

FLUE GAS DESULPHURIZATION BY SPRAY DRY SCRUBBING



This dissertation is submitted in fulfillment of the requirement for the Doctor of Philosophy:

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Declaration

I Lawrence Koech, declare that, to the best of my knowledge, my dissertation is the result of my original work except otherwise stated. It has not been submitted in candidature for any degree in any university or institution. Due references in literature were stated and acknowledged wherever other sources were involved according to the standard referencing practices.



Lawrence Koech

30th March 2022

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Abstract

Post combustion sulphur dioxide (SO_2) emission is a major problem facing coal-based power plants. Increased awareness of the detrimental effects of SO_2 on human health and the environment has prompted increased pressure to equip power plants with flue gas desulphurization (FGD) systems. FGD is a commercially proven technology for removal of SO_2 from flue gas which is considered as a significant pollutant to the environment. Spray dry scrubbing (SDS) process represents a type of semi-dry FGD which is a low-cost retrofit SO_2 control technology that could be used in already existing coal-fired power plants.

This study explored the experimentation on the performance of a laboratory-scale spray dryer involving flue gas desulphurization (FGD). The experimentation involved test done to investigate the effects of spray characteristics i.e., inlet gas phase temperature, approach to saturation temperature, and calcium to sulphur ratio on SO_2 removal efficiency using hydrated lime as a sorbent. Results indicated improved SO_2 removal efficiency with increasing the stoichiometric ratio and decreasing the temperature and approach to saturation temperature. An absorption efficiency of SO_2 beyond 90% was achieved at a stoichiometric ratio of 2.5. A high degree of conversion of calcium was realized at low stoichiometric ratios with a maximum utilization of 94% obtained at a stoichiometric ratio of 1.5.

This study also investigated the interaction effects of independent variables on SO_2 absorption using response surface methodology. By analyzing the influence of stoichiometric ratio, inlet gas phase temperature, slurry solid concentration and slurry pH, a predictive quadratic model was developed correlating the independent variables and SO_2 removal efficiency. Although all independent variables had impact SO_2 removal efficiency, stoichiometric ratio was found to have the largest influence. The recommended optimal conditions for SO_2 absorption were inlet gas phase temperature of 140°C , stoichiometric ratio of 2, slurry solid concentration of 8% and slurry pH of 10 to achieve 90% SO_2 removal efficiency.

An investigation into performance of relevant spray drying FGD sorbents was carried by evaluating different sorbents namely: hydrated lime, limestone and trona. Results show that trona had better performance characteristics with the highest SO_2 absorption efficiency when compared to hydrated lime and limestone under the same operating conditions. The analysis of the desulphurization product revealed that trona has better sorbent conversion and utilization in comparison with

limestone and hydrated which contained high concentration of unreacted sorbent in the desulphurization product.

Keywords: spray drying, desulphurization, semi-dry FGD sorbents, experimentation, optimization.

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1. Introduction

The combustion of Sulphur containing fossil fuels in power plants such as coal leads to the release of SO₂ which is harmful to the human health and causes damage to the natural environment. Environmental regulations on air emission are becoming increasingly stringent and therefore coal-fired power plants have been hard-pressed to adopt flue gas desulphurization (FGD) technology to curb SO₂ emission to the environment.

There are three types of FGD: wet, semi-dry and dry FGD systems. Wet FGD technology has been predominantly used in most coal fired plants in the past because of the availability of sorbent (limestone) and high SO₂ removal efficiency realized (Soud, 1995). Despite this, it has drawbacks stemming from high capital cost and large solid waste materials which needs comprehensive wastewater treatment. This has made both dry and semi-dry FGD technologies attractive alternatives due to the ease of product handling and less space requirement (Xu et al., 2000). However, dry, and semi-dry FGD technologies have not been widely used in the past because of high sorbent cost, low sorbent utilization and lower desulphurization efficiencies compared to wet FGD technology (Soud, 1995; Zhou et al., 2005).

Spray dry technology is a type of semi-dry FGD system which uses finely sprayed lime slurry to contact it with hot flue gas containing SO₂. It uses atomizers or fluid nozzles to disperse lime slurry which comes in contact with hot flue gas resulting in SO₂ removal by chemical absorption (Hill and Zank, 2000; Scala et al., 2004). The heat contained in flue gas dries the slurry thereby losing water by evaporation resulting in dry products which are collected using particulate control device (Heebink et al., 2007). The dry product is mostly calcium sulphite which precipitates due to its low solubility in water. Powder particles are taken up by flue gas which are collected by electrostatic precipitator or a bag filter. This type of FGD technology has received much attention in the recent years for use in coal-fired power plants mostly due to the cost and less space requirement.

There are challenges associated with the application of spray dryers in coal-fired plants. It is mostly limited to power plants which use low sulphur coal (usually 1-2%) because of low desulphurization efficiency (Srivastava and Jozewicz, 2001; Kadja and Bergeles, 2003). Low desulphurization efficiency is mainly caused by short residence time of the sorbent in the dryer and shorter constant drying period (Xu et al., 2000). High SO₂ removal is normally achieved during the constant drying

period (when the sorbent is still moist) and this can be elongated by use of deliquescent additives (Srivastava and Jozewicz, 2001; Stein et al., 2002). Deliquescent additives enhance the solubility of calcium hydroxide thereby keeping the sorbent moist which means more SO₂ in flue gas can be removed. Liu (2005) investigated the reaction between Ca(OH)₂ and SO₂ in the presence of HCl and deliquescent additives. By addition of CaCl₂ which is an organic hygroscopic salt, SO₂ removal was greatly improved. Similarly, Izquierdo et al., (2000) examined the reaction between Ca(OH)₂ and SO₂ in a fixed bed reactor at low temperatures using different organic additives. CaCl₂ and NaOH were found to increase the reaction rate of Ca(OH)₂ while NaCl had the least effect on the reaction rate.

Because of low sorbent utilization, lime spray drying produces a dry product consisting of calcium sulphite-hemihydrate and unreacted calcium hydroxide, making it less attractive commercially than gypsum produced in wet FGD system (Ma et al., 2000; Erdöl-Aydın and Nasün-Saygılı, 2007). To improve this, part of the solid product is always recycled into the feed with lime slurry. This necessitates the use of high stoichiometric ratio of calcium to sulphur in order to achieve the desired high SO₂ absorption efficiency (90-95%). This in turn translates to excess sorbent usage and incomplete conversion of calcium hydroxide (Hill and Zank, 2000). Klingspor (1987) performed experiments using a laboratory scale spray dryer to determine the effect of grinding the recycle product on SO₂ removal. Enhanced SO₂ removal and improved sorbent utilization was realized because grinding of the solid waste exposes more unreacted Ca(OH)₂ in the core of the particle for reaction with SO₂. Xu et al., (2000) proposed a powder-particle spouted bed reactor for lime spray drying. High SO₂ removal efficiency and better sorbent utilization was achieved when the reactor was used due to elongated sorbent residence time.

The performance and reactivity of slaked lime in a spray dryer can also be improved by activation using hydrating agents which are siliceous in nature such as fly ash. It has been proven that the addition of fly ash into slaked lime improves its SO₂ removal efficiency and utilization by making it more porous (Davini, 1996; Lin et al., 2003). The reactivity of slaked lime depends on its porosity and surface area which is enhanced when a siliceous material is added. The reaction between active silica in siliceous material and slaked lime is a pozzolanic reaction resulting in calcium-silicate-hydrate which is a fibrous gel and thus improves the specific surface area (Maina and Mbarawa, 2011). The removal of SO₂ will then be enhanced because increased surface area exposes more calcium ions which are active compounds during chemisorption reaction.

1.1. Problem statement

South Africa heavily depends on coal for electricity generation with 77% of its energy sources coming from coal. Most coal-fired power plants have no FGD systems in place and therefore substantial amount of sulphur dioxide is released into the environment during combustion. Power plants have been hard-pressed to meet the international environmental regulations monitoring air quality and consequently, there is a need to restrict sulphur dioxide emission. Due to scarcity and depletion of water sources, power plants are also trying to adopt technologies that minimize water usage. Dry and semi-dry FGD systems are low-cost retrofit sulphur dioxide control technologies that require low water usage. Spray dry technology represents a semi-dry FGD system that has received growing interest due to the reduced installation and operating cost requirement, ease of retrofit to existing plants and ease of product handling which requires no sludge handling equipment. However, its performance is characterized by low sorbent utilization and low sulphur dioxide removal efficiency when compared with wet FGD technology. This has limited its application to low sulphur coal plants. To realize the desired sulphur dioxide removal efficiency, a high lime stoichiometric ratio is used leading low sorbent utilization. Low desulphurization efficiency in spray dryer FGD system is also attributed to the short time spent by the sorbent slurry droplet when it is still moist (constant rate drying period). This is the period which accounts for most of sulphur dioxide removal before the falling rate drying period where little or no sulphur dioxide removal takes place. Despite the substantial amount of research previously done, there is little research done on the absorption of sulphur dioxide in the falling rate drying period of the spray chamber. There is also lack of suitable data for laboratory scale spray dryers worldwide.

1.2. Main objective

The purpose of this research is to investigate the performances of spray dry scrubbing FGD using a laboratory scale scrubber by establishing optimum operating condition relevant to the process.

1.2.1. Specific objectives

- 1) To develop detailed literature survey on spray drying FGD with competing technologies with applicable sorbents

- 2) To design and construct of a suitable spray dryer pilot plant and commission with the relevant advanced measuring equipment.
- 3) To identify and evaluate different sorbents suitable for spray dry scrubbing and perform detailed experimental characterization and screening.
- 4) To conduct detailed parametric study to identify interaction of variables for drying and drying/adsorption respectively using existing statistical methods.
- 5) To identify important operating parameters for detailed experimentation and validation with results from other models.

2. Literature Review

2.1. Energy Trends

Energy plays a fundamental role in the development of a nation; it is the backbone of the economy which is relied upon by its citizens. The world is heavily dependent on energy and mineral resources particularly on fossil fuels. There has been an increasing energy demand globally due to economic growth and industrialization which has been experienced in both developed and developing countries. The demand for energy is expected to be still on the rise for an unforeseeable future as more energy is needed in rural parts of developing countries for agriculture, domestic use, transportation, and industrial development (Revelle, 1979). It is becoming necessary to supply larger quantities of energy with great efficiency to meet the growing demand of emerging economies and rapid growing of developing countries.

There are several sources of energy that are currently being used in the world. They are categorized as: fossil fuel, renewable energy sources and nuclear sources (Balat and Ayar, 2005). The world market largely relies on energy from fossil fuels, petroleum crude oil and natural gas which all account for around 80% of the total world energy sources (Bauen, 2006). Renewable energy sources accounts for 14%, while nuclear energy accounts for 6% of the world's primary energy. Globally, electricity has been mostly produced by coal (39%), followed by hydro power (18%), nuclear power (17%), natural gas (16%) and crude oil (9%) (Fridleifsson, 2003). The remaining 2% are new renewable sources. Figure 2:1 shows world energy sources. Energy is mostly distributed among commercial, residential, transport and industrial sectors with the transport sector mostly using petroleum oil while other sectors use mostly fossil fuel.

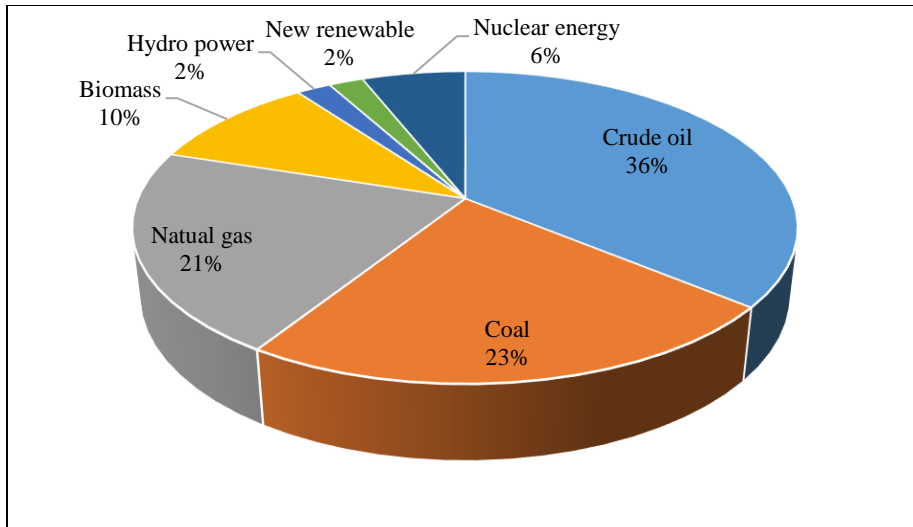


Figure 2:1: World energy sources (adapted from Goldemberg, 2001).

It is evident that fossil fuel has been the principal source of energy mostly for industrial use in most countries worldwide. South Africa being one of the most industrialized country in Africa, its economy is heavily dependent on the energy sector which accounts for 15% of the GDP (Rozpondek and Siudek, 2009). It has large coal reserves which is the main source for electricity generation with over of 77% of its power demands depending on it (Menyah and Wolde-Rufael, 2010). There has been a growth in the use of coal in South Africa over the last few decades and this is expected to continue over the next few years as it is putting up more coal-fired power stations to meet the growing energy demands and consumption (Winkler, 2007). Due to its abundance and reliability, it implies that coal will remain as a primary source of energy in South Africa and the rest of the world. Other sources of energy in South Africa include nuclear energy, natural gas, renewable energy, crude oil, and hydro power. South Africa's energy sources are depicted in Figure 2:2.

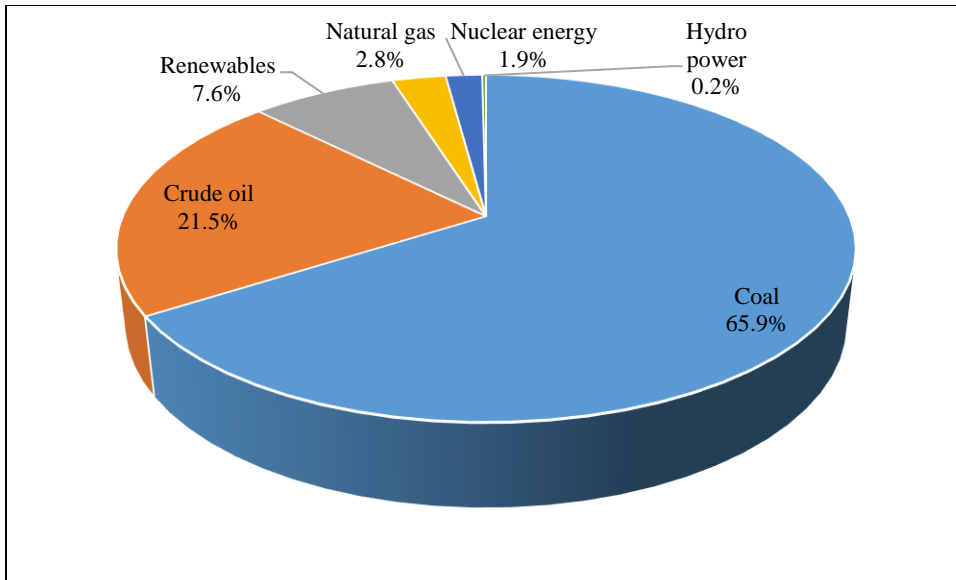


Figure 2:2: South Africa's primary energy supply-2006 (adapted from Subramoney et al., 2010).

2.2. Pollution Sources

The use of fossil fuel as a primary source of energy has been mainly due to its availability and reliability in most countries. It is also due to the industrial energy demand in emerging economies which has increased the use of coal, thereby aggravating attempts to control environmental pollution. Its use especially coal, has raised concerns due to its detrimental pollution effects on the environment and urban pollution. The use of coal especially in emerging economies will still be on the rise because it is a major source of energy. South Africa has huge coal reserves which is an obvious indicator that coal will remain as the primary source of energy for the next few decades.

Some of the environmental pollution stemming from the burning of coal include carbon emission, release of nitrous gases and release of sulphur dioxide gas to the environment. Fossil fuel combustion is a major contributor to carbon emission which accounts for 98% of the total carbon emissions (Demirbaş, 2006; Katsouyanni, 2003). It emits gases such as CO₂, SO₂, NO_x, HC, O₃ and CO which cause global warming, acid rain and urban pollution (Bose, 2000). It is particularly SO₂ and NO_x causing acid rain which damage vegetation and the ozone layer.

Emission from combustion of fossil fuel can be reduced through the use of efficient energy technologies, low carbon energy supply and reduced energy demand (Bauen, 2006). Major technological advancements are essential especially for developing countries with enormous coal reserves in order to mitigate environmental pollution. These technologies include flue gas desulphurization (FGD) technologies and carbon capture & storage (CCS) among others. Electricity generation in South Africa is massively reliant on coal and it's therefore faced with environmental gaseous pollutants emanating from coal-fired stations mainly SO₂ gas. Power stations have been hard-pressed to meet international emission regulations on air quality standards and have therefore adopted the use of FGD technologies in new power generation utilities. This has seen Eskom install FGD system in its newly constructed power utility at Kusile.

The occurrence of SO₂ in the environment is mostly due to the use of fossil fuel, with coal and crude oil containing 1-2% sulphur by weight (Smith et al., 2011). Coal is mostly composed of organic matter and pyrite which gets oxidized and released as SO₂ to the environment during combustion (Cheng et al., 2003). This shows that sulphur content in coal is directly proportional to the concentration of SO₂ released. It is therefore necessary to burn low-sulphur coal in order to reduce SO₂ emission in coal-fired power plants (Xu et al., 2000).

2.3. Effects of Sulphur Dioxide

Although there are several sources of gas pollutants, it is the widespread combustion of coal in power utilities that has been known to be a major source of sulphur dioxide bearing adverse effects both on the environment and human health. Sulphur dioxide is an anthropogenic gas which also comes from smelting of sulphidic ores, petroleum refining, photochemical production of volatile sulphur in the oceans and volcanoes (Kampa and Castanas, 2008; Vestreng et al., 2007). Globally, there has been an increase of SO₂ emission which is attributed to widespread use of fossil fuel due to industrialization in emerging economies especially those without proper pollution control technologies. There is always the risk of human exposure to SO₂ as well as the effect it has on vegetation, animals, or any material.

Long term exposure to particulate matter causes severe effects to human life in terms of overall health burden. Areas close to industrial zones have experienced deposition of sulphuric acid and atmospheric sulfate loading which can be detrimental to the ecosystem, harming aquatic animals and plants (Castanas and Kampa, 2007). Sulphur dioxide release to the environment leads to the formation of sulfate aerosols which tend to make clouds more reflective and change their lifetime causing net cooling (Smith et al., 2011). It was reported by (Joint and World Health Organization, 2006) that a significant reduction in life expectancy of the average population will be experienced if the present levels of SO₂ are to continue. It is known to cause chronic respiratory diseases, allergic reactions, brain damage and susceptibility to bacterial infections (Treissman et al., 2003). It is therefore crucial to reduce SO₂ emissions to levels which have no effects on human life (Vestreng et al., 2007).

Acidification deposition of SO₂ on the environment has mainly contributed to ecological degradation which has affected aquatic and terrestrial organism either by direct dry or wet deposition through chemical changes in soil, groundwater, and surface water (Mylona, 1996). The deposition of SO₂ in rivers triggers an imbalance in water pH (mostly decreasing below 5) causing aquatic animals like fish to die due to intolerable living conditions. A decline in fisheries was recorded in Southern Norway in rivers and lakes in the early 19th century (Muniz, 1984). Over the same period, a decrease in the growth of certain tree species and severe damage to aquatic ecosystem was reported in Europe, which was caused by acidification of water (Mylona, 1996).

Other adverse effects caused by acid rains stemming from SO₂ emission also include degradation of forests resulting in soil erosion and eventual destruction of natural habitats to many animals. SO₂ released reacts with water in the atmosphere to form sulphurous acid which easily gets oxidized to sulphurous and sulphuric acid. Acidic pollutants mainly caused by SO₂ resulted in widespread foliar disease in southern Germany in the 1970s which extended from industrial zones to remote areas after some time (UN-Economic Commission for Europe, 1984). This became a serious matter in most parts of Europe due to slow weathering of rock and bedrock. Buildings, architectural structures and infrastructures like railway lines and bridges are also affected by acid rains due to its corrosive nature.

2.4. Emission Control

With the rapid pollution by electric utility boilers used in coal-fired power plants, it is becoming necessary to have air emission pollution control as a legal requirement. Coal is still a major source of power in most countries; therefore, the efficiency of coal combustion and emission control are the two most critical factors to be considered in pollution mitigation. The use of low sulphur containing coals can also be a way of mitigating SO₂ pollution.

The growing concern has led to the adoption of laws and regulations enforced by the governments and international bodies focusing on environmental pollution mitigation measures. To protect human life and ecological environment, it necessary to set emission limits and air quality targets that are sufficient to improve the ambient air quality (Wang and Hao, 2012). The Geneva Convention held in 1979 on Air Pollution was aimed at protecting the environment. This was after it was demonstrated by researchers that there is an interrelationship between SO₂ emission from industries and the environmental degradation experienced at that time (Popp D, 2001). This marked the beginning of adoption of laws and regulations focused on environmental protection throughout the world and increased awareness on importance of environmental protection. In South Africa, the Air Quality Act (AQA) by the National Environmental Management was enacted in 2004 which provides national ambient quality norms and standards on air quality monitoring and evaluation. It is aimed at reducing/eliminating respiratory and other diseases through implementation of air pollution mitigation measures. These laws ensure power plant utilities are compliant with the air quality regulations. Intensive efforts have been made to implement these laws all over the world with the aim of reducing air pollution.

To comply with the enforced environmental laws and regulations, coal power plants are obligated to invest in pollution abatement equipment by installing scrubbers, retrofitting existing boiler units, and repowering/regenerating units (Yaisawarng and Klein, 1994). There are different categories of pollution control technologies that have been pursued by electric power utilities (Taylor et al., 2005):

1. Using tall gas stacks to disperse emissions away from the immediate areas
2. Using intermittent controls which involves routine operational adjustments to reduce power plant SO₂ emissions in response to atmospheric conditions
3. Pre-combustion reduction of sulphur from fuel e.g., coal washing/switching
4. Post-combustion SO₂ removal from flue gas e.g., FGD technology

Power plants can also ensure compliance with the emission laws and regulations especially regarding SO₂ emission through burning low sulphur-containing fuel or adopting renewable energies (Streeter, 2016). This is mostly hampered by the un-availability of renewable energy sources and complications relating to restructuring power plants from using coal to natural gas. This has made post-combustion technologies for treatment of SO₂ in flue gas to be technically feasible in industries especially using FGD which has demonstrated to be an appropriate technology for treatment of flue gas in coal-fired power plants. FGD systems are capable of high SO₂ removal efficiency, and it involves a substantial capital cost.

2.5. Flue gas desulphurization (FGD)

Coal-fired power plants are based on combustion of coal which generates numerous pollutants including acid gases such as sulphur dioxide (SO₂) sulphur trioxide (SO₃), hydrogen fluoride (HF), hydrogen chloride (HCl), nitrogen oxides (NO_x), mercury and particulate matter (Miller and Miller, 2010). Acid gases have adverse effects on human health which may contribute to an increase in mortality, serious illness or pose potential hazards to human health (Kampa and Castanas, 2008). Acid gases also cause serious damage to vegetation, aquatic life, and man-made structures when it precipitates as acid rain. This has led to strict environmental and air quality legislations that have been enacted both locally and internationally to monitor ambient air pollution particularly from industries. These legislations have had a tremendous impact on improving air quality and have resulted in the development and deployment of many innovative air pollution control technologies.

Fuel sulphur content in coal varies depending on the source. During coal combustion, sulphur-oxides (SO_x), mainly SO₂, are formed through oxidation of sulphur and released to the atmosphere. The atmospheric SO₂ is an air pollutant responsible for respiratory problems and acid rain (Benko and Mizsey, 2007). With increasing awareness of the detrimental effects of SO₂ on human health and the environment, it is becoming appropriate to build power plants with flue gas desulphurization (FGD) systems to curb SO₂ emission. The implementation of the use of FGD systems has largely been as a result of environmental regulations which are continuously becoming stringent. Power plants can also utilize low-sulphur fuels, natural gas or adopt renewable energy as alternative sources of energy to coal to limit emission of SO₂ to the environment (Streeter, 2016). Types of FGD systems include wet systems e.g., wet limestone system, semi-dry systems e.g., lime spray drying and dry systems e.g., duct sorbent injection.

FGD systems were first commercially used in the early 1970s both in the United States and Japan, thereafter, expanding rapidly to Europe in the 1980s (Soud, 2000). They have been notably used in several countries seeking to minimize the effect of increased air, water, and solid pollutants. This led to a significant decrease in air pollution in 1990s and 2000s which is attributed to the use of FGD systems in power plants especially in developed countries (Nolan, 2000). FGD technology has seen its first application in South Africa in its new power utility at Kusile and it is expected to be implemented in all new and existing coal power utilities.

FGD technology has proven to be one of the most efficient systems adopted worldwide for removal of SO₂ from flue gas in coal power plants. It is a scrubbing system that uses an adsorbent medium to interact with flue gas containing sulphur in an absorber or a scrubber to form a high solid sulphur slurry (Córdoba, 2015). Traditionally, a sorbent rich in alkali (calcium or magnesium) reacts with sulphur forming a solid stable product CaSO₄ which can easily be disposed of. Lime and limestone are the most commonly used medium as a sorbent in FGD systems because of their calcium abundance and availability. Other sorbents used include magnesium, seawater, sodium, and amine among others.

2.6. FGD processes

Commercialized FGD technologies can be classified as regenerative and once-through systems depending on the process handling of the resultant solids generated (Ortiz and Ollero, 2008; Srivastava and Jozewicz, 2001). In once-through systems, the spent sorbent is often disposed of as waste or utilized as a byproduct, this requires continuous delivery of fresh sorbent. In a regenerative system, the sorbent is regenerated or recycled back into the system with no waste produced (Jafarinejad, 2016; Vega et al., 2019). Both once-through and regenerative systems can be further classified as dry, semi-dry and wet FGD processes as shown in Figure 2:3 for major FGD processes. Wet and semi-dry FGD processes use chemical absorption to remove SO₂ using slurries such as slaked lime or limestone. Dry FGD process applies physical or chemical sorption on the sorbent to remove SO₂.

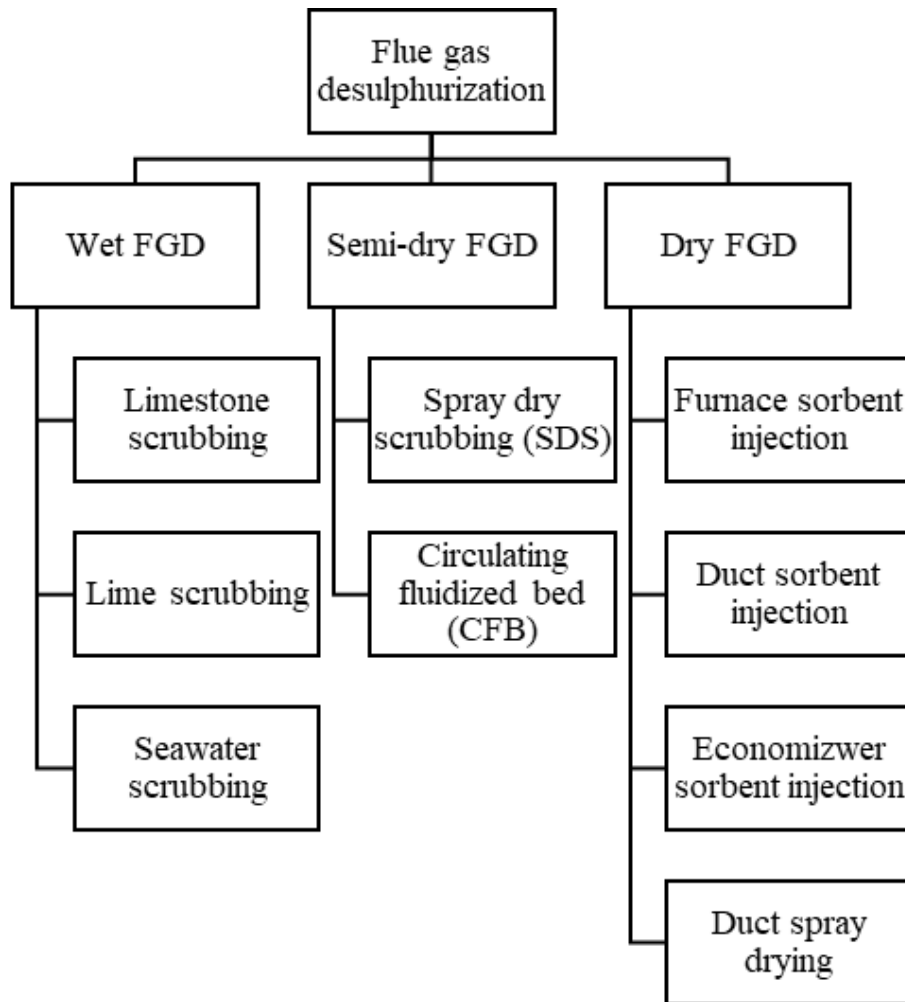


Figure 2:3: Classification of major FGD processes (adapted from Córdoba, 2015)

2.7. Wet FGD Processes

Wet FGD technology is the most commonly used commercial scrubbing system in power plants due to its reliability and high SO₂ removal efficiency. It accounts for up to 87% of the total worldwide FGD capacity (Benko and Mizsey, 2007; Cheng and Zhang, 2018). It uses either lime or limestone as a sorbent forming gypsum as a product. The reliability and availability of the sorbent, the formation of a stable sellable product (gypsum) and high SO₂ removal efficiencies have made wet FGD technology a choice for many power utilities. This technology has low operational costs due to the availability of the sorbent; however, it has a significantly high capital cost.

Typically, in a wet FGD system, flue gas at high temperature enters the absorber through the flue gas duct situated slightly above the slurry tank. Limestone slurry is prepared by crushing or milling limestone into fine powder of the desired particle size before mixing with a proportionate amount of water in the slurry tank. It is then pumped into the absorber where it is dispersed via spray nozzles. The flue gas comes in contact with dispersed slurry counter-currently, effectively increasing the gas-liquid interaction and subsequently removing SO_2 from flue gas. SO_2 in flue gas reacts with calcium in slurry forming CaSO_3 and CaSO_4 which drops into the slurry tank. At the same time, air is injected into the slurry tank to enhance oxidation of CaSO_3 to CaSO_4 which is a stable product. The slurry tank provides sufficient time for complete reaction between the slurry and dissolved SO_2 , and for dissolution of the fine limestone particles. For effective utilization of the sorbent, the slurry is usually recirculated into the absorber using a circulation pump with the slurry entering the absorber via spray nozzles located at the top of the absorber. Clean flue gas, free of SO_2 leaves the top of the absorber through the outlet duct before entering the chimneys (Jin et al., 2006; Nolan et al., 2004; Zhong et al., 2008). A typical wet FGD system is shown in Figure 2:4.

