

# Chapter III

## Experimental

### **3.1. Apparatus/Instruments/reagents for experimentation**

The various apparatus and instruments used to conduct experiments for simultaneous removal of SO<sub>2</sub> and NO from simulated gas stream were shown in Table 3.1.

#### **3.1.1. Gas cylinders with two stage pressure regulators**

Gas cylinders were used as sources of SO<sub>2</sub>, NO, N<sub>2</sub> and CO<sub>2</sub> to simulate the gas stream. The SO<sub>2</sub>, NO and CO<sub>2</sub> cylinders were balanced with N<sub>2</sub> after the maximum requirement that meets the stack exit concentration. The exit of the gas cylinder was fitted with two stage pressure regulator which helps to show the cylinder pressure and exit stream pressure. The SO<sub>2</sub> (1.04 % SO<sub>2</sub> & balanced N<sub>2</sub>), N<sub>2</sub> (100% N<sub>2</sub>) and CO<sub>2</sub> (20% CO<sub>2</sub> & balanced N<sub>2</sub>) cylinders were supplied by BOC India Limited, India with purity 99% of

each cylinder. The source of NO cylinder (0.5% NO & balanced N<sub>2</sub>) was Inox Air Products Limited with purity 99%.

**Table 3.1.** Apparatus used for experimentation

<b>S. No.</b>	<b>Instrument/Apparatus</b>	<b>Specifications</b>	<b>Sources</b>
1.	Gas mixing cum pressure releasing chamber	Borosilicate glass column Internal diameter: 0.05 m; height: 0.3 m; coil of 8 turns made from borosilicate glass tube of 0.008 m internal diameter (coil diameter: 0.055 m)	Precision Instruments, Varanasi, India
2.	Spray column with distributor	Borosilicate glass column Internal diameter: 0.03 m; height: 0.6 m; distributor tip diameter: 0.08 m; number of holes: 20	Precision Instruments, Varanasi, India
3.	Bubble column	Borosilicate glass column Internal diameter: 0.03 m; height: 0.3 m;	Precision Instruments, Varanasi, India

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4.	Magnetic stirrer vessel	Borosilicate glass column Internal volume: 250 cm <sup>3</sup> ; height: 0.15 m	Precision Instruments, Varanasi, India
5.	Magnetic stirrer hot plate	Temperature 0-100 °C; agitation speed 0-1500 rpm	Remi Equipment's Ltd., India
6.	pH analyzer	Model LI614	Elico India Ltd., India
7.	Tubing	3/8" internal diameter	Mayur rubber and plastic agency, Varanasi, India
8.	Mass flow controllers	0-200 ppm; model: D07-19B	Beijing Seven Star Electronics Co. Ltd., Beijing, China
9.	Digital readout box	0-200 ppm; model: D08-2F	Beijing Seven Star Electronics Co. Ltd., Beijing, China
10.	Multi flue gas analyzer	SO <sub>2</sub> : 0-10000 ppm; NO: 0-2000 ppm; CO <sub>2</sub> : 0-200000 ppm; model: Gas-board 3800 P	Wuhan Cubic Optoelectronics Co. Ltd., Wuhan, China
11.	Submersible pump	0-150 L/h; model: Usha-1195	Khaneja Electronic, Varanasi, India

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12.	Gas flow meter	0-2000 mL/min; model: GSI-301	Test Master Pvt. Ltd., Mumbai.
13.	Joints	Tee, cross, union	Precision Instruments, Varanasi, India

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### **3.1.2. Mass flow controllers and digital read out box**

To maintain the gas stream flow stable mass flow controllers were used. During experiments for large concentrations (>2000 ppm) gas flow meters were used. These gas flow meters are made of glass and contain an operating nob which helps to control the flow rate and the flow rate was measured in cc/min. The flow rate was adjusted according to the initial concentration with help of multi gas flow meter. For the minute concentration (0-2000 ppm), the initial concentration was monitored itself with mass flow controllers containing mass flow sensors adjusted with digital read out box. With use of these sensors we can easily know the concentration of inlet flow stream can be easily known. These mass flow controllers (model: D07-19B) and digital readout box (model: D08-2F) were purchased from Beijing Seven Star Electronics Co. Ltd, Beijing, China with range 0-2000 ppm.

### **3.1.3. Gas mixing cum pressure releasing chamber**

Gas mixing cum pressure release chamber was made of borosilicate glass with internal diameter 0.05 m and height 0.3 m. It contains coil of 8 turns made of borosilicate glass with internal diameter 0.008 m at the exit. It contains 4 inlets with controlling valves at the entrance with internal diameter 0.008 m. This mixing chamber was used to mix the gas streams from different cylinders and to prepare simulated gas stream to reach the desired concentrations of stack gases. The coil at the exit was provided to increase the contacting zone for the incoming gas streams and also to create turbulence so that the gaseous particles were mixed properly. The source for the gas mixing and pressure releasing chamber was Precision Instruments, Varanasi, India.

### **3.1.4. Tubing**

Throughout the experiment, plastic tubing was used of 3/8-inch diameter supplied by Mayur Rubber and Plastic agency, Varanasi, India. This tubing helps in joining the instruments and also ensures the flow of gas stream in rest of the experimental section. For liquid circulation, same diameter tube was used but the thickness of the tube was less in comparison with the gas tubing.

### **3.1.5. Joints**

Cross and Tee joints are used which helps to assemble the experimental setup. These are made of borosilicate glass. The source of these joints was Precision Instruments, Varanasi, India.

### **3.1.6. Absorption columns**

Three types of absorption columns were used during the experiments of simultaneous removal of SO<sub>2</sub> and NO. One was bubble column generally a borosilicate gas bubbler with internal diameter 0.03 m and height 0.3 m. It also contains a closure with a gas inlet and gas outlet provisions. The inlet and outlet were connected with two glass tubes of internal diameter 0.005 m where inlet tube for introduction of the gas stream was extended to the bottom of the column and outlet glass tube is at the surface to near the top of the bubble column. Here the mixing of the gas and liquid phase was done with the help of gas bubble liquid interfacial area while flowing the gas from bottom to the top surface of liquid in the column. Being a vertical column, the gas stream was released at the bottom of the column and the gas bubble travels throughout the column to the top. During the process, the solutes SO<sub>2</sub> and NO transfer from the bubbles to the absorbing solution. Water bath was provided to surround the column for temperature variation. The maximum capacity of the bubble column with respect to effective volume of the absorbent was 200 cm<sup>3</sup>.

