

Factors Affecting the Rate of Absorption of Sulfur Dioxide into Fly Ash Suspensions

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Abstract

The absorption rate of sulfur dioxide into aqueous suspensions of lignite fly ash was experimentally investigated using lab-scale continuously stirred tank reactor. The effects of SO₂ inlet concentration, suspension concentration, and temperature were evaluated and reported. Concurrent gas absorption and alkalinity leaching from ash particles produced 1.5 to 4.0 times higher concentrations of Ca and Mg alkalinity and thus much higher SO₂ removal capacity compared to consecutive leaching and gas absorption due to the role of pH and chemical changes associated with it. Data on SO₂ solubility in ash suspension and pH as well as stoichiometric relations among chemical reactions are used to correlate absorption rate to alkaline metals leaching rate. Initial absorption was found to be a function of inlet SO₂ concentration and independent of suspension concentration due to quick surface leaching. In the later stages, the absorption rate becomes a strong function of the leaching rate connected to alkalinity release from the interior surfaces of ash particles.

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Keywords: Flue gas, desulfurization, sulfur dioxide, fly ash, absorption, leaching, calcium, magnesium, kinetics

1. Introduction

Fly ash is a problematic fine powder waste captured by air-pollution control equipment after fossil fuel combustion processes in power plants and other industrial activities. Due to its physical and chemical properties as well as massive production rate, this material threatens human health and all elements of the environment making fly ash management with safe disposal a big challenge (Baig and Yousaf, 2017; Blissett and Rowson, 2012). Several hundred million tons of fly ash are produced annually from power plants worldwide, with less than 50% being utilized and reused, mostly in civil engineering (construction) and agricultural (ameliorating soil conditions) applications (Yao et al., 2015). Fly ash particles captured by air pollution collection devices are transported via wet sluicing to lagoons, dry handling to landfill or reuse destination (Ritter, 2016; Ahmaruzzaman, 2010).

However, fly ash has the potential to be a resource material rather than being solely a hazardous waste. It can be used as raw material for geopolymers having adsorption and ion exchange properties to remove many air and water and wastewater pollutants (Ge et al., 2018; Blissett and Rowson, 2012; Swanepoel and Strydom, 2002). One practical and sustainable option for the power industry is the recycling and utilization of fly ash as scrubbing medium in both wet and dry flue-gas desulfurization (FGD) systems. Fly ash is known to provide alkaline species upon leaching in water which are capable of neutralizing acidic stack gases, particularly, SO₂, and the material has attracted researchers over the past decades (Li et al., 2008). This capability has been investigated, particularly by using fly ash as an

inexpensive supplement to lime or seawater in conventional wet scrubbing systems, or as the sole absorbent for FGD of low-sulfur power plants (International Energy Agency, 2020; Back et al., 2019; Liao et al., 2012). More research is needed for a better understanding of the kinetics of sulfur dioxide scrubbing in fly ash media in order to design and optimize the scrubbing process system. The main objective of this study is to evaluate the rate of SO₂ absorption into fly ash suspensions at key operating conditions in a three-phase stirred tank slurry reactor. A theoretical chemical and mass transfer analyses are used to arrive at a simple correlation for the rates of simultaneous alkalinity leaching and gas absorption processes.

2. Methodology

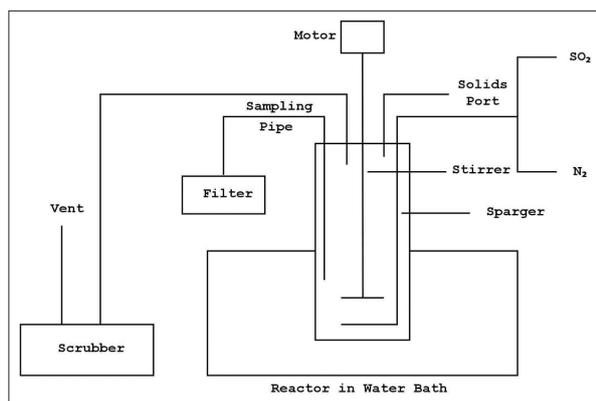
Fly ash from lignite coal is used as a source of alkalinity. The chemical composition for the ash used in this study is given in Table 1 (Al-Haj Ali, 1989). A stirred vessel was used to carry out both leaching and gas absorption experiments. The reactor consisted of a four-liter vessel of Pyrex glass, 14 cm in diameter and 34 cm in height equipped with a four-bladed turbine impeller which is 6.4 cm in diameter and 1.27 cm in width. The impeller was fitted by a 1.27 cm motor shaft which, in turn, was fitted by a mechanical seal and bearings to the reactor cover. The cover was provided with adequate ports for feeding the solid particles, temperature measurement, liquid sampling and gas exit. The cover, shaft, turbine, sparger, sampling pipe and fittings were all stainless steel. A schematic diagram illustrating the experimental setup is shown in Figure 1

Table 1. Chemical composition (weight percent) of fly ash size cuts used in the study

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO ₂	P ₂ O ₅	LOI*
53-63µm	48.0	22.2	5.83	12.7	4.31	2.00	1.22	0.77	0.01	0.26	0.82
63-75µm	47.3	22.0	6.49	12.9	4.44	2.01	1.22	0.78	0.02	0.26	0.83

*Loss on Ignition

For absorption experiments, SO₂ was diluted in nitrogen to the desired inlet gas concentration by setting the appropriate flow rates of SO₂ while maintaining the flow rate of nitrogen constant. Gases were fed to the reactor by means of a 0.5 cm diameter stainless steel ring sparger installed through the reactor cover. Before that, they passed through a long tubing to allow for better mixing. The sparger ring was provided with sixteen perforations, 0.05 cm diameter each. Each gas was delivered at 1.36 atm. For leaching experiments, only nitrogen was allowed to pass through the reactor. SO₂ and N₂ flow meters were calibrated by the soap-bubble method and wet-test meter, respectively. Effluent gases from the reactor were passed through a twenty-liter container with 20% sodium hydroxide to remove unreacted SO₂, followed by a vent to allow non-absorbed gases to pass to the fume hood.