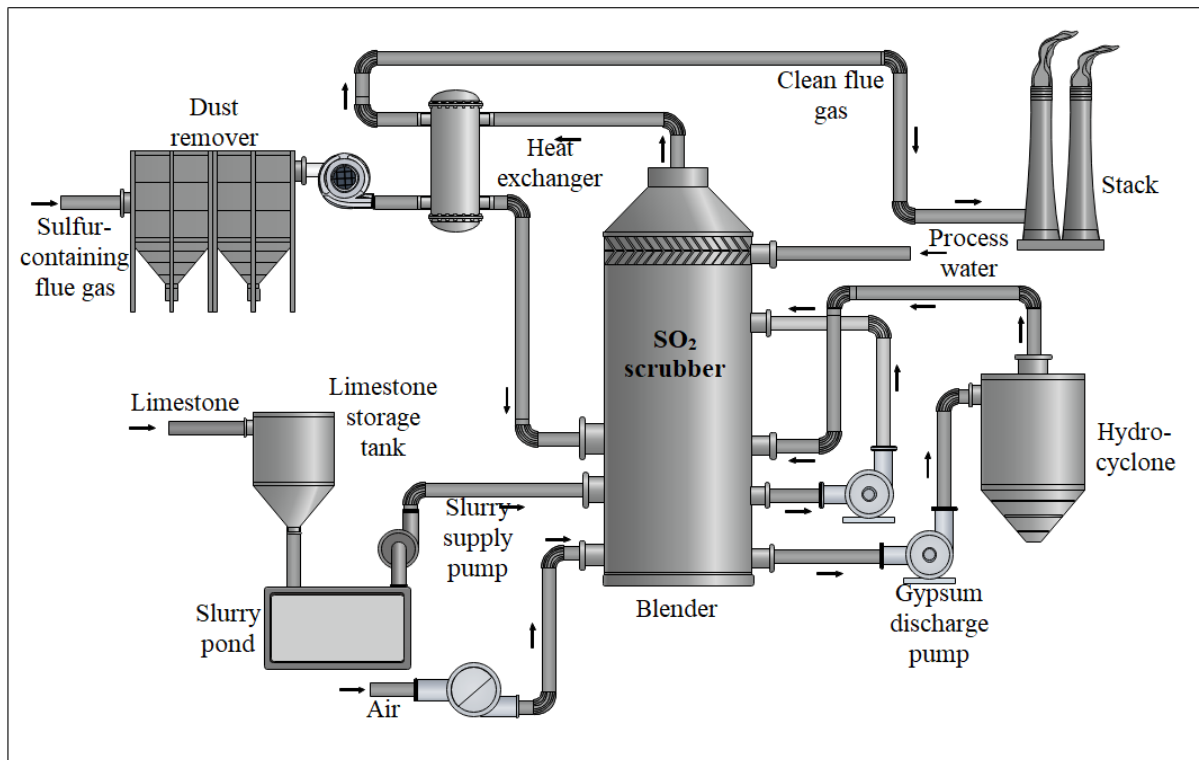
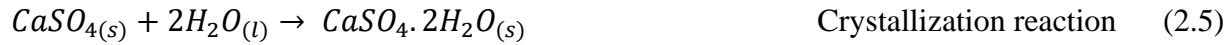
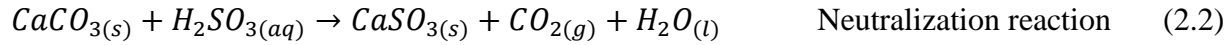
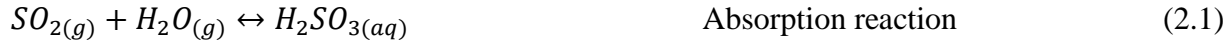
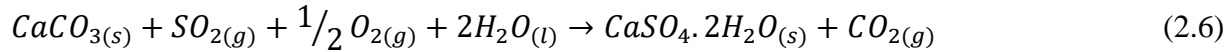


Figure 2:4: Typical limestone wet FGD system (adapted from Miller and Miller, 2010)

The following are the basic reactions that take place in both the absorber and the recycle tank of a wet FGD limestone system (Michael Walsh A, 2008; Xiaowen, 2019):



An overall equation involving the reactions above leading to the formation of $CaSO_4 \cdot 2H_2O$ (gypsum) is represented by equation 6.



The performance of a wet FGD system is greatly influenced by gas-liquid phase mass transfer of Ca^{2+} ions in liquid phase and SO_2 into the slurry (Kiil et al., 1998). This is further influenced by the rate of dissolution of limestone in the system which directly influences the concentration of Ca^{2+} in the slurry and consequently the rate of SO_2 absorption. Other significant operating variables include slurry pH and stoichiometry, reaction temperature, slurry particle size and the type of sorbent used. To improve wet FGD SO_2 removal efficiency, organic acids are used as additives in the sorbent slurry and maintaining the operating pH at around 4.5 - 6.0 which has been found to be an optimum range (Karatepe, 2000). Other wet FGD technologies include a magnesium-based system, dual alkali process, sodium-based process, organic-based process, ammonia-based process, and seawater process. Each process differs with varying degree of SO_2 removal efficiency.

2.8. Semi-dry FGD process

2.8.1. Spray Dry Absorption (SDA)

Spray drying absorption process uses alkaline solution (mainly hydrated lime) as a sorbent. It is finely dispersed using spray nozzles or atomizer in a reaction chamber where it intimately comes in contact with flue gas containing SO_2 . The dispersed slurry is introduced at the top of the reaction chamber flowing downwards and reacting with flue gas to form $CaSO_3$ and $CaSO_4$ (Karatepe,

2000; Maryamchik, 2019). A dry product is collected at the bottom of the reaction vessel from flue gas before passing to the particulate collector. A particulate control device is used to collect unreacted sorbent particles and fly ash where part of it is recycled back into the slurry feed system and the rest is disposed of in landfills. This process requires significantly less water compared to the wet FGD system and has low capital and operating cost. However, it is a technology that is used for control of SO₂ in power utilities that burn low to medium-sulfur coal thereby limiting its application in high-sulfur coal utilities (Srivastava, 2000).

2.8.2. Circulating Fluidized Bed (CFB)

CFB technology uses a slurry composed of hydrated lime as a sorbent to mix with humidified flue gas. The slurry is injected into the bottom of the reaction chamber to flow co-currently with flue gas dispersing it through the chamber to a particulate collection device located downstream (Neathery, 1996). The flue gas is fed into the CFB through venturi nozzles at the bottom of the reactor causing turbulent flow. Water is sprayed as the flue gas moves up the reactor to increase its moisture content which accelerates chemical reactions (Moganelwa et al., 2018). It is recommended to use appropriate height of CFB to allow adequate residence time for the reactions to take place. Flue gas dries the sorbent as it interacts with it resulting in good SO₂ mass transfer conditions due to mixing of solids and gas (Srivastava and Jozewicz, 2001). Figure 2:5 shows a circulating fluidized bed system.

Particulate control (e.g., fabric filter plant) is a downstream process designed to be part of CFB SO₂ removal process which separates solids from flue gas. Solids are part of entrained sorbent which is composed of spent and unreacted sorbent. Particulate control allows further desulphurization to take place consequently providing approximately 10% additional removal efficiency (Moganelwa et al., 2018). The entrained solids are usually recycled into the reactor vessel as dry powder, leading to improved sorbent utilization (Neathery, 1996). Equations 2.7 and 2.8 represent the reaction between the sorbent and SO₂ contained in flue gas for a CFB desulphurization system (Neathery, 1996):



The optimum temperature for the above reaction is 70 – 90°C which can be achieved through quenching of the flue gas in the reactor. Pressurized water is provided through nozzles to ensure homogeneous distribution in the reactor. To avoid condensation of water, the process must be operated above the dew point (Moganelwa et al., 2018).

CFB technology is increasingly getting attention because it has lower capital costs similar to spray dry absorption with potentially high SO₃ removal and lower PM emissions. It also produces a dry waste by-product which does not require sludge handling equipment and related operational and maintenance requirements (Moretti et al., 2012). This process can achieve SO₂ removal efficiency of approximately 98% depending on the conditions of application.

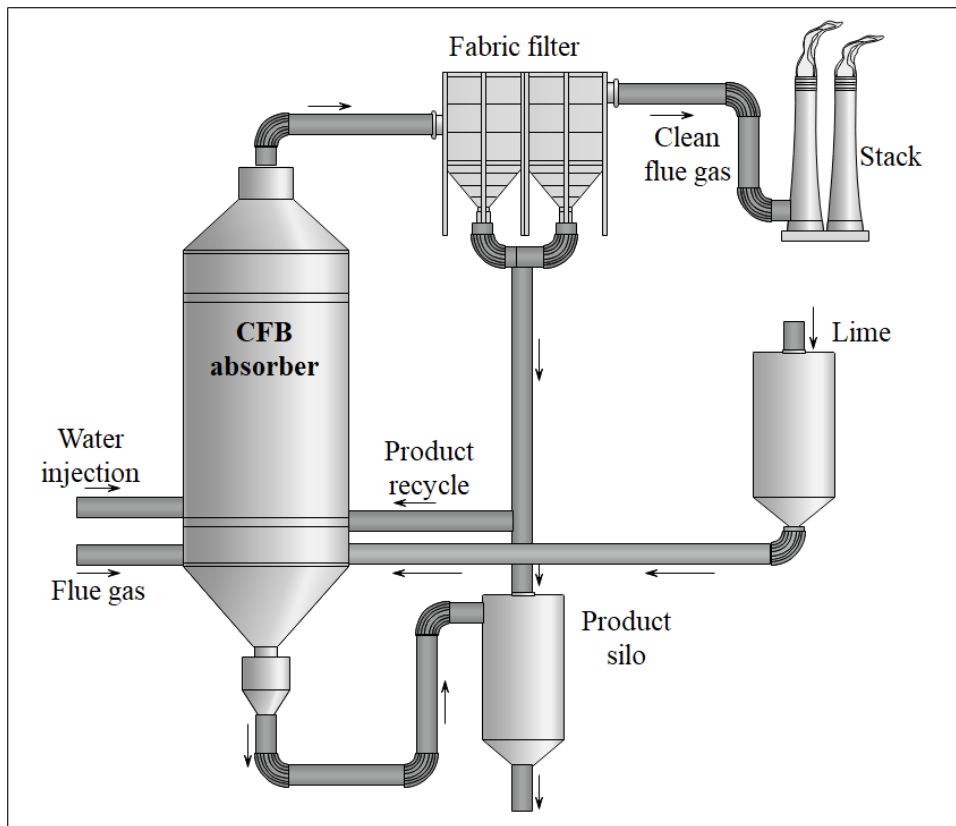


Figure 2:5: Circulating fluidized bed scrubbing system (adapted from Li et al., 2011)

2.9. Dry FGD Processes

Dry FGD technology has attracted a lot of attention over wet FGD technology for various reasons ranging from less waste handling due to dry product and smaller footprint requirement. It offers more economical advantage than wet FGD technology due to their lower capital cost and ease of

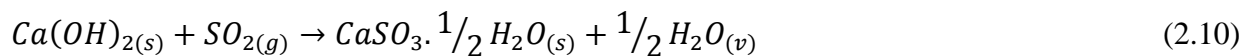
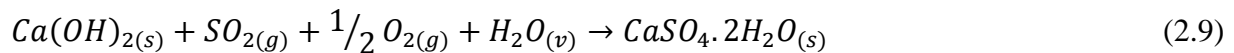
retrofitting to existing plants to meet emission regulations (Sanders et al., 1995). It has great application potential in areas where water shortage is severe. However, they are characterized by significantly lower SO₂ removal efficiency of about 50 to 60% for calcium-based sorbents (Ortiz and Ollero, 2008). It is typically used in smaller coal-fired power utilities that burn low to medium sulphur coal.

In dry FGD system, flue gas containing SO₂ is contacted with an alkaline sorbent either through injection or spraying the sorbent into a flue gas stream. SO₂ in flue gas will react with the sorbent resulting in a dry waste product which is easier to dispose of. A further classification of the dry FGD processes results in the following different sorbent injection processes (Srivastava and Jozewicz, 2001).

- Furnace sorbent injection
- Duct spray drying
- Duct sorbent injection
- Economizer sorbent injection

2.9.1. Duct sorbent injection

It is a post-combustion desulphurization process involving the use of humidified flue gas using water spraying and injection of a sorbent which is mostly hydrated lime into the ductwork downstream of the pre-heater (Garea et al., 2001). The injection section is located ahead of the particulate collection system (either electrostatic precipitator, bag filter or both). Flue gas is humidified to temperatures within limits of adiabatic saturation temperature using water (Keeth et al., 1991). The sorbent (ca [OH]₂) reacts with SO₂ in flue gas to form calcium sulphate and calcium sulphite as shown in equation (9) and (10):



Due to high flue gas temperature, the water droplets vaporize before entering the particulate control device. The particulate control device collects fly ash and unreacted sorbents where part of it is recycled and the rest is disposed of in landfills (Keeth et al., 1991). Due to short residence time in the duct, it requires a highly reactive sorbent to achieve the desired SO₂ removal.

This process is an attractive retrofit technology due to its smaller footprint, low capital cost and produces a dry product with no dewatering system required. The sorbent and humidification water are directly injected into the existing flue gas path, and thus no separate SO₂ absorption vessel necessary (Miller and Miller, 2010). This generally offers competitive advantage compared to the wet limestone process. This process, however, has its drawbacks as compared to the wet limestone process which include low SO₂ removal efficiencies (30 – 70%) for ca/S molar ratio of 2.0, high sorbent cost, and increased fly ash resistivity and dust loading potentially causing reduced SO₂ absorption efficiency (Miller and Miller, 2010).

2.9.2. Furnace sorbent injection

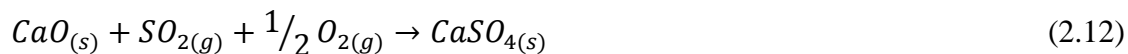
This technology uses dry pulverized sorbents (such as hydrated lime, limestone, or dolomite) which is directly injected into the furnace cavity of the boiler at a high temperature (800 – 1100°C) calcining it prior to reacting with SO₂ to produce CaSO₄ (Karatepe, 2000). The residence time for the reaction in the furnace is 1 – 2 seconds. Due to high furnace temperatures, the sorbents decompose instantly and become porous with high surface areas (Miller and Miller, 2010).

Based on limestone sorbent, the following reactions take place in the furnace:

- Rapid calcination of limestone to quicklime



- Diffusion of SO₂ to the surface of the particle and reaction with CaO to form calcium sulphate



Using hydrated lime as a sorbent, the following reactions occur in the furnace:



This process does not require a separate SO₂ absorption vessel due to direct injection to the flue gas path. This reduces the complexities associated with handling the reagent and thus lowers the operating and maintenance cost and eliminates problems such as plugging, scaling and corrosion associated with reagent slurry handling. Due to less equipment needed for this process, it has lower

power requirement. The dry product produced also eliminates the need for a comprehensive sludge dewatering system (Keeth et al., 1991; Miller and Miller, 2010).

Using Ca/S molar ratio of 2.0, this can achieve around 15-40% SO₂ removal using limestone as a sorbent and around 50-80% using hydrated lime. Hydrated lime is more effective than limestone, but it is expensive. Generally, this process has low SO₂ removal efficiency because of low sorbent utilization, and it thus requires high sorbent injection rates. It has high corrosion potential and solid deposition at the point of humidification. The increased particle loading, and ash resistivity can always reduce the efficiency of the electrostatic precipitator (ESP) used which might necessitate addition particle collection devices (Keeth et al., 1991; Miller and Miller, 2010).

2.9.3. Duct spray drying

Duct spray drying process uses lime slurry as a sorbent which is directly sprayed into the ductwork upstream of the particulate control device. The sorbent slurry is first dispersed using a rotary atomizer into the ductwork allowing maximum interaction with the flue gas. The ductwork is designed to provide sufficient residence time (1 - 2 seconds) allowing evaporation of the moisture in the slurry and subsequently reacting SO₂ (Carpenter, 2012). This technology is characterized by low capital cost and no process water is produced making it one of the attractive technologies for retrofitting existing power plants (Srivastava, 2000).

2.9.4. Economizer sorbent injection

Hydrated lime is normally used as a sorbent in this process where it is injected into the flue gas stream near the economizer inlet. Effective SO₂ removal is achieved at optimum temperature range of 500 – 570°C where the sorbent reacts with SO₂ to form CaSO₃. At this temperature range, part of the slurry (Ca[OH]₂) decomposes to form a reactive CaO which easily reacts with SO₂ forming CaSO₃ and CaSO₄ (Carpenter, 2012; Srivastava and Jozewicz, 2001). However, due to low economizer temperatures, only 10% of hydrated lime is converted to quicklime and the unconverted hydrated lime reacts with SO₂ to form calcium sulphite according to the equation below (Miller and Miller, 2010).



The efficiency of this process could be significantly improved by spraying additional water into the ductwork which hydrates any unreacted CaO.

2.10.FGD Technical Comparison

In the past, wet FGD technology has predominantly been used for SO₂ removal. It has lower operational costs and uses readily available sorbent which can be recycled into numerous products such as gypsum. Despite this, wet FGD has various disadvantages ranging from high capital cost, production of excessive waste, scaling in mist eliminators and its inability to capture SO₃ and mercury (Srivastava, 2000). It also has effluent discharge which requires comprehensive wastewater treatment, and this adds on the capital and operating costs. On the other hand, there has been increased interest in dry and semi-dry FGD technologies owing to their ability to remove mercury, acid gases, particles and SO₂ from flue gas at rates well above the legislative targets. They require minimum water usage and have low liquid discharge which is crucial to most power plants that are required to reduce their water consumption capacities.

Table 2.1 presents a key technical comparison between different FGD technologies that are commercially used i.e., spray dry absorption, circulating fluidized bed scrubber, sorbent injection processes, and the wet FGD (Carpenter, 2012; Karatepe, 2000; Koralegedara et al., 2019; Srivastava and Jozewicz, 2001). Spray dry absorption technology consumes relatively low amount of water (about 60% less) compared to the limestone wet FGD and requires less capital and operation costs than rival technologies (Carpenter, 2012). However, limestone wet FGD has slightly higher SO₂ removal efficiency, but it has high capital cost.

Table 2:1: FGD Key technical comparison (Carpenter, 2012; Karatepe, 2000; Koralegedara et al., 2019; Srivastava and Jozewicz, 2001)

Type of FGD	Sorbent	By-products	Max Sulphur content	fuel	Max SO ₂ removal efficiency	Capital Cost
Wet FGD						
• Limestone scrubbing	Limestone	Gypsum, sludge, wastewater	3.5%		95 – 99%	High
• Lime scrubbing	Lime	Gypsum, sludge, wastewater	3.5%		95 – 99%	High
• Seawater scrubbing	Seawater (NaCl) and limestone or lime	Waste treated seawater	3.5%		95 – 99%	High
Semi-dry FGD						
• Spray dry absorption	Lime or hydrated lime	Calcium sulphate, sulphite, fly ash	<2.5%	calcium	90 – 95%	Low
• Circulating fluidized bed (CFB)	Lime and recycled solids	Calcium sulphite	<3.5%		95 – 98%	Low
Dry FGD						
• Furnace injection	sorbent Hydrated limestone	lime, Calcium sulphate	N/A		40 – 80%	Low
• Duct injection	sorbent Hydrated lime	Calcium sulphate, sulphite	N/A	calcium	30 – 70%	Low
• Economizer injection	sorbent Hydrated lime	Calcium sulphite	N/A		N/A	Low

In comparison with the wet FGD process, spray dry absorption offers some advantages which include (Miller and Miller, 2010; Rogoff and Screve, 2011; Scala et al., 2004):

- Production of a dry waste byproduct that requires no sludge handling equipment and associated operating and maintenance requirements.
- Superior and simultaneous removal of acid gases, fine particles, and trace metals
- No scaling and corrosion problems enabling the use of cheaper materials for construction
- Mild steel can be used rather than expensive alloys due to high pH of slurry and dry solids.
- Smaller space needed and the possibility of easily retrofitting existing plants
- No reheating required due to unsaturated flue gas exiting the absorber. This reduces steam consumption and capital cost.
- Flexibility in operation with regard to varying boiler load
- Less overall energy consumption on account of low less pumping power needed.
- Reduced installation and operating costs.
- Extended equipment life
- No condensation plume since flue gas temperature is above the dew point

Some of the disadvantages of lime spray drying process include:

- To achieve greater SO₂ removal efficiencies, a higher reagent feed ratio than the conventional system (about 1.5 moles Ca[OH]₂ per SO₂) should be used.
- The reagent used as a sorbent (Ca[OH]₂) is expensive compared to limestone, this increases the operating cost.
- Potential clogging and erosion of spray nozzles during operation
- Calcium sulphite is a major product in the process where less than 25% is oxidized to calcium sulfate.
- To achieve required SO₂ removal in high-sulphur coal, a higher inlet flue gas temperature will be required resulting in reduced boiler efficiency.

2.11. Spray Drying Absorption FGD Technology

Spray drying absorption process is based on a concept that has been refined over the years into an effective system. It is increasingly becoming an attractive alternative due to the ease of product handling and low capital investment (Scala et al., 2004). The process consists of four operations: sorbent preparation, the spray chamber, particulate collection, and product handling (Heebink et al., 2007). This scrubbing process utilizes either limestone (pre-calcined CaO), lime slurry (hydrated lime) or sodium carbonate prepared in a slurry tank where it is continuously mixed to prevent sedimentation or agglomeration (Yang and Kim, 2000). Lime slurry ($\text{Ca}[\text{OH}]_2$) is the most commonly used sorbent because it is highly reactive towards SO_2 compared to limestone and it is cheaper than sodium carbonate. The slurry is introduced at the top of the reaction chamber through the spray nozzles or atomizers which disperses it into hot flue gas in the chamber cooling it from around $150\text{ }^\circ\text{C}$ to as low as $17\text{ }^\circ\text{C}$ above the adiabatic water saturation temperature. The spray nozzles atomize the slurry to form fine mist of droplets containing the $\text{Ca}[\text{OH}]_2$, which reacts with SO_2 contained in flue gas as it flows downwards through the chamber. The gas residence time in the scrubber is 12 to 17 seconds which is sufficient time to allow SO_2 and other gases to react with the sorbent and for water evaporation (Carpenter, 2012). The dispersal of the slurry allows maximum interaction between flue gas and the slurry resulting in a dry product mainly consisting of CaSO_3 and small amounts of CaSO_4 (Carpenter, 2012; Wang et al., 2019).

Part of the dry product is collected at the bottom of the reaction chamber with the remaining solids collected in particulate control device (i.e., ESP or fabric filter/baghouse) as flue gas passes through. To improve sorbent utilization, part of the collected dried product is normally recycled back into the slurry vessel. The particulate control device is an integral part of the FGD system where particles continue to react with SO_2 in the gas and where removal of SO_3 takes place. To ensure effective system performance, critical variables should be closely monitored. Figure 2:6 shows a schematic diagram for a spray dry absorber FGD process using hydrated lime as a sorbent.

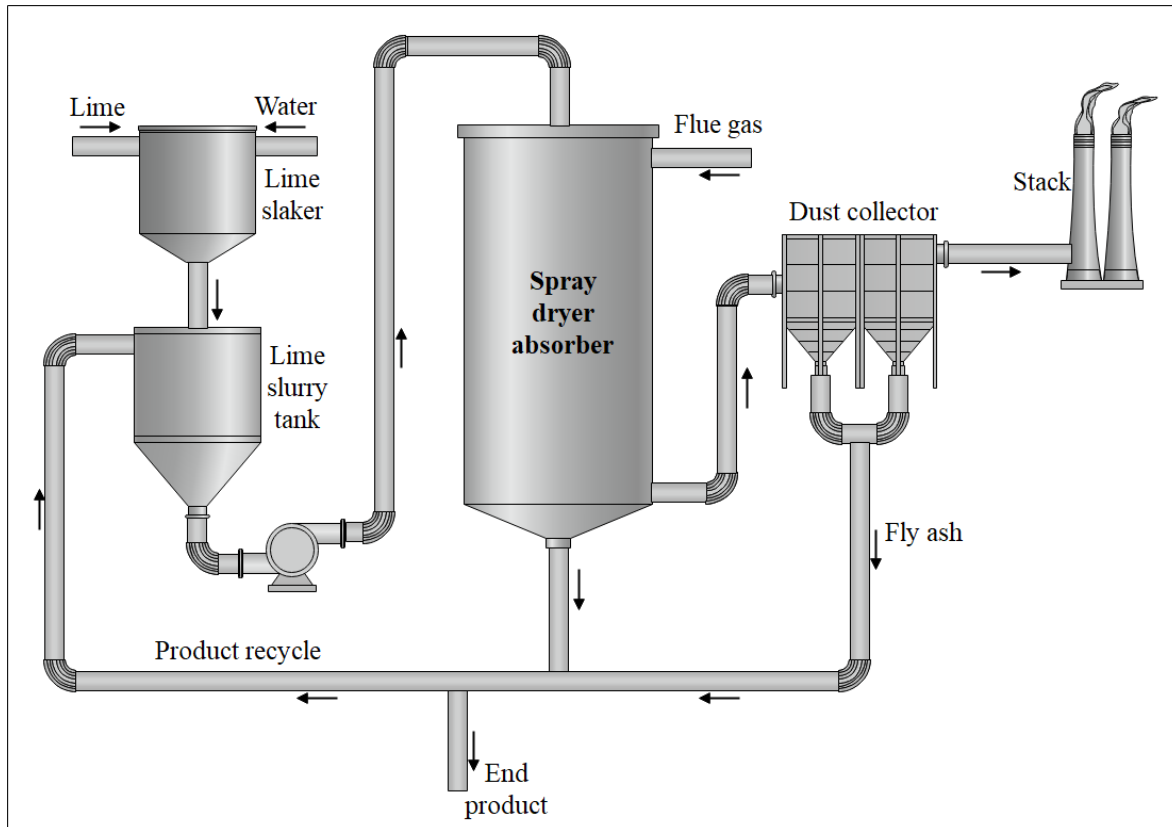


Figure 2:6: Lime Spray drying FGD process (adapted from Feng et al., 2014)

2.12. Sorbents for Spray Drying Absorber FGD

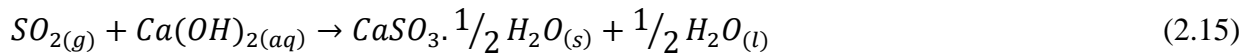
Sorbents play a significant role in the performance and removal of SO_2 in a spray dry absorber process. The choice of the sorbent used varies depending on the SO_2 removal and design requirement of the spray dryer. This requires a critical assessment of both capital and operating cost of the plant. Besides, the performance of sorbents depends on numerous variables such as temperature, particle size, sorbent dispersion, morphology, residence time and reactivity (Carpenter, 2012). Sorbent quality largely influences the performance of the process, operating cost, and the quality of the final product. There is a wide range of materials that can be readily used as sorbents but SO_2 is acidic in nature, and this forms a basis for its removal by use of appropriate alkali sorbent. Potential sorbents used in spray dry absorbers are either calcium or sodium-based sorbents

2.12.1. Calcium-based sorbents

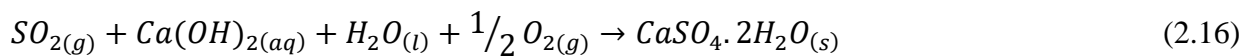
Calcium based sorbents are the most commonly used in spray dry FGD processes mainly due to their availability and reactivity towards SO₂ (Srivastava and Jozewicz, 2001). In a spray dry absorber FGD process, the sorbent comes into contact with a stream of heated flue gas which reacts with SO₂ to form a dry sulphate or sulphite product collected at the bottom of the spray dryer. Limestone which a raw material used for the preparation of hydrated lime is naturally occurring and is easily found throughout the world. It is mainly composed of calcium carbonate (CaCO₃) which varies depending on the source. Lime is produced by calcination of limestone which releases CO₂ to leave CaO which is then hydrated to obtain hydrated lime (Ca[OH]₂) (N. Karatepe et al., 1998).

Modern spray drying systems mostly utilize hydrated or slaked lime (calcium hydroxide) which is more reactive than limestone and is cheaper than sodium-based sorbents (Carpenter, 2012). Hydrated lime is normally introduced into the absorber as a slurry from the top of the spray chamber through rotary atomizers. The slurry is obtained by mixing lime with excess water and keeping close control of the amount of fresh lime to maintain the required level of alkalinity necessary to achieve the desired level of SO₂ removal. This occurs in a reaction vessel at atmospheric pressure.

The reaction between hydrated lime and SO₂ follows the general equation below:

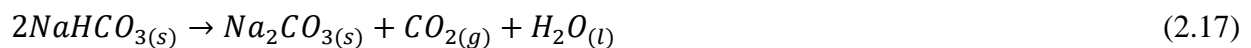


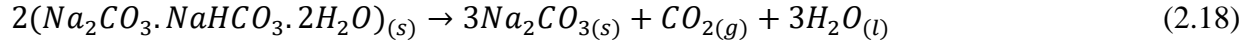
A smaller portion of SO₂ may react with O₂ in flue gas and Ca[OH]₂ to form Calcium Sulphate Dihydrate [28]



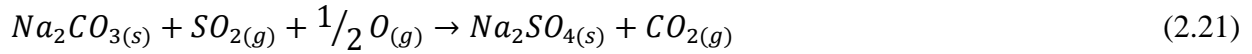
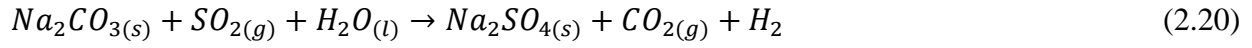
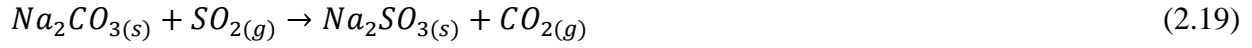
2.12.2. Sodium-based sorbents

(Vernon and Jones, 1993) Sodium bicarbonate and trona decompose thermally when introduced into flue gas at temperatures above 125°C (Carpenter, 2012).





Sodium carbonate then reacts with SO₂ as follows:



To improve the performance and reactivity of the sorbents used in spray dry absorbers, materials such as fly ash, can be mixed with sorbents containing calcium to form hydrated calcium silicates and aluminates (Wang and Keener, 1996). Similarly, the use of deliquescent salts additives in a spray dryer has a considerable effect on SO₂ removal efficiency due to their moisture retention capacity on the surface of the Ca[OH]₂ slurry droplets consequently enhancing SO₂ liquid phase reaction (Wey et al., 2003).

2.13. Operating parameters for spray drying absorption FGD

The performance of lime spray drying technology is greatly sensitive to several factors which affect its operation and maintenance. Numerous studies have been conducted focused primarily on the operating variables which directly affect SO₂ removal in a spray dryer (Klingspor, 1987; Izquierdo et al., 2000; Stein et al., 2002; Song and Park, 2001; Yang and Kim, 2000). Both evaporation and SO₂ absorption have been found to significantly affect the desulphurization efficiency of a spray dryer. These are mainly controlled by the spray dryer operating variables which should be maintained at their optimum conditions to achieve desired absorber performance. These variables include approach to saturation temperature, humidification, slurry concentration, droplet size, particle size among others (Karatepe et al., 1998).

2.13.1. Humidification

Humidity plays a significant role in the reaction between SO₂ and calcium hydroxide in a lime spray dryer. Numerous studies have pointed that the presence of water vapour (humidity) has a strong influence on the conversion of SO₂ in a lime spray dryer. Klingspor et al., (1984) conducted a study on similarity between lime and limestone and found out that no reaction occurs at low relative humidity below 20% even though SO₂ and water can be adsorbed into the droplet solid surface. With increased relative humidity, water is preferentially adsorbed onto the solid surface and consequently, less SO₂ is adsorbed due to intermolecular forces. This leads to the absorption of SO₂ into the adsorbed water and thus forming complexes where sulfur atom is bound to oxygen atom of water. Their studies concluded that at relative humidity below 70%, the reaction rate is independent on SO₂ concentration, and it gradually becomes more dependent above this value.

In a similar study by Ruiz-Alsop and Rochelle (1986), it was shown that the chemical reaction at the droplet surface is rate controlling at high relative humidity and SO₂ concentrations. On the other hand, diffusion through the product layer is rate controlling at low values of relative humidity and SO₂ concentrations. This was in agreement with a study by Izquierdo et al., (2000) who performed experiments to determine kinetic of reaction between SO₂ and Ca[OH]₂ and found out that at constant temperature, there was a corresponding increase in the reaction rate with an increase in the relative humidity. Their study indicated that the presence of water vapour in solids favours the reaction between SO₂ and Ca[OH]₂ which can be enhanced by use of organic additives which modifies the moisture content of the solids.

Generally, the presence of water in flue gas plays a critical role in the removal of SO₂ in a spray dryer owing to increased reactivity of the sorbent towards SO₂. Experimental results obtained by Liu et al., (2002) indicated that there was an exponential increase on SO₂ removal when the relative humidity is increased to values above 40%. Ruiz-Alzop and Rochelle (1986) also found an overall increase in SO₂ removal with increase in the relative humidity. A sharp decrease was observed at the reaction rate at low relative humidity but rather slower at higher relative humidity. Zhang et al., (2006) performed experiments using a modified sorbent and found an increase in the removal of SO₂ with corresponding increase in the relative humidity in the range of 0-20%. This was however found to decline when the relative humidity was increased beyond 20% due surface-catalyzed reaction. This is shown in Figure 2:7 below.

