

# The Performance of Hydrated Lime Derived from Industrial Brine Sludge Waste in Spray Dry Scrubbing of SO<sub>2</sub> †

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**Abstract:** Spray dry scrubbing is a popular method for removing sulphur dioxide (SO<sub>2</sub>) gas from industrial flue gases, with hydrated lime (Ca[OH]<sub>2</sub>) being a preferred sorbent due to its high reactivity. This study investigated the feasibility of using Industrial Brine Sludge Waste (IBSW) from the chlor-alkali industry as a source of Ca[OH]<sub>2</sub>. XRF analysis revealed that IBSW had a high content of CaO (89.05%), making it a suitable starting material for the production of a calcium-based sorbent. A laboratory-scale spray dry scrubber was used to test the performance of the prepared Ca[OH]<sub>2</sub> sorbent. The desulphurization efficiency was analyzed by investigating how the SO<sub>2</sub> capture in the spray dryer was influenced by the inlet flue gas temperature (120–180 °C), slurry pH (6–12), Ca:S ratio (1.0–2.5), and sorbent particle size (–45µm to –90µm). The highest SO<sub>2</sub> capture rate of 88.54% was achieved under the following conditions: inlet flue gas temperature of 120 °C, Ca:S ratio of 2.5, particle size of –45µm, and a slurry pH of 12. The results suggest that IBSW can be a viable starting material for producing Ca[OH]<sub>2</sub> sorbent, which could then be utilized in the spray dry scrubbing process to remove SO<sub>2</sub> from industrial flue gases.

**Keywords:** Industrial waste; spray drying; hydrated lime; desulphurization

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## 1. Introduction

In recent years, the rapid industrialization observed in developing countries has led to an increase in the demand for electricity. To meet this demand, more power plants are being built, resulting in increased coal combustion. According to the World Nuclear Association [1], South African coal-fired power plants provide 95% of the country's electricity needs and 45% of the electricity needs of the rest of Africa. During coal combustion, the sulphur in coal is oxidized to form sulphur dioxide (SO<sub>2</sub>), which is released as flue gases into the environment. Coal-fired power plants are responsible for 66% of global SO<sub>2</sub> emissions, with 98% of these emissions coming from coal-fired power plants [2]. The release of SO<sub>2</sub> into the atmosphere is not only detrimental to the environment but also to human health. Inhaling the toxic gas may cause throat inflammation, hair loss, respiratory illnesses, and impaired vision [3]. Additionally, atmospheric SO<sub>2</sub> is linked to the formation of acid rain, which negatively affects the ecosystem. To comply with stringent local and international SO<sub>2</sub> emission regulations, power plants are equipped with flue gas desulfurization (FGD) units that use efficient sorbents to control SO<sub>2</sub> release.

Flue gas desulfurization (FGD) techniques are categorized into three types: wet, semi-dry, and dry FGD. Wet FGD systems have been found to be reliable for various fuels

and are commonly used in commercial power plants to achieve efficiencies of over 98% [4]. Among the FGD processes, semi-dry FGD (typically spray dry absorbers) comes second after conventional wet scrubbers. One notable advantage of spray dry absorbers is that they produce a dry by-product, which is easy to handle. Additionally, they consume less energy, have a smaller space requirement, and have a lower installation cost than wet scrubbers. They are also highly flexible in handling varying boiler loads, and affordable construction materials can be used to make the scrubber since no corrosion or scaling issues arise [5]. Semi-dry FGD is most appropriate for incinerators that need to eliminate multiple pollutants, including dioxin, hydrogen chloride, and SO<sub>2</sub> [6]. However, for power plants that burn high-sulfur coal for economic reasons, wet scrubbers are preferred over semi-dry FGD [7].

In the chlor-alkali industry, the disposal of industrial brine sludge waste (IBSW) has posed significant environmental concerns. This waste contains high levels of calcium, magnesium, and sulphates and is typically discarded in landfills [8]. However, upon leaching, this waste can have significant detrimental effects on the ecosystem. To mitigate this problem, IBSW can be converted into a useful or less harmful product. As IBSW contains a substantial amount of calcium and magnesium, it can serve as a potential sorbent or be used in sorbent preparation. A study by Masilela et al. [9] examined the feasibility of using IBSW as a sorbent in wet FGD and concluded that it is a practical and viable option in this context.

In this study, IBSW was utilized as a starting material for the preparation of hydrated lime, which was subsequently utilized as a sorbent in a laboratory-scale spray dry scrubber to evaluate its efficiency in SO<sub>2</sub> uptake. Additionally, the degree of sorbent utilization was investigated under varying experimental conditions, including the gas phase inlet temperature, pH of the lime slurry, stoichiometric ratio, and sorbent particle size.

