with Ca, coming from the CaCO_3 , S and Al^{3+} , coming from the SO_4^{2-} and Al^{3+} in the mine water. Further studies will be carried out to determine: (i) the value of the contaminated pigment; and (ii) if the pigment impurity can be improved through an acid wash.

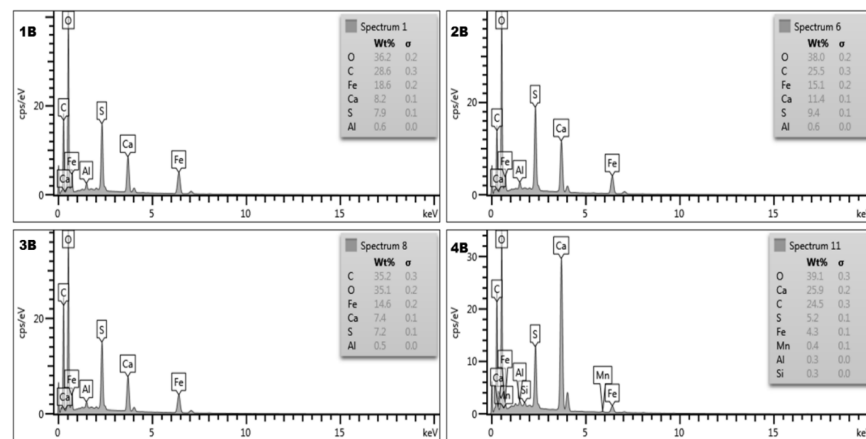


Figure 16. Energy dispersive spectroscopy (EDS) plots of nanoparticles samples produced from AMD. 1B = (25 °C-CaCO₃ as alkali); 2B = Goethite (150 °C-CaCO₃ as alkali); 3B = Goethite (300 °C-CaCO₃ as alkali); 4B = Hematite (800 °C-CaCO₃ as alkali).

3.4. Alkali Selection

3.4.1. CaCO₃

OLI software was used to identify which alkali (CaCO₃, Na₂CO₃ and Ca(OH)₂) will be most suitable for removal of the residual metals in solution after removal of Fe³⁺ with CaCO₃ (Tables 4–7). Na₂CO₃ will only be attractive if the pre-treatment stage is combined with reverse osmosis to achieve complete desalination. If only the pre-treatment stage is used for water treatment, sodium carbonate is disqualified due to the negative impact of sodium on the environment. Ca(OH)₂ would be an attractive option as it can remove HCO₃[−] as CaCO₃ and the residual metals as hydroxides, including Mg²⁺.

Table 4. Removal of Fe³⁺ and other metals with only CaCO₃ at 1 atm (OLI simulation).

	pH	Pressure [atm] (Y2)	Fe(+3) Aq [mg] (Y2)	Fe(OH) ₃ (Bernalite)—Sol [mg] (Y2)	CO ₂ —Vap [mg] (Y2)	Al(+3) Aq [mg] (Y2)	MnCO ₃ (Rhodochrosite)—Sol [mg] (Y2)	Na(+1) Aq [mg] (Y2)	Mg(+2) Aq [mg] (Y2)	Ca(+2) Aq [mg] (Y2)	CaSO ₄ ·2H ₂ O (Gypsum) [mg] (Y2)	C(+4) Aq [mg] (Y2)	CaCO ₃ (Calcite)—Sol [mg] (Y2)	S(+6) Aq [mg] (Y2)	Cl(−1) Aq [mg] (Y2)
0	2.5	1.0	2000	0	0	300	0	100	200	300	0	0	0	3074	150
1000	2.6	1.0	1690	593	0	300	0	100	200	604	416	120	0	2997	150
2000	2.6	1.0	1314	1313	0	300	0	100	200	590	2194	240	0	2666	150
3000	2.7	1.0	938	2033	0	300	0	100	200	577	3971	360	0	2335	150
4000	2.7	1.0	562	2751	360	300	0	100	200	564	5745	382	0	2004	150
5000	2.8	1.0	192	3460	794	300	0	100	200	554	7509	383	0	1676	150
6000	3.5	1.0	4.0	3820	1228	226	0	100	200	549	9252	385	0	1351	150
7000	3.7	1.0	1.4	3825	1663	50	0	100	200	546	10,983	386	0	1029	150
8000	5.5	1.0	0.0	3827	1645	0	194	100	200	618	12,397	468	0	765	150
9000	5.9	1.0	0.0	3827	1417	0	385	100	200	756	13,228	593	171	611	150
10,000	5.9	1.0	0.0	3827	1417	0	385	100	200	756	13,228	593	1171	611	150