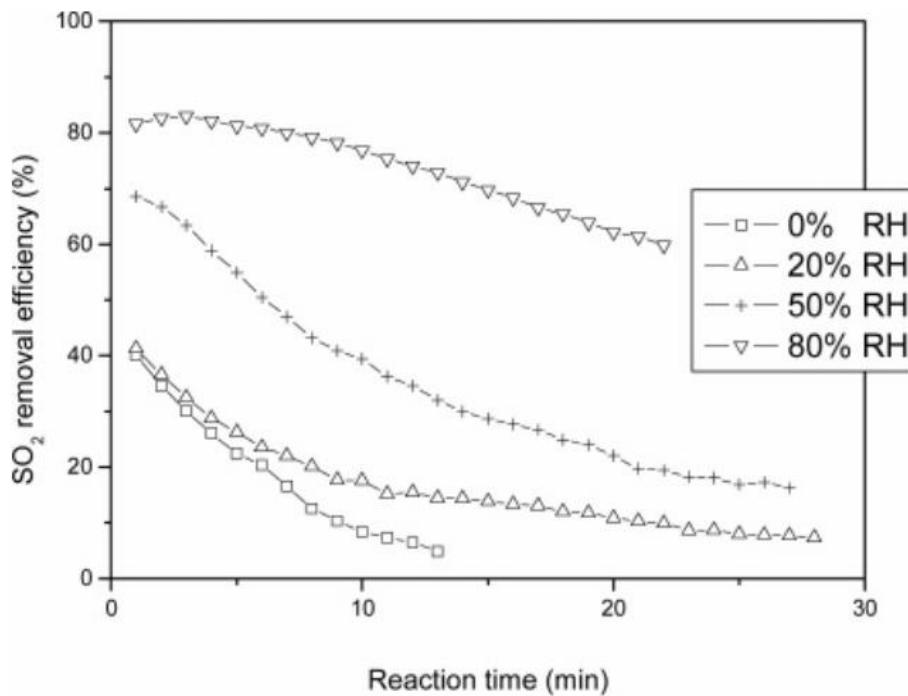


Figure 2:7: Effect relative humidity on SO₂ removal efficiency (adapted from Zhang et al., 2006)

2.13.2. Approach to saturation temperature (AST)

To maximize the removal of SO₂ from flue gas, a close approach to saturation temperature should be maintained. An optimum approach to saturation temperature of between 10°C to 15°C has been found to be effective (Srivastava, 2000). This can be controlled by varying the amount of water content in the feed slurry which can either lower the flue gas temperature to safe margin above the

saturation temperature when more water is added or increase the approach to saturation temperature when less water is used. Spray dry scrappers are designed efficiently to allow as much water as possible to enter the spray and allow close approach of the exit flue gas temperature to the flue gas saturation temperature. This close approach to the saturation temperature reduces the driving force for evaporation which increases evaporation time and enhances liquid gas interaction. Higher inlet temperatures (at high approach to saturation temperature) significantly lower the removal of SO₂ due to increased driving force for evaporation. The rapid evaporation caused by this effect reduces the much-needed contact time between the slurry droplet and the flue gas (Yang and Kim, 2000). The increase in SO₂ removal at lower approach to saturation temperature values is attributed to slower evaporation rate which increases the interaction between the droplet slurry and SO₂ (Scala et al., 2005). This was also observed by Newton et al., (1990) whose results indicated decreased calcium utilization with increase in approach to saturation temperature. This was attributed to an increase in both the quantity of spray and the lifetime of the droplet as the approach to saturation temperature decreases. Experiments conducted by Wang and Keener (1996) also found a dramatic increase in the removal of SO₂ with decreasing approach to saturation temperature. Xu et al., (2000) using a powder-particle spouted bed spray dryer showed that SO₂ removal from the spray dryer decreased with increasing approach to saturation temperature. It was however observed that lower approach to saturation temperature values have little effect on the SO₂ removal. A typical relationship between approach to saturation temperature and SO₂ removal efficiency is shown in Figure 2:8.

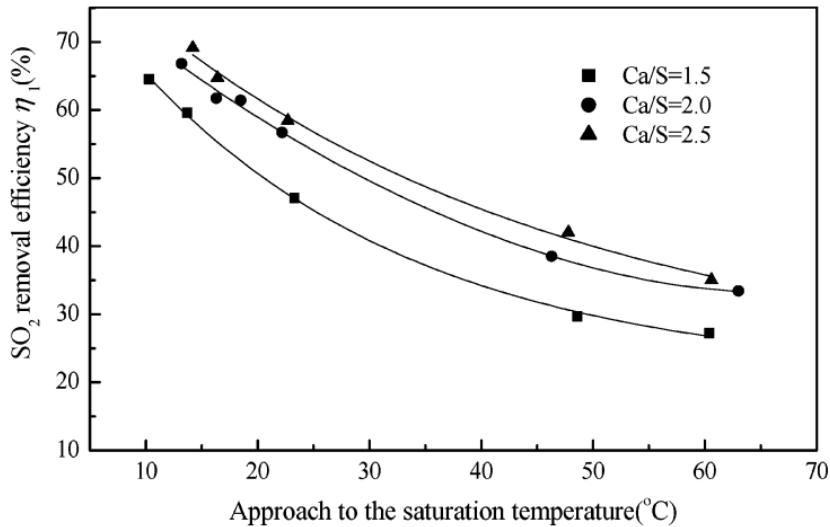


Figure 2:8: Effect of approach to saturation temperature on SO₂ removal (Zhou et al., 2005)

2.13.3. Droplet size

The size of the droplet in a spray dryer influences SO₂ removal capacity by altering the lifetime of the droplet. Increased droplet size effectively leads to an increase in the droplet lifetime but reduces the external mass transfer rate. The droplet size in a spray dryer can be controlled by varying slurry and atomizing air feed rates as indicated by Scala et al., (2005). It was described that lower atomization air flow rates lead to larger droplet sizes, and this was evident in their experiments which showed enhanced spray dryer performance at low atomization air flow rates. This phenomenon corroborates the findings of Newton et al., (1990) and Roop and Pflug Jr (1984) whose studies concluded that droplet sizes below 10-20 μm lead to poor calcium utilization and in turn lower the overall efficiency of the spray dryer. They explained that increasing droplet size results in corresponding increase in the droplet lifetime as well as decrease in the external mass transfer.

Smaller droplet sizes in a spray dryer heightens drying which corresponds to falling relative humidity and eventually lowers SO₂ absorption efficiency. This was investigated by Oh et al., (1999) who found a significant drop in the relative humidity with decreasing droplet diameter. It was also concluded that with sufficient retained moisture content, a higher conversion can be achieved with smaller droplets. Larger droplets can retain moisture longer and this can enhance the reaction of the slurry with SO₂. However, larger droplets do not have high conversion and may leave the spray dryer with unreacted parts of the droplet. The experiments conducted by Oh et al.,

(1999) showed improved SO₂ removal efficiency with increased droplet sizes. This was attributed to increased time of water retention in the droplet raising the overall SO₂ removal in the droplet suggesting a direct effect of the droplet size on SO₂ removal.

On the other hand, smaller droplet sizes can also lead to increased absorption reaction of SO₂ into the droplet due increased surface area of the droplets for both external mass transfer of SO₂ and evaporation (Newton et al., 1990). However, increased rate of evaporation reduces the droplet's lifetime and eventually impacts negatively on the absorption of SO₂. A study by Oh et al., (1999) concluded from their experiments that higher conversion is achieved with smaller droplets, but they quickly dry up. Larger droplets were found to enhance conversion by reaction with SO₂ due to higher moisture retention capacity or prolonged wet absorption stage. Their general observation was decreased SO₂ removal with decreasing droplet diameter but there was incomplete conversion in larger droplets.

2.13.4. Flue gas SO₂ concentration

High concentrations of SO₂ in flue gas has been found to have a significant influence on the reaction rate of Ca[OH]₂ and SO₂. Increased SO₂ concentration at constant operating conditions in a spray dryer decreases SO₂ removal efficiency due to rapid depletion of liquid phase alkalinity. Experiments performed by Izquierdo et al., (2000) indicated that the reaction rate is not dependent on the partial pressure of SO₂ for concentration less than 3000 ppm. A similar observation was noted by Ruiz-Alsop and Rochelle (1986) who found out that SO₂ concentration ranging from 0 to 4000 ppm does not significantly influence the reaction rate as well as temperatures ranging from 30°C to 90°C and 17-90% relative humidity.

Liu et al., (2002) investigated the effect of SO₂ concentration on the reaction rate of SO₂ and Ca[OH]₂ by maintaining relative humidity at 75±5%. This led to an increase in the removal efficiency of SO₂ with increasing SO₂ concentration at the inlet. To further illustrate their findings, they performed SO₂ mass balance around the spray dryer and found increased amount of Sulphur retained in the spray dryer ash as SO₂ concentration is increased. Their results matched with what was observed by Klingspor et al., (1984) and Ruiz-Alsop and Rochelle (1986) on the maintaining the relative humidity above 70%.

Using a spray-dry scrubbing pilot plant, Karlsson and Klingspor (1987) found no significant effect of the SO₂ concentration levels on the removal of SO₂. By varying SO₂ inlet concentration from

500 to 1000 ppm in their experiments, their results revealed that there was a drop in SO₂ removal efficiency. There was no significant drop in SO₂ removal efficiency with further increase in inlet SO₂ concentration which was directly attributed to the changing drying conditions.

2.13.5. Sorbent stoichiometry and sorbent utilization

Stoichiometric ratio for spray drying system is defined as the ratio of mols of the absorbent to the mols of SO₂ inlet to the scrubber. To enhance the removal of SO₂ in a spray dryer, a high stoichiometric ratio must be utilized through the use of a highly soluble and sufficiently reactive sorbent. However, this is an uneconomical operation because large amount of the sorbent is needed and this makes the spray drying process economically viable only for plant burning low to medium Sulphur containing coal (Scala et al., 2005). Stoichiometric ratio is a direct indication of the concentration of lime in the slurry which in turn affects moisture evaporation rate in the droplet.

Experiments conducted by Scala et al., (2005) showed that there was increased SO₂ removal in the spray dryer with increased calcium to Sulphur ratio. This was attributed to increased concentration of the active component (Ca[OH]₂) in the slurry which lessens the liquid mass transfer resistance in the droplet. Ma et al., (2000) also investigated the effect of calcium to Sulphur ratio on SO₂ removal and their findings presented a similar trend where there was increased SO₂ removal with matching increase in calcium to Sulphur ratio. From their findings, there was consistent increase in SO₂ removal efficiency for calcium to Sulphur ratio ranging from 1.0 to 2.0 and no further enhancement of the SO₂ removal was achieved beyond that range.

A study by Newton et al., (1990) found out that increased stoichiometric ratio increases the slurry concentration at the initial stages of the droplet's life due to increased concentration of sorbent particles at the droplet surface. This eventually results in decreased liquid phase mass transfer resistance. Their experiments found minimal effects of the stoichiometric ratio over the rest of the droplet's life which is limited by either liquid-phase mass transfer of the sulphur species through the layer of calcium sulphite or external mass transfer.

To maintain a high stoichiometry, sufficient amount of the sorbent must be utilized. And due to the nature of lime droplets during the reaction system, the outer regions become covered by the reaction products while the central regions remain unreacted. This will necessitate employing a recycle stream of ground dried product into the feed slurry to expose the unreacted core which

effectively improves sorbent utilization in the spray dryer. The relationship between sorbent stoichiometry and the removal efficiency of SO₂ is shown in Figure 2:9.

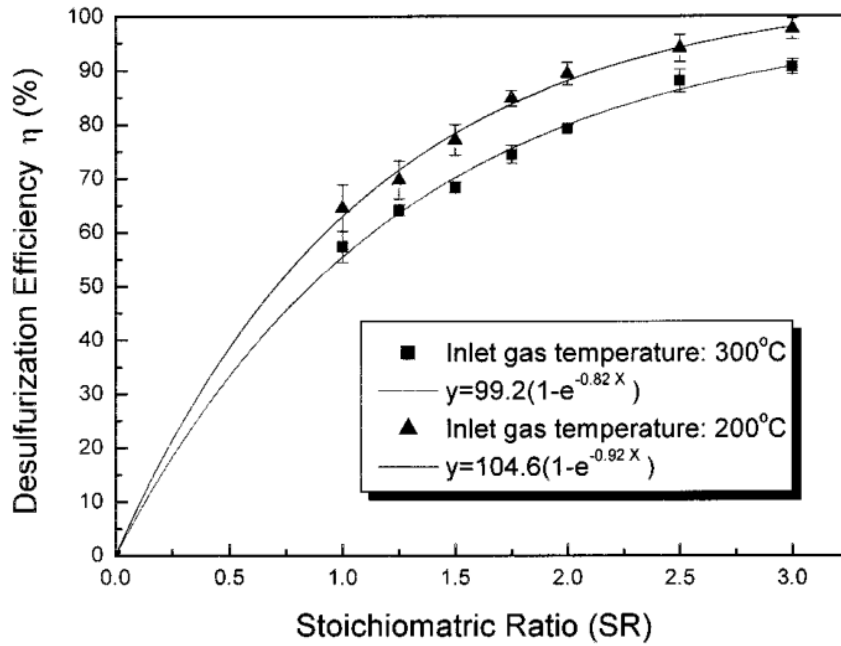


Figure 2:9: Effect of different stoichiometric ratios on desulphurization efficiency (adapted from Yang and Kim, 2000)

2.14. Proposal for improvement

The performance of a lime spray dryer can be improved in numerous ways ranging from addition of deliquescent salts to the feed slurry, recycling part of the dried product and the use of siliceous materials. Organic salt additives such as NaOH, CaCl₂, NaCl etc. could be added into the feed slurry to improve SO₂ absorption through prolonged retention of water moisture content in the droplet. This increases the liquid phase reaction for SO₂ removal (Wang and Keener, 1996). Additive siliceous materials involve the use of materials such as fly ash which mostly contains SiO₂ Fe₂O₃, CaO and Al₂O₃ compounds (Ho and Shih, 1992). They react with lime slurry forming calcium silicate complex compounds which are highly reactive towards SO₂ and eventually enhancing the utilization of Ca[OH]₂. Dried product from the spray dryer containing partially unreacted Ca[OH]₂ can also be utilized by grinding and recycling into the feed slurry to further react with SO₂. Recycling increases the concentration of lime in the slurry and ultimately improving lime utilization and SO₂ removal efficiency as well (Garea et al., 1997).

2.14.1. Use of organic salts

The use of organic salts as additives in lime spray drying improves SO₂ removal capacity by limiting evaporation of water moisture in the droplet. Prolonged retention of water moisture in the droplet enhances the reaction between SO₂ and unreacted Ca[OH]₂ in the droplet. Generally, the possible reasons for improved SO₂ removal upon using organic salts as additives include (Wang and Keener, 1996; Yoon et al., 1986):

- Additives are hygroscopic, retaining moisture content on the sorbent surface
- Additives enhance basicity of the sorbent
- Additives alter the lime particles physical properties i.e., specific surface area
- Additives increase the solubility of the lime (Ca[OH]₂) in the slurry.

A study by Wey et al., (2003) found significant increase in SO₂ removal efficiency from 72 to 86% from the use of NaHCO₃ as an additive. Apart from its ability to limit evaporation, it was explained that NaHCO₃ modifies the moisture content of the slurry at specific humidity and acts as co-sorbent due to its alkalinity. Research conducted by (Wang and Keener, 1996) focused on NaHCO₃, NaCl, CaCl₂ and NaOH as additives in a lime spray dryer and observed improved SO₂ capture. A significant improvement was observed with the use NaOH at lower approach to saturation

temperatures (less than 16.7°C). There was relatively lower SO₂ removal improvement on the use of CaCl₂ due to its lower affinity to water when combined with Ca[OH]₂. A general trend of improved SO₂ capture with increased additive concentration was observed with high reaction rate at the beginning (lower concentration of the additive). High concentrations of the additive in the slurry resulted in low reaction rate which was attributed to either gas phase resistance or lime particle dissolution rate resistance. The effect of different additives on SO₂ removal efficiency is depicted in Figure 2:10

Liu (2005) employed the use of CaCl₂ and observed an improved SO₂ removal efficiency with increased concentrations of the additive due to its hygroscopic property which retains moisture content on the droplet surface. The use of CaCl₂ was also observed to positively alter the specific surface area of the sorbent through increased cohesivity of lime particles resulting in droplet coagulation and consequently forming coarse particles with enhanced specific surface area compared to original Ca[OH]₂ particles.

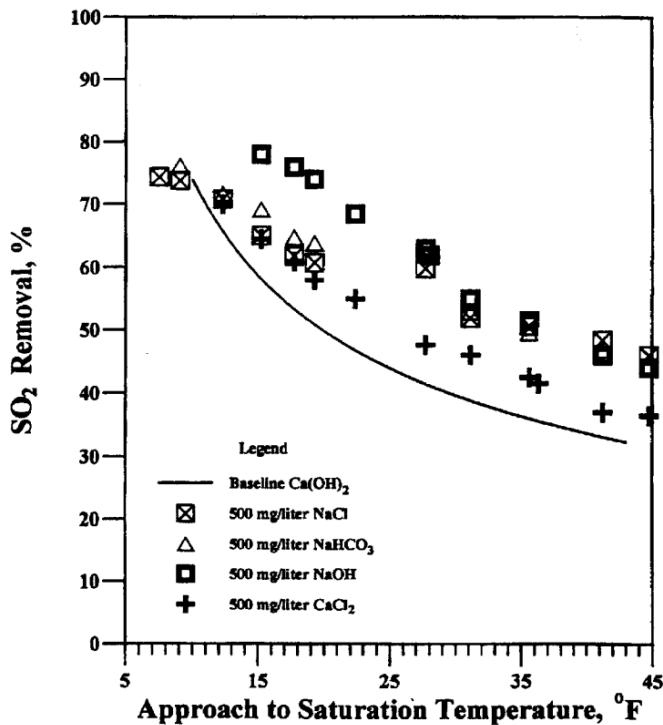


Figure 2:10: Effect of different additives on SO₂ removal efficiency (Wang and Keener, 1996)

2.14.2. Recycling of dried product

Electric power utilities utilizing low to medium sulfur coal could improve their sorbent utilization by recycling part of the dried product from the spray dryer. This is part of design and operations improvement on commercial spray dryers. Due to instantaneous reaction between SO_2 and the droplet, a reaction product precipitates on the droplet surface thereby limiting further reaction between $\text{Ca}[\text{OH}]_2$ and SO_2 stemming from increased diffusion resistance through the ash layer (Klingspor, 1987). The unreacted core of the dry product containing $\text{Ca}[\text{OH}]_2$ can be exposed through grinding for further reaction.

Recycling of spent or used sorbent increases its utilization through exposure of partially reacted sorbents for further reaction with SO_2 in flue gas. Klingspor (1987) investigated the effect of grinding and recycling part of dry product focused particularly on the performance of a pilot plant spray dryer. The results presented showed significant positive effect on the stoichiometric ratio and subsequent improvement in sorbent utilization and SO_2 capture. The increase in sorbent utilization increases sorbent reactivity towards SO_2 due to reduced dissolution rate resistance. This leads to a resistance shift to gas film control.

2.14.3. Utilizing siliceous materials

The performance of a lime spray dryer can be greatly enhanced through addition of siliceous materials on the sorbent. This is in effect more beneficial when utilized as part of the recycle stream with $\text{Ca}[\text{OH}]_2$ than when $\text{Ca}[\text{OH}]_2$ is used alone. Wey et al., (2003) conducted experiments using SiO_2 as an additive and observed an increase from 72.49 to 80.88% SO_2 removal efficiency. This was attributed to its pozzolanic properties which reacted with $\text{Ca}[\text{OH}]_2$ to form hydrated calcium silicates in the presence of moisture. The complex compound formed was found to exhibit higher specific surface area compared to pure $\text{Ca}[\text{OH}]_2$ and it eventually exposes more Ca ions for reaction with SO_2 .

In a similar study, Ho and Shih (1992) investigated the application of fly ash as a sorbent additive and observed increased sorbent utilization but no improvement on SO_2 removal efficiency. An improvement on both sorbent utilization and SO_2 removal efficiency was only observed after addition of CaSO_3 and/or CaSO_4 along with fly ash to the lime slurry. This was mainly attributed

to increased presence of calcium containing compounds from pozzolanic reaction which are more reactive towards SO_2 than pure $\text{Ca}[\text{OH}]_2$. With a focus of the effect of fly ash on the specific surface area, Nakamura et al., (1991) studied the reactivity of fly ash and lime slurry to be used as a sorbent in a mini-pilot spray dryer. They reported an improvement of up to 30% on the removal of SO_2 over the use of $\text{Ca}[\text{OH}]_2$ alone. Lin et al., (2003) observed a significant increase in sorbent reactivity towards SO_2 when fly ash was added into $\text{Ca}[\text{OH}]_2$ slurry. This was as a result of increased specific surface area from around $10 \text{ m}^2/\text{g}$ of sorbent to a minimum of $30 \text{ m}^2/\text{g}$ of sorbent when fly ash was introduced as seen in Figure 2:11.

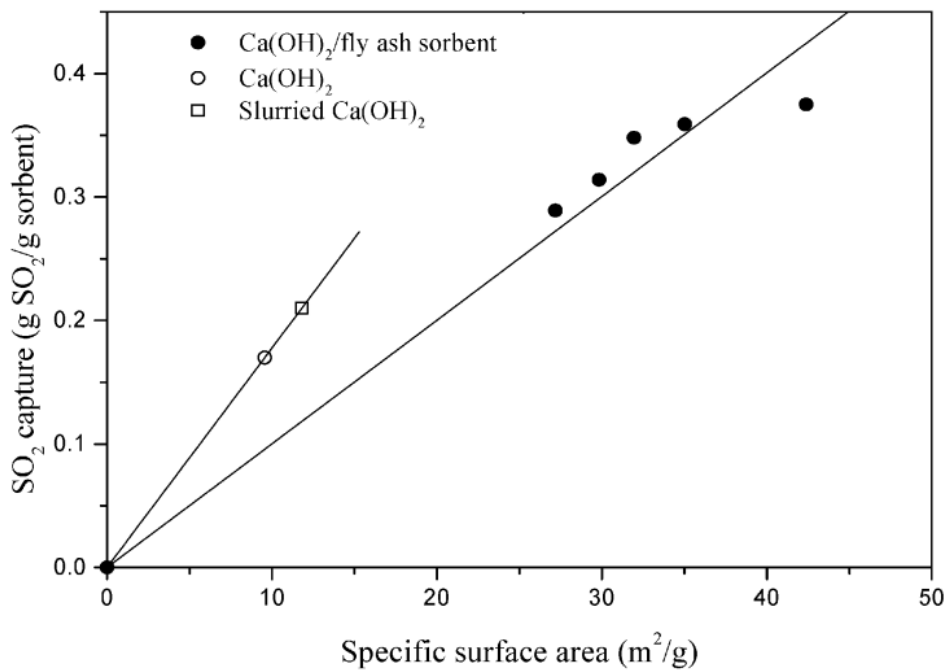
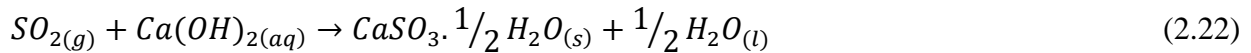


Figure 2:11: Effect of specific surface area on desulphurization efficiency using different sorbents (Lin et al., 2003)

2.15. Sulphation process in lime spray drying FGD

In a spray drying process, hot flue gas comes in contact with the slurry droplets leaving the atomizers. Due to high temperature in the chamber, water evaporates from the sprayed droplet as well as the droplet absorbs SO₂ in the spray chamber leading to complex heat and mass transfer occurring simultaneously (Scala et al., 2004). This consequently affects the desulphurization efficiency due to the two counter diffusion processes i.e., water evaporation and SO₂ absorption through the porous lime particle (Hill and Zank, 2000; Partridge et al., 1990). This reaction follows the overall reaction represented by equation (2.22) below to produce a dry product calcium sulphite.



A free-falling slurry droplet in a spray dryer consist of suspended lime particles which begin to dissolve immediately thereby saturating the water in the droplet as SO₂ is absorbed on the droplet surface. The dissolved reactants in the droplets reacts instantaneously forming an insoluble precipitate (reaction product) on the reaction front. The surface of the droplet being the reaction front shall form a spherical outer shell with the core of the droplet consisting of unreacted Ca[OH]₂ (Hill and Zank, 2000). This follows spray drying sequence as depicted in Figure 2:12. The spray drying process has been identified to have two drying phases (Scala et al., 2004; Srivastava, 2000; Neathery, 1996; Erdöl-Aydin and Nasün-Saygili, 2007):

- **Constant rate drying period:** This is just after the atomizers where droplets decelerate to reach their terminal velocity and rapid evaporation begins, consequently concentrating lime particles inside the droplet. The droplets contain discrete particles which are in constant random motion with interspatial distances between them within the droplet. As evaporation continues, the droplet shrinks homogeneously in size and the distance between particles is reduced until particle surfaces touch (Getler et al., 1979). Simultaneously, SO₂ diffuses from the bulk gas region to the moisture layer on the surface of lime particles and reacts with dissolved lime. This forms a reaction product which precipitates on the surface of the droplet acting as a barrier thus limiting both water evaporation and SO₂ absorption. This drying phase has been suggested to be controlled by the gas phase mass transfer rate surrounding the droplet or by chemical reactions neutralizing SO₂ within the droplet (Dlouhy and Gauvin, 1960).

- **Falling rate drying:** The inner core of the reaction product (agglomerate) formed contains unreacted $\text{Ca}[\text{OH}]_2$ which is a result of evaporation of the moisture inside the particles dominating the process over SO_2 absorption. Water recedes into the porous agglomerate of the reaction product. Desulphurization in this phase takes place through diffusion of SO_2 through the dried reaction products of the lime and SO_2 , causing a gas-solid reaction with the unreacted core of lime particle. The particles continue to expand leading to increased resistance to diffusion which reduces chemical reaction and subsequently, the absorption of SO_2 is reduced when the particles achieve equilibrium moisture content. This forms a dry final product which collected at the bottom of the reaction chamber. The final moisture content in the droplet is a dependent on vapour pressures, SO_2 diffusion rate and the temperature difference between the droplet and the flue gas (Neathery, 1996; Getler et al., 1979).

Dantuluri (1988) indicated that the drying process is best described by the following steps which occur in both constant rate drying and falling rate drying periods:

1. Diffusion of the reactants in the flue gas into the liquid droplet
2. Chemical reaction on the liquid phase
3. Diffusion of the reactants and reaction products through the pores of the particle consisting of reacted and unreacted cores.

The figure below represents the drying sequence of the atomized droplet in the spray chamber.

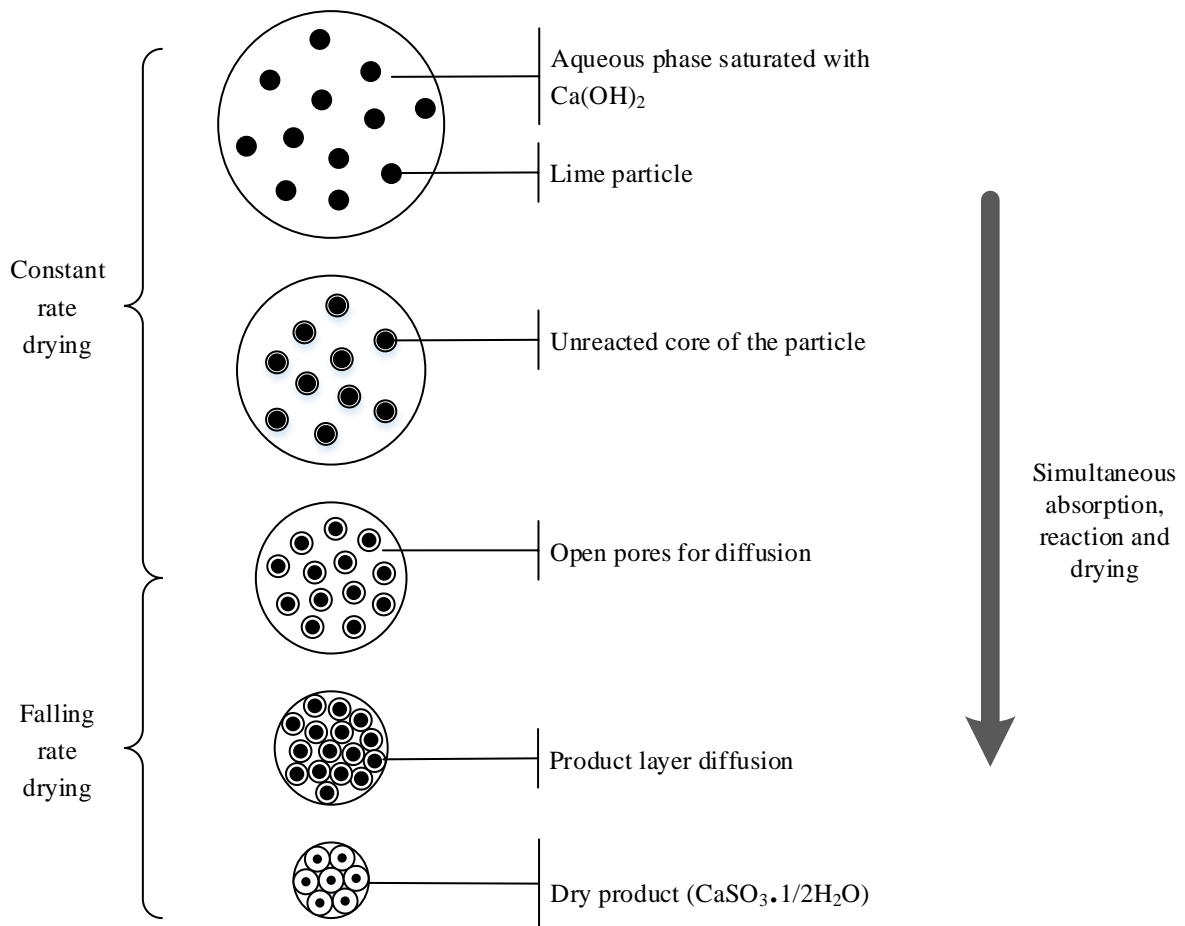


Figure 2:12: Droplet drying sequence in a lime spray dryer (adapted from Getler and Shelton, 1979).

2.16. Process Chemistry

During the reaction process, heat, and mass transfer between alkali in the finely dispersed lime slurry and SO₂ from the gas phase take place simultaneously resulting in a series of reactions and eventually drying of reacted products (Srivastava, 2000). The gas and the liquid phase mass transfer resistances strongly affect the removal efficiency of SO₂ in the spray drier because of the counter diffusion of SO₂ and evaporating moisture from the slurry droplets (Hill and Zank, 2000). Lime (CaO) is the primary source of alkaline solution used for SO₂ absorption in a spray dryer. It dissolves readily in water to form slaked lime (Ca[OH]₂). The absorption of SO₂ into Ca[OH]₂ slurry is regarded as an instantaneous reaction involving 3-phase gas absorption processes which include: diffusion of solute gas, dissolution of Ca[OH]₂ particles and chemical reaction (Partridge et al., 1990).

The overall equation for SO₂ absorption in a lime spray dryer represented in equation (2.14) can be subdivided into series of steps as shown below: (Hill and Zank, 2000; Scala et al., 2004; Erdöl-Aydin and Nasün-Saygili, 2007).

- a) Gas phase diffusion of SO₂ from the gas bulk to the droplet surface
- b) The absorption of SO₂ at the droplet surface



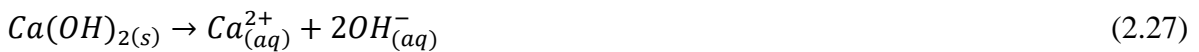
- c) Formation of sulphurous acid



- d) Dissociation of sulphurous acid into ionic sulphur species



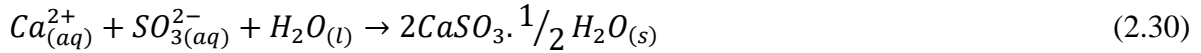
- e) Liquid phase diffusion of sulphur species inside the droplet (towards the droplet centre)
- f) Dissolution of Ca[OH]₂ at the outer shell of the unreacted core



- g) Liquid phase diffusion of alkaline species towards the droplet surface.
- h) Neutralization reaction between alkaline species and acid species at the reaction front



i) Reaction to form calcium sulphate-hemihydrate



The above ionic reactions strongly depend on the presence of water in the slurry droplet. They are considered instantaneous reactions in the presence of water and very slow in its absence. Other variables including the droplet size, surface area have been identified to affect the reactivity too (Erdöl-Aydin and Nasün-Saygili, 2007; Scala et al., 2004).

