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Recovery and Reuse of SO₂ from Thermal Power Plant Emission

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1. Introduction

Thermal power plants are major sources of air pollutants. Three major air pollutants emitted from thermal power plant are Suspended Particulate Matter (SPM), Sulphur di oxide – (SO₂), Sulphur tri oxide (SO₃), and (NO₂, NO₃). The amount of pollutants emitted from any power plant depends upon the type of the fuel used, burning method and type of control equipment. These pollutants finally found in ambient air. Coal is re-emerging as a the dominant fuel for power generation in various power plants. ¹ Various coal such as petcock, lignite, bituminous etc. used in power plants in which % S have 6.0 %, 4.0 % and 3.8 % respectively. The common elements in fuel are Carbon, which is principle combustible constitute of all fossils. Oxygen, nitrogen, hydrogen, and Sulphur (S) are not combustible elements. Sulphur in coal cannot be destroyed it can only be converted to one form to another During the combustion process , Sulphur react with oxygen and formed SO₂ and SO₃.

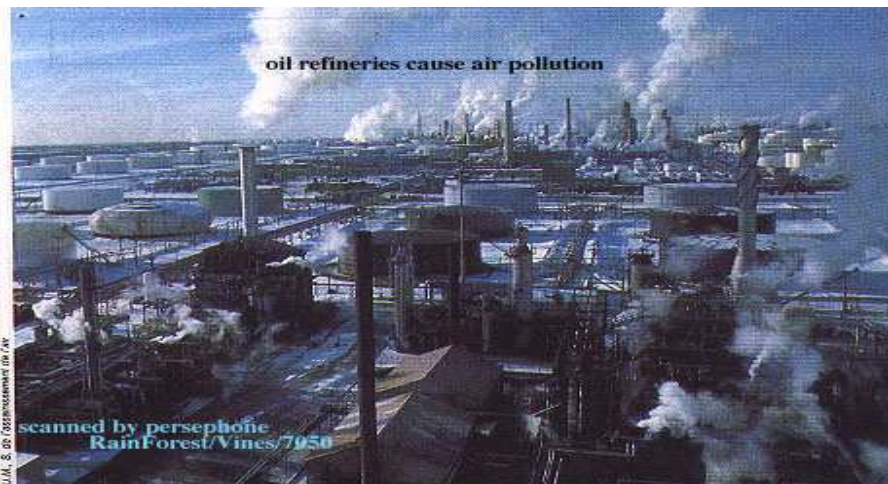
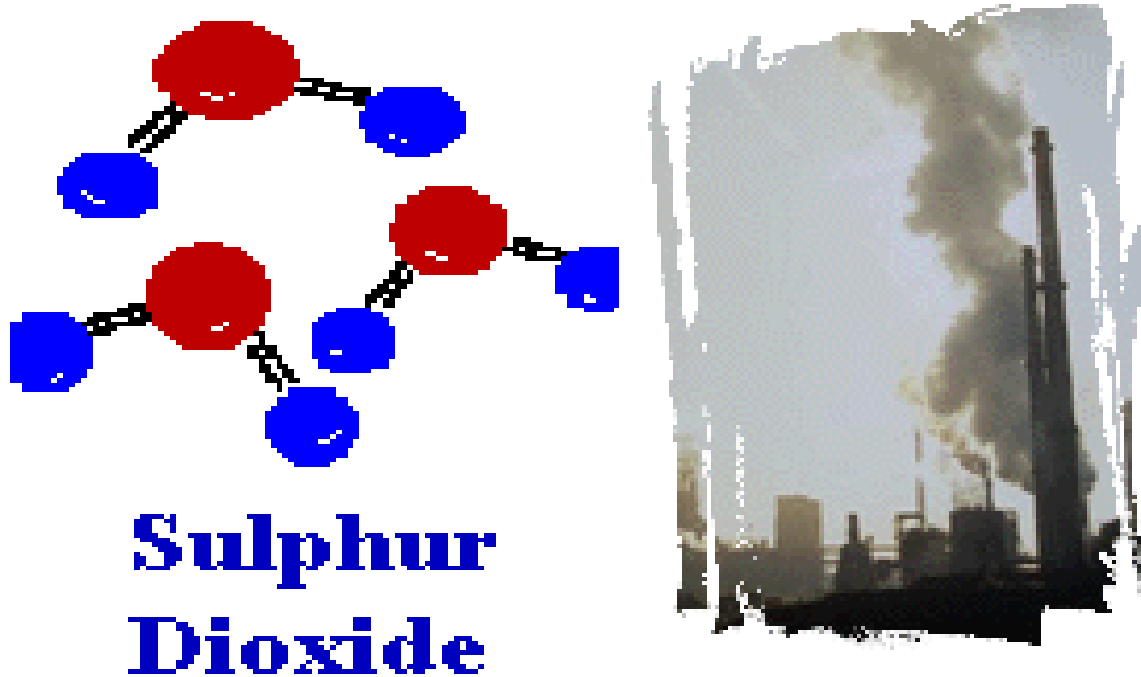
SO₂ is a major constituent in air pollution.² and affects the environment by no. of ways like acid rain, corrosions and severe damage to the health. SO₂ causes a wide variety of health and environmental impacts because of the way it reacts with other substances in the air. Particularly sensitive groups include people with asthma who are active outdoors and children, the elderly, and people with heart or lung disease. Intensity of SO₂ emission can be observed by following example. “ A typical 6 MW power generation unit using furnace oil containing 2 % Sulphur will emit 388 tons of SO₂ per year, based upon 320 working days or A 22.5 MW power generation unit will emit 1690 tons of SO₂ per year by using Pet Coke.”³⁻⁴

2. Review of literature

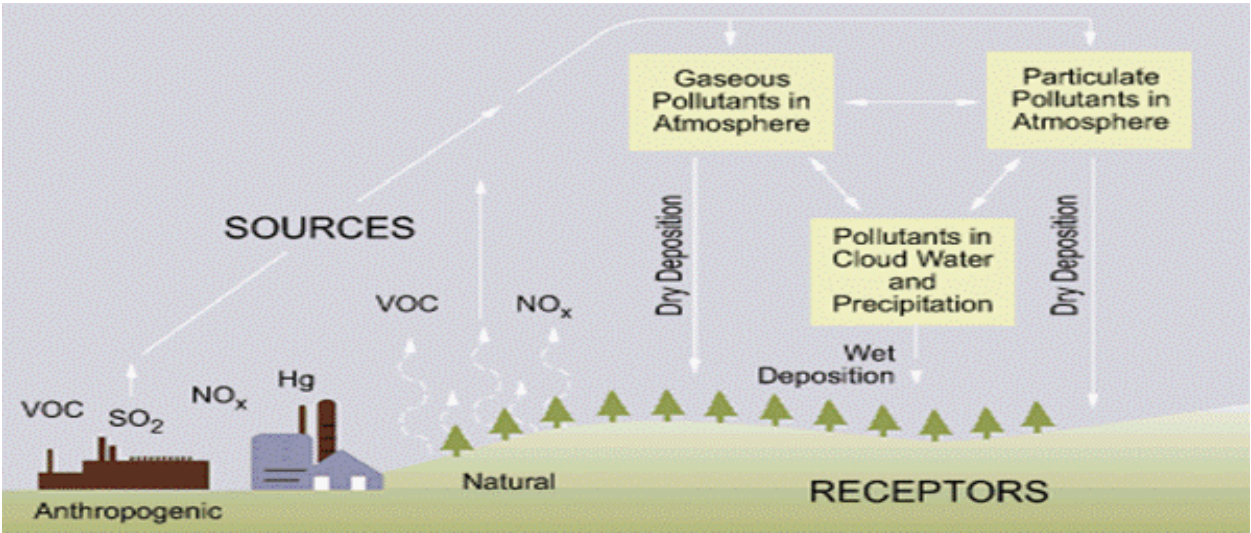
The acid rain problem is mainly attributed to anthropogenic sulphur dioxide and, to a lesser extent, nitrogen oxide emissions. Sulphur dioxide can be directly removed from the atmosphere through dry or wet deposition. The main sink of atmospheric SO₂, however, is the oxidation to SO₄²⁻ in the gas phase and in the liquid phase of clouds, fog and rain. These processes are, besides the oxidation of nitrogen compounds, the major source of acidity in acid rain or acid fog. The relative importance of different pathways for atmospheric oxidation of sulphur dioxide can vary under different conditions such as relative humidity,

intensity of solar radiations, temperature and degree of air pollution. Under favourable conditions the oxidation of sulphur dioxide can occur in the atmospheric aqueous phase at significantly faster rates than in the gas phase. It is believed that, on a global scale, more than 70% of the global oxidation of SO_2 to SO_4^{2-} occurs within cloud droplets (Langner and Rodhe 1991). The oxidation of sulphur dioxide has been one of the most frequently studied reactions in aqueous atmospheric droplets. Three reaction pathways are considered to be dominantly responsible for oxidation of SO_2 in atmospheric water droplets. These are the oxidation of dissolved SO_2 by H_2O_2 , O_3 and O_2 in the presence of transition metal ions as catalysts (Seinfeld and Pandis 1998; Warneck et al. 1996). In acid solutions the major oxidant is H_2O_2 , whereas the role of O_3 becomes more important above pH 6 (Calvert et al. 1985; Ibusuki et al. 1990; Seinfeld and Pandis 1998). Oxidation by molecular oxygen may also be important if cloud water contains sufficient amount of transition metal ions (e.g., Fe, Mn) for autocatalytic reactions to occur. This process may play an important role in highly industrialized areas where various transition metals are present in atmospheric water in relatively high concentrations (Seigneur and Saxena 1984). Catalytic autooxidation of S(IV) is the subject of a number of studies (e.g. Penkett et al. 1979; Pasiuk-Bronikowska and Bronikowski 1981; Martin 1984; Martin and Hill 1987; Ibusuki and Takeuchi 1987; Kraft and van Eldik 1989; Grgić et al. 1991, 1992; Berglund and Elding 1995; Novič et al. 1996; Turšič et al. 2003). It is claimed that at pH 4, transition metal catalysed pathways could account for up to half of the oxidation of S(IV) to S(VI) (Graedel et al. 1985). According to present knowledge, iron(II/III) and manganese (II/III) are the most important catalysts in atmospheric droplets (Coichev and van Eldik 1994; Brandt and van Eldik 1995; Seinfeld and Pandis 1998). These metals are the only efficient catalysts at low pH. In addition, both iron and manganese are common constituents of tropospheric aerosols and water droplets even in remote areas due to their generation from erosion of the earth's crust. Other transition metals such as Cu(II), Co(III), Sc(III), Ti(III), V(III) and Cr(III), are also catalysts, but with a substantially lower effect on the reaction rate (Ibusuki et al. 1990; Grgić et al. 1991; Sedlak and Hoigné 1993). The catalytic oxidation of S(IV) is a free radical chain reaction. Its mechanism and kinetics are so complex and sensitive to the conditions under which the process occurs that even a minor change in experimental conditions can cause a change of the dominant path of the reaction course, and thus lead to diverse results. Despite numerous studies of the metal catalysed S(IV) oxidation there still exist serious discrepancies in rate expressions, rate constants, pH dependencies, activation energies, reaction mechanisms etc. Recent studies show that the sulphur(IV) oxidation in atmospheric water droplets can be affected by other reactions. In particular, organic chemistry may be especially important. Organic compounds may dissolve into water droplets and react with sulphydryl radicals and transition metal ions, and thus alter the rate of catalytic S(IV) oxidation (Martin et al. 1991; Pasiuk-Bronikowska et al. 1997; Grgić et al. 1998; Pasiuk-Bronikowska et al. 2003a,b; Ziajka and Pasiuk-Bronikowska 2003, 2005). Recently, the inhibiting effect of such organic ligands as oxalate, acetate and formate in the iron-catalyzed autooxidation of sulphur(IV) oxides in atmospheric water droplets has been suggested. Grgić et al. (1998, 1999) and Wolf et al. (2000) reported the strong inhibiting effect of oxalate on the Fe-catalysed S(IV) oxidation in aqueous acidic solution. Acetate and formate also inhibit the reaction, but to a much lesser extent than oxalate (Grgić et al. 1998). Very recently, the influence of some low weight mono- (formic, acetic, glycolic, lactic) and di-carboxylic acids (oxalic, malic, malonic) on the Mn(II)-