**Figure 1.** Schematic diagram illustrating the experimental setup.

A variable speed stirrer capable of providing up to 2000 rpm of impeller speed was used. The speed was adjusted and monitored using a strobe light. All the reactor experiments were carried out at a constant temperature. Isothermal conditions were maintained by immersing the reactor in a constant-volume water bath. For the leaching experiments, the pH of the water was adjusted to the desired level prior to the addition of the solids. For the absorption experiments, the pH of the water was not adjusted; rather it remained in the range of 5.4-5.6 due to the acidic nature of aqueous species present. The suspension pH was not controlled in order to quantify the changes caused by ash leaching, gas absorption or both. Initial pH was adjusted to 2.0 or 6.0 for leaching-only experiments (without SO₂ absorption) using 2.0 N nitric acid.

Ash suspensions were prepared by the addition of an accurately weighted amount of ash powder to a volume of 2 L of distilled water in the reactor at the desired conditions of the experiment (stirring, temperature and initial pH). Solids were fed by a funnel through a designated port in the reactor

cover and it was completed within ten to twenty seconds. Samples were withdrawn from the reactor at the desired times (3, 5, 10, 15, 30, 45, 60 min ... etc.) through a sampling pipe into a vacuum filtration system. About 5-10 cm³ of filtrate were collected through 0.45µm pore-size membranes into a screw-capped test tube. Part of the filtrate was used to measure the leachate pH and the rest was used for the determination of dissolved metal concentrations.

Three types of analyses were performed on liquid samples, namely, determination of dissolved Ca or Mg concentrations released during leaching, both in the absence and the presence of gas absorption using a Perkin Elmer atomic absorption spectrophotometer; determination of concentrations of absorbed sulfur S(IV) species was done using iodometric titration, and measurement of pH was conducted using a digital pH meter. The chemical composition of ash particles (expressed as weight percent of CaO and MgO among other components) are conducted using X-ray spectrophotometry. The composition of the gas feed to the reactor was analyzed by a Hewlett Packard gas chromatography Model 5890A to verify the percentage SO₂ in the N₂/SO₂ mixture set by adjusting the individual gas flow rates (Al-Haj Ali, 1989).

3. Results and Discussion

In the absence of SO₂ gas, leaching experiments in the reactor at specified conditions produced the results shown in Table 2. The alkaline species leached out in significant amounts from fly ash particles are Ca and Mg cations, with Na and K cations being undetectable. Lower pH is favorable to dissolve more Ca and Mg due to the effect of acid-base interaction, which is also confirmed in other reported studies (Gao et al., 2011; Gitari et al., 2009). Dissolved calcium concentrations produced are quite higher than those of magnesium, an observation which can be explained by the fact that calcium hydroxide is far more soluble in water than magnesium hydroxide. The solubility product (K_{sp}) of Ca(OH)₂ at 25°C is 5.02 x10⁻⁶ mol/L compared to 5.61 x10⁻¹² mol/L for Mg(OH)₂ (Lide, 2003). Therefore, these two metal ions are responsible for the alkaline character of the ash suspensions.

Table 2. Concentrations of dissolved alkaline metals after 60 minutes of leaching in reactor

Cation	Concentration (mg/L)	
	pH 2.0	pH 6.0
Ca ²⁺	164	55
Mg ²⁺	35	1
Na ⁺	nil	Nil
K ⁺	nil	Nil

Results of concentration (for dissolved sulfur or Ca and/ or Mg) versus time obtained from experiments on SO_2 absorption into pure water as well as leachate (solid-free) and suspensions of fly ash will be presented and discussed to illustrate the effect of selected operating conditions on gas absorption rate. A theoretical analysis will also be presented and applied to the experimental data. The total concentration of S(IV), including both concentrations of unhydrolyzed $\text{SO}_{2(\text{aq})}$ and bisulphite ions (HSO_3^-), was determined experimentally by the iodometric titration. Since the reactor was purged with nitrogen before the SO_2 flow started and there was no oxygen in the feed gas, no oxidation took place in the reactor and, therefore, no sulphate (SO_4^{2-}) was formed. The ash powder was added three minutes before SO_2 was sparged in and the pH increased to around 10. All experiments showed that as soon as the gas was introduced into the liquid phase, the suspension pH dropped sharply due to the rapid absorption of SO_2 , and then it stabilized at a value in the range of 5.4-5.6, which is considered to be initial pH for absorption study. The pH profiles of the three-phase system during simultaneous leaching and gas absorption under selected process parameters are reported.

3.1 Effect of Temperature

The effect of suspension temperature on the total concentration of aqueous sulfur, S(IV), obtained by the absorption of SO_2 into lignite ash suspensions is shown in Figure 2. The experiments were carried out at 20, 40, and 55°C while keeping the suspension concentration at 10 g/L and the SO_2 inlet concentration at 0.5 mol %. S(IV) values obtained at 55°C are slightly less than those obtained at lower temperatures, which can be attributed to lower gas solubility at the gas-liquid interface. Other studies also indicated that the negative effect of temperature on SO_2 solubility is slightly higher than its positive effect on diffusivity (Ma et al., 2019).