The second column was semi batch magnetic stirrer vessel (known as agitated column) of conical borosilicate glass vessel with 250 cm<sup>3</sup> internal volume, covered with borosilicate glass closure with inlet for gas flow into the absorbing solution and outlet for gas flow exit. This was operated with help of magnetic stirrer. The heating for this agitated liquid bed was provided with help of hot plate magnetic stirrer. Cooling was provided with the help of water bath temperature indicator surrounded by the column, to maintain the uniform temperature of the liquid.

Third column was a spray column used for continuous mode of absorption of SO<sub>2</sub> and NO by the absorbent. The internal diameter of the spray column was 0.055 m and the height of the column was 0.6 m. The column consists of a liquid distributor at the top of the column and gas distributor at the bottom of the column. The inlet of the distributor was connected with 0.008 m tube where the outlet was conical shaped flat at the bottom. The distributor outlet consists several holes each of 0.001 m diameter. The number of holes were more at liquid distributor as compared to gas distributor. The gas-liquid contact zone (the distance between tips of the distributors) is about 0.4 m height. The both distributors were arranged in such a way that the gas stream was in proper contact with the liquid. There was a gas out let at the top of the column and the liquid was collected at the bottom of the column and stored in the storage tank for recirculating. The liquid was recirculated throughout the column by using submersible pump. The temperature throughout the process was controlled with the help of water bath having temperature controller.

All the equipments were made of borosilicate glass and procured from Precision Instruments, Varanasi, India.

### **3.1.7. Submersible pump**

The submersible pump was used to circulate the liquid stream in continuous operation. The maximum capacity of the pump was 150 liters per hour. The source of the pump was Khaneja electronics, Varanasi, India. (model: Usha-1195)

### **3.1.8. Liquid storage tank**

Liquid storage tank was a borosilicate glass tank open to atmosphere with 20 liter capacity with internal diameter of 0.15 m.

### **3.1.9. Gas flow meter**

The glass flow meter works on the water displacement principle. Here the total gas flow through the exit was monitored by gas flow meter. Source of gas flow meter was Test Master Pvt. Ltd., Mumbai with capacity of 0-2000 mL/min. (model: GSI-301)

### **3.1.10. Silica gel column**

Silica gel column was a long cylindrical borosilicate glass column closed at the bottom and consists of inter changeable closure fitted with one inlet introduced to the bottom of the column and the outlet at the top of the column. The column was filled with silica gel.

### **3.1.11. Multi flue gas analyzer**

The analyzer works on the principle of micro-flow non-dispersive infrared sensor (NDIR) to measure SO<sub>2</sub>, NO, CO, CO<sub>2</sub> and electro chemical sensors to measure O<sub>2</sub>. The multi flue gas analyzer was obtained from Wuhan Cubic Optoelectronics Co. Ltd., Wuhan, China with model number Gas-board 3800 P. The maximum range of analyzer was SO<sub>2</sub>: 0-10000 ppm, NO: 0-2000 ppm, CO: 0-2000 ppm, CO<sub>2</sub>: 0-25% and O<sub>2</sub>: 0-25% to check the concentration of the constituents present in the gas stream.



### **3.1.12. Temperature controlled water bath**

This temperature controlled water bath was used to provide the heat and maintain constant temperature of the absorbent inside the absorption column. The range of the temperature controller was 0-100 °C. The source of this instrument was Narang Scientific Works Pvt. LTD, New Delhi, India.

### **3.1.13. pH meter**

The pH meter was used to measure the pH of the absorbent in the experiment. It consisted of digital pH indicator with probe. The source of this instrument was Elico India Pvt. Ltd India. It was calibrated with help of 3 standard buffer samples with pH 4, 7 and 9.2. Once the pH analyser was calibrated it was subjected to measure the samples during experimentation.

### **3.1.14. Reagents**

The reagents used were of analytical reagent grades. These are sodium hypochlorite solution, ammonia solution, buffer tablets, hydrochloric acid, NaOH and calcium hypochlorite. The detailed specifications of the reagents were given in Table 3.2. The gases used to prepare the simulated gas stream were also listed in the Table 3.2.

**Table 3.2.** The purities and specifications of gases and chemicals used for experimentation

S.NO.	Chemical/ gas	Specification (purity)	Source
1.	NaClO	Molecular weight:74.4 g/mol; CAS No. 7681-52-9 (Minimum assay 4% w/v; 99 % purity)	Thermo Fisher Scientific India Pvt. Ltd., Mumbai, India
2.	NaOH	Molecular weight: 39.997 g/mol, CAS No. 1310-73-2 (Minimum assay: 99%; 99 % purity)	RFCL Limited, India
3.	Ca(OCl) <sub>2</sub>	Molecular weight: 142.98 g/mol, CAS No. 7778-54-3 (Minimum assay 35% available chlorine; 99 % purity)	SD Fine chemical Pvt. Ltd., India
4.	Ammonia solution	Molecular weight: 17.03 g/mol, CAS No. 1336-21-6 (Minimum assay 30% a/v; 99 % purity)	Thermo Fisher Scientific India Pvt. Ltd., Mumbai, India
5.	HCl	Molecular weight: 36.46 g/mol, CAS No. 7647-01-0 (AR Grade; 99 % purity)	RFCL Limited, India
6.	N <sub>2</sub> gas	N <sub>2</sub> : 100% by volume (99.99% purity)	BOC Pvt. Ltd., Mumbai, India
7.	SO <sub>2</sub> gas	SO <sub>2</sub> : 1.04 % by volume with	BOC Pvt. Ltd., Mumbai,

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		remaining N <sub>2</sub> gas (99.99 % purity)	India
8.	NO gas	NO: 0.5 % by volume with rest of N <sub>2</sub> gas (99.99% purity)	BOC Pvt. Ltd., Mumbai, India
9.	CO <sub>2</sub> gas	CO <sub>2</sub> : 20 % by volume with balanced N <sub>2</sub> gas (99.99% purity)	BOC Pvt. Ltd., Mumbai, India
10.	Buffer tablets	pH: 4, 7, and 9.2	Thermo Fisher Scientific India Pvt. Ltd., Mumbai, India

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### 3.2. Methodology adapted

Initially the simulated gas stream was prepared for desired stack concentrations of SO<sub>2</sub> and NO. Then the experimentation was carried out in a semi batch operation in bubble column to determine the saturation data. The experimental setup was fabricated for semi batch bubble column to conduct the experiments for simultaneous removal of SO<sub>2</sub> and NO. During the estimation of saturation time the major operating parameters tested for the process in bubble column were time, temperature, and absorbent concentration.

