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Sodium-based flue gas desulphurisation for the South African coal-fired power industry a review

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ABSTRACT

A comprehensive review of sodium-based flue gas desulphurisation is presented in this article. The paper provides a comparison of various sodium-based technologies with regards to sulphur removal efficiency, sorbent cost, by-product valorisation and overall process economics. More emphasis was placed on dry sorbent injection (furnace sorbent injection, economizer sorbent injection, duct sorbent injection) and semi-dry flue gas desulphurisation. Particular effort was devoted in identifying state-of-the-art technologies and potential research gaps in a summarized way. In water-scarce countries, where sodium-based technologies are more economically feasible, and duct sorbent injection processes are favourable, it is recommended to use sodium-based absorbents since they will have higher sorbent utilization and improved electrical resistivity (compared to their calcium-based and/or magnesium-based sorbent equivalents). However, the check-and-balance of the associated advantages and disadvantages are a pivotal determinant of the sorbent choice. Apart from sulphur dioxide abatement, the additional advantages of sodium-based absorbents include its high sulphur trioxide removal efficiency as well as its hydrogen fluoride and hydrogen chloride removal capability. A scarcity in literature, especially as it relates to application in the South African coal-fired power generation industry, necessitates the need for further research with particular focus on local sodium-based absorbent markets, the physiochemical properties and sulphur dioxide reduction potential of locally acquired sodium-based absorbents, modelling of sulphation reaction kinetics in semi-dry and dry application, as well as the techno-economic feasibility of sorbent based technologies for the South African power industry.

1. Introduction

In 2019 global anthropogenic activities alone contributed close to 69 % of the total SO_2 emissions, with coal-fired power generation accounting close to 36 % of the global value (Dahiya et al., 2020). Countries such as the United States of America (Srivastava and Jozewicz, 2001), India (Garg et al., 2002), China (Yan and Wu, 2017), Europe (Smith et al., 2011) and South Africa (Pretorius et al., 2015) have shown to be the main contributors to global SO_2 emissions mainly as a result of fossil fuel-based electricity generation. More specifically in 2019, South Africa ranked 7th with a total anthropogenic SO_2 emission rate of close to 1200 kt per annum of which 95 % of this value could be related to coal-fired power generation (Dahiya et al., 2020). A significant reduction (between 37 and 40 %) in global SO_2 emissions has, however, been observed over a ten-year period as measured between 2008 and 2009. This marked improvement could be largely attributed to the

List of abbreviations: ACP, aqueous carbonate process; ANN, artificial neural networks; BET, brunauer, Emmett and teller; CAPEX, capital expenditure; CDS, circulating dry scrubbers; CFB, circulating fluidized bed; CFD, computational fluid dynamics; DFFE, department of forestry, Fisheries & environment; DSI, dry / duct sorbent injection; EC SC, emissions control specialisation centre; EPA, environmental protection agency; EPPEI, eskom power plant engineering institute; EPRI, electric power research institute; ESI, economizer sorbent injection; ESP, electrostatic precipitator; FGD, flue gas desulphurisation; FFP, fabric filter plant; FSI, furnace sorbent injection; IEA, international energy agency; MES, minimum Emission Standards.

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strengthening of emissions standards and legislation, a reduction in coal usage as well as an increased application of SO_2 emissions control technologies in some of the top emitting countries (Dahiya et al., 2020). The promulgation of more stringent SO_x regulations by various regulatory bodies across the world has also subsequently prompted the South African government to further amend its Minimum Emission Standards (MES), in terms of Section 21 of the National Environmental Management: Air Quality Act, 2004 (Act No. 39 of 2004) (NEMAQA), in 2018 and 2019 (Department of Forestry, Fisheries & Environment (DFFE), 2004 & 2019; Gubb, 2009; Ross, 2012).

For coal-fired power generation industries several pre- and post-combustion abatement technologies are currently available to control atmospheric releases of SO_2. Of these available technologies flue gas desulphurization (FGD), as a post-combustion abatement solution is mostly favoured due to its technical and economic feasibility as opposed to pre-combustion technologies. It is projected that the global market size for FGD will increase by as much as $ 7.2 billion over the next 6 years, growing at a CAGR (Compound Annual Growth Rate) of 4.3 %, as the demand to install FGD systems or retrofit existing systems increases to meet the stringent legislative requirements (Bloomberg, 2022). This is especially of significance for developing countries, such as South Africa, where fossil fuels remain the primary source of energy for the unforeseeable future due to the relatively slow implementation of renewable energy generation alternatives (Koech et al., 2021). Presently, there is broad range of available commercial regenerative and non-regenerative FGD processes in wet, semi-dry and dry application (Carpenter, 2012; Lisnic and Jinga, 2018; Srivastava and Jozewicz, 2001; Vernon and Jones, 1993). Wet FGD (WFGD) is by far the most common technology, accounting over 80 % of the total installed capacity worldwide, while semi-dry and dry processes are reported to only account for less than 10 % (Carpenter, 2012; Cordoba, 2015; Srinivasn, 2004). In addition, lime ($Ca(OH)_2$ or CaO) and limestone ($CaCO_3$) are mostly favoured as suitable absorbents for WFGD due to its abundance and availability.(Carpenter, 2012). However, growing concerns with respect to the high process water consumption rates for WFGD as well as the effective management of FGD by-products has sparked renewed interest in dry and semi-dry technologies, especially in water-scarce or semi-arid regions, to minimize operational expenditure and utility demands (Koech et al., 2021).

Although there is a strong drive for South Africa's energy sector to transition to a more sustainable and renewable future, it is foreseen that coal-fired power generation will remain a key component of the energy mix for at least the short to medium term (Strickroth et al., 2020). The efficient control of emissions (within regulated limits and standards,) during pulverized coal combustion will therefore become ever increasingly more important as the country battles to address the persistent threat to energy security, whilst also ensuring environmental compliance. To this extent South Africa's major state-owned utility company, Eskom, implemented six wet flue gas desulphurization (WFGD) units (the first in South Africa and Africa) as part of its new 4800 MWe Kusile power station in the Mpumalanga region. To date 4 of the 6 units at Kusile have achieved beneficial operation. Furthermore, two retrofit technology selection studies performed in 2014 and 2018 also recommended the use of WFGD technology for Eskom's operational 4800 MWe Medupi power station in the Waterberg region (Bagus et al., 2018; Eskom, 2018; Harris et al., 2014). Both studies considered limestone and lime (quick and hydrated) as absorbents, while only spray dry absorbers / scrubbers (SDA/SDS) and circulating fluidized bed (CFB) absorbers were used in the comparison with WFGD technologies. Although the focus was more on calcium-based sorbents, a recent feasibility study conducted in 2019 further concluded that direct sorbent injection (DSI) was not technically feasible for the Medupi power station due to an uncertainty in sorbent quality and availability, the configuration of the existing dust handling facilities as well as concerns related to waste management (Eskom, 2019). The study could, however, have benefitted from a more detailed account of not only the performance, techno-economics, co-emission reduction benefits and regional / local availability of both natural occurring or alternative absorbents (e.g., sodium-based absorbents) used in semi-dry and dry application but also the valorisation potential of the subsequent FGD by-products. The use of sodium carbonate (Na_2CO_3) as a sorbent for acid gas abatement dates back to the 1980s (Kimura and Smith, 1987; Mocek et al., 1983). In the 1990s, the approach was widely used in Waste to Energy (WtE) plants (Vehlow, 2015), following the NEUTREC process (marketed by Solvay S. A.) through the injection of $NaHCO_3$ in the flue gas and its subsequent solid waste collection (be it by fabric filter or electrostatic precipitator). Literature review publications that focus more in depth on sodium-based FGD systems are, however, relatively scarce when compared to similar works based on calcium-based technologies. The objective of this paper was therefore to systematically review the available literature on sodium-based FGD as a means of evaluating recent developments as well as further research opportunities to contribute to the body of knowledge. Knowledge gained through this approach is also intended to better inform not only future technical feasibility studies but also local energy and environmental policies as well as industry-specific emissions control technology roadmaps.

2. Review methodology and approach

A systematic, in-depth review of available literature (past 40 years) was performed to compare several technical, operational and economical aspects related to sodium-based FGD. Databases from ScienceDirect, Scopus, the Electric Power Research Institute (EPRI), the International Energy Agency (IEA) and the Environmental Protection Agency (EPA) constituted the primary resources for this systematic review, whilst news articles, OEM (original equipment manufacturers) brochures, governmental policy documents, engineering contractor's case studies and business cases were also occasionally consulted. The paper commences with a brief overview of commonly known sodium-based FGD processes, with specific emphasis placed on direct sorbent injection (DSI) and its associated technical and operational aspects affecting absorbent efficiency and downstream processing. The review then proceeds further by reflecting on recent developments with respect to non-conventional sodium-based absorbents as well as recent advances for elucidating and improving sodium-based absorbent performance. Further considerations with respect to sodium-based DSI are then summarized, followed by a critical assessment of the research carried out to date. The latter was aimed at identifying potential research gaps to stimulate further research in the field of sodium-based FGD and its applicability and or feasibility within the South African coal-fired power generation sector. In comparison to other publications in the field of FGD, the review presented in this paper follows a holistic approach by not only focusing on absorbent characteristics and performance but also taking into consideration other facets of technology selection, such as the valorisation potential of produced FGD by-products.

3. A review of sodium-based flue gas desulphurization processes

3.1. General overview of flue gas desulphurization

Commercial flue gas desulphurization (FGD) processes are commonly based on the contact and/or reaction of an acidic gas (e.g., SO_2, SO_3, HF, HCl etc.) with an alkaline sorbent (e.g., calcium-, sodium- or ammonium-based) to produce sulphates and/or sulphites and by-products. Depending on the fate of the sorbent, FGD can be broadly categorized into two main categories, namely, regenerative and non-regenerative processes. For regenerative processes, the spent sorbent is recovered via thermal or chemical treatment processes while concentrated SO_2 is also generated and further processed to desired products e.g., elemental sulphur, H_2SO_4, etc. In contrast, for non-regenerative processes, the absorbents are not recycled (Lisnic and Jinga, 2018; Srivastava and Jozewicz, 2001). Classification of FGD processes depends

on the aggregation state of the sorbent, namely, wet processes (solution or suspension) which consume the largest amount of water followed by semi-dry processes (sorbent with controlled humidity) and dry processes (zero humidification) (Mchabe, 2020). Generally, regenerative processes cut across the spectrum of wet, semi-dry and dry flue gas desulphurization processes. Limestone ($CaCO_3$) is the most widely used calcium-based sorbent in FGD processes (Carpenter, 2012; Cordoba, 2015; Srivastava and Jozewicz, 2001), owing to its availability and relatively low cost. Other calcium-based absorbents include quicklime (CaO) and slaked lime ($Ca(OH)_2$). It is important to bear in mind that both quicklime and slacked lime can be derived from limestone through calcination (quicklime), and calcination and quenching (slaked lime). It has been reported by various authors (Carpenter, 2012; Maina, 2012; Pandey et al., 2005; Poullikkas, 2015; Siagi et al., 2007) that quicklime is more reactive than limestone. The reactivity was attributed to various factors namely: higher surface area, porosity, etc.

Slaked lime has been reported to have an even higher surface area and porosity than both quicklime and limestone (Maina, 2012; Sasaoka et al., 1998), and as a result is generally more reactive. Other common absorbents used include sodium-based compounds (sodium carbonate, sodium bicarbonate, nahcolite and trona), magnesium carbonate and ammonia (Carpenter, 2012; Muzio and Arand, 1981; Pflughoeft-Hassett et al., 2009; Pilat and Wilder, 2007). These absorbents also react with SO_2 and SO_3 in the flue gas to produce a mixture of sulphite and sulphate salts, and in some instances also produce other sulphate and bisulphate compounds. The proportions of these products are dependent on the process conditions (Carpenter, 2012; Kong and Wood, 2011; Pflughoeft-Hassett et al., 2009; Pilat and Wilder, 2007). The commonly used, naturally occurring sodium-based absorbents include trona, nahcolite and sodium bicarbonate ($NaHCO_3$) (Muzio and Arand, 1981; Sahu, 2013). These sodium-based absorbents have been reported to be more reactive than hydrated lime during dry injection (Carpenter, 2012). Both sodium bicarbonate and trona have also been found to be more reactive to SO_2 than sodium carbonate (Na_2CO_3) due to a higher surface area for reaction as a result of a phenomenon known as the "*popcorn*" effect (the generation of micropores during water and CO_2 generation and subsequent release from the sorbent particles).