Table 5. Removal of Fe^{3+} and other metals with only CaCO_3 at 0.1 atm (OLI simulation).

CaCO_3 [mg]	pH	Pressure [atm] (Y2)	Fe(+3) Aq [mg] (Y2)	$\text{Fe}(\text{OH})_3$ (Bernalite)—Sol [mg] (Y2)	CO_2 —Vap [mg] (Y2)	Al(+3) Aq [mg] (Y2)	MnCO_3 (Rhodochrosite)—Sol [mg] (Y2)	Na(+1) Aq [mg] (Y2)	Mg(+2) Aq [mg] (Y2)	Ca(+2) Aq [mg] (Y2)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Gypsum) [mg] (Y2)	C(+4) Aq [mg] (Y2)	CaCO_3 (Calcite)—Sol [mg] (Y2)	S(+6) Aq [mg] (Y2)	Cl(−1) Aq [mg] (Y2)
0	2.5	0.1	2000	0	0	300	0	100	200	300	0	0.0	0	3074	150
1000	2.6	0.1	1690	593	413	300	0	100	200	603	420	7.3	0	2996	150
2000	2.6	0.1	1314	1313	853	300	0	100	200	589	2200	7.3	0	2665	150
3000	2.7	0.1	938	2033	1292	300	0	100	200	575	3978	7.4	0	2333	150
4000	2.7	0.1	562	2752	1732	300	0	100	200	563	5753	7.4	0	2003	150
5000	2.9	0.1	192	3460	2171	300	0	100	200	552	7518	7.4	0	1674	150
6000	3.5	0.1	4	3820	2611	225	0	100	200	546	9263	7.4	0	1349	150
7000	3.7	0.1	1	3825	3051	49	0	100	200	543	10,996	7.5	0	1026	150
8000	6.6	0.1	0	3827	3141	0	353	100	200	579	12,564	28.7	0	734	150
9000	6.8	0.1	0	3827	3122	0	390	100	200	590	12,693	39.3	896	710	150
10,000	6.8	0.1	0	3827	3122	0	390	100	200	590	12,693	39.3	1896	710	150

Table 6. Removal of remaining metals with Na_2CO_3 after Fe^{3+} removal with CaCO_3 (OLI simulation).

Na_2CO_3 [mg/L]	pH	Ca(+2) Aq [mg] (Y2)	CaCO_3 (Calcite)—Sol [mg] (Y2)	Fe(+2) Aq [mg] (Y2)	FeCO_3 (Siderite)—Sol [mg] (Y2)	Mn(+2) Aq [mg] (Y2)	S(+6) Aq [mg] (Y2)	Cl(−1) Aq [mg] (Y2)	C(+4) Aq [mg] (Y2)
0	6.8	584	0	18.2	18.2	21.0	729	150	24.54
200	7.0	532	150	11.0	33.2	12.6	735	150	25.76
400	7.0	459	331	9.5	36.3	10.9	735	150	26.03
600	7.1	387	512	8.1	39.3	9.3	735	150	26.34
800	7.2	315	692	6.6	42.3	7.6	735	150	26.69
1000	7.3	243	872	5.2	45.3	5.9	735	150	27.10
1199	7.4	171	1051	3.7	48.3	4.2	735	150	27.59
1399	7.6	100	1229	2.3	51.3	2.4	735	150	28.22
1599	8.1	30	1403	0.9	54.2	0.7	735	150	29.34
1799	9.4	2	1473	0.3	55.3	0.0	735	150	43.28
1998	9.6	1	1475	0.3	55.3	0.0	735	150	65.73

Table 7. Removal of remaining metals with Ca(OH)₂ after Fe³⁺ removal with CaCO₃ (OLI simulation).

