

ENHANCED ABSORPTION OF SO₂ BY SUPPORTED LIQUID PHASE

THESIS

*Submitted in the Partial Fulfillment of the Requirement
For the Award of the Degree of*

**Master of Technology
In
Gas Engineering**

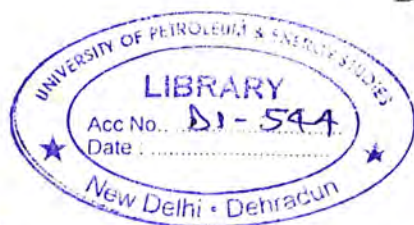
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**College of Engineering
University of Petroleum & Energy Studies
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May 2007**

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भारतीय पेट्रोलियम संस्थान

वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद्
हरिद्वार रोड, मोहकम्पुर
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TO WHOM SO EVER IT MAY CONCERN

This is to certify that Mr. D. Arulvalavan, M. Tech Student in Gas Engineering from University of petroleum and energy studies, Dehradun, was associated in the team working on project "Enhance Absorption of SO₂ by Supported Liquid Phase" at Indian Institute of Petroleum, Dehradun, from Feb. 16th, 2007 to May 11, 2007.

During his stay he has worked very diligently and has shown grasp on the subject and willingness to learn. He is a sincere hardworking boy with initiative. He has also shown good team spirit and is amicable.

I wish him success in his future endeavors.

Dr. Asha Masohan,
(Scientist "F")

11.5.07

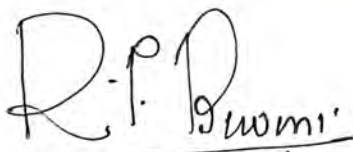


UNIVERSITY OF PETROLEUM & ENERGY STUDIES

CERTIFICATE

This is to certify that the project work entitled “Enhanced Absorption of SO₂ by Supported Liquid Phase ” submitted by D.Arulvalavan in partial fulfillment of the requirements for the award of the degree of Master Of Technology (Gas Engineering) at college of engineering, University of Petroleum and Energy Studies, is a record of the work carried by him at Indian Institute of Petroleum under the guidance of Dr. Asha Masohan Scientist F, Indian Institute of Petroleum Dehradun and Dr. R. P Badoni Distinguished Professor, COE, UPES.

To the best of my knowledge, the contents of this project work did not form a basis of the award of any previous degree or published material by any one else.



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M.TECH. GAS ENGG.

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PREFACE

Reduction of emissions of air pollutants is required for industrial operations; in particular, SO_2 and NO_x are the main targets to be reduced. Removal of SO_2 from stack gases has been the subject of more research than any other gas purification process, because of the detrimental effect of SO_2 on the environment. A great number of flue gas desulphurization processes have been developed throughout the world. Various separation techniques employed to separate SO_2 from flue gases require regeneration of solvents and it involves loss of solution by vaporization/condensation. Moreover, this process involves increased cost imparted by pumps and other utilities required, and the cost of solvents. In order to overcome these kinds of drawbacks and to improve the efficiency of absorption, a novel separation process is desired to be developed.

In recent years, a number of authors have pointed out the significance of vapor-phase reaction systems catalyzed by a liquid solution contained within the pores of an inert solid matrix. Such catalysts have been designated as Supported Liquid-Phase Catalysts (SLPC). In SLPC, the liquid-phase catalyst is coated onto the walls of a porous support as an ultra-thin film, with supported liquid and it, thus, effectively combines the attractive features of homogeneous catalysis such as high specificity, mild conditions, and molecular dispersion of catalytic species, with those of heterogeneous catalysis such as large interfacial area, lack of corrosion, use of packed-bed reactors, and facile separation of catalyst from products.

On similar laws by utilizing the technique of supported liquid phase, the absorbing solvent can be impregnated over a bed of solid to separate SO_2 from gaseous mixture. This technique will reduce loss of solvent since the solvent is immobilized and can be used for longer hours without the loss in activity or selectivity. This would be more economical than the other methods since it requires no pumping.

1. INTRODUCTION

In our world of rapid industrialization, it is imperative that all countries find a cost-effective way to reduce pollution. Reduction of emissions of air pollutants is required for industrial operations. In particular, SO₂ and NO_x are the main targets to be reduced. Removal of SO₂ from stack gases has been the subject of more research than any other gas purification process, because of the detrimental effect of SO₂ on the environment. When sulfur dioxide combines with water, it forms sulfurous acid, which is the main component of acid rain. Acid rain falls can cause deforestation, acidify waterways to the detriment of aquatic life and corrode building materials and paints.

For years, the most prevalent means of pollution control were command-and-control reduction methods. Command-and-control methods rely on government bureaucrats to set pollution standards and then enforce them by monetary fines. Beginning in the late 1960's the thought of using economic incentives to control pollution levels started to emerge and by 1975; the first permit trading programs had begun. Permit trading programs work by allowing pollution sources that decrease discharges more than the set standard to amass pollution permits. Other firms that cannot meet standards can then buy up these permits. In theory incentive, based programs are said to be better than traditional command-and-control programs because they are more cost-effective in the short-run, increase incentives to seek out new technology in the long run, reduce the costly burden of information gathering for regulatory bureaucrats, and are more flexible. On the other hand, there have been some criticisms of these new programs, one of which is that permit trading will lead to condensed areas of pollution known as "hot-spots". As part of the Clean Air Act Amendments, various countries enacted The Acid Rain Program to achieve a decrease in sulfur dioxide (SO₂) which is the leading cause of acid rain.

2. PRIMARY POLLUTANTS OF ENVIRONMENT

The six primary pollutants of air are listed below:

OZONE (O₃)

Nature and Sources of the Pollutant: Ground-level ozone (the primary constituent of smog) is the most complex, difficult to control, and pervasive of the six principal pollutants. Unlike other pollutants, ozone is not emitted directly into the air by specific sources. Ozone is created by sunlight acting on nitrogen oxides (NO_x) and volatile organic compound (VOC) emissions in the air. There are literally thousands of sources of these gases. Some of the more common sources include gasoline vapors, chemical solvents, combustion products of various fuels, and consumer products. They can originate from large industrial facilities, gas stations, and small businesses such as bakeries and dry cleaners. Often these "precursor" gases are emitted in one area, but the actual chemical reactions, stimulated by sunlight and temperature, take place in another. Combined emissions from motor vehicles and stationary sources can be carried hundreds of miles from their origins, forming high ozone concentrations over very large regions.

Health and Other Effects: Scientific evidence indicates that ground-level ozone not only affects people with impaired respiratory systems (such as asthmatics), but healthy adults and children as well. Exposure to ozone for 6 to 7 hours, even at relatively low concentrations, significantly reduces lung function and induces respiratory inflammation in normal, healthy people during periods of moderate exercise. It can be accompanied by symptoms such as chest pain, coughing, nausea, and pulmonary congestion. Recent studies provide evidence of an association between elevated ozone levels and increases in hospital admissions for respiratory problems in several cities. Results from animal studies indicate that repeated exposure to high levels of ozone for several months or more can produce permanent structural damage in the lungs. Environmental Protection Agency (EPA) health-based national air quality standard for ozone is 0.12 ppm

(measured at the highest hour during the day). Ozone is also responsible for several billion dollars of agricultural crop yield loss each year. Ozone also damages forest ecosystems.

NITROGEN DIOXIDE (NO₂):

Nature and Sources of the Pollutant: Nitrogen dioxide belongs to a family of highly reactive gases called nitrogen oxides (NO_x). These gases form when fuel is burned at high temperatures, and come principally from motor vehicle exhaust and stationary sources such as electric utilities and industrial boilers. A suffocating, brownish gas, nitrogen dioxide is a strong oxidizing agent that reacts in the air to form corrosive nitric acid, as well as toxic organic nitrates. It also plays a major role in the atmospheric reactions that produce ground-level ozone or smog.

Health and Other Effects: Nitrogen dioxide can irritate the lungs and lower resistance to respiratory infections such as influenza. The effects of short-term exposure are still unclear, but continued or frequent exposure to concentrations that are typically much higher than those normally found in the ambient air may cause increased incidence of acute respiratory illness in children. Nitrogen oxides are important in forming ozone and may affect both terrestrial and aquatic ecosystems. Nitrogen oxides in the air are a potentially significant contributor to a number of environmental effects such as acid rain and eutrophication in coastal waters. Eutrophication occurs when a body of water suffers an increase in nutrients that reduce the amount of oxygen in the water, producing an environment that is destructive to fish and other animal life.

PARTICULATE MATTER (PM-10 and PM-2.5):

Nature and Sources of the Pollutants: Particulate matter is the term for solid or liquid particles found in the air. Some particles are large or dark enough to be seen as soot or smoke. Others are so small they can be detected only with an electron microscope. Because particles originate from a variety of mobile and

stationary sources (diesel trucks, wood stoves, power plants, etc.), their chemical and physical compositions vary widely.

Health and Other Effects: Major concerns for human health from exposure to particulate matter are effects on breathing and respiratory systems, damage to lung tissue, cancer, and premature death. The elderly, children, and people with chronic lung disease, influenza, or asthma, tend to be especially sensitive to the effects of particulate matter. Acidic particulate matter can also damage manmade materials and is a major cause of reduced visibility.

SULFUR DIOXIDE (SO₂):

Nature and Sources of the Pollutant: Sulfur dioxide belongs to the family of sulfur oxide gases (SO_x). These gases are formed when fuel containing sulfur (mainly coal and oil) is burned, and during metal smelting and other industrial processes.

Health and Other Effects: The major health concerns associated with exposure to high concentrations of SO₂ include effects on breathing, respiratory illness, alterations in pulmonary defenses, and aggravation of existing cardiovascular disease. Major subgroups of the population that are most sensitive to SO₂ include asthmatics and individuals with cardiovascular disease or chronic lung disease (such as bronchitis or emphysema) as well as children and the elderly.

LEAD (Pb):

Nature and Sources of the Pollutant: Smelters and battery plants are the major sources of the pollutant "lead" in the air. The highest concentrations of lead are found in the vicinity of nonferrous smelters and other stationary sources of lead emissions.

Health Effects: Exposure to lead mainly occurs through inhalation of air and ingestion of lead in food, paint, water, soil, or dust. Lead accumulates in the body in blood, bone, and soft tissue. Because it is not readily excreted, lead can also affect the kidneys, liver, nervous system, and other organs. Excessive exposure

to lead may cause anemia, kidney disease, reproductive disorders, and neurological impairments such as seizures, mental retardation, and/or behavioral disorders. Even at low doses, lead exposure is associated with changes in fundamental enzymatic, energy transfer, and other processes in the body. Fetuses and children are especially susceptible to low doses of lead, often suffering central nervous system damage or slowed growth. Recent studies show that lead may be a factor in high blood pressure and subsequent heart disease in middle-aged white males. Lead may also contribute to osteoporosis in postmenopausal women

CARBON MONOXIDE (CO):

Nature and Sources of the Pollutant: Carbon monoxide is a colorless odorless poisonous gas formed when carbon in fuels is not burned completely. It is a byproduct of motor vehicle exhaust, which contributes more than two-thirds of all CO emissions nationwide. In cities, automobile exhaust can cause as much as 95 percent of all CO emissions. These emissions can result in high concentrations of CO, particularly in local areas with heavy traffic congestion. Other sources of CO emissions include industrial processes and fuel combustion in sources such as boilers and incinerators. Despite an overall downward trend in concentrations and emissions of CO, some metropolitan areas still experience high levels of CO.

Health and Other Effects: Carbon monoxide enters the bloodstream and reduces oxygen delivery to the body's organs and tissues. The health threat from CO is most serious for those who suffer from cardiovascular disease. Healthy individuals are also affected, but only at higher levels of exposure. Exposure to elevated CO levels is associated with visual impairment, reduced work capacity, and reduced manual dexterity, poor learning ability, and difficulty in performing complex tasks.

National air Quality Monitoring Programme (NAMP):

Central Pollution Control Board of our country is executing a nation-wide programme of ambient air quality monitoring known as National Air Quality Monitoring Programme (NAMP). The network consist of 308 operating stations covering 115 cities/towns all States and Union Territories of the country.

The objectives of the N.A.M.P. are to determine status and trends of ambient air quality; to ascertain whether the prescribed ambient air quality standards are violated; to Identify Non-attainment Cities; to obtain the knowledge and understanding necessary for developing preventive and corrective measures and to understand the natural cleansing process undergoing in the environment through pollution dilution, dispersion, wind based movement, dry deposition, precipitation and chemical transformation of pollutants generated.

Under N.A.M.P., four-air pollutants *viz.*, Sulphur Dioxide (SO₂), Oxides of Nitrogen as NO₂ and Suspended Particulate Matter (SPM) and Respirable Suspended Particulate Matter (RSPM/PM₁₀), have been identified for regular monitoring at all the locations. The monitoring of meteorological parameters such as wind speed and direction, relative humidity and temperature was also integrated with the monitoring of air quality.

The monitoring of pollutants is carried out for 24 hours (4-hourly sampling for gaseous pollutants and 8-hourly sampling for particulate matter) with a frequency of twice a week, to have 104 observations in a year. The monitoring is being carried out with the help of Central Pollution Control Board, State Pollution Control Boards, Pollution Control Committees; National Environmental Engineering Research Institute (NEERI), Nagpur. N.A.M.P. is being operated through various monitoring agencies, large number of personnel and equipment are involved in the sampling, chemical analyses, data reporting etc. It increases the probability of variation and personnel biases reflecting in the data, hence it is pertinent to mention that these data be treated as indicative rather than absolute.

Enhanced Absorption of SO₂ by Supported Liquid Phase

National Ambient Air Quality Standards:

Table 1 (Source: Central Pollution Control Board)

Pollutants	Time-weighted average	Concentration in ambient air			Method of measurement
		Industrial Areas	Residential, Rural & other Areas	Sensitive & Areas	
SulphurDioxide (SO ₂)	Annual Average*	80 µg/m ³	60 µg/m ³	15 µg/m ³	- Improved West and Geake Method - Ultraviolet Fluorescence
	24 hours**	120 µg/m ³	80 µg/m ³	30 µg/m ³	
Oxides of Nitrogen (NOx)	Annual Average*	80 µg/m ³	60 µg/m ³	15 µg/m ³	- Jacob & Hochheiser Modified (Na-Arsenite) Method
	24 hours**	120 µg/m ³	80 µg/m ³	30 µg/m ³	Gas Phase Chemiluminescence
Suspended Particulate Matter (SPM)	Annual Average*	360 µg/m ³	140 µg/m ³	70 µg/m ³	High Volume Sampling, (Average flow rate not less than 1.1 m ³ /minute).
	24 hours**	500 µg/m ³	200 µg/m ³	100 µg/m ³	
Respirable Particulate Matter (RPM) (size less than 10 microns)	Annual Average*	120 µg/m ³	60 µg/m ³	50 µg/m ³	Respirable particulate matter sampler
	24 hours**	150 µg/m ³	100 µg/m ³	75 µg/m ³	
Lead (Pb)	Annual Average*	1.0 µg/m ³	0.75 µg/m ³	0.50 µg/m ³	ASS Method after sampling using EPM 2000 or equivalent Filter paper
	24 hours**	1.5 µg/m ³	1.00 µg/m ³	0.75µg/m ³	
Ammonia	Annual Average*	0.1 mg/ m ³	0.1 mg/ m ³	0.1 mg/m ³	
	24 hours**	0.4 mg/ m ³	0.4 mg/m ³	0.4 mg/m ³	
Carbon Monoxide (CO)	8 hours**	5.0 mg/m ³	2.0 mg/m ³	1.0mg/ m ³	Non Dispersive Infra Red Spectroscopy (NDIR)
	1 hour	10.0 mg/m ³	4.0 mg/m ³	2.0 mg/m ³	Spectroscopy

* Annual Arithmetic mean of minimum 104 measurements in a year taken twice a week 24 hourly at uniform interval.