After estimation of saturation and feasibility data in the sense of effective removal, the experiments were subjected to semi batch agitated column. Because in bubble column only axial mixing were taken place. To improvise the contact between gas and liquid the experimentation was carried out in semi batch agitated column where both axial and radial mixing takes place. Here the experimental setup was fabricated for semi batch

magnetic stirrer vessel to conduct the experiments for simultaneous removal of SO<sub>2</sub> and NO. The semi batch operation was performed with different operating conditions such as operating time, reaction temperature, initial NO concentration, initial SO<sub>2</sub> concentration and initial pH. This semi batch operation using magnetic stirrer vessel was performed for three different sets of absorbents NaClO, Ca(OCl)<sub>2</sub> and NaClO/NaOH blend. The initial feasibility and optimum operating conditions with these absorbents were estimated and the best effective absorbent was selected as NaClO for conducting the further experiments of simultaneous removal of SO<sub>2</sub> and NO.

As NaClO was selected effective absorbent, and the process was considered to continuous mode of operation. Here, initially, fabrication of spray column was done. The major operating parameters involved in continuous phase operation were reaction temperature, time, absorbent concentration, initial SO<sub>2</sub> concentration, pH change, initial CO<sub>2</sub> concentration and NO concentration. The obtained results showed NaClO as prominent absorbent for simultaneous removal of SO<sub>2</sub> and NO. The kinetics of the process in laboratory conditions were studied over best suitable absorbent NaClO.

As NaClO has a capability to remove NO/SO<sub>2</sub>, and able to produce nitrate/sulphate, influences of NH<sub>3</sub> addition to the absorbent so that it can produce ammonium based nitrate/sulphate. The experiments were done with NaClO/NH<sub>3</sub> blend; initially feasibility was tested for the process. Then semi batch operation was carried out with various operating parameters reaction time, temperature, mole ratio, initial pH, SO<sub>2</sub> concentration and NO concentration. Finally, the process was conducted in a continuous spray column with similar operating parameter. This data will help to scale up the process. The proposal for feasibility of the power plant suitable to thermal power plants

was given. The design of bio layers around the process was also proposed, in order to use the spent absorbent.

### **3.3. Experimental procedure**

The experimentation was performed based on the objective of the experiment. The main intension of this experiment was to select a suitable solvent for the process, check the feasibility of the process and to develop a process for continuous operation. Initially the experimentation was carried out to check the efficiency of the absorbent has for removal of SO<sub>2</sub> and NO simultaneously. The operation was preceded to semi batch operation to obtain optimum results. For semi batch operation, the gas phase was sent continuously into the stable liquid absorbent to study the operating conditions and to obtain optimum operating variables. These established operating variables would be helpful to proceed for continuous phase operation.

In the course of experiments, Initially the performance of bubble column using chemical absorbent NaClO was done for simultaneous removal of SO<sub>2</sub> and NO under various operating parameters. The process was followed by experimentation in the semi batch agitated vessel with NaClO, Ca(OCl)<sub>2</sub> and NaClO/NaOH as absorbents for simultaneous removal of SO<sub>2</sub> and NO under various conditions. Comparison of results was done with different absorbents for selection of suitable chemical absorbent which lead to high removal efficiencies of SO<sub>2</sub>/NO. Then experimentation was done with suitable absorbent NaClO to see the effect of various parameters on simultaneous SO<sub>2</sub> and NO removal for continuous study. The effect of additive NH<sub>3</sub> to NaClO was studied for simultaneous removal of SO<sub>2</sub> and NO in semi batch and continuous operation.

### **3.3.1. Absorption in bubble column with NaClO**

A schematic diagram of simultaneous SO<sub>2</sub> and NO removal process for experimental setup was shown in Figure 3.1. The absorption of SO<sub>2</sub> and NO from simulated gas stream in semi batch bubble column with NaClO was essentially divided into three major steps. The major steps were preparation of simulated gas stream, absorption of SO<sub>2</sub> and NO in the process and analysis of the streams.

Simulated gas stream preparation was an important task, and it should resemble the composition of industrial stack outlet gas stream. During the preparation of simulated gas stream, the gas stream was prepared in such a concentration level where it happens to be the desired concentration of stack gases for SO<sub>2</sub> and NO related to coal fired power plants. Here three different gas cylinders containing SO<sub>2</sub> with balance N<sub>2</sub>, NO with balance N<sub>2</sub> and N<sub>2</sub> alone, fitted with 2-stage pressure regulators, were used as source of the gas streams. The flow rates of gaseous streams were controlled by the pressure regulators and mass flow controllers with digital read out box and then followed by stainless steel needle valves to enter gas mixing and pressure release chamber for proper mixing. After getting the desired concentration of SO<sub>2</sub> and NO, the gas stream from the mixing chamber was fed into the bubble column containing a fixed volume of absorbing solution (aqueous NaClO). The column was connected to two valves. One is concerned about injection of gas stream in liquid phase and other was for outlet to either analysis or by-pass section, whenever required. The main intention of carrying out this experiment was to determine the saturation time for the process.

In this bubble column, the gas was continuously mixed in absorbent in form of bubbles at the bottom of the column to carry out absorption of both SO<sub>2</sub> and NO by the absorbent. The operating conditions for this experiment were shown in Table 3.3.

In the analysis section, the gas stream was initially dried with help of silica column and further this gas stream was analyzed with multi flue gas analyzer. Before the absorption process initially the gas stream was bypassed through T-joint and cross-joint present after gas mixing chamber through silica column to analyzer for analysis of gas stream. The absorbed gas was sent to atmosphere through gas flow meter to measure the amount of gas flow throughout the process.