Ca(OH) ₂ [mg/L]	pH	Fe(+2) Aq [mg] (Y2)	FeCO ₃ (Siderite)—Sol [mg] (Y2)	Fe(OH) ₂ (Amakinite)—Sol [mg] (Y2)	Mn(+2) Aq [mg] (Y2)	MnCO ₃ (Rhodochrosite)—Sol [mg] (Y2)	Na(+1) Aq [mg] (Y2)	Ca(+2) Aq [mg] (Y2)	C(+4) Aq [mg] (Y2)	CaCO ₃ (Calcite)—Sol [mg] (Y2)	CaSO ₄ ·2H ₂ O (Gypsum) [mg] (Y2)	Cl(−1) Aq [mg] (Y2)	Ca(OH) ₂ (Portlandite)—Sol [mg] (Y2)
0	6.8	18.2	18.2	0.0	21.0	21.9	100	584	24.5	0	34	150	0
100	8.8	13.2	11.2	13.5	13.7	37.2	100	569	0.7	191	0	150	0
200	9.6	0.4	0.0	42.8	14.7	35.1	100	577	0.3	206	176	150	0
300	9.7	0.3	0.0	42.9	15.0	34.5	100	584	0.3	207	376	150	0
400	9.7	0.3	0.0	43.0	12.9	0.0	100	590	0.3	237	529	150	0
500	9.8	0.2	0.0	43.1	9.6	0.0	100	599	0.3	237	723	150	0
600	9.9	0.2	0.0	43.2	6.3	0.0	100	609	0.3	237	914	150	0
700	10.0	0.1	0.0	43.3	3.0	0.0	100	620	0.3	237	1099	150	0
800	10.7	0.0	0.0	43.4	0.2	0.0	100	637	0.2	237	1257	150	0
900	11.4	0.0	0.0	43.4	0.0	0.0	100	676	0.2	237	1323	150	0
999	11.6	0.0	0.0	43.4	0.0	0.0	100	717	0.2	237	1379	150	0

Tables 4 and 5 show the results when CaCO₃ was used for Fe³⁺ removal as Fe(OH)₃ (Bernalite) at pH 3.5, at 1.0 and 0.1 atm pressure, respectively. Fe³⁺ removal was achieved at a dosage of 5000 mg/L at pH 3.5, Al³⁺ at a dosage of 7265 mg/L at pH 4.0 as Al(OH)₃ (Gibbsite), Fe²⁺ and Mn²⁺ at a dosage of 8830 mg/L at pH 6.6. At 0.1 atm C⁴⁺ (CO_{2aq}) was removed to 39.3 mg/L (as C) (Table 5) compared to 592.9 mg/L (as C) (Table 4). This was confirmed by the larger mass of CO₂ vapor removed from solution at 0.1 atm (3122 mg CO₂ at a CaCO₃ dosage of 10,000 mg to 1 L), than in the case of 1 atm (1416 mg CO₂ from L). This finding was in line with Henry's law which stipulates that the solubility of a gas is related to the partial pressure. Fe²⁺ and Mn²⁺ were also removed faster at 0.1 atm than at 1.0 atm due to the removal of CO₂, which resulted in the shift of the equilibrium from HCO₃[−] to CO₃^{2−}. Tables 8 and 9 calculate the CaCO₃/Metals removal eq/eq ratio needed for the removal of each metal with CaCO₃. For Fe³⁺ and Al³⁺ the ratio was 1, while for Fe²⁺ and Mn²⁺, that were removed at the higher pH value of 6.6, the ratio was 2. The difference in equivalent CaCO₃/Metal ratios can be explained by the escape of CO₂ in the case of Fe³⁺ and Al³⁺ (Equation (4)), and by HCO₃[−] that remained in solution in the case of Fe²⁺ and Mn²⁺ (Equation (5)).