2.17. Absorption and reaction rate mechanisms in lime spray drying: Droplet phase.

Majority of the models developed for lime spray drying have combined both heat and mass transfer models with a focus on a single droplet for two phase flow of gas and liquid (slurry) in a spray dryer. This generally takes into consideration the resistance of both gas and liquid phases during the SO₂ absorption process. The liquid phase resistance involves mass transfer and chemical reaction encompassing both absorption reaction of SO₂ with Ca[OH]₂ and dissolution of Ca[OH]₂ (Partridge et al., 1990). For a single droplet in a lime spray dryer, the mass transfer and SO₂ absorption model is represented in Figure 2:13 which includes gas, liquid, and solid phases.

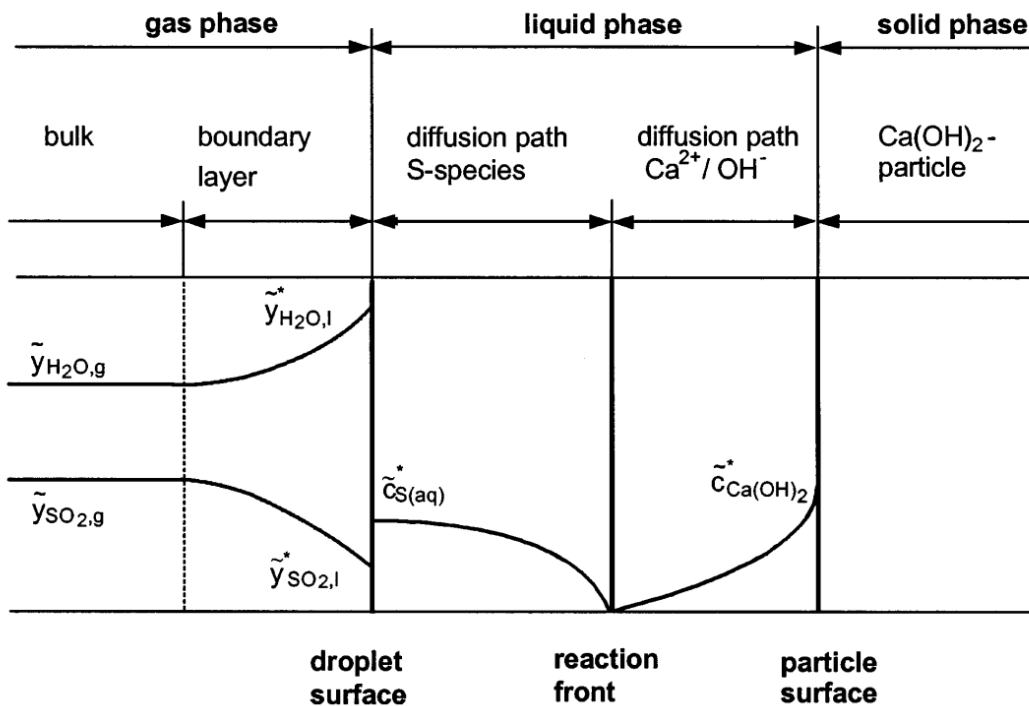


Figure 2:13: Mass transfer and reaction model for a single lime slurry droplet (adapted from Hill and Zank, 2000)

The desulphurization process in a lime spray dryer is a complex process consisting of series of sub-processes as shown in equations 2.23 to 2.30. The process consists of simultaneous heat and mass transfer involving several drying phases and reactions between gas and liquid. The ionic reactions are considered instantaneous with the rate controlling step being either gas diffusion or solid dissolution rate (Hill and Zank, 2000). In the liquid phase, there is a high SO₂ diffusion through the droplet surface which is accelerated by the relative droplet velocity. In this phase, rate of dissolution of solid phase (Ca[OH]₂) is considered the rate limiting step with the mass transfer rate dependent on solid properties (slurry solubility, particle size and shape) and liquid pH and composition. As the droplet dries up to form a solid particle with the reaction products on its surface, the resistance to diffusion through the reaction product layer shall then be considered rate controlling (Getler et al., 1979).

A study conducted by Babu et al., (1984) suggested that the reaction kinetics in the liquid phase is much faster than the diffusion rates of dissolved sulphur species and the sorbent. This is similar to

observation made by Ruhland et al., (1991) who also suggested that ionic reactions advance rapidly, resulting in SO₂ hydration being rate controlling in the process.

Earlier studies on desulphurization kinetics had varied observations on the controlling factors in lime spray drying process. A model developed by Jozewics and Rochelle (1984) indicated that the rate of SO₂ capture is controlled by external SO₂ mass transfer. This model ignored the dissolution rate of Ca[OH]₂ and its diffusivity effects which may affect the absorption of SO₂. A study by Karlsson and Klingspor (1987) also concluded that external SO₂ mass transfer is the rate controlling in the removal of SO₂ as well as the dissolution of the sorbent. It was observed that the diffusion of SO₂ from the gas bulk to the droplet surface was rate limiting step when excess lime is used. Subsequent studies have provided detailed accounts of the desulphurization process in lime spray drying. Damle and Sparks (1986) demonstrated that liquid phase mass transfer occurs faster by taking into consideration dissolution of lime, liquid-liquid reaction between the sorbent in the slurry droplet and dissolved SO₂, external SO₂ mass transfer and absorption of SO₂ on the droplet surface.

Newton et al., (1990) developed a model representing the reaction between SO₂ and the slurry droplet which considered internal liquid phase mass transfer of the film interface and bulk liquid region. Based on their model, they concluded that particles do not circulate inside the slurry droplet which causes accumulation of sorbent particles on the surface of the slurry droplet as evaporation continues. A similar account was observed by Harriott and Kinzey (1986) who gave a detailed description of the desulphurization process by illustrating that sorbent particles inside the droplet do not circulate and the reaction between dissolved SO₂ and calcium species occur at the reaction front which recedes inwards towards the centre of the particle as the reaction continues. This conclusion was in agreement with the findings of Constan and Calvert (1960) who showed that no internal circulation in a falling slurry droplet occurs for diameters less than 1 mm due insignificant droplet size and viscosity of lime suspension.

Hill and Zank (2000) studied the absorption of SO₂ in a spray dryer using lime and found that the absorption process is limited by the drying conditions. They found out that the presence of water during the reaction process had significant effect on the absorption rate of SO₂. Their experiments showed decreased absorption efficiency due to additional liquid phase mass transfer resistances and due to decreased stoichiometric ratios. Based on already available results, Scala et al., (2004)

developed a model for SO₂ absorption in a rigid droplet in a spray dryer which was used to predict the performance of the spray dryer under different operating conditions. It was established that the main controlling resistances to SO₂ absorption are the liquid phase at the column entry (near atomizer) and gas phase at the exit of the column. Both resistances i.e., liquid phase and the gas phase resistances were however found to be controlling over the constant rate drying phases.

The absorption of SO₂ in a lime spray dryer is regarded as instantaneous reaction where it mainly occurs in the constant rate period. Partridge et al., (1990) developed a model focused on the constant rate period based on the film theory and regards slurry droplets with discrete sorbent particles evenly scattered around the droplet. Their model indicated combined resistance flux (gas phase mass transfer, liquid phase mass transfer and sorbent dissolution) as the rate controlling at the initial stage before gas phase resistance becomes rate controlling. This was attributed to decreasing concentration of SO₂ with time as the reaction takes place. Their findings concluded that the absorption of SO₂ in a spray dryer is generally controlled by the gas phase resistance in a typical spray drying conditions. A study on the absorption kinetics of SO₂ onto lime slurry by Ruhland et al., (1990) considered two limiting factors in their reaction model: SO₂ absorption onto Ca[OH]₂ solution and absorption into a concentrated suspension of lime. When using a high solid content, the reaction was found to be controlled by absorption onto concentrated suspension of lime slurry at constant pH. The main resistance to mass transfer was found to be the absorption of SO₂ onto Ca[OH]₂ slurry.

While hydrated lime is considered to be one of the most attractive sorbent for SO₂ removal in spray drying processes due to its high specific surface area and abundant pores in its reactive form, some research studies have focused on the alternative sorbents such as limestone and trona. On the use of limestone as a sorbent, Brogren and Karlsson (1997) developed a model based on a penetration theory that calculated the rate of absorption of SO₂ into a limestone slurry droplet. The model developed quantified the mass transfer within the scrubber as well as evaluated the effect of reactions with finite SO₂ mass transfer. Their study concluded that the removal of SO₂ in the scrubber is largely controlled by the liquid phase mass transfer due to low limestone dissolution at the gas-liquid interface especially at low pH and during low internal circulation inside the droplet. In a similar study, Stromberg and Karlsson (1988) performed experiments by utilizing finely ground limestone in a spray dry scrubbing process and observed that the gas-solid reaction depends on the surface area, while the gas-liquid-solid reaction rate is dependent on the particle size.

Contrary to the case in lime-based scrubber process, their experiments indicated significant effect of removal of SO₂ in the fabric filter which could be improved further by increasing the bag filter area.

The use of trona as a sorbent in spray dryer for SO₂ removal was studied by Aydin and Saygili (2007) who developed a model incorporating mass and heat transfers which was in good agreement with the experimental data. It was found out that the absorption efficiency of SO₂ in the spray dryer was significantly decreased when operated under excess trona due to additional liquid phase mass transfer resistances for SO₂. In a similar study using trona and slaked lime for SO₂ removal in a spray dryer, Dogu et al., (1992) majorly focused on the effects of operating variables on the scrubbing efficiency of the spray dryer. Their findings indicated that a higher scrubbing efficiency was achieved using trona compared to slaked lime under low relative humidity (less than 5%) which is due high reactivity of trona towards SO₂. This was further enhanced by simultaneous decomposition of NaHCO₃ to Na₂CO₃ and sorption reaction at elevated temperatures beyond 110°C. It was also found out that higher conversion of the sorbent could be obtained when a bag filter is fitted to the spray dryer.

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3. Experimentation of SO₂ absorption using lime spray drying.

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3.1. Abstract

This paper presents the findings of an experimental investigation on the performance of a laboratory-scale spray dryer involving flue gas desulphurization (FGD). Using commercial hydrated lime as a sorbent, systematic set of experiments were performed to integrate drying, evaporation and SO₂ absorption capacity of the spray dryer. The experimentation involved accurate measurement of the process conditions within the spray dryer space such as temperature and SO₂ concentration along the spray chamber by varying the input and output variables. Tests were done to investigate the effects of spray characteristics i.e., inlet gas phase temperature (120 – 180 °C), approach to saturation temperature (5.6 – 14.6 °C), and calcium to sulphur ratio (1 - 2.5) on SO₂ removal efficiency. The performance of the spray dryer was further evaluated based on the degree of conversion of calcium (sorbent utilization) after SO₂ absorption. Results indicated remarkable improvement on SO₂ removal efficiency with increasing the stoichiometric ratio and decreasing the temperature. An absorption efficiency of SO₂ beyond 90% was achieved at a stoichiometric ratio of 2.5. A high degree of conversion of calcium was realized at low stoichiometric ratios with a maximum utilization of 94% obtained at a stoichiometric ratio of 1.5. The analysis of the final desulphurization product revealed the presence of sulphites with better conversion achieved at a stoichiometric molar ratio of 1.5. Significant amount of unreacted sorbent (63.43%) was observed at a stoichiometric ratio of 2, while samples collected at stoichiometric ratio of 1.5 had the lowest concentration of unreacted Ca[OH]₂ (41.23%).

Key words: spray drying, desulphurization, evaporation, sorbent utilization, conversion.

3.2. Introduction

FGD technology has proven to be one of the most efficient systems adopted worldwide for the removal of SO₂ from flue gas in coal power plants. It is a scrubbing system that utilizes an adsorbent medium to interact with flue gas containing sulphur dioxide in an absorber or a scrubber to form a high solid sulphur slurry (Córdoba, 2015). Traditionally, an alkali rich sorbent containing either calcium or magnesium reacts with sulphur forming a solid end-product which can easily be disposed. This makes lime (Ca[OH]₂) and limestone (CaCO₃) as the most widely used as sorbents in FGD processes due to their availability and calcium abundance. Among others, magnesium, seawater, sodium, and amine are used as sorbents for FGD.

Spray drying absorption process is a type semi-dry FGD system that consists of four main features: slurry preparation, the spray chamber, particulate collection, and product handling. This scrubbing process utilizes either limestone (pre-calcined CaO), lime slurry (hydrated lime) or sodium carbonate prepared in a slurry tank where it is continuously mixed to prevent sedimentation or agglomeration (Yang and Kim, 2000). Lime slurry (Ca[OH]₂) is the most commonly used sorbent because it is highly reactive towards SO₂ compared to limestone and it is cheaper than sodium carbonate. The slurry is introduced on top of the reaction chamber through the spray nozzles or atomizers which disperses it into hot flue gas in the chamber. The spray nozzle atomizes the slurry to form fine mists of droplets containing the Ca[OH]₂, which reacts with SO₂ contained in flue gas as it flows downwards through the chamber. The dispersal of the slurry allows maximum interaction between the flue gas and the slurry resulting in a dry product mainly consisting of CaSO₃ and small amounts of CaSO₄ (Wang et al., 2019; Carpenter, 2012).

Spray drying absorption process for FGD is a low-cost retrofit SO₂ control technology which could be used in already existing coal-fired power plants. It is increasingly becoming an attractive alternative due to the ease of product handling and smaller footprint requirement when compared to wet FGD system (Katolicky and Jicha, 2013; Shanshan et al., 2020; Scala et al., 2004). However, it has low sorbent utilization and low SO₂ removal efficiency when compared with wet FGD technology. SO₂ removal efficiency hardly exceeds 70% when a calcium to sulphur ratio of 1:2 is used and this has limited its application to low sulphur coal plants (Scala et al., 2004). To achieve the desired SO₂ removal efficiency, a high lime stoichiometric ratio is necessary leading low sorbent utilization. Low desulphurization efficiency is also attributed to the short time spent by the

sorbent slurry droplet when it is still moist (constant rate drying period). This is the period which accounts for most of SO₂ removal before the falling rate drying period where little or no SO₂ removal takes place (Neathery, 1996).

The study consists of sets of experiments conducted to integrate drying, evaporation and SO₂ absorption by varying inlet gas temperature (120 - 180 °C), approach to saturation temperature (5.6 - 14.6 °C), slurry solid content (6 - 12%), and calcium to sulphur molar ratio (1 - 2.5). The experimentation involved accurate measurement of the process conditions within the spray dryer to obtain both axial and radial profiles while controlling the input and output variables such as flowrates, inlet temperatures, sorbent utilization and efficiency (calculated).

3.3. SO₂ reactions in lime spray dryer

During the reaction process, the interaction between alkali in the finely dispersed lime slurry and SO₂ from the gas phase takes place simultaneously resulting in a series of reactions and eventually drying of reacted products. The absorption of SO₂ into Ca[OH]₂ slurry is regarded as an instantaneous reaction involving multiphase absorption processes which include diffusion of solute gas, dissolution of Ca[OH]₂ particles and chemical reaction (Partridge et al., 1990). The absorption of SO₂ in a lime spray dryer follows the reaction path described below (Erdöl-Aydin and Nasün-Saygili, 2007; Hill and Zank, 2000; Scala et al., 2004):

j) Gas-phase diffusion of SO₂ from the gas bulk to the droplet surface

k) The absorption of SO₂ at the droplet surface



l) Formation of sulphurous acid



m) Dissociation of sulphurous acid into ionic sulphur species



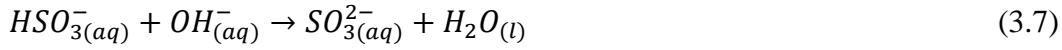
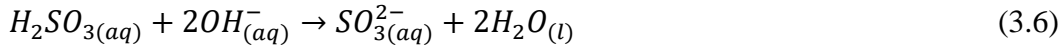
n) Liquid phase diffusion of sulphur species inside the droplet (towards the droplet centre)

o) Dissolution of Ca[OH]₂ at the outer shell of the unreacted core



p) Liquid phase diffusion of alkaline species towards the droplet surface.

q) Neutralization reaction between alkaline species and acid species at the reaction front



r) Reaction to form calcium sulphate-hemihydrate.



The above ionic reactions strongly depend on the presence of water in the slurry droplet. They are considered instantaneous reactions in the presence of water and very slow in its absence (Erdöl-Aydin and Nasün-Saygili, 2007; Scala et al., 2004).

3.4. Experimental

A systematic experimentation program was used to evaluate drying and SO₂ absorption behaviour of the spray dryer by varying the main operating variables in addition to controlling the input and output variables such as flowrates, temperatures concentrations and efficiency. The range of process conditions used for this study are presented in Table 3:1. All experiments in this study were conducted using a laboratory-scale Buchi B290 Mini Spray Dryer obtained from Buchi, Switzerland. A schematic of the experimental setup is shown in Figure 3:1 and it comprises of the following main systems:

3.4.1. Slurry preparation

Lime slurry was prepared using the commercial hydrated lime by mixing it externally with an appropriate proportion of water in a vessel. The contents in the vessel were stirred continuously using a magnetic stirrer to inhibit sedimentation and agglomeration. The slurry was then supplied continuously through a feeding line connected through a peristaltic pump fitted in the spray dryer to the fluid nozzle in the spray chamber. Compressed air was used to atomize (disperse) the slurry into fine droplets which are subsequently dried in the spray chamber. The chemical composition of the hydrated lime used is presented in Table 3:2.

3.4.2. Spray drying chamber.

The spray dryer consisted of a unit which controls the airflow rate, air temperature and the spray injection conditions of the simulated flue gas into the drying chamber. The spray chamber is 0.6m high and 0.16m in diameter made of borosilicate glass 3.3 providing gas mean residence time of 1.0 – 1.5 seconds. The spray dryer is also equipped with an electric heater to provide the desired temperature in the inlet gas. SO₂ gas is dosed into the inlet air stream at a controlled rate to simulate the conditions prevailing in a coal-fired power plant's flue gas. The temperature of the flue gas is monitored at the entry and exit point in the chamber. The flowrates of both SO₂ and the ambient air streams were regulated using appropriate flow meters to achieve the desired SO₂ concentration in the simulated flue gas.

The slurry is introduced into the spray chamber through a two-fluid nozzle which disperses the slurry producing droplets which then interacts with hot flue gas in co-current flow. The two-fluid nozzle comprises of a nozzle tip with nozzle cap of different diameters to allow variation of droplet sizes in the spray chamber. The stoichiometric ratio was controlled by varying the slurry feed rate and concentration of the feed slurry which also regulates the spray dryer outlet temperature and determines the approach to saturation temperature (AST). The flue gas temperature, relative humidity and SO₂ concentration were measured at various positions along the spray chamber height as shown in Figure 3:1 to obtain respective radial profiles.

3.4.3. Flue gas analysis

The simulated flue gas is obtained by mixing 99% SO₂ with inlet air by means of flow controllers to maintain the required flue gas volume flow and inlet SO₂ concentration. The concentration of SO₂ in the gas stream was analyzed using a Testo 340 combustion gas analyzer. The desulphurization efficiency was determined directly on the basis of concentrations of SO₂ at the inlet and outlet.

$$\eta = \frac{N_{SO_2,i} - N_{SO_2,o}}{N_{SO_2,i}}$$

Where $N_{SO_2,i}$ and $N_{SO_2,o}$ are the concentrations of SO₂ entering and leaving the spray chamber respectively.

3.4.4. Characterization

The Branauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume of the hydrated lime sorbent were determined from the N₂ adsorption-desorption isotherms at 77 K using Micromeritics ASAP™ 2020 Porosity Analyzer. Qualitative analysis of the sorbent was determined by x-ray diffraction (XRD) technique using Malvern Panalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K α radiation. The phases present were identified using X'Pert Highscore plus software. The functional groups present in the final desulphurization product were determined by Fourier Transform Infrared (FTIR) analysis using Perkin-Elmer Spectrum Two™ machine. Scanning Electron Microscopy (SEM) machine equipped with Energy Dispersive Spectroscopy (EDS) was used to determine the morphological structures of the samples and to detect chemical elemental composition on the surface of the final desulphurization product. The decomposition properties of various compounds in the final desulphurization products were assessed using SDT Q600 TGA analyzer.

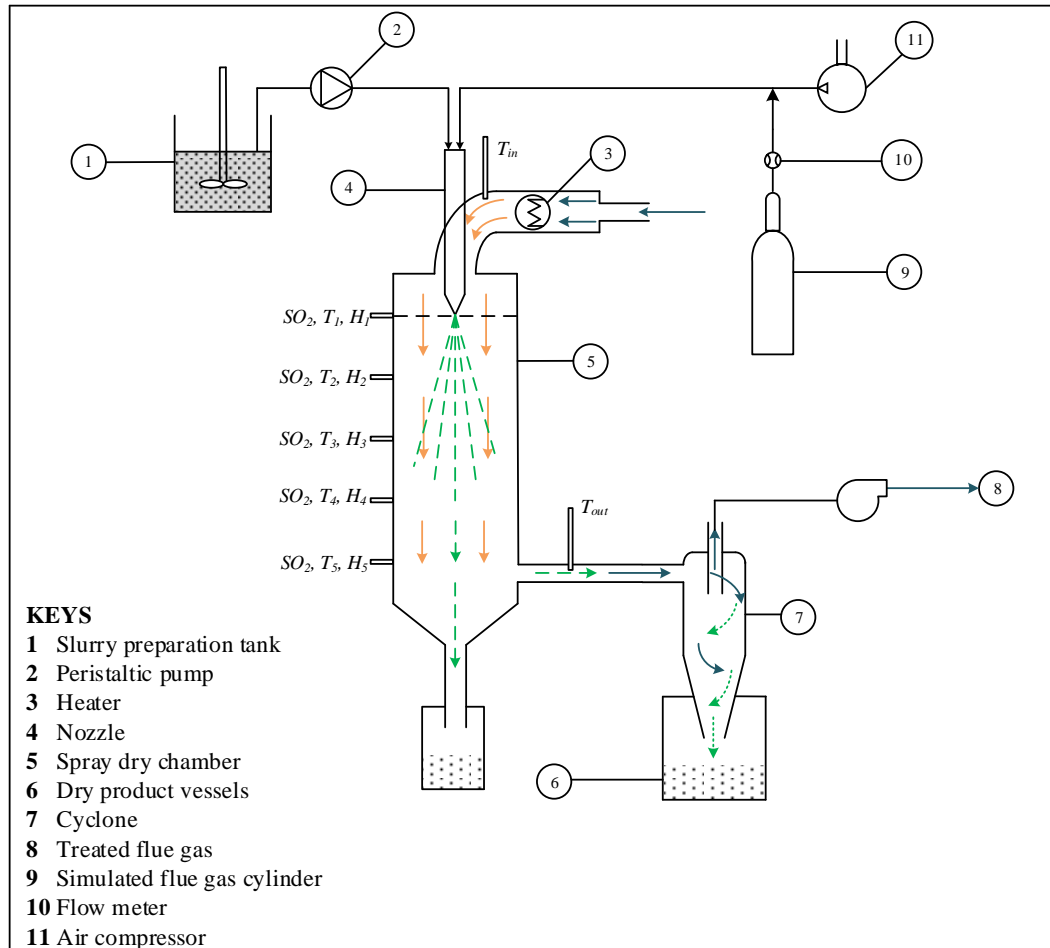


Figure 3:1: Lime spray drying experimental setup.

Table 3:1: Spray dryer specifications and experimental conditions

Variables	Ranges
Inlet air temperature (°C)	120 - 180
Feed air flow rate (m ³ /h)	20 - 35
Slurry solid concentration (%)	6 - 12
Atomizing air flowrate (l/h)	350 - 750
Calcium to sulphur ratio	1 - 2.5
Flue gas SO ₂ concentration (ppm)	500 - 2000
Approach to saturation temperature (°C)	5 - 20

3.5. Results and discussion

3.5.1. Sorbent physical and chemical properties

The chemical composition of hydrated lime determined by XRF analysis is given in Table 3:2. From the analysis, the sorbent is mainly composed of CaO with a content of 89.55% which is crucial in the total sulphation of the sorbent. Impurities consisted of SiO₂, MgO, and Al₂O₃ with trace amounts of K₂O, Mn₃O₄, TiO₂ and Na₂O.

Table 3:2: Chemical composition of hydrated lime

	Content %								
	SiO ₂	Al ₂ O ₃	K ₂ O	Mn ₃ O ₄	CaO	MgO	TiO ₂	Na ₂ O	SrO
Lime	7.38	0.79	0.05	0.12	89.55	1.12	0.06	0.23	0.19

The x-ray diffraction (XRD) pattern in Figure 3:2 revealed portlandite (Ca[OH]₂) as a major crystalline phase in the sorbent. The analysis also indicated the presence of quartz crystalline phase which appears as mild hump on the diffraction patterns. The specific surface area determined by BET surface area analysis was found to be 4.24 m²/g. The adsorption-desorption isotherm plot in Figure 3:3 indicates that the sorbent used belongs to a typical type II isotherm in accordance with IUPAC classification. This indicates a multilayer adsorption property associated microporous materials (Hadjar et al., 2008). This demonstrates that the particles are mesopores having their pore diameters larger than micropores. Pore sizes between 2 and 100 μm have been identified as the effective zone for the sulphation reaction between SO₂ and sorbent (Garea et al., 1997; Lee et al., 2005).

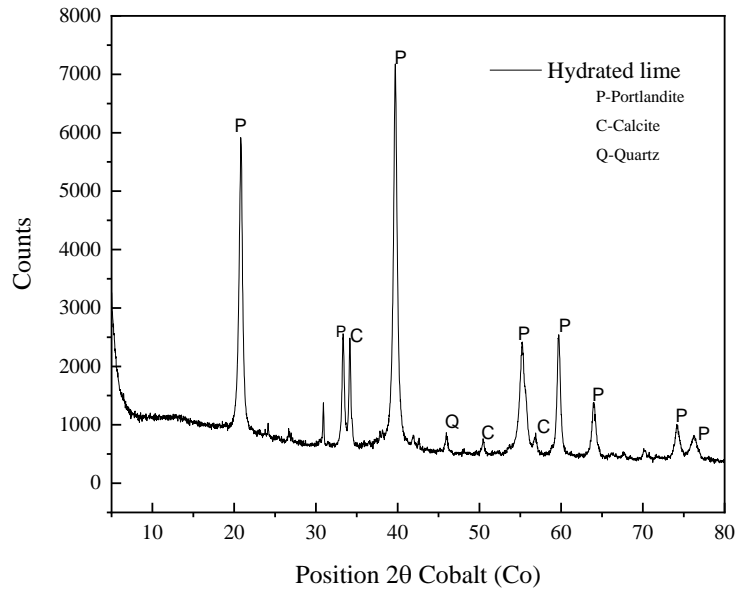


Figure 3:2: XRD diffraction pattern for hydrated lime

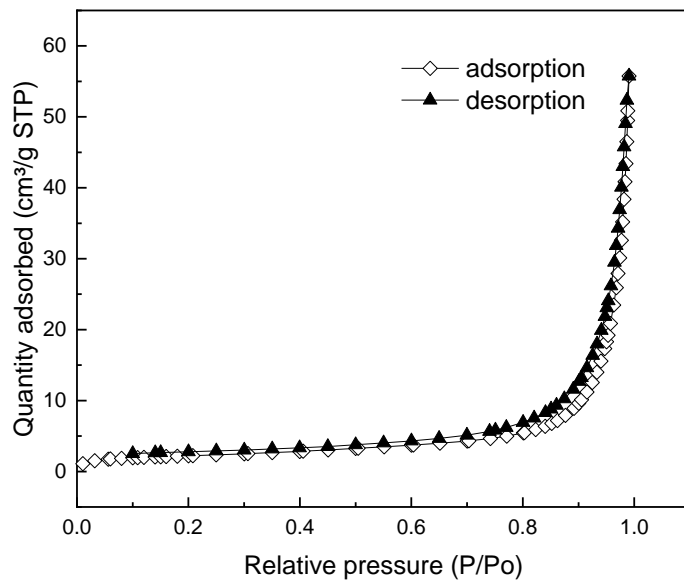


Figure 3:3: Nitrogen adsorption/desorption isotherm linear plot for hydrated lime.

3.5.2. Spray drying desulphurization variables.

3.5.2.1. Effect of stoichiometric ratio on SO₂ absorption

Stoichiometric ratio is an expression for the ratio of moles of fresh sorbent to the moles of SO₂ in flue gas. It is an indication of the rate of consumption of the sorbent which is a critical economic

consideration in the process. It is also one of the key parameters necessary during the design stage of a spray dryer (Yang and Kim, 2000). For lime spray drying process, stoichiometric ratio is evaluated as:

$$SR = \frac{\text{Moles of } Ca(OH)_2 \text{ in feed slurry}}{\text{Moles of } SO_2 \text{ in flue gas}}$$

In this study, experiments were conducted by varying the stoichiometric ratio from 1 to 2.5 at a constant temperature of 140 °C. This was varied by regulating the amount of Ca[OH]₂ in the feed slurry. The results for this experiment are represented in Figure 3:4. The results indicate a rapid rise in the desulphurization efficiency with an increase in the stoichiometric ratio and this is attributed to the increase in the slurry concentration which reduces the droplet liquid-phase mass transfer resistance for SO₂ (Scala et al., 2004; Newton et al., 1990). A high SO₂ absorption efficiency beyond 80% was achieved for stoichiometric of 2.5. However, the economic analysis of lime and solid waste disposal costs requires lower stoichiometric ratios for this process (Sahar and Kehat, 1991). Furthermore, high stoichiometric ratios lead to poor sorbent utilization, this is due to the nature of lime droplets during the reaction system where the outer regions become covered by the reaction products while the central regions remain unreacted.

The results also indicate an almost linear increase in SO₂ absorption from the nozzle tip before it levels off towards the exit of the spray chamber for the range of the stoichiometric ratio used. As the droplet leaves the nozzle, there is high concentration of sorbent particles near the surface of the droplet which reduces the liquid-phase mass transfer resistance (Newton et al., 1990). As the droplet continues to drop, additional external resistances due to mass transfer or liquid-phase mass transfer of reactant species (sulphur) through the layer of CaSO₃ will limit the absorption of SO₂. This is evident in the levelling of the graphs towards the exit of the spray chamber for stoichiometric ratio between 1.5 and 2.5.

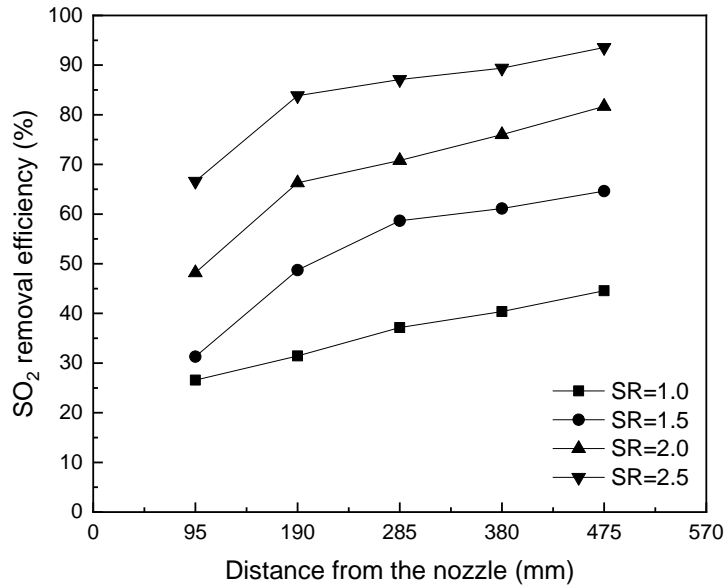


Figure 3:4: The effect of stoichiometric ratio on SO₂ removal efficiency (inlet air flowrate, 35m³/h; slurry federate, 15ml/min, temperature, 140 °C).