** 24 hourly/8 hourly values should be met 98% of the time in a year. However, 2% of the time, it may exceed but not on two consecutive days.

3. SOURCES OF SO₂ EMISSIONS

- Industry sources
- Diffuse sources, and industry sources included in diffuse emissions data
- Natural sources
- Transport sources
- Consumer products that may contain sulfur dioxide

Industry sources

Fossil fuel combustion sites particularly coal burning power plants; industrial processes such as wood pulping, paper manufacture, petroleum and metal refining and metal smelting, particularly from sulfide containing ores, e.g. lead, silver and zinc ores all emit sulfur dioxide to air.

The figure below shows the amount of gaseous pollutants emitted during combustion of coal (main source of SO₂ emission) at various level of air supply.

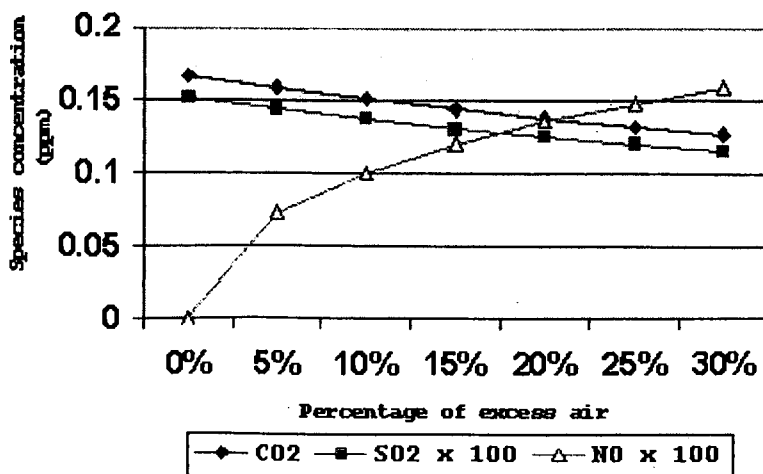


Fig 01: Combustion products/kg of coal

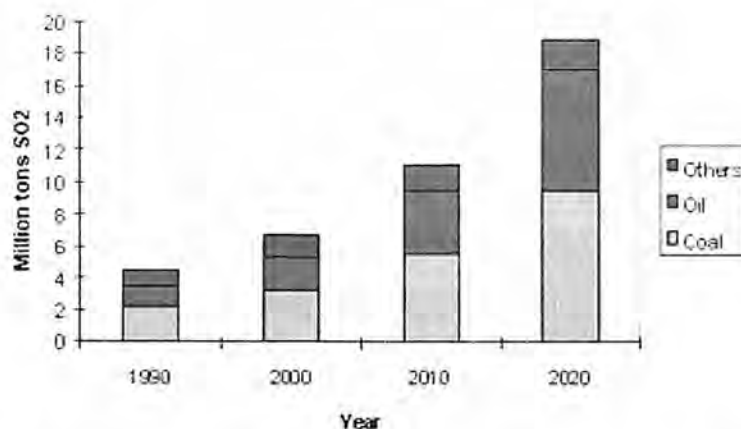


Fig 02: SO₂ Emissions, by fuels, under the reference scenario for India

(Source: RAINS-ASIA Model, Version 7.02)

Diffuse sources and industry sources included in diffuse emissions data

Small textile bleaching and food preserving facilities and wineries, fumigation activities all emit sulfur dioxide to air.

Natural sources

Geothermal activity, including hot springs and volcanic activity; sulfur dioxide is produced from the natural decay of vegetation on land, in wetlands and in oceans all emit sulfur dioxide to air.

Transport sources

Vehicle exhaust.

Consumer products that may contain sulfur dioxide

Some solvents, dechlorination agents, bleaches and fumigation products.

4. HEALTH AND ENVIRONMENTAL IMPACTS OF SO₂

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.

Respiratory Effects from Gaseous SO₂

Peak levels of SO₂ in the air can cause temporary breathing difficulty for people with asthma who are active outdoors. Longer-term exposures to high levels of SO₂ gas and particles cause respiratory illness and aggravate existing heart disease.

Respiratory Effects from Sulfate Particles

SO₂ reacts with other chemicals in the air to form tiny sulfate particles. When these are breathed, they gather in the lungs and are associated with increased respiratory symptoms and disease, difficulty in breathing, and premature death.

Visibility Impairment

Haze occurs when light is scattered or absorbed by particles and gases in the air. Sulfate particles are the major cause of reduced visibility in many parts of the U.S., including our national parks.

Acid Rain

SO₂ and nitrogen oxides react with other substances in the air to form acids, which fall to earth as rain, fog, snow, or dry particles. Some may be carried by the wind for hundreds of miles.

Plant and Water Damage

Acid rain damages forests and crops, changes the makeup of soil, and makes lakes and streams acidic and unsuitable for fish. Continued exposure over a long time changes the natural variety of plants and animals in an ecosystem.

Aesthetic Damage

SO₂ accelerates the decay of building materials and paints, including irreplaceable monuments, statues, and sculptures that are part of our nation's cultural heritage.

5. SCENARIO OF SO₂ EMISSIONS

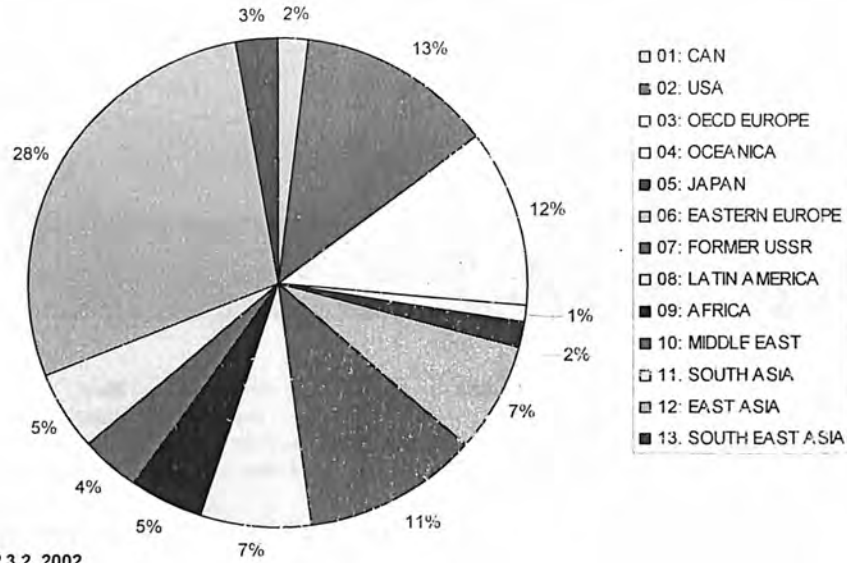


Fig 03: Global SO₂ Emissions

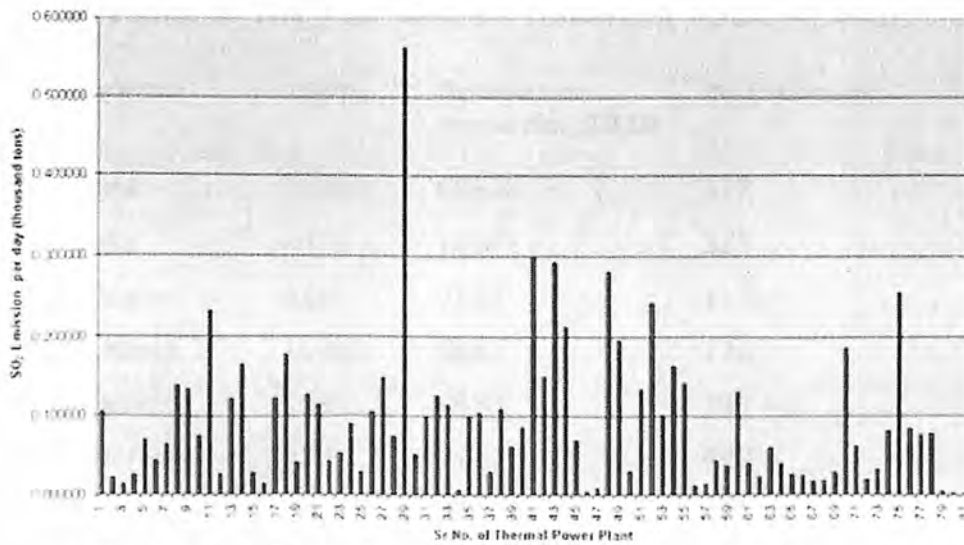


Fig 04: SO₂ Emissions/day from Indian Power Plants

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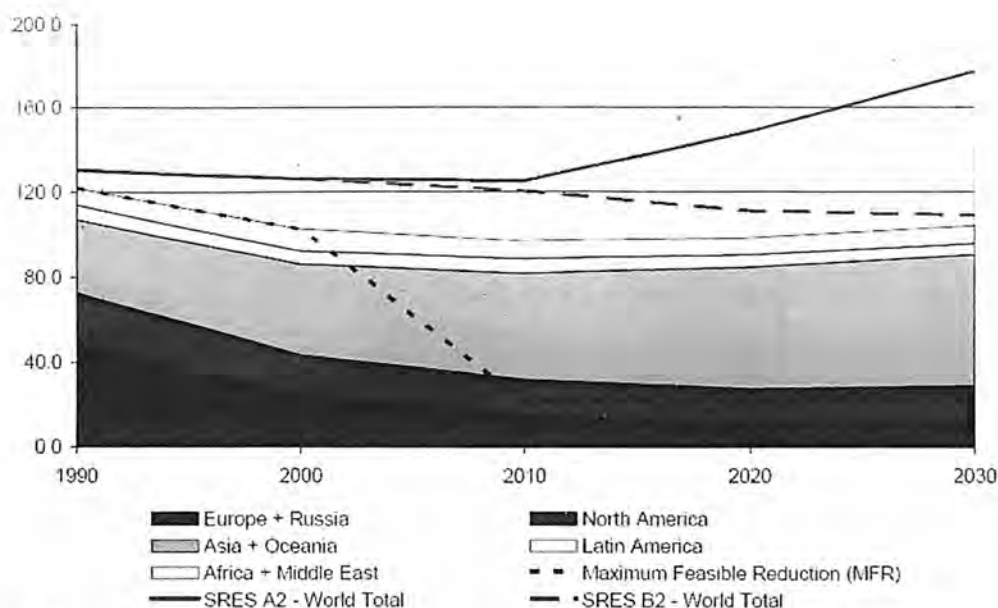


Fig 05: Projected development of anthropogenic SO₂ emissions by world region (Million tons SO₂) (Source: www.iiasa.ac.at/rains/global_emissions)

Table 02: Sulphur Dioxide Emissions In 1990 And For The Reference Scenario In The Year 2020 (In Thousand Tones Of SO₂)

Country	1990	Reference scenario, 2020	% Increase
China	21908	60688	177
India	4472	18549	315
Pakistan	614	7527	1126
S. Korea	1640	5537	238
Thailand	1038	4638	347
Indonesia	630	3162	402
Philippines	391	2037	421
Japan	835	1120	34
Asia Total	33675	110,478	228

Source: RAINS-Asia: An assessment model for acid deposition in Asia, The World Bank, Washington D.C., 1997.

6. LITERATURE STUDIES

POSSIBLE METHODS OF REDUCING SO₂ EMISSIONS

Energy conservation

Increased thermal efficiency

Alternative fuels

- Low sulphur fuels

Alternative sources of energy

- Nuclear power
- Solar power
- Tidal power
- Wave power
- Wind power
- Geothermal power

Combined heat and power schemes

Alternative combustion methods

- Fluidized bed combustion
- Gasification

Removal of sulphur from fuel

Removal of SO₂ from flue gases

Sulphur dioxide emissions from existing plant can be reduced either by removing sulphur from the coal before combustion or by removing sulphur dioxide during combustion or from the flue gases after combustion.

Categorization of sulfur dioxide removal process:

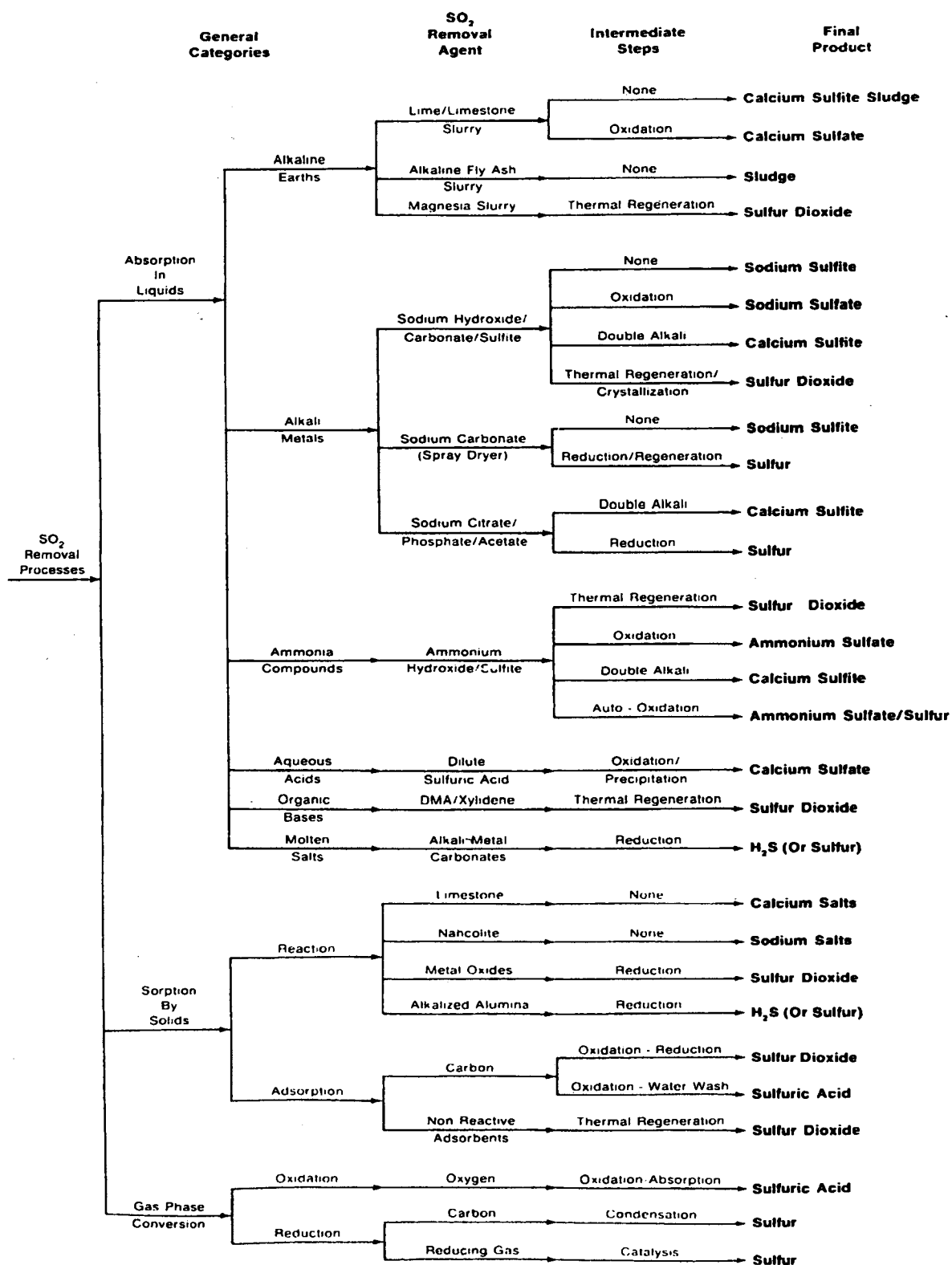


Fig 06: Categorization of sulfur dioxide removal process

SO₂ REMOVAL PROCESSES FOR FURNACE AND UTILITY STACK GASES

(14)