When CO₂ was stripped to low levels, e.g., 0.1 atm, FeCO₃ (Equation (6)), MnCO₃ and CaCO₃ started to form at lower CaCO₃ dosages than when the atm was 1. In the case of CaCO₃ the remaining Ca²⁺ in solution at 0.1 atm was 590.5 mg/L compared to 756.3 mg/L at 1 atm. The 590.5 mg/L at 0.05 atm was mainly linked to SO₄^{2−}, while the difference between 756 and 590 was due to Ca(HCO₃)₂ in solution.

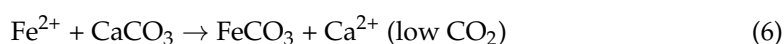
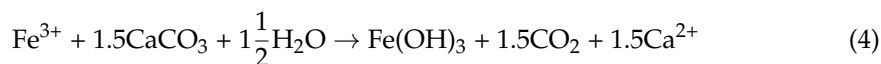


Table 8. Mole ratio of Alkali dosage/Metals removed at 1 atm.

Parameter	Unit	Metal			
		Fe ³⁺	Al ³⁺	Fe ²⁺	Mn ²⁺
Initial conc.	mg/L	2000.0	300.0	200.0	200.0
pH		3.5	3.8	6.6	6.6
q mass	g	18.6	9.0	27.9	28.0
Acc. CaCO ₃ dosage	mg/L	5000.0	7265.0	8047.5	8830.0
CaCO ₃ dosage	mg/L	5000.0	2265.0	782.5	782.5
CaCO ₃ eq mass	g	50.0	50.0	50.0	50.0
CaCO ₃ /Metal rem	mol/mol	0.9	1.4	2.2	2.2

Table 9. Mole ratio of Alkali dosage/Metals removed at 0.1 atm.

Parameter	Unit	Metal			
		Fe ³⁺	Al ³⁺	Fe ²⁺	Mn ²⁺
Initial conc.	mg/L	2000.0	300.0	200.0	200.0
pH		3.5	3.8	6.6	6.6
q mass	g	18.6	9.0	27.9	28.0
Acc. CaCO ₃ dosage	mg/L	5000.0	7265.0	8047.5	8830.0
CaCO ₃ dosage	mg/L	5000.0	2265.0	782.5	782.5
CaCO ₃ eq mass	g	50.0	50.0	50.0	50.0
CaCO ₃ /Metal rem	mol/mol	0.9	1.4	2.2	2.2
CO ₂ (aq)	mg/L	7.4	7.5		39.3
CO ₂ (vap)	mg	2171.4	3050.7		3122.2

3.4.2. Na₂CO₃ and Ca(OH)₂

Section 3.4.1 showed that CaCO₃ can remove Fe³⁺ and Al³⁺ in quantities equivalent to the CaCO₃ dosage. This is due to the escape of CO₂ at the low pH where it precipitated as hydroxides. Fe²⁺ and Mn²⁺ were only removed as carbonates at excess dosages of CaCO₃. CO₂ stripping was needed for precipitation of FeCO₃ and MnCO₃ in the absence of excess CaCO₃ dosages. Ca²⁺ could only be precipitated when CO₂ stripping was applied. The aim of this section was to evaluate Na₂CO₃ and Ca(OH)₂ for removal of Fe²⁺, Mn²⁺ and Ca²⁺. Ca(OH)₂ or CaO is of great interest as the OH[−] will convert the HCO₃[−] to CO₃^{2−}, which is the ideal anion for removal of Fe²⁺, Mn²⁺ and Ca²⁺ as carbonates. Tables 6 and 7 show the results when Na₂CO₃ and Ca(OH)₂ were used, respectively, for removal of 584.1 mg/L Ca²⁺, 18.2 mg/L Fe²⁺, 21 mg/L Mn²⁺ and 200 mg/L Mg²⁺, the metals left in solution after Fe³⁺ and Al³⁺ were removed with CaCO₃ at pH 6.8. A dosage of 1600 mg/L Na₂CO₃ was needed to remove Fe²⁺, Mn²⁺ and Ca²⁺ to low levels as FeCO₃ (Siderite), MnCO₃ (Rhodochrosite) and CaCO₃ (Calcite), respectively. The pH was raised to 8.1. A dosage of 800 mg/L Ca(OH)₂ was needed to remove Fe²⁺, Mn²⁺ and Mg²⁺ to low levels as Fe(OH)₂ (Amakinite), Mn(OH)₂ (Pyrochroite) and Mg(OH)₂ (Brucite), respectively. The pH was raised to 10.5. Ca(OH)₂ will be the preferred alkali to use for removal of Fe²⁺, Mn²⁺ and Mg²⁺ to low levels in the case where water is not desalinated, as no Na⁺ is added to the water. Na⁺ affects the suitability of treated water for further uses such as irrigation. Na₂CO₃ will be the preferred alkali to use if desalination is needed after the pre-treatment stage, as Ca²⁺ can be removed as CaCO₃. This way gypsum scaling of the RO membranes is avoided.