3.2. Wet sodium-based FGD processes

3.2.1. Soda ash wet scrubber

A variety of different wet scrubber technologies are currently available for FGD and include spray towers, venturi scrubbers, packed towers as well as trayed towers. Spray towers are commonly more preferred for large-scale FGD application given its better slurry handling capability (US EPA, 2003). An example of a sodium-based, non-regenerative wet FGD process is the soda ash scrubber, of which an illustrative schematic can be found in the works of Pandey et al. (2005). A soda ash scrubber operates on similar principles to that of a wet limestone scrubber i.e., SO_2 and SO_3 species in the flue gas dissolves in water to produce sulphurous and sulphuric acids that consequently reacts with the dissolved alkaline sorbent to produce sulphite and sulphate salts. The produced salts precipitate out of solution, depending on their respective saturation points and relative solubilities (Pandey et al., 2005). When both reactants and products are soluble, the need for technologies to handle solid waste products is eliminated (Schnelle et al., 2015). For both soda ash and caustic soda the sulphation process entails several dissolution, dissociation and aqueous phase reactions (more details provided in the works of Pandey et al. (2005)) to produce more specifically sodium bisulphite ($NaHSO_3$) and or sodium sulphite (Na_2SO_3) (Pandey et al., 2005). It has been reported that this process is able to achieve SO_2 removal efficiencies of between 90 and 95 % when sodium-based alkalis are used (US EPA, 2021). However, soda ash or caustic soda scrubbing processes are costly (Pandey et al., 2005) but to offset significant operational expenditures, lime or limestone may be introduced into the process, thereby implementing 'dual-alkali treatment' which produces a calcium-sulphite-rich sludge (Satriana, 1981). In 1998 the global installed capacity equipped with wet sodium-based (i.e., Na_2CO_3) FGD was mainly located in the United States and amounted to 2756 MWe, which represents only a mere 1.4 % of the global total of installed wet FGD capacity (Srivastava, 2000). More recently, another 11 sodium-based wet FGD units, associated with a coal-fired power generation capacity of 6322 MWe, were installed at US power plants (US EPA, 2019).

3.2.2. Dual-alkali scrubbers

The first dual-alkali units in the United States were brought online in 1974 (Donahue et al., 1980; VanNess et al., 1979). The process is based on two sets of chemical reactions. First, sodium-based alkali solution (e.g., NaOH or Na_2CO_3) reacts with the SO_2 in the flue gas. The second set of chemical reactions involve the spent alkali solution and lime, to regenerate and recover the sodium-based sorbent. The process is more suitable on particulate-free systems but can be employed for flue gas treatment (high concentration and low concentration) on both coal-fired and oil-fired plants (Donahue et al., 1980). The dual-alkali process incorporates three main unit operations namely: absorption, chemical regeneration, and solids dewatering. During absorption, flue gas from the facility's dust collection plant (electrostatic precipitator (ESP) or baghouse / fabric filter plant (FFP)) is introduced at the bottom of a scrubber, and proceeds to the reaction zone, where the gas is thoroughly mixed with the alkali solution (fresh makeup NaOH/Na_2CO_3 solution and the recycled Na_2SO_3 solution). As the flue gas stream reaches its adiabatic saturation temperature, SO_2 is removed through the subsequent production of sodium bisulphite ($NaHSO_3$), sodium sulphite (Na_2SO_3) and sodium sulphate (Na_2SO_4). In regenerative mode the spent scrubber solution is reacted with lime to regenerate the sodium-based sorbents and produce calcium sulphite and sulphate ($CaSO_3$ & $CaSO_4$) (Donahue et al., 1980). Hereafter the thickened slurry is dewatered, and the filtered liquor recycled back to the system. High SO_2 removal efficiencies in the order of 85 to 95 % have been reported by various workers (Córdoba, 2015; Donahue et al., 1980; Poullikkas, 2015; Srivastava and Jozewicz, 2001). The advantages of the dual-alkali process include, amongst other factors: (1) a high availability as the process is relatively free from plugging and scaling, (2) a low energy requirement (2 to 3 % of the total plant energy input), (3) a relatively pure gypsum by-product, as well as (4) minimal corrosion and erosion problems. However, drawbacks of this process include: (1) process complexity, (2) high operational cost due to reagents, (3) the formation of sodium salts on the filter cake, (4) particulate emissions due to misting, (5) complexity in process retrofit and additional capital expenditure due to the requirement of extra auxiliary equipment as well as (6) blockages in areas where low temperatures are common.

3.2.3. Wellman-Lord's sodium sulphite process

Over the past two decades publications on the Wellman-Lord process focused primarily on gas purification from harmful components (Dzhonova-Atanasova et al., 2013; Yildirim et al., 2012; Srivastava and Jozewicz, 2001) and has been reported to be applied in about 40 operating installations in Japan, USA, and Germany. The main advantage of the process is the relatively low sorbent demand and low waste production (Yildirim et al., 2012). In this process, either sodium sulphite (Na_2SO_3) or sodium sulphate (Na_2SO_4) solution is employed to absorb SO_2 from the flue gas. The process constitutes the following unit operations: a flue gas pre-treatment step, a SO_2 absorption unit as well as an absorbent regeneration and sulphate removal section. Flue gas compression is facilitated via the venturi pre-scrubber where after the waste stream is neutralized (by alkaline fly ash and/or lime/limestone) and deposited in a precipitator as a 5 wt. % suspension. Regeneration of Na_2SO_3 produces a concentrated SO_2 stream, which may be converted into a saleable product such as liquid SO_2, sulphuric acid, or elemental sulphur. It is important to bear in mind that, despite the targets of regenerating all the sodium sulphite and/or sodium bisulphite, minor

irreversible oxidation reactions may occur, leading to the formation of sodium sulphate (Pandey et al., 2005). It has been reported by Pandey et al. (2005) that this process is able to achieve a SO_2 removal efficiency of up to 95 %. Recently a review conducted by Dzhonova-Atanasova et al. (2013) provided useful insights into improving the energy efficiency of the Wellman-Lord process. From this review it is noteworthy to mention that the final concentration of sodium bisulphite in the absorber also determines the process efficiency and is dependent on the initial quantity of sodium sulphite fed into the absorption column. Operational concentrations are therefore usually close to saturation. The lower solubility of Na_2SO_3 (as compared to $NaHSO_3$) also creates the possibility of further saturating the partially unreacted solution to increase the $NaHSO_3$ concentration resulting in a subsequent reduction in the energy demand (i.e., steam consumption in this case) per unit of SO_2 absorbed (Dzhonova-Atanasova et al., 2013). The process has the advantage of producing a relatively pure SO_2 product stream via the regenerative step, while the largest drawbacks of this process include the high capital investment for additional equipment required for the recirculation of the absorbent as well as the significant amount of steam required for solution regeneration (Dzhonova-Atanasova et al., 2013). Despite this the operational costs have, however, been reported to be a similar order of magnitude to that of wet limestone FGD (Pandey et al., 2005).

3.2.4. Sodium carbonate eutectic process

This process takes advantage of the eutectic temperature of sodium carbonate (Na_2CO_3) (i.e., 425°C). The absorption of SO_2 proceeds according to Reaction R1 (Kumar and Jana, 2021; Pandey et al., 2005).

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \quad (1)$$

The regeneration of sodium carbonate is given by Reaction R2:

$$Na_2SO_3 + CO + 2H_2 \rightarrow Na_2CO_3 + H_2S + H_2O \quad (2)$$

The H_2S produced in Reaction R2 can be processed to yield valuable products (e.g., elemental S by Claus process).

3.2.5. Airborne process™

One of the emerging technologies, as it relates to sodium-based FGD, is the Airborne process™. This emissions abatement process is an amalgamation of the wet sodium scrubbing process and dry sorbent injection of sodium bicarbonate. Mortson & Xia (2006) reported removal efficiencies of 99.9 % for SO_2, 99.9 % for SO_3, 99 % for NO_x, 99 % for mercury from their bench-scale and pilot scale demonstration tests. Carpenter (2013) reported that the proprietary $NaHCO_3$ regeneration component has been demonstrated at a commercial sodium sulphate mine in Ormiston, SK, Canada. However, the integrated Airborne technology still needs to be demonstrated on commercial scale. The Airborne Process™ consists of four main unit operations, namely dry sorbent injection, wet scrubbing, oxidant wash and sorbent regeneration/fertiliser production (Carpenter, 2013). In the first step, dry $NaHCO_3$ is injected into the flue gas downstream of the particulate control device employed within the combustion process (e.g., fabric filter plant or electrostatic precipitator). Here the $NaHCO_3$ thermally decomposes to form porous sodium carbonate particles with a large surface area which are highly reactive to acid gas species. It has been found that Na_2CO_3 produced in this way is a significantly better absorbent than commercially produced analogues. SO_2 and SO_3 react with the Na_2CO_3 and $NaHCO_3$ to form Na_2SO_4. After the direct sorbent injection step, a mixture of flue gas and sorbent is then introduced at the bottom of a wet scrubber unit where the flue gas contacts the sodium scrubbing solution counter currently. The formed Na_2SO_4 is dissolved into the solution whilst any unreacted SO_x are also removed. The spent sodium scrubbing solution is collected and withdrawn from the bottom of the scrubber into an oxidizing unit where aeration is carried out to convert sodium sulphite (Na_2SO_3) in the spent solution to Na_2SO_4. Hereafter, the solution is conditioned with Na_2CO_3 to adjust the pH to enable the precipitation and removal (filtration) of heavy metal compounds to increase the purity of the final products. The resulting spent solution is then finally mixed with ammonium bicarbonate (NH_4HCO_3) to not only regenerate the $NaHCO_3$ through the process of precipitation but also to produce ammonium sulphate as a high-quality fertiliser by-product (Carpenter, 2013). Apart from the regeneration benefit, the Airborne process™ also has the following additional advantages: (1) lower total power consumption (3 %), (2) lower capital and operating costs than separate conventional pollutant control technologies (SCR, limestone wet scrubber, wet ESP and activated carbon injection) as well as lower water consumption than wet limestone scrubbers (Carpenter, 2013; Mortson and Telesz, 2001; Zhu 2010).

3.3. Semi-dry, sodium-based FGD processes

The semi-dry desulphurization process emanates from taking advantage of the sensible heat of evaporation of the desulphurization slurry moisture from the sorbent particles. A predetermined amount of water is introduced, either to form a film around solid particles or as to introduce the sorbent as a highly concentrated slurry. During the process, SO_2 and SO_3 reacts with the solid sorbent directly. To ensure an efficient process, absorbents need to be characterized by a high specific surface area and porosity. Similar to the wet FGD process, the products from semi-dry, sodium-based FGD include sodium sulphites and - sulphates (Na_2SO_3 and Na_2SO_4). Generally, semi-dry processes can be categorized into: (1) spray dry scrubbers, (2) duct spray dry process and (3) circulating dry scrubbers (Carpenter, 2012). Other semi-dry scrubbing technologies include gas suspension absorption (GAS) and Alstom's Novel Integrated Desulphurization (NID™) system (Carpenter, 2012). Publications on sodium-based, semi-dry FGD processes are relatively scarce in literature with most, only briefly referring to the use of these absorbents without providing any detailed technical information e.g., SO_2 removal efficiencies, average water consumption rates, proven commercial facilities or demonstrations and cost estimates. The use of sodium-zinc sorbent as a substitute for the traditional semi-dry FGD technologies has, however, been proposed by Zhang et al. (2015).