<p>Dry absorption process</p> <p>1. Limestone injection</p> <p>2. USBM alkalized Alumina</p> <p>3. Mitsubishi H. I. Manganese dioxide (DAP, Mn)</p> <p>4. Grillo mixed metal oxides (Germany)</p> <p>5. Still lignite ash (Germany)</p>	<p>Uses injection of dry Limestone into furnace.</p> <p>Uses alkalized alumina to absorb SO₂ and produces H₂S-rich stream for further processing to elemental sulfur.</p> <p>Uses manganese dioxide to absorb SO₂ and produces ammonium sulfate by-product.</p> <p>Uses manganese dioxide and magnesium Hydroxide to absorb SO₂ and produces SO₂ rich stream for further processing to sulfuric acid.</p> <p>Uses ash from lignite coal to absorb SO₂, and produces SO₂ rich stream for further processing to sulfuric acid.</p>
<p>Wet absorption process</p> <p>6. Combustion Engineering</p> <p>7. A. B. Bacha (Sweden)</p>	<p>Uses addition of alkaline earth additive to furnace followed by wet scrubbing with limestone slurry. Produces solids waste.</p> <p>Uses limestone wet scrubbing to Remove SO₂ and produces sludge.</p>

Enhanced Absorption of SO₂ by Supported Liquid Phase

8. Zurn	Uses wet scrubbing with native coral marl. Produces calcium sulfite/sulfate sludge.
9. U.O.P.-TCA Scrubber	Special "hollow spheres" scrubber used in wet scrubbing systems employing various solutions. Produces throwaway sludge.
10. U.O.P. Sulfoxel	Uses two stages of wet scrubbing to remove SO ₂ and produce liquid sulfur.
11. Mitsubishi new lime	Uses wet scrubbing with lime slurry and produces gypsum as by-product.
12. Davy Power gas. Wellman Lord	Uses sodium sulfite wet scrubbing and produces SO ₂ rich stream for further processing to sulfur or sulfuric acid.
13. Atomic International Molten carbonate)	Uses mixture of molten carbonates to remove SO ₂ , by scrubbing and produces H ₂ S rich stream for further processing to sulfur
14. Atomic International wet carbonate	Use aqueous solution of carbonates to remove SO ₂ .
15. Mitsubishi ammonia	Involves reaction of SO ₂ with NH ₃ and H ₂ O to produce ammonium sulfate by-product.
16. Showa Denko Ammonia	Uses injection of NH ₃ in flue gas to react with SO ₂ Produces ammonium sulfate byproduct.

Enhanced Absorption of SO₂ by Supported Liquid Phase

17. Showa Denko sodium sulfite	Uses sodium sulfite solution to Scrub out SO ₂ , and produces gypsum
18. Electricite de France ammonia	Uses variation Of Showa Denko's process and produces ammonium sulfate.
19.FMC	Uses double alkali process, with Caustic soda and lime to produce gypsum.
20. Envirotech	Uses caustic soda/lime double alkali scheme.
21. EDF-Kuhlman (France)	Uses ammonia/lime double alkali scheme.
22. General Motors	Uses caustic soda/lime double alkali scheme.
23. C.E.A. (U.S.A)	Uses caustic soda/lime double alkali scheme.
24. Research-Cottrell	Uses slurry of limestone to absorb SO ₂ from flue gas. Produces sludge waste for disposal. .
25. Wade's wet-scrubber	Uses special Linac contactor and ammonical-solution wet scrubbing. Produces ammonium sulfate.
26. Bufete Industrial (Marino) ammonia (Mexico)	Uses NH ₃ , vapor to react directly with SO ₂ in flue gas. Produces ammonium sulfate.
27. Stone & Webster/ Ionics	Uses aqueous caustic wet scrubbing. Regeneration produces SO ₂ rich stream for further processing to sulfuric acid.

Enhanced Absorption of SO₂ by Supported Liquid Phase

28. Chemico Basic	Uses magnesium oxide slurry wet scrubbing. Separate regeneration step produces SO ₂ rich stream for further processing to sulfuric acid.
29. Bischoff (Germany)	Uses lime slurry wet scrubbing. Produces waste sludge.
30. Kureka caustic soda (Japan)	Uses aqueous caustic wet scrubbing to produce sodium sulfite by-product.
31. Peabody soda ash	Uses soda ash slurry wet scrubbing. Produces waste sludge.
32. Consol's potassium salts	Uses potassium salts solution to remove SO ₂ . Produces H ₂ S rich stream for further processing to sulfur.
33. Hitachi caustic soda	Uses aqueous caustic. Wet scrubbing to produce sodium sulfite by-product.
34. Chiyoda (Thoroughbred 101)	Uses dilute sulfuric acid wet scrubbing to remove SO ₂ . Produces gypsum as byproduct.
35 Monsanto Calsox	Uses an organic liquid /lime double alkali scheme to produce a CaSO ₃ / CaSO ₄ cake.
Catalytic oxidation processes	
36. Monsanto Cat-Ox	Involves catalytic oxidation of SO ₂ to SO ₃ and wet absorption to produce 78% sulfuric acid.

Enhanced Absorption of SO₂ by Supported Liquid Phase

<p>37. Kiyoura T.I.T</p> <p>Wet and dry adsorption processes</p>	<p>Involves catalytic oxidation of SO₂ to SO₃ and reaction with NH₃ to form ammonium sulfate.</p>
<p>38. Lurgi Sulfacid (wet process) (Germany)</p>	<p>Uses fixed bed of carbon to adsorb SO₂ and produces 70% sulfuric acid.</p>
<p>39. Hitachi carbon (wet process)</p>	<p>Uses fixed bed of carbon to adsorb SO₂ and produces dilute sulfuric acid (10-15%).</p>
<p>40. AIST (wet process) (Japan)</p>	<p>Uses carbon to adsorb SO₂ and produces dilute sulfuric acid (10-20%).</p>
<p>41. Reinluft (dry process) (Germany)</p>	<p>Uses moving bed of carbon (char) to adsorb SO₂ and produces SO₂ rich stream for further processing.</p>
<p>42. Westvaco (dry process)</p>	<p>Uses fluidized bed of carbon to adsorb SO₂ and produces elemental sulfur.</p>
<p>43. Sumitomo-Kansai (dry process)</p>	<p>Uses carbon to adsorb SO₂, and it Produces SO₂ rich stream for further processing.</p>
<p>44. Foster-Wheeler- Bergbau Forschung (dry process)</p>	<p>Uses char (carbon to adsorb SO₂ and produces SO₂ rich stream for further processing in FW Resox Process-to produce elemental Sulfur.</p>

Enhanced Absorption of SO₂ by Supported Liquid Phase

45. Shell flue gas desulfurization (dry process)	Uses fixed bed of copper oxide to Adsorb SO ₂ Regeneration produces an SO ₂ rich stream for further processing.
46. B&W Esso (dry process)	Uses special material to adsorb SO ₂ from flue gas.
Miscellaneous new processes (under development / Developed)	
47. A. J. Telle	Involves chromatographic approach to adsorb SO ₂ and produces SO ₂ rich stream for further processing.
48. J. Sieth & Siemens	Uses ferrous oxide to adsorb SO ₂ .
49. USBM Mitsubishi	Uses Red Mud absorbent in process similar to USBM alkalized alumina process.
50. USBM phosphate rock	Uses phosphate rock to absorb SO ₂ .
51. USBM MnO ₂	Involves absorption of SO ₂ by MnO ₂ in dry gas phase. Hope to produce elemental sulfur.
52. Kennecott MnO ₂ nodules	Uses naturally occurring MnO ₂ nodules to absorb SO ₂ , and produces SO ₂ rich stream.
53. Chevron Research	Is a catalytic reduction process to reduce SO ₂ , to sulfur.

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54. Princeton Research	Is a catalytic reduction process, which reduces SO ₂ , directly to sulfur.
55. Amine absorption (A. D. Little)	Uses high-temperature amine absorption of SO ₂ , from flue gas.
56. Allied Chemical	Removes SO ₂ from iron-ore roaster gases. May be applied to flue gas.
57. United Int'l. Research	Uses catalytic oxidation to convert SO ₂ into weak sulfuric acid.
58. Esso fuel-oil desulfurization	Injects fuel in bed of lime where sulfur reacts to form calcium sulfide.
59. NAPCA coal	Uses injection of coal into molten bed of iron where sulfur forms slag that rises to surface.
60. B&W wet MgO ₂	Uses wet magnesium oxide to absorb SO ₂ from flue gas.
61. USBM catalytic reduction	Uses injection of coal into molten metals, which causes SO ₂ to, be converted into sulfur.
62. Catalytic-IFP (ammonia) (France)	Uses NH ₃ to capture SO ₂ and uses Liquid phase Claus reaction to convert SO ₂ into sulfur.

Enhanced Absorption of SO₂ by Supported Liquid Phase

63. Union Carbide Purva Siv-S	Uses molecular sieves to adsorb SO ₂ from flue gas.
64. Mitsubishi manganese oxyhydride	Uses manganese oxyhydride to absorb SO ₂ , from flue gas.
65. USBM- Bumines citrate	Uses solution of citrate with H ₂ S to reduce SO ₂ to sulfur.

GAS SEPARATION PRINCIPLES:

1. Absorption with reaction (10):

Chemical absorption of gaseous pollutants in a suitable medium is one of the most promising routes for waste gas treatment because of the selectivity in the absorption allowed, and because of the possible regeneration of both the absorption medium and the absorbed species.

The recovery or removal of a variety of solutes, through reactions, from diverse gaseous mixtures, continues to occupy an important role in industry. Reactions are sometimes deliberately imposed to realize higher rates of absorption provide much higher capacity per unit volume of the absorbent and allow higher extent of separations to the desired solute. In order that bulk separations are economically attractive, the reactions ought to be reversible with temperature variations between absorption and desorption often not greater than 100-120 °C. In many cases, the removal of a number of solutes, at low levels, to vanishing levels, below even 1 ppm, is realized through reactions only and in such cases, the reactions could well be irreversible. The manipulation of chemistry, thermodynamics, kinetics and hydrodynamics often permits selectivity with respect to the desired solute, in the presence of other solutes.

The range of gas-liquid contactors is so broad that contact time can be varied from a microsecond to a few seconds. Further, in continuous absorbers, with essentially plug flow, co current versus counter-current mode of contacting can bring about considerable changes in selectivity when simultaneous absorption of two or more solutes is encountered. The theory of gas absorption with reaction, involving single or multiple solutes, one or more dissolved reactants, irreversible or reversible reactions, complex reactions, simultaneous absorption desorption, etc. has been developed sufficiently well. It is often feasible to utilize data from carefully planned laboratory experiments to approach the design of large plants,

without recourse to pilot plant work; modern computational methods allow a more rigorous design procedure to be adopted. In most cases in practice, alternative separation processes can be considered. However, absorption with reaction continues to have a niche in several areas.

Role of Fine Particles:

An analysis of different situations encountered in the wet scrubbing process, especially when the reactant particles are smaller than the diffusional scales of the diffusant (sulfur dioxide) in the liquid phase, brings out the role of fine sorbent particles in a very effective manner.

A necessary condition for the intensification in the specific rate of absorption of SO₂ (species A) to occur is the depletion of the dissolved reactant (OH⁻ or CO₃²⁻, species B) near the gas-liquid interface. This allows for a driving force for the release (dissolution) of B from the micro particles to be established. The situation for which this dissolution will prove to be of maximum benefit is the case of instantaneous reaction between A and B, since here depletion of B is maximum and very close to the interface the concentration of B is zero, thus leading to the highest possible driving force for dissolution.

The simple model proposed by Ramachandran and Sharma under some reasonable assumptions, gives the following equation for the prediction of the specific rate of absorption:

$$R_A = (B_s/Z) [DB K_{sL} a_p]^{1/2}$$

$$\text{Provided, } (B_s/Z) [DB K_{sL} a_p]^{1/2} / K_L > 5.$$

Thus for small size articles, say, less than 5 μ m, the specific rate becomes inversely proportional to the particle size. This finding is of great practical relevance and more so, with slaked lime as on hydration of calcium oxide it is possible to manipulate conditions, which do not require extra energy, to give very small particle sizes of calcium hydroxide approaching sub-micron dimensions.

Role of Additives

In some of the processes, such as the Saarberg - Holter process of Lodge-Cottrell, formic acid is added to the liquid phase, greatly increasing the solubility of the calcium by a factor as high as 800 and thereby enhancing the specific rate of absorption of SO₂. The formic acid maintains the pH of the solution between 4.2 and 5.2 causing the calcium formate to react with the dissolved SO₂ in the spray droplets to form calcium bisulfite rather than calcium sulfite. This bisulfite is then oxidized to calcium sulfate by sparged air (into the liquid sump) aided by a propeller mixer. The advantages of using formic acid thus include elimination of calcium sulfite deposits on the sides of the scrubber tower and because of the enhanced solubility of liquid to gas ratio may be reduced.

Role of Fine Bubbles

In some plants, which are specifically designed to make sulfites for pulp plants, where three phase-sparged reactors are used, we may encounter problems associated with fine bubbles whose characteristic dimension is less than the diffusion film thickness of gas-liquid and solid-liquid films. The existence of fine bubbles can make a marked difference to the specific rate of absorption of sulfur dioxide.

2. Adsorption (15):

Adsorption is to be carefully distinguished from absorption. The later term implies that a substance is uniformly distributed throughout the body of a solid. McBain suggested the use of the term sorption to describe the process in which both absorption and adsorption takes place simultaneously.

Adsorption not necessarily a surface phenomena always. It may as well be a chemical process involving a chemical interaction between the surface atoms and the atoms of adsorbate. This type of adsorption is known as Chemisorption.

Because of adsorption, there is decrease in residual forces along the surface of the adsorbent. Consequently, there is decrease of surface energy, which appears as heat. Adsorption, therefore, is invariably accompanied by decrease in enthalpy of the system, i.e., ΔH of the process is invariably negative. Further, since the adsorbate changes from the more gaseous state to less random adsorbed state on the surface of the solid, adsorption is also accompanied by decrease in entropy of the system, i.e., $T \Delta S$ of the process is also negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a spontaneous process, the free energy change given by the expression

$$\Delta G = \Delta H - T\Delta S.$$

Should be negative. Since ΔH and ΔS are both negative, it is evident that ΔH should have a sufficiently high negative value so that the net result of the expression on the right hand side of the equation is negative.

Factors influencing adsorption:

The magnitude of gaseous adsorption depends upon the following factors:

- Temperature
- Pressure
- Nature of gas and
- Nature of the adsorbent

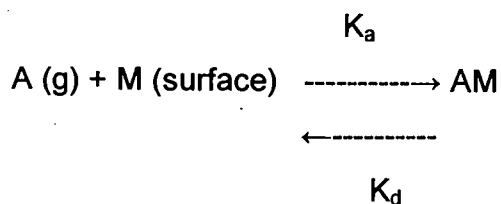
Effect of Temperature and Pressure: since adsorption is invariably accompanied by evolution of heat, therefore in accordance with Le Chatelier's principle, the magnitude of adsorption should increase with fall in temperature. This actually happens. Further, since adsorption of a gas leads to decrease of pressure, the magnitude of adsorption increases with increase in pressure. Thus, decrease of temperature and increase of pressure both tend to increase in the magnitude of adsorption of gas on a solid.