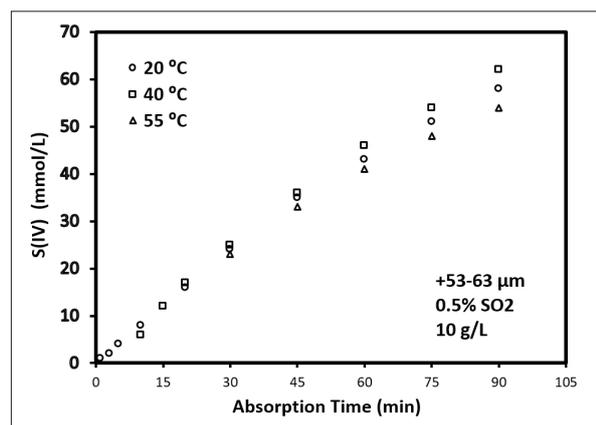


Figure 2. Effect of suspension temperature on absorbed S(IV) concentration.

Temperature is expected to have a dual effect on the overall process of SO_2 removal by suspensions of sparingly soluble solids. The dissolution of alkaline compounds in the solid particles gets a small enhancement as temperature is increased due to the increase in their solubility and ionic diffusivities, while the solubility of the gas is decreased by about 50% when the temperature is increased from 20°C to 40°C. The outcome of these two opposing effects will depend on the characteristics of the medium and the experimental

conditions including the temperature level. Due to the insignificant influence of temperature on the absorption rate, the process can be assumed to be controlled by mass transfer rather than chemical reaction kinetics. Further experiments were conducted at 40°C.

3.2 Absorption in Water, Clear Solution, and Suspension

The results of absorption experiments using the three different media are shown in Figure 3. In one experiment, inlet concentration of SO_2 of 0.5 mol % was allowed to equilibrate with distilled water in the stirred tank reactor at 40°C. The solution is saturated with dissolved unhydrolyzed SO_2 and bisulphite ions [total S(IV)] in 20-30 min levelling off at 11 mmol/L. Another absorption experiment was carried out in which the absorbing medium is a clear solution of ash leachate. A leaching-only experiment was conducted in the reactor using 10 g ash/L at initial pH of 5.5 and 40°C for sixty minutes. The suspension was filtered, ash particles were discarded, and a filtrate was added to the reactor as a medium for SO_2 absorption. The S(IV) concentration leveled off at 45-60 minutes at 21 mmol/L, twice as much as S(IV) in water.

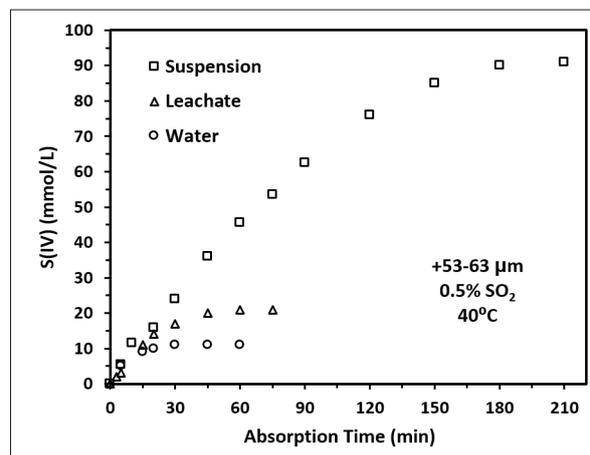


Figure 3. Comparing SO_2 absorption into water, leachate solution and suspension.

In a third experiment, concurrent leaching from suspension (at 10 g/L) and gas absorption are allowed to proceed for the same conditions above. It can be seen that during the first 10-15 minutes of contact, the rate of absorption was the same regardless of the type of absorbing medium as indicated by the initial slopes. After sixty minutes, the solution of leachate solution absorbed twice as much SO_2 as pure water at the given conditions. When ash suspension was allowed to release the alkalinity simultaneously with absorption, the amount of the gas absorbed after sixty minutes (and later times) increased to more than four times as much as that of the solid-free leachate solution. This large difference in the absorption capabilities of the suspension and leachate reflects a corresponding large difference in the amount of available soluble Ca and Mg. Since this alkalinity is produced by the continuous dissolution of the alkaline metals in the ash, the concurrent use of a suspension rather than a leachate solution is necessary to enhance leachable alkalinity and maximize the scrubbing ability of the ash. In order to achieve this, the conditions that favor the dissolution of Ca and Mg, in particular, high suspension concentration and a lower pH, should be maintained.

3.3 Effect of Suspension Concentration

The effect of ash suspension concentration or slurry density on the change of S(IV) concentration with time is shown in Figure 4. The inlet SO₂ concentration was kept constant at 0.5 mol %. In the first 20-30 minutes, gas absorption capability of the suspension is quite independent of the amount of solids present due to the readily soluble and sufficient Ca and Mg released from external particle surfaces. After this initial period, S(IV) concentration increased gradually with the increasing of suspension concentration (5, 10 and 20 g/L) to level-off at different times depending on the quantity of alkalinity provided by each suspension concentration. The same trend is reported by Liao et al. (2012) who experimentally studied the SO₂ removal in coal fly ash slurries.