3.5.2.2. Effect on inlet gas phase temperature on SO₂ absorption

The absorption of SO₂ was studied with varying inlet gas temperatures ranging from 120 to 180 °C at a constant stoichiometric ratio of 1.5. These temperatures corresponded to outlet temperature values of 35 and 48°C, respectively. Figure 3:5 shows the experimental findings where it was observed that an increase in the inlet gas temperature causes a decrease in the absorption efficiency of SO₂. This is attributed to accelerated drying rate caused by increased gas-phase temperature in the spray chamber. Higher inlet gas temperatures create a substantial temperature difference between the bulk gas and the droplets which causes rapid evaporation and subsequently reducing the necessary contact time for chemisorption reaction (Scala et al., 2004; Yang and Kim, 2000). Highest SO₂ removal efficiencies beyond 80% were obtained for temperatures of 120 and 140 °C at the chamber height of $z = 485 \text{ mm}$. This is because lower temperatures allow close temperature difference between the gas bulk and the droplet is necessary to provide adequate lifetime for SO₂ absorption because of reduced evaporation.

In the spray chamber, the reactivity of the slurry droplet towards SO₂ is strongly dependent on the moisture retention capacity of the droplet. The reactions as shown in equations 1 – 8 are considered to occur in the aqueous phase, and thus rapid moisture loss through evaporation hinders the necessary reactions (Erdöl-Aydin and Nasün-Saygili, 2007). This is evident in the SO₂ absorption

findings as shown in Figure 3:5 where there is a steady rise in the absorption efficiency at the top section of the spray dryer (0 to 285mm) before almost levelling off towards the chamber exit. The steady rise in the absorption of SO₂ over the range of temperatures is attributed constant rate drying period where the droplet still contains sufficient moisture for chemisorption reaction (Mei et al., 2020). As the droplet leaves the atomizer, rapid evaporation begins and consequently concentrating lime particles inside the droplet. Simultaneously, SO₂ diffuses from the bulk gas region to the moisture layer on the surface of lime particles and reacts with dissolved lime. This forms a reaction product which precipitates on the surface of the droplet acting as a barrier thus limiting both water evaporation and SO₂ absorption (Wey et al., 2003).

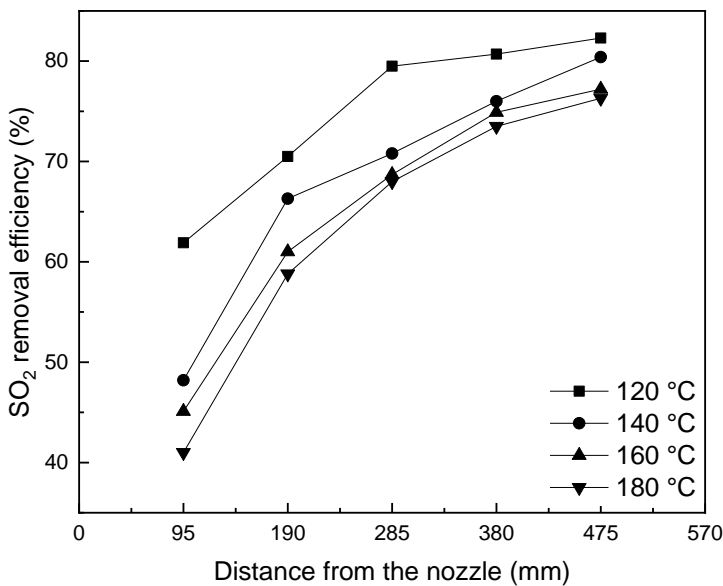


Figure 3:5: SO₂ removal efficiency at different temperatures (inlet air flowrate, 35m³/h; lime slurry solid concentration, 6%; slurry feed rate, 15ml/min)

3.5.2.3. Effect of approach to saturation temperature on SO₂ absorption

Approach to saturation temperature is a critical process parameter in spray drying that is used to express the influence of gas relative humidity on SO₂ absorption. It is defined as the difference between the gas temperature and the adiabatic saturation temperature inside the spray chamber (Ma et al., 2000). To achieve high SO₂ absorption rates, a close approach to saturation temperature must be maintained in a spray dryer which reduces the driving force for evaporation (Li et al., 2004; Srivastava, 2000). In this study, the approach to saturation temperature was varied by regulating the amount of water in the feed slurry. Experiments were conducted for values of the

approach to saturation temperature ranging from 5 to 15 °C. The findings for this experiment are represented in Figure 3:6, where it was observed that SO₂ absorption improved significantly with decreasing approach to saturation temperature. This trend is in good agreement with spray dryer performance trends reported in literature. The results showed that an absorption efficiency of about 55-70% was achieved at the higher approach to saturation temperatures (13 - 16 °C) while at low approach to saturation temperature of 5 °C, an absorption efficiency of 70-89% was achieved. The highest absorption efficiency of 89% was achieved when an approach to saturation temperature of 5 °C was used with stoichiometric ratio of 2.5. At low approach to saturation values, there is high gas relative humidity and thus there is reduced rate of evaporation. This therefore promotes dissociation and dissolution of the reacting species in the droplets leading to remarkable improvement of SO₂ absorption. Extremely low values of approach to saturation temperature will however cause incomplete drying of the slurry and excess consumption of water. It is therefore necessary to maintain the value of AST at optimum level to avoid agglomeration of fluidized particles and solid deposits on the spray dryer wall (Xu et al., 2000; Zhou et al., 2009). The results indicate the significant influence of the approach to saturation temperature on the absorption of SO₂ in the spray dryer. The reaction between Ca[OH]₂ and SO₂ in the spray dryer is heavily dependent on the droplet's moisture retention capability. This occurs in the aqueous phase, and thus rapid loss of moisture by evaporation impedes the necessary reactions (Ma et al., 2000).

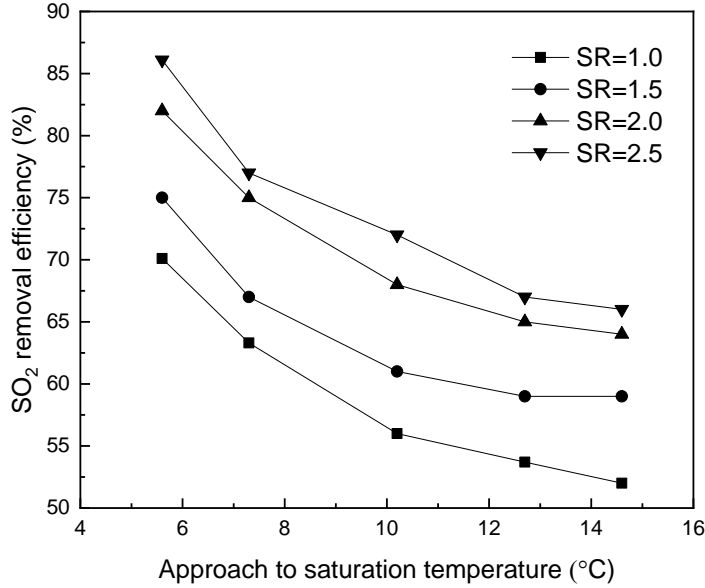


Figure 3:6: Effect of approach to saturation temperature on SO₂ removal efficiency under different stoichiometric ratios (inlet air flowrate, 35m³/h; slurry federate, 15ml/min, temperature, 140 °C)

3.5.2.4. Sorbent utilization

The performance of the spray dryer was also evaluated based on the degree of conversion of calcium (calcium utilization) after SO₂ absorption which is calculated as (Scala et al., 2005):

$$x_{Ca} = \frac{N_{SO_2,i} - N_{SO_2,o}}{N_{Ca_i}}$$

Where,

$N_{SO_2,i}$ is the molar concentration of SO₂ in the entering gas.

$N_{SO_2,o}$ is the molar concentration of SO₂ in the exiting gas.

N_{Ca_i} is the molar concentrations of calcium in the feed slurry.

Figure 3:7 represents experimental results for the influence of inlet gas phase temperature (140 - 180 °C) and stoichiometric ratio (1.0 - 2.5) on the degree of conversion of calcium and SO₂ removal efficiency. The results show decreasing degree of conversion of calcium and SO₂ removal efficiency with increasing temperature. Higher temperatures accelerate the droplet evaporation rate thereby limiting its lifetime for both calcium conversion and SO₂ absorption. Experimental results also show that a high degree of conversion of calcium was achieved at low stoichiometric ratios.

The maximum value of 94% was achieved at a stoichiometric ratio of 1.5 for inlet gas temperature of 140 °C. The results also indicate increasing SO₂ absorption efficiency with increasing stoichiometric ratio due to negligible internal mass transfer resistances for SO₂ at high stoichiometric ratios (Hill and Zank, 2000). It is however advisable to operate the spray dryer with minimum stoichiometric ratio to reduce the operating cost and wet deposition on the walls of the chamber (Ollero et al., 1997).

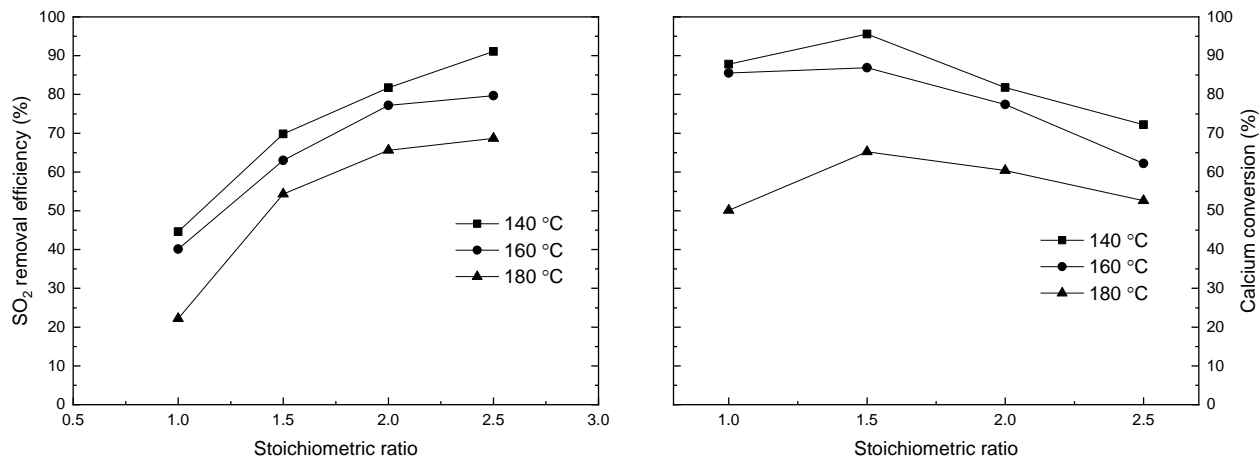


Figure 3:7: The effect of Ca:S ratio and inlet gas temperatures on SO₂ removal efficiency (%) and calcium conversion (%) respectively.

3.5.3. Characterization of the spray drying product

3.5.3.1. SEM and EDS analysis

The surface morphologies of the final dried products after desulphurization obtained by SEM analysis were used to assess the influence of the spray drying conditions on the hydrated lime particles. Figure 3:8 shows the micrographs obtained under varying stoichiometric molar ratios of 1.0, 1.5 and 2.0 respectively. It was observed from the micrographs that the samples obtained at stoichiometric ratio of 1.0 and 2.0 had porous irregular particles with relatively rough surfaces. This is attributed to products of desulphurization and agglomeration of partially reacted sorbent particles forming larger aggregates (Scala et al., 2005). Extensive agglomeration was observed on the sample obtained at a stoichiometric ratio of 2.0 which retained higher moisture content on the surface of the sorbent leading to a higher desulphurization activity. The sample obtained at a stoichiometric ratio of 1.5 was observed to be plate-like and needle-like shaped particles which is

typical of calcium sulphite and gypsum particles (Küspert and Krammer, 2012). They are also mainly composed of depleted sorbent particles after reaction with SO_2 . This is in agreement with the experimental findings where the highest sorbent utilization of 94% was realized at a stoichiometric ratio of 1.5.

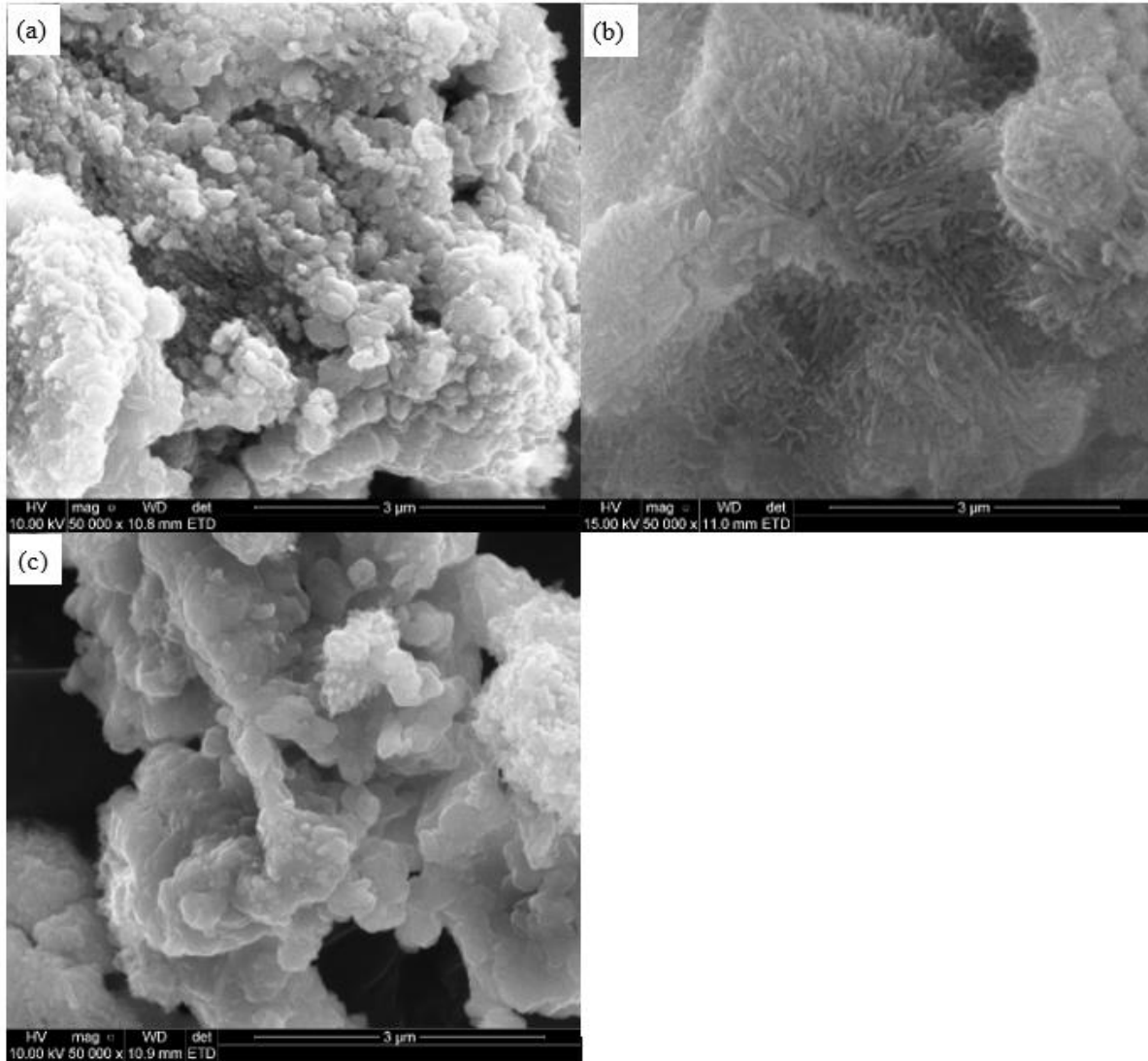


Figure 3:8: SEM micrographs for desulphurization products obtained at (a) $\text{SR}=1.0$, (b) $\text{SR}=1.5$ and (c) $\text{SR}=2.0$.

The samples were further tested by EDS (Energy-Dispersive Spectroscopy) analysis to obtain their respective normalized elemental compositions as presented in Table 3:3. The elemental compositions indicated increased concentration of calcium mass percentage (from 64.19 to 68.5%) with increasing stoichiometric molar ratio. This is mainly due to increased concentration of lime

introduced into the feed slurry to achieve the required stoichiometric ratio. The results also indicate the highest concentration of sulphur (8.95% by mass) for the sample collected at stoichiometric ratio of 1.5 compared to the samples collected at stoichiometric ratio of 1.0 and 2.0, which contained 4.72 and 7.79 mass percentage, respectively. The presence of sulphur element in the dried product indicates the absorption of SO₂ into the sorbent to form SO₃ and SO₄ salts (i.e., CaSO₃ and CaSO₄). High concentration of sulphur on the final product at a stoichiometric ratio of 1.5 is due to high desulphurization activity per mass of the sorbent. This led to improved sorbent conversion which was confirmed by the theoretical evaluation of the degree of conversion at different stoichiometric ratios. Based on EDS analysis and the evaluation of sorbent utilization, it can therefore be concluded that effective utilization of the of hydrated lime in the spray dryer can be achieved when stoichiometric ratio of 1.5 is used.

Table 3:3: Surface chemical composition by EDS analysis

	SR = 1.0	SR = 1.5	SR = 2.0
Ca	64.19	65.87	68.50
S	4.72	8.95	7.79
O	31.09	25.18	23.71
Total	100.00	100.00	100.00

3.5.3.2. FTIR analysis

Samples of the dried product collected after desulphurization were analysed using infrared FTIR with a spectral range of 4500 – 350 cm⁻¹. Figure 3:9 illustrates FTIR analysis spectra of the desulphurization products at different stoichiometric ratios ranging from 1.0 to 2.0. The spectral profiles as seen in the figure show strong broad absorption band around 938 cm⁻¹ and at 650 cm⁻¹ which are assigned to calcium sulphite hemihydrate (Guan et al., 2011). The sulphate ions had characteristic minor absorption band at 1120 – 1170 cm⁻¹ (Böke et al., 2004). As observed in the spectra, the sample collected at a stoichiometric ratio of 1.5 had a huge calcium sulphite hemihydrate spectrum at 938 cm⁻¹. This is due to the significant proportion of sulphite formed in the final product resulting from high sorbent conversion as observed at a stoichiometric ratio of 1.5. This was confirmed by the chemical analysis which revealed a strong presence of 24.57%

CaSO₃·0.5H₂O in the final desulphurization product. The infrared profiles also show significant changes on the absorption bands around 1413 and 3642 cm⁻¹ which were identified as calcite and portlandite respectively (Laperche and Bigham, 2002). The conversion of the sorbent accounts for the changes in the infrared absorption bands for portlandite and calcite at different stoichiometric ratios as illustrated in Figure 3:9. The depleted portlandite peak for the collected sample at stoichiometric ratio of 1.5 is evidence of high sorbent conversion with corresponding huge peaks at around 938 cm⁻¹ for sulphite. Highest portlandite peaks at stoichiometric ratios of 1.0 and 2.0 demonstrate significant proportion of unreacted sorbent as confirmed by EDS analysis and the evaluation of unreacted Ca[OH]₂ by TGA analysis.

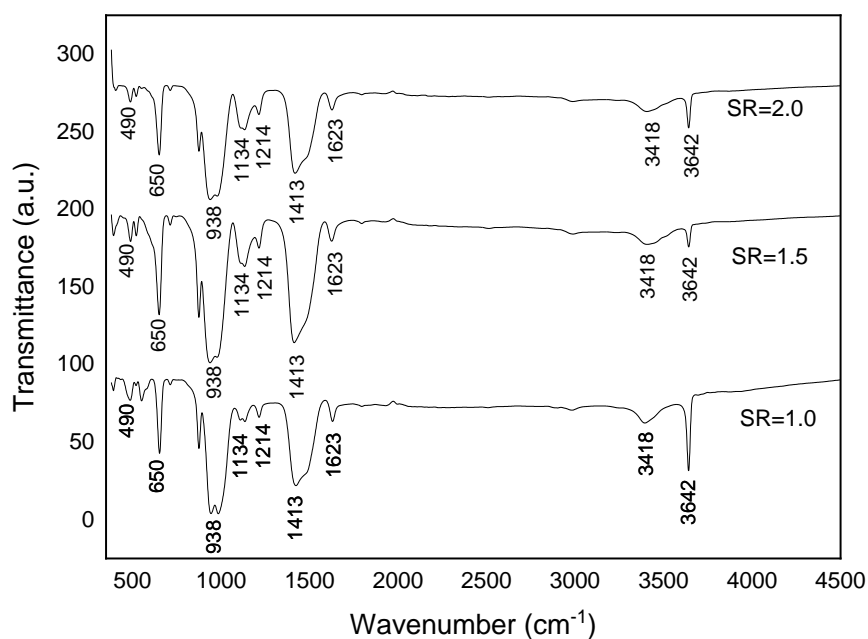


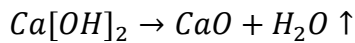
Figure 3:9: FTIR spectra for desulphurization products under varying stoichiometric ratios.

3.5.3.3. Evaluation of unreacted Ca[OH]₂ by TGA analysis

Thermogravimetric analysis of the final product was conducted to verify and assess the decomposition of various compounds at different temperatures. Different samples of the final desulphurization product were collected under varying experimental conditions (i.e., with SR of 1.0, 1.5 and 2.0) and analysed by TGA. Their composition was evaluated based on the weight loss at different temperatures as shown in Figure 3:10 for a sample collected at a stoichiometric ratio of 2.0. For all the samples analysed, there was weight loss recorded between 350 - 450 °C which was attributed to the release of water of crystallization due to the decomposition of unreacted

Ca[OH]₂ in the collected sample (Kim and Olek, 2012). Further weight loss was recorded between 550 - 750 °C, which was attributed to the release of carbon during decomposition of CaCO₃ in the sample (VGB PowerTech, 2008). The presence of CaCO₃ as also observed in FTIR analysis was associated with the contamination during sample preparation. This forms part of the unreacted sorbent fraction in the final product. Over the range of temperatures used, the decomposition of the final desulphurization product follows the reaction path below:

- Between 350 - 450 °C (release of water of crystallization)



- Between 550 - 750 °C (release of carbon dioxide)

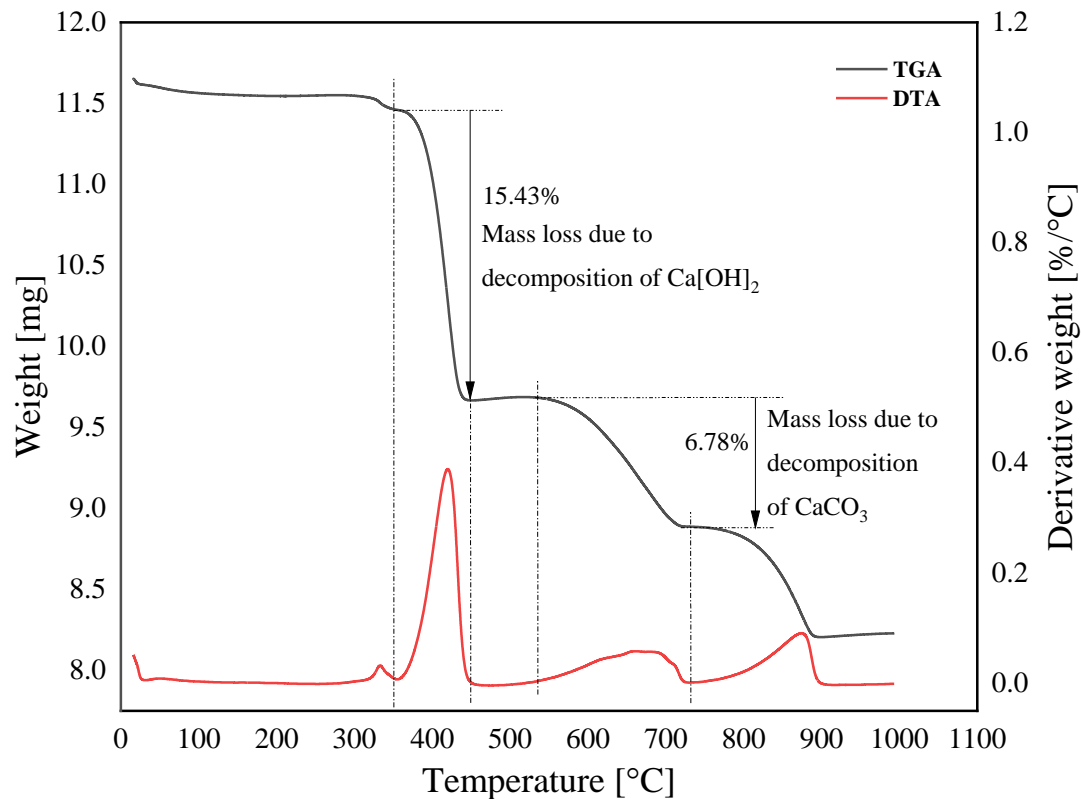
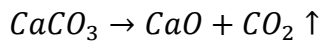


Figure 3:10: TGA and DTA curves for desulphurization product at stoichiometric of 2.0

The content of unreacted $Ca[OH]_2$ in the final product was evaluated as (Kim and Olek, 2012):

$$Ca[OH]_2 \text{ content} = \frac{MW \text{ of } Ca[OH]_2}{MW \text{ of dehydrated water}} \times wt \text{ loss between } 350 - 450^\circ C$$

$$Ca[OH]_2 \text{ content} = \frac{74}{18} \times 15.43 = 63.43\%$$

$CaCO_3$ content in the final product was evaluated as (VGB PowerTech, 2008):

$$CaCO_3 \text{ content} = \frac{MW \text{ of } CaCO_3}{MW \text{ of Carbon dioxide}} \times wt \text{ loss between } 550 - 750^\circ C$$

$$CaCO_3 \text{ content} = \frac{100}{44} \times 6.78 = 15.41\%$$

Table 3:4: Final product composition under different stoichiometric ratios (TGA and XRF analysis)

	$CaSO_3 \cdot \frac{1}{2}H_2O$	<i>Unreacted</i> $Ca[OH]_2$	SO_2 removal efficiency
SR=1.0	11.68%	46.87%	45%
SR=1.5	24.57%	41.23%	65%
SR=2.0	21.74%	63.43%	82%

Figure 3:10: TGA and DTA curves for desulphurization product at stoichiometric of 2.0

The content of unreacted $Ca[OH]_2$ in the final product was evaluated as (Kim and Olek, 2012):

$$Ca[OH]_2 \text{ content} = \frac{MW \text{ of } Ca[OH]_2}{MW \text{ of dehydrated water}} \times wt \text{ loss between } 350 - 450^\circ C$$

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$$CaCO_3 \text{ content} = \frac{100}{44} \times 6.78 = 15.41\%$$

Table 3:4 shows the evaluated compositions of gypsum and unreacted $Ca[OH]_2$ in the samples analysed by TGA and XRF analysis. The results demonstrate that the samples collected for the experiment with SR of 2.0 had the highest SO_2 removal efficiency of 82%. However, the analysis by TGA shows that it had considerable amount of unreacted $Ca[OH]_2$ remaining in the final product. This reveals poor sorbent conversion at high stoichiometric ratio. Both experiments conducted with SR of 1.0 and 1.5 exhibited better sorbent conversion due to lower concentration of unreacted $Ca[OH]_2$ but with relatively lower SO_2 removal efficiencies of 45 and 65% respectively when compared to the experiment conducted with SR of 2.0. The analysis also shows higher concentrations of $CaSO_3 \cdot \frac{1}{2}H_2O$ for experiments with SR of 1.0 and 1.5 compared to SR of 2.0. The operating conditions at SR of 1.5 yielded the highest concentrations of 24.57% for $CaSO_3 \cdot \frac{1}{2}H_2O$, which indicates better sorbent conversion.

3.6. Conclusion

An experimental study on the absorption of SO₂ from flue gas by means of a laboratory scale spray dryer was carried out under different operating conditions. Results indicate decreased absorption of SO₂ at high gas phase temperatures due to rapid evaporation. SO₂ absorption efficiency of up to 80% was achieved at a gas phase temperature of 120 °C. Results also indicated significant improvement of SO₂ beyond 80% absorption at high stoichiometric ratios due to reduced liquid-phase mass transfer resistances. A high absorption efficiency was achieved at low approaches to saturation temperatures for all range of stoichiometric ratios used. However, there was incomplete drying of the slurry at low values of approach to saturation temperature due to excess consumption of water. Analysis of the degree of conversion of calcium indicated high utilization at low stoichiometric ratios with maximum utilization obtained at Ca:S ratio of 1.5. Characterization of the final product revealed better sorbent conversion of 94% at a stoichiometric ratio of 1.5. TGA analysis generally indicated poor conversion sorbent conversion in the spray dryer. The concentration of unreacted Ca[OH]₂ ranging from 41 – 64% in the final desulphurization product was achieved for experiments conducted stoichiometric ratios ranging from 1.0 - 2.0.

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4. Optimization of spray drying variables for desulphurization using response surface methodology.

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4.1. Abstract

An investigation was undertaken to determine the performance of a laboratory-scale spray dryer (semi-dry process) involving flue gas desulphurization (FGD) to contribute to the understanding, modelling and design of an industrial process. The study consisted of a systematic experimentation programme using response surface methodology with a lab scale spray dryer to optimize the absorption of SO₂. Parametric tests were conducted to analyse the influence of stoichiometric ratio (0.5-2.5), inlet gas phase temperature (120-200°C), slurry solid concentration (6-14%) and slurry pH (4-12) on SO₂ absorption efficiency. The axial profiles of SO₂ within the absorber space indicated two drying regimes i.e., constant rate and falling rate drying periods within the spray dryer. A predictive quadratic model correlating independent variables and the response was developed based on experimental findings. The model was found to provide a suitable fit with an R-squared coefficient of 0.93. The recommended optimal conditions for SO₂ absorption were inlet gas phase temperature of 140°C, stoichiometric ratio of 2, slurry solid concentration of 8% and slurry pH of 10 which gave 90% SO₂ removal efficiency. The desulphurization product was characterized using XRD, FTIR and SEM to determine mineral compositions under varying operating conditions.

Key words: Spray drying absorption, semi-dry FGD, experimentation, sorbents, optimization.

4.2. Introduction

The removal of pollutant gases such as SO₂ and NO_x has gained a lot of interest for many years. They mostly emanate from the combustion of sulphur-containing coal in power plants resulting in emission of pollutant gases. Other pollutant gases generated from the combustion of coal include SO₃, HCl, HF and particulate matter (Miller and Miller, 2010). The emission and dispersion of these gases causes serious environmental pollution and adverse effects on human health (Kampa and Castanas, 2008). This has resulted in the enactment of stringent laws and regulations governing industrial air pollution particularly SO₂ and subsequently necessitated the need to implement flue gas cleaning processes such as flue gas desulphurization (FGD) units in both new and existing power plants.

FGD technologies can be categorized as wet, dry, and semi-dry based on the state of the active ingredient applied (Katolicky and Jicha, 2013). Spray drying absorption (SDA) is a type of semi-dry FGD technology that has received much attention in the recent years for use in the coal-fired power plants. It is an attractive alternative to the wet FGD system due to smaller footprint requirement, ease of product handling, low capital cost, ease of retrofit to existing plants and less water consumption (Wang et al., 2015; Xie et al., 2017; Xu et al., 2000). SDA mostly utilizes hydrated lime slurry as a sorbent which is sprayed via the spray nozzle at the top of the absorption chamber to react with SO₂ contained in flue gas. The desulphurization occurs on the surface of the droplet containing lime sorbent particles resulting in the formation of CaSO₃ and CaSO₄ (Katolicky and Jicha, 2016; Maryamchik, 2019). A final dry product is collected at the bottom of the absorption chamber before passing through a particulate collection device.

Despite its ability to remove SO₂ beyond legislative limits, the application of SDA in coal-fired power plants has been limited by high sorbent cost, low sorbent utilization and lower SO₂ removal efficiency compared to the wet FGD technology. It is therefore necessary to improve its desulphurization efficiency and sorbent utilization to make it more attractive in the industry. The reaction between hydrated lime (Ca[OH]₂) and SO₂ in the absorption chamber is an adsorption controlled reaction that mainly depends on a variety of factors such as sorbent surface properties, particle size, slurry solid concentration, humidity, approach to saturation temperature among others (Gassner et al., 2014). Numerous experimental studies have been conducted focused primarily on the operating variables which directly affect SO₂ removal in a spray dryer (Izquierdo

et al., 2000; Karlsson and Klingspor, 1987; Song and Park, 2001; Stein et al., 2002; Yang and Kim, 2000). Both evaporation and SO₂ absorption significantly affect the desulphurization efficiency of a spray dryer. These are mainly controlled by the spray dryer operating parameters which should be maintained at their optimum conditions to achieve desired absorber performance.