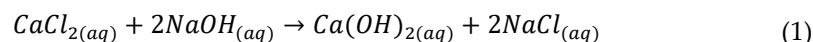
## 2. Materials and Methods

### 2.1. Materials

The initial material for this study, IBSW, was obtained from a local chlor-alkali industry in South Africa. Analytical-grade hydrochloric acid and sodium hydroxide were procured from Sigma Aldrich, South Africa, and 99.99% pure SO<sub>2</sub> gas was supplied by Afrox. X-ray fluorescence (XRF) analysis of the IBSW revealed its chemical composition, with major components comprising 89.05 wt.% CaO, 4.65 wt.% MgO, 1.12 wt.% Na<sub>2</sub>O, 0.68 wt.% Fe<sub>2</sub>O<sub>3</sub>, and 0.84 wt.% SiO<sub>2</sub>.

### 2.2. Methods

A specific amount of the IBSW sample was added slowly to 2 M HCl with constant stirring to ensure the neutralization of the acid. The mixture was then subjected to centrifugation using a Hermle Z 366 to separate the solid residue from the supernatant, which contained a solution of CaCl<sub>2</sub>. The solution was then filtered using a vacuum filtration system. The resulting clear filtrate of CaCl<sub>2</sub> was subsequently reacted with 2 M NaOH to form Ca(OH)<sub>2</sub>, according to the equation 1 below:



The precipitate (Ca(OH)<sub>2</sub>) was then centrifuged using Hermle Z 366 equipment, rinsed with ultrapure water then dried in an oven. Prepared Ca(OH)<sub>2</sub> was then crushed and sieved to obtain different particle sizes ranging from -45 to -90 m. It was then stored in an airtight container to be used for analysis and desulphurization tests.

The scrubber used in this study is a laboratory-scale Buchi mini spray dryer B-290. The full set up consisted of flue gas preparation, lime slurry preparation, spraying drying chamber, product collection section and gas analysis. The feed slurry was prepared by mixing the prepared sorbent with distilled water at predetermined ratio to obtain the calculated weight fraction. The slurry mixture was stirred continuously to ensure proper

mixing. A peristaltic pump was used to continuously feed the lime slurry into the reactor vessel through a two-fluid nozzle at the top of the spray chamber to atomize the slurry into fine droplets. The temperature of the inlet gas was regulated a gas heater at the entry into the spray chamber. To confirm the reproducibility of results, all measurements were done in triplicates. The flue gas was generated by dosing 99% of pure SO<sub>2</sub> into a stream of atmospheric air using flow controllers to obtain required inlet concentration of SO<sub>2</sub> measured in ppm. The concentration of SO<sub>2</sub> on entry and exit points was analyzed using Testo 340 combustion gas analyzer. The readings were taken before and during the desulphurization process. The efficiency of SO<sub>2</sub> uptake ( $\eta$ ) was calculated using the formulae below.

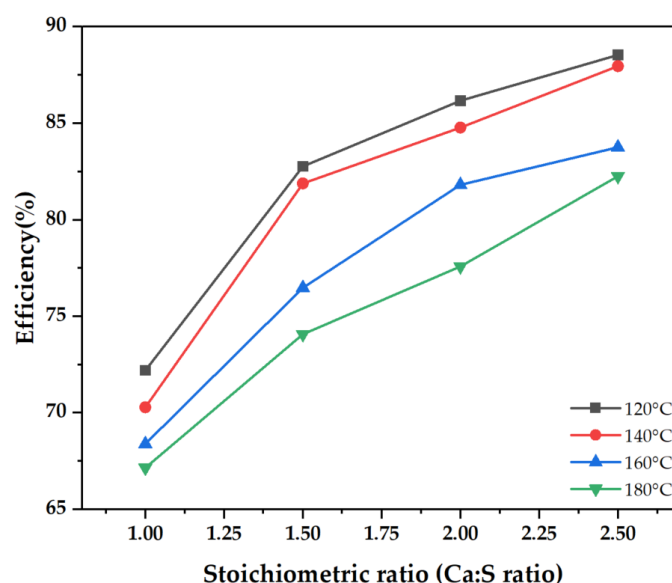
$$\eta = \frac{N_{SO_2,i} - N_{SO_2,o}}{N_{SO_2,i}} \quad (2)$$

where,  $N_{SO_2,i}$  and  $N_{SO_2,o}$  are the inlet and outlet sulphur dioxide concentration in ppm respectively.