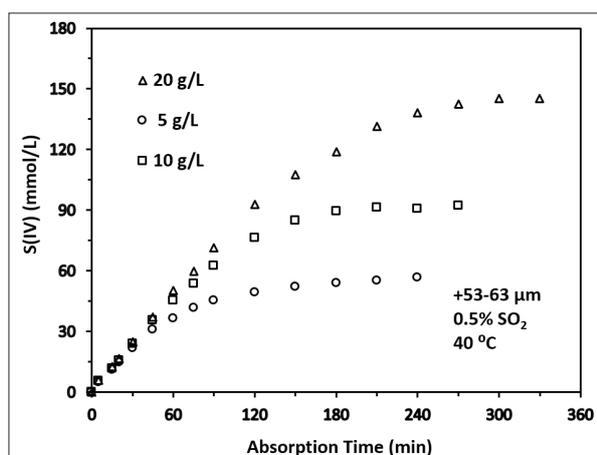


Figure 4. Effect of suspension concentration on the amounts of S(IV) absorbed.

3.4 Comparing Leached Metal Cations with and without Absorption

The concentrations of Ca and Mg species released from ash during SO₂ absorption at different suspension concentrations are shown in Figure 5 (a,b). To further illustrate the significant differences between gas absorption capabilities of concurrent absorption/ leaching and leaching prior to absorption, the concentrations of Ca or Mg released from ash in the absence of SO₂ are plotted in Figure 6 (a,b). A comparison of data in these two Figures indicate that the concentrations of metals released during absorption increased by a factor of 1.5- 2.0 and 1.5- 4.0 times for Ca and Mg, respectively compared to those in the absence of SO₂. This comparison is based on values obtained at contact times at 60 and 180 minutes, when the curves started to level off. Moreover, dissolution of Ca and Mg in the presence of absorbed SO₂ continued for much longer times before the concentrations reached a constant value. The large increase in dissolved Ca and Mg concentrations can be explained by fast chemical reactions between acidic species produced by the hydrolysis of SO₂ (bisulphite ions) with alkaline metal ions (Ca²⁺ and Mg²⁺). These reactions are given and discussed later along with the effect of pH on the concurrent leaching and absorption processes.

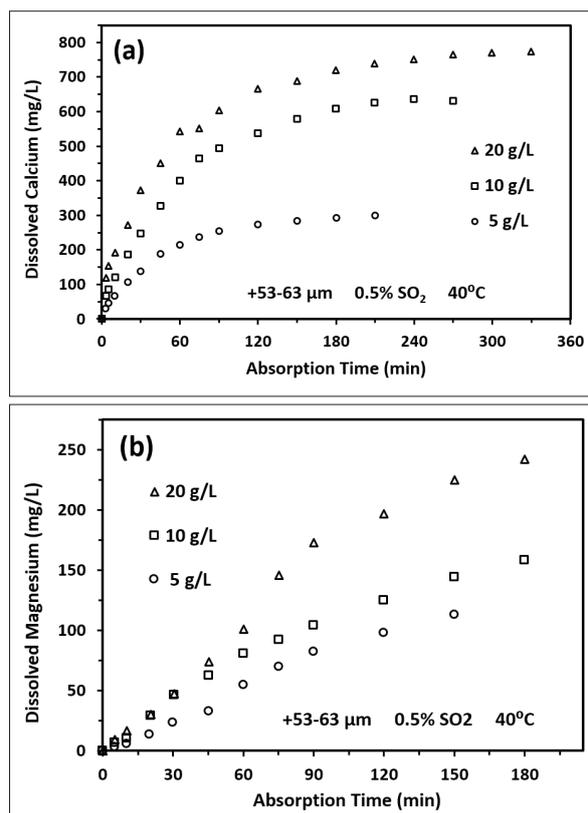


Figure 5. (a, b). Concentrations of Ca and Mg released from ash suspensions during SO₂ absorption.

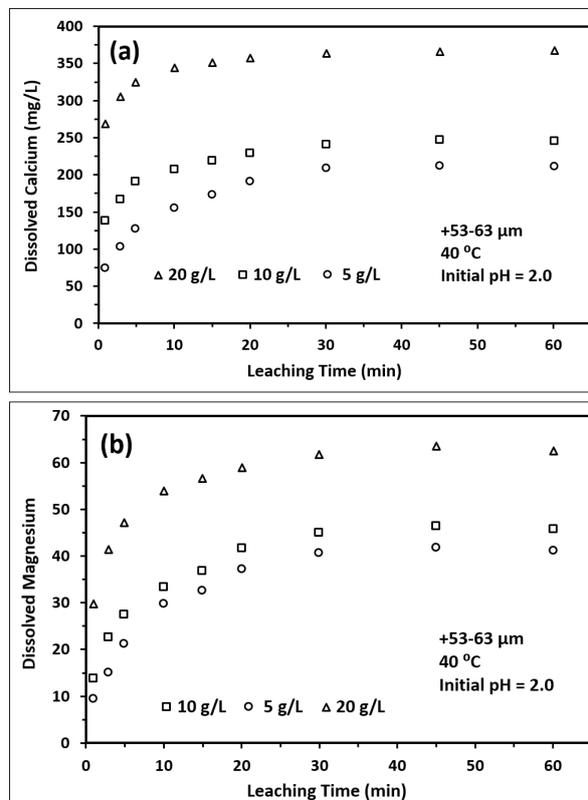


Figure 6. (a, b). Concentrations of Ca and Mg released from ash suspensions prior to SO₂ absorption.