3.5. Feasibility

Table 10 compares the feasibility of pre-treatment with Na_2CO_3 for the removal of Fe^{3+} , Al^{3+} , Fe^{2+} , Mn^{2+} and Ca^{2+} with Table 11 where CaCO_3 , $\text{Ca}(\text{OH})_2$ and Na_2CO_3 were used, in combination with gypsum crystallization. In the latter case CaCO_3 was used for removal of Fe^{3+} and Al^{3+} , $\text{Ca}(\text{OH})_2$ for the removal of Fe^{2+} , Mn^{2+} , and Na_2CO_3 for the removal of Ca^{2+} associated with SO_4^{2-} . In the case of Na_2CO_3 , the TDS increased from 12,660 mg/L in the Feed to 13,684 mg/L due to the replacement of metal ions (Fe^{3+} , Al^{3+} , Fe^{2+} , Mn^{2+} and Ca^{2+}) with Na^+ in solution. In the case where CaCO_3 was used for the removal of Fe^{3+} and Al^{3+} , $\text{Ca}(\text{OH})_2$ for the removal of Fe^{2+} , Mn^{2+} , and Na_2CO_3 for the removal of Ca^{2+} , the TDS dropped from 12,661 mg/L to 2288 mg/L, due to gypsum precipitation. During treatment with calcium alkalis, the Na^+ concentration increased only to 980 mg/L, compared to 4118 mg/L in the case of Na_2CO_3 treatment. Another benefit of using calcium alkalis was that of reduced chemical cost, namely ZAR29.43/ m^3 versus ZAR48.46/ m^3 . In both cases the cost can be recovered from the value of pigment. For an Fe^{3+} concentration of 2000 mg/L, and a pigment price of ZAR20/kg, the potential income from pigment amounts to ZAR122.71/ m^3 . The capital cost in both cases was estimated at ZAR10,000,000/(ML/d) or ZAR3.65/ m^3 (term = 120 month; interest = 6%/a) and the electricity cost at ZAR2.16/ m^3 (Electricity price = ZAR1.50/kWh).

Table 10. Chemical cost and water quality when acid mine water is treated with Na_2CO_3 for removal of Fe^{3+} , Al^{3+} , Fe^{2+} , Mn^{2+} and Ca^{2+} .

Compound	Unit	Composition			Price	Cost	Value
		Feed	$\text{Fe}(\text{OH})_3$	Other Metals	ZAR/t	ZAR/ m^3 Feed	ZAR/ m^3 Feed
Flow Feed	m^3/h	40.0	40.0	40.0			
Na_2CO_3	mg/L		5958.8	3300.6	5000.0	46.30	
Na_2CO_3	mg/L				5000.0	0.00	
Product water							
pH			3.2	5.7			
TDS	mg/L	12,660.9	13,241.8	13,684.2			
H^+	mg/L	5.0	0.0	0.0			
Na^+	mg/L	100.0	2685.9	4118.3			
Mg^{2+}	mg/L	200.0	200.0	200.0			
Fe^{3+}	mg/L	2000.0	0.0	0.0			
Al^{3+}	mg/L	300.0	300.0	0.0			
Fe^{2+}	mg/L	200.0	200.0	0.0			
Mn^{2+}	mg/L	200.0	200.0	0.0			
Ca^{2+}	mg/L	300.0	300.0	10.0			
SO_4^{2-}	mg/L	9205.9	9205.9	9205.9			
Cl^-	mg/L	150.0	150.0	150.0			
Cations	meq/L	196.0	196.0	196.0			
Anions	meq/L	196.0	196.0	196.0			

Table 11. Cont.