### 3. Results and Discussion

#### 3.1. Effect of Inlet Flue Gas Temperature and Stoichiometric Ratio

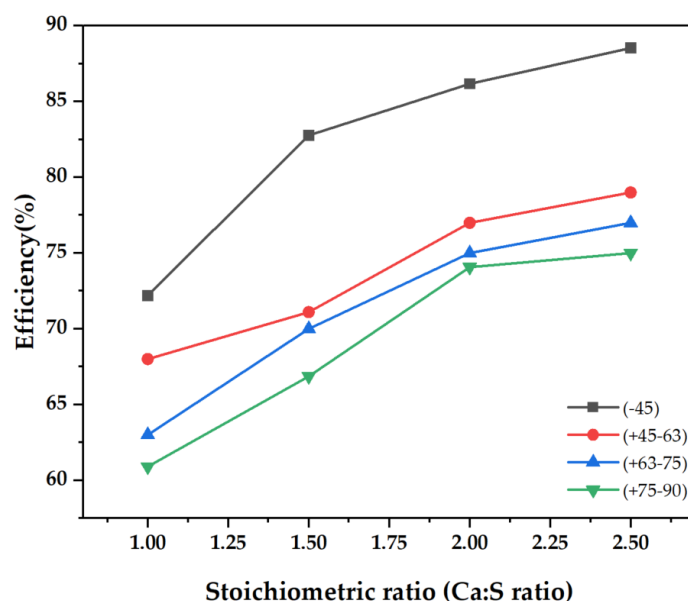
Figure 1 illustrates the experimental findings of SO<sub>2</sub> removal efficiency as a function of Ca/S ratio at different inlet gas temperatures ranging from 120 to 180 °C. Experiments were conducted under the following conditions: slurry weight fraction of 10%, SO<sub>2</sub> flue gas concentration of 500 ppm, and the slurry feed rate was adjusted according to the desired Ca/S ratio. The experimental findings show that high SO<sub>2</sub> capture was achieved at low gas inlet temperatures. At a Ca/S of 1.5, the desulphurization efficiency was 82.8% when the inlet temperature was 120 °C and 74.1% when the inlet temperature was 180 °C. This implies that the SO<sub>2</sub> removal efficiency improved by 8.7% at low temperature. Lower temperatures slow down the evaporation of the water in the spray dryer, therefore elongating the droplet lifetime. Since the reaction and absorption of SO<sub>2</sub> only occur in the presence of water, the prolonged droplet lifetime allows more chemisorption reaction between SO<sub>2</sub> and hydrated lime [10]. As the desulphurization process is entirely dependent on droplet lifetime in a spray chamber [11], lower temperatures are associated with high relative humidity, which is a conducive environment for SO<sub>2</sub> capture.



**Figure 1.** Spray dryer desulphurization efficiency as a function of stoichiometric ratio for different inlet flue gas temperature.

### 3.2. Effect of Sorbent Particle Size

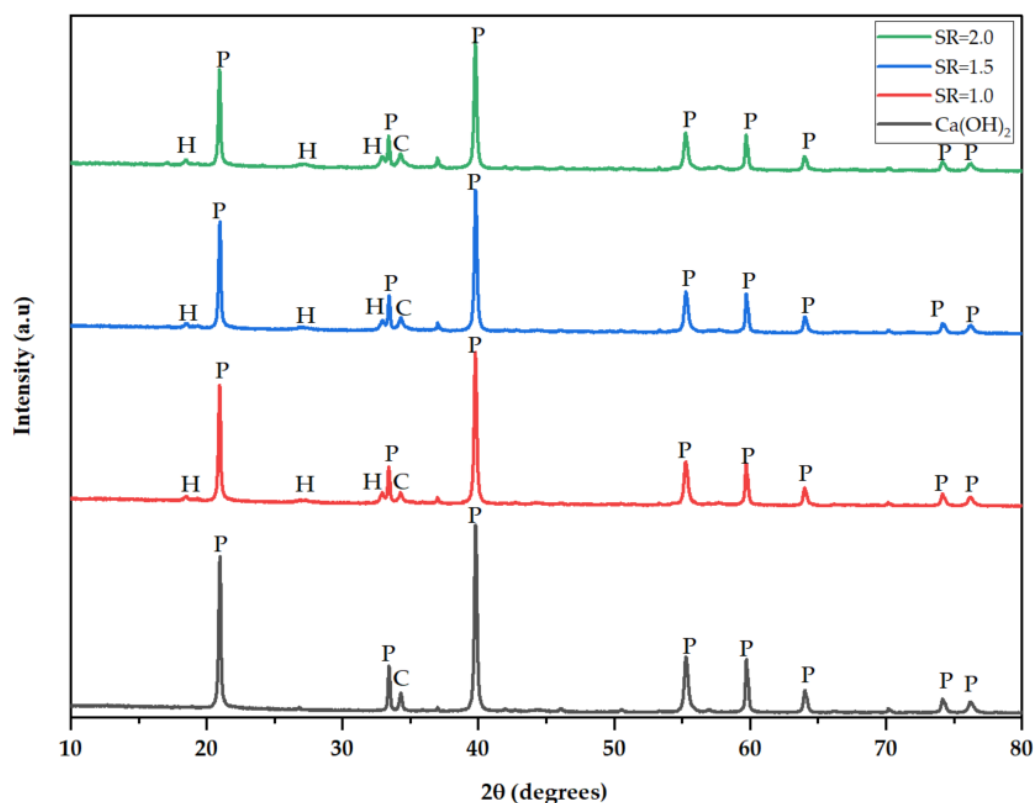
Figure 2 illustrates the experimental findings on the effect of the particle size of the prepared  $\text{Ca}[\text{OH}]_2$  on the  $\text{SO}_2$  capture in the spray dryer. Sorbent particle size was varied from  $-45 \mu\text{m}$  to  $-90 \mu\text{m}$  while maintaining gas inlet temperature at  $140 \text{ }^\circ\text{C}$ , solid weight concentration at 10% and  $\text{SO}_2$  concentration at 500 ppm. Sorbent particle size has great influence on  $\text{SO}_2$  capture as observed from the figure. There was a remarkable improvement in the efficiency by 30% when the grain size reduced from  $-90 \mu\text{m}$  to  $-45 \mu\text{m}$ . This is attributable to the larger surface area on finer grain size of  $\text{Ca}[\text{OH}]_2$  which exposes more of the  $\text{Ca}^+$  ions to the chemisorption process [12]. This observation is also in agreement with research done by Liu et al., [13] who investigated the influence of particle size of waste concrete powder. The authors established that the finest particle size gave the highest  $\text{Ca}^{2+}$  releasing rate hence a high  $\text{SO}_2$  capture.