3.5 Effect of SO₂ Inlet Concentration

Results of S (IV) concentrations versus absorption time at three different SO₂ inlet concentrations (expressed as mol percent SO₂ in N₂/SO₂ mixture) and constant suspension concentration (10 g/L) are plotted in Figure 7. At any given time, S (IV) increased with increasing the SO₂ gas inlet concentration since more SO₂ will dissolve in solution accordingly. Similar results are reported in the literature including those of Ma et al. (2019) who studied SO₂ scrubbing by seawater and Liao et al. (2012) who studied the SO₂ removal in fly ash slurries at inlet gas concentrations 1000-10000 mg SO₂/m³.

A reactor model based on mass balance is useful in expressing initial absorption rates, at which most of the gas is removed in the early stages of the process. Based on the assumption of a well-mixed gas phase, a mass balance for SO₂ over the entire gas volume in the reactor, V_g, at any time, t, gives:

$$Q C_{gf} - Q C_g - r V_L = V_g (dC_g/dt) \quad (1)$$

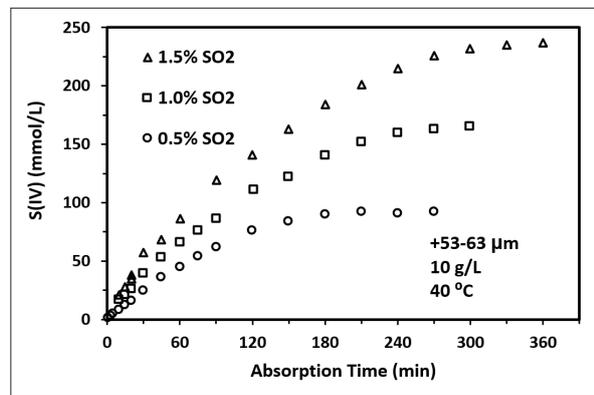


Figure 7 Effect of SO₂ inlet concentration on the amounts of S(IV) absorbed.

The accumulation term (dC_g/dt) can be neglected because of the small values of both the gas volume, V_g, and the rate of change in the gas concentration with time. The gas volume (or holdup) in the reactor was estimated to be about 100 cm³ which is only 5% of the liquid volume (2 L). Also, the variation of exit gas-phase concentration, C_g, with time is not high especially at the later stages of absorption, thus:

$$C_{gf} - C_g = r (V_L/Q) = V_L/Q (dC_T/dt) \quad (2)$$

$$C_g = C_{gf} - (V_L/Q) (dC_T/dt) \quad (3)$$

When the percentage of SO₂ removal [calculated as $\{(C_{gf} - C_g)/C_{gf}\} \times 100\%$] is close to 100%, the exit concentration of SO₂ is very small compared to the inlet concentration; therefore, C_g can be neglected. In general, SO₂ removal efficiencies close to 100% were obtained during the initial stage of absorption when the liquid phase contained abundant alkalinity. Assuming that the gas is well-mixed, the absorption rate is given by:

$$dC_T/dt = Q (C_{gf}/V_L) \quad (4)$$

The equation above suggests that if the volume of the liquid and the volumetric flow rate are fixed, initial absorption rate depends only on the concentration of SO₂ in the feed. This is demonstrated by the slopes of S(IV)

concentration vs. time lines shown in Figure 8 (a), which are calculated by linear regression (equations and correlation coefficients given on the Figure), then plotted against the inlet SO₂ concentrations as shown in Figure 8 (b). The slope of the resulting line is 3.0 min⁻¹ (also from linear regression), which is close to the ratio of $Q/V_L = 6.5 \text{ L}\cdot\text{min}^{-1}/(2\text{L})$, or 3.25 min⁻¹. Furthermore, equation (4) suggests that as long as the SO₂ removal is close to 100%, the rate of absorption does not depend on the absorption medium. This conclusion is essentially confirmed by the values of the initial rates obtained from a number of representative experiments, which are presented in Table 3. It is important to note that these initial rates were obtained at high levels of solution pH which prevailed at the beginning of the experiments.

Table 3. Initial rates of SO₂ absorption for different media and conditions

SO ₂ Inlet Concentration	Medium*	Initial Rate (mmol/L/min)
0.5 mol % (0.005 atm = 0.195 mmol/L)**	Pure water	0.76
0.5 mol %	Clear leachate solution	0.81
0.5 mol %	Suspension at 10 g/L	0.79
0.5 mol %	Suspension at 20 g/L	0.80
1.0 mol % (0.010 atm = 0.390 mmol/L)	Suspension at 10 g/L	1.52
1.5 mol % (0.015 atm = 0.585 mmol/L)	Suspension at 10 g/L	2.00

*Other conditions were fixed ** Using ideal gas law

3.6 The Role of pH

The values of pH during SO₂ absorption into ash suspensions are given in Table 4 at different ash suspension concentrations and SO₂ inlet concentrations. It can be seen that during the initial stage of absorption, there was a sharp drop in the pH which lasted for few minutes, after which the suspension pH stabilized at a value in the acidic range for the rest of the experiment. This relatively constant pH level is the resultant of the effects of the two concurrent processes of gas absorption and leaching of alkaline metals. The hydrolysis of absorbed (aqueous) SO₂ to bisulphite ions results in producing constant supply of hydrogen ions which will drive dissolution of alkaline metal oxides through reaction with hydroxide ions produced by the alkalinity leaching process. Maintaining a low pH throughout the absorption process is important to enhance and further the dissolution of alkaline species from the ash particles (chemical equations given below). The fact that the overall pH level is low eliminates any possibility of absorbing a fraction of SO₂ which is present in the actual power plant flue gas in 50-100 times as much as SO₂. Moreover, carbon dioxide may be absorbed in the scrubbing solution when the pH is higher than 7.0. In industrial scale scrubbing processes and in the presence of oxygen in the flue gas, lower pH will speed up the oxidation from sulphite to sulphate (Poullikkas, 2015; National Lime Association, 2003).