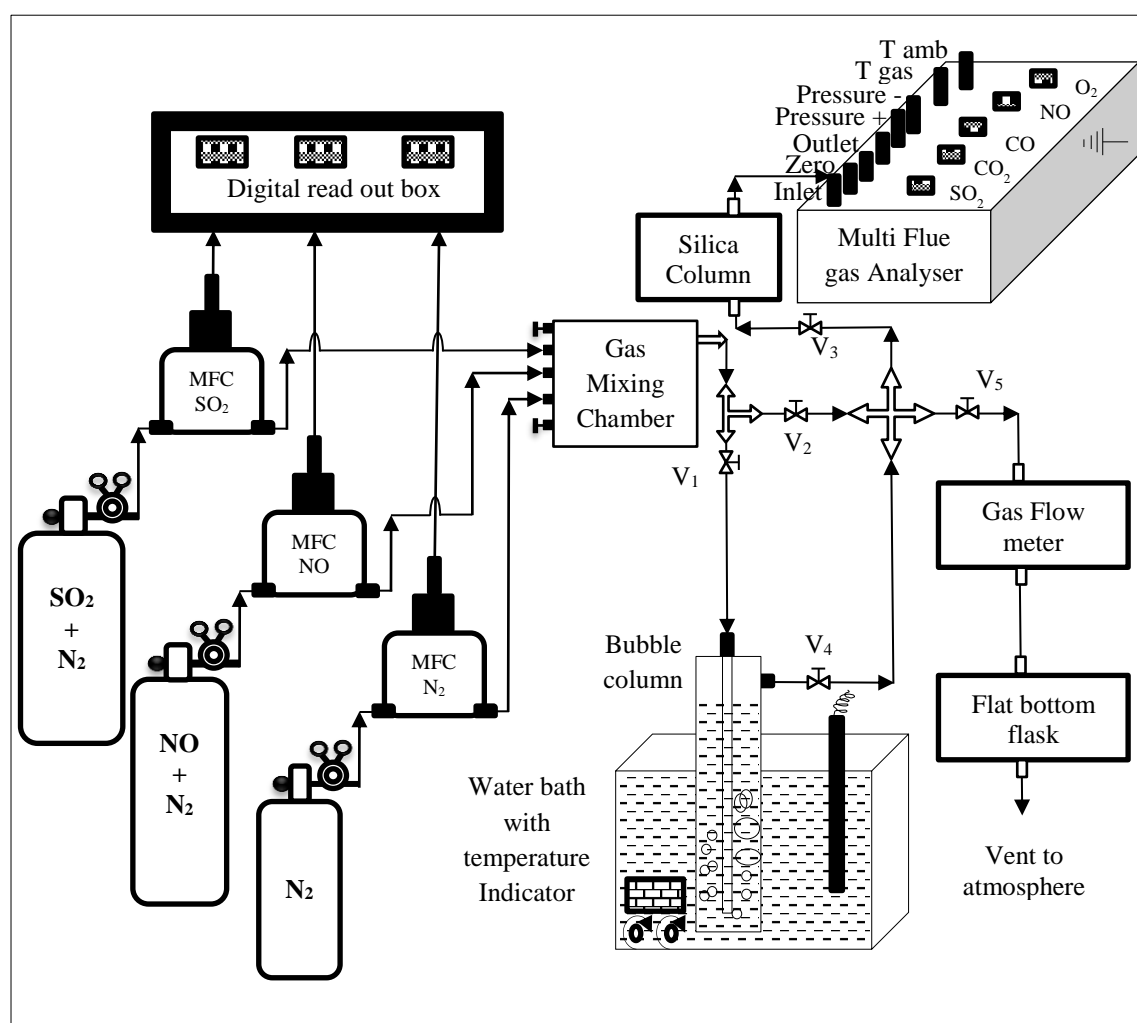
**Table 3.3.** Experimental conditions and sample description, for bubble column with NaClO

S. No.	Parameters	Condition	Accuracy/Purity
1.	Time	0-360 min	-
2.	NaClO concentration	0.004-0.032 M	99.00 %
3.	Absorbent temperature	283-325 K	±1K
4.	Initial NO concentration	6348 ppm	99.99 %
5.	Initial SO <sub>2</sub> concentration	1804 ppm	99.99 %
6.	Initial pH	5.6	±0.1
7.	pH of distilled water	6.85	-

The gases were mixed in a gas mixing cum pressure releasing chamber and sent for analysis in multi flue gas analyzer. The flow rates were adjusted with help of mass flow controllers and the pressure regulator till it showed the desired initial concentrations of SO<sub>2</sub> and NO in multi flow gas analyzer. The outlet of gas mixing chamber was a coil of 8 turns to provide a large time space for the gases so that proper mixing was done before entering the absorption process. During analysis of inlet gas stream, inlet valve V<sub>1</sub> was kept closed due to which gases were not passed into absorber vessel. Other valves V<sub>4</sub> and V<sub>5</sub> were also closed during this period. The valves V<sub>2</sub>, and V<sub>3</sub> were kept opened and gases were passed in flue gas analyzer. After maintaining desired concentration of NO/SO<sub>2</sub> in inlet gas stream, valve V<sub>1</sub> was opened and valve V<sub>2</sub> was closed permanently. Then the gases could pass through reactor and escaped from the system via valves V<sub>4</sub> and V<sub>5</sub>. In the analyzer, fixed amount of gas was passed and the vent was sent to atmosphere through gas flow meter. After regular time interval of 10 min the NO/SO<sub>2</sub> composition in the outlet gas stream were measured by flue gas analyzer. The sufficient amount of gas was passed in to analyzer for measuring the concentration of NO/SO<sub>2</sub> in exit gas. For concentration of NO/SO<sub>2</sub> in outlet gas stream, valves V<sub>1</sub>, V<sub>3</sub>, V<sub>4</sub> were opened and V<sub>2</sub>, V<sub>5</sub> valves were closed and the gas stream was passed into analyzer. After measuring the outlet concentration, valves V<sub>2</sub>, V<sub>3</sub> were closed and V<sub>1</sub>, V<sub>3</sub>, V<sub>5</sub> valves were opened through which gas could pass through flat bottom flask containing large volume of absorbing solution to ensure that all the remaining SO<sub>2</sub> and NO present in the outlet gas stream were absorbed. Finally exhaust gas was vented out into the atmosphere.