3.3.1. Spray dry scrubbers

Carpenter (2012) indicated that in the spray dry scrubbing (SDS) processes, a concentrated lime slurry (a few systems use a sodium carbonate solution) is introduced into the top of the absorber vessel through rotary atomizers or dual fuel nozzles. These atomize the slurry creating a fine mist of droplets containing the reagent, which reacts with SO_2 and SO_3 in the downward flowing flue gas to form calcium sulphite and sulphate ($CaSO_3$ and $CaSO_4$). Although the work of Dantuluri (1988) focused primarily on calcium-based absorbents, it was also stated that sodium carbonate solution (Na_2CO_3) can be utilized during the semi-dry scrubbing process (e.g., spray using an atomizer into a drying vessel). Srivastava and Jozewicz (2001) as well as US EPA (2003) highlighted that the spray dry scrubbers typically use lime (CaO) as sorbent, owing to its lower price as compared to its sodium-based sorbent counterpart. Although cheaper than wet scrubbing, SDSs are normally restricted to power plants with a capacity lower than 400 MW as larger power plants require multiple absorber systems which may reduce its capital cost advantage (Carpenter, 2012; US EPA, 2003). Further advantages offered by semi-dry FGD includes low water consumption (~60 % less than wet FGD), low energy consumption (0.3 – 1.0 %), opportunity to use low quality steel, minimal scaling and plugging problems, no need for sludge handling equipment, etc. However, operational expenditure for SDS is higher due to low sorbent utilization, increased frequency of maintenance on FFPs because of greater wear as well as higher sorbent and waste disposal costs when compared to wet FGD (Carpenter, 2012). A critical review conducted by Koech et al. (2021) on recent developments with respect to spray dry FGD, albeit more focused on the use of traditional calcium-based sorbents, identified the need for further research as it relates to droplet–gas absorption kinetics, accurate process

optimization employing advance parametric studies and computational fluid dynamics modelling, spray dry FGD waste management as well as the quantification of multiple pollutant removal efficiencies.

3.4. Dry sodium-based FGD processes

3.4.1. Brief overview of dry sodium-based FGD scrubbers

The application of dry FGD scrubber technology presents a viable option to the power utility and industrial sector (both locally and internationally, especially in water scarce countries) receiving increased pressure to retrofit their facilities with SO_2 abatement technologies, to reduce emissions to the allowable country specific, emission limits. The selection of dry scrubbing technology, like other technologies, is influenced by unit size, unit age, fuel usage, financial base, geographic location, etc. During the dry scrubbing process, the sorbent reacts with SO_2 to form a dry product containing sulphates and sulphites. After the scrubbing section, the mixture of spent sorbent material and fly ash can be removed from the gas stream by either ESP or FFP. The spent sorbent is usually disposed of, but in some cases, it may be regenerable or have commercial end uses (Miller et al., 1979; Yeh et al., 1982). When nahcolite (or any synthetic form of sodium bicarbonate) and/or trona are injected post-combustion (above 125°C), they thermally decompose according to Reactions R3 and R4 to form sodium carbonate, carbon dioxide (CO_2) and water:

$$2\boldsymbol{NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O} \quad (3)$$

$$2(\boldsymbol{Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O}) \rightarrow 3\boldsymbol{Na_2CO_3 + CO_2 + 5H_2O} \quad (4)$$

The evolution of water vapour and CO_2 during the thermal decomposition process results in the formation of microporous sorbent particles with surface areas 5 to 20 times larger than the original particle surface area (Carpenter 2012; Kong and Wood, 2010). This relatively high surface area increases the reaction rate between Na_2CO_3 and SO_2. The produced sodium carbonate intermediate reacts with SO_2 or SO_3 to produce sodium sulphite (Na_2SO_3) or sodium sulphate (Na_2SO_4) according to the following reaction schemes:

$$\boldsymbol{Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2} \quad (5)$$

$$\boldsymbol{Na_2CO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2} \quad (6)$$

$$\boldsymbol{Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2} \quad (7)$$

Recycled and/or make-up $NaHSO_3$ and Na_2SO_3 react with SO_3 in the flue gas according to:

$$NaHSO_3 + \boldsymbol{SO_3 \rightarrow NaHSO_4 + SO_2} \quad (8)$$

$$Na_2SO_3 + 2SO_3 + H_2O \rightarrow 2NaHSO_4 + SO_2 \quad (9)$$

Wilhelm (2004) reported that reactions R8 and R9 will be given by reactions R10 and R11, when the molar ratio of Na:SO_3 exceeds 1.

$$2NaHSO_3 + SO_3 \rightarrow Na_2SO_4 + 2SO_2 + H_2O \quad (10)$$

$$Na_2SO_3 + SO_3 \rightarrow Na_2SO_4 + SO_2 \quad (11)$$

Zhu (2010) reported that side reactions between $NaHCO_3$ and NO takes place (reaction R12), when a small portion of NO is converted to NO_2, to subsequently produce $NaNO_3$ (thus reducing NO_x emissions). The removal of $NaNO_3$ is given by Reaction R12 and R13 (Johnson et al., 2005)

$$2NaHCO_3 + SO_2 + NO + O_2 \rightarrow Na_2SO_4 + NO_2 + H_2O + 2CO_2 \quad (12)$$

$$2NaHCO_3 + 2NO_2 + \frac{1}{2}O_2 \rightarrow 2NaNO_3 + H_2O + 2CO_2 \quad (13)$$

Some of the measures suggested by Zhu (2010) for avoiding brown stack plume, includes adding urea to $NaHCO_3$, high temperature injection, and using low NO_x burners. Johnson et al. (2005) and Kong & Balland (2011) further reported that Na_2CO_3 also can remove HCl and HF according to Reactions R14 and R15:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2 \quad (14)$$

$$Na_2CO_3 + 2HF \rightarrow 2NaF + H_2O + CO_2 \quad (15)$$

In comparison to calcium-based absorbents (e.g., limestone and lime), sodium-based absorbents are significantly more reactive when injected as dry powders (Yeh et al., 1982; Zhu, 2010). In general, the advantages offered by dry FGD scrubbing includes no or lower process water requirements, lower capital and operating costs, less space required than wet FGD systems, etc. However, for sodium-based absorbents, the disadvantages include, amongst others: (1) leaching of landfilled solid by-products, (2) CO_2 production (contributing more to the GHG emissions burden) and (3) lower SO_2 removal efficiency when compared to wet FGD.

3.4.2. Sodium-based, dry sorbent injection processes

Dry sorbent injection, in which the sorbent (e.g., trona, nahcolite, $NaHCO_3$, etc.) is injected directly either into the furnace or post-furnace, offers a low cost FGD alternative due to the lower capital cost incurred because of equipment installation and or modification (Muzio and Often 1987; Often et al., 1987). Dry injection technologies have been under investigation since the 1960s and are in some cases not considered popular due to several reasons, e.g., SO_2 removal efficiencies not always greater than 90 %, lower value and solubility of solid by-products (Muzio and Often 1987). More recently though, dry sorbent injection has been classified (as per the European BREF - best available technology reference documents) as the best available technique for no less than seven different manufacturing industries in the European Union, i.e., ceramics, common wastewater, iron & steel making, large combustion plants glass, cement & lime, and waste incineration (Balland et al., 2017). As a measure of its increasing relevance, one might also consider the installation of 14 dry sorbent injection systems at power stations in the USA (US EPA, 2019). Fig. 1 below provides a schematic overview of the typical injection locations (Carpenter, 2012).

To illustrate the performance capability of sodium-based sorbents, a full-scale dry sorbent injection test campaign was successfully conducted in 2011 on a commercial scale power generation unit (Unit 3 - 150 MW) of the Battle River Station of ATCO Power, using both trona and pre-milled $NaHCO_3$ as absorbents (EPRI, 2011). Sorbent injection was facilitated via 12 lances into two ducts downstream of the secondary air heater. A SO_2 removal efficiency of 45.6 % and 57.6 % was achieved for trona (injection rate of 3.4 ton/h and unit load of 110 MW) and $NaHCO_3$ (injection rate of 1.9 ton/h and unit load of 70 MW) respectively. At full load and an injection rate of 4.3 ton/h a SO_2 removal efficiency of 50.7 % was achieved for $NaHCO_3$ (EPRI, 2011). Sorbent injection systems are best suited for coal-fired power stations, using low to medium sulphur coals, with capacities less than 300 MWe and moderate SO_2 removal requirements (Carpenter, 2012; US EPA, 2019; Zhou et al., 2010). For South Africa's power utility company, Eskom, DSI therefore provides a suitable option for power stations that have derated capacities and are close to reach their end of useful life. Exceptions on the rule do exist as is evident from the installation and demonstration of DSI systems on boilers with generation capacities of up to 1300 MWe (Campobenedetto and Silva, 2011).

Dry sorbent injection processes are categorised according to the following distinct injection locations: (1) Furnace Sorbent Injection (FSI), (2) Economiser Sorbent Injection (ESI), (3) Duct Sorbent Injection (DSI) and (4) hybrid systems (mostly a combination of the furnace and duct injection systems or may involve humidification of the flue gas). These processes employ the pneumatic transportation of the powdered sorbent, via injection lances, into the designated injection locations, whilst the solid by-products (i.e., sulphites and sulphates) are collected with the fly ash using the appropriate particulate matter control device

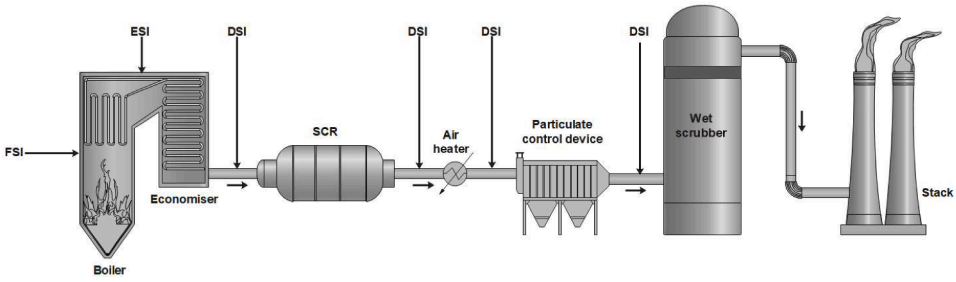

Fig. 1. Possible sorbent injection locations (adapted from Carpenter, 2012).

(ESP or FFP). Fabric filters have been found (Carpenter, 2012) to generally achieve higher SO_2 removal efficiencies than ESPs due to a prolonged reaction time because of the additional flow resistance provided by the FFP filter cake. Sahu (2013) reported that various researchers and vendors investigated trona (unmilled Solvay T200 (D50 = 30 μm)) injection at the economizer inlet, air heater inlet, and the ESP inlet locations, over temperatures of 374 °C, 288 °C and 110 °C, respectively.

Furnace sorbent injection (FSI). Furnace sorbent injection involves the direct injection of the sorbent into the top part of the boiler/furnace (where the operational temperatures typically range between 750 and 1230ºC). FSI is the simplest and most cost-effective, commercial FGD technology to install. Operating costs can, however, be high due to low or insufficient sorbent utilization (Carpenter, 2012). It should be noted that the addition of solid absorbents via FSI can, however, reduce boiler efficiency especially if injection is facilitated directly into the combustion zone. Limestone, dolomite and dolomite ($CaCO_3.MgCO_3$) are mostly employed for FSI, whilst literature on injection of sodium-based absorbents remains scarce and can be attributed mainly to high operational temperatures in the furnace. At these temperatures (generally higher than the normal boiling point of sodium-based absorbents) sodium-based absorbents are expected to melt and cause slagging or fouling within the furnace. These melted absorbents have been also reported to be poisonous to Selective Catalytic Reduction (SCR) catalysts (Blythe, 2004).

Economizer sorbent injection (ESI). ESI involves the injection of sorbent into the economizer of a coal-fired boiler at operational temperatures ranging between 300 and 650ºC (Carpenter, 2012). An ESI study performed on a 90 MW boiler (combusting bituminous coal with 0.7 wt. % S), using trona (normalized stoichiometric ratio of 2.5) as sorbent resulted in a 50 % SO_2 removal efficiency. Furthermore, reducing the d_{50} particle size of the trona sorbent from 30 μm to 13.7 μm improved the SO_2 removal efficiency to 74 % for a trona normalized stoichiometric ratio of 3.5. A computational fluid dynamics (CFD) study conducted by Cremer et al. (2008) to optimize the injection location and distribution of trona concluded that a SO_2 removal efficiency of 80 % and 90 % could be achieved for a normalized trona stoichiometric ratio of 2.5 and 3.5, respectively. For calcium-based ESI, it has been shown that the injection of water in the ducting between the air heater and dust collection device could increase the SO_2 removal efficiency to up to 80 %. The increased efficiency could mainly be attributed to the hydration of any unreacted CaO. This approach may present a means to also improve the SO_2 removal efficiency of sodium-based sorbents although the theory stands to be tested (Srivastava and Jozewicz, 2001). Despite its advantages ESI is not currently in commercial use which may warrant further investigation.