catalysed S(IV) oxidation has also been investigated (Grgić et al. 2002; Podkrajšek et al. 2006). It has been established that mono-carboxylic acids inhibit the oxidation, with the strongest influence 2 J Atmos Chem (2008) 60:1-17 found for formic acid. The lowest inhibition was caused by acetic acid. From among dicarboxylic acids, oxalic acid slows down the S(IV) oxidation, although to a lesser extent than mono-carboxylic acids, while malic and malonic acids have practically no influence. The effect of organic compounds in atmospheric water on the transition metal-catalysed oxidation of sulphur(IV) is not fully known yet and more work in this area is needed to understand these processes better. The purpose of the present study was to study the kinetics of the Mn(II)-catalysed S(IV) oxidation and to determine the inhibiting effect of acetic acid on this process under different experimental conditions representative for heavily polluted areas. The experiments were carried out at Mn(II) and CH₃COOH concentrations in the range 10⁻⁶-10⁻⁵ and 10⁻⁶-10⁻⁴ mol/dm³, respectively, and at initial pH of the solution in the range 3.5-5.0; initial concentrations of S(IV) were around 10⁻³ mol/dm³. S(IV) liquid-phase concentration of 1×10⁻³ mol/dm³ corresponds to 0.6 ppm SO₂ in the gas phase over a solution of pH=5, or 7 ppm over a solution of pH=4, or 20 ppm over a solution of pH=3.5. Such high SO₂ gas-phase concentrations are found in heavily polluted areas as well as in power plant and volcanic plumes. In highly polluted locations, for example in large urban areas where coal is used for domestic heating purposes, or for poorly controlled combustion in industrial installations, SO₂ concentrations are rather high and vary between 0.1 and 0.5 ppm, and sometimes they are even higher (Ferrari and Salisbury 1999). High sulphur dioxide concentrations are being recorded in some of the megacities in developing countries where burning of coal is the main source of energy. The greatest problems related to sulfur dioxide occur in Asia (mainly in Chinese cities and some Middle-East cities such as Teheran, Tbilisi and Istanbul)(Baldasano et al. 2003). In Asia there are cities [e.g. Guiyang (424 µg/m³), Chongqing (340 µg/m³)] with average annual values of more than six times the WHO guideline value (Baldasano et al. 2003). Also in Africa some of the urban areas, and especially industrial areas, experience high concentrations of sulphur dioxide (WHO 2006). Weekly average concentrations in Zambia's copper belt (Nkana, Mufulira and Luanshya) were found to range from 167 to 672 µg/m³, the highest weekly average being 1,400 µg/m³. Studies undertaken on the impact of the Selebi Phikwe copper smelter in Botswana show that there are large areas experiencing concentrations above 100 µg/m³. Short term measurement indicated 1-h average concentrations of more than 1,000 µg/m³ (WHO 2006). Also some of the heavily industrialized areas in Europe may still be experiencing high levels of sulphur dioxide. In some cities in the north western corner of the Russian Federation, close to large primary smelters, daily concentrations of sulphur dioxide exceed 1,000 µg/m³ (WHO 2006). From the point of view of atmospheric chemistry, especially fast chemical reactions, concentrations averaged for shorter periods e.g., for 1 h or even for several minutes, are more relevant. These concentrations are closer to actual concentrations at which fast reactions proceed in the atmosphere. Concentrations averaged for shorter periods are considerably higher than those averaged for longer periods. Peak concentrations over shorter averaging periods may still be very high, both in cities with a high use of coal for domestic heating and when plumes of effluent from power station chimneys fall to the ground (fumigation episodes). Transient peak concentrations of several thousand



Snap. 1. Photographs showing air pollution by industries along with molecular structure of SO₂.



Snap. 2. Photographs showing Acid rain effect of SO₂.



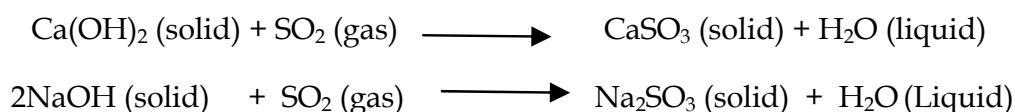
Snap. 3. Photographs showing Acid rain effect of SO₂ on monuments of India.

microgram per cubic meter are not uncommon (WHO 2000). Concentrations of SO_2 can reach tens of parts per million in power plant (Jaakkola et al. 1998) and volcanic plumes (Gauthier and Le Cloarec 1998; Shinohara 2005). Under stable atmospheric conditions, SO_2 may be transported relatively great distances at appreciable concentrations. In very stable power station plumes SO_2 concentrations may be greater than 1.0 ppm over 70 km from their source (Stephens and McCaldin 1971). *J Atmos Chem* (2008) 60:1–17 3

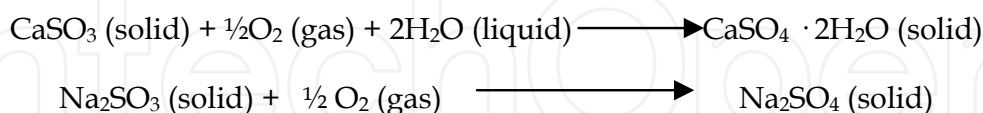
Concentrations of Mn(II) and acetic acid in solutions used in our experiments correspond to those found in rain-, cloud- and fogwater in heavily polluted urban and industrialized areas. Manganese is one of the most abundant transition metals in atmospheric liquid phases (wet aerosol, cloud, fog, rain). The only source of these metals in the atmospheric aqueous phase is the dissolution of aerosol particles incorporated in water droplets. The common particles containing trace metals are emitted from both anthropogenic (fossil fuel combustion, industrial processes) and natural (windblown dust, weathering, volcanoes) sources. Particles from anthropogenic sources contribute significantly to metal distribution in atmospheric droplets due to their high metal content and solubility. In consequence, trace metal concentrations in atmospheric waters are higher in urban and industrial areas (Colin et al. 1990). In atmospheric waters, manganese is mainly found as Mn(II), which is more soluble than manganese(III) (Deutsch et al. 1997). Mn(II) exhibit a large variation in solubility dependent on the nature of the particles, but this solubility is pH-independent (Millet et al. 1995). Concentrations of Mn in rainwater are typically lower than those observed in fog and cloud water samples. In urban and industrial areas manganese concentrations range from 10^{-7} to 10^{-6} mol/dm³ in rain (Deutsch et al. 1997; Patel et al. 2001), and from 10^{-6} to 10^{-5} mol/dm³ in fog- and cloudwater (Millet et al. 1995; Brandt and van Eldik 1995). Acetic acid is one of the most abundant carboxylic acids in the troposphere and it is found in rain, clouds, fogs, and aerosol particles from remote to highly polluted urban areas. The atmospheric sources of carboxylic acids are numerous and they comprise: primary biogenic emissions, primary anthropogenic emissions and photochemical transformations of precursors in aqueous, gaseous, and particulate phases (Chebbi and Carlier 1996). Direct anthropogenic emissions of carboxylic acids (e.g. from incomplete combustion of fossil fuels, wood and other biomass material) and/or photo-oxidation of anthropogenic organic compounds are the main sources of these compounds in urban and industrial environments (Chebbi and Carlier 1996; Kawamura et al. 1996). Concentrations of organic acids are generally elevated in the urban as compared with the nonurban atmosphere (Meng and Seinfeld 1995). In urban sites concentrations of acetic acid range from 10^{-7} to 10^{-5} mol/dm³ in rain (Chebbi and Carlier 1996; Kawamura et al. 1996), and from 10^{-6} to 10^{-4} mol/dm³ in cloud and fogwater (Meng and Seinfeld 1995; Brandt and van Eldik 1995; Millet et al. 1996; Raja et al.

3. Basics and scopes of the work – Flue Gas Desulphurization (FGD)

Flue gas desulphurization (FGD) is the current state-of-the art technology used for removing sulphur dioxide from the exhaust flue gases in power plants. SO_2 is an acid gas and thus the typical sorbent slurries or other materials used to remove the SO_2 from the flue gases are alkaline. The reaction taking place in wet scrubbing using $\text{Ca}(\text{OH})_2$ and NaOH slurry produces CaSO_3 and Na_2SO_3 and can be expressed as:

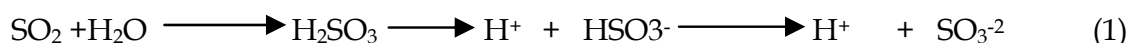


Some FGD systems go a step further and oxidize the CaSO₃ and Na₂SO₃ to produce marketable CaSO₄ · 2H₂O (gypsum) and Na₂SO₄ (Sodium Sulphate):⁵⁻⁶

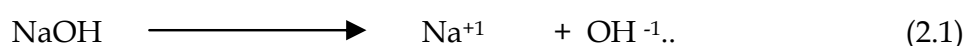
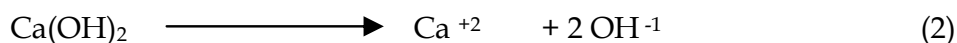


3.1 Mechanism

When sulfur dioxide (SO₂) in the flue gas contacts scrubber slurries, the pollutant transfers from the gas to the liquid phase, where the following equilibrium reactions are fundamentally representative of the transfer process.



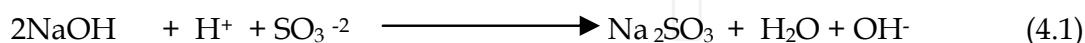
when lime hydrated powder or caustic flakes introduced to water will raise the pH according to the following mechanism.



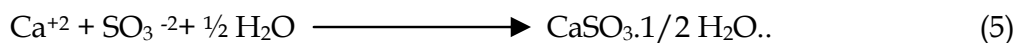
However, Ca(OH)₂ is only slightly soluble in water, so this reaction is minor in and of itself. In the presence of acid, calcium hydroxide reacts much more vigorously and it is the acid generated by absorption of SO₂ into the liquid that drives the lime dissolution process.



Equations 1, 2 and 3 when combined illustrate the primary scrubbing mechanism.



In the absence of any other factors, (for example, oxygen in flue gas) calcium and sulfite ions will precipitate as a hemihydrate, where water is actually included in the crystal lattice of the scrubber byproduct.



However, oxygen in the flue gas has a major effect on chemistry, and in particular on byproduct formation. Aqueous bisulfite and sulfite ions react with oxygen to produce sulfate ions (SO₄²⁻).



Approximately the first 15 mole percent of the sulfate ions co-precipitate with sulfite to form calcium sulfite-sulfate hemihydrate $[(\text{CaSO}_3 \cdot \text{CaSO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}]$. Any sulfate above the 15 percent mole ratio precipitates with calcium as gypsum.



Calcium sulfite-sulfate hemihydrate is a soft, difficult-to-dewater material that previously has had little practical value as a chemical commodity. Gypsum, on the other hand, is much easier to handle and has practical value. These factors are driving utilities to install forced oxidation systems for gypsum production.

There are three control technologies which have major application in the field of Sulphur dioxide control.⁷⁻⁸

- Adsorption.
- Catalytic Oxidation / reduction.
- Absorption.

Adsorption is a control technology for control of SO_2 from stack gases but suffers from several following drawbacks viz:

1. Higher energy requirements.
2. Penetration of SO_2 in the granule is difficult.
3. Highly active absorbent surfaces cause oxidation of SO_2 to SO_3 which react with moisture in flue gases to form acid.
4. Regeneration techniques are costlier.