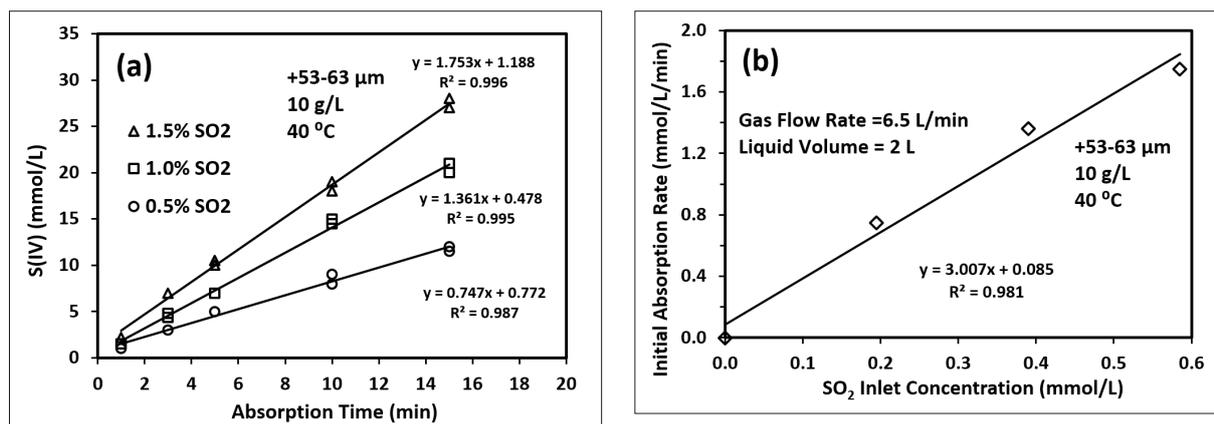


Figure 8. (a, b). Initial SO₂ absorption rates as a function of gas inlet concentration.

Table 4. Suspension pH during absorption into ash suspensions at different conditions

Time (min)	Suspension concentration (g/L) (SO ₂ inlet concentration = 0.5%)			SO ₂ inlet concentration (Suspension concentration = 10 g/L)		
	5	10	20	0.5%	1.0%	1.5%
0	9.6	9.9	10.3	9.9	9.75	10.1
1	7.0	7.1	7.35	7.1	6.6	6.8
3	3.7	3.7	3.8	3.7	2.9	2.7
5	3.55	3.5	3.7	3.5	2.8	2.6
10	3.4	3.35	3.55	3.35	--	2.5
15	--	3.25	--	3.25	2.75	--
20	3.2	3.35	3.4	3.35	--	2.5
30	3.1	3.3	3.4	3.3	2.6	2.45
45	3.0	3.3	3.3	3.3	2.6	2.4
60	3.0	3.25	3.35	3.25	2.65	2.45
75	2.95	3.25	3.35	3.25	2.5	2.5
90	3.05	3.2	3.4	3.2	2.5	2.5

3.7 Solution Chemistry

The results discussed earlier have demonstrated that after the initial drop from highly alkaline to acidic levels, the pH was never greater than 4.5 in any of the absorption experiments performed in this study. In this pH range, the predominance diagram of sulfur species (Beyad et al., 2014) shows that the only important species in the liquid phase are the aqueous molecular SO₂ and bisulphite ion. The sulphite ion does not exist in the solution during this period due to lower pH. Based on this, the following equations represent the reactions taking place in the mixed three-phase system

(Slack et al., 1972):

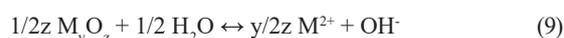
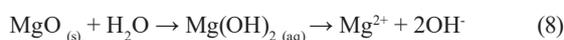
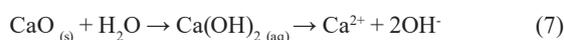
Gas Absorption by water:



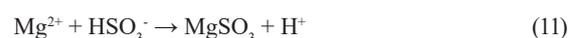
Absorbed Gas Hydrolysis:



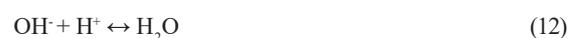
Metal Dissolution:



Metal-Sulfur Reactions:



Acid-Base Neutralization:



In the chemical model above, it is assumed that alkaline ions other than Ca and Mg are negligible (Table 2). According to Uchida et al. (1975), the reaction between absorbed gas (SO₂) and dissolved solid species [Ca(OH)₂ or Mg(OH)₂], is fast and thus the overall absorption process rate is controlled by the slower step of diffusional mass transfer. The fast reactions among aqueous species (Equations 10 and 11) do enhance the solid leaching rate and accordingly the gas absorption rate. The total concentration of sulfur compounds in solution [S(IV)] at constant pH is the sum of the concentrations of molecular SO_{2(aq)} and the bisulphite ions, HSO₃⁻:

$$C_T = C_A + C_B \quad (13)$$

The solubility of SO₂ gas in a solution (Equation 5) can be expressed in terms of Henry's law constant, H, defined as C_A/p_{SO₂}. Henry's law constant for SO₂ in water can be

calculated from the following equation at 40°C (Rabe and Harris, 1963):

$$H = \exp [(2851.1/T) - 9.3795] \quad (14)$$

For a pressure of 1 atm, the solubility is 763 mmol/L and for 0.005 atm it is only 3.8 mmol/L. Therefore, the main component of S(IV) is bisulfite ions, that is, $C_A \ll C_B$.