Duct sorbent injection (DSI). DSI involves the injection of the sorbent directly into the ducting between different unit operations within the coal-fired power generation process (refer to Fig. 1). Depending on the sorbent used, the system is suitable for the removal of not only SO_2 and SO_3 but also HCl and HF. The DSI technology has also been shown to enhance mercury removal and is currently also in commercial use in several power stations across the US (Carpenter, 2012).

Low temperatures (typically between 120 and 180°C) within the ducting (below the melting point of sodium carbonate, sodium sulphite and sodium sulphate) makes the technology suitable to employ sodium-based absorbents for FGD (e.g., nahcolite, trona, sodium carbonate etc.).

Chemical reactions previously discussed mentioned (thermal decomposition and SOx removal) are also applicable in the case where sodium-based absorbents are used during DSI. In summary the advantages of sodium-based duct sorbent injection, more specifically, include:

- Sodium-based absorbents are more reactive (70 to 90 % removal efficiency) than their calcium-based counterparts (50 to 75 % removal efficiency) and do not require any flue gas humidification (Carpenter, 2012; VanDerWerff, 2011).
- Both $NaHCO_3$ and trona have been shown to reduce NO_x emissions by around 10–25 % without an SCR (Maziuk, 2007).
- Sodium-based absorbents decrease fly ash resistivity which in turn may also result in the improvement of ESP performance (Carpenter, 2012).
- Sodium-based DSI also offers a multipollutant reduction co-benefit through the enhancement of mercury, SO_3, HF and HCl removal (Carpenter, 2012).

Drawbacks of sodium-based duct sorbent injection, more specifically, include:

- Higher running costs due to the higher raw material costs as compared to lime and limestone (Carpenter, 2012).
- The recovered fly ash/ Na2SO4 mixture has been reported to have a little economic value (high sodium content makes it unsuitable for cement/concrete use) (Carpenter, 2012).
- Na2SO4 is water soluble which makes waste disposal difficult and also poses a significant environmental risk (Sahu, 2013).
- Trona has been reported to be more difficult to handle than hydrated lime due to its small particle size (approximately 28 μm average particle size), its cohesiveness, affinity for moisture, and its temperature sensitivities (Ritzenthaler, 2007; Ritzenthaler et al., 2007).
- The formation of liquid sodium bisulphate (NaHSO4) at temperatures greater than 185ºC, which can deposit on the air heater and duct, causing build-up and plugging. Soot blowing might therefore be required on a regular basis, which in turn may increase operational expenditure (Kong and Wood, 2010).
- Dry sodium-based sorbent injection chemical reactions are also known to reduce NO to NO_2 (Sahu, 2013; Smith et al., 1997) which in turn can result in an increase in NO_2 emissions burden (brown plume from the stack).

3.4.3. *Comparative assessment between direct sorbent injection processes*

A comparative assessment between the SO_2 and SO_3 emissions reduction performance of ESI and DSI technology is provided in Table 1.

Table 1
Comparison of sorbent injection systems.

Injection System	Sorbent	Product	SO_2 removal efficiency (%)	SO_3 removal efficiency (%)
ESI	Trona	Na_2SO_3	50 - 80	-
		Na_2SO_4		-
DSI	Na_2CO_3	Na_2SO_3	-	90 - 98 (Solution Injection)
	$NaHCO_3$	Na_2SO_4	-	
	Trona	Na_2SO_3	70 - 90	$\geq$ 90
		Na_2SO_4	70 −80	$\geq$ 90
		Na_2SO_3		
		Na_2SO_4		
	Na_2SO_3	Na_2SO_4	-	90 - 98 (Solution Injection)
		$NaHSO_4$	-	
	$NaHCO_3$	Na_2SO_4	-	91 - 98 (Solution Injection)
		$NaHSO_4$	-	

FSI has been excluded from this comparison as sodium-based absorbents have been reported to be incompatible with the typical high temperatures experienced in pulverized fuel boilers. Table 1 was adapted from the table provided by Carpenter (2012) and is based on the collective work of Benson et al. (2003), Blythe (2004), Commission (2006), Cremer et al. (2008), Srivastava & Jozewicz (2001) and VanDerWerff (2011). SO_2 and SO_3 removal efficiencies quoted in the table above are typical ranges reported in literature and will be site and operations specific. As an example, a power generation facility equipped with a fabric filter plant will generally achieve a higher (5–10 %) SO_x removal efficiency than one with ESPs as the filter cake on the fabric filter increases the surface area and contact time for the SO_2/SO_3 to react with the sorbent. An even distribution of the sorbent across the boiler/duct and an adequate residence time at the proper temperature are critical for high SO_x removal efficiencies.

A higher SO_2 reduction (up to 90 %) can be achieved when injecting dry sodium-based absorbents into the flue gas duct. Although ESI can achieve 50–80 % SO_2 reduction, it is not currently in commercial use (Carpenter, 2012). In most cases, SO_3 control efficiencies of 70 % to 90 % are required to appreciably lower, or eliminate, plume opacity due to the increased SO_3 concentration from the oxidation of SO_2 to SO_3 in the SCR unit. DSI is more efficient at removing both furnace- and SCR-generated SO_3, capturing over 90 % with sodium-based absorbents (Carpenter, 2012). Sodium bisulphite, sulphite and carbonate can also be injected as solutions as part of the duct spray dry process to remove 90–98 % of the SO_3. Flue gas humidification or conditioning with SO_3 coupled with the injection of sodium-based absorbents can possibly also increase fly-ash reactivity (reduction of resistivity) leading to a subsequent increase in ESP performance.

However, as stated above, trona is more difficult to handle than hydrated lime (Carpenter, 2012). Caution is expressed when employing humidification as part of sodium-based direct sorbent injection as the formation of liquid $NaHSO_4$ can result in unacceptable fouling within parts of the duct and downstream equipment. Another concern with the use of both sodium and calcium-based absorbents is the effect collected spent sorbent on the market value and saleability of the fly ash. Pre-collection of the fly ash may resolve this concern. Finally, another major drawback with the carbonate-type absorbents is the generation of CO_2 from the reactions with SO_2 and SO_3, which inevitably increases total CO_2 emissions from the coal-fired power plant (Carpenter, 2012).

4. Factors affecting the efficiency of dry sodium-based FGD processes

The SO_2 removal efficiency of sodium-based absorbents is dependent on several factors. Muzio and Arand (1981) quantified the effects of the following process parameters on the dry SO_2 removal process: (1) sorbent type (i.e., nahcolite, trona, commercial sodium bicarbonate), (2) normalized stoichiometric ratio (NSR), (3) sorbent particle size, (4) baghouse temperature, (5) air-to-cloth ratio, (6) cleaning cycle time, (7) sorbent injection schedule (continuous and batch), (8) injection at temperatures up to 427 °C, (9) pre-decomposition of the nahcolite as well as (10) initial SO_2 concentration. Yeh et al. (1982) investigated the effects of baghouse temperature and cleaning cycle time, sorbent particle size, sorbent/sulphur ratio, location of sorbent injection point, and sorbent injection schedule (batch or continuous). The same authors (Muzio and Arand, 1981; Yeh et al., 1982) reported that, except for baghouse cleaning cycle rate, each parameter had a significant effect on SO_2 removal efficiency.

4.1. Sorbent type, particle size and stoichiometric ratio

Amongst all available sodium-based absorbents (e.g., thermonatrite, trona, nahcolite, natron, dawsonite, gaylussite, shortite, burkeite and hanksite), the most used and studied sodium-based absorbents are commercial sodium bicarbonate, trona and nahcolite (Kostick, 1994). Consequently, this section of the paper focuses solely on the effect of these absorbents on SO_2 removal efficiency. Muzio & Arand (1981) and Yeh et al. (1982) compared the SO_2 removal efficiencies of nahcolite and trona whereas Smith et al. (1997) compared the SO_2 removal rates between 11 μm diameter sodium bicarbonate and 10 μm sodium sesquicarbonate (trona) at flue gas temperatures 204 – 210 °C; SO_2 concentrations between 450 and 500 ppm; and 2.5 s in-duct residence time. Muzio & Arand (1981) reported that the behaviour of nahcolite was similar to that of commercial $NaHCO_3$, despite the fact that the latter had a relatively lower SO_2 removal efficiency. Smith et al. (1997) reported that both trona and $NaHCO_3$ were able to achieve 70 % SO_2 removal with $NaHCO_3$ exhibiting a higher utilization of sodium when compared to trona. As such, sodium bicarbonate can achieve 70 % SO_2 removal at a lower molar ratio of sodium to SO_2 than trona, (i.e., 2Na/S) of 1.9 and 0.9, for trona and sodium bicarbonate, respectively.

Furthermore, the investigation of Smith et al. (1997) indicated that $NaHCO_3$ fines (mean particle diameter of 11.2 μm) had the highest SO_2 removal efficiency. Their findings show that $NaHCO_3$ exhibits a significantly larger SO_2 removal efficiency than trona within the NSR (normalized stoichiometric ratio) range of 0.5 to 2.5 (e.g., for $NaHCO_3$ a NSR of 1 is required to achieve 50 % SO_2 removal efficiency, whilst for trona a SO_2 removal efficiency of only 34 % is achieved at the same NSR level). These observations are also in agreement with what was observed by other investigators (Carson, 1980; Keener and Davis, 1984; Muzio and Sonnichsen, 1984; Shah et al., 1978; Stern 1978). An inverse linear relationship between SO_2 removal and mean particle diameter was observed by Yeh et al. (1982) i.e., SO_2 removal increased with the decrease in mean particle diameter.

The same authors (Smith et al., 1997; Carson, 1980; Keener and Davis, 1984; Muzio and Sonnichsen, 1984; Shah et al., 1978; Stern 1978) reported SO_2 removal efficiencies of up to 90 % for absorbents with mean particle diameters of less than 65 μm. Muzio & Arand (1981) reported that decreasing the nahcolite particle size improved the SO_2 removal efficiency, particularly at cycle times shorter than 60 min (50 % removal for 37 μm nahcolite compared to 30 % for 74 μm nahcolite over a 60-minute cycle time at a NSR of 0.8). The work of Keener & Davis (1984) also confirmed the dependence of the SO_2 removal rate of Na_2CO_3 on particle size (in the range of 20 to 200 μm) for temperatures less than 232°C. Accordingly, for a reaction period of 600 s, SO_2 removal rates of close to 50 %, 35 % and 20 % was respectively achieved for 20, 90 and 200 μm particles. In contrast, however, it was found that the $NaHCO_3$ sulphation reaction was less dependent on particle size. Keener & Davis (1984) ascribed this to the probable enhancement of sorbent particle characteristics because of thermal decomposition which occurred during the reaction.

Stoichiometric ratio is another important factor that affects the SO_2 removal efficiency of sodium-based absorbents. A study by Yeh et al. (1982) reported an SO_2 removal of 90 % for a Na_2/S ratio of 1.3 while using $NaHCO_3$ of particle size 32 μm in a baghouse at 204.44 °C when coal of 1.6 % S was combusted. $NaHCO_3$ utilization was estimated at 70

%. To study the effect of stoichiometric ratios, some authors (e.g., Muzio and Arand, 1981) employed the phenomenon known as normalized stoichiometric ratio (NSR), which is described as the measure of the amount of sodium injected relative to the sulphur in the flue gas as measured by a continuous SO_2 monitor. A NSR of 1 therefore implies that 2 mol of Na per mole of SO_2, which is the stoichiometric requirement to form sodium sulphate, Na_2SO_4. For nahcolite a SO_2 removal efficiency of 67 % can be achieved when a NSR of 1.0 is used (Muzio and Arand, 1981). For trona, the same authors reported a SO_2 removal efficiency of 40 % at NSR of 1.0, and a SO_2 removal efficiency of 70 % at NSR of 3.0.