Catalytically oxidation / reduction is a control technology for control of from stack gases but suffers from several following drawbacks viz:

1. Higher energy requirements
2. Large equipment size.
3. Costly Catalysts.
4. Regeneration and disposal of catalysts is also a problem
5. Contractor design is complex.

Absorption is a control technology for control of SO_2 from stack gases is most widely practiced.

However this technology also suffers from following drawbacks:

1. Stack gas cooling and reheating is required.
2. Mist elimination is required.

However these problems can be easily encountered with proper engineering design used. Besides this less operator's intensiveness, less cost and ease of handling of liquid sorbent makes it an attractive option. It is one of the most widely used control technology employed for removal of SO_2 ⁹⁻¹⁰

4. Material and methods

All experiments were conducted on Stack monitoring Kit (Model No. and Make -VSS1, 141 DTH -2005,Vayubodhan). First of all Stack monitoring kit of SO₂ monitoring were set up for experiment at *chimney* inlet of Boiler of thermal power plant. Flue gas containing SO₂ were supplied from *chimney* via probe connected with flexible pipe of stack monitoring kit. The flow of flue gas were controlled using an inlet line Rota meter and was maintained at a value of 3 liter per minute and other end of flexible pipe carrying air and SO₂ respectively were connected to a impinger of 10 cm diameter and 100 cm length. The impinger were filled with 100 ml of scrubbing media in this experiment i.e. Sludge solution, Calcium hydroxide solution, Sodium hydroxide solution.

The concentration of SO₂ in flue gases was first measured by Stack monitoring Kit.

$$C_{SO_2} = \frac{K_2 (V_t - V_{tb}) N (V_{soln})}{V_{m(std)} * V_a}$$

C_{SO_2} = Concentration of sulphur dioxide, dry basis converted to standard conditions, mg/NM³.

N = Normality of barium per chlorate titrant mili equivalent/ml.

K_2 = 32.03 mg/meq.

V_t = Volume of barium per chlorate titrant used for the sample, ml.

V_{tb} = Volume of barium per chlorate titrant used for the blank, ml

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, NM³.

V_a = Volume of sample aliquot-titrated, ml.

Five sets of reading were taken by varying concentration of every solution. 100 ml of solution were taken in first two different impinges for better absorption of SO₂ and 30 ml of H₂O₂ was taken in the third for determination of remaining SO₂. Respective sulphate were formed in solution. Dissolved sulphate were extracted from solution by heating till dryness. Three parameters regards to % SO₃ (gravimetric), % SO₂ (Volumetric) and % alkalinity were analyzed in precipitate. The methods used as Indian standard method from bureau of Indian standard.¹¹⁻¹⁶ During the experiments pipette out 10 ml of NaOH solution in every 15 minutes and pH were analyzed, titrate with 1M oxalic acid determination for fall in conc. of NaOH. Similarly Experiments were conducted on Indirect Flow (By taking water in first impinger) and Direct Flow (Without Water in First impinger). Similarly all experiments were conducted at different temperatures and at different times of interval for reaction. Operating condition of SO₂ absorption is given in table - 1. Experimental set up shown in figure - 12 and schematic diagram of experimental protocol shows in figure - 11

| S. No. | Operating Condition | Value |
|--------|--|---------------------------|
| 1 | Initial Concentration of Scrubbing media | Varying |
| 2 | pH of solution | Varying |
| 3 | Total liquid hold up | 100 ml |
| 4 | Temperature of solution | Varying |
| 5 | Time period for reaction | Varying |
| 6 | Flow of flue gas in impinger | 3 LPM |
| 7 | SO ₂ load in flue gas | 3000 – 3200 ppm |
| 8 | Flue gas Temperature | 135 °C |
| 9 | Flue gas flow in duct of ESP O/L | 150522 M ³ /hr |
| 10 | Pet Coke Feeding Rate | 13 Ton/ hr |
| 11 | Lime Stone Feeding Rate | 1.0 Ton/hr |

Table 1. Operating condition of SO₂ absorption in Scrubbing media.

| S. No | Concentration of Sludge Sample (%) | Initial Concentration of SO ₂ at I/L of absorbing media (ppm) | Concentration of SO ₂ at O/L of absorbing media (ppm) | Recovery of SO ₂ (%) |
|-------|------------------------------------|--|--|---------------------------------|
| 1 | 5.00% | 2950 | 1134 | 62.56 |
| 2 | 10.00% | 2950 | 1205 | 60.18 |
| 3 | 15.00% | 2950 | 1444 | 52.08 |
| 4 | 20.00% | 2950 | 1734 | 42.25 |
| 5 | 25.00% | 2950 | 1795 | 40.16 |

Table 2. Effect of Conc. of sludge solution and recovery of SO₂.

| S. No | Concentration of Sludge Sample (%) | Yield of precipitate (g) | Mg ⁺² | Percent CaSO ₄ | Percent SO ₂ (By Volumetric) | Percent Alkalinity | L/G ratio |
|-------|------------------------------------|--------------------------|------------------|---------------------------|---|--------------------|-----------|
| 1 | 5.00% | 5.25 | 7.72 | 5.54 | 2.6 | 0.0014 | 33.89 |
| 2 | 10.00% | 10.56 | 5.91 | 5.20 | 2.44 | 0.0028 | 50.84 |
| 3 | 15.00% | 15.56 | 4.34 | 3.65 | 1.72 | 0.0144 | 67.79 |
| 4 | 20.00% | 20.56 | 2.55 | 3.09 | 1.45 | 0.0158 | 84.74 |
| 5 | 25.00% | 25.89 | 1.95 | 1.73 | 0.81 | 0.0201 | 101.69 |

Table 3. Analysis results of precipitate which was prepared by sludge solution and SO₂.

| S. No | Concentration of Ca(OH) ₂ (%) | Initial Concentration of SO ₂ at I/L of absorbing media (ppm) | Concentration of SO ₂ at O/L of absorbing media (ppm) | Recovery of SO ₂ (%) |
|-------|--|--|--|---------------------------------|
| 1 | 5.00% | 2980 | 621 | 80.15 |
| 2 | 10.00% | 2980 | 739 | 76.2 |
| 3 | 15.00% | 2980 | 898 | 70.85 |
| 4 | 20.00% | 2980 | 1097 | 64.18 |
| 5 | 25 .00% | 2980 | 1279 | 58.06 |

Table 4. Effect of Conc. of Ca(OH)₂ solution and recovery of SO₂.

| S. No. | Concentration of Ca(OH) ₂ Sample | Yield of precipitate (g) | Mg ⁺² | Percent CaSO ₄ | Percent SO ₂ (By Volumetric) | Alkalinity Percent | L/G ratio |
|--------|---|--------------------------|------------------|---------------------------|---|--------------------|-----------|
| 1 | 5.00% | 5.55 | 3.61 | 8.75 | 4.12 | 0.02 | 33.55 |
| 2 | 10.00% | 10.89 | 2.41 | 7.51 | 3.53 | .0216 | 50.33 |
| 3 | 15.00% | 15.06 | 1.96 | 7.34 | 3.45 | .0252 | 67.11 |
| 4 | 20.00% | 20.42 | 1.29 | 5.03 | 2.36 | .0324 | 83.89 |
| 5 | 25.00 % | 25.18 | 1.24 | 4.18 | 1.96 | .0540 | 100.67 |

Table 5. Analysis results of precipitate which was prepared by Ca(OH)₂ solution and SO₂.

| S.No. | Concentration of NaOH (%) | Initial Concentration of SO ₂ at I/L of absorbing media (ppm) | Concentration of SO ₂ at O/L of absorbing media (ppm) | Recovery of SO ₂ (%) |
|-------|---------------------------|--|--|---------------------------------|
| 1 | 5 % | 3067 | 75 | 97.96 |
| 2 | 10 % | 3067 | 158 | 95.08 |
| 3 | 15 % | 3067 | 306 | 90.18 |
| 4 | 20 % | 3067 | 324 | 88.02 |
| 5 | 25 % | 3067 | 455 | 85.19 |

Table 6. Effect of Conc. of NaOH solution and recovery of SO₂.

| S. No. | Concentration of NaOH Sample | Yield of precipitate (g) | Percent SO ₃ (By gravimetric method) | Percent Na ₂ SO ₄ | Percent SO ₂ (By volumetric) | Percent Alkalinity | L/G ratio |
|--------|------------------------------|--------------------------|---|---|---|--------------------|-----------|
| 1 | 5 % | 4.88 | 20.76 | 35.49 | 39.21 | 0.62 | 16.30 |
| 2 | 10 % | 9.76 | 5.67 | 17.00 | 25.61 | 1.17 | 32.60 |
| 3 | 15 % | 14.15 | 1.49 | 9.81 | 20.54 | 1.64 | 48.90 |
| 4 | 20 % | 18.62 | 0.52 | 5.77 | 19.47 | 1.68 | 65.21 |
| 5 | 25 % | 23.28 | 0.24 | 3.99 | 17.62 | 1.75 | 81.51 |

Table 7. Analysis results of precipitate which was prepared by NaOH Solution and SO₂.

| S. No. | Time (Min.) | pH of solution | Volume of 1 M Oxalic acid consumed in titration using phenolphthalein indicator (ml) | Conc. of NaOH (%) |
|--------|-------------|----------------|--|-------------------|
| 1 | 0 | 12.57 | 20.05 | 80.06 |
| 2 | 15 | 10.62 | 15.56 | 62.2 |
| 3 | 30 | 8.82 | 3.5 | 14.2 |
| 4 | 45 | 7.95 | 1.23 | 4.8 |
| 5 | 60 | 5.62 | 0.56 | 2.2 |
| 6 | 75 | 4.75 | 0.32 | 1.2 |

Table 8. Effect of pH of NaOH solution for absorption of SO₂.

| S. No. | Flow of SO ₂ gas | Initial Concentration of SO ₂ (ppm) | Concentration of SO ₂ after formation of Sodium sulphate (ppm) | Recovery (%) |
|--------|-----------------------------|--|---|--------------|
| 1 | Direct | 3050 | 145 | 95.25 |
| 2 | Indirect | 3050 | 1818 | 59.62 |

Table 9. Effect of direct and indirect flow of flue gases in NaOH solution and removal efficiency of SO₂.

| S. No. | Flow of SO ₂ gas | Yield of precipitate (in gm) | % SO ₃ (Gravimetric) | % Na ₂ SO ₄ | % SO ₂ (Volumetric) | Alkalinity (%) |
|--------|-----------------------------|------------------------------|---------------------------------|-----------------------------------|--------------------------------|----------------|
| 1 | Direct | 9.55 | 1.79 | 3.17 | 39.21 | 1.12 |
| 2 | Indirect | 9.02 | .233 | .413 | 20.01 | 1.72 |

Table 10. Analysis results of precipitate which was prepared by varying the flow of flue gases in NaOH solution.

| S. No. | Temperature of NaOH solution | Initial Conc. of SO ₂ (ppm) | Conc. of SO ₂ after formation of Sulphate(ppm) | Recovery (%) |
|--------|------------------------------|--|---|--------------|
| 1 | 20-25 °C | 3080 | 302 | 90.18 |
| 2 | 25-30 °C | 3080 | 566 | 81.62 |
| 3 | 30-35 °C | 3080 | 675 | 78.08 |

Table 11. Effect of temperature of NaOH solution and recovery of SO₂.

| S.No | Temperature of NaOH Solution | Yield (g) | % SO ₃ | % SO ₂ | % Na ₂ SO ₄ | % Alkalinity |
|------|------------------------------|-----------|-------------------|-------------------|-----------------------------------|--------------|
| 1 | 20-25°C | 9.77 | 0.62 | 38.72 | 1.100 | 1.68 |
| 2 | 25-30°C | 9.25 | 0.42 | 31.92 | 0.745 | 1.80 |
| 3 | 30-35°C | 9.06 | 0.22 | 17.87 | 0.390 | 1.95 |

Table 12. Analysis results of precipitate which was prepared by different temperature of NaOH solution and SO₂.

| S.No | Time for reaction(Min) | Initial conc. of SO ₂ (ppm) | Conc. of SO ₂ after formation of SO ₄ (ppm) | Recovery (%) |
|------|------------------------|--|---|--------------|
| 1 | 20 | 3075 | 761 | 75.25 |
| 2 | 40 | 3075 | 609 | 80.18 |
| 3 | 60 | 3075 | 360 | 88.27 |

Table 13. Effect of time intervals of reaction and recovery of SO₂.

| S.No | Time of Reaction (Min) | Yield (g.) | % SO ₃ | % SO ₂ | % Na ₂ SO ₄ | % Alkalinity |
|------|------------------------|------------|-------------------|-------------------|-----------------------------------|--------------|
| 1 | 20 | 8.62 | 1.63 | 26.68 | 2.89 | 1.16 |
| 2 | 40 | 8.95 | 2.35 | 29.34 | 4.17 | 0.96 |
| 3 | 60 | 9.02 | 3.06 | 36.51 | 5.03 | 0.75 |

Table 14. Analysis results of precipitate which was prepared by different times of intervals of reaction between NaOH solution and SO₂.