The removal efficiency of SO<sub>2</sub> and NO were analyzed for every 10 min throughout the process keeping other feasibility parameters such as absorbent concentration, absorbent temperature, pH, initial SO<sub>2</sub> concentration, initial NO concentration, etc. frozen. This leads to estimation of optimal time for the process. After the optimum time, the saturation time of absorbent was determined to calculate the kinetic parameters.

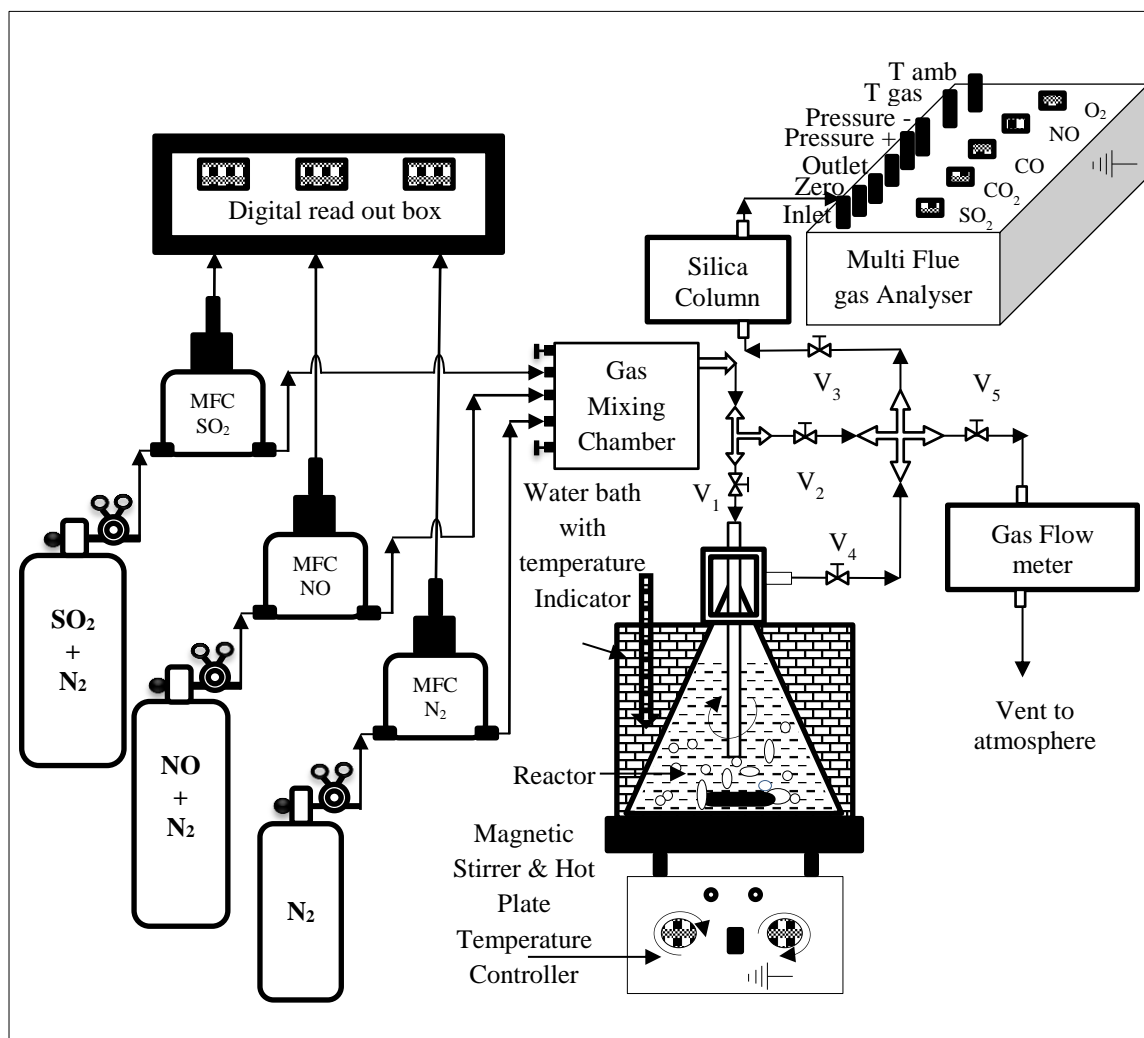


**Figure 3.1.** Experimental set-up for simultaneous absorption of SO<sub>2</sub> and NO in bubble column

The operating parameters such as time, absorbent temperature, pH, initial SO<sub>2</sub> concentration, initial NO concentration, etc. were kept frozen and the absorbent concentration was varied to determine the optimum concentration feasible to the process. The reaction temperature change with respect to steady operating conditions in terms of removal efficiency for simultaneous absorption of SO<sub>2</sub> and NO. The feasible temperature range which can provide best results during simultaneous removal of SO<sub>2</sub> and NO was estimated. The change in absorption of SO<sub>2</sub> and NO with initial pH was found by maintaining initial SO<sub>2</sub> concentration, initial NO concentration, initial NaClO concentration, and reaction time constant. For the acidic conditions 0.1N HCl, and for basic conditions 0.1N NaOH solution were used.

Experimentation was carried out to study the change in removal efficiency of SO<sub>2</sub> and NO for simultaneous absorption with respect to initial SO<sub>2</sub> concentration keeping the remaining operating parameters constant. The experiments were performed by considering concentration range 0 to 7000 ppm to check the feasibility consideration and industrial stack concentration resemblance. Effect of various initial concentration of NO on simultaneous removal of SO<sub>2</sub> and NO to select an optimal range feasible for the process was carried out by varying NO concentration 0 to 1000 ppm with constant operating parameters reaction temperature, initial SO<sub>2</sub> concentration, initial NaClO concentration and reaction time.