A comparison between SO_2 removal efficiencies and NSR during sodium injection trails for commercial demonstration (22 MW and 100 MW) showed close agreement with the work of Muzio & Arand (1981). From the demonstration-scale results it was concluded that sodium bicarbonate (or nahcolite) is the most effective, with a SO_2 removal efficiency of 80 % at a NSR of 1, while trona could only achieve a 67 % removal efficiency at a similar NSR. In addition, Na_2CO_3 was found to be relatively unreactive (only between 5 and 15 % SO_2 removal efficiency), although other investigations (Albin, 1986; Hooper and Bland, 1985; Muzio and Often, 1987) have shown higher removal efficiencies. Similar observations with respect to the effect of stoichiometric ratio was made by Pilat & Wilder (2007) and Walawska et al. (2014).

4.2. Sorbent injection schedule

Yeh et al. (1982) studied the effect of sorbent injection schedule on both SO_2 removal efficiency and sorbent utilization. During the investigation two experimental sets were employed, namely: (1) a comparison of continuous injection to a 1 min on / 1 min off injection regime and (2) a comparison of continuous injection to a 3 min on / 1 min off injection regime. The findings from this study are summarised in Table 2, clearly illustrating the higher SO_2 removal efficiencies and sorbent utilization obtained for both experimental sets.

Muzio and Arand (1981) tested the performance of nahcolite on SO_2 removal efficiency by comparing batch and continuous injection schedules into the baghouse inlet. Their injection schedule results were classified as follows: (I) continuous injection, steady-state level, maximum removal, (II) continuous injection, 90-minute average removal, (III) bag precoated (batch), 90-minute average removal and (IV) continuous injection for 54 % of 90-minute cycle, 90-minute average removal. These tests were conducted under NSR of 0.9, 200-mesh (74 μm) nahcolite and an injection temperature of 132.2 °C. It was evident from their results that during continuous injection, the SO_2 level at the baghouse outlet reaches a steady-state level (around 40 min) and maintains this level for the remainder of the test period. In contrast, the SO_2 concentration rapidly went through a minimum for the batch injection experiment and steadily rises again as the nahcolite, which was precoated on the bags, is consumed. Their findings illustrated the improvements made in SO_2 removal efficiency by either precoating the bags or injecting at a rate such that the total amount of sorbent is injected during the first 54 % of the cycle. In both cases, SO_2 removal increases from about 50 % for continuous injection to 66 % for the batch and semi-batch feeding of the nahcolite over a 90-minute test period.

Table 2
Effect of sorbent injection schedule (taken from Yeh et al., 1982).

Sorbent Injection Schedule	Na_2/S Ratio	SO_2 Removal Efficiency (%)	Sorbent Utilization (%)
Experimental set 1			
Continuous	1.30	77.6	59.7
1 min on: 1 min off	1.30	58.6	45.1
Experimental set 2			
Continuous	0.95	65.1	68.5
3 min on: 1 min off	0.98	48.0	49.0

4.3. Injection location

From the field tests conducted by various vendors and researchers, Sahu (2013) reported that one set of tests focused on the effect of injection position on the SO_2 removal efficiency of trona. The positions that were considered include the economizer inlet, the air heater inlet, and the ESP inlet. The reported, respective average temperatures recorded in those positions were 374 °C, 288 °C and 110 °C respectively. These tests were primarily carried out using an as-received, unmilled Solvay T200 material (D_{50} of 30 μm). From the experiments it was concluded that the highest SO_2 removal efficiency was realized during injection at the economizer inlet (ranging between 48 and 55 % for NSRs between 2.3 and 2.5), followed by the air heater (ranging between 42 and 43 % for NSRs between 2.1 and 2.5) and then the ESP inlet (ranging between 30 and 35 % for NSRs between 2.6 and 2.7)

According to Yeh et al. (1982) no significant effect of injection location (baghouse inlet versus duct injection upstream of air heater inlet) was observed when using sorbent with a mean particle size of 32 μm. However, for sorbent particles with a mean particle size of 69 μm SO_2 removal efficiencies were reported to decrease from 87 % when injecting upstream, to 64 % when injecting at the baghouse inlet. Similarly for 180 μm particles, a decrease from 64 % to 43 % was reported respectively. The authors attributed these observations to particle separation and settling, i.e., the coarser and heavier particles separate from the flue gas and settle out before chemical reactions can progress further. To better compare the effect of particle size and injection location, the authors maintained the baghouse temperature at 204.4 °C, whilst using a Na_2/S of 1.5 and particle sizes of 32, 69 and 180 μm. Muzio & Arand (1981) also made consistent reports whilst comparing the SO_2 removal efficiency on the duct and on the inlet of the baghouse. In their studies using trona at a NSR of 2, they reported SO_2 removal efficiencies of 70 to 78 % for duct injection as compared to the 50 to 62 % observed at the inlet to the baghouse.

4.4. Operating temperature

The effect of baghouse temperature using $NaHCO_3$ on SO_2 removal efficiency was investigated by Yeh et al. (1982) and their findings indicated that the SO_2 removal efficiency increases with an increase in temperature and reaches a plateau around 204.44 °C. Consistent reports were also made by Muzio & Arand (1981), who reported that for trona, nahcolite and synthetic Na_2CO_3, the SO_2 removal efficiency was enhanced by higher temperatures. For nahcolite, it was observed that a maximum SO_2 removal efficiency is achieved around 288 °C. Furthermore, Smith et al. (1997) reported that the humidification of the flue gas to a 15.6 °C saturation temperature increased SO_2 removal by up to 20 % when injecting trona (at constant Na_2/S ratios). More recently, Lu et al. (2022) investigated the dry desulphurization performance of $NaHCO_3$ ($d_{10} = 3.2$ μm; $d_{50} = 13.2$ μm; $d_{90} = 33.5$ μm) in a fixed bed experimental assembly and concluded that SO_2 removal efficiency remained relatively constant (between 95 and 100 %) over the temperature range of 100 to 190°C. Hereafter, it reduced significantly (to close to 60 % SO_2 removal efficiency at 220°C) with further temperature increases. Although the authors do not offer an explanation to the observed SO_2 removal trend it is believed that it can be ascribed to a change in sorbent physical characteristics (specific surface area) as a result of the thermal decomposition of $NaHCO_3$. As an example, Walawska et al. (2014) have shown that the BET (Brunauer, Emmett and Teller) surface area of $NaHCO_3$ increases, depending on the mechanical activation method employed, by a factor between 3 and 10 when thermally activated at 300°C. A more in-depth investigation with respect to the relationship between SO_2 removal efficiency, sorbent physical properties and temperature could therefore provide useful for future comparative studies between different sodium-base absorbents.

4.5. Sulphur content in coal

As coal is heterogenous in nature it can contain different concentrations of organic sulphur and inorganic sulphur. The proportions of these two main forms of sulphur may also vary from coal seam to coal seam; and even if the total sulphur is the same the total amount of sulphur released as SO_x can vary significantly under identical combustion conditions. Yeh et al. (1982) investigated SO_2 removal with nahcolite while combusting three different coals: Kentucky coal (1.0 wt. % S), Pittsburgh coal (1.6 wt. % S) and West Virginia coal (3.1 wt. % S).

The baghouse temperature was maintained between 204 and 216 °C during their investigation. From their investigation it was concluded that a SO_2 removal efficiency of 90 % and sorbent utilization of 82 % was achieved for the Pittsburgh Coal, whilst the Kentucky coal showed a similar trend. However, the reported SO_2 removal efficiencies achieved when burning the West Virginia coal were lower than those obtained for the other two coals. The effect of sulphur content was further investigated whilst employing trona as a sorbent. From these experiments it was observed that the difference in SO_2 removal efficiencies of Pittsburgh coal and that of West Virginia coal was more pronounced.

4.6. Inlet SO_2 concentration

Pilat & Wilder (2007) studied the effect of the inlet SO_2 concentration on the removal efficiency at flue gas temperatures ranging between 204 and 210 °C with a 2.5 s in-duct residence time. During the study five test series were executed using 11 mm MMD $NaHCO_3$ particles whilst spiking the flue gas with pure SO_2 (concentrations ranging between 300 and 2600 ppm). From the results it was deduced that the inlet SO_2 concentration had very little effect on the SO_2 removal efficiency of the small 11 mm MMD $NaHCO_3$ particles.

Pilat & Wilder (2007) attributed their observations to the fact that similar reaction rate limiting steps were dominant throughout this 300–2600 ppm concentration range and that no gas phase diffusion limitations were present. Their report was consistent with the work of Davis et al. (1978), who concluded that the inlet SO_2 concentration had no effect on its removal efficiency. However, a study examining the removal efficiency of a bench-scale thin-bed of nahcolite performed by Stern (1978) suggested a dependence on SO_2 concentration. Stern's bench scale studies concluded that SO_2 removal efficiencies increased with increasing inlet SO_2 concentrations. A theoretical model predicting a higher SO_2 removal efficiency with higher inlet SO_2 in the 200–3000 ppm SO_2 concentration range at 127°C was also presented by Wu et al. (2004).

4.7. Residence time in the duct

As previously discussed, the dry absorbents can be injected either at the inlet to the baghouse (downstream of the heat exchanger) or into the high temperature duct. The residence time of the combustion products and dry sorbent in suspension in the duct from the point of injection to the heat exchanger is normally determined to be in the range of 2 s. In an actual utility boiler, residence times between the convective section and the air preheater are on the order of 0.5 s, and temperatures are approximately 427 °C.

The residence times through the air heater are in the order of 0.5 s, with temperatures close to 149 °C. The residence time in the duct between the air heater and the particulate collection device is on the order of a few seconds (Muzio and Arand, 1981). Pilat & Wilder (2007) studied the effect of in-duct residence time on SO_2 removal efficiency for flue gas temperatures ranging between 204 and 210 °C and SO_2 inlet concentrations ranging between 350 and 380 ppm. Significant SO_2 removal efficiencies (between 35 and 70 %) were achieved within a 3 s duct residence time at a temperature of 204.4 °C. The findings of Pilat and Wilder (2007) were, however, not in agreement with the model predictions of Wu et al. (2004) who reported very small SO_2 concentration changes (less than 5 %) for a 1 s sorbent particle duct residence time at a gas velocity of 15 m/s, particle diameter of 5–10 mm, and temperatures in the 120–210.8 °C range.

4.8. Baghouse air-to-cloth ratio

The baghouse air-to-cloth ratio is defined as the actual volumetric flow rate through the baghouse divided by the area of the bags. This is effectively the velocity of the gases through the bags. Thus, the air-to-cloth ratio determines the relative residence time as the gases pass through the filter cake (Muzio and Arand, 1981). Muzio and Arand (1981) varied the air-to-cloth ratio by lowering the firing rate which simulates low load operation of a utility system; and by removing half the bags from the baghouse. Increasing the air-to-cloth ratio from 2 to 4 by removing the bags had essentially no effect on the SO_2 removal process while using nahcolite injection into the baghouse.

The same authors reported that increasing the air-to-cloth ratio and (thus decreasing the residence time of the gas as it passed through the filter cake containing the sodium) could be expected to reduce the effectiveness of the SO_2 removal process. Results of these tests at NSRs of 0.93 and 2.33 indicated that there was no significant difference between the SO_2 removal efficiencies at air-to-cloth ratios of 3 or 4 either for the removal based on the steady-state SO_2 level or the integrated removal for a 60-minute cycle time. At a NSR of 0.93, the SO_2 removal based on the steady-state level was somewhat lower at the high air-to-cloth ratio, although it appears to be within the margin of error of the data.

4.9. ESP operation

Pilat & Wilder (2007) also studied the effect of ESP corona voltage on the SO_2 removal efficiency, whilst performing $NaHCO_3$ injection at 204°C with an absorbent particle size of 11 μm and SO_2 inlet concentration of 350 ppm. Results from this campaign are summarized in Table 3, where a decrease in ESP corona voltage can be observed to result in a slight increase in the SO_2 removal efficiency. According to the authors, lower Corona voltages probably increased the gas-particle contact time in the ESP due to lower dust collection efficiencies.