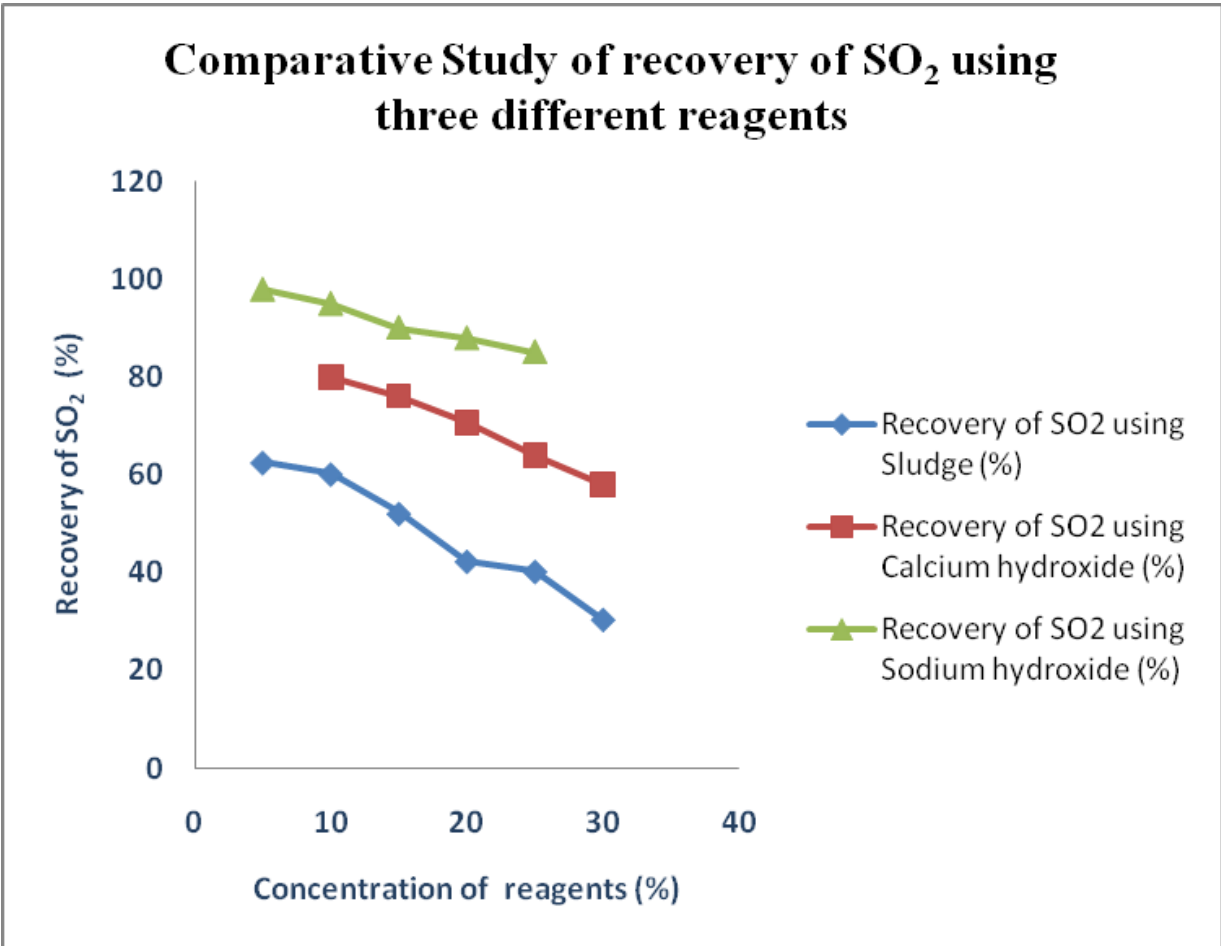


Fig. 1. Comparative Study of recovery of SO₂ with three different reagents.

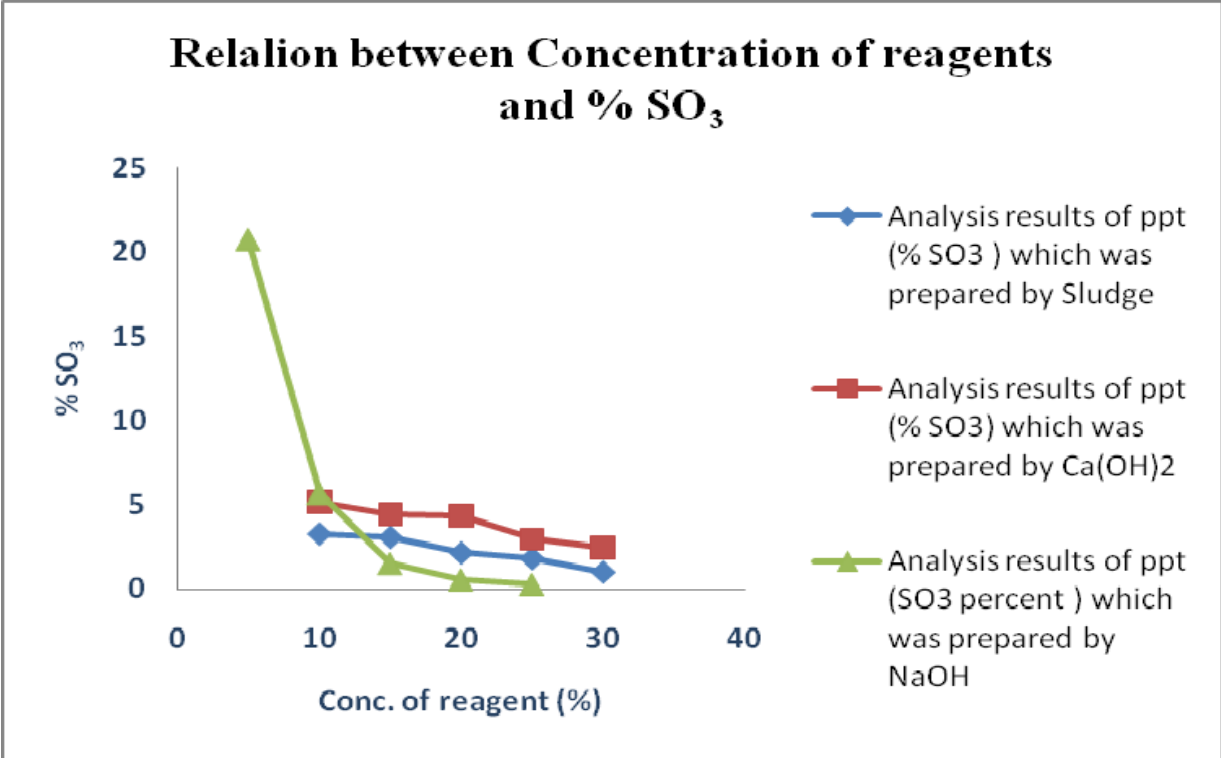


Fig. 2. Comparative Study of Conc. of three different reagents with % SO₃ (Gravimetric) of precipitate.

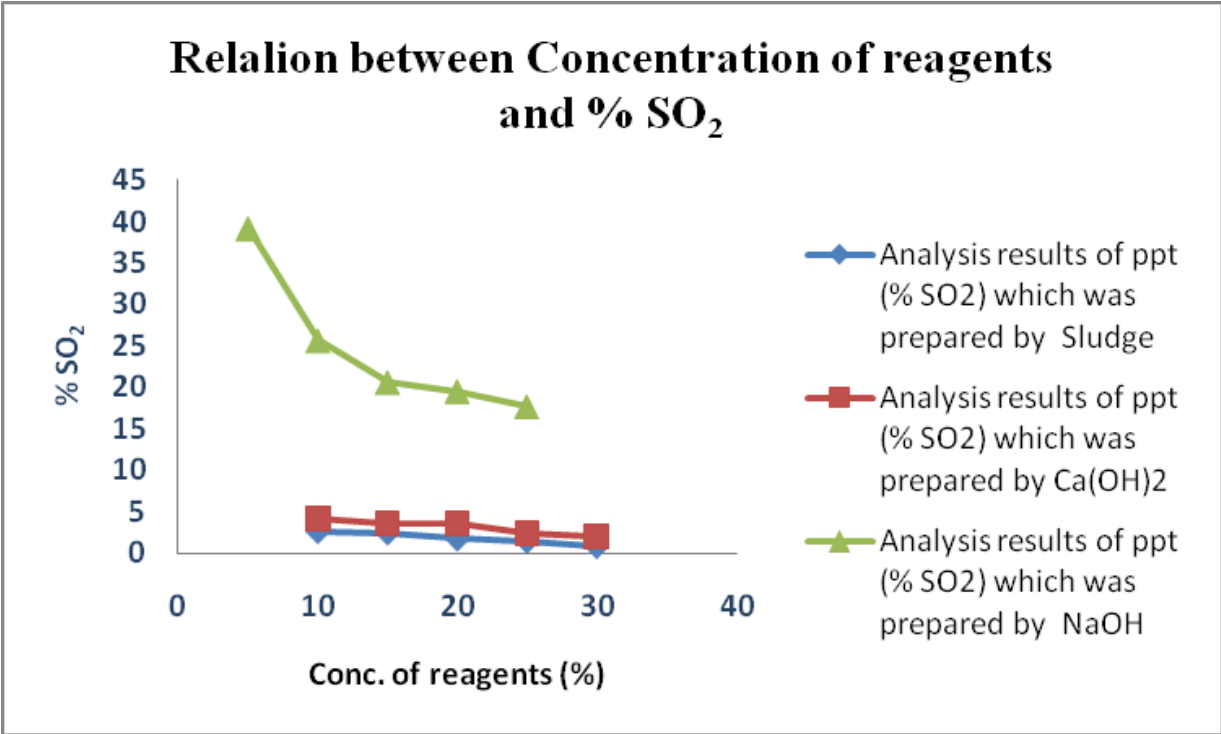


Fig. 3. Comparative Study of Conc. of three different reagents with % SO₂ (Volumetric) of precipitate.