In this study, a systematic approach using central composite design (CCD) was used to assess the influence of spray characteristics on the desulphurization efficiency using commercial hydrated lime as a sorbent. This was performed using a laboratory scale spray dryer by varying the spray characteristics such as stoichiometric ratio (0.5 – 2.5), inlet gas phase temperature (120 - 200°C), slurry solid concentration (6 – 14%) and slurry pH (4 - 12) which were chosen as independent variables. These limits were based on the results of trial experiments on the present work and considering SO₂ concentrations in industrial flue gas. RSM was then applied to assess the cross-influences of the variables on SO₂ removal efficiency. Optimization was carried out for the process variables with an aim of maximizing SO₂ removal efficiency. Using CCD, a predictive quadratic model was developed, relating the desulphurization efficiency and the spray characteristics. The experimental results were compared with the theoretical results obtained from the model to verify the accuracy and validity of the model.

4.3. Experimental

The absorption experiments were conducted in a laboratory scale Buchi B290 mini spray dryer. A schematic of the spray dryer is shown in Figure 3:1. The overall setup consisted of the following subsystems: sorbent slurry preparation, spray drying absorption chamber, flue gas analysis and other accessories.

Simulated flue gas was obtained by mixing 99% SO₂ with ambient air at controlled rate to achieve the required inlet SO₂ concentration. To achieve the desired inlet temperature, flue gas is heated using an electric heater located above the chamber before entering the spray chamber. The feed slurry comprised of commercial grade hydrated lime mixed with water using pre-determined ratios. Table 4:1 presents a summary of the chemical and physical properties of the hydrated lime used. The pH of the slurry was adjusted by adding 0.1M HCl into the feed slurry. The feed slurry was then injected into the spray dryer via a two-fluid nozzle located at the top of the spray chamber. The nozzle disperses the slurry into fine droplets which comes in contact with the heated flue gas in a co-current flow in the spray chamber. A final dry product is collected at the bottom of the

chamber and captured by the cyclone separator. Throughout each experimental run, SO₂ concentration was monitored along the spray chamber using Testo 340 combustion gas analyzer. This was done by continuously sampling the flue gas at 5 different points as depicted in Figure 3:1.

The hydrated lime sorbent was characterized using Nitrogen Branauer-Emmett-Teller (Micromeritics ASAP™ 2020 Porosity Analyzer) to determine their specific surface area. Qualitative analysis of the sorbent and final desulphurization product was determined by x-ray diffraction (XRD) technique using Malvern Panalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K α radiation. The phases present were identified using X'Pert Highscore plus software. Scanning Electron Microscopy (SEM) machine equipped with Energy Dispersive Spectroscopy (EDS) was used to observe the morphological structures and to detect chemical elemental composition on the surface of the samples. Fourier Transform Infrared (FTIR) analysis using Perkin-Elmer Spectrum Two™ machine was used to determine the functional groups present in the samples. The morphological structures of the samples were determined by Scanning Electron Microscopy (SEM) machine.

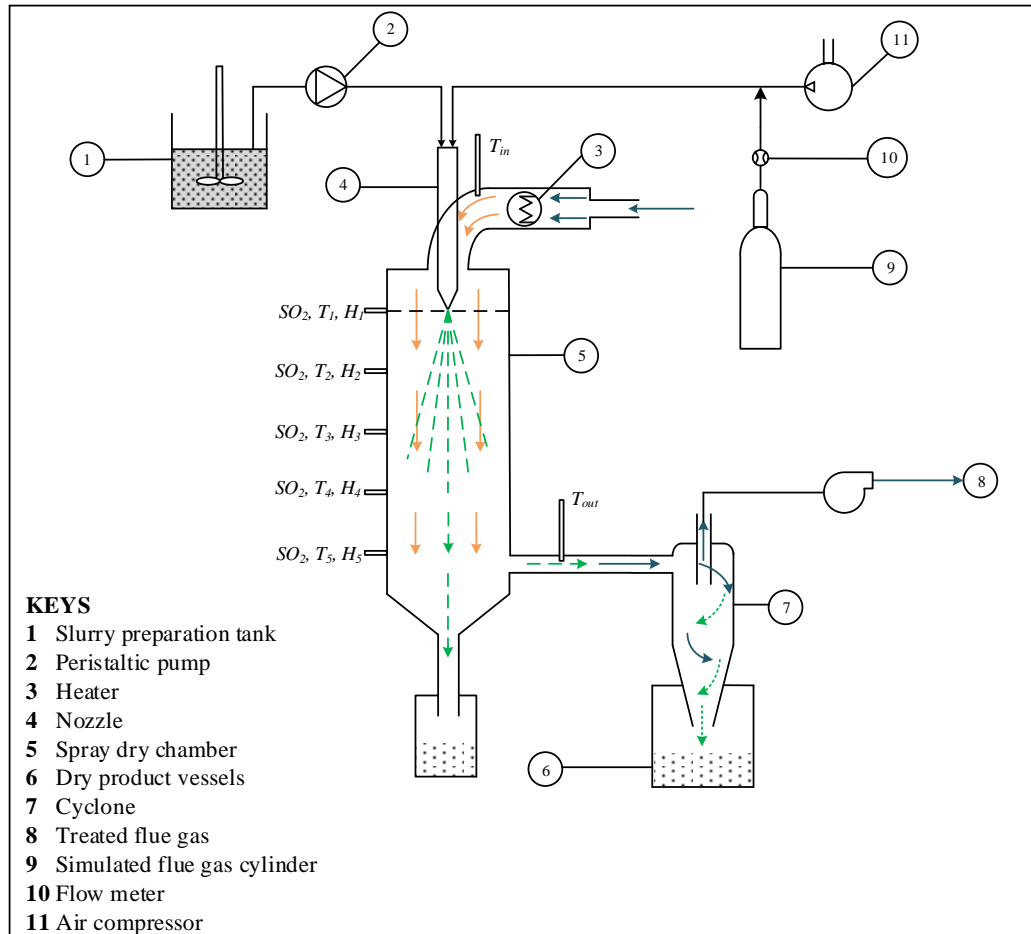


Figure 4:1: Lime spray drying experimental setup.

Table 4:1: Sorbent properties.

Property	Ca[OH] ₂
Composition (XRF)	89 wt% CaO
Average particle size	<75 μm
BET surface area (N ₂)	4.24 m ² /g

4.4. Design of experiments and statistical analysis

In this study, response surface methodology (RSM) was used to optimize the experimental conditions for the absorption of SO₂ from flue gas using a laboratory scale spray dryer. RSM is a mathematical and statistical technique useful for the modelling and analysis of problems in which

a response of interest is influenced by several variables, with an objective to optimize this response (Myer and Montgomery, 2002). A full factorial design consisting of independent variables that were investigated is shown in Table 4:2. A central composite design component with quadratic model and $\alpha=2$ in the Design Expert Software v13.0.1.0 was used to analyse the effects of process variables (inlet gas phase temperature, stoichiometric ratio, slurry solid content and slurry pH) on SO₂ absorption efficiency. Alpha (α) is the axial distance from the centre point and makes the design rotatable. The full factorial design comprising of 30 experiments is shown in Table 4:3 with the response.

Table 4:2: Process parameters.

Independent variable	Code	$\alpha = -2$	$\alpha = -1$	$\alpha = 0$	$\alpha = 1$	$\alpha = 2$
Inlet gas temperature (°C)	x_1	120	140	160	180	200
Stoichiometric ratio (Ca:S)	x_2	0.5	1.0	1.5	2.0	2.5
Slurry solid concentration (wt%)	x_3	6	8	10	12	14
Slurry pH	x_4	4	6	8	10	12

The experimental data obtained were fitted into a second-order polynomial model and regression coefficients were obtained. The second-order polynomial model used in the response surface analysis was as follows:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j$$

Where Y is the predicted SO₂ absorption efficiency (ppm), b_0 is offset term, b_i are the linear coefficients, b_{ii} are the quadratic coefficients, b_{ij} are the interaction coefficients, and $x_{i,j=1,2,\dots,n}$ are the coded values for the independent variables investigated. The significance of the second-order model was evaluated by analysis of variance (ANOVA) and a lack of fit test which was then used to optimize spray dryer absorption efficiency for all the independent variables investigated. The model adequacy was evaluated based on the R-squared statistic (R^2).

Table 4:3: Full factorial design matrix of experiments and results.

Run	Temperature (°C)	Stoichiometric ratio (Ca:S)	Solid content (%)	Slurry pH	SO ₂ removal efficiency (%)
1	160	1.5	10	8	77
2	160	1.5	10	8	77
3	160	0.5	10	8	48
4	200	1.5	10	8	65
5	180	2	8	6	60
6	160	1.5	10	8	77
7	180	2	8	10	79
8	180	1	12	10	59
9	140	1	8	10	69
10	160	1.5	10	8	77
11	180	2	12	6	67
12	140	1	8	6	65
13	160	1.5	10	8	77
14	160	2.5	10	8	86
15	140	2	12	6	84
16	180	1	12	6	54
17	140	1	12	10	72
18	180	2	12	10	76
19	160	1.5	10	8	77
20	180	1	8	10	59
21	140	1	12	6	67
22	160	1.5	10	4	72
23	160	1.5	14	8	80
24	180	1	8	6	53
25	120	1.5	10	8	88
26	140	2	12	10	93
27	140	2	8	6	80
28	160	1.5	10	12	80
29	140	2	8	10	89
30	160	1.5	6	8	70

4.5. Results and discussion

4.5.1. Sorbent characterization

Chemical analysis (XRF) of the commercial hydrated lime used a sorbent in this study indicated significant presence of Ca expressed as CaO (89.55 wt%) which is an active component in the chemisorption reaction. This was evident from XRD analysis which revealed strong presence of Ca[OH]₂ (portlandite) peaks appearing at $2\theta = 20.9, 33, 39.5, 55, 59.5, 64$ and 74° as shown in Figure 4:2. The diffraction patterns also revealed mild presence of quartz (SiO₂) appearing at $2\theta = 24, 31, 42.5, 47, 49$ and 53.5° . The presence of calcite peaks in the sample is attributed to the re-carbonation of Ca[OH]₂ by reaction with SO₂ in the atmosphere (Bigham et al., 2005). This could also have been due to contamination during preparation for XRD analysis. The surface morphology of the sorbent obtained from SEM analysis indicated a porous particle surface with rough texture as shown in Figure 4:3. This contributes to a high specific surface area as indicated in the N₂ BET surface area analysis of 4.24 m²/g which is adequate surface area beneficial for desulphurization in spray drying.

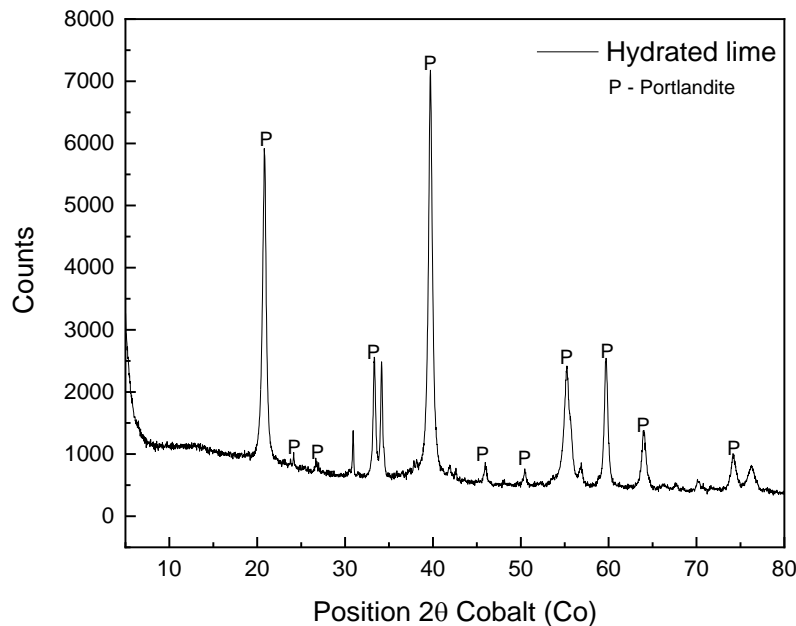


Figure 4:2: XRD diffraction pattern for hydrated lime sorbent.

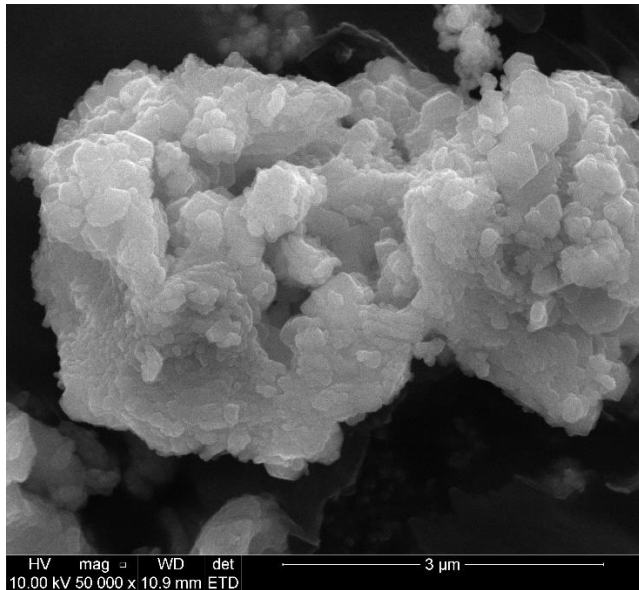


Figure 4:3: SEM image for hydrated lime sample.

4.5.2. SO₂ absorption profile within the absorber

A critical aspect of this study was to accurately measure the process conditions within the absorber space. This involved the sampling of the flue gas at different chamber heights to obtain axial profile by analysis for SO₂ concentration. Figure 4:4 shows SO₂ absorption curves for randomly selected experimental runs (experiments 1, 4, 15 and 17) along with their respective experimental conditions. The results depict a steady increase in the absorption of SO₂ along the spray chamber for all the selected runs. As shown in Figure 4:4, there was a steady rise in the absorption of SO₂ between 0 and 285 mm from the nozzle for all the selected experiments. This was attributed to the constant rate drying period in the spray chamber where the droplets rapidly lose moisture and therefore concentrating the lime particles inside the droplet (Katolicky and Jicha, 2013). The absorption efficiency was generally constant beyond 285 mm from the nozzle where particles are already formed, and a product precipitate ($CaSO_3 \cdot \frac{1}{2}H_2O$) is formed on the surface of the droplet. This acts as a barrier and limits reaction and absorption of SO₂. This is considered to be the falling rate drying period where water recedes into the porous agglomerate of the particle (Neathery, 1996).

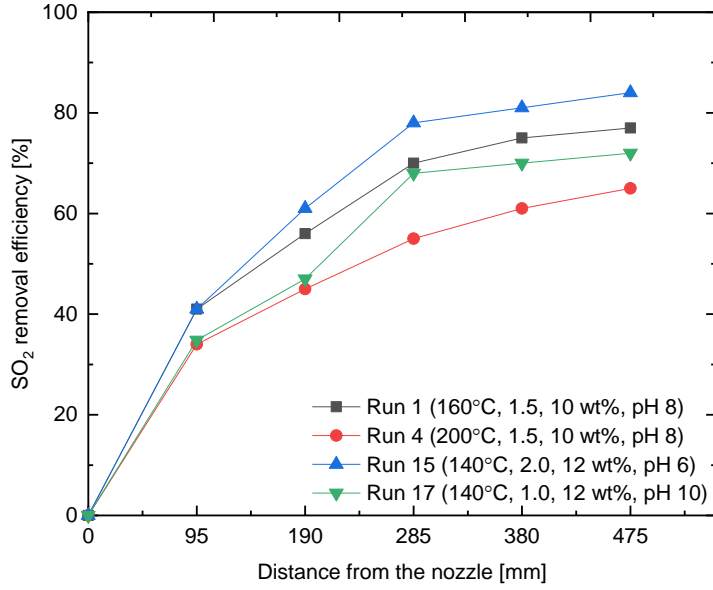


Figure 4:4: SO₂ absorption profiles for selected experiments.

4.5.3. Model fitting

A full design matrix of experiments comprising of all the independent variables and the response (SO₂ absorption efficiency) for all experiments is presented in Table 4:3. The percentage removal range of SO₂ was between 48 and 93%. The correlation between the independent variables and the responses was developed using CCD based on the experimental findings. From CCD, the predictive quadratic model for SO₂ removal efficiency was obtained in terms of coded factors as shown below:

$$Y = 77 - 6.58x_1 + 8.58x_2 + 1.58x_3 + 3.42x_4 - x_1x_2 - 0.5x_1x_3 + 1.75x_1x_4 + 0.375x_2x_3 + 1.63x_2x_4 - 0.625x_3x_4 - 0.667x_1^2 - 3.04x_2^2 - 1.04x_3^2 - 0.792x_4^2$$

Y – SO₂ removal efficiency (%)

x_1 – Temperature (°C)

x_2 – Stoichiometric ratio

x_3 – Slurry solid concentration (%)

x_4 – Slurry pH

The coded equation was useful in identifying the relative impact of the experimental variables by comparing the model coefficients. Analysis of variance (ANOVA) was carried out to determine

the significance test for the predictive model and the individual model terms. The results for lack of fit test and ANOVA are presented in Table 4:4. The model F-value of 28.33 and p-value of less than 0.0001 confirm that the selected model is a suitable fit. The p-values were also used to check the model terms, which indicate that the model term is significant if this value is less than 0.0500. In this case, all four model terms x_1, x_2, x_3 and x_4 have significant effect of SO₂ absorption efficiency. All interaction effects of the model terms except x_2x_4 are non-significant with p-values greater than 0.1000. The analysis also shows that the quadratic effects of all variables except x_2^2 were non-significant bearing p-values greater than 0.1000.

The precision of the predictive model was validated by assessing the linear relationship between experimental and predicted values. Figure 4:5 shows a regression graph for experimental and predicted values showing an acceptable fit of the data points along the line of unit slope. This gave an R-squared (R^2) value of 0.93 for the quadratic model which implies that the entire response variation can be attributed to the quadratic model.

Table 4:4: Analysis of variance (ANOVA) for the quadratic model.

Source	Sum of squares	F-value	p-value	
Model	3495.20	28.33	< 0.0001	Significant
x_1 - Temperature	1040.17	118.05	< 0.0001	
x_2 - Stoichiometric ratio	1768.17	200.67	< 0.0001	
x_3 - Slurry solid concentration	60.17	6.83	0.0196	
x_4 - Slurry pH	280.17	31.80	< 0.0001	
x_1x_2	16.00	1.82	0.1978	
x_1x_3	4.00	0.4540	0.5107	
x_1x_4	9.00	1.02	0.3282	
x_2x_3	2.25	0.2554	0.6207	
x_2x_4	42.25	4.80	0.0448	
x_3x_4	6.25	0.7093	0.4129	
x_1^2	12.19	1.38	0.2578	
x_2^2	253.76	28.80	< 0.0001	
x_3^2	29.76	3.38	0.0860	
x_4^2	17.19	1.95	0.1828	

Residual	132.17
Lack of Fit	132.17
Pure Error	0.0000
Cor Total	3627.37

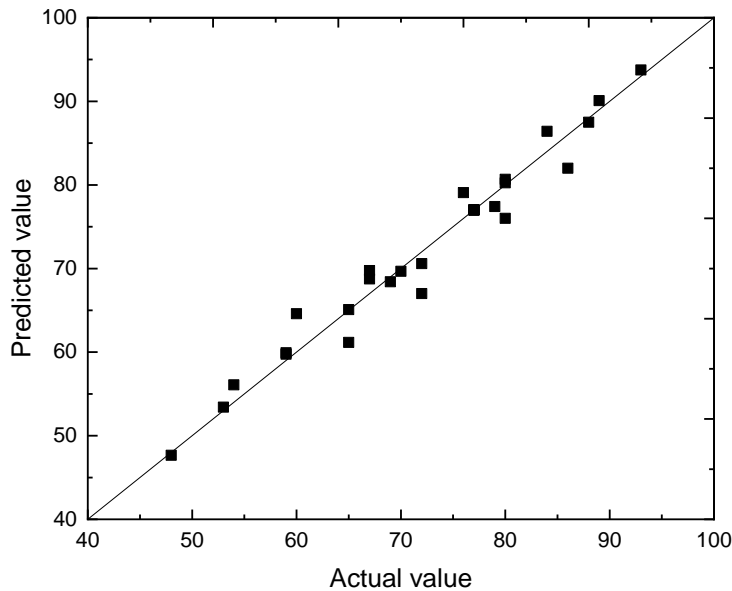


Figure 4:5: Regression graph of the predicted and experimental values.

4.5.4. Influence of spray drying parameters on SO₂ absorption.

SO₂ removal efficiency obtained under different experimental conditions ranged from 48 – 93%. The effects of all interactions of the independent variables on SO₂ absorption were represented using 3D surface plots generated by the variation of two independent parameters while keeping the other two constant at their respective central points. This gave six 3D surface response plots as shown in Figure 4:6 - Figure 4:11 which provide information of the effect of each independent variable and their interactive effects on the response (SO₂ removal efficiency).

The interactive effects of the temperature (A) and the stoichiometric molar ratio (B) on SO₂ removal efficiency under constant values of solid concentration (10%) and slurry pH (8) is shown in Figure 4:6. Stoichiometric ratio in lime spray drying is the ratio of the mols of the reactant in the feed slurry to the mols of SO₂ inlet into the scrubber. The variation of the stoichiometric molar ratio directly impacts the absorption efficiency in spray drying. From Figure 4:6, an increase in the absorption efficiency was observed with increasing stoichiometric molar ratio. Improved SO₂

removal at high stoichiometric molar ratios is due to increased concentration of the reactant ($\text{Ca}[\text{OH}]_2$) which maintains the reaction front at the droplet surface and consequently reduces the liquid mass transfer resistance (Hill and Zank, 2000). This was also observed in Figure 4:9 and Figure 4:10 which depict significant influence of the stoichiometric ratio on SO_2 removal efficiency. On the other hand, increasing inlet gas phase temperature impacts negatively on SO_2 absorption efficiency as observed from the model plot in Figure 4:6. Higher inlet gas phase temperatures cause rapid evaporation and reduces the contact time necessary between the droplet and the flue gas (Yang and Kim, 2000). This eventually reduces the removal of SO_2 due to increased driving force for evaporation. A similar effect was also observed in subsequent model plots in Figure 4:9 and Figure 4:10. From the model plot in Figure 4:6, the interactive effects of the temperature and the stoichiometric ratio show higher absorption efficiency of 89% at a temperature of 140°C and a stoichiometric molar ratio of 2 compared to 58% absorption efficiency at 180°C and a stoichiometric molar ratio of 1.

The combined effects of temperature (A) and slurry solid concentration (C) at constant values of stoichiometric ratio (1.5) and slurry pH (8) is shown in Figure 4:7. Slurry solid concentration was observed to have relatively less influence on SO_2 absorption efficiency. There was a slight increase in the efficiency from 67 - 69% when solid concentration was varied from 8% to 12% which was attributed to the increase in the number of reactants (lime particles) available in the slurry for reaction with SO_2 (Scala et al., 2005). This also due to the constant stoichiometric molar ratio of 1.5 used which maintained constant molar ratio of the feed reactants (calcium in slurry and sulphur in flue gas) with varying solid concentrations. Their combined effects show better SO_2 absorption efficiency at low temperatures and high slurry solid concentration. Hence highest absorption efficiency of 84% was observed at lower temperature of 140°C with 12% slurry solid concentration compared to an absorption efficiency of 67% at 180°C with 8% slurry solid concentration. The combined effects of the slurry solid concentration and the stoichiometric ratio is shown in Figure 4:9. The absorption efficiency of SO_2 was found to be significantly improved by 21% (62-83%) when both variables were increased from 8-12% for solid concentration and 1-2 for stoichiometric molar ratio. This illustrates the dominant influence of the stoichiometric ratio on the absorption of SO_2 despite minimal effects of other independent variables.

Figure 4:10 illustrates the interactive effects of the slurry pH and the stoichiometric molar ratio on SO_2 absorption efficiency. This was conducted while keeping the inlet gas phase temperature and

solid concentration constant at their respective central points. The model plot portrays a slight decrease in SO₂ absorption efficiency from 66% to 63% when the slurry pH was decreased from 10 to 6. The decreasing absorption at lower pH is due to increasing concentration of HCl that was used to adjust the slurry pH. The acidic solution of HCl is stronger than the sulphurous acid formed from absorption of SO₂ onto the slurry droplet (Guo et al., 2020). Strong presence of HCl at lower pH increases the concentration of Cl⁻ ions present in the slurry, which will inhibit the dissolution of lime (Ca[OH]₂) particles i.e., diffusion of H⁺ and Ca²⁺ ions within the droplet (Zheng et al., 2002). The presence of HCl in the droplet containing Ca[OH]₂ will result in the formation for CaCl known for its hygroscopic properties. This prolongs the drying of the droplet in the spray chamber and eventually enhances SO₂ absorption. However, it has been reported that the presence of both CaCl and Ca[OH]₂ in a droplet leads to the formation of Ca[OH]₂.CaCl.H₂O complex salt which has a weaker affinity for water (Wang and Keener, 1996). This will impede further absorption of SO₂ in the droplet at high concentrations of CaCl. A similar trend of decreasing SO₂ absorption at lower pH is illustrated in the model plots shown in Figure 4:8 and Figure 4:11. The combined effects from the model plot in Figure 4:10 depicts a more significant effect on SO₂ absorption. A maximum SO₂ absorption efficiency of 87% was obtained at a stoichiometric molar ratio of 2 and a slurry pH of 10.

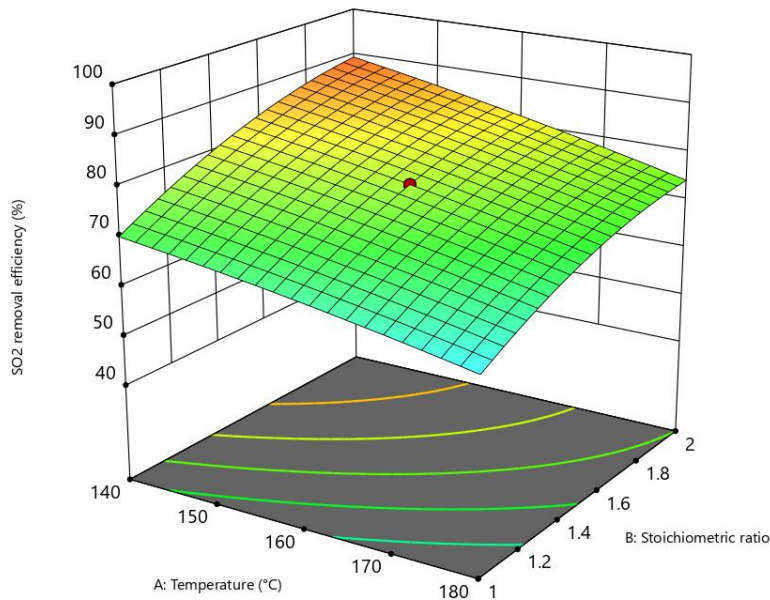


Figure 4:6: Interactive effects of inlet gas phase temperature and stoichiometric ratio on SO₂ removal efficiency.

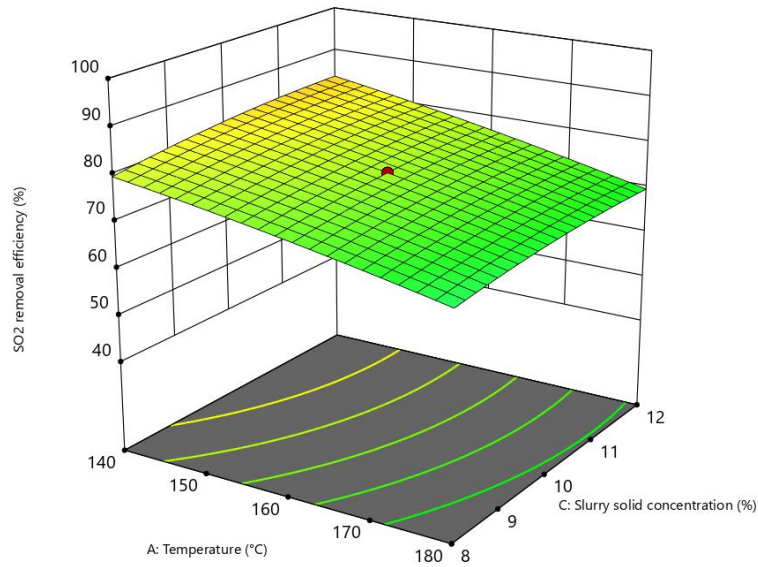


Figure 4:7: Interactive effects of inlet gas phase temperature and slurry solid concentration on SO₂ removal efficiency.

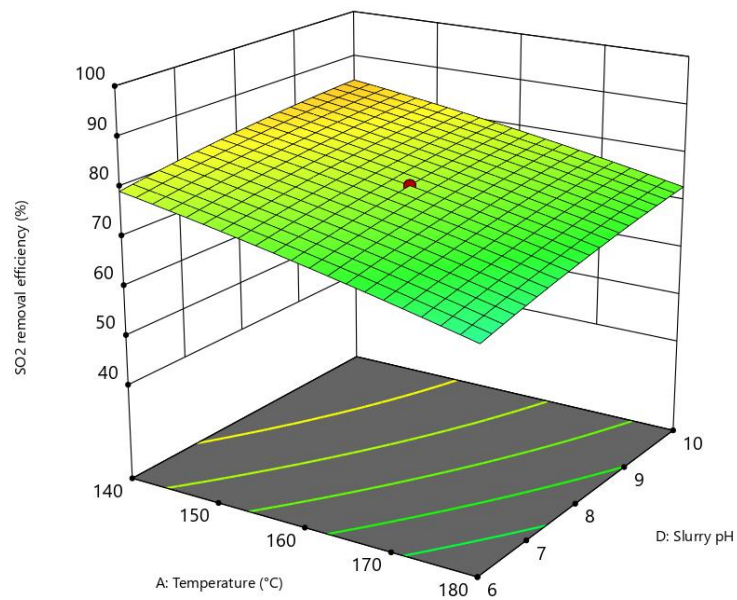


Figure 4:8: Interactive effects of inlet gas phase temperature and slurry pH on SO₂ removal efficiency.

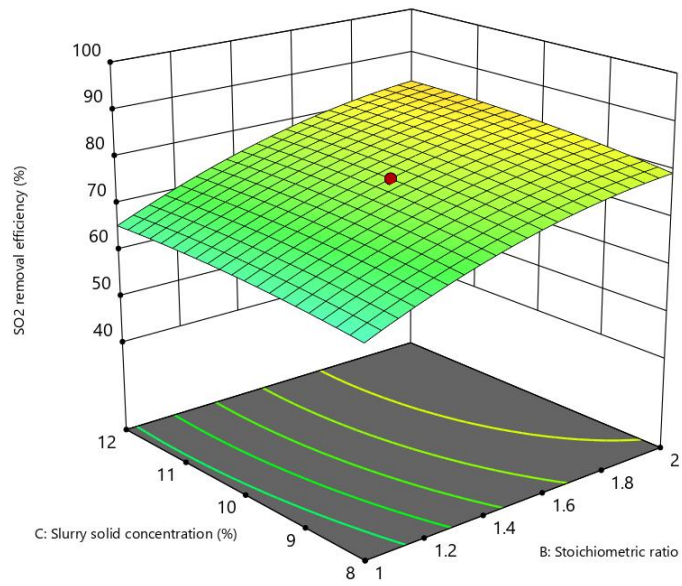


Figure 4:9: Interactive effects of stoichiometric ratio and slurry solid concentration on SO₂ removal efficiency.

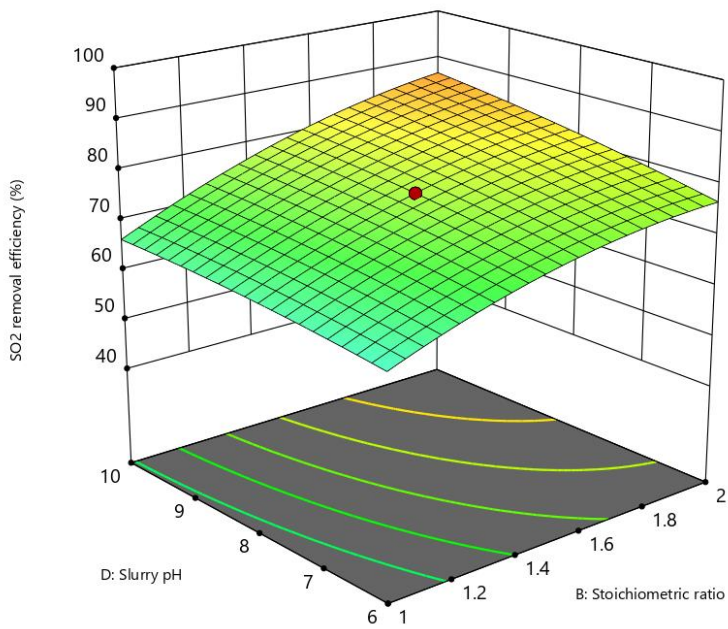


Figure 4:10: Interactive effects of stoichiometric ratio and slurry pH on SO₂ removal efficiency.