Nature of gas and adsorbent: it has been that the more readily soluble and easily liquefiable gases such ammonia, hydrochloric acid, chlorine and sulphur dioxide are adsorbed more than the so called permanent gases such hydrogen, nitrogen and oxygen. The reason is that Vander Waals or inter molecular forces which are involved in adsorption are, more predominant in former category than in the later category of gases.

The Langmuir theory of adsorption:

In 1916, Langmuir proposed his theory of adsorption of gas on the surface of solid. He considered the surface of the solid to be made up of elementary sites each of which could adsorb one gas molecule. It is assumed that all adsorption sites are equivalent and the ability of the gas molecule to get adsorbed to any site is independent of whether or not the neighboring sites are occupied. It is further assumed that a dynamic equilibrium exists between the adsorbed molecules and free molecules.

If A is the gas molecule and M is the surface site, then



Where K_a and K_d are rate constants for adsorption and desorption, respectively. The rate of adsorption is proportional to the pressure of A, P_a and the number of vacant sites on the surface $N(1-\theta)$ where N is the total number of sites, and θ is the fraction of surface occupied by the gas molecules, i.e.,

$$\Theta = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}}$$

Thus, rate of adsorption = $K_a P_a N (1-\theta)$, the rate of desorption is proportional to the number of adsorbed molecules, $N\theta$.

Thus, rate of desorption = $K_d N\theta$

FLUE GAS DESULFURIZATION TECHNOLOGIES

There are well over one hundred different flue gas desulphurization processes available in various degrees of development, ranging from the laboratory scale to full-scale commercial units. Those processes that have been developed to commercial scale are all capable of removing 90% of the sulphur dioxide from the flue gases.

Sulfur dioxide removal processes can be classified into four categories:

1. Absorption by non-regenerable and regenerable solutions.
2. Adsorption on solid bed.
3. Direct conversion to sulfur.
4. Direct conversion to sulfuric acid.

NON-REGENERABLE PROCESS (13)

Once-through Processes:

The first FGD units installed in the world, at Battersea and Bankside, were once-through processes, which made use of the natural alkalinity of the River Thames. The river water was passed through the FGD plant and then, after suitable processing, discharged back to the river. The only other process in this category is one, which uses seawater as the scrubbing liquid. However, for a modern large power station, the natural alkalinity of the cooling water would not be sufficient and addition of extra lime or limestones or more seawater would be required. The dispersion of effluents from the seawater process in estuaries or the sea, and the effects of the effluents on marine life, has not been fully elucidated. Further works developed new processes eliminated these processes, which is potentially the cheapest.

Lime/Limestone Processes

In these processes, the alkaline absorbent liquor is recirculated in a closed loop. The sulphated reaction products are separated off and fresh absorbent is added. The only water usage is to cover losses by evaporation and that entrained with the product. A purge is sometimes required to control impurity levels. A quencher is used to cool the flue gases to avoid concentration changes in the absorber due to evaporation.

The vast majority of scrubbing systems installed use limestone as the alkali to neutralize sulphur dioxide. The resulting reaction product, a calcium sulphite/sulphate mixture, is then disposed of in ponds or disused mines. This mixture is very difficult to de-water and forms a thixotropic solid commonly known as 'sludge'. Fixation methods, including mixing with fly ash, cement, lime, soil etc. are often used to stabilize the sludge. The costs of disposal add significantly to the overall cost of the process. Such a process is considered unacceptable for use.

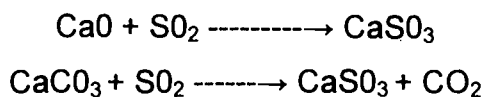
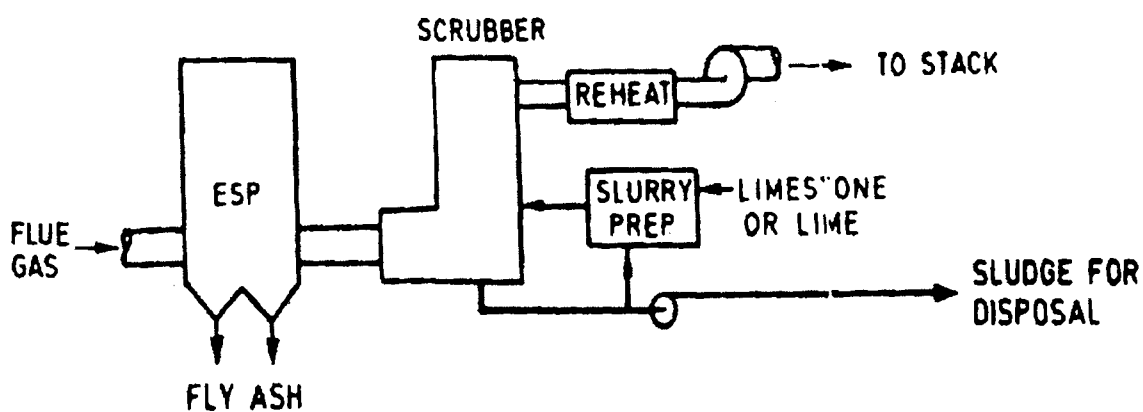


Fig 07: Lime/Limestone Processes

Gypsum Processes

Since the disposal of sulphite/sulphate sludges is difficult, there has been an incentive to produce a more amenable product. Gypsum (CaSO₄.2H₂O) is such a material as it can be sold for the manufacture of plasterboard, bag plaster or 'as a cement setting retardant. Gypsum can also be used for landfill if suitable disposal sites are available. The lime/limestone process can be made to produce gypsum by the addition of an oxidation step in which calcium sulphite is oxidized to gypsum by air injection. Oxidation is usually carried out at a lower H than that used for absorption. Intentional oxidation can also be carried out in the scrubber loop.

Some of the processes produce gypsum of marketable quality and only these are considered for use. These processes are the most common in use worldwide except in the US and even there some plant is being converted to produce gypsum.

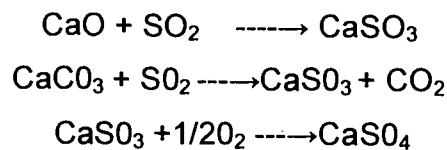
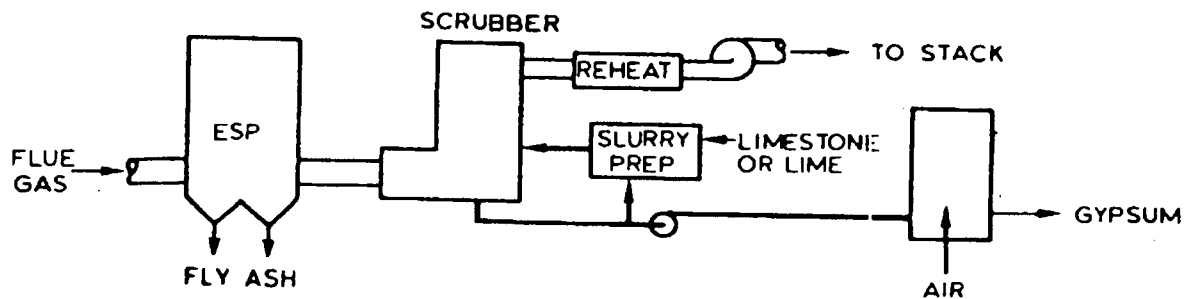


Fig 08: Gypsum Processes

REGENERABLE PROCESSES (13):

In these systems, the absorbent is chemically or thermally regenerated for re-use and a saleable product (liquefied SO₂ sulphur or sulphuric acid) is generated. Ideally, there should be no disposal problems but all the processes produce some by-products, which means that there is, still a need for absorbent make-up and for by-product disposal.

The most widely used regenerable flue gas desulphurization system is the Wellman-Lord process.

As a matter of fact, various regenerative processes for SO₂ removal from waste gases have been developed: the media used for the absorption can be polyether, as in Solinox–Linde process, amines (Hofmann and Wanderwerf, 1946; Balej & Regner, 1956), ketones, glycol ethers (Heartel, 1985; Sciamanna & Lynn, 1988), esters, urea (Suszka, 1989; van Dam, Lamine, Roizard, Lochon, & Roizard, 1997; van Dam, Corriou, Midoux, Lamine, & Roizard, 1999) or heterocyclic compounds (Adams, Kruus, & Patrabooy, 1983; Suszka, 1989).

Apart from some amines, the regenerative absorption relies upon the reversible formation of a complex between sulfur dioxide and the solvent molecule at low/ambient temperature, which can decompose at higher temperatures: this decomposition allows the regeneration of the two species.

Wellman-Lord Process

The Wellman-Lord system employs absorption of sulphur dioxide in a concentrated solution of sodium sulphite and regeneration of the resultant bisulphate rich solution by steam stripping in an evaporator crystallizer. The process produces a pure concentrated sulphur dioxide gas stream, which can be converted to sulphur or sulphuric acid. Considerable quantities of impure sodium sulphate are produced, a by-product which must be disposed of.

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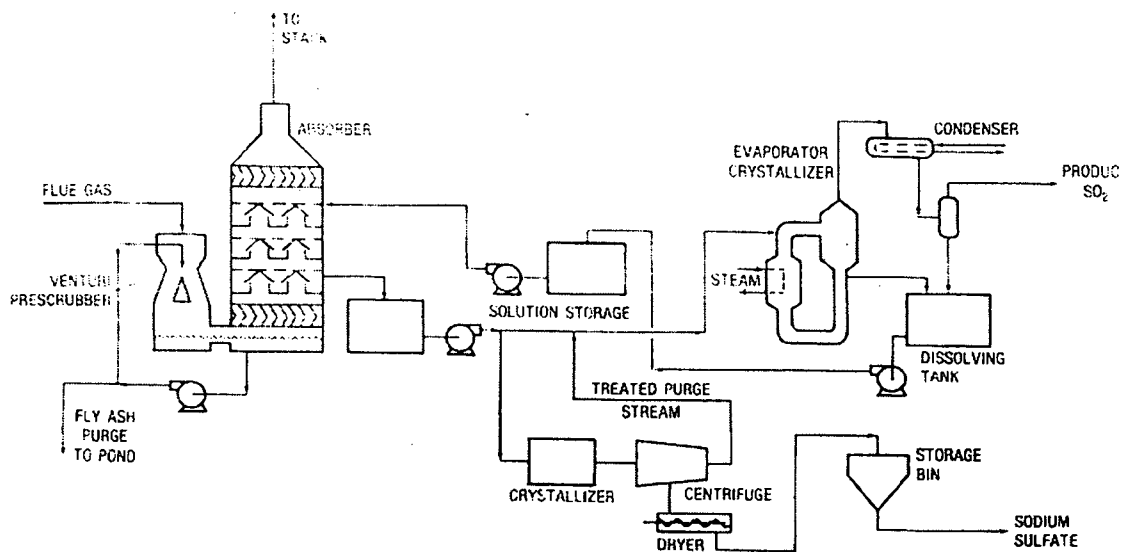


Fig 09: Wellman-Lord Process

Magnesium Oxide Process

In this process, aqueous slurry of magnesium hydroxide is used to absorb sulphur dioxide. The resulting magnesium sulphite is then calcined to release sulphur dioxide and to regenerate the absorbent. The sulphur dioxide produced is available for conversion to either sulphuric acid or sulphur.

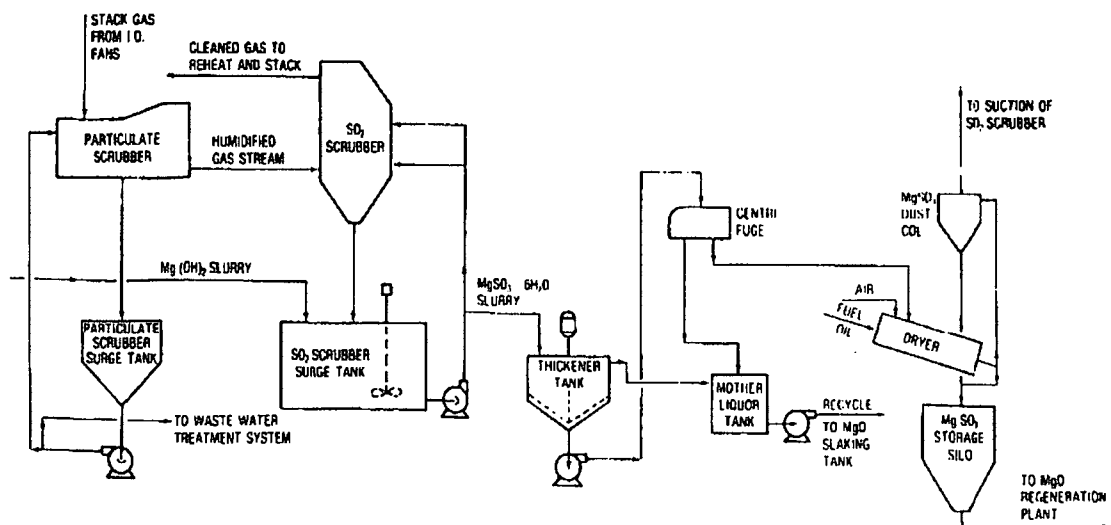


Fig 10: Magnesium Oxide Process

Spray Drying Processes:

During the past few years, the use of spray driers for the absorption of sulphur dioxide has attracted increasing attention. The spray drier in effect replaces the absorber in a wet system, but is situated upstream of the dust collector. The sulphur dioxide absorbent can be lime, sodium carbonate or bicarbonate. A mixture of fully reacted and unreacted absorbent is produced which is collected in an electrostatic precipitator or bag filter together with fly ash. By adding an extra small dust collector up stream of the spray drier the fly ash and spray dry Product can be essentially collected separately.

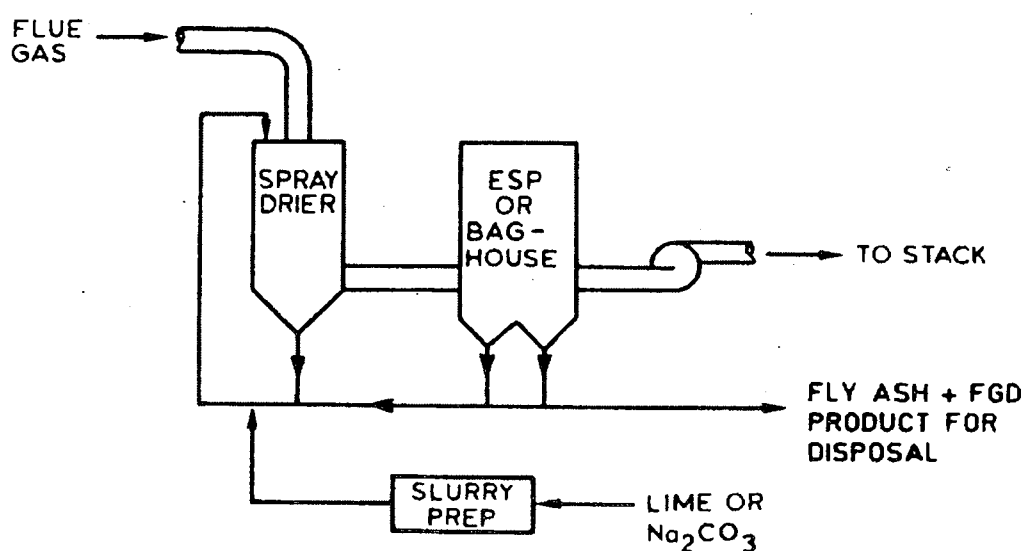
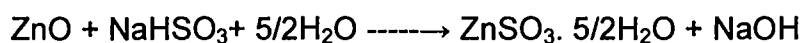


Fig 11: Spray Drying Process

Zinc Oxide Process

H.F. Johnstone and A.D. Singh at the Engineering Experimental Station of the University of Illinois as a portion of a research project sponsored by the Commonwealth Edison Company and several other utility companies developed the zinc oxide process. The process has not been used commercially; however, a considerable amount of pilot-plant work has been done on it, and features of the process design have been worked out in considerable detail. The process is

illustrated in figure below. The flue gases are contacted with a solution of sodium sulfite and bisulfite, and sulfur dioxide is absorbed, thus causing an increase in bisulfite content. The solution is next passed into a clarifier, in which particulate matter removed from the gas stream is separated, and finally into a mixer in which it is treated with zinc oxide. At this point, the original ratio of sulfite to bisulfite is restored, and zinc sulfite is precipitated in accordance with the following reactions:



After agitation to promote crystal growth, the precipitate is removed by settling and filtration, and the filter cake is dried and calcined. Calcining of the zinc sulfite results in a gas containing 70% water and 30% sulfur dioxide, which may be cooled, dried, and compressed to produce a nearly pure liquid sulfur dioxide as the final product. Zinc oxide obtained in the calciner is recycled to the process. As in most processes for recovery of sulfur dioxide from flue gas, oxidation of sulfur dioxide to sulfate introduces a complication. In this case, the sulfate is removed as calcium sulfate which is formed by treatment with lime.