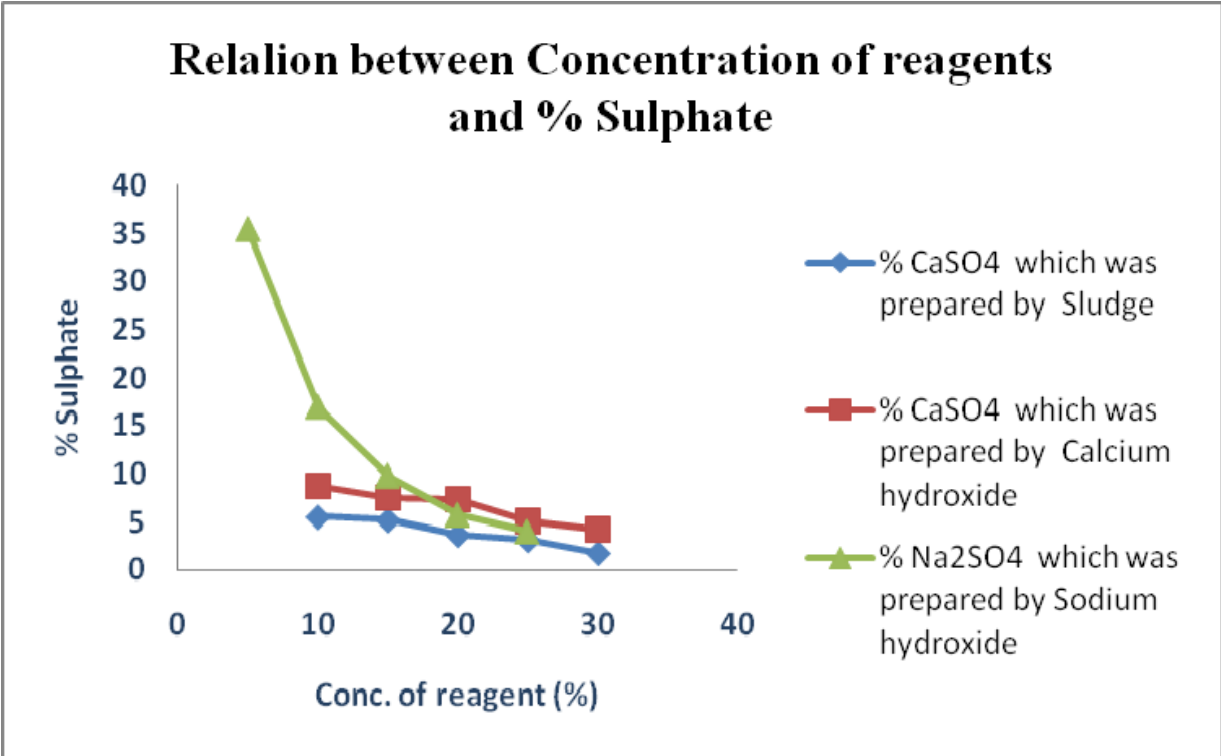


Fig. 4.Comparative Study of Conc. of three different reagents with % sulphate of precipitate.

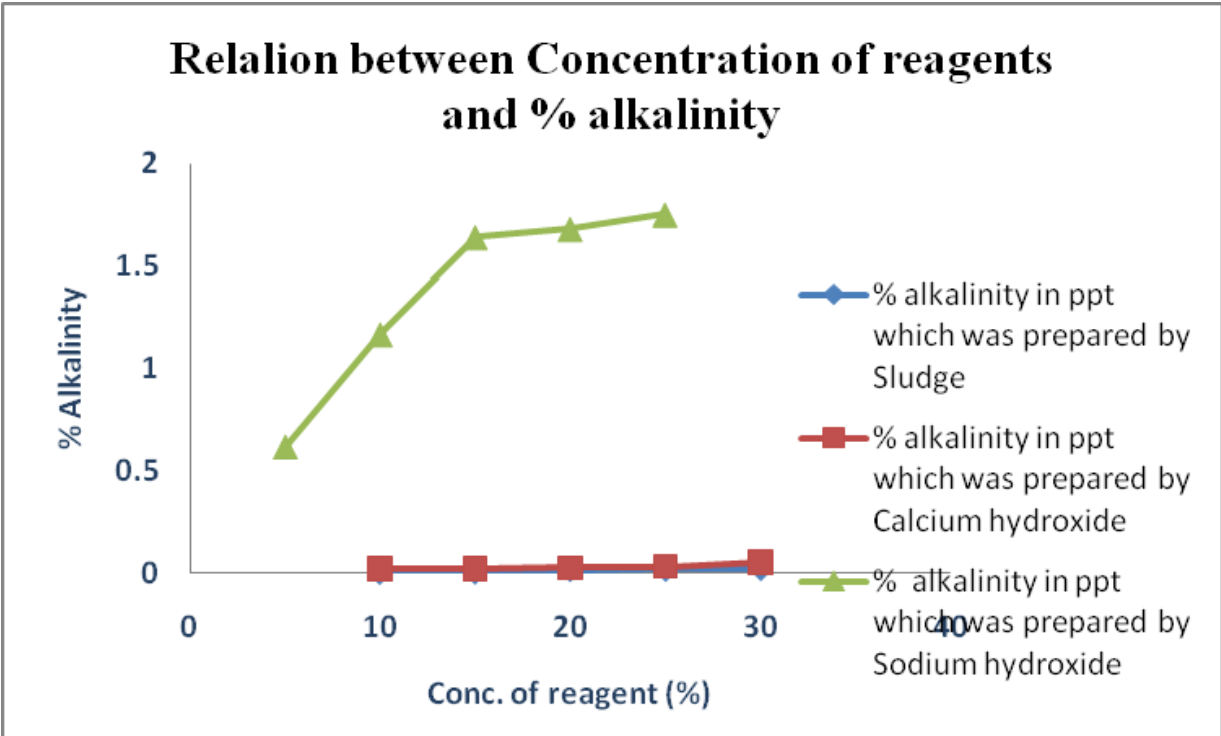


Fig. 5. Comparative Study of Conc. of three different reagents with % alkalinity.

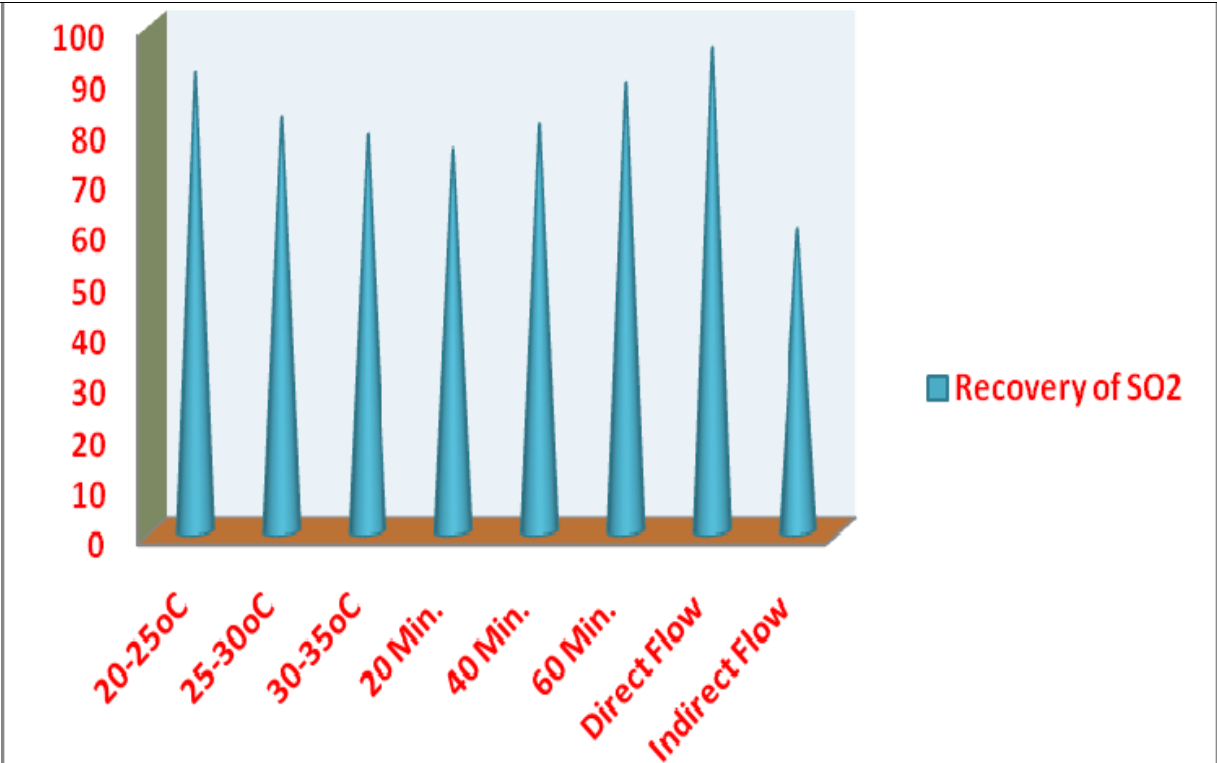


Fig. 6. Comparative Study of recovery of SO₂ with different parameters.

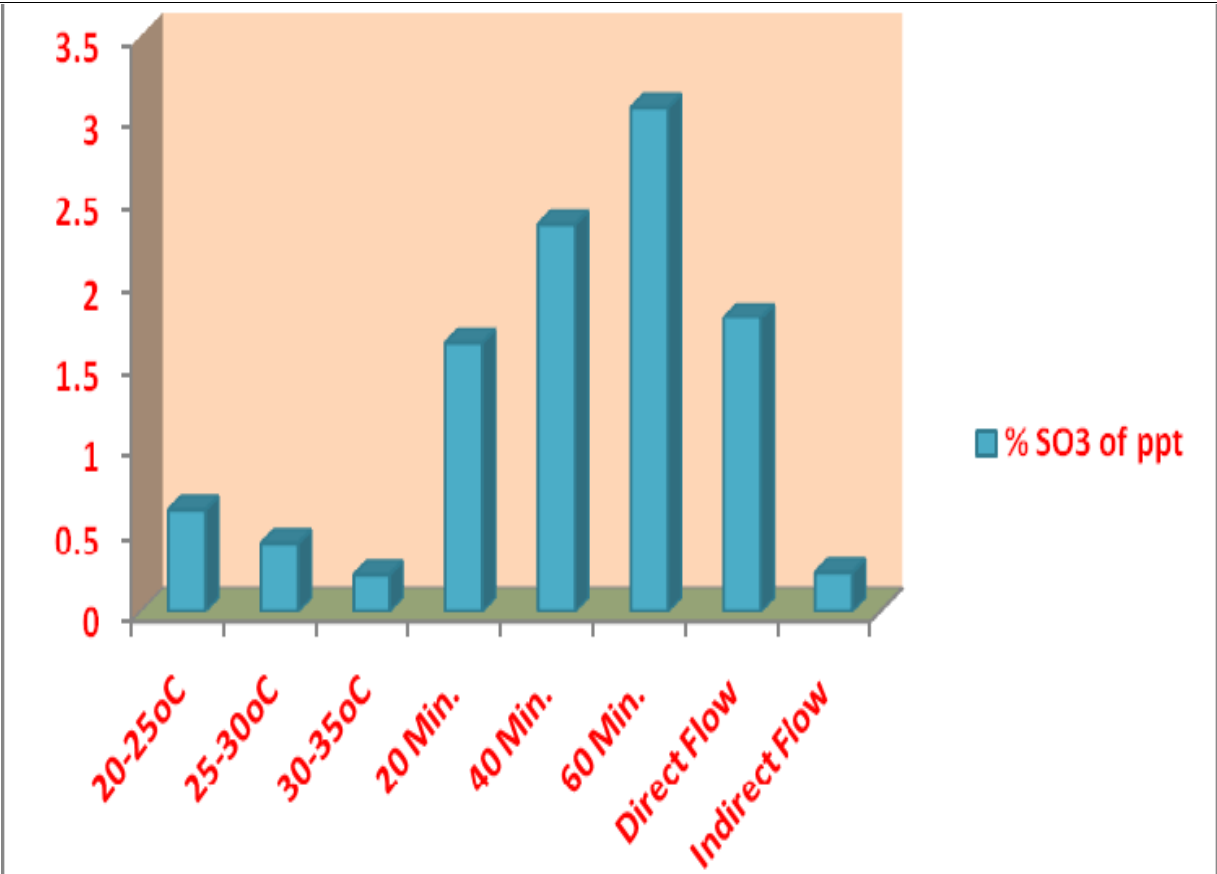


Fig. 7. Comparative Study of % SO₃ of precipitate with different parameters.