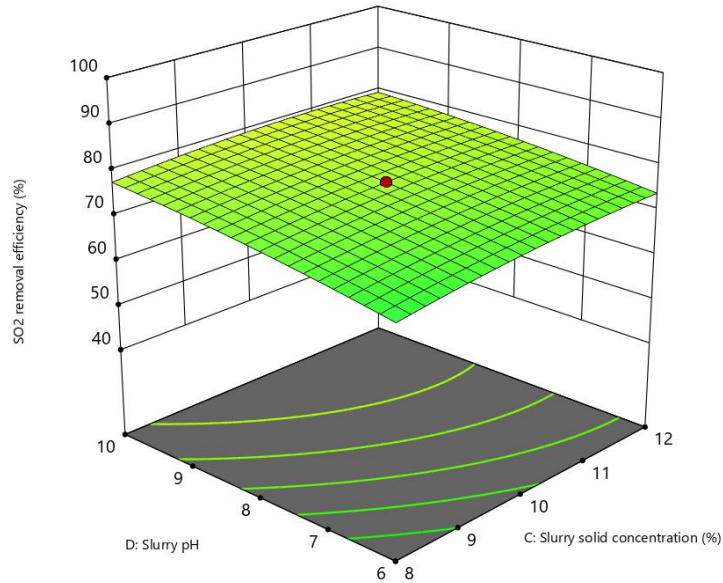


Figure 4:11: Interactive effects of slurry solid concentration and slurry pH on SO₂ removal efficiency.

4.5.5. Optimization of desulphurization variables

Spray drying absorption involves scrubbing of SO₂ from flue gas by contacting it with alkaline (lime) slurry. Efficient SO₂ removal requires operation of the spray dryer at most appropriate conditions of the variables. In the present study, independent variables were evaluated to get optimal conditions necessary to achieve maximum SO₂ absorption. Design expert v13.0.1.0 was used to generate the set of optimum conditions of independent variables with the predicted values of the response i.e., SO₂ removal efficiency using numerical optimization function called desirability. Desirability function is an objective function the most commonly used for optimization of responses. It is based on the idea that the "quality" of a product or process that has multiple quality characteristics, with one of them outside of some "desired" limits, is completely unacceptable (Heckert *et al.*, 2002). The method assigns a "score" between 0 (least) and 1 (most) to a response and chooses factor settings that maximize that score. If any of the responses falls outside their desirability range, the overall function becomes zero (Amjed *et al.*, 2017). Optimization criteria chosen for all independent variables and responses is shown in Table 4:5:

Table 4:5: Criteria for numerical optimization of SO₂ absorption in a spray dryer.

Variable/Response	Goal	Lower limit	Upper limit
x_1 : Inlet gas temperature	minimize	140	180
x_2 : Stoichiometric ratio	in range	1	2
x_3 : Slurry solid concentration	minimize	8	12
x_4 : Slurry pH	maximize	6	12
SO ₂ removal efficiency	maximize	48	93

The optimum process conditions and response were generated from the software. The optimum conditions for independent variables based on the highest desirability value were found to be at inlet gas phase temperature of 140°C, stoichiometric molar ratio of 2, slurry solid concentration of 8% and slurry pH of 10. These set of optimum conditions produced SO₂ removal efficiency of 90% with a desirability of 0.98. To verify the optimization results, experiments were conducted under the recommended optimal conditions for SO₂ absorption. Experiments under these conditions gave 91.2% SO₂ removal efficiency with an error of 1.33% which is within the acceptable limits.

4.5.6. Analysis of the desulphurization products

The mineralogical composition of the final desulphurization products was conducted by both XRD and XRF analyses. Figure 4:12 shows XRD patterns for final desulphurization product samples obtained at different experimental conditions (i.e., at SR 1.0 and 2.0 respectively). The figure reveals the presence of both portlandite (Ca[OH]₂) and hannebachite (CaSO₃.0.5H₂O) in the final desulphurization products which was also observed by Bigham (2005). The desulphurization samples had residual peaks of Ca[OH]₂ appearing at $2\theta = 20.9, 34, 40, 55$ and 60° which indicates incomplete reaction of Ca[OH]₂ in the final product. Low sorbent utilization is a major drawback in lime spray drying which in this case was observed by the significant presence of portlandite in the final desulphurization product. This is in agreement with the observation made by Zhou et al., (2009) and Bigham et al., (2005) on XRD analysis of semidry FGD products. The diffraction patterns also show the presence of CaSO₃.0.5H₂O in both final products appearing at $2\theta = 18.5$

and 27.5°. $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ is a desulphurization product resulting from a reaction between SO_2 and $\text{Ca}[\text{OH}]_2$ in the spray dryer. This is evident from SEM micrographs illustrated in Figure 4:13(b) with SR of 1.0 which were observed to have needle-like shaped particles deposited on the sorbent surface, a common physical characteristic for calcium sulphite and gypsum particles (Küspert and Krammer, 2012). Poor sorbent utilization and conversion due to high stoichiometric ratio of 2.0 resulted in particles of partially unreacted sorbent forming larger aggregates as depicted in Figure 4:13(c). Figure 4:13(a) is the raw hydrated lime sorbent showing a relatively porous material before exposure to desulphurization.

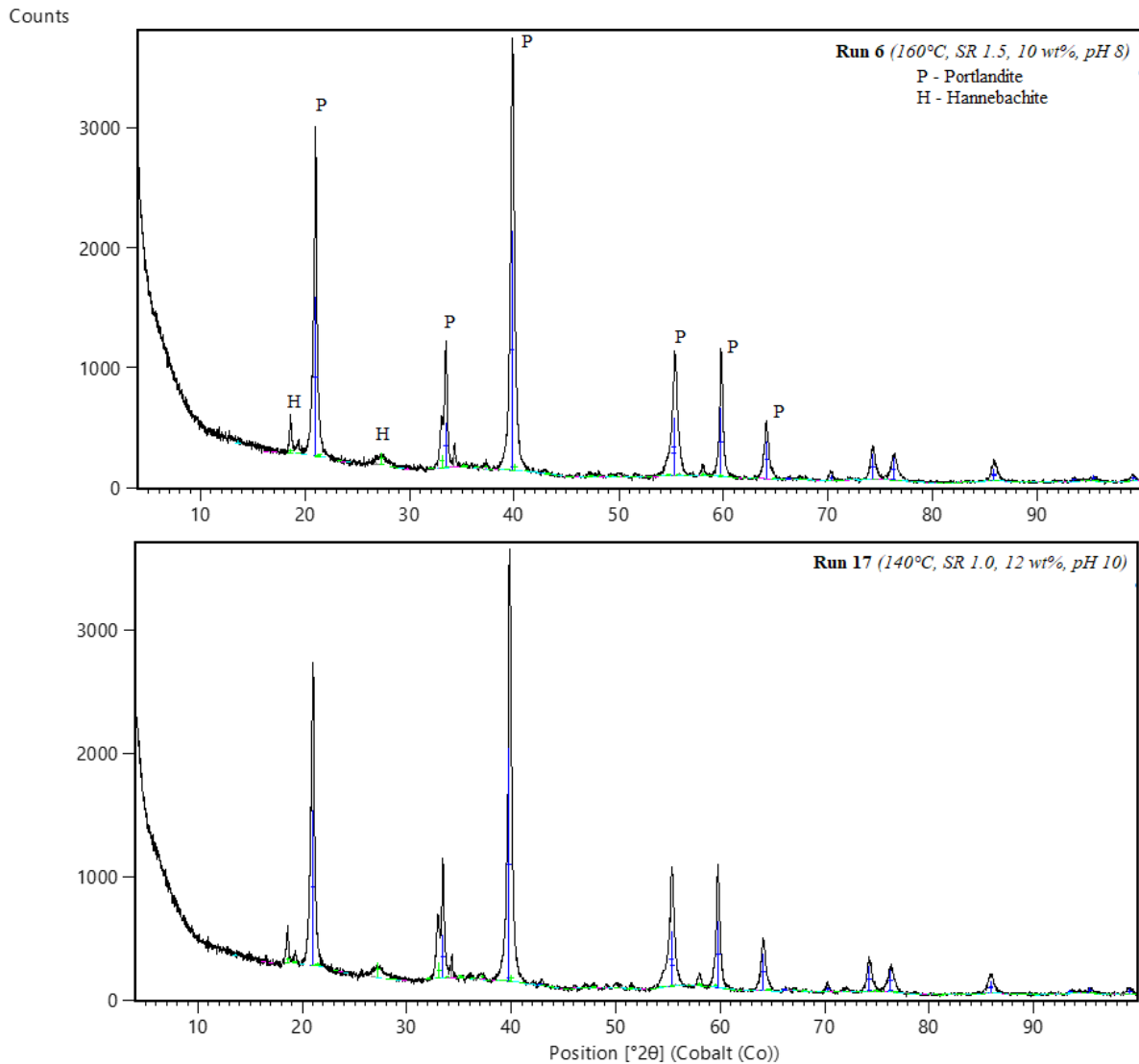


Figure 4:12: XRD patterns for final desulphurization products (experiment 6 and 17).

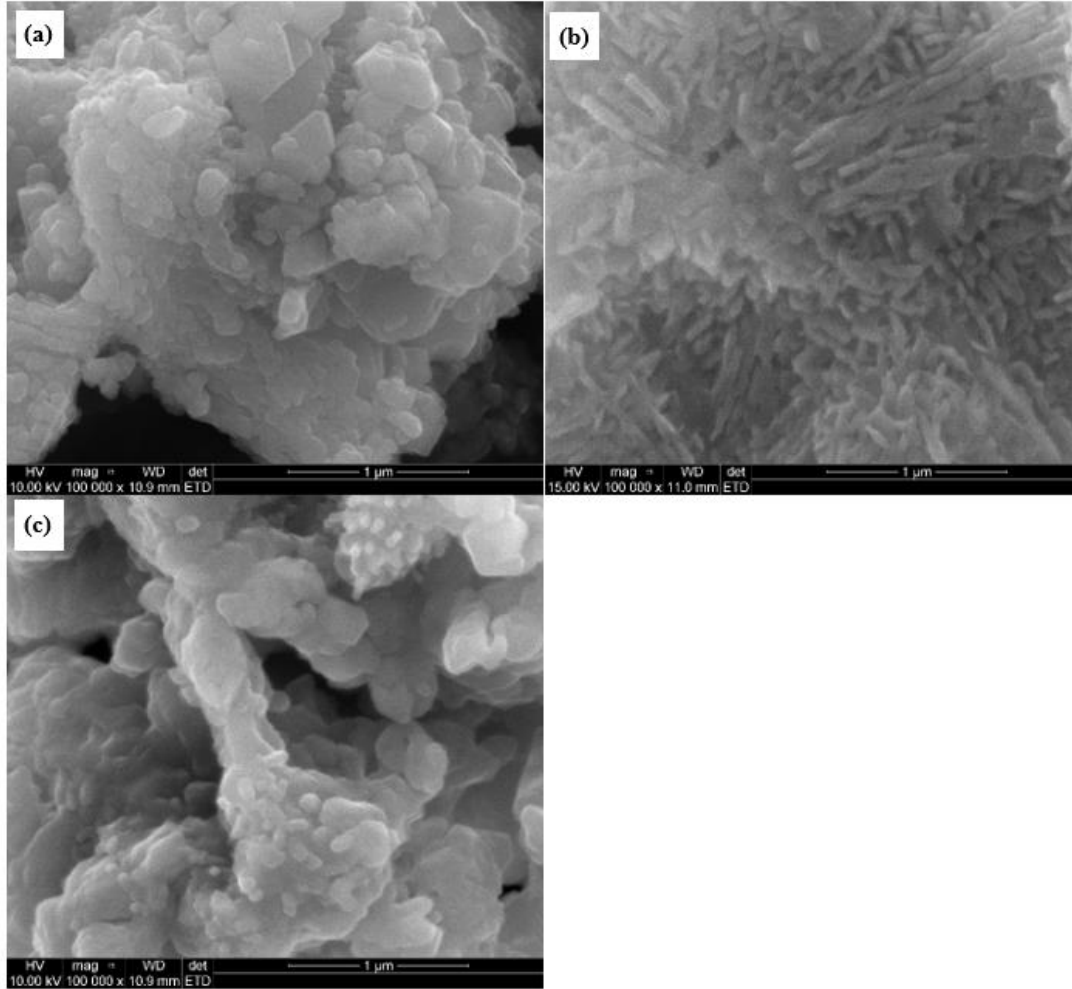


Figure 4:13: SEM micrographs for (a) hydrated lime sorbent, (b) final desulphurization product (140°C, SR 1.0, 8 wt%, pH 10), and (c) final desulphurization product (140°C, SR 2.0, 12 wt%, pH 6).

Table 4:6 shows the quantitative mineralogical compositions for hydrated lime and final desulphurization products measured by XRF analysis. The analysis shows a decline in CaO content from 89 wt% for raw hydrated lime sorbent to 75 wt% at SR of 1.0 and 78 wt% at SR of 2.0. A higher concentration of CaO in the desulphurization product at SR of 2.0 is due to the excess use of the sorbent. This implies that part of $\text{Ca}[\text{OH}]_2$ reacted with SO_2 resulting in the formation of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ in the final product (Xie et al., 2017). This is evident from the presence of SO_3 in the final products as observed in Table 4:6. From the analysis, a higher concentration of 14% SO_3 in the final product was achieved at SR of 1.0 compared to 11% SO_3 at SR of 2.0. This indicates better sorbent conversion at lower stoichiometric ratios as also observed in SEM and FTIR analyses.

Table 4:6: Mineralogical compositions of hydrated lime and desulphurization products at different stoichiometric ratios.

Oxide	Hydrate lime	Desulphurization products	
		SR=1.0	SR=2.0
Al ₂ O ₃	0.78	0,04	0,01
K ₂ O	0.05	0,02	0,02
CaO	89.55	75,77	78,08
MgO	1.12	0,62	0,60
TiO ₂	0.06	0,04	0,03
SO ₃	0.13	13,74	11,76

Figure 4:14 shows normalized FTIR spectra for hydrated lime and the desulphurization products at SR of 1.0 and 2.0 respectively. The IR spectra for both desulphurization products reveal strong bands appearing 652, 938 and 988 cm⁻¹ which are attributed to calcium sulphite hemihydrate, a product of desulphurization reaction involving Ca[OH]₂ and SO₂. Other bands assigned to sulphite ions appear at 652 and 712 cm⁻¹ (Guan et al., 2011; Pekov et al., 2012). These bands confirm the presence of sulphur oxide content as detected by XRF analysis for both desulphurization products. Both samples of the desulphurization products had similar functional groups appearing across the spectral range. The IR spectra for hydrated lime sorbent differ from the desulphurization products and do not contain sulphite bands. It has strong bands appearing at 712, 875, and 1401 cm⁻¹ representing the presence of portlandite (Ca[OH]₂) in the raw sorbent. The other main differences between hydrated lime and desulphurization products are the relative intensities of portlandite peaks. These absorption bands are significantly diminished in the desulphurization products confirming the absorption of reaction between Ca[OH]₂ and SO₂.

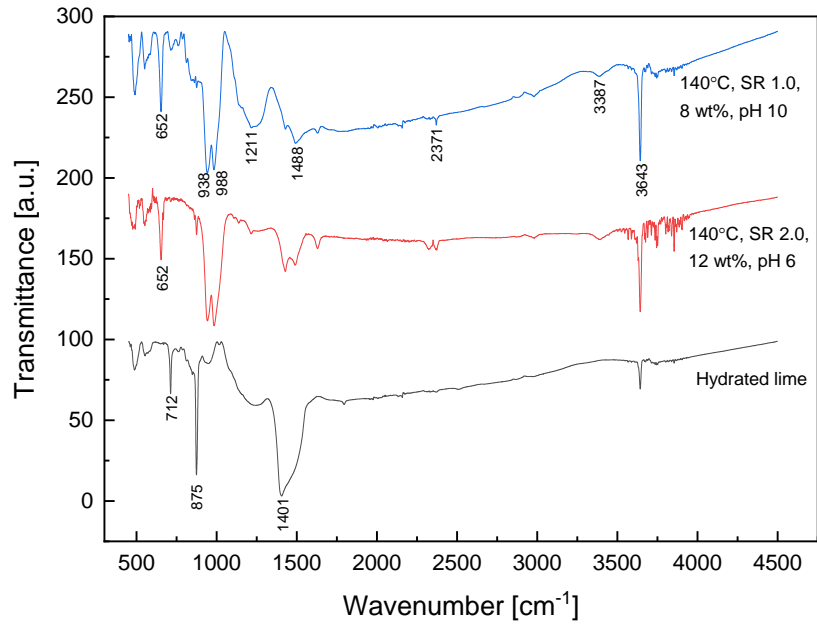


Figure 4:14: FTIR spectra for hydrated lime and final desulphurization products.

4.6. Conclusion

This study presents the findings of the influence of spray drying characteristics on SO₂ absorption efficiency. RSM was used to analyse and optimize the independent variables which include inlet gas phase temperature, stoichiometric molar ratio, slurry solid content and slurry pH. A predictive quadratic model correlating the variables and response was developed using CCD. The analysis of the model was found to best describe the relationship with a regression coefficient of 0.93 when compared to the experimental data. The model results indicated stoichiometric molar ratio as a variable with significant influence on the absorption of SO₂. Under the recommended optimal conditions of inlet gas phase temperature of 140°C, stoichiometric ratio of 2, slurry solid concentration of 8% and slurry pH of 10, a removal efficiency of 90% for SO₂ can be achieved. The analysis of the desulphurization product by XRD, FTIR and SEM confirm the presence of hannebachite (CaSO₃·0.5H₂O), a product of desulphurization reaction. Residual Ca[OH]₂ in the final product reveal poor conversion especially at high stoichiometric ratios. This study contributes to the understanding of the interactive effects of the variables on the absorption of SO₂ and will help on efficient operation in spray drying FGD.

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5. Comparative study of sorbents for spray drying FGD

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5.1. Abstract

This study presents the findings of an investigation into spray drying absorption of SO₂ from flue gases. The experimentation involved the evaluation of different sorbents (i.e., hydrated lime, limestone and trona) with relevant properties for spray dry flue gas desulphurization (FGD). Experiments were conducted to explore the effects of spray characteristics on SO₂ removal efficiency using the selected sorbents. Results show that trona has better performance characteristics with the highest SO₂ absorption efficiency of 94% at an inlet gas phase temperature of 120°C and a stoichiometric molar ratio of 1.5. Under the same operating conditions, hydrated lime and limestone achieved 82 and 76% SO₂ removal efficiency respectively. The analysis of the desulphurization product by XRF and FTIR analytical methods revealed the presence of SO₃ in the samples; a product of desulphurization reaction. Significant proportion of unreacted sorbent was observed when hydrated lime and limestone sorbents were used. The evaluation of the degree of conversion also revealed that trona had the highest conversion of 96% at a stoichiometric ratio of 1.0. Hydrated lime and limestone had 63 and 59% conversion respectively under the same operating conditions.

Keywords: spray drying, desulphurization, sorbents, experimentation.

5.2. Introduction

Flue gas desulphurization (FGD) is a commercially proven technology for removal of SO₂ from flue gas which is considered as a significant pollutant to the environment. There are three types of FGD for removal of SO₂ from flue gas namely: dry, semi-dry and wet FGD technology. Wet limestone FGD process accounts for up to 87% of the market share of the FGD systems that are currently used in large utility boilers (Moganelwa et al., 2018; Ortiz and Ollero, 2008). It has been a choice for many utility plants due to its reliability, high SO₂ removal efficiency and availability of the sorbent (limestone). On the other hand, interest in the use of spray drying FGD technology has predominantly increased in the last decade. This is mainly due to variety of factors including reduced installation and operating cost requirement, ease of retrofit to existing plants due to less space requirement and ease of product handling which requires no sludge handling equipment and associated maintenance and operating costs (Miller and Miller, 2010; Rogoff and Screve, 2011; Scala et al., 2004). Despite the high reagent cost and low reagent utilization for dry and semi-dry processes, they have proven to have the ability to remove SO₂ from flue gas well above legislative limits (GEA Niro, 2020).

In the spray drying process, a concentrated sorbent slurry is introduced at the top of the absorber via two-fluid nozzle or rotary atomizers. This produces fine mist of droplets containing the sorbent which reacts with SO₂ contained in the untreated flue gas from the boiler. The water in the slurry will humidify and allow cooling of the flue gas from higher temperatures to about 17 °C above the water saturation temperature (EPRI, 2007). This requires careful control of the amount of water fed into the spray dryer to avoid complete saturation of the flue gas. The residence time in the absorption chamber is sufficient to allow SO₂ and other gases such as SO₃ and HCl to react with the sorbent (Carpenter, 2012). In the spray chamber, evaporation of water and drying of the droplet takes place as it flows downwards concurrently forming a dry waste product containing sulphite and sulphate salts (Carpenter, 2012). Part of the dry waste is collected at the bottom of the absorber while the remaining suspended solids are removed by the particulate control device such as baghouse or ESP (Srivastava, 2000).

The operating cost in an FGD process mainly depends on the amount and type of sorbent used, water, electricity consumptions, maintenance, and the end-product disposal cost. Over time, remarkable strides have been made to improve the efficiency of this process. Spray dry scrubbing

process utilizes several sorbents for absorption of SO₂ from flue gas. It uses appropriate alkali sorbents which are either calcium or sodium based. The most commonly used sorbents include hydrated lime, pre-calcined limestone or sodium carbonate which are typically prepared by continuously mixing in a slurry tank to avoid sedimentation and agglomeration (Yang and Kim, 2000). Although hydrated lime (Ca[OH]₂) is expensive compared to limestone, it has been extensively used in spray drying FGD processes due to its reactivity towards SO₂. Trona has been tested and proven to be more reactive with greater conversion levels approaching unity (Erdöl-Aydin and Nasün-Saygılı, 2007). This provides the possibility of using alternative sorbents in spray dry scrubbing process to improve its performance against the well-established wet FGD technology.

The selection of better performing sorbent poses a great challenge to FGD in power utilities due to crucial requirements and compatibility. Despite the capabilities shown by existing spray drying scrubbers using hydrated lime as a sorbent, there is still dominant challenge of poor sorbent utilization. In this study, appropriate sorbents (i.e., hydrated lime, limestone, and trona) for spray dry scrubbing FGD process were identified through detailed parametric experiments. The sorbents were characterized and subjected to varying experimental conditions to compare their performances on SO₂ absorption in a spray dryer. The spray drying characteristics such as inlet gas phase temperature, stoichiometric ratio, slurry concentration and flowrate were closely monitored while controlling the input and output state variables. The potential of absorbing SO₂ at low stoichiometric ratios was explored which offers significant advantage for high sulphur coal-based power plants.

5.3. Experimental

Experiments in this study were carried out using a co-current flow laboratory-scale Buchi B290 Mini Spray Dryer. A schematic of the spray dryer is shown in Figure 5:1. It comprises of slurry preparation, spray drying chamber, flue gas analysis and other accessories. The spray chamber is made of a cylindrical borosilicate glass 3.3 with a diameter of 0.16 m and a height of 0.6 m allowing a mean residence time of 1 – 1.5 seconds. In this study, three different sorbents for desulphurization in SDS were identified and investigated namely: hydrated lime, trona and limestone. Their chemical and physical properties are summarized in Table 5:1. The respective sorbent slurries were prepared by continuously mixing the sorbent with appropriate amount of

water in a reaction vessel to obtain the desired solid concentration. The prepared sorbent slurry was then introduced via a two-fluid nozzle into the spray dryer at controlled feed rate to maintain the required stoichiometric molar ratios.

The simulated flue gas was generated by blending 99% SO₂ with ambient air at controlled flow to achieve the desired inlet SO₂ concentration. The temperature of the inlet flue gas was regulated using an electrical heater located at the spray chamber entry. The two-fluid nozzle in the spray chamber disperses the sorbent slurry to produce fine droplets to come into contact with the heated flue gas. In the spray chamber, simultaneous drying, evaporation, and absorption takes place resulting in a final dry product collected at the bottom of the chamber and captured by the cyclone separator. In order to carry out desulphurization studies, the spray chamber was modified to allow multiple measurement of SO₂ concentration along the chamber. Throughout each experimental run, the flue gas flowed continuously, and the sorbent slurry was also sprayed continuously. Flue gas was continuously sampled at 5 different points (95 mm apart) along the chamber as shown in Figure 5:1 for temperature (°C) and SO₂ concentration (ppm). The ranges of operating parameters used for this study are presented in Table 5:2.

A variety of characterization techniques were used to determine the physical and chemical properties of the sorbent and the dry desulphurization product. Micromeritics ASAP™ 2020 Porosity Analyzer for Brunauer-Emmet-Teller (BET) surface area analysis was used to determine the N₂ adsorption-desorption isotherms at 77K for the samples. The chemical composition in the samples was determined using X-ray fluorescence (XRF) analysis. X-ray diffraction (XRD) technique using Malvern Panalytical Aeris diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K α radiation was used to determine the qualitative analysis of the samples. The phases present were identified using X'Pert Highscore plus software. The functional groups present in the samples were determined by Fourier Transform Infrared (FTIR) analysis using Perkin-Elmer Spectrum Two™ machine. The morphological structures of the samples were examined using scanning electron microscopy (SEM) machine.

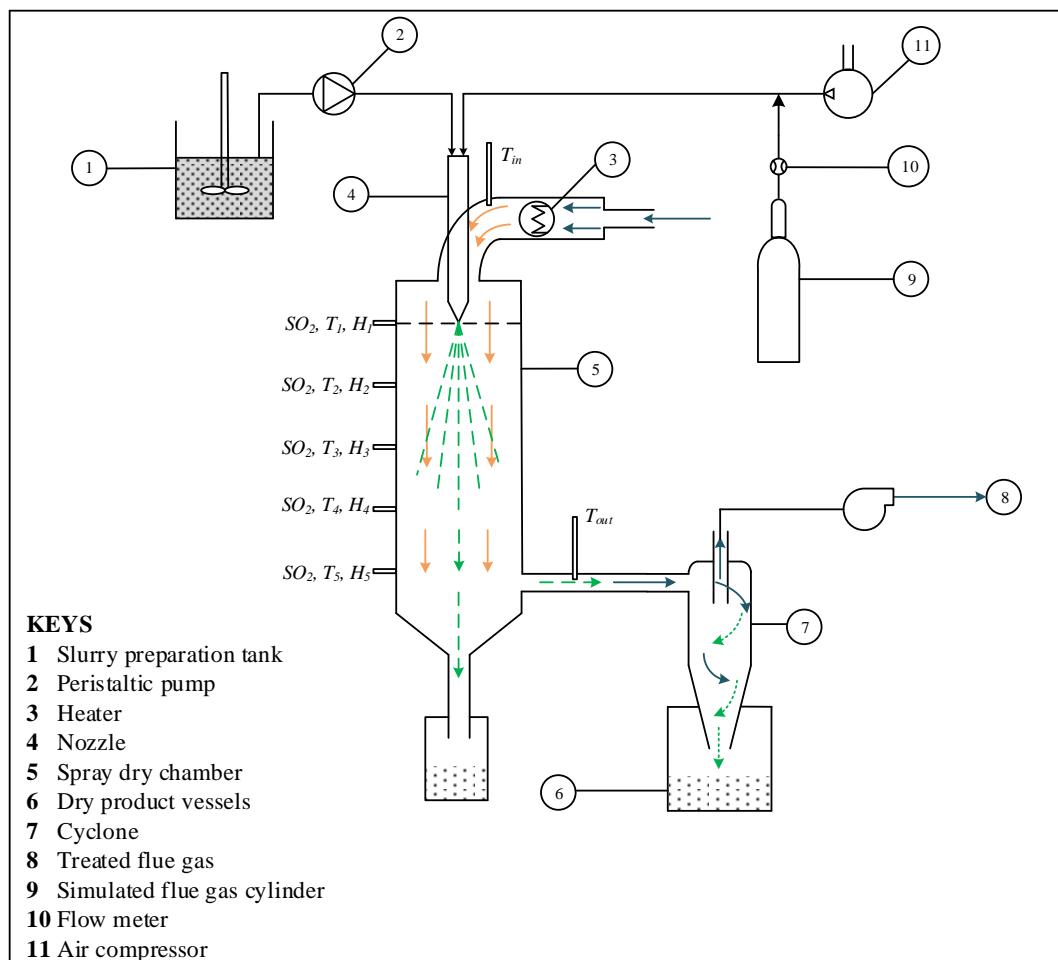


Figure 5:1: Lime spray drying experimental setup.

Table 5:1: Chemical and physical properties for the hydrated lime, trona and limestone sorbents used.

		Hydrated lime	Trona	Limestone
Components	SiO ₂	7.38%	0.05%	1.37%
	Al ₂ O ₃	0.79%	0.02%	0.40%
	K ₂ O	0.05%	0.02%	0.08%
	Mn ₃ O ₄	0.12%	0.15%	1.09%
	CaO	89.55%	0.13%	94.53%
	MgO	1.12%	0.02%	2.03%
	TiO ₂	0.06%	0.01%	0.01%

	Na ₂ O	0.23%	99.39%	0.02%
	SrO	0.19%	0.06%	0.01%
	ZrO ₂	0.02%	0.02%	0.01%
	SO ₃	0.13%	0.02%	0.17%
	Fe	0.34%	0.10%	0.28%
	P	0.03%	0.01%	0.01%
N ₂ BET Surface area (m ² /g)		4.24	0.36	2.51

Table 5:2: Process parameters

Process parameter	Range
Inlet air temperature (°C)	120 – 180
Feed air flow rate (m ³ /h)	20 – 35
Slurry solid concentration (%)	6 – 12
Atomizing air flowrate (l/h)	350 – 750
Calcium to sulphur ratio	1 – 2
Flue gas SO ₂ concentration (ppm)	500 – 2000

5.4. Results and discussion

5.4.1. Analysis of sorbent properties

The components of the respective sorbents used in this study were analyzed using both XRF and XRD analytical methods. Table 5:1 shows the chemical composition of the sorbents determined by XRF analysis while the diffraction patterns of the sorbents are represented in Figure 5:2. Chemical analysis indicates various components identified in each sorbent with CaO being a dominant component for both hydrated lime and limestone having 89.55 and 94.53% relative phase amounts, respectively. This is evident in the diffraction patterns which indicates limestone having calcite (CaCO_3) as a major crystalline component appearing at $2\theta = 34.5, 42, 46, 50.5, 56$ and 57° . Similarly, hydrated lime contains portlandite ($\text{Ca}[\text{OH}]_2$) as a major crystalline component appearing at $2\theta = 20.9, 33, 39.5, 55, 59.5, 64$ and 74° . From the XRF results, hydrated lime also contains low concentration of SiO_2 (7.38%), which appears on the diffraction pattern as quartz at $2\theta = 24, 31, 42.5, 47, 49$ and 53.5° . Trona sorbent on the other hand has significant concentrations of Na_2O (99.39%) from XRF analysis. This is a major component in trona identified as Nahcolite (NaHCO_3) from the diffraction patterns appearing at $2\theta = 21.1, 35.2, 38.5, 40$ and 67.5° . In general, the contents CaCO_3 , $\text{Ca}[\text{OH}]_2$ and NaHCO_3 in the respective sorbents are crucial in the total sulphation capacity values of their slurries. The reactivity of these major components towards SO_2 also play an important role in their sulphation capacities. The N_2 BET surface areas for the selected sorbent are presented in Table 5:1. Hydrated lime sorbent has the highest specific surface area of $4.24 \text{ m}^2/\text{g}$ while limestone had a specific surface area of $2.51 \text{ m}^2/\text{g}$. Trona on the other hand had relatively low specific surface area of $0.36 \text{ m}^2/\text{g}$ which could be considered as low porosity material.