Lime is added to a clarified side stream of the solution; this results in the precipitation of insoluble calcium sulfite to form slurry which is added to the main solution-stream leaving the gas washer. The resulting thin slurry is passed into a clarifier. The calcium sulfite and any fly ash which may have been picked up are then removed as slurry. This slurry is acidified by contacting it with a portion of the product sulfur dioxide. Acidification results in conversion of the calcium sulfite to the more soluble bisulfite form and reaction of the dissolved calcium ions with any sulfate present in the solution to form calcium sulfate, which is relatively insoluble under these conditions. Precipitated calcium sulfate and undissolved ash are removed together in a small filter. The resulting desulfated solution

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containing dissolved calcium bisulfite is then treated with lime to form the slurry, which is recycled to the process.

The zinc oxide process is not being applied commercially since the recent economic evaluations have not shown it to be economically competitive with other processes, however, it should be noted that this process has been developed very thoroughly with regard to chemical-engineering design data. Much of the work may be useful in connection with other systems particularly the studies of tower packing and the use of wet cyclone scrubbers.

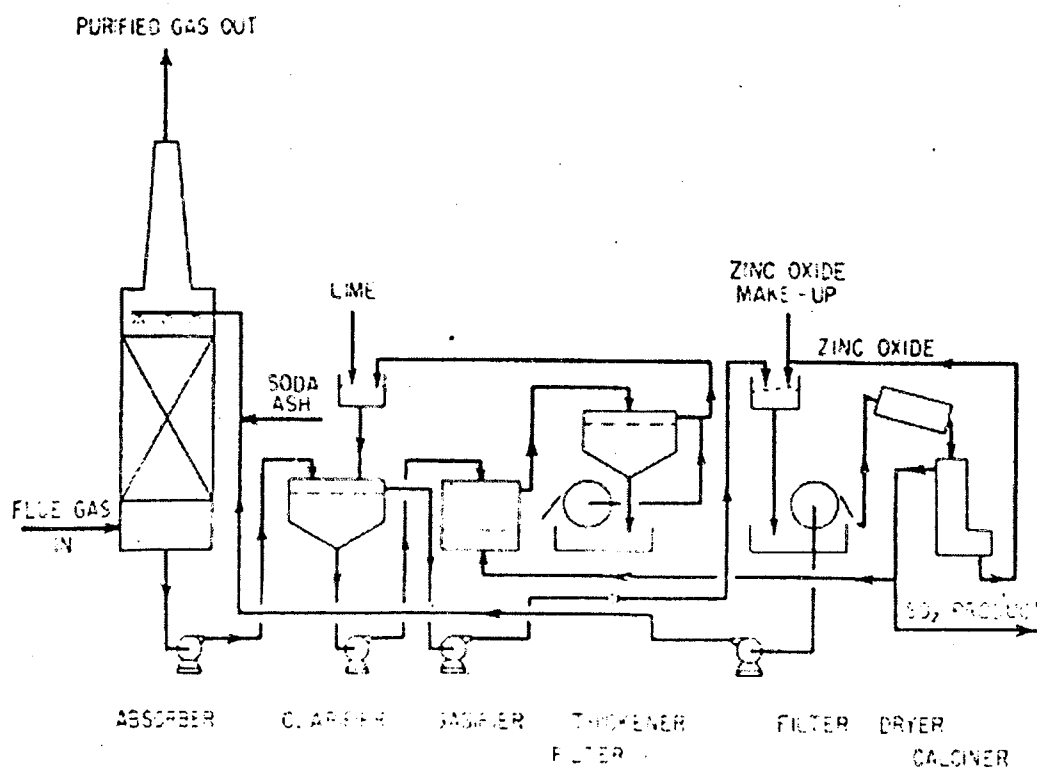


Fig 12: Zinc oxide process

DISADVANTAGES OF EXISTING PROCESSES

One of the drawbacks of limestone scrubbing is the damage to construction materials by corrosion and erosion. Although the scrubber slurry is not highly acidic (pH 5.0 to 5.5), it has the capability of corroding carbon steel and several alloys used in the construction of equipment. Many systems use a pre scrubber before the main scrubber as a method of removing particulate matter and other impurities that are undesirable in gypsum destined for later use.

Wet scrubbing process utilizes large quantity of water producing a wet waste product (sludge), which has high disposal costs. In summary, waste management is a major issue for those flue gas desulphurization technologies which involve wet scrubbing. Water management could be a major issue, depending upon regional and other water demands. In addition, it is applicable for large-scale applications of SO₂ removal.

The spray dry process tends to have a lower capital but higher running cost than wet processes, and hence, becomes more economically attractive for older plant or plant with a low load factor only. It may also be more suitable for smaller plant where the disposal of the product may not be so difficult.

Advanced post combustion cleaning technologies encompass two approaches:

(a) Using the existing flue gas ductwork to inject a sorbent; and (b) inserting one or more separate vessels into the downstream ductwork where pollutant absorbents are added. Using a separate vessel allows a greater residence time for the absorbent to react, but the vessel is larger than the ductwork used with in-duct sorbent injection and is costlier to install. In-duct sorbent injection works inside the ductwork leading from the boiler to the smoke stack, Sulphur absorbers (such as hydrated lime) are sprayed into the centre of the duct. By

controlling the humidity of the flue gas and the spray pattern of the sorbent, 50-70% of the sulphur dioxide can be removed which is very low efficient as compared to other FGD processes.

Selective additives, such as adipic acid, may remove more than 90% of the sulphur dioxide. The reaction produces dry particles that can be collected downstream. Because the plant's existing ductwork is used, extensive new construction is not needed. This makes in-duct sorbent injection an attractive option for retrofitting smaller, older plants where space requirements might be limited. However, the cost of additives is a major concern.

When separate vessels are used, one or more process chambers are inserted in the flue gas ductwork, and various sorbents are injected to remove the pollutants. Generally, the separate vessels provide a longer residence time for the absorbent to react with the gas, and pollutant capture is greater. Although more costly than in-duct injection, this approach has the potential of capturing more than 90% of the pollutants. Owing to the cost and added size requirements, the use of separate vessels tends to be more suitable to new plant applications or to plants that can accommodate the additional size requirements. Technologies such as the spray dryer and selective catalytic reduction represent approaches that use separate vessels.

7. SUPPORTED LIQUID PHASE CATALYSIS

HOMOGENEOUS & HETEROGENOUS CATALYTIC METHODS:

Catalytic methods have generally utilized solid phase or liquid phase catalysts, each type being characterized by certain advantages and disadvantages. The solid forms of catalysts when used with gaseous or liquid reactants have good physical strength and may be provided with large surface areas to obtain effective contacting area for the reactants. However, the solid phase catalysts suffer certain disadvantages, such as not containing a high degree of dispersion of active sites. The active sites are in general disposed on the surface of crystallites in such a way that they are often in close proximity. This has the effect of limiting selectivity. For example, sequential reactions leading to side products may occur readily when there is high density of active sites.

The liquid phase catalyst generally employed with gaseous reactants, for example, in a sparged or stirred reactor, overcome some of the selectivity and activity limitation of solid catalyst; but the effective interface area for reaction is relatively small, and the liquid diffusion path are relatively long, so that the efficiency is not always sufficient for industrial reactions. Furthermore, the requirement for the proper agitation or sparging of liquid reaction systems imposes severe limitations upon the gas flow rates and other parameters of the reactor so that considerable equipment is necessary to provide the proper sparging or mixing conditions. It is also found that the use of liquid phase catalysts composed of solution of salts of metals usually results in attrition and plating out of the metals on walls of the reactor system, so that the catalyst is lost and the reactor conversion efficiency decreases.

It is possible to provide the combination of liquid-and-solid phase catalyst in a single unitary, multiphase catalytic entity. The multiphase catalysts are composed of a porous solid support having a liquid phase catalyst present. The liquid phase catalysts may be a single component which is liquid under reaction

conditions(3), and may also be comprised of a liquid solvent containing dissolved or dispersed catalytic components such as metal salts. The liquid phase catalyst is dispersed upon porous supports or substrates.

The multiphase catalyst supplies a supported liquid phase but externally behaves like a solid catalyst, which is free flowing, and can be used in fixed or fluidized bed reactors while at the same time providing the advantages of liquid catalysts, including the selectivity, which is provided by the dispersed catalyst component in melt or solution form. An advantage over the solid catalysts is that the this multiphase catalysts operate at less severe reaction conditions of temperature and pressure, while providing higher gas liquid interfacial areas and considerable reduced liquid diffusion paths in comparisons to typical liquid phase catalytic systems.

The growth of homogenous catalytic process is primarily due to their selectivity and activity performance. These qualities satisfy current needs for processes of high efficiency, which operate under relatively mild conditions with few by-products.

Supported Liquid-Phase Catalysts (SLPC).

In recent years, a number of authors have pointed out the significance of vapor-phase reaction systems catalyzed by a liquid solution contained within the pores of an otherwise inert solid matrix. Such catalysts have been designated as Supported Liquid-Phase Catalysts (SLPC).

SLP consists of a liquid phase catalyst dispersed within a porous support to occupy a part of the pore space. The gaseous reactants diffuse through the residual pore space as well as the dispersed liquid phase and undergo homogenous catalytic reaction in the liquid phase to produce volatile products, which then diffuse back out of the porous support.

In SLPC, the liquid-phase catalyst is coated onto the walls of a porous support as an ultra-thin film, much as in a chromatographic packing with supported liquid and it, thus, effectively combines the attractive features of homogeneous catalysis such as high specificity, mild conditions, and molecular dispersion of catalytic species, with those of heterogeneous catalysis such as large interfacial area, lack of corrosion, use of packed-bed reactors, and facile separation of catalyst from products. The technique is suitable for low temperature gas-phase reactions as well as for liquid-phase reactions in which the catalyst and reactant phases are immiscible.

Hence it is a hybrid system that retains the advantage of homogenous catalysts such as product selectivity, and mild operation conditions and, at the same time, provides the advantages of heterogeneous catalysts such convenient handling, large interfacial areas, and consequently small liquid diffusion paths, ease of separation of catalyst from product, and use of conventional equipment like packed-bed and fluidized-bed reactors. Its major limitation is that the reactants and the products must be in gaseous or vapor form at reaction conditions while the catalyst solution should be essentially nonvolatile. SLPC are simple to prepare and generally reproducible, provided the soluble metal complex is stable under reaction condition. It may be a reliable method for measuring reaction rate constants in liquid phase at high temperature and pressure. Just as liquid chromatography.

Advantages of SLPC:

The use of SLPC eliminates the problems of catalyst attrition, plating of the catalyst on the reactor walls, as well as fouling and corrosion of reactor because there is no free catalyst solution present in direct contact with reactor system walls and components. It also eliminates the problems of separation of catalyst from the product while permitting the existence of long gas-liquid contact times.

In addition, various gas separation techniques employed to separate SO₂ from flue gases such as absorption using solvents like Amine Solutions require

regeneration of solvents and it involves loss of solution by vaporization or condensation. Moreover, this process involves increased cost imparted by pumps and other utilities required, and the cost of amine solutions. This technique will reduce loss of solvent since the solvent is immobilized and the solvent can be used for longer hours without the loss in activity or selectivity. The process would be more economical than the other methods since it requires no pumping

METHODS OF IMMOBILIZING CATALYSTS:

Supported liquid-phase catalysts may be prepared by various impregnation techniques, depending on the nature of the catalytic solution involved. In some cases, the catalytic agent may be solid at ambient conditions but liquefied under reactor operating conditions (3), as in the oxidation of SO₂. In other cases the catalyst remains as a liquid solution throughout, as in the case of hydroformylation of propylene catalyzed by RhCl(CO)- (PPh₃), dissolved in a nonvolatile solvent, butyl benzyl phthalate (Rony, 1969).

Immobilization may be achieved in one of several ways, (a) Chemisorption of a metal complex onto a solid support. (b) Physical absorption of a complex on a support. (c) Entrapment of metal complexes via in situ synthesis with in zeolites. (d) Dissolution of a complex in a nonvolatile solvent which is absorbed onto the surface of a support i.e. SLP (supported liquid phase). The first three of these methods have not provided a commercially viable heterogeneous catalyst.

The draw back of these immobilization methods is that they are not applicable for liquid reactants that are miscible with the film that resides on a high surface area hydrophilic support, such as CPG (controlled pore glass) or silica gel and is composed of water-soluble organometallic complexes and water. Reactions of liquid phase water insoluble organic reactants take place at the film-organic interface. SAP (supported aqueous phase) catalysis differs significantly from SLP catalysis in that SLP is used for gas phase reactants where SAP is specifically

designed for liquid phase reactants. Additionally, with SLP catalysis, the reaction proceeds homogeneously; in SAP catalysis it occurs at the interface. Although aqueous acids or bases supported on solids have been known for decades. SAP catalysis differs significantly in that they contain organometallic complexes as the active sites. The hydrophilic nature of the ligands and the support creates interaction energies sufficient to maintain the immobilization. Thus, the SAP catalysts are designed to efficiently conduct catalytic reactions at interfaces.

SAP catalysis, the catalytic phase, immiscible with organic phase containing the reactants/products, consists of an aqueous solution of a water-soluble organometallic catalyst. To provide for the necessary interfacial area required the reaction to proceed at a reasonable rate; the catalyst phase is immobilized in the pores of a high surface area solid. Since the catalysis proceeds at interface between an organic phase containing the reactant and the product and an aqueous phase containing the catalytic species, SAP catalysis is usable with liquid reactants. SAP catalysis displays good activity for hydroformylation of oleyl alcohol.

MECHANISM OF SLPC (17):

In SLP catalysts, a thin ionic liquid catalyst layer is immobilized on the surface of a highly porous inorganic material by physisorption. The homogeneous catalyst is immobilized in the ionic liquid by ionic ligands or its ionic nature.