## 3.3.2. Absorption in magnetic stirrer vessel



**Figure 3.2.** Experimental setup for simultaneous absorption of SO<sub>2</sub> and NO in magnetic stirrer vessel

In bubble column, standard liquid absorbent was kept in absorber in which gas was injected at the bottom of the column so that the gas bubble can travel axially throughout the liquid be inside the column. The residence time is a depending factor to obtain the

efficient results. Here a magnetic stirrer vessel was introduced to reduce the contact time and improve the mixing between the dissolved gas and liquid absorbent. Here both axial and rotational mixing can be performed. This helps in finding out the maximum removal capability of the absorbent to remove both SO<sub>2</sub> and NO simultaneously. The experimental setup for semi batch magnetic stirrer vessel was quite like the set up explained for the bubble column. The schematic diagram of simultaneous SO<sub>2</sub> and NO removal in semi batch stirred vessel was shown in Figure 3.2. The absorption of SO<sub>2</sub> and NO from simulated gas stream in semi batch magnetic stirrer was carried out vessel with three different absorbents NaClO, Ca(OCl)<sub>2</sub> and NaClO/NaOH.

#### **3.3.2.1. Absorption in magnetic stirrer vessel with NaClO**

The experimentation to conduct simultaneous removal of SO<sub>2</sub> and NO using NaClO solution in semi batch magnetic stirrer vessel was shown in Figure 3.2. The experimentation performed was like as the procedure explained in the bubble column. Here the absorption column was replaced by the magnetic stirrer vessel. The desired gas stream resembling the stack gas concentrations of SO<sub>2</sub> and NO was fed into the stirrer vessel containing a fixed volume of aqueous NaClO as absorbent. In this column, continuous mixing of absorbent with gas was carried out by hot plate magnetic stirrer where both SO<sub>2</sub> and NO were absorbed by the absorbing solution. The operating conditions for this experiment were shown in Table 3.4.

**Table 3.4.** Experimental conditions and sample description for magnetic stirrer vessel with NaClO

S. No.	Parameters	Condition	Accuracy/Purity
1.	NaClO concentration	0.002-0.01 M	99.00 %
2.	Absorbent temperature	293-323 K	±1K
3.	Initial NO concentration	508.27-816.67 ppm	99.99 %
4.	Initial SO <sub>2</sub> concentration	4170.69- 7135.97 ppm	99.99 %
5.	pH of distilled water	6.85	-

Initially the temperature in the column was calibrated to minimize the temperature difference between bottom and top of absorbent bed. The experimentations were performed by varying operating parameters such as absorbent concentration (0.002-0.01 M), reaction temperature (293-323 K), initial NO concentration (508.27-816.67 ppm), initial SO<sub>2</sub> concentration (4170.69- 7135.97 ppm) and initial pH (3-10). The magnetic stirrer resolves the best feasible conditions for the absorbent at which it can ensure to show maximum capability.

### 3.3.2.2. Absorption in magnetic stirrer vessel with Ca(OCl)<sub>2</sub>

This process was concerned about the instantaneous removal of SO<sub>2</sub> and NO with a complex absorbent calcium hypochlorite (Ca(OCl)<sub>2</sub>) for simulated gas stream. The Ca(OCl)<sub>2</sub> was used to improvise the oxidation rate to convert NO to NO<sub>2</sub> and further reaction lead to absorption of SO<sub>2</sub>, NO and NO<sub>2</sub>. In this process concentrations of SO<sub>2</sub>

and NO were taken as like the desired concentrations of SO<sub>2</sub> and NO in flue gas emission. The detailed schematic of experimental setup was shown in Figure 3.2. including with three major sections such as a simulated flue gas preparation section, a magnetic stirrer vessel and a flue gas analysis section.

**Table 3.5.** Experimental conditions and sample description for magnetic stirrer vessel with Ca(OCl)<sub>2</sub>

<b>S. No.</b>	<b>Parameters</b>	<b>Condition</b>	<b>Accuracy/Purity</b>
1.	Ca(OCl) <sub>2</sub> concentration	1-7 g/100 ml	99.00 %
2.	Absorbent temperature	293-323 K	±1K
3.	Initial NO concentration	200-900 ppm	99.99 %
4.	Initial SO <sub>2</sub> concentration	1000- 6000 ppm	99.99 %
5.	pH of distilled water	6.85	-
6.	Time	0-120 min	--

A simulated gas stream has been prepared during the process. This gas stream was subjected to absorption and the effective parameters such as absorbent concentration, operating temperature, initial pH, initial SO<sub>2</sub> concentration and initial NO concentration were varied to study the feasibility of Ca(OCl)<sub>2</sub> as absorbent for integrative absorption of SO<sub>2</sub> and NO. The experimental conditions for the process were tabulated in Table

3.5. The proper mixing of  $\text{Ca}(\text{OCl})_2$  is required because it can't immediately dissolve in water.

### 3.3.2.3. Absorption in magnetic stirrer vessel with NaClO/NaOH

The detailed experimental procedure described in section 3.3.1 was followed in this section. This process considers magnetic stirrer vessel as absorption column and NaClO/NaOH as absorbent shown in Figure 3.2. Here the absorbent blend was taken into consideration to increase the removal efficiency of NO. The experimental conditions with sample description were given in Table 3.6.

**Table 3.6.** Experimental conditions and sample description for magnetic stirrer vessel with NaClO/NaOH

S. No.	Parameters	Condition	Accuracy/Purity
1.	NaClO concentration	0.024 M	99.00 %
2.	Absorbent temperature	293-323 K	$\pm 1\text{K}$
3.	Initial NO concentration	850 ppm	99.99 %
4.	Initial $\text{SO}_2$ concentration	6829 ppm	99.99 %
5.	pH of distilled water	6.85	-
6.	Time	0-120 min	--
9.	Absorption blend ratio	0.5-4	--

Several reactions were occurred when simulated gas stream entered into the column in which agitation was done by a hot plate magnetic stirrer. The concentrations of SO<sub>2</sub> and NO<sub>x</sub> were noted by multi flue gas analyzer prior and after absorption at a specific time to calculate the removal efficiencies of SO<sub>2</sub> and NO. Then, the exhaust gas stream was discharged into the environment after being treated by the exhaust gas processing unit. To avoid damage to the flue gas analyzer; the silica gel column was used to remove the moisture content from the gas stream prior to the analyzer. The major influencing parameters studied in this process were reaction temperature, molar ratio and reaction time.