At a higher stoichiometric ratio and upstream residence time(i.e., 1.5 and 5 s), if was found that both the upstream and downstream SO_2-removal efficiencies increased by a factor of between 2 and 3 (i.e., 25 to 75 % and 40 to 80 % respectively). The relative increase in SO_2 removal across the ESP appeared to depend on the extent of SO_2 removal (SO_2 reaction with the sorbent) upstream of the ESP.

5. Developments related to other sodium-based absorbents

Kumar & Jana (2021) recently published a review paper in which they provided a critical review of advances made in absorbents and techniques for both wet and dry FGD. In the review a comprehensive account of absorbent performance is provided for not only the more commonly known and used absorbents (i.e., limestone and lime) but

Table 3
Effect of ESP corona voltage on SO_2 removal efficiency (adapted from Pilat and Wilder, 2007).

Duct residence time (s)	SO_2 inlet concentration (ppm)	Stoichiometric ratio	Corona voltage (kV/cm)	SO_2 removal efficiency (%)	
				ESP Inlet	ESP Outlet
2.5	350	1.0	2.6	25	40
2.5	350	1.0	1.3	–	45
2.5	350	1.0	0.0	–	45
5.0	350	1.5	2.6	75	80
5.0	350	1.0	2.6	–	52
5.0	350	1.0	1.3	–	60
5.0	350	1.0	0.0	–	63

also sodium-based absorbents. A summary of other (apart from Na_2CO_3, $NaHCO_3$, nahcolite and trona) sodium-based absorbents investigated for application in FGD, as adapted from the work performed by Kumar & Jana (2021), is summarized in Table 4. A few additional and noteworthy sodium-based absorbent studies have, however, been found by the authors of this review paper and reference to these publications (**) are therefore subsequently included in Table 4 to supplement the review provided by Kumar & Jana (2021)

The work of Chang and Rochelle (1981) revealed that the SO_2 absorption rate increased with increasing NaCl concentration and reaching a maximum value around 0.4 M NaCl. Furthermore, at constant HCl concentration and temperature no significant change could be observed in the mass transfer rate for a change in SO_2 concentration. Experiments performed in a sieve tray column, maintaining an acidic environment, indicated removal efficiencies of 36 – 72 % for NO_x and 88 – 100 % for SO_2 respectively (Chien and Chu, 2000). The removal efficiency was also found to increase with an increase in L/G ratio.

Table 4
Summary of other sodium-based sorbent research performed (adapted from Kumar and Kana, 2021).

Type of absorbent	Composition of SO_2	Experimental parameters	Type of contactor	Reference
NaCl, H_2O and HCl	Pure and dilute 0.0002 – 0.98 bar	25 °C, 1 atm	Stirred tank reactor (300 rpm)	Chang & Rochelle (1981)
NaOH with 5 × 10^{-3} wt. % sodium lauryl sulphate (SLS)	Pure	25 ± 2 °C, 1 atm	Sphere and cylinder column reactor	Vazquez et al. (1988)
NaOH (0 – 0.9 M)	Dilute	25 – 50 °C	Packed column	Schultes (1998)
NaOH & $KmnO_4$	Dilute and mixture with NO	50 °C, 1 atm	Stirred tank reactor	Chu et al. (2001)
NaClO with NaOH	300 – 800 ppm	65 °C, pH 7, L/G ratio: 5 – 10 L/m^3	Sieve tray column	Chien & Chu (2000)
$NaClO_2$	SO_2: 0 – 1500 ppm NO: 100 – 800 ppm	25 – 65 °C pH 4 – 10	Bench-scale spraying column	Chien et al. (2003)
NaClO with $NaClO_2$ (molar ratio of 4)	2000 mg/m^3	50 °C, 1 atm, pH 5.5	Bubbling reactor	Zhao et al. (2010)
**$C_9H_8Na_2O_4$ (Sodium humate)	SO_2: 1100 - 2700 ppm NO_2: 340 ppm	25 – 85 °C 1 atm 0.01 – 12 g/ml pH 4 - 10	Bubbling reactor	Sun et al. (2010)
**$C_9H_8Na_2O_4$ sludge (Sodium humate)	2000 - 3000 ppm	25 - 65 °C 1 atm 0.12 m^3/h (gas) pH 3 - 11	Bubbling reactor	Zhao & Hu (2013)
**Na_2HPO_4, α-amino acid salts (sodium glycinate & sodium lysinate)	1000 - 1800 ppm	25 - 60 °C 1 atm L/G ratio: 0.005 – 0.01	Gas-liquid contactor (Packed Bed)	Rahmanim et al. (2015)
$NaClO_2$	300 – 600 ppmv	27 W power supply	Wet electrostatic precipitator	Park et al. (2017)
NaOH, Na_2SO_3 & CaO	2000 ppm	50 °C, 1 atm	Hollow fibre membrane reactor	Joo et al. (2020)
**NaOH, $NaHCO_3$, Na_2CO_3, Na_2SO_3	SO_2: 371 – 3500 ppm CO_2: 15 vol. %	Ambient T & P L/G ratio: 12.5 – 37.5	Hollow fibre membrane reactor	Park et al. (2021)

Contrary to the use of inorganic sodium-based absorbents, Sun et al. (2010) investigated the SO_2 removal performance of an organometallic sodium-based absorbent (i.e., sodium humate) at varying absorbent concentrations, pH, temperature, gas flowrate, O_2 concentration as well as SO_2 and NO_2 inlet concentrations. The investigators were able to achieve SO_2 removal efficiencies of more than 98 % and prescribed an absorbent concentration of 0.06 mg/L and a pH of 4.5 for optimum SO_2 removal performance. A similar study was also performed in 2013 by Zhao & Wu (2013) using sodium humate extracted from sludge collected from the thickening tank of a wastewater treatment plant. Comparable SO_2 removal efficiencies were observed whilst the authors also make a compelling case for employing or repurposing readily available, industrial or commercial waste materials as a cost-effective means of combatting the emissions of harmful pollutants. To the best of the author's knowledge, no publications currently exist where either a waste, sodium-bearing stream or organometallic sodium-based absorbent, such as sodium humate, is used for either semi-dry or dry FGD application. A further addition to the focus area of non-conventional sodium-based absorbents is the comparative, sulphation performance study conducted by Rhamani et al. (2015) wherein the effect of SO_2 inlet concentration, process temperature and liquid/gas ratio on SO_2 removal efficiency of α-amino salts (sodium glycinate and sodium lysinate) was investigated. Based on the experimental results, the amino acid solutions showed good SO_2 removal efficiencies with sodium lysinate being the superior.

A completely different approach to FGD was followed by Park et al. (2017). The authors investigated both NO and SO_2 removal efficiencies in a wet ESP by making use of $NaClO_2$ as absorbent. From the study it was determined that NO and SO_2 removal rates of 34.8 – 72.9 mmol/m^3.s and 36.6 – 84.7 mmol/m^3.s could be respectively achieved by varying the molar concentration of the absorbent. Another novel approach w.r.t. FGD was the utilization of a polypropylene hollow fibre membrane reactor by Joo et al. (2020) and Park et al. (2021) to study the SO_2 removal efficiency using different absorbents (refer to Table 4). A 99.9 % removal efficiency was achieved by using lower CaO concentrations as compared to NaOH. No significant membrane deterioration was observed even after multiple weeks of operation (Joo et al., 2020). The study of Park et al. (2021) is also only one amongst a very few studies where pollutant removal efficiencies were evaluated in the presence of two or more gaseous pollutants. From the results it was evident that in the presence of both CO_2 and SO_2, SO_2 removal performance decreases due to fouling ("corrosion") of the membrane contactors' potting material. However, the authors believe that this problem might be overcome by using a potting material with high chemical stability.

6. Further considerations for sodium-based dry sorbent injection

When selecting the most appropriate FGD process, one needs to consider several factors including: electricity generation capacity of the associated power plant, fuel type, fuel-to-sulphur ratio, availability, and price of the absorbent to be used, absorbent type, potential market for FGD by-products, waste disposal and management, as well as environmental factors (e.g., waste disposal and wastewater treatment). From the preceding discussions and based on available SO_2 removal efficiency data, dry, sodium-based sorbent injection might be considered a viable option for FGD, especially for a semi-arid country like South Africa. The sections to follow seek to highlight some further operational and technical aspects to consider for semi-dry and or dry, sodium-based FGD.

6.1. Potential impact on particulate matter emissions

The dry sorbent injection process has the potential to increase the particulate matter (PM) burden from ESPs due to an increased load on especially ESP ash handling systems (i.e., hoppers, fans, blowers, ducts, etc.). The subsequent increase in PM emissions can be attributed to

increased quantities of unreacted sorbent and FGD reaction products (e.g., sorbent with SO_2, HF, HCl etc.) yielded during the FGD process. Both the unreacted sorbent and the resulting products do not only increase the loading, but will also alter the physicochemical properties of the solids to be handled by the ESP. The capacity of the ESP with respect to the particulate loading, electrical resistivity of the particles, particles size distribution, sulphuric acid mist concentration etc., will need to be thoroughly considered to ensure optimum ESP performance. Electrical resistivity dictates the ease or difficulty by which ash particles are charged during ESP operation. According to Sahu (2013), sodium-based absorbents have the added advantage of reducing ash resistivity and increase overall ESP performance. Flue gas conditioning with SO_3 (which converts to sulphuric acid mist in the presence of water vapour) exhibits the same effect and according to Blythe (2004), sodium-based sorbent has the affinity for preferentially absorbing sulphuric acid mist. Upgrading and retrofitting existing ESPs to accommodate for these combined FGD solutions can, however, result in tens of millions (USD) in additional expenditure (Sahu 2013). For power generation facilities equipped with fabric filter plants (FFP), an increase in particulate matter burden through the flue gas stack can also occur due to more frequent bag failures (e.g., mechanical degradation) from a higher particulate loading which induces greater wear on the FFP bag filters (Carpenter, 2012).

6.2. Potential leachability of FGD by-products

An environmental concern may arise from the leaching of Na_2SO_3 and or Na_2SO_4 (products of $NaHCO_3$ or trona flue gas desulphurization) during and after landfill disposal. This can be attributed to the higher solubility of these products as compared to the limestone / lime analogues (i.e., $CaSO_3$ and $CaSO_4$), The leachability of these sodium sulphite/sulphate products depends on several factors which include (1) moisture conditioning and handling, (2) water consumption during landfill dust control, (3) compaction of the wetted FGD products as well as (4) pelletization (Madsen, 2017). The aforementioned factors have been reported to have a substantial impact on the hydraulic conductivity and leaching behaviour (Madsen, 2017). On evaluating the impact of trona injection and its effect on the resulting ash product, Wang and Su (2011) concluded the following:

- The injection of trona altered the physicochemical properties of the fly ash, e.g., the specific surface area, particle morphology and microstructure. It also resulted in an increase in sodium, sulphur and carbonate concentration.
- An increase in fly ash solubility, pH, and leachability of anionic elements including fluoride, sulphate, chloride, and trace oxyanions of concern especially As and Se was observed.
- Compared to the conventional fly ash, trona ash leached significantly more As and Se in all conditions, including varying leaching time, pH, storage time conditions. Multiple factors may contribute to the enhanced As and Se leaching from trona ash, including more alkaline pH, greater ash solubility, presence of high concentrations of competing anions (such as sulphate and carbonate), and a greater Se (VI) fraction in trona ash.
- The increased solubility of the produced fly ash will most probably increase the leachability of As and Se into groundwater which therefore necessitates the need for lining of landfills.

6.3. Potential impact on CO_2 emissions

The chemical reactions involved in semi-dry and dry sodium-based sorbent FGD processes were discussed previously or can be found elsewhere (Carpenter, 2012; Pandey et al., 2005). Noticeably, is the fact that all these chemical reactions produce CO_2, the greenhouse gas. Studies that focus on the emissions of CO_2 (or more specifically multi-pollutant emissions control performance of absorbents), while using sodium-based absorbents, are scarce in literature. The thermal decomposition of sodium bicarbonate/trona/nahcolite will vary along the different injection locations, according to local temperatures. Furthermore, lower temperatures (60 – 70 °C) have been reported to favour CO_2 capture (Liang et al., 2004) by sodium-based absorbents, whilst temperatures above 120 °C have been reported to favour decomposition.