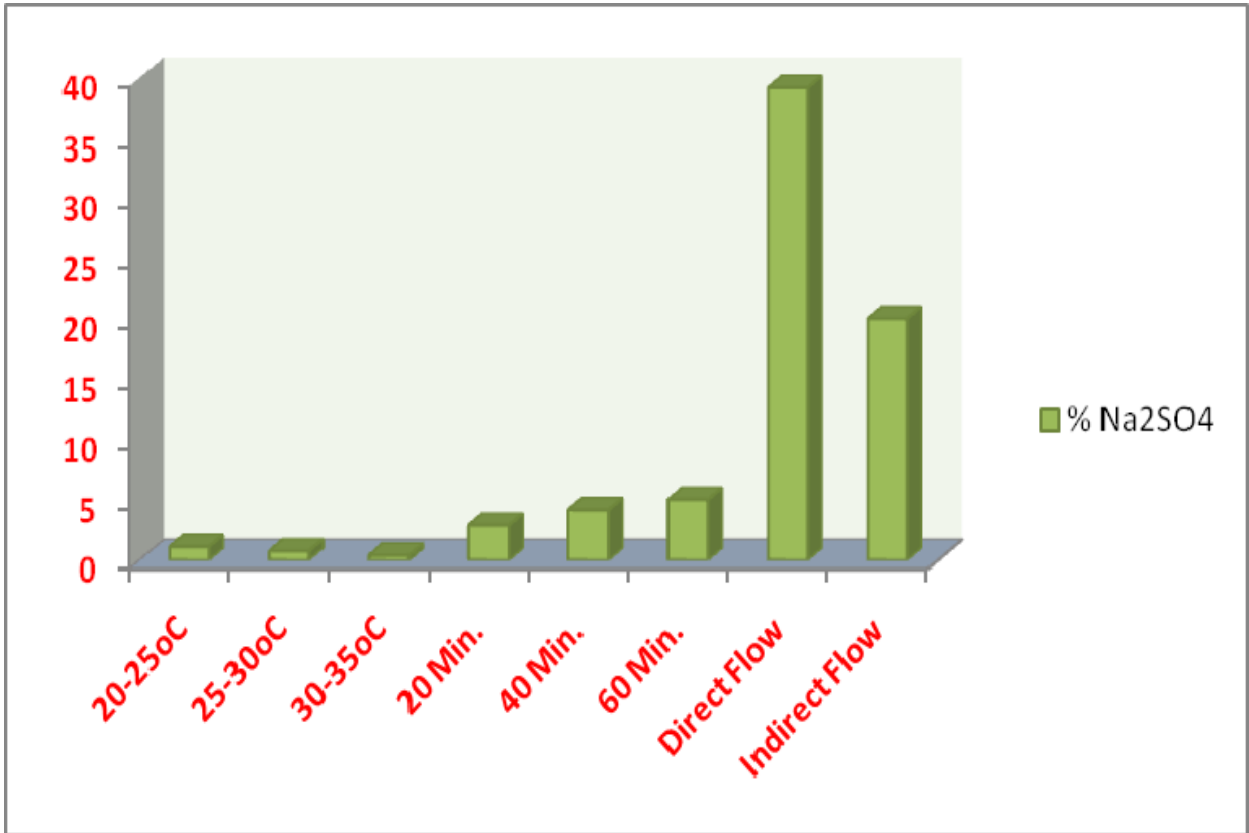


Fig. 8. Comparative Study of % Sulphate of precipitate with different parameter.

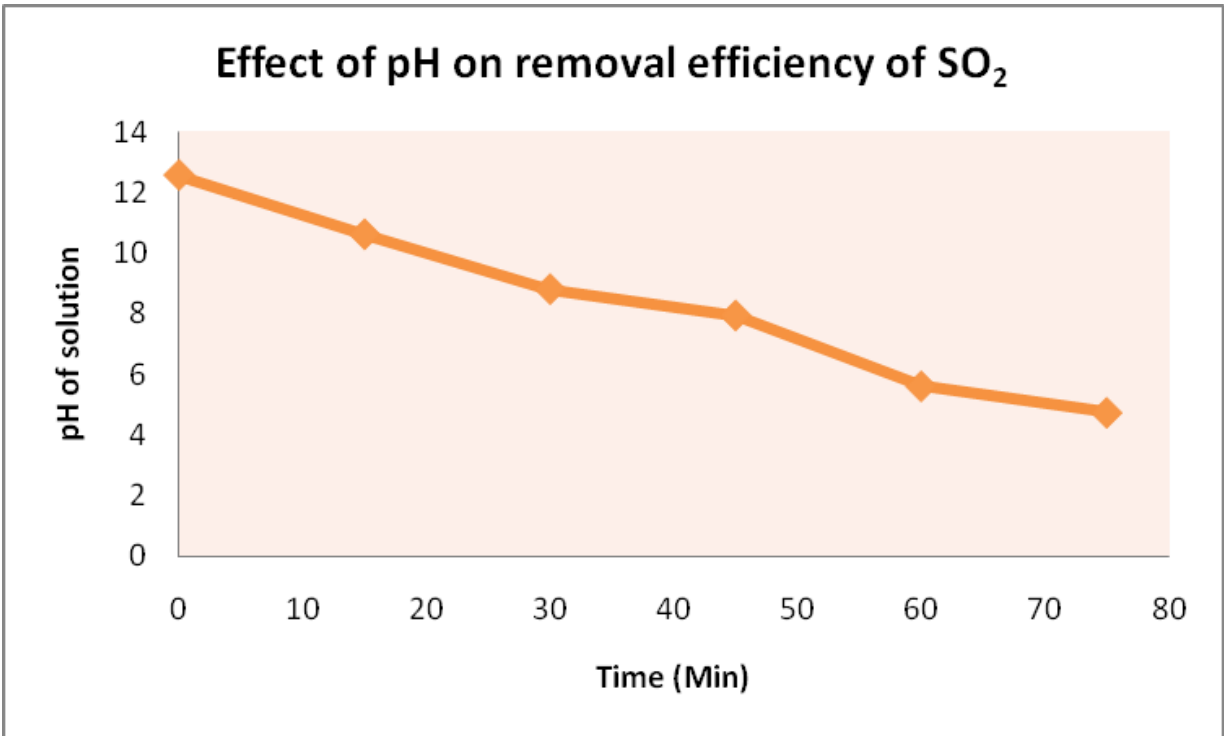


Fig. 9. Figure depicting relation between pH of NaOH solution and absorption of SO₂.

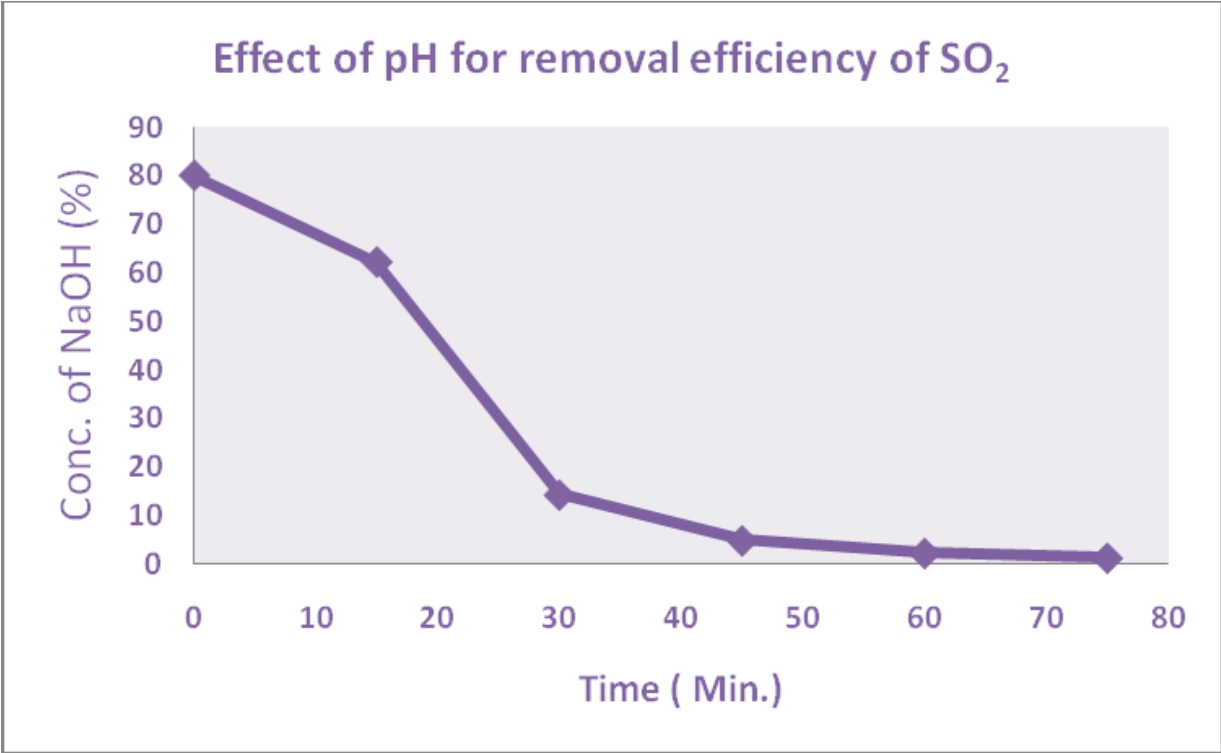


Fig. 10. Figure depicting relation between time period and falls in conc. of NaOH.

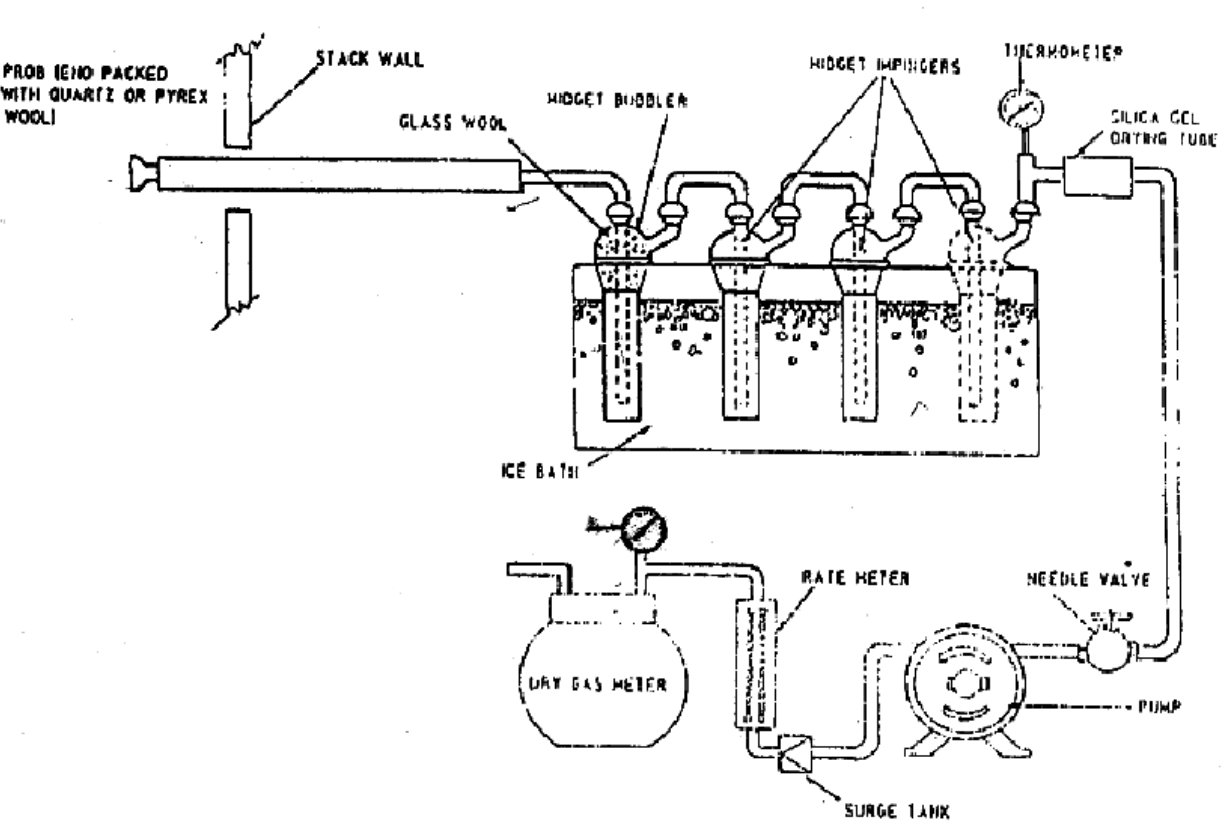


Fig. 11. Schematic diagram of experimental protocol.