### **3.3.3. Absorption in continuous spray column with NaClO**

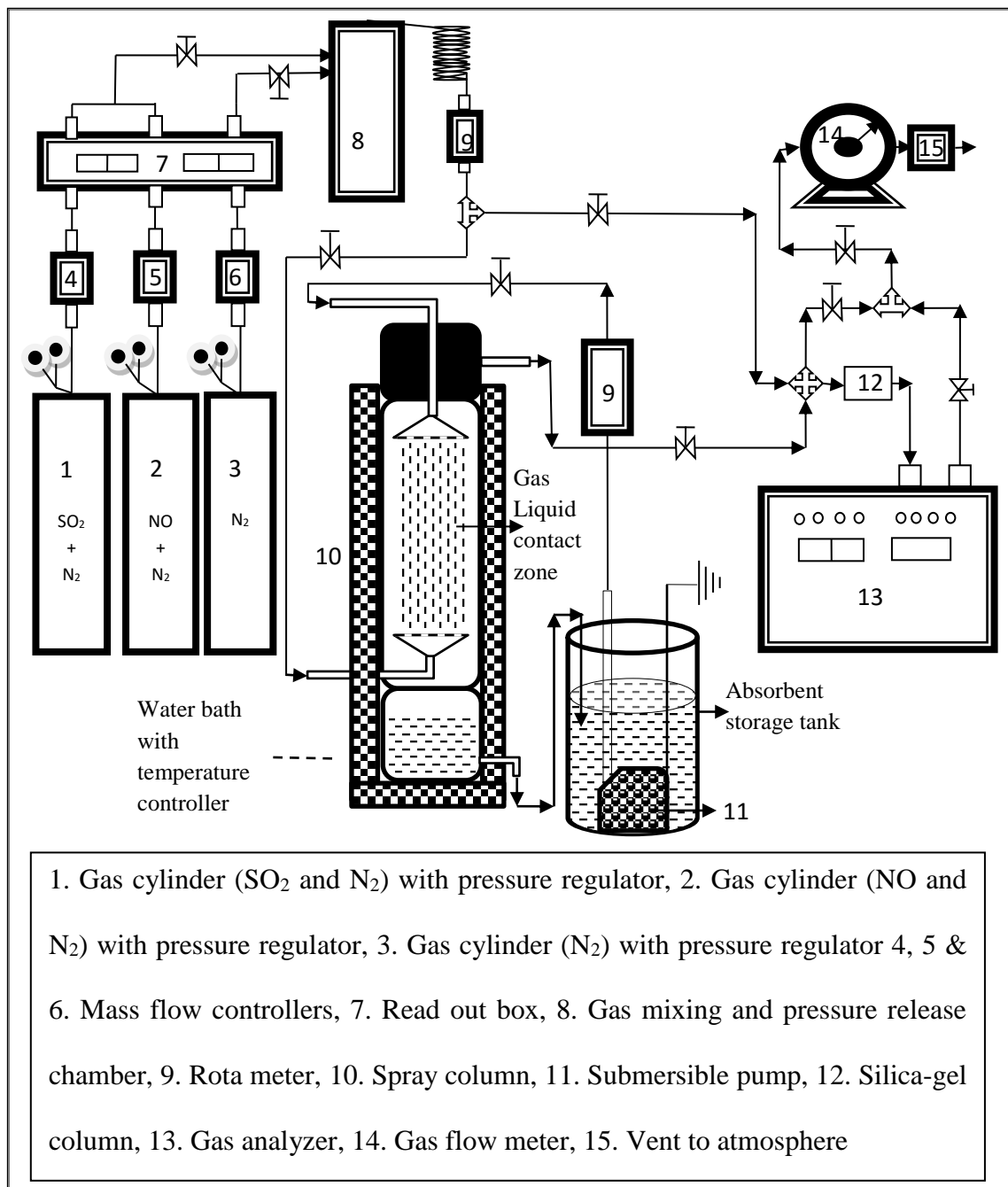
As the absorbent can remove both SO<sub>2</sub> and NO in semi batch operation, further experiments were conducted in continuous mode operation with the use of spray column. The magnetic stirrer vessel in Figure 3.2 was replaced by a spray column as shown in Figure 3.3. During the continuous process, additional absorbent storage tank, spray column and submersible pump were incorporated in the experimental setup as shown in Figure 3.3. The experimental conditions used in continuous spray column were shown in Table 3.7.

During the process, the absorbent was kept in a storage tank, here the liquid is circulated with the help of submersible pump. The column was kept inside a water bath equipped with temperature controller to monitor the temperature variation. The collecting tank at the bottom of the absorber helps to re-circulate the solution till the total solution reaches saturation and to maintain time lag between observations. During the experimentation, initially gas was introduced in to the column before releasing the liquid to avoid the



back pressure so that the liquid be not allowed of traveling through gas distributor. The experimentation was carried out by considering several operating parameters with obtained optimum values in semi batch operations.

The simulated gas stream was prepared with the usage of gases from two different gas cylinders containing SO<sub>2</sub> with balance N<sub>2</sub> (No.1) and NO with balance N<sub>2</sub> (No.2) fitted with 2-stage pressure regulators. This system urged with further inclusion of another cylinder containing N<sub>2</sub> (No.3) so that the concentration of the gas stream can be varied in the inlet of spray column during experimental runs. The flow rates of gaseous streams were controlled by mass flow controllers (4, 5 and 6) with digital read-out box (7) and then followed by stainless steel needle valves to enter gas mixing and pressure release chamber (8) for proper mixing of gas streams. After obtaining the predetermined concentration of SO<sub>2</sub> and NO, the gas stream from the mixing cum pressure releasing chamber was introduced into the spray column (10) where the gas stream was contacted with the spray of aqueous NaClO solution circulated with submersible pump (11). Column consists of spray distributor at the top which provides uniform distribution of liquid inside the column. The distributor is made of glass which is assigned as closed tube discharge system containing special outlets of diameter 1 mm each on the underside of the distribution exit to distribute the liquid in spray column. In this absorption column, continuous spraying of absorbing solution was accomplished where both SO<sub>2</sub> and NO were absorbed by the absorbing solution. The liquid circulation was controlled with use of rotameter (16) aliened to the liquid circulating stream.