6.4. Cost implications

The capital cost and energy consumption of direct sorbent injection systems have been found to be considerably lower in comparison to semi-dry and wet FGD processes due to their simplicity, lower water consumption and relative ease to handle and manage dry products from the process. Capital / installation costs have been quoted to range between 8 and 12 US$/kW for SO_2 control and 4 to 8 US$/kW for SO_3/H_2SO_4 control (Campobenedetto and Silva, 2011).

Higher values (around 20 US$/kW) have, however, been quoted by Staudt et al. (2011) for a basic injection system with storage silo. Operational costs will be plant and location specific and are influenced by various factors including mining and transportation of raw material (e.g., trona), production of raw material (e.g., sodium carbonate), material preparation (milling) and storage, PM control equipment upgrades / modifications (e.g., ESP) and landfill upgrade. Operational and capital expenditures will be higher in cases where additional storage and materials handling are necessary. However, this is still lower than the capital cost for wet or dry scrubbers (approximately 400 US$/kW) (Campobenedetto and Silva, 2011). A comparative / indicative cost estimate for different SO_2 abatement retrofit options, including for dry sorbent injection with sodium-based absorbent, was recently conducted by Jacobs (2021) for the Vales Point power station (2 × 600 MW) in New-South Wales, Australia. The study confirmed the lower capital expenditure and higher operational costs for dry sorbent injection (in this case furnace sorbent injection) as can be seen in Table 5.

A large fraction of the operating cost can be attributed to the price of the sorbent used in FGD. In general, the sodium-based absorbents are more expensive than the calcium-based absorbents. Srinivasn (2004) assessed and compared the raw material cost of natural occurring absorbents for the US market (i.e., limestone, hydrated lime, trona and $NaHCO_3$) and found the cost of trona to be significantly lower (approximately a factor 2) than $NaHCO_3$. This aspect will however need to be assessed on a country specific basis. Furthermore, sorbent utilization in dry based FGD processes is normally lower than in wet based processes, therefore resulting in higher control costs in terms of cost per tonne of SO_2 reduced. The use of real time, continuous measurement of SO_2 and SO_3 in the power plant stacks could lower the sorbent injection rate, with consequent cost savings.

6.5. Potential abrasiveness of absorbents

Of all the natural occurring sodium-based absorbents (e.g., sodium bicarbonate, trona and nahcolite), trona has been found to be the most abrasive (VanDerWerff, 2011). The abrasive nature of trona can be attributed to its silica (SiO_2) content, a factor that must be considered

Table 5
Comparative estimate of SO_2 abatement options for Vales Point Power Station (adapted from Jacobs, 2021).

Technology &. Techno-economic aspect	Furnace Sorbent Injection	Semi-Dry (SDA)	Wet Scrubber	Seawater Scrubber
Sorbent	Sodium-based	Lime	Limestone	Seawater
CAPEX (US$/kW)	41 – 58*	117 – 361	233 – 426	175 – 321
OPEX (US$/kW-y)	18 – 23*	6 – 9	5 – 9	4 – 6

* Based on sodium-based absorbent price of 371 US$ per tonne and 70 % collection efficiency of bag filter plant.

during the design of the process of the pneumatic injection system to ensure operational and mechanical integrity throughout the operational lifecycle of the facility. Premature and frequent failures may result in higher operational costs.

6.6. Valorisation potential of FGD by-products and recovery of spent sorbents

Desulphurization by-products derived from the use of sodium-based sorbents in FGD have numerous applications ranging from metallurgy (mineral processing), wood processing, glass manufacture, commercial and household laundry detergents and chemical industry among others. One of the most notable uses of Na_2SO_4 is the Kraft Process (sulphate process) for wood pulp manufacturing to produce paper products and building supplies (Bajpai, 2018). This process utilizes heat reduction process to convert Na_2SO_4 to Na_2SO_3 which breaks the bond in wood cellulose making it malleable and able to be extruded (Bajpai, 2018). Na_2SO_4 is also one of the main raw materials in glass manufacturing process as a fining agent chiefly because it provides the necessary alkali base, prevents sum formation, and removes air bubbles from molten glass during glass refining process (Global Markets Insights, 2021).

The application of Na_2SO_4 in mineral processing has been tested as an additive in pyrometallurgy to obtain ferronickel concentrates from nickel laterite ores (Jiang et al., 2013). This has been effectively tested by several researchers showing significant improvement in nickel extraction with high recovery from laterite ores (Jiang et al., 2013; Li et al., 2012a; Li et al., 2012b). Other applications of Na_2SO_4 include textile production industry (as a catalyst for colour fixation and absorption of dyes on fabrics), in households and commercial detergent and soap manufacturing process (as a pH neutralizer and to maintain the viscosity of the finished product), and in pharmaceutical industry (as laxative and food additive) (Global Markets Insights, 2021). On the other hand, Na_2SO_3 can be used as a depressant in the processing of complex ores by selective floatation in media with high ion content. Due to its oxidising and reducing properties, Na_2SO_3 has been used as a reagent to depress pyrite in copper sulfides (Molaei et al., 2018), copper depressant in molybdenite ores (Suyantara et al., 2021) and arsenopyrite from gold ores (Kydros et al., 1993).

For most sorbent injection processes, FGD products and spent absorbent is normally collected with the fly ash fraction in the power station's main dust collection device (i.e., ESP or FFP). Consequently, for sodium-based FGD this solid waste mixture has little economic value (e.g., cement manufacturing) if the sodium content is too high and may also result in higher disposal costs due to the higher solubility of sodium-based FGD products (Carpenter, 2012). In addition, significant amounts of unreacted sorbent might be lost which may subsequently result in higher operational costs if not recovered or regenerated. Collecting fly ash before the sorbent injection location presents one practical solution but would require a secondary dust collection device to recover the spent sorbent and FGD by-product. This could increase capital expenditure due to the installation of additional unit operations. Salmenoja et al. (2020) has, however, proposed a process of directly recovering Na_2SO_4 in fly ash (patented for a recovery boiler of a chemical pulp mill) which can be considered as a possible alternative for sorbent and FGD recovery from a fly ash mixture. Several other methods for the recovery and regeneration of sodium compounds from dry FGD wastes have also been reviewed and proposed by EPRI (1981) and Detourney & Coustry (2010) and include amongst others the Aqueous Carbonate Process (ACP), carbonation, evaporative crystallization, acidification with H_2SO_4, dissolution accompanied by electrodialysis and the Ampot process. The presence of similar key industries (e.g., glass manufacturing, paper and pulp, textiles, mining and minerals beneficiation) within the South African economic sector, combined with the potential of the aforementioned FGD by-product recovery and regeneration schemes, therefore creates the opportunity for potential markets to be explored for utilizing and recovery of waste products from semi-dry and dry, sodium-based FGD.

6.7. Improving sorbent performance with additives and activation technologies

In recent years, several research and technology development studies have been performed to improve absorbent performance but also to lower operational costs of semi-dry and dry FGD systems. Some studies have focused specifically on the addition of additives whilst others have considered alternative absorbent activation strategies to enhance the SO_2 removal efficiency during semi-dry and or dry FGD. França et al. (2020) investigated the effect of seven additives (magnesium hydroxide, ammonium nitrate, ammonium acetate, ammonium phosphate, sodium hydroxide, citric acid, and urea) on the SO_2 removal efficiency of Ca$(OH)_2$ during semi-dry FGD. In their experiments, two concentrations (2 and 4 wt. %) of additives were applied to Ca$(OH)_2$ slurries of 10 and 20 wt. % respectively. From the results it was concluded that the ammonium additives (especially ammonium nitrate) increased the SO_2 removal efficiency by as much as 13.5 % when compared to the highest SO_2 removal efficiency when only using Ca$(OH)_2$. Very few research papers do, however, consider the effect of additives (e.g., urea and ammonia) on the SO_2 removal efficiency of sodium-based sorbents in either semi-dry or dry application (Bland, 1990; Darmastaedter, 1990; Hooper, 1988). Unfortunately, a thorough review of more recent literature (past 10 years) produced no meaningful results which therefore creates the opportunity for further research in the field of sodium-based FGD additives and their effects.

For dry scrubbing purposes, $NaHCO_3$ is generally pulverized into fine particles (~ 20 μm) to increase the absorbent specific surface area and subsequently enhance SO_2 removal efficiency. However, the storage and transport of this ultrafine reagent is characterized by several operational issues (e.g., bridging and or blocking) which requires the costly addition of a dispersing agent to prevent occurrence. As a means of investigating possible solutions to overcome these issues Hwang et al. (2021) evaluated the pollutant removal efficiency of porous $NaHCO_3$ produced via thermal vacuum treatment from coarse $NaHCO_3$. Although tested for HCl removal from flue gas, the optimum conditions for enhanced specific surface area and effective HCl removal was determined to be 180 °C, 30 kPa and a residence time of 1 h. Absorbent activation using mechanical and thermal techniques was also investigated by Walawska et al. (2014). In their study, $NaHCO_3$ and Na_2CO_3 was subjected to various grinding techniques (fluid bed opposed jet mill, fine impact mill and electromagnetic mill) followed by thermal activation and subsequent evaluation of the SO_2 removal efficiency. A comparison between the different milling techniques revealed that electromagnetic grinding produced an absorbent with the highest specific surface area and SO_2 removal efficiency.

A 19.8 % improvement on SO_2 removal efficiency was observed between the SO_2 removal efficiencies of the finest milled $NaHCO_3$ (6.7 μm) and ungrounded absorbent. Furthermore, thermal activation at 300°C showed that absorbent surface area could be increased by at least a factor 13 (from 0.6 to 8.6 m^2/g). Although the preceding studies have been more fundamental in nature, technology optimization efforts and commercial trials have also proven to be useful in improving dry FGD. One such an example is the SORBMIX technology offered by Mobotec which, in contrast to a conventional injection lance protruding into the flue gas duct for mixing, uses a boosted air jet with high velocity to effectively mix the dry FGD sorbent into the flue gas (Liu, 2015). The technology also has the following added advantages: more operational flexibility by being able to handle various load ranges and reduced maintenance and operational issues when compared to conventional lances. An industrial scale SORBMIX trial (~ 774 kg/kWh inlet SO_2) conducted over a 12-hour period, at various stoichiometric ratios (Ca/S of between 2.5 and 7.5) indicated, on average, an 8 to 10 % improvement in SO_2 reduction made by SORBMIX as compared to the standard injection lance setup.

6.8. Optimization of abatement performance using modelling techniques

Over the past two decades several papers have focused their attention more on the use of both fundamental and advanced modelling techniques as a means of not only gaining insight into the mechanistic processes of desulphurization but also to optimize desulphurization efficiency through more reliable and accurate FGD system design and simulation. Kinetic studies of the semi-dry and or dry sulphation reaction of sodium-based sorbents are relatively rare in literature with only a few publications cited (Bibalani and Ebrahim, 2022; Keener and Khang, 1993; Kimura and Smith, 1987; Wu et al., 2004). One example is the comprehensive study performed by Bibalani & Ebrahim (2022) on Na_2CO_3 at various operating temperatures and SO_2 concentrations (i.e., 100 – 250°C and 0.13 – 1.12 vol. % respectively). Modelling studies of this nature normally consider the order of reaction to be either fractional (e.g., 0.5) or 1st order, whilst the preferred kinetic models employed include the random pore model, shrinking core model, modified grain model or the volume reaction model. In their study, the authors developed and evaluated a sophisticated random pore model, which accounts for the whole pore size distribution (the reader is referred directly to the paper for more details on the governing equations). This is a substantial improvement on the modelling approaches of Keener and Khang (1993) and Kimura & Smith (1987) who failed to consider absorbent specific surface area as well as diffusional resistances during the sulphation reaction. For the experimental temperature range investigated, Bibalani & Ebrahim (2022) determined the activation energy to be 22.5 $kJ.mol^{-1}$, the diffusion coefficient (D_P) of SO_2 through the product layer to range between 12×10^{-19} and 15×10^{-18} $m^2.s^{-1}$ and the surface rate constant (k_S) to range between 8.8×10^{-6} and 9.1×10^{-5} $m.s^{-1}$. A comparative overview of rate constants and applied kinetic models for various other absorbents are also included in the works of Bibalani & Ebrahim (2022).