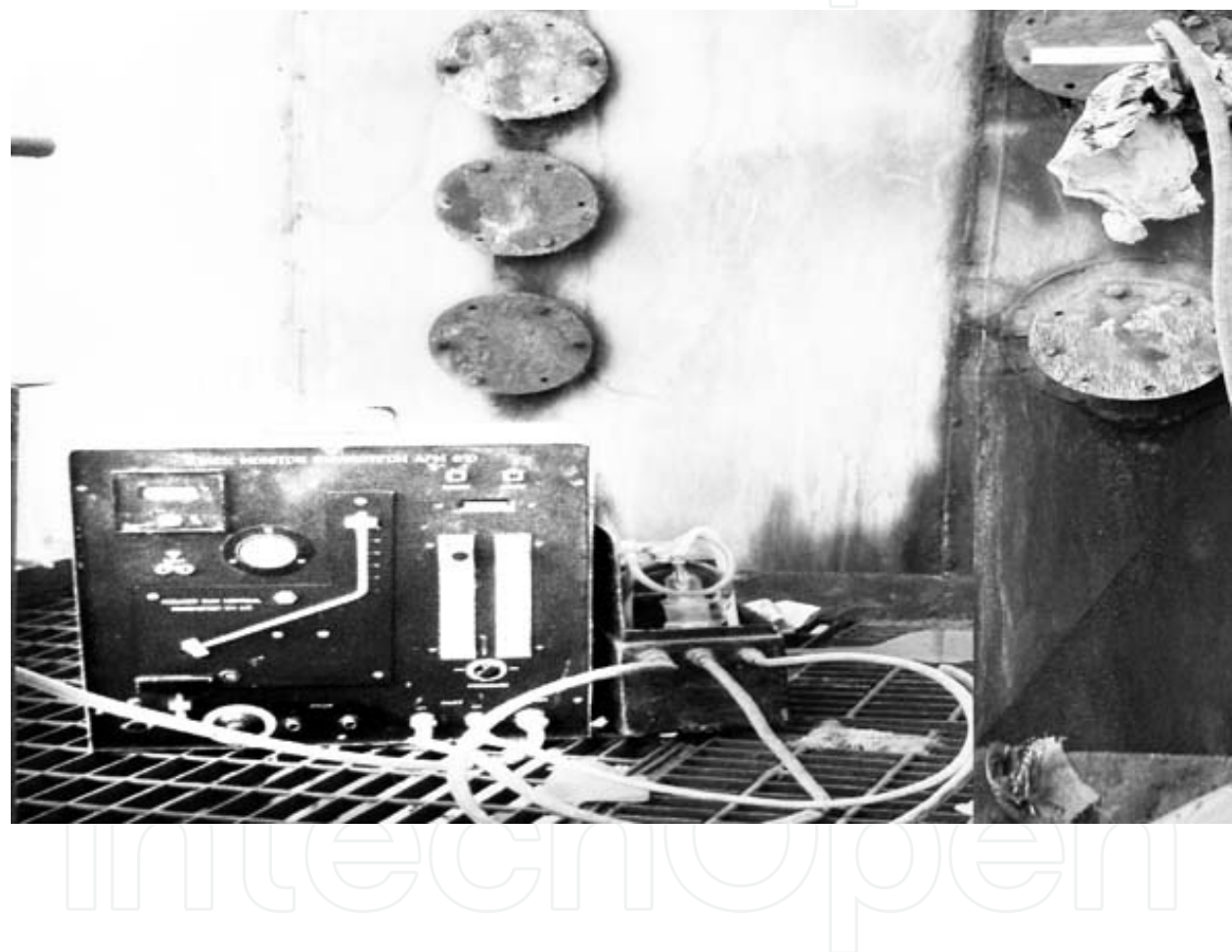


Fig. 12. Experimental Set Up by using SO₂ monitoring kit for absorption of SO₂.



Fig. 13. Experimental Set Up by research scholar using SO₂ monitoring kit.

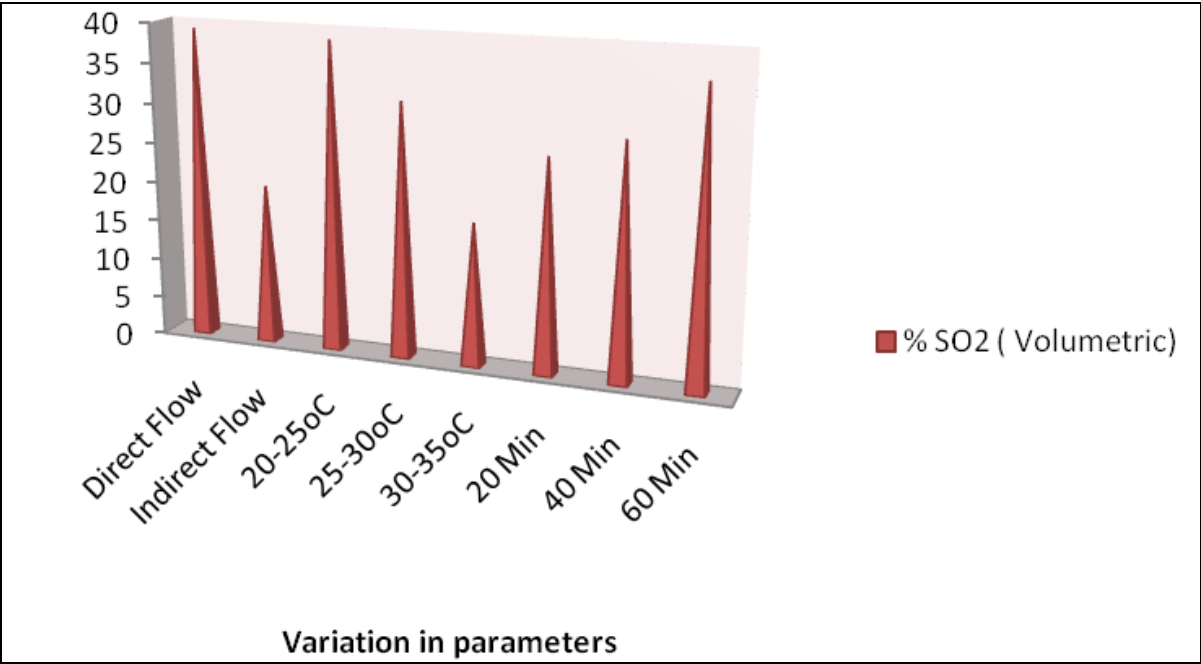


Fig. 14. Comparative Study of % SO₂ (Volumetric) with different parameters.

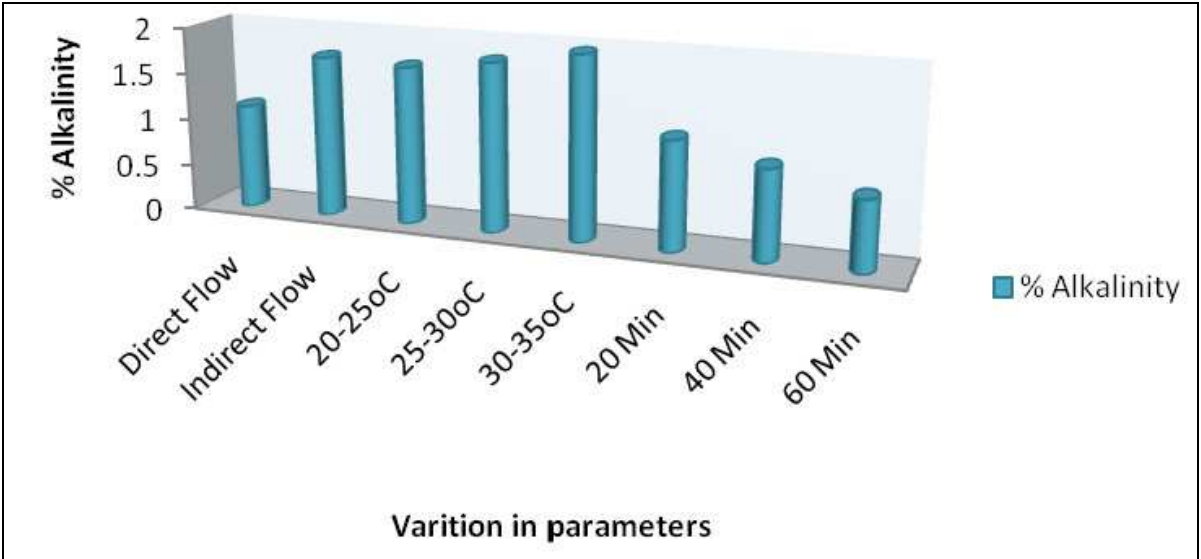


Fig. 15. Comparative Study of % Alkalinity with different parameters.

5. Result and discussion

Table -2 to 7 reports that relation between recovery of absorption of SO₂ using varying concentration of Sodium hydroxide, Calcium hydroxide, and Sludge with analysis results of precipitate. As can be seen from figure - 1 that recovery of SO₂ using, Calcium hydroxide, and Sludge is far below that using Sodium hydroxide. Figure -2 shows the results of % SO₃ (Gravimetric) of precipitate which was prepared by three different reagents and SO₂ contained in flue gases. It is reported that % SO₃ is higher in case of NaOH as to others. Figure -3 shows the results of % SO₂ (Volumetric) of precipitate which was prepared by three different reagents and SO₂ contained in flue gases. It is reported that % SO₂ is higher

in case of NaOH as to others. Figure -4 shows the results of % respective Sulphate of precipitate which was prepared by three different reagents and % SO₂ in flue gases. Figure -5 shows the results of % alkalinity of precipitate which was prepared by three different reagents. We know that alkalinity is the reverse of % SO₂ and it is confirmed by figure -5. Figure -9 and table -8 reports that effect of pH of NaOH solution and absorption of SO₂ and it is confirmed that when increase in the time period for absorption of SO₂ in NaOH solution, then there is a significant decrease in pH. Figure -10 reports that with the increase of time period for absorption of SO₂ in NaOH solution there is a significant decrease in conc. of NaOH Solution. Table -9 shows recovery of SO₂ using different parameters like time period for reaction, temperature of Solution and flow of flue gases in impingers with analysis results of precipitate. Figure -6 reports that recovery of SO₂ with different parameters. Figure -7 reports that % SO₃ in precipitate which was prepared by exhaust SO₂ using different parameters. Figure -8 reports that amount of % Sulphate which was prepared by SO₂ using different parameters. Figure -14 reports that amount of % SO₂ (Volumetric) which were prepared by exhaust SO₂ using different parameters. Figure -8 reports that amount of % Alkalinity which were prepared by SO₂ using different parameters.