**Figure 3.3.** Experimental set-up for simultaneous absorption of  $\text{SO}_2$  and  $\text{NO}$  in spray column

**Table 3.7.** Experimental conditions in continuous spray column with NaClO

S. No.	Parameter	Condition	Accuracy/purity
1.	Gas flow rate	600 mL/min	±2 mL/min
2.	Liquid flow rate	1500 mL/min	±2 mL/min
3.	Absorbent temperature	283 – 323 K	±1K
4.	Absorbent concentration	0.004 – 0.032 M	99%
5.	Initial SO <sub>2</sub> concentration	2431.75 – 6816.67 ppm	99%
6.	Initial NO Concentration	431.75 -816.67 ppm	99%
7.	Initial CO <sub>2</sub> concentration	50000 ppm	99%
8.	Initial pH	4.1 – 9.2	-
9.	Time	0 – 180 min	-

The measurements of inlet gas stream composition were carried out with the use of infrared flue gas analyzer (13) (model: gas-board 3800 P, Wuhan Cubic Optoelectronics Co. Ltd., Wuhan, China) by passing the simulated gas stream directly to the analyzer through silica-gel column (12). This analysis was carried out till the desired concentrations of SO<sub>2</sub> and NO were obtained in the gas stream. Experimentation was initiated and progressed with inlet gas stream of fixed SO<sub>2</sub> and NO concentration after being entered into the spray column followed by contacting with a particular concentration of absorbent as sprayed liquid. Then the gas stream was permitted to pass through flue gas analyzer for a set quantity of gas for analysis and vent (15) can release

the rest of the gas stream to atmosphere through gas flow meter (14). The reading of SO<sub>2</sub> and NO concentrations recorded by the analyzer was noted for a regular time interval of 20 min.

During the experimentation for studying study the effect of CO<sub>2</sub> addition to the simulated gas stream, the N<sub>2</sub> gas cylinder (No.3) was replaced with CO<sub>2</sub> gas cylinder containing CO<sub>2</sub> with balance N<sub>2</sub>. The experimental study of CO<sub>2</sub> was carried out due to presence of high CO<sub>2</sub> concentration in industrial stack gases so that used in this research continuous process can be implemented to pilot plant scale which can be scaled up easily to industrial scale. By including CO<sub>2</sub> gas cylinder with the mass flow controller (6) simulated gas stream equivalents to stack gases was prepared in gas mixing chamber (7). The analysis of CO<sub>2</sub> added simulated gas stream was carried out in similar pattern as described above. Initially the inlet concentrations were measured by passing the CO<sub>2</sub> added simulated gas stream directly through the multi-gas analyzer (13) and followed by treated gas stream using absorbent in spray chamber (10).

Effect of various initial concentration of CO<sub>2</sub> on simultaneous removal of SO<sub>2</sub> and NO to select an optimal range feasible for the process was carried out at CO<sub>2</sub> concentration of 50000 ppm with constant operating parameters like reaction temperature, initial SO<sub>2</sub> concentration, initial NaClO concentration, initial NO concentration and reaction time.

#### **3.3.4. Feasibility of NaClO/NH<sub>3</sub> blend for NH<sub>3</sub> as additive**

Initial feasibility of the process was investigated with use of absorbent blend on simultaneous removal of SO<sub>2</sub> and NO by varying the basic parameters such as process temperature, initial absorbent concentration, initial pH, and change in initial SO<sub>2</sub> concentration and initial NO concentration. Another important parameter concerned to

this experiment was blend ratio in NH<sub>3</sub>-NaClO solution. These feasibility operations were studied initially with exact mole ratio in semi batch magnetic stirrer vessel and then implemented to continuous operation using spray column.

**Table 3.8.** Experimental conditions and sample description for magnetic stirrer vessel with NaClO/NH<sub>3</sub>

<b>S. No.</b>	<b>Parameters</b>	<b>Condition</b>	<b>Accuracy/Purity</b>
1.	NaClO concentration	0.032 M	99.00 %
2.	Absorbent temperature	283-333 K	±1K
3.	Initial NO concentration	200-1845 ppm	99.99 %
4.	Initial SO <sub>2</sub> concentration	214-8216 ppm	99.99 %
5.	pH of distilled water	6.85	-
6.	Contact time	0-180 min	--
9.	Mole ratio of NH <sub>3</sub> to NaClO	0-3.04	--

#### **3.3.4.1. Absorption in semi batch magnetic stirrer vessel with NaClO/NH<sub>3</sub> blend**

The schematic for conducting experiments on simultaneous SO<sub>2</sub> and NO removal process using NaClO/NH<sub>3</sub> for experimentation is shown in Figure 3.2. The detailed description of experimentation was explained in section 3.3.1. The flow rates of three gas cylinders with 2 stage pressure regulators connected to mass flow controllers were monitored with use of digital read out box. The absorption of SO<sub>2</sub> and NO was done

with help of magnetic stirrer vessel containing NaClO/NH<sub>3</sub> solution as an absorbent. The required heating for the process was provided by the hot plate fitted with temperature controller. The hot plate also consists of a magnetic stirrer which agitates the solution for proper mixing in between absorbent and the gas stream. This agitation helps the bubble breakage of gas stream in the solution to enhance the reaction rate. The experimental conditions for the process was given in Table 3.8.

Being a semi-batch operation, the major parameters studied during the process were operation temperature, concentration of absorbent, pH of absorbent, rate of mixing, initial SO<sub>2</sub> concentration, initial NO concentration and mass transfer parameters for the process. Experimentation was carried out to study the change in removal efficiency of SO<sub>2</sub> and NO for simultaneous absorption with respect to initial SO<sub>2</sub> concentration keeping the remaining operating parameters constant. The experiments were performed by considering SO<sub>2</sub> concentration ranges where the initial range was 0 to 2000 ppm and next range was 2000 to 8000 ppm. The reason for considering two ranges is that minute range helps for feasibility consideration and major range is considered for industrial stack concentration resemblance.

#### **3.3.4.2. Absorption in continuous spray column with NaClO/NH<sub>3</sub> blend**

The experimental setup was same for the experimentation as explained in section 3.3.3 expect NaClO/NH<sub>3</sub> blend as absorbent. The NaClO/NH<sub>3</sub> blend showed excellent removal of both SO<sub>2</sub> and NO in magnetic stirred vessel. Therefore, NaClO/NH<sub>3</sub> blend was used for further experimental runs in spray column. The major operating parameters for this study were absorbent temperature, initial SO<sub>2</sub> concentration initial NO concentration, molar ratio of NaClO/NH<sub>3</sub> blend and contact time.