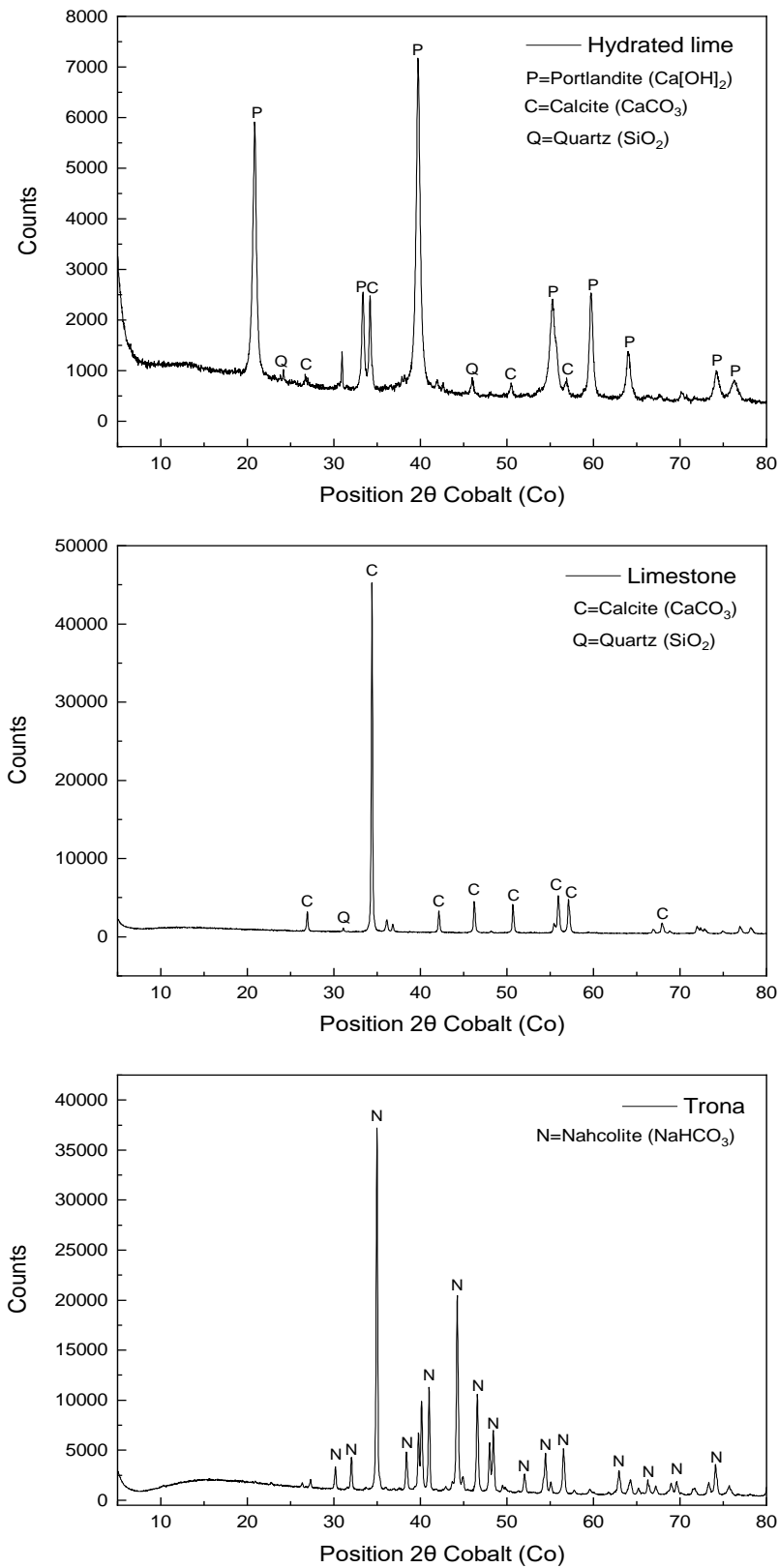


Figure 5:2: XRD diffraction patterns for hydrated lime, limestone and trona sorbents.

5.4.2. Effects of spray drying desulphurization variables

5.4.2.1. Effect of stoichiometric molar ratio

Stoichiometric molar ratio in a spray drying absorption system is defined as the ratio of mols of fresh absorbent to the mols of SO₂ inlet to the scrubber. This ratio is critical for the performance of spray dryer because it indicates the consumption of the sorbent which is an important economic consideration in the process (Ollero et al., 1997). Experiments were performed for the selected sorbents investigated under varied stoichiometric molar ratios ranging from 1 to 2.5. This was investigated by regulating the slurry flowrate and concentration while keeping a constant gas phase SO₂ concentration of 1000 ppm and inlet gas phase temperature at 140 °C. Figure 5:3 illustrates the effect of stoichiometric molar ratio on SO₂ removal efficiency for hydrated lime, limestone and trona respectively. Generally, the results show improved SO₂ removal efficiency at high stoichiometric molar ratios for all sorbents. For the range of sorbents studied, there was a steady increase in the removal efficiency when the stoichiometric molar ratio was varied from 1 to 2.5. It was observed that trona has high SO₂ absorption efficiency up to 98% at SR=2.0 compared to 94% SO₂ removal efficiency at SR=2.5 for hydrated lime and 59% SO₂ removal efficiency at SR=1.75 for limestone. On the other hand, poor reactivity of limestone towards SO₂ in a spray drying system is evident from low SO₂ absorption efficiencies over the range of experimental conditions with a maximum absorption value of 59% at a stoichiometric ratio of 1.75. From the range of experiments conducted, it can be noted that the hydrated lime had a maximum SO₂ absorption value of 94% at stoichiometric molar ratio is 2.5. Although this was case, significant deposition of the sorbent on the spray chamber wall was observed at stoichiometric ratios beyond 2.0. Furthermore, the use high stoichiometric ratios in the experiments led to poor sorbent utilization as observed in the chemical analysis of the dried sorbent (Table 5:3) and the evaluation of the degree of conversion (Figure 5:5). The results are in good agreement with the performance trends reported in literature where it has been reported that at high stoichiometric molar ratio, there is increased sorbent particle concentration near the surface of the droplet which reduces the liquid-phase mass transfer resistance (Hill and Zank, 2000; Newton et al., 1990). High sorbent particle concentration also reduces the amount of water in the droplet and in turn increases the droplet count. This subsequently increases the surface area for mass transfer of SO₂ (Ollero et al., 1997).

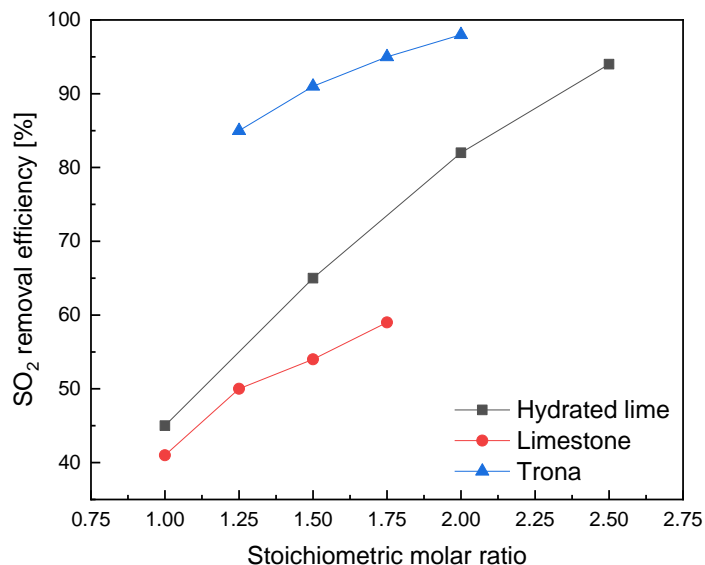


Figure 5:3: Effect stoichiometric molar ratios on SO₂ removal efficiency for hydrated lime, limestone and trona.

5.4.2.2. Effect of inlet gas phase temperature

Several experiments were performed to demonstrate the influence of inlet gas phase temperature on absorption efficiency of SO₂ in the spray dryer. This was investigated by varying the inlet gas temperature between 120 - 180 °C, while all other parameters were kept constant. Figure 5:4 illustrates the influence of inlet gas phase temperature on SO₂ absorption efficiency for the three sorbents. The results show a steady drop in the absorption efficiency with increasing temperature for all sorbents. This is attributable to accelerated evaporation rate at high temperatures which significantly reduces the period necessary for SO₂ absorption in the dryer. The absorption of SO₂ in a spray dryer is an aqueous reaction and thus the rate of evaporation is crucial in determining the overall SO₂ capture. Trona was observed to exhibit the highest absorption efficiency of up to 96% at 120 °C compared to both hydrated lime (82%) and limestone (76%). This proves that it is highly reactive towards SO₂ especially above 110 °C which has been reported to decompose NaHCO₃ component in trona at this temperature (Erdöl-Aydin and Nasün-Saygili, 2007). Limestone on the other hand exhibited lower absorption efficiencies over the range of temperatures investigated with a significant drop at elevated temperatures. Sorbent dissolution contributes significantly towards its reactivity with SO₂ in the spray dryer. High temperatures mostly impede dissolution of limestone resulting in poor reactivity towards SO₂ are observed in the experimental findings.

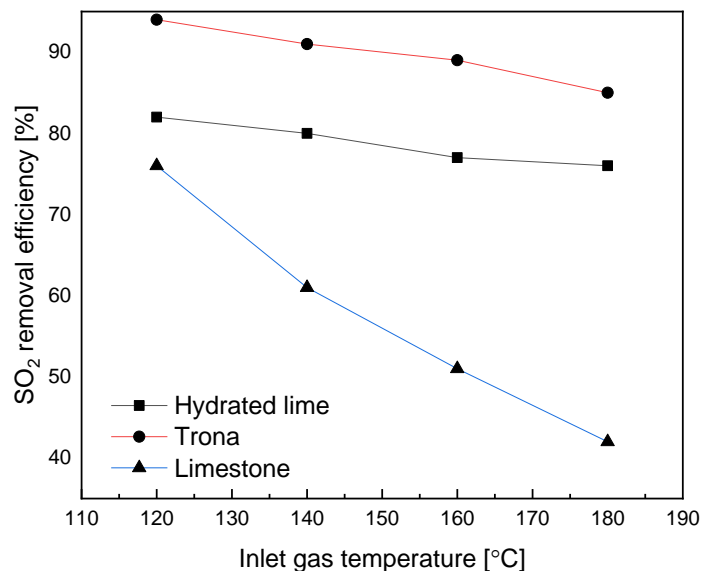


Figure 5:4: Effect of inlet gas phase temperature on SO₂ removal efficiency.

5.4.2.3. Sorbent utilization and conversion

Chemical analysis of the final products collected after desulphurization was carried out to determine sulphite content from the spray dryer. The concentration of sulphite in the dried product is a direct indication of the utilization of the sorbent. Table 5:3 shows chemical analysis of the dried product at different stoichiometric ratios for all the sorbents studied. A general trend observed from this was the increasing concentration of unreacted sorbent (Ca[OH]₂, CaCO₃, and Na₂CO₃) with increasing stoichiometric molar ratios. The final product collected from trona had significant concentrations of 44.4% Na₂CO₃ at a stoichiometric molar ratio of 2.0 compared to 34.7% Na₂CO₃ concentration for the desulphurization product collected at a stoichiometric molar ratio of 1.0. Although there was poor sorbent utilization at high stoichiometric ratio of 2.0, a high SO₂ removal efficiency of 98% was achieved for trona sorbent. Significant fraction of unreacted Na₂CO₃ (low sorbent utilization) leads to increased absorption reaction between SO₂ and the sorbent resulting in high SO₂ absorption efficiency at high stoichiometric molar ratio. Table 5:3 also shows relatively better sorbent utilization at low stoichiometric ratio of 1.0 for both hydrated lime and limestone due to the lower concentrations of unreacted Ca[OH]₂ (53.4%) and CaCO₃ (73.3%) respectively in comparison with the stoichiometric ratio of 2.0. The relatively high concentrations of unreacted Ca[OH]₂ (60.2%) and CaCO₃ (77.5%) at stoichiometric ratio of 2.0 for hydrated lime and limestone respectively is indication of low sorbent utilization.

Table 5:3: Desulphurization product compositions at varying stoichiometric ratios

	SR = 1.0	SR = 1.5	SR = 2.0
Hydrated lime			
Ca[OH] ₂	53.4	57.6	60.2
CaSO ₃	43.6	40.2	38.1
Limestone			
CaCO ₃	73.3	74.5	77.5
CaSO ₃	21.7	24.6	21.7
Trona			
Na ₂ CO ₃	34.7	35.6	44.4
Na ₂ SO ₃	63.3	62.7	53.8

A theoretical evaluation of the utilization of the sorbent was evaluated based on the degree of conversion of the sorbent after SO₂ absorption. This was evaluated as follows:

For hydrated lime and limestone:

$$x_{Ca} = \frac{N_{SO_2,i} - N_{SO_2,o}}{N_{Ca_i}}$$

Where N_{Ca_i} is the molar concentration of calcium in the feed slurry.

For trona:

$$x_{Na} = \frac{N_{SO_2,i} - N_{SO_2,o}}{N_{Na_i}}$$

Where N_{Na_i} is the molar concentration of sodium in the feed slurry.

Figure 5:5 illustrates the degree of conversion evaluated for hydrated lime, trona and limestone respectively under varying inlet gas phase temperatures (120 - 180°C) and stoichiometric molar ratios (1.0 - 2.5). Generally, there was a high conversion for all sorbents at low temperatures with the highest conversion observed at 120°C. Trona was observed to have the highest conversion of

up to 96% at 140°C using Ca:S ratio of 1.0, while hydrated lime and limestone achieved a maximum conversion of 63% and 59% respectively at 140°C. It has been reported that an increase in temperature causes a decrease in trona microporosity and macropore surface area and leads to a decrease in active surface area of Na_2CO_3 (Doğu et al., 1992). This is evident from the significant drop in the conversion of trona at higher temperatures of 160 and 180°C. Besides better absorption properties of trona towards SO_2 compared to both hydrated lime and limestone, it also had the highest sorbent conversion. Hydrated lime and limestone had poor sorbent utilization as observed in chemical analysis of the dried product and it will require recirculation of significant amount of the spent sorbent to improve its utilization. Hydrated lime exhibited better conversion when utilized as a sorbent in the spray dryer as shown in Figure 5:5 in comparison with limestone sorbent. This is due to high reactivity towards SO_2 contributed by various factors such as relatively high sorbent specific surface area. Low conversion for all the sorbents at high temperature of 180°C was observed and this was mainly due to accelerated droplet evaporation rate which limits its lifetime for conversion and SO_2 absorption. The results also show a consistent trend of decreased conversion of the sorbent with increasing stoichiometric molar ratios for all sorbents investigated. This trend is in good agreement with literature which is due to negligible internal mass transfer resistances for SO_2 at high stoichiometric ratios (Hill and Zank, 2000; Scala et al., 2005). In general, trona has better performance characteristics on the absorption of SO_2 compared to hydrated lime and limestone due to high absorption efficiencies under varying experimental conditions and better sorbent utilization and conversion.

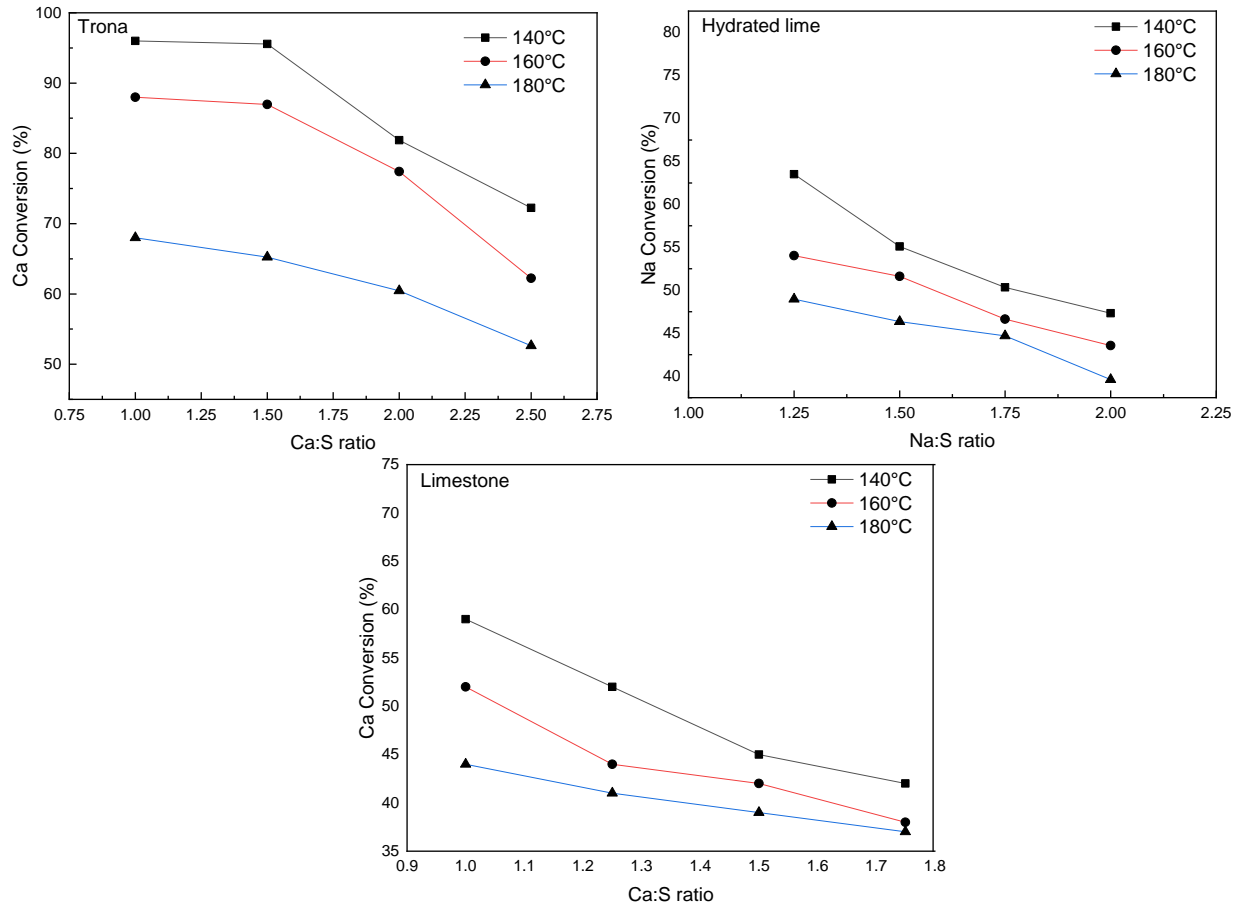


Figure 5:5: Evaluated degree of conversion at different stoichiometric ratios for hydrated lime, trona and limestone.

5.4.3. Analysis of final product

5.4.3.1. SEM analysis

Scanning electron microscopy (SEM) analysis was performed to observe the changes in the chemical and crystal structures of the sorbent samples during desulphurization. Figure 5:6(a-c) shows SEM micrographs for desulphurization product samples for hydrated lime, limestone and trona sorbents respectively. The samples were collected under the same experimental conditions with an inlet gas phase temperature of 140°C and stoichiometric ratio of 1.5. Figure 5:6(a) represent SEM micrograph for hydrated lime desulphurization product which reveals particles with rough surfaces agglomerated together. These are products of desulphurization which include partially reacted particles aggregating to form larger particles. This is also observed in Figure

5:6(b) SEM micrograph for limestone desulphurization product. It shows more aggregated particles which potentially limits exposure of unreacted particles resulting in poor sorbent utilization as confirmed by XRF analysis (Table 5:3). Figure 5:6(c) shows SEM micrograph for trona desulphurization product which reveal spherical particles with mostly smooth surfaces. The effect of desulphurization on trona is evident from the relative roughness observed on some particles and the needle-like shaped crystals on the particle surfaces.

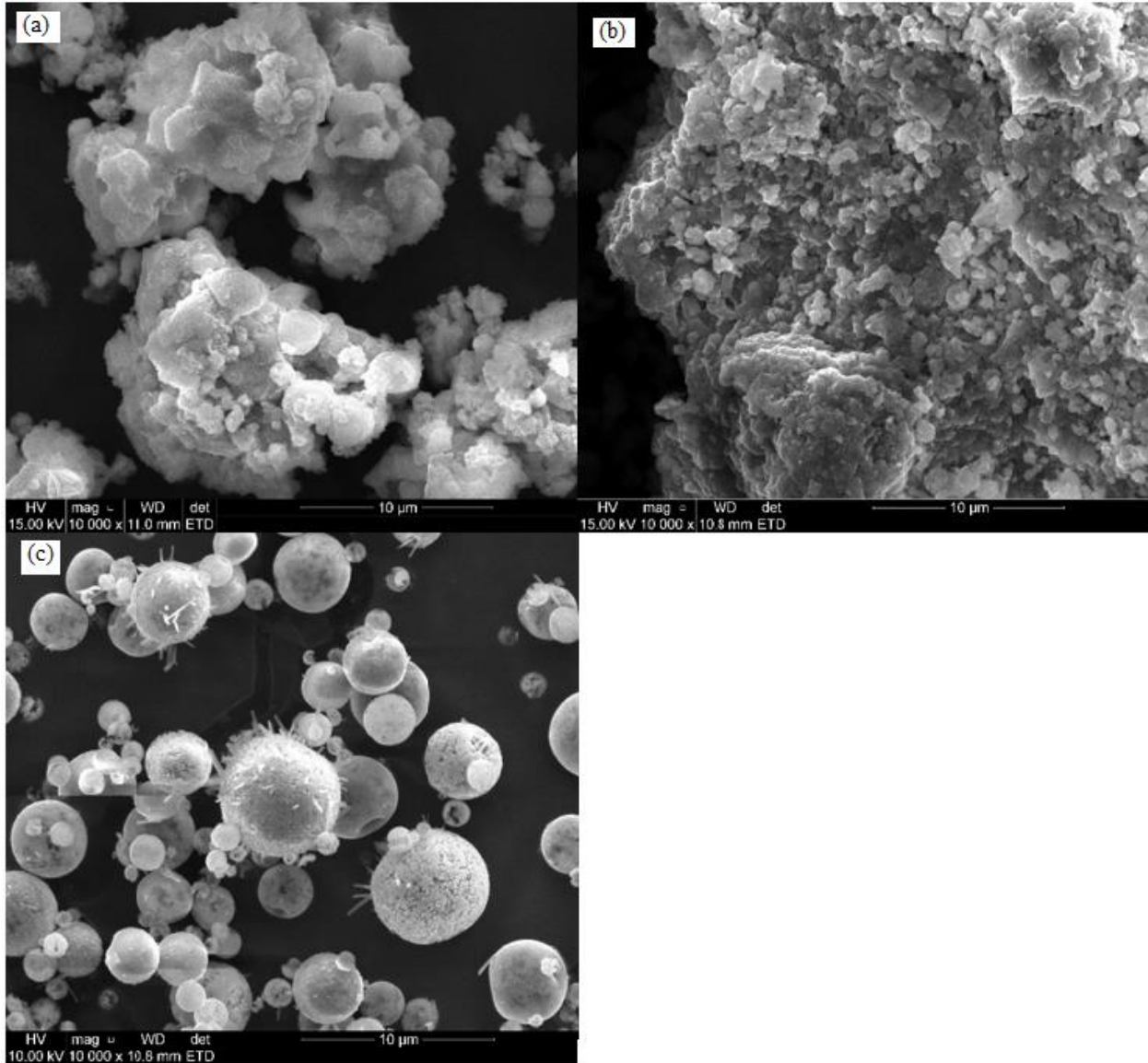


Figure 5:6: SEM micrographs of desulphurization products for (a) hydrated lime, (b) limestone, and (c) trona.

5.4.3.2. FTIR analysis

The functional groups on the surface of the desulphurization product samples were determined by FTIR analysis with a spectral range of 350-4500 cm^{-1} . Figure 5:7 shows the FTIR spectra for desulphurization products of hydrated lime, limestone and trona sorbents respectively. The FTIR spectrum of limestone desulphurization product shows strong absorption bands at 2520, 1402, 874 and 712 cm^{-1} which represent the presence of unreacted CaCO_3 (calcite) in the sample (Hamed et al., 2014). This confirms poor sorbent conversion as observed by XRF analysis and the evaluation of the degree of conversion. Similarly, the FTIR spectrum of hydrated lime desulphurization product shows absorption bands appearing at 712, 875 and 1413 cm^{-1} representing the unreacted $\text{Ca}[\text{OH}]_2$ (portlandite) in the sample. The spectra for both hydrated lime and limestone desulphurization products reveal absorption bands appearing at 652, 938 and 988 cm^{-1} attributable to $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ (Navarrete et al., 2021; Pekov et al., 2012). This corresponds with the XRF findings showing the presence of sulphite in the samples. Relatively high intensity of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ spectrogram in hydrated lime desulphurization product especially at 652 and 938 cm^{-1} is evidence of better sorbent conversion compared to limestone. The FTIR spectrum of trona desulphurization product shows strong presence of sulphite ions appearing around 1000-940 cm^{-1} and 650-520 cm^{-1} . This is a product of the absorption reaction between the sorbent and SO_2 resulting in the formation of sulphite salt. The absorption bands appearing at 1726 and 1432 cm^{-1} represent unreacted Na_2CO_3 in the desulphurization product.

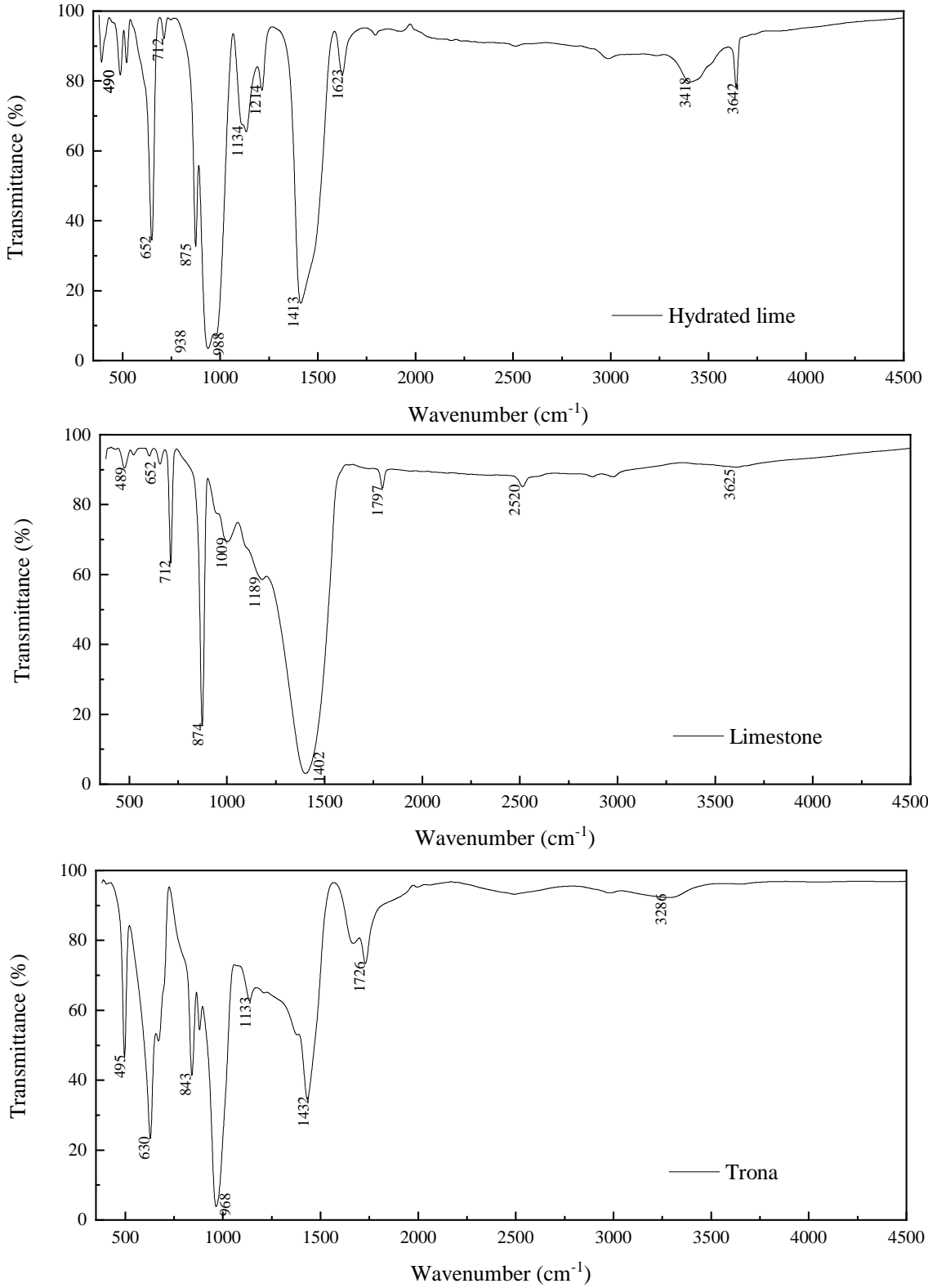


Figure 5:7: Desulphurization product FTIR spectra for hydrated lime, limestone and trona sorbents.

5.5. Conclusion

This study involved desulphurization experiments in a spray dryer using relevant sorbents (hydrated lime, limestone and trona) to compare their performance characteristics towards the absorption of SO₂. Trona and hydrated lime exhibited the highest SO₂ absorption efficiency of 98 and 82% respectively at a stoichiometric ratio of 2.0 compared to 59% for limestone. Although all sorbents exhibited poor SO₂ removal at elevated temperatures, limestone had a significant drop in the removal efficiency from 76 to 42% between 120 and 180°C due to poor dissolution properties at elevated temperatures. XRF and FTIR analysis of the desulphurization product indicated significant conversion and utilization of the trona sorbent. High concentration of the unreacted sorbent for both hydrated lime and limestone was observed in their respective final product samples. Generally, trona sorbent performed better compared to hydrated lime and limestone sorbents.

5.6. Bibliography

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Conclusion

This study aimed at investigating the performances of a laboratory scale spray dryer for SO₂ absorption to determine the effects of spray drying variables on SO₂ removal efficiency. It also aimed at evaluating the optimum operating conditions for SO₂ absorption using response surface methodology and finally investigating the performance characteristics of the relevant sorbents for spray drying SO₂ absorption.

Results from the investigation of the performance of the spray dryer revealed better SO₂ absorption at lower inlet gas phase temperatures than at high temperature due to rapid evaporation in the spray chamber. SO₂ absorption efficiency of up to 80% was achieved at an inlet gas phase temperature of 120 °C. High stoichiometric ratios beyond 1.5 were found to improve SO₂ removal efficiency beyond 80%, however there was poor sorbent utilization observed on analysis of the desulphurization product. Maximum sorbent utilization of 94% was achieved at a stoichiometric ratio of 1.5 and an inlet gas phase temperature of 140°C. High SO₂ absorption efficiency was realized at low values of approach to saturation temperature due to excess moisture which enhances the reaction between SO₂ and Ca[OH]₂.

Response surface methodology was used to analyse and optimize the independent variables (inlet gas phase temperature, stoichiometric molar ratio, slurry solid content and slurry pH). A predictive quadratic model correlating the variables and SO₂ removal efficiency was developed using CCD which was found to best describe the relationship with a regression coefficient of 0.93. The model results indicated stoichiometric molar ratio as a variable with largest influence on the absorption of SO₂. The recommended optimal conditions for SO₂ absorption in the spray dryer are inlet gas phase temperature of 140°C, stoichiometric ratio of 2, slurry solid concentration of 8% and slurry pH of 10, to achieve SO₂ removal efficiency of 90%.

The performance characteristics of the selected sorbents was investigated through experimentation to determine their performance and reactivity towards SO₂ using the spray dryer. The selected sorbents were hydrated lime, limestone and trona. Trona sorbent showed better performance characteristics towards the absorption of SO₂ with the highest SO₂ removal efficiency of 98% at a stoichiometric ratio of 2.0. Hydrated lime and limestone sorbents had relatively lower removal efficiencies under the same operating conditions. An investigation into sorbent utilization and

conversion indicated significantly high concentration of unreacted sorbent for hydrated lime and limestone. Trona on the other hand had relatively low concentration of the unreacted sorbent.