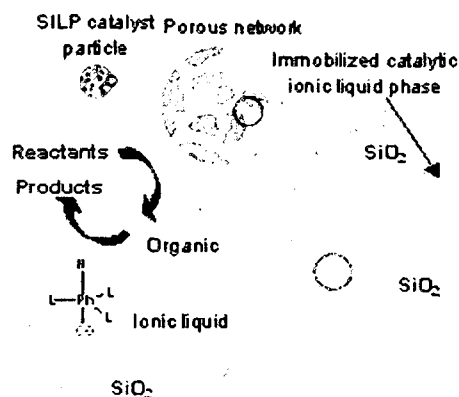
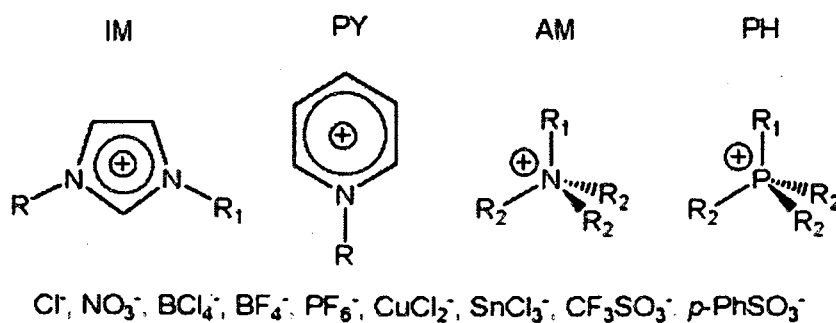


Fig 13: Gas-phase hydroformylation of propene over SiO₂ Support

Ionic liquids (IL's) are per definition molten salts having a melting point < 100 °C. They have no measurable vapor pressure below their decomposition temperature, i.e. they do not evaporate and are easy to maintain. Physical properties and chemical characteristics of IL's can in general be adjusted by suitable choice of anion/cation. For this reason, IL's have been referred to as "designer solvents". Adjustable physical properties include, e.g. thermal stability, temperature window for the liquid range, density, viscosity, solvation strength, solubility and miscibility with other liquids.

The chemical characteristics involves acidity, coordination ability and stability against acids/bases and oxidation. Combined, these properties are of importance when the IL's have to function as solvent in catalytic systems. In the Figure below some of the most important IL anions and cations are shown.



Important cations and anions in ionic liquids

IM: imidazolium, PY: pyridinium, AM ammonium, PH: phosphonium.

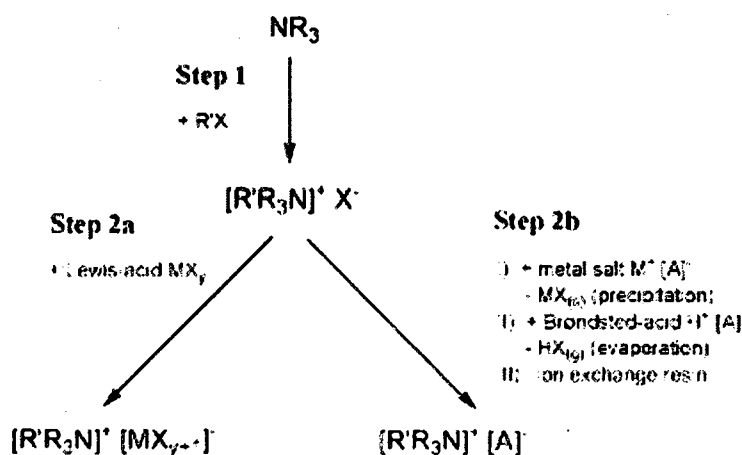
R = methyl.

R1 = methyl, ethyl, butyl.

R2=ethyl, butyl, hexyl, octyl, phenyl.

Preparation of IL's generally follows the same preparation procedure, as illustrated for N-containing IL's in the Figure below. In the first step (step 1) an amine (NR₃) is alkylated with an alkyl halide (R'X) generating an ionic liquid, [R'R₃N] +X⁻, containing the corresponding quarternized amine cation and the anion from the Alkylation agent. The anion in the primary IL can afterwards be

exchanged to other anions by reaction with a Lewis-acid MX_y (e.g. AlCl_3) generating $[\text{R}'\text{R}_3\text{N}]^+ + [\text{MX}_{y+1}]^-$ ionic liquids (Step 2a), or by addition of metal ions generating a metal halide precipitate (e.g. AgCl), addition of a Brønsted-acid and subsequently removal of hydrogen halide (e.g. HCl) or by ion exchange procedures, e.g. using columns (step 2b, I-III), respectively. Salts based on the imidazolium (IM) cation have received special attention in connecting with hydroformylation. This involves in particular salts containing the 1-n-butyl-3-methylimidazolium cation such as the bis (trifluoromethanesulfonyl) amide salt, $[\text{BMIM}][(\text{CF}_3\text{SO}_2)_2\text{N}]$. This salt is relatively easy to prepare in high purity and easy to handle due to high oxygen/water stability and acid/base resistance the $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ anion possesses. In addition, the PF_6^- anion possesses a low coordination ability, which diminishes its interference during catalysis due to its lower tendency for complex formation. Several recent reviews have been published about IL's where details concerning synthesis, properties, characterization and use of IL's in multiphase catalysis are discussed more thoroughly.



General preparation procedure to N-containing ionic liquids

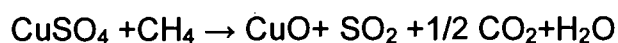
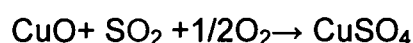
8. RECENT DEVELOPMENTS IN SLP

1. Novel Separation Process of Gaseous Mixture of SO₂ and O₂ with Ionic Liquid for Hydrogen Production in Thermochemical Sulfur-Iodine Water Splitting Cycle (8):

Sulfur-iodine cycle is the most promising thermochemical cycle for water splitting to produce hydrogen, which can replace the fossil fuels in the future. As a sub-cycle in the thermochemical Sulfur-iodine water splitting cycle, sulfuric acid (H₂SO₄) decomposes into oxygen (O₂) and sulfur dioxide (SO₂) which should be separated for the recycle of SO₂ into the sulfuric acid generation reaction (Bunsen Reaction). Conventional gas separation processes are Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA), and solvent absorption. PSA and TSA are energy intensive processes to control the pressure and temperature in a large system. Absorption process is not attractive for the high temperature process because of the volatile property of the solvent. A novel separation process needs to be proposed to compensate the demerits of conventional gas separation methods for the high temperature-gaseous SO₂/O₂ mixture. Ionic Liquid is not volatile even at high temperature, which can improve absorption process utilizing organic solvents by eliminating the issue of volatility of the solvents. In addition, a continuous process can be realized by recycling non-volatile ionic liquid at high temperature. Cost of gas separation process can be reduced by avoiding PSA and TSA and by operating absorption system relatively at high temperature by ionic liquid process compared to the solvent absorption. In this study, absorption process of SO₂ by ionic liquid is investigated. At first, the best ionic liquid for SO₂ absorption is selected by combining anions and cations. With TGA/DTA analysis operating temperature windows of each ionic liquid are determined. After that, absorption and desorption properties of SO₂ by each ionic liquid are examined. Moreover, IR analysis is executed before and after the absorption of SO₂ to verify the absorption mechanism.

2. SO₂ adsorption and thermal regeneration over activated carbon-supported copper oxide catalysts (4):

The mechanisms of SO₂ adsorption and regeneration over activated carbon-supported copper oxide sorbent/catalysts were carried out to curtail the large amounts of potential hazardous waste. Based on thermodynamics, the selection of regenerable sorbent/catalysts has often pointed towards copper oxides, because the sulfation reaction becomes highly favored if copper is kept in the usual states of oxidation (Cu⁺ or Cu²⁺). The reactions are as follows,



Studies were carried out in a fixed-bed reactor equipped with a non-dispersive infrared gas analyzer to detect the reaction products, by using X-ray powder diffraction (XRPD), and temperature-programmed desorption (TPD) experiments to characterize the nature of the sulfate species and surface oxygen complexes. The results indicate that SO₂ was catalytically oxidized to SO₃ over a copper phase in the presence of gaseous oxygen, and then reacted with a copper site to form a sulfate linked to copper without desorption into the gas phase. The activated carbon support did not participate in this sulfation reaction. After the adsorption of SO₂, the exhausted sorbent/catalysts could be regenerated by direct heat treatment in inert gas at temperatures between 260 and 480°C, while the neighboring surface oxygen complexes on the carbon surface were acting as the reducing agents to reduce CuSO₄ to Cu. During the subsequent adsorption process, the copper is rapidly oxidized by oxygen in the flue gas.

9. SLP EXPERIMENTAL STUDY

The whole study consists of various steps from loading to regeneration, which are as given below:

1. Degasification of solid support
2. Estimation of Pore volume of the solid support
3. First Loading: Loading of HB on the solid support
4. Second Loading: Loading of Solvent on solid support after first loading
5. Absorption
6. Regeneration

PREPARATION OF SUPPORT:

This chapter discuss preparation of support in the desired organic absorbent (AM), for absorption of SO₂, was loaded onto the support by dissolving solvent (HB). For uniform loading on support, the above solution was diluted in a low boiling (LB) Volatile solvent, which is then evaporated off.

Affinity of high boiling (HB) towards SO₂

High boiling solvents are those, which generally have high boiling ranges. A suitable high boiling will be the one, which does not absorb SO₂ and holds the absorbing solvent firmly on to the support and prevents thermal sintering of supports at operating conditions (5).

Rough estimation of pore volume using H₂O

Knowledge of pore volume is very important as for as loading is concerned. More the pore volume more will be the surface for molecules to immobilize.

Known weight say (w₁) gm of support SP was taken and boiled in distilled H₂O for one hour and then filtered by using ordinary filter paper, excess adhering water was removed by filtration and rest of the wet SP was weighed.

Wt of SP before boiling = w₁ gm

Wt of SP after boiling = w₂ gm

Increase in weight = (w₂-w₁) gm

Therefore, rough pore volume of SP is (w₂-w₁)/w₁ cc per gm of SP.

Solubility of Solvent

Both high boiling solvent (HB) and low boiling solvent (LB) were so taken that solvent (AM) was soluble in both of them. This helps in uniform distribution of solvent over the support when loaded.

Components of loading are

- Support
- High boiling solvent
- Absorbent
- Low boiling solvent

High boiling solvent (HB): These are the solvents, which have high boiling point ranges and remain stable at high temperatures. These are used here so that they could firmly attach to the outer surface of support. In addition, remain stable at high temperatures. Basic requirement is to form a layer (monomolecular will be preferred one). The formation of uniform layer will serve two purposes viz. proper bonding with absorbent, which will lead to proper immobilization of absorbent onto the support. Second purpose will be to deactivate the support, which will ensure that all the reactions are occurring on absorbent but not on support or HB (no affinity for SO₂). High boiling liquid includes high boiling substituted or non-substituted aromatic hydrocarbons.

Absorbent: The solvent, which is going to react with (absorbate) SO₂, is the absorbent. This forms a monomolecular layer (maybe multi-layer, as the exact model is not known) on HB. The absorbed gas (SO₂) may be pure or mixture with other gases viz. SO₂-N₂.

Low boiling solvents (LB): These are volatile solvents having low boiling range. LB was used to impregnate desired amount of absorbent (desired loading).

Calculations of loading experiments:

Let,

- X - wt. of HB-1, gm
- Y - wt. of Am-1, gm
- M1 - mol.wt. of HB-1, gm/mol
- M2 - mol.wt. of Am-1gm/mol
- ρ1 - density of HB-1, g/cc
- ρ2 - density of Am-1, g/cc
- V - Total pore volume, cc

$$(X/\rho_1) + (Y/\rho_2) = 0.25(V) \dots\dots\dots (1)$$

Where 0.25 is for 25% loading.

For Equi. Molar condition,

$$X/M1 = Y/M2 \dots\dots\dots (2)$$

$$X = (M1/M2) * Y \dots\dots\dots (3)$$

Substitute (3) in (1)

$$((M1/M2) * Y) * \rho_1 + (Y/\rho_2) = 0.25 * (V) \dots\dots\dots (4)$$

The values of M1, M2, V, ρ1, ρ2 are known

So that we can calculate Y, Hence X also.

DEGASIFICATION:

About 35 gm of fresh Support - SP, taken in a beaker was boiled in distilled water for one hour and then filtered to remove any excess water. Wet SP collected on filter paper was transferred to a bowl and kept in oven at 250⁰C for 1 ½ hour for the purpose of degasification. The obtained SP was kept in desiccator for cooling.

First Loading:

30 gm of degasified SP was taken and its total pore volume was calculated. The required amount of low boiling solvent (LB) as per the loading conditions was taken and its volume was made upto the total pore volume of the degasified SP taken, with LB whichever dissolves the HB completely. The made-up solution was homogenized well, added to the degasified SP, and mixed well until it was homogenized. It was kept in the open space to remove the high volatile liquid, and it was dried over the mantle at low temperatures if necessary.

Second Loading:

In the case of AM's having two active groups, one is highly basic and other is weakly basic. The high basic AM group is deactivated with the acid by which it forms a salt – an intermediate product. The intermediate salt formed helps the other Am group in absorbing the SO₂.

The required amount of solvent AM was taken and the acid was added, as required, to it in drops for the purpose discussed above to prepare the half salt. The prepared half salt was made upto the remaining pore volume of loaded SP with any of the highly volatile liquid which dissolves the salt completely. It was mixed well, added to the SP, and homogenized. Then it was kept for drying to remove the volatile liquids and any moisture content due to water added for rinsing.

Care was taken during drying such that we were not losing any weight. Some moisture content was retained to maintain the stoichiometric ratio.

Apparatus/Reagents used for adsorption-desorption experiments:

Column: The column used for experiments is a double-jacketed column in which the temperature was maintained by oil bath.

Specifications of column:

Material = glass

Enhanced Absorption of SO₂ by Supported Liquid Phase

Type = Double – jacketed

Inner-diameter = 0.5 “

Outer-diameter = 1.1 “

Height = 27 ½ “

Effective height (30 gm of activated carbon) = 25 “

Flow meter: Flow rate of gases either SO₂ or N₂ was checked by soap bubble in 25 or 100 ml burette. Gas was passed from the bottom of the column, which takes bubble of soap with it and time of ascending of bubble calculated that gives the flow rate in sec/ml, inverse of this gives cc/sec.