Compound	Unit	Composition						Price	Cost	Value
		Feed	Fe(OH) ₃	Al(OH) ₃	Other Metals	CaSO ₄ Crystal	CaCO ₃	ZAR/t	ZAR/m ³ Feed	ZAR/m ³ Feed
HCO ₃ [−]	mg/L			500.0	500.0	500.0	200.0			
OH [−]	mg/L						0.0			
Cations	meq/L	196.0	204.2	204.2	204.2	48.1	43.2			
Anions	meq/L	196.0	204.2	204.2	204.2	48.1	43.2			
SO ₄ ^{2−} (OLI)						1503				
Sludge										
Fe(OH) ₃	mg/L		3826.3		0.0					
Al(OH) ₃			0.0		866.7					
FeCO ₃			0.0		414.9					
MnCO ₃			0.0		418.6					
CaCO ₃	mg/L						245.9			
Products										
Pigment	mg/L		5470					20,000		109.41
Al(OH) ₃	mg/L			866.7						
CaSO ₄ ·2H ₂ O	mg/L					13,425		20.0		0.27
CaCO ₃	mg/L						2650	500.0		1.33
Water	mg/L							12.0		11.70
Energy usage	kWh/m ³		0.6		0.6		0.6			
Energy usage	kWh/m ³		0.6		0.6		0.6	1.2	2.16	
Total									29.43	122.71

4. Conclusions

The following conclusions were made: (i) the rate of gypsum crystallization, in the absence of Fe³⁺, is influenced by the over saturation concentration in solution, the seed crystal concentration and temperature; (ii) gypsum crystallization from an over-saturated solution, in the presence of Fe(OH)₃ sludge, required an inhibitor dosage of 100 mg/L to keep gypsum in solution for a period of 30 min; (iii) gypsum crystallization from an over-saturated solution, in the presence of both, Fe(OH)₃ sludge and CaCO₃ reactant, required a higher inhibitor dosage than 100 mg/L to keep gypsum in solution for a period of 30 min. A dosage of 200 mg/L kept gypsum in solution for the total reaction period; (iv) when only Fe(OH)₃ is present in the slurry, gypsum inhibition is more effective when Fe(OH)₃ sludge is allowed to settle after the initial mixing; (v) when both Fe(OH)₃ and CaCO₃ are present in the slurry, gypsum inhibition is more effective when the inhibitor is added over a period of time (10 min), rather than applying the total dosage at time zero; (vi) Fe(OH)₃ can be changed to yellow pigment (Goethite) by heating to 150 °C and to red pigment (Hematite) by heating to 800 °C. Pigment of nano particle size was produced; (vii) in the case of Na₂CO₃, the TDS increased from 12,660 mg/L in the Feed to 13,684 mg/L due to the replacement of metal ions (Fe³⁺, Al³⁺, Fe²⁺, Mn²⁺ and Ca²⁺) with Na⁺ in solution. In the case where CaCO₃ was used for the removal of Fe³⁺ and Al³⁺, Ca(OH)₂ for the removal of Fe²⁺, Mn²⁺, and Na₂CO₃ for the removal of Ca²⁺, the TDS dropped from 12,661 mg/L to 2288 mg/L due to gypsum precipitation. The alkali cost in the case of calcium alkalis amounted to ZAR29.43/m³ versus ZAR48.46/m³ in the case of Na₂CO₃. In both cases the value of pigment recovered from mine water containing 2000 mg/L Fe³⁺ amounted to ZAR122.71/m³ when the price of pigment was taken at ZAR20/kg.

The capital cost in both cases was estimated at ZAR10,000,000/(ML/d) or ZAR3.65/m³ (term = 120 month; interest = 6%/a) and the electricity cost at ZAR2.16/m³ (Electricity price = ZAR1.50/kWh).

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