To further modelling efforts, Wu et al. (2004) developed and evaluated a mathematical model to simulate dry sorbent ($NaHCO_3$ in this case) duct injection across a fabric filter. The developed model employs parallel reaction kinetics and assumes that the process is composed of an initial stage where absorbent interacts with SO_2 in the duct followed by sorbent collection and further reaction on the fabric filter. Various pilot and demonstration scale operational results were used to validate and assess the model against typical operational parameters (temperature, particle size, residence time, NSR, SO_2 concentration and decomposition time). From the model validation and sensitivity analysis it was concluded that the SO_2 removal efficiency within the duct is negligibly small for most operational conditions, whilst significant SO_2 abatement occurs across the fabric filter cake (Wu et al., 2004). The most notable findings made during this modelling investigation was the effect of particle size and flue gas / filtration temperature on SO_2 removal efficiency. Accordingly, 10 μm absorbent particles showed a monotonic decrease in removal efficiency (from approximately 69 to 35 %) with an increase in flue gas temperature, whilst for the other particle sizes (20, 50 and 70 μm) the removal efficiency first increased then decreased. The flue gas temperature associated with each local maxima for SO_2 removal also decreased almost linearly with an increase in flue gas temperature. For the fabric filter bag modelling analysis (at a given particle size), it was shown that although the optimum filtration temperature (local maxima around 127°C) for SO_2 removal does not change significantly with a change in SO_2 concentration, the maximum SO_2 removal efficiency does however increase with an increase in SO_2 concentration (Wu et al., 2004).

Other more advanced modelling approaches have also started to gain popularity, with a few studies employing response surface methodologies (RSM), artificial neural networks (ANN) and computational fluid dynamics (CFD) (Heiszwolf and Nyssen, 2016; Makomere et al., 2023). The purpose of these advanced modelling studies, although historically more focused on calcium-based sorbents, is not only to evaluate the statistical significance of several operational parameters but also to understand two-phase flow phenomena inside the duct and optimize the location and the number of injection points as a means of improving absorbent utilization and SO_2 sulphation efficiency. A comprehensive review of the application of CFD for semi-dry flue gas desulphurization has also been recently provided by Lerotholi et al. (2022). Although computationally intensive, these studies offer a cost-effective means to benchmark and screen FGD technologies to be installed in new coal-fired power stations or retrofitted to older facilities.

7. Research gaps and significance for the south african power industry

The generation of additional taxable CO_2 as well as the increase in the life-cycle cost for waste disposal (gypsum by-product disposal) are amongst the factors which could result in the sustained net negative operational expenditure of wet FGD units currently installed in South Africa's power industry (Bagus et al., 2018; Strickroth et al., 2020; Gruenewaldt, 2013; Campbell, 2015; Vosloo, 2018; Koralegedara et al., 2019). Another threat to the successful implementation and sustainable operation of wet FGD technology is the scarcity, quality, and transportation cost of limestone in South Africa (Strickroth et al., 2020). The Kusile Power Station is currently supplied with limestone from the Idwala Industrial Holdings (Pty) Ltd quarry in Danielskuil in the Northern Cape (more than 700 km away from the Kusile Power Station). The challenge is, therefore, to evaluate and select economically viable and sustainable SO_2 abatement technologies for further roll-out to South Africa's ageing coal-fired power industry. It is also not advisable that a "one size fits all" approach is followed, but rather a life cycle and risk-based cost benefit approach be applied taking into consideration the expected remaining operational life and emissions apportionment of each power station in the fleet. The preceding paragraphs of this paper have listed several advantages (e.g., higher cost of sodium as compared to lime/limestone, but higher utilization) of utilizing sodium-based absorbents over the more commonly used calcium-based absorbents. A number of available processing technologies (several small-scale and a few full-scale commercial applications in practice) also makes sodium-based FGD an attractive option to the utility industry (Srinivasn, 2004). Literature and research performed on the emissions reduction performance and economic feasibility of implementing sodium-based FGD for the power generation industry in South Africa is relatively scarce and almost non-existing. Based on the findings made during this review the main areas of further research therefore include:

- An evaluation of the general availability, market (potential suppliers), location, and associated costs of both natural occurring and synthetic sodium-based absorbents (e.g., trona, nahcolite, NaHCO3) in South Africa. As an example, it is known that Botash SA (Pty) Ltd (a partner / subsidiary of Idwala Industrial Holdings (Pty) Ltd) is an industrial supplier of both NaHCO3 (derived from nahcolite) and soda ash (Na2CO3). Botash SA operates as an agent for Botswana Ash SA which is the supplier of choice for natural sodium products in Africa. The Botash SA operational facility is conveniently located in Alrode, Alberton where its Natalspruit depot comprises of both a 24,000 Mt bulk storage (3 silos) facility and a 2000 m2 warehouse facility (Botash SA, 2021).
- As sodium-based absorbents are generally known to be more expensive than their calcium-based counterparts, further effort is also required to investigate the feasibility of repurposing sodium-bearing waste streams (e.g., industrial brines, caustic scrubber streams, etc.) as low-cost or cost-effective alternatives. This approach also resonates well with the current global effort to stimulate circular economies as a means of eliminating waste and pollution through the circulation of raw materials and products (United Nations Industrial Development Organization (UNIDO), 2023).
- Assess the physiochemical characteristics (e.g., specific surface area, chemical composition / purity, particle size distribution, etc.) of locally sourced natural occurring, waste bearing and or synthetic

sodium-based absorbents (inorganic and organometallic) in South Africa and benchmark against published information on sodium-based absorbents used for FGD studies internationally. A detailed understanding of each absorbents physiochemical comparison could provide useful to draw meaningful conclusions with respect to the absorbent's desulphurization performance under different operating conditions.

- Evaluate the effect of different operational variables (temperature, SO2 concentration, particle size, NSR, etc.) on the SO2 removal efficiency of the locally acquired sodium-based absorbents during semi-dry and dry FGD tests and benchmark against published results on sodium-based FGD. Here the application of statistical sound parametric and optimization studies (e.g., RSM) could play an important role in evaluating multi-variate effects during desulphation using sodium-based sorbents (extracted from waste, natural occurring and synthetic). Of particular importance is the inclusion of multipollutant and additive studies to assess the individual pollutant removal efficiencies in typical, simulated flue gas mixtures (mixtures of SO2, CO2, Hg, etc.). This, to the authors knowledge, is a significant gap in the current body of knowledge.
- Kinetic studies of the semi-dry and or dry sulphation reaction of sodium-based sorbents are relatively rare in literature and therefore, presents an ideal opportunity for further contribution to the body of knowledge. A thorough kinetic and modelling study on the SO2 removal efficiency of various locally sourced, sodium-based absorbents is imperative to gain further insight in the design and selection of suitable semi-dry and dry FGD technologies to be employed in the South African power generation sector. These fundamental studies can be further supplemented by more advanced modelling approaches such as CFD.
- Perform a techno-economic study to evaluate the economic feasibility (and to compare to limestone wet FGD) of retrofitting existing power stations with sodium-based FGD technologies. A similar approach can be followed as was done for the technology selection studies performed by Bagus et al. (2018) and Harris et al. (2014). A more recent study which focused on a first order technoeconomic comparison between the wet FGD and Sulfacid® SO_2 abatement technologies can also provide useful information in this regard (Strickroth et al., 2020). The proposed techno-economic study should not only be limited solely to sodium-based absorbents and technologies but should also take into consideration hybrid and regenerative technologies (e.g., dual-alkali process). Although not done for the utility sector, a publication on the operation of a concentrated model dual-alkali scrubber plant at the Lonmin smelter has provided useful insight on the rationale of technology selection and the plant performance thus far (Bezuidenhout et al., 2012).

8. Conclusions

SO_x emission control technologies with varying water demands are available globally for use in response to stringent emissions regulations. Low-water to no-water technologies are attractive to arid and drought vulnerable regions/countries like South Africa. There is, therefore, a need for FGD systems offering low water consumption, high SO_2 and SO_3 removal efficiencies, high reliability, low capital, operating and maintenance costs, low auxiliary power consumption and marketable FGD by-products. A review of publications on technologies that employ sodium-based absorbents are scarce, thus, necessitating a need to evaluate this aspect in this paper.

Wet scrubbers (sodium-based or calcium-based), result in up to 10 – 15 % of the evaporative water losses of water-cooled coal-fired power plants. In facilities that employ dry/air cooling, the water usage due to wet scrubber can reach in the order of 40 to 70 %. Sodium-based wet scrubber technologies available in literature includes soda ash wet scrubber, dual-alkali scrubber, Wellman-Lord process, Airborne process etc.

Semi-dry scrubbing systems (sodium-based or calcium-based), namely spray dry scrubbers (SDSs) and circulating dry scrubbers (CDSs), consume about 60 % less water than wet scrubbers. Their advantages include lower investment costs (than a similar sized wet scrubber), limited production of wastewater, dry by-products, lower parasitic power consumption, a smaller footprint (which may be easier for retrofit applications), and additionally capture over 95 % of the SO_3, HCl, HF and oxidised mercury. It is important to highlight that general literature and review publications on semi-dry processes that employs sodium-based absorbents are scarce.

Processes that commonly utilizes sodium-based absorbents are sorbent injection processes. They have zero water usage or a minimal amount in cases where the flue gas is humidified to improve performance. They have been reported to be simple to install and operate, easy to retrofit with their small space requirements, and produce no wastewater. In addition, they also remove, to some extent, HCl, HF and mercury species present in the flue gas. By-products are dry and therefore easier to handle and manage as compared to the wet by-products from wet scrubbers. Their capital cost and energy consumption of the sorbent injection systems have also been reported to be significantly lower than the semi-dry and wet FGD processes. Parasitic power consumption has been reported to be around 0.2 % of electric capacity.

The drawbacks of dry sorbent inject includes higher operating costs due to the high price and consumption of the sorbent. The bulk of the operating cost is the price of the sorbent. Trona, though, is more difficult to handle than hydrated lime due to its small particle size (28 μm), its cohesiveness, and affinity for moisture. In addition, care must be taken to avoid the formation of liquid $NaHSO_3$ which can foul the downstream equipment and ductwork. Solid by-products are of less economic value and pose danger of leaching when landfilled. The sorbent injection systems are best suited for use in small (300 MWe) power plants that utilise low to medium sulphur coals, and where only a moderate SO_2 removal efficiency is required.

Poor sorbent utilisation and SO_2 removal efficiency (as compared to wet FGD technologies) of the absorbents are also major setbacks, although this can be improved through the use of additives and sorbent activation strategies. The efficiency of sodium-based FGD process has been reported to be influenced by various factors, e.g., physicochemical properties of the absorbents, sodium to sulphur stoichiometric ratio, sorbent injection schedule, injection location, operating temperature, sulphur content in coal, inlet SO_2 concentration, sorbent resident time in the duct, baghouse air-to-cloth ratio, ESP operation, etc. To conclude, high removal efficiencies of SO_2, SO_3, HCl and HF with trona, nahcolite and sodium bicarbonate have been demonstrated at many power plants over the years. Its low capital cost makes dry sorbent injection even more attractive in today's difficult economic environment. Further research work is also recommended to strengthen especially the South African knowledge base with respect to the sodium-based sorbent market, the physiochemical properties and SO_2 reduction potential of locally acquired sodium-based absorbents (both in diluted SO_2 but also simulated flue gas streams), reaction rate modelling studies as well as its techno-economic feasibility for the South African utility industry. Additionally, it is recommended to consider the reusability of the generated waste products from sodium-based dry FGD.

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Author contributions

D. Mchabe conceived the original idea for the paper (on request from Eskom and as part of its EPPEI Task Force program) and prepared the first draft (i.e., overview of processes, reaction chemistry and effect of process parameters). B.B. Hattingh and L. Koech further developed the

manuscript with the support from H.L. Rutto and H.W.J.P. Neomagus to include aspects related to other non-common Na-based sorbents, reaction modelling, absorbent benefits and disadvantages, cost considerations, gaps for further research, etc. All authors reviewed and approved the final manuscript before submission to the journal.

Data and availability

Data sharing is not applicable. The authors confirm that the data analysed in this study were a re-analysis of existing data, which are openly available at locations cited in the reference section.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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