3.8 Stoichiometric Relationships

The constant pH after 10-15 minutes of absorption implies that the hydrogen ion concentration is constant. To satisfy the dissociation equilibrium constant of water (Equation 12), the concentration of the hydroxide ion should also be constant. Therefore, the rate of the generation of hydroxide ions by the dissolution of metal compounds from ash (Equation 9) is equal to the rate of the generation of hydrogen ions by the hydrolysis of the dissolved SO_2 (Equation 6). The latter rate is also equal to the rate of generation of bisulfite ions from the same reaction:

$$d[H^+]/dt = d[OH^-]/dt \quad (15)$$

$$d[H^+]/dt = d[HSO_3^-]/dt = dC_B/dt \quad (16)$$

$$d[OH^-]/dt = (y/2z) d[M^{2+}]/dt = dC_m/dt \quad (17)$$

From the abovementioned stoichiometric relations, the following relationship equation between the rates of metal leaching and bisulfite ions production is obtained:

$$dC_m/dt = (y/2z) dC_B/dt \quad (18)$$

Stoichiometric relations also indicate that the rate of SO_2 absorption from the gas phase by the liquid medium should be equal to the rate of increase in the total concentration of S(IV) in solution, C_T , and it is given by:

$$dC_T/dt = dC_A/dt + dC_B/dt \quad (19)$$

Substituting for the bisulfite term from equation (18):

$$dC_T/dt = dC_A/dt + (2z/y) dC_m/dt \quad (20)$$

Which can also be represented by:

$$R_{\text{Absorption}} = R_A + (2z/y) R_{\text{Leaching}} \quad (21)$$

R_A denotes the rate of transfer of molecular SO_2 from gas-liquid interface to bulk liquid (mmol $SO_{2(aq)}/L/min$). Both $R_{\text{Absorption}}$ and R_{Leaching} were calculated based on the experimental data of S(IV) vs. absorption time [Figure 4] as well as dissolved calcium plus magnesium (leached out during SO_2 absorption) vs. leaching time [Figure 5 (a, b)].

The rates calculated using data obtained at different suspension concentrations of 5, 10, and 20 g/L are plotted according to the model expressed in equation 21 and the results obtained from linear regression are given in Table 5. The linear plots are shown in Figure 9, which indicates that gas absorption rates are strongly dependent on alkalinity leaching rates. In the special case of $z/y = 1$ (Equations 7-9) applicable to the leaching of calcium and magnesium only, the slope is 2, which lies in the above range of slopes. Other values for the slope may be obtained depending on the complexity of the mixture where other sources of alkalinity

or acidity are involved. Figure 9 also indicates that the rate of transfer of molecular SO_2 from gas-liquid interface to bulk liquid, R_A , increased with the increasing of the suspension concentration. This can be explained by the fact that at higher alkalinity, hydrolysis reaction (Equation 6) is shifted to bisulphite formation and more $SO_{2(aq)}$ is needed to maintain the equilibrium. Overall, such a simple stoichiometric model developed in this work can be useful in evaluating the interdependency of gas absorption and alkalinity leaching rates on each other in ash-based scrubbing media.

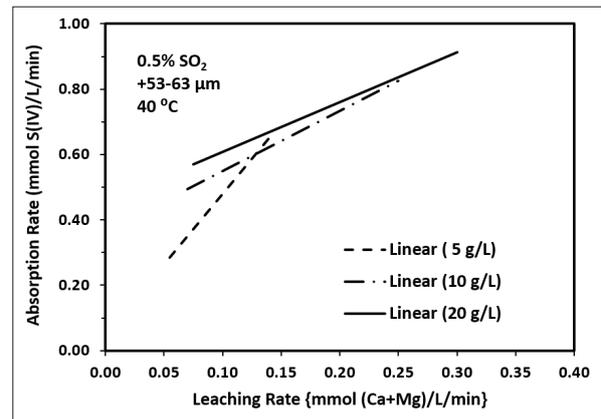


Figure 9. Correlation between SO_2 gas absorption and alkalinity leaching rates.

Table 5. Linear regression analysis of absorption- leaching rates correlations

Condition	Slope (2z/y)	Intercept (R_A)	Correlation Coefficient (R^2)
5 g/L	4.968	0.011	0.990
10 g/L	1.986	0.345	0.987
20 g/L	1.404	0.478	0.967

5. Conclusions

Several conclusions can be deduced from this study. Leaching of calcium and magnesium from ash particles constitute the effective soluble alkalinity for SO_2 absorption through neutralization reaction. Leaching rate depends on factors in the solid, liquid, and gas phases that determine the extent of Ca and Mg dissolution and hence subsequent gas absorption. In the initial stage of absorption (10-15 min), absorption rate is independent of the aqueous medium and function only of inlet gas concentration. The use of a solid/liquid suspension rather than a leachate or extract solution of ash is necessary to maximize the amount of alkalinity for higher SO_2 removal. Simultaneous alkalinity dissolution and gas absorption result in a constant pH that is maintained over most of the contact time between the three phases, and the value of which depends on the conditions prevailing in the reactor. The concentrations of total aqueous sulfur species, or S(IV) increased significantly with increasing the inlet concentration of SO_2 and suspension concentration not affected by suspension temperature or particle size within the tested period of contact time of ninety minutes. The overall conclusion is that fly ash-water suspensions are an attractive and cost-effective medium for SO_2 removal from low-sulfur fossil fuel flue gas.