Manometer: 3

Manometer is simple equipment used to measure the p by h method

$$P = h \rho g$$

EXPERIMENTAL PROCEDURE:

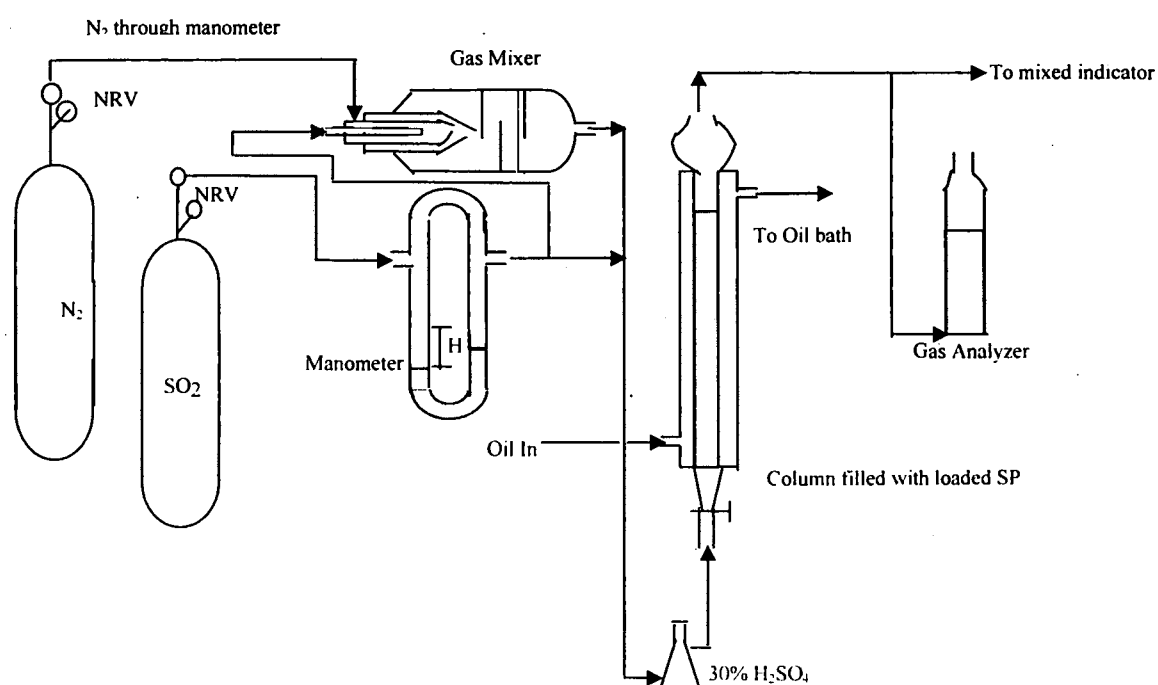


Fig 14: Experimental Set up

Adsorption and desorption of SO₂ on Loaded Carbon

ADSORPTION:

Loaded SP was packed into the column randomly. Flow rate of SO₂ was set at the desired value by a simple flow meter assembly and maintained. Then SO₂ stream connected at the bottom of column. At the outlet, an indicator for gas analysis was connected with off gas. The Indicator has greenish color and as SO₂ starts coming out it frequently changes to dirty yellow. When SO₂ is adsorbed onto the column the indicator changes color and gas stream is disconnected after checking the flow rate once again. The total time of adsorption was noted down and the flow rates were checked at the end of experiment. The room temperature was noted down and the pressure drop through the set-up was noted.

DESORPTION BY N₂ STRIPPING:

Temperature of oil bath was raised to 120⁰C, and N₂ flow rate was set and passed from the top of the column, simultaneously oil bath was connected to the outer jacket of the column. The rate of regeneration was calculated by taking the samples at fixed intervals. The completion of regeneration was checked with appropriate indicator.

N₂ flow rate was checked and stopped. During desorption off gas was collected in H₂O₂ and then titrated against NaOH.

10. CALCULATION OF GAS ADSORBED AND DESORBED

Gas adsorbed:

$$\text{Volume of gas passed, } V_1 = \text{flowrate} \times \text{time} \quad (1)$$

By gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (2)$$

Where P_1 , V_1 and T_1 are pressure, volume, and temperature at standard conditions i.e. at 760 mm of Hg, and 25 °C and P_2 , V_2 , and T_2 are pressure, volume and temperature at N.T.P.

$$\text{Volume at NTP, } V_2 = \frac{P_1 (760) \times V_1 \times T_2 (273)}{P_2 (760) \times T_1 (273 + RT)} \quad (3)$$

$$\text{Gas sorbed, gm} = \frac{64 \times V_2}{22400}$$

Gas desorbed can be calculated in the following manner:

$$\text{Gas desorbed, gm} = \frac{\text{Normality (NaOH)} \times \text{titer value} \times 32}{1000} \quad (4)$$

Percentage of recovered gas:

$$\% \text{ recovery} = \frac{G_{\text{desorbed}}}{G_{\text{sorbed}}} \times 100 \quad (5)$$

12. RESULTS & DISCUSSIONS

Cumulative accumulation of SO₂ on column

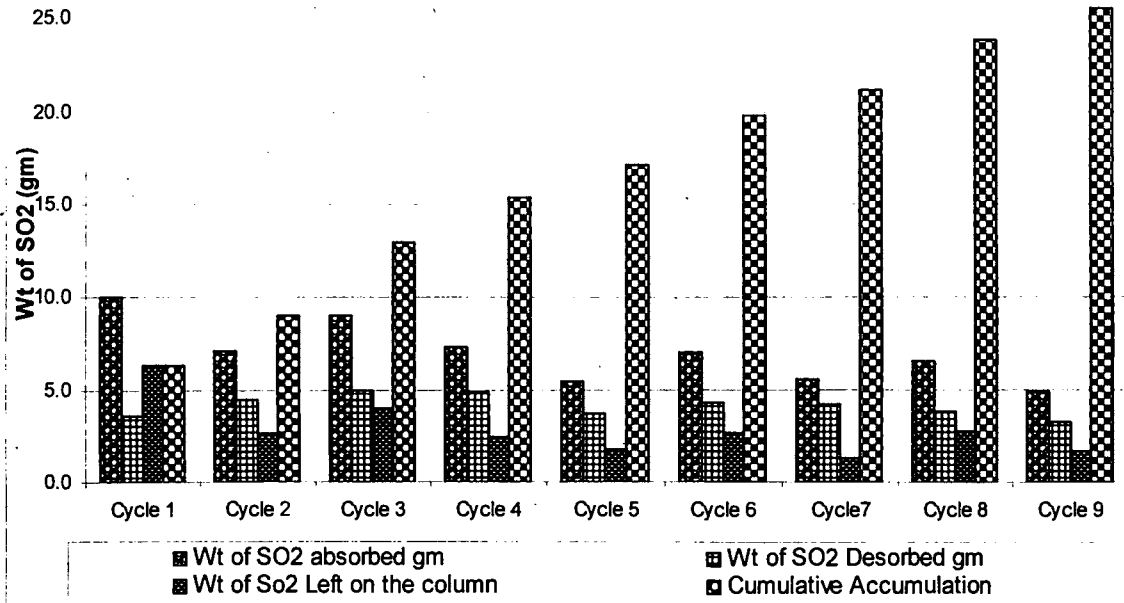


Fig15: 50% loading of AM-1

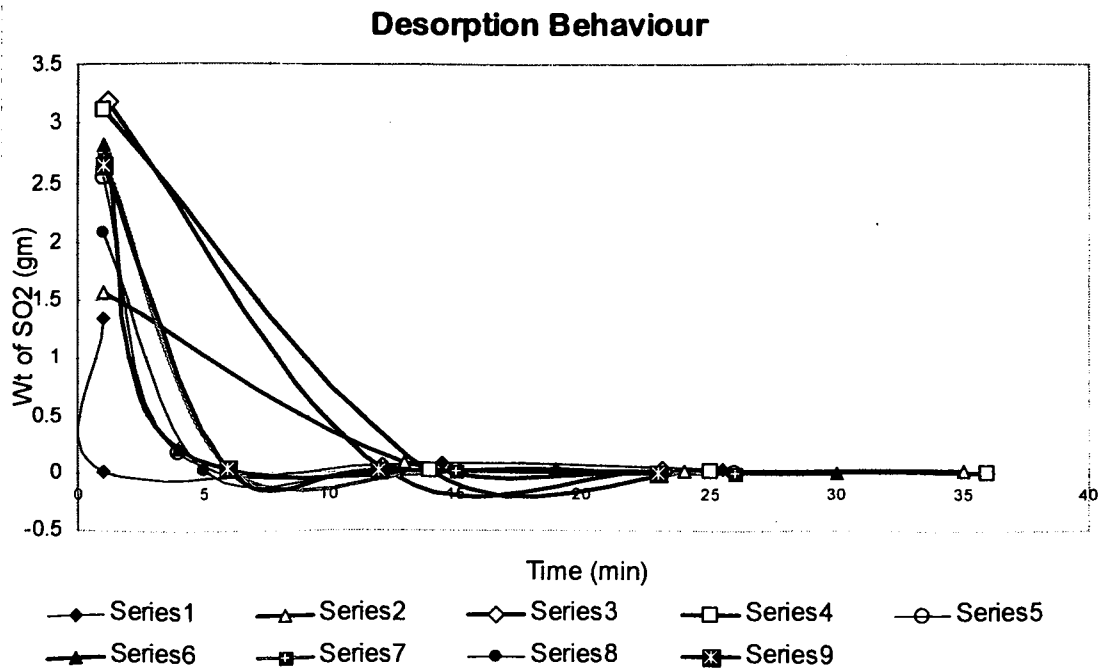


Fig 16: 50% loading of AM-1

The Fig 15 shows that the amount of SO₂ absorbed per cycle steadily decreases in each subsequent cycle of the experiment. In addition, irrespective of the extent of adsorption amount of SO₂ regenerated remained practically the same. The amount of SO₂ absorbed in the first cycle of a particular day was the highest and decreased in the subsequent cycles.

This was ascribed to the probable slow desorption of SO₂ from the support overnight, and the time left between the cycles were not enough for the bed to get cooled which, also decreases the amount of SO₂ absorbed.

Fig 16 reveals that most of the SO₂ was desorbed in first few minutes itself. Regeneration was carried out at two different flow rates of N₂. The results showed that when we doubled the N₂ stripping flow rate desorption rate was increased thus, reducing the time of desorption. However, the amount of SO₂ desorbed is same. This observation was found consistent in subsequent experimental studies too.

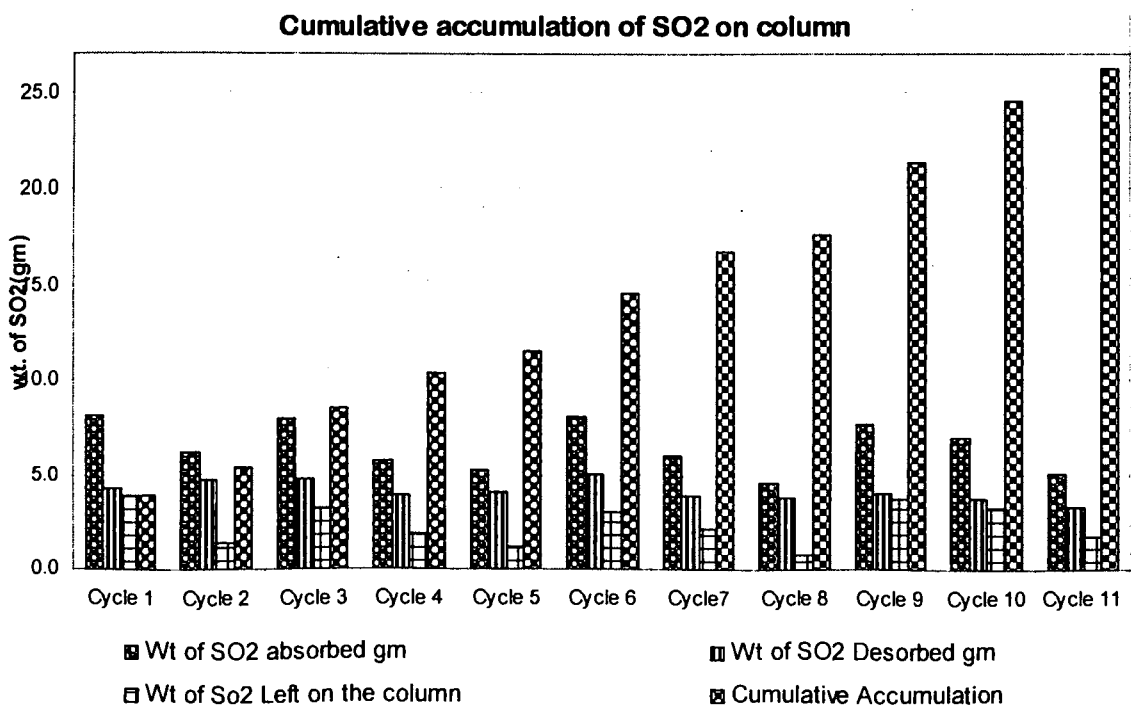


Fig 17: 50% Loading Of AM-2

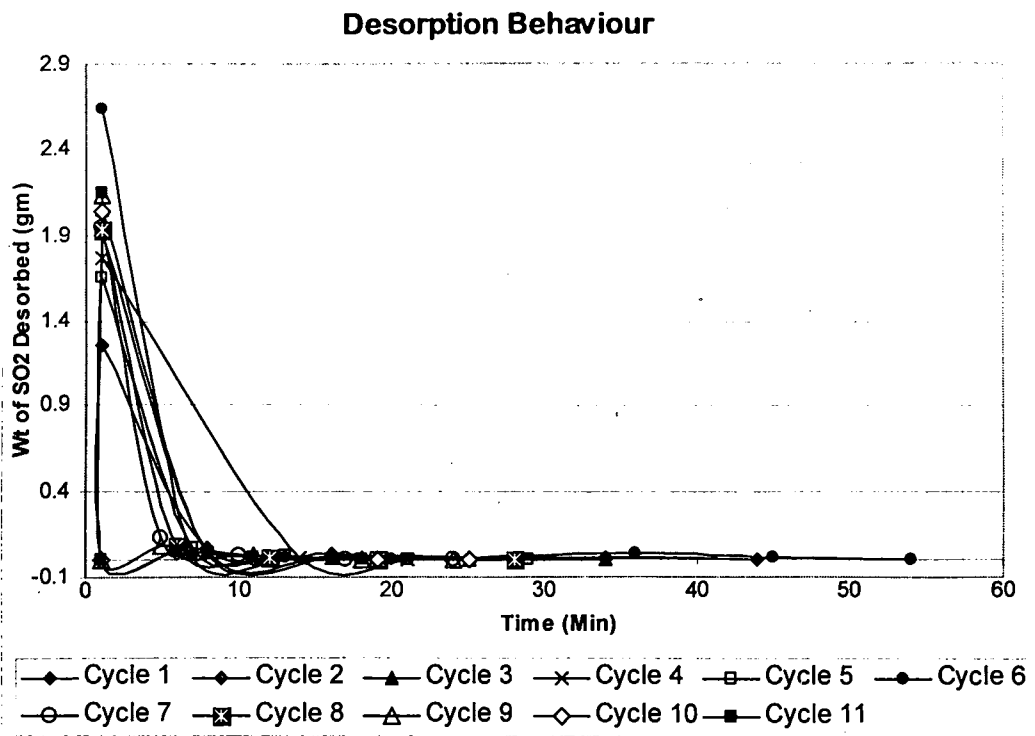


Fig 18: 50% Loading Of AM-2

Fig 17 shows that, the results were similar as noted in the case of 50% loading of AM-1, however there were slight variations in the amount of SO₂ absorbed/desorbed. This condition showed better absorption in the later cycles of the experiment than AM-1, (which has given notable depletion in the absorption amount.).

Fig 17 shows the average regeneration was around 4.0 gm of SO₂/cycle as compared to 3.6 gm SO₂/Cycle for AM-1 from fig15.