6. Conclusion

From the comparative study of three different reagent regarding to removal of SO₂, it is observed that Sodium hydroxide is superior as compare to calcium hydroxide and sludge. The initial rate of absorption is higher for Sodium hydroxide as compared to calcium hydroxide and Sludge. All the absorption methods coupled with a chemical reaction. It may be suggested that Sulphur dioxide is a weak acid and it is a well known fact that reaction of a weak acid with a strong base is fast, meaning stronger the base faster would be the reaction Therefore Sodium hydroxide is a strong base compared to calcium hydroxide and sludge so this evident that Sodium hydroxide is a better solvent for removal of SO₂.

The lower Conc. of the reagent is found to be optimum. Increasing conc. of solution is not very fruitful for maximum absorption of SO₂ in exhaust flue gases. This is because of load of SO₂ in flue gases is very low (at ppm level), so the reagent remains as it is in solution after completely absorption of SO₂.

The pH of the solution should be alkaline. Because of nature of SO₂ is acidic and reaction is restricted in acidic solutions

The temperature of solution should be lower i.e. 20- 25 °C. Because of at higher temperature reversible reaction may be take place and partially formed product may be change in to initial reactants.

The time period of the absorption of SO₂ should be maximum for completely absorption of SO₂.

The direct flow of flue gases in to impingers containing solution will results maximum absorption of SO₂ instead of indirect flow of flue gases because of in indirect SO₂ react with water form sulfurous acid.

On the basis of our study we can recommended that if flue gas desulphurization system (FGD System) is set up before Chimney then maximum SO₂ is trapped, resulting lowers the SO₂ conc. in environment and lowers the air pollution.

7. FGD design and equipment

7.1 Purpose

Air pollution is one of the very important issues world-wide. The wet limestone-gypsum process has been the most popular method adopted to eliminate SO₂ emitted from thermal Power Stations. However, due to the relatively high construction cost, its further implementation has inevitably limited and the development of more economical FGD technology has been sought.

Hence, Hitachi Compact FGD System was developed, for the purposes of simplification and cost reduction utilizing features of the latest FGD technology fully. The first System was delivered to Peoples Republic of China under the "Green Aid Plan", which has been organized and managed by the Ministry of International Trade and Industry (MITI), Japan, in order to implement their policy to transfer environmental preservation technology to neighbouring countries and it contributes to global environmental preservation and the technologies, such as, higher gas velocity in the absorber and adoption of horizontal flow spray absorber instead of conventional vertical flow spray absorber shortened duct length. Eventually it helps to accomplish a lower construction cost.

7.2 Performance

The absorption and forced oxidation mechanisms are the same as the conventional wet limestone gypsum FGD technology, so it is possible to achieve more than 80% of SO₂ removal efficiency. Also, because of higher gas velocity under the same conditions of gas versus liquid ratio, it is possible to maintain the same SO₂ removal efficiency.

In the method of horizontal spray tower, it is possible to achieve high dust removal efficiency as in the vertical spray tower.

7.3 Special features

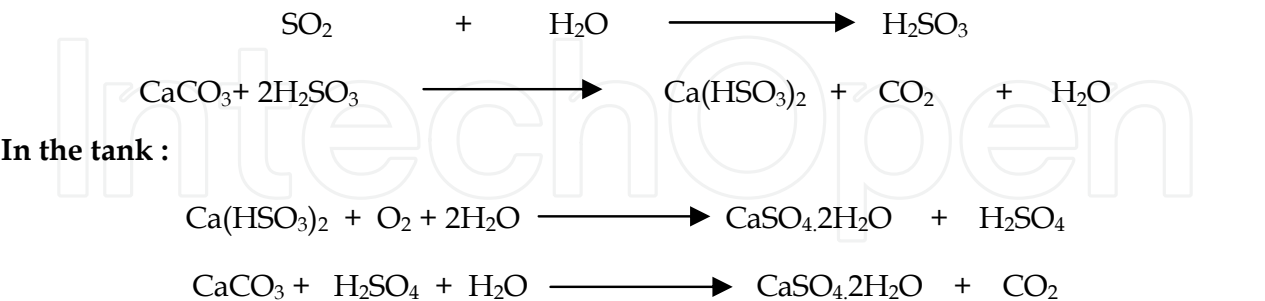
1. Absorber, having functions of dust removing, SO₂ absorbing, SO₂ oxidization simultaneously
2. Adoption of horizontal flow spray absorber and simplified flue duct make a compact arrangement.
3. Use of limestone of easy handling and low cost
4. High Ca utilization factor
5. Complete oxidation in the absorber
6. High dust removal efficiency at spray part
7. Re-use of by-product gypsum as salable gypsum
8. Easy to retrofit to existing plant

7.4 Process description

The SO₂ contained flue gas flow into FGD system through duct. The SO₂ is absorbed and removed by the chemical reaction of limestone slurry sprayed through horizontal flow

spray as an absorbent. By injecting air in the absorber tank, the absorbed and removed SO₂ forms gypsum, then, the gypsum slurry is delivered outside system, as in the method of latest wet limestone gypsum FGD system.

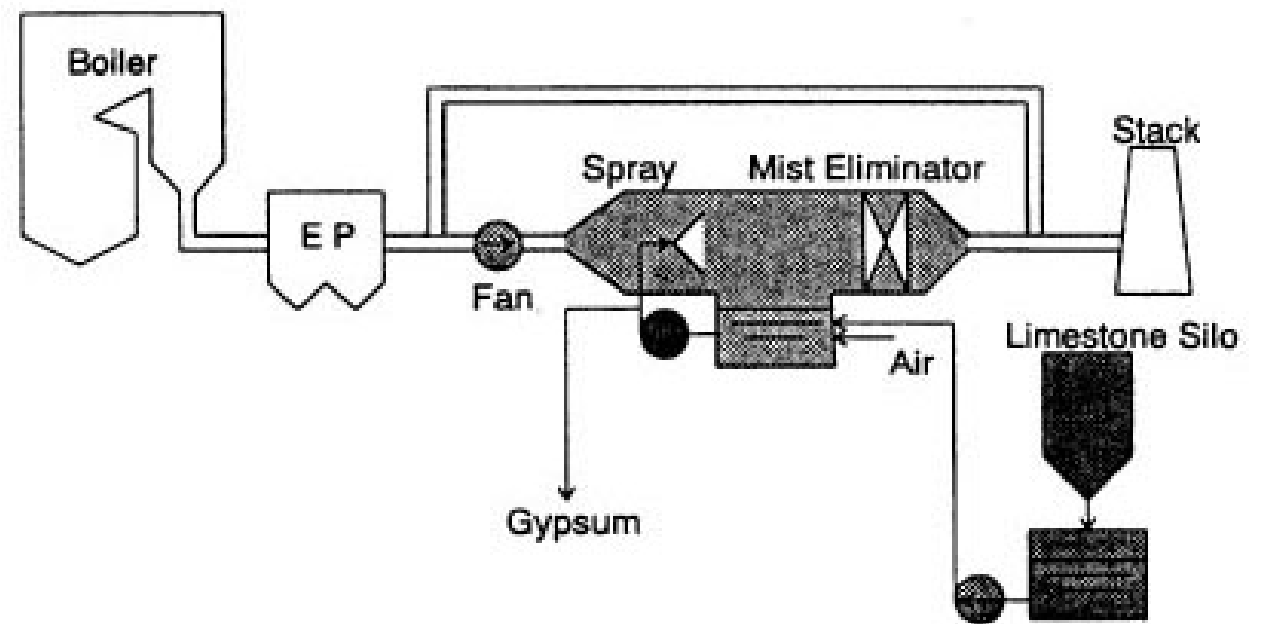
In the absorber :



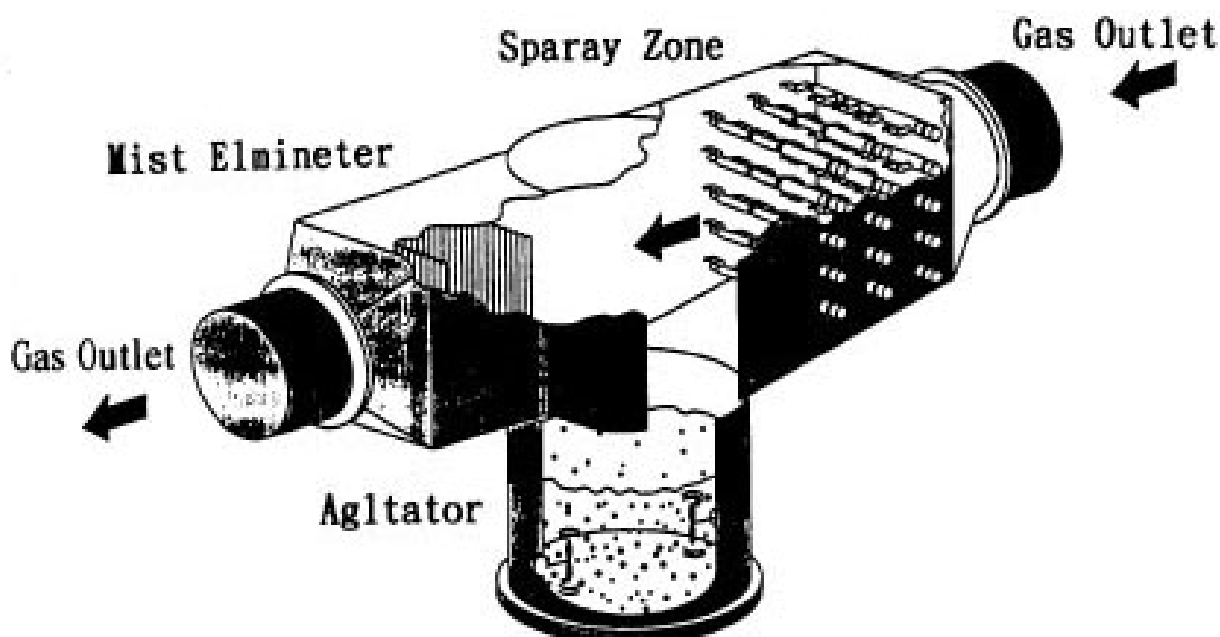
It shows the same reaction characteristics as in conventional one. From the absorbing tower’s structural view point, adoption of higher gas velocity and horizontal spray tower eliminate certain portion of duct for up and down and both of Duct’s capacity and system’s cost can be reduced tremendously.

Also, it is possible to reduce both auxiliaries and installation space by making the system compact.

7.5 Process flow sheet



7.6 Outline of absorber



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Air Pollution - Monitoring, Modelling, Health and Control

Edited by Dr. Mukesh Khare

ISBN 978-953-51-0381-3

Hard cover, 254 pages

Publisher InTech

Published online 21, March, 2012

Published in print edition March, 2012

Air pollution has always been a trans-boundary environmental problem and a matter of global concern for past many years. High concentrations of air pollutants due to numerous anthropogenic activities influence the air quality. There are many books on this subject, but the one in front of you will probably help in filling the gaps existing in the area of air quality monitoring, modelling, exposure, health and control, and can be of great help to graduate students professionals and researchers. The book is divided in two volumes dealing with various monitoring techniques of air pollutants, their predictions and control. It also contains case studies describing the exposure and health implications of air pollutants on living biota in different countries across the globe.

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Arun Kumar Sharma, Shveta Acharya, Rashmi Sharma and Meenakshi Saxena (2012). Recovery and Reuse of SO₂ from Thermal Power Plant Emission, Air Pollution - Monitoring, Modelling, Health and Control, Dr. Mukesh Khare (Ed.), ISBN: 978-953-51-0381-3, InTech, Available from: <http://www.intechopen.com/books/air-pollution-monitoring-modelling-health-and-control/air-pollution-recovery-and-reuse-of-so2-from-flue-gases-of-thermal-power>

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