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Nomenclature

C_{gf} : Feed concentration of gaseous SO_2 , mmol/L of gas mixture,

C_g : Exit concentration of gaseous SO_2 , mmol/L of gas mixture,

C_m : Concentration of metal ions (Ca^{2+} and Mg^{2+}) from dissolution of ash alkalinity, mmol/L,

C_A : Concentration of aqueous SO_2 , mmol/L,

C_B : Concentration of bisulphite ion (HSO_3^-), mmol/L,

C_T : Concentration of total dissolved sulfur (IV), both $SO_{2(aq)}$ and HSO_3^- , in the bulk liquid, mmol/L,

K_{sp} : Solubility product, mol/L

p_{SO_2} : partial pressure of SO_2 in the gas feed to the reactor, atm,

Q_g : Gas volumetric flow rate to the reactor, L/min,

R_A : Rate of transfer of molecular SO_2 from gas-liquid interface to bulk liquid, mmol $SO_{2(aq)}$ /L/min,

V_L : Volume of liquid phase in the reactor, L.

References

- Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science* 36: 327-363.
- Al-Haj Ali, A. (1989). Characterization of the alkaline metal dissolution and sulfur dioxide absorption of fly ash slurries, Ph.D. Thesis, McGill University, Montreal, Canada.
- Al-Harashsheh, A.M., Shawabkeh, R.A., Al-Harashsheh, M.S. Batiha, M.M. (2011). Removal of sulfur dioxide by a slurry of Jordanian oil shale ash. *Energy Sources, Part A: Recovery Utilization, and Environmental Effects* 34 (1): 90-98.
- Back, S.K., Mojjammal, A.H., Jo, H.H., Kim, J.H., Jeong, M.J., Seo, Y.C., Joung, H.T., Kim, S.H. (2019). Increasing seawater alkalinity using fly ash to restore the pH and the effect of temperature on seawater flue gas desulfurization. *Journal of Material Cycles and Waste Management* 21 (4): 962-973.
- Baig, K.S. and Yousaf, M. (2017). Coal fired power plants: Emission problems and controlling techniques. *Journal of Earth Science and Climatic Change* 8 (7): 404.
- Beyad, Y., Burns, R., Puxty, G., Maeder, M. (2014). A speciation study of sulfur (IV) in aqueous solution. *Dalton Transaction* 43 (5): 2147-2152.
- Blissett, R.S. and N.A. Rowson. (2012). A review of the multi-component utilization of coal fly ash. *Fuel* 97: 1-23.
- Lide, D.R. (Ed.). (2003). Solubility constants for compounds at 25°C. In "CRC Handbook of Chemistry and Physics", 84th Edition, National Institute of Standards and Technology, CRC Press, Boca Raton, USA.
- Gao, R., Pan, W., Zhang, X., Xu, H., Ren, J. (2011). Dissolution rate of magnesium hydrate for wet flue gas desulfurization. *Fuel* 90 (1): 7-10.
- Ge, J.C., Yoon, S.K., Choi, N.J. (2018). Application of fly ash as an adsorbent for removal of air and water pollutants. *Applied Sciences* 8 (7): 1116-1140.
- Gitari, W., Fatoba, O., Petrik, L., Vadapalli, V. (2009). Leaching characteristics of selected South African fly ashes: Effect of pH on the release of major and trace species. *Journal of Environmental Science and Health- Part A* 44 (2): 206-220.
- International Energy Agency, <https://www.iea-coal.org/wet-scrubbers-SO2-control>, visited on 31/05/2020.
- Li, L., Fan, M., Brown, R.C., Kozeil, J.A., van Leeuwen, J. (2008). Reduction of SO_2 in flue gas and applications of fly ash: A review. *Power Plant Chemistry* 10 (5): 291-301.
- Liao, Y., Zhai, M., Li, F., Shi, W., Zhang, Y., Dong, P. Experimental study on desulfurization of fly ash slurry. *Applied Mechanics and Materials* 148-149: 487-490.
- Ma, Y., Xu, L., Zhou, J., Yang, K., Li, G. (2019). Experimental investigation of seawater scrubbing of SO_2 in turbulent contact absorbers and spray towers. *Environment Protection Engineering* 45 (3): 39-53.
- National Lime Association (2003). Wet flue gas desulfurization technology evaluation, Report of Project No. 11311-000, NLA, Chicago, IL, USA, pp. 50.
- Poullikkas, A. (2015). Review of design, operating, and financial considerations in flue Gas desulfurization systems. *Energy Technology and Policy* 2 (1): 92-103.
- Rabe, A. E. and Harris, J. F. (1963). Vapour liquid equilibrium data for the binary system, sulfur dioxide and water. *Journal of Chemical Engineering Data* 8 (3): 333-336.
- Ritter, S.K. (2016). A new life for coal ash. *Chemical and Engineering News* 94 (7): 10-14.
- Slack, A.V., Falkenberry, H.L., Harrington, R.E. (1972). Sulfur oxide removal from waste gases. *Journal of the Air Pollution Control Association* 22 (3): 159-166.
- Swanepoel, J. and Strydom, C. (2002). Utilization of fly ash in a geopolymeric material. *Applied Geochemistry* 17: 1143-1148.
- Uchida, S., Koide, K., Shindo, M. (1975). Gas absorption with fast reaction into a slurry containing fine particles. *Chemical Engineering Science* 30: 644-646.
- Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S., Xi, Y.Q. (2015). A comprehensive review on the applications of coal fly ash. *Earth-Science Reviews* 141: 105-121.