**Figure 2.**  $\text{SO}_2$  removal efficiency as a function of stoichiometric ratio for different sorbent particle sizes.

### 3.3. Mineralogical Composition of the Desulphurization Products

Figure 3 presents XRD diffractograms of the sulphation products collected under different process conditions. This analysis technique is crucial as it provides mineralogical data about a compound. The dominant mineral in the prepared sorbent is portlandite, accounting for 91.9% of the total composition. The XRD spectrum of the sulphation products indicates a decrease in portlandite and the emergence of hannebachite with an increase in stoichiometric ratio. The five typical peaks observed at  $2\theta$  angles of  $20.98^\circ$ ,  $33.43^\circ$ ,  $39.77^\circ$ ,  $55.28^\circ$ , and  $59.72^\circ$  correspond to portlandite and are similar to those reported by Mardiana et al. [14]. The emerging peaks at  $2\theta$  angles of  $32.9^\circ$  and  $36.99^\circ$  are for hannebachite formed after the absorption process. This supports the experimental findings showing that desulphurization efficiency increases with an increase in SR forming a desulphurization product containing sulphite (Hannebachite).



**Figure 3.** XRD spectrum of prepared hydrated lime and sulphation products sampled at different stoichiometric ratios of 1.0, 1.5 and 2.0, respectively (P—Portlandite, H—Hannebachite, C—Calcite).

#### 4. Conclusions

This research paper investigated the feasibility of utilizing industrial by-product solid waste (IBSW) as a source of hydrated lime for desulphurization purposes. The results showed that  $\text{Ca}[\text{OH}]_2$  was successfully synthesized from the waste with a purity of 91.9%. The prepared sorbent was then used in a spray dryer, and a desulphurization test was conducted. The  $\text{SO}_2$  removal efficiency of up to 89% was achieved at a gas phase inlet temperature of 120 °C and Ca/S ratio of 2.5. The study also found that a low gas phase inlet temperature can slow down the evaporation of the water fed into the spray dryer, thereby elongating the droplet lifetime and creating more time for ionic reactions to occur between  $\text{SO}_2$  and  $\text{Ca}[\text{OH}]_2$ . Additionally, high stoichiometric ratios were found to increase desulphurization by reducing additional liquid mass transfer resistance. Furthermore, the study observed that high  $\text{SO}_2$  capture was achieved with a particle size of  $-45$ , due to the increased surface area. XRD analysis conducted on the sulphation products indicated the presence of unreacted portlandite ( $\text{Ca}[\text{OH}]_2$ ) and hannebachite ( $\text{CaSO}_3$ ).

**Author Contributions:** L.K. and B.J.C. outlined the methodology used in the study. B.J.C. performed the experiments and wrote the first draft of the manuscript. H.L.R. and L.K. edited and drafted the final version of the manuscript. All authors have read and agreed to the published version of the manuscript.

**Data Availability Statement:** All experimental data reported in this study will be provided upon request.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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