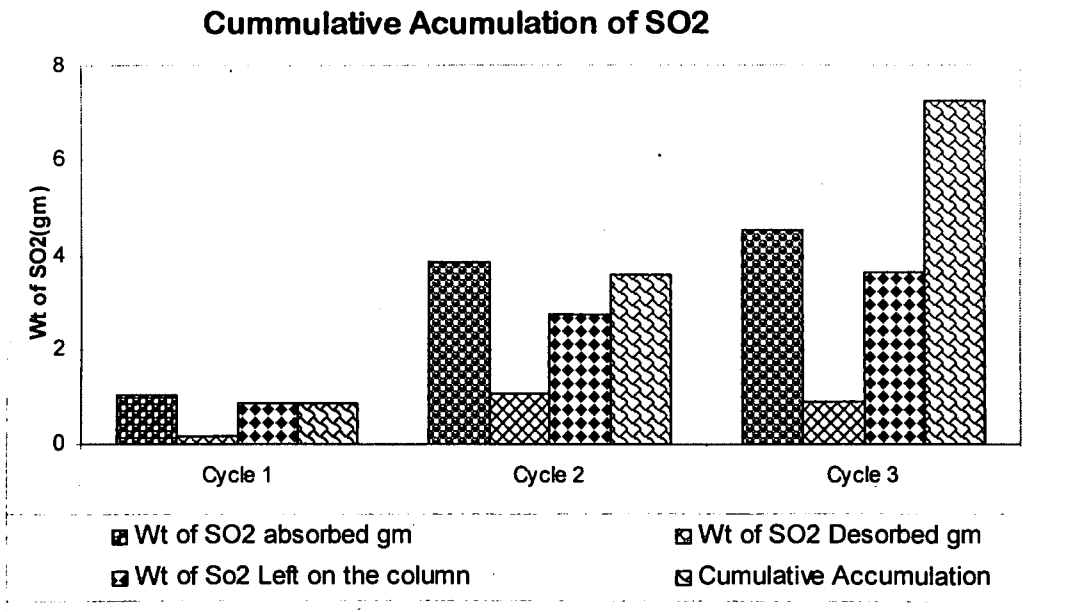


Fig 19: 70% Loading of AM-2

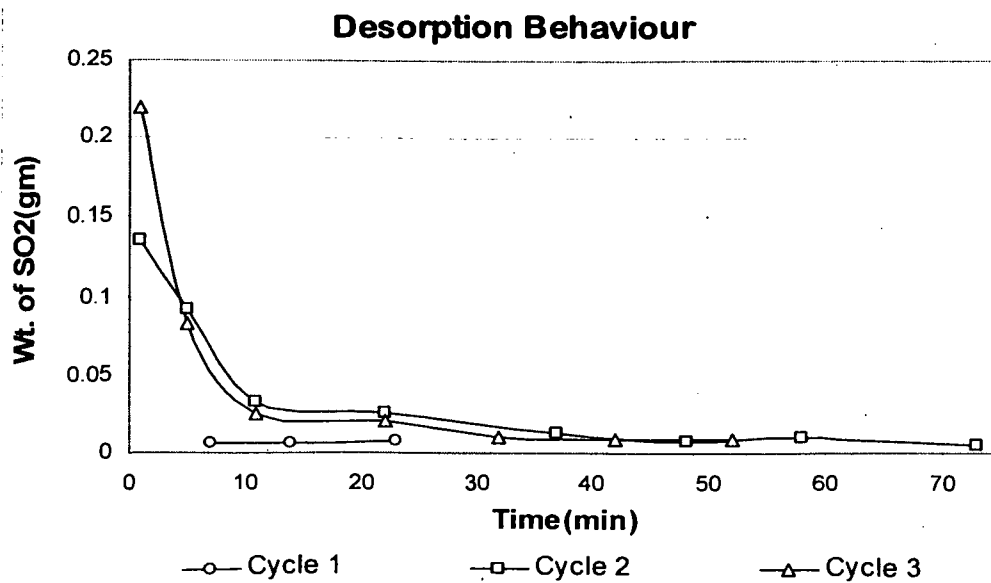


Fig 20: 70% Loading of AM-2

From fig 19 & 20, SO₂ absorption / desorption performance for 70% loading was not satisfactory since it has shown negligible amounts of absorption and desorption.

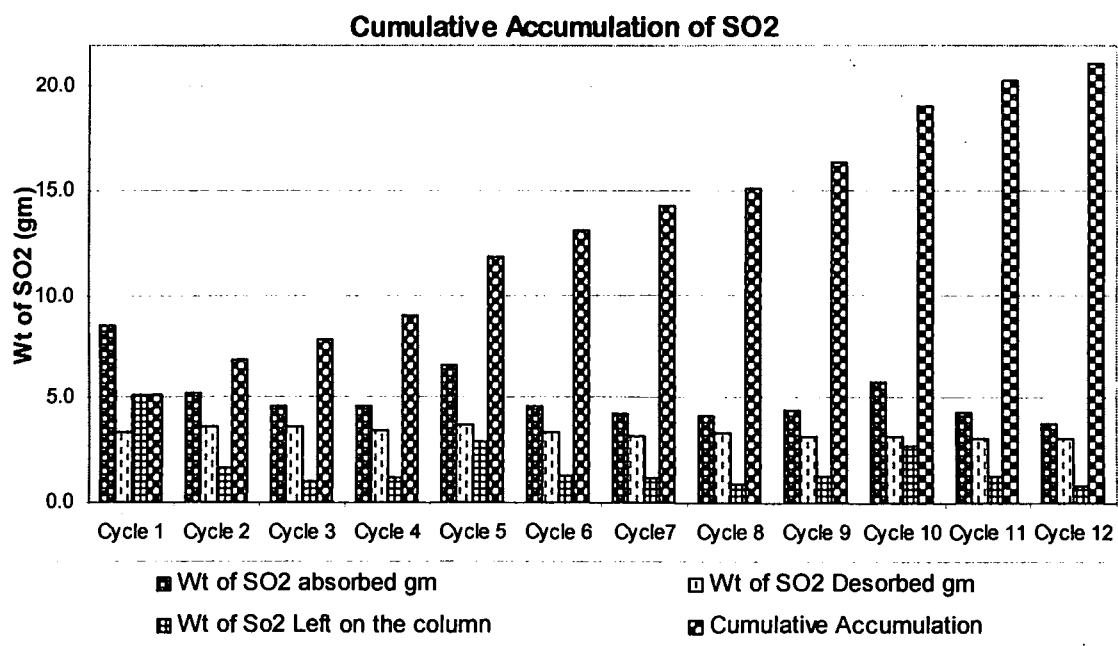


Fig 21: 25% Loading of AM-2

From fig 21, it is clear that this support had shown better consistency for SO₂ absorption. However, the net amounts were comparatively less than the 50% loaded support.

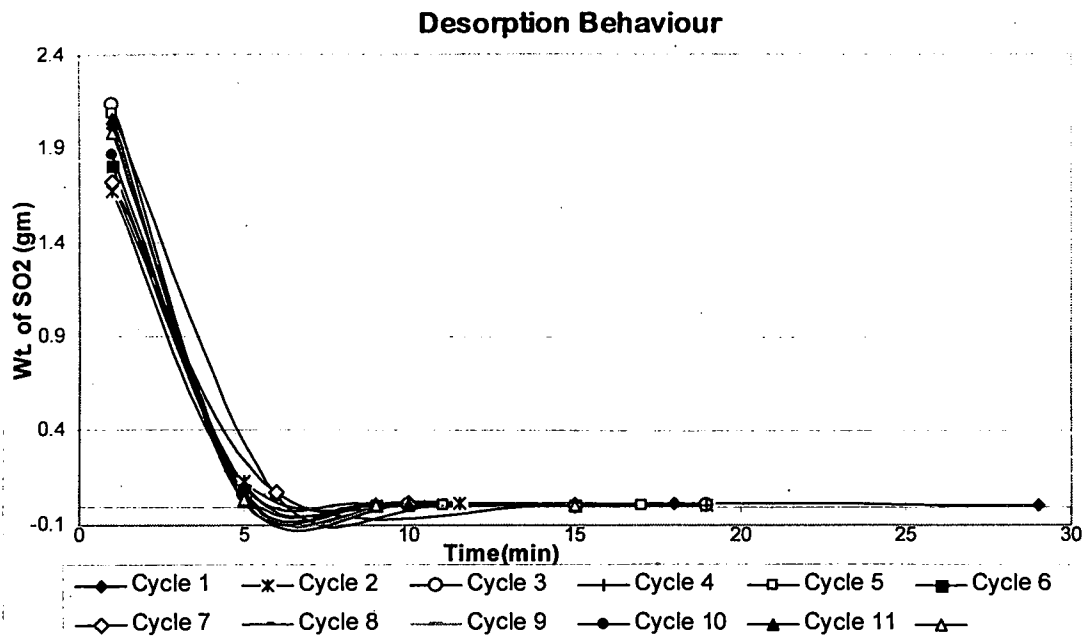


Fig 22: 25% Loading of AM-2

Fig 22 shows that the regeneration rate in case of 25% loading was similar as compared to previous experimental condition of 50% loaded support and had shown better consistency for SO₂ desorbed. However, the net amounts were comparatively less than the 50% loaded support. However, it had shown lower regeneration amounts than 50% loaded support.

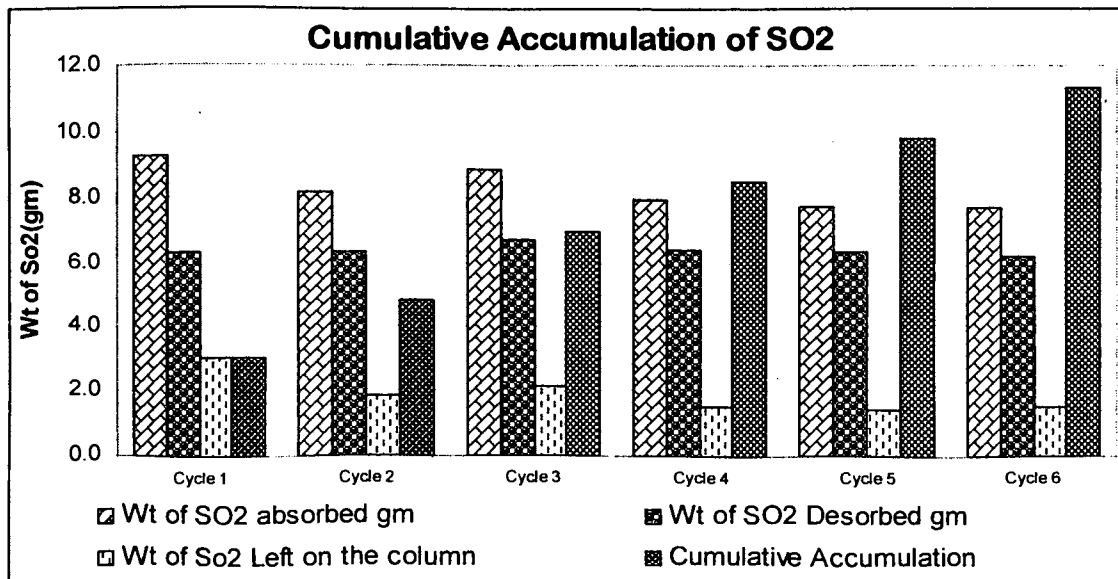


Fig 23: 0% loading of solvent

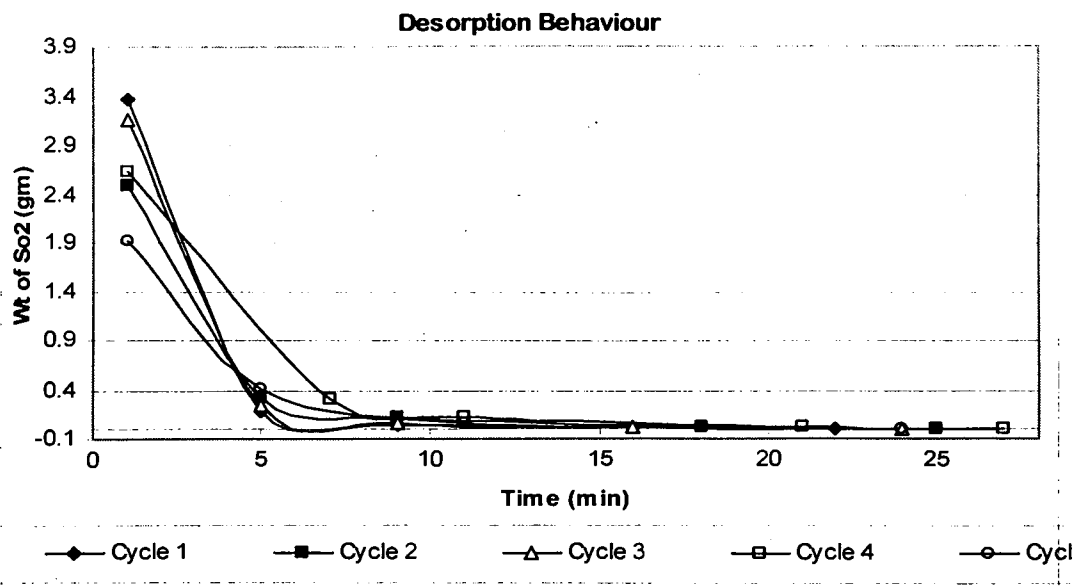


Fig 24: 0% loading of solvent

The amounts of SO₂ absorbed and desorbed were the highest in case of unloaded SP. This is explained due to the availability of larger interfacial surface area, due to which the gas molecules were diffused without any liquid film resistance.

From the above figures, it is clear that the amount of SO₂ left on the column is accumulated which should be trapped in the support. However, it was found that it was not accumulated in the bed after the experiments. The reason for which is not yet explained until some further studies are done. The effect of loading was noted clear from the results. It seems that there exists an optimum loading between 25% and 50% loading and needs to be further confirmed by experiments.

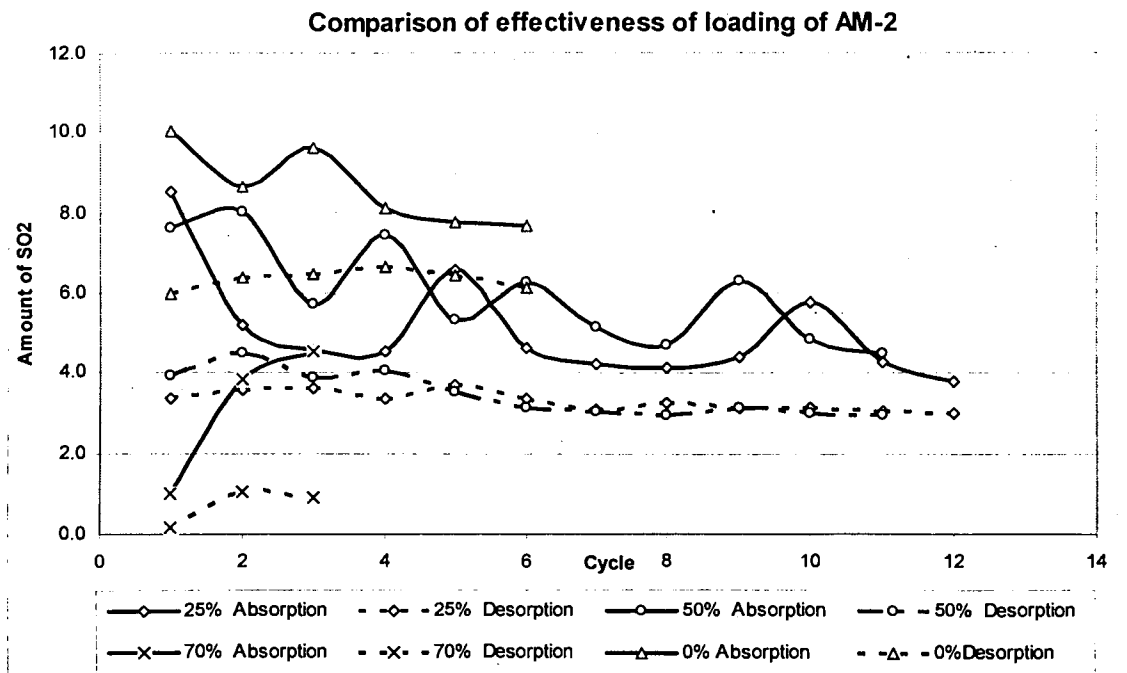


Fig 25: Comparison of Effectiveness of Loading

Fig 25 compares the effect extent of loading collectively on SP support. As discussed earlier, this graphical representation points to some optimum loading of the solvents between 25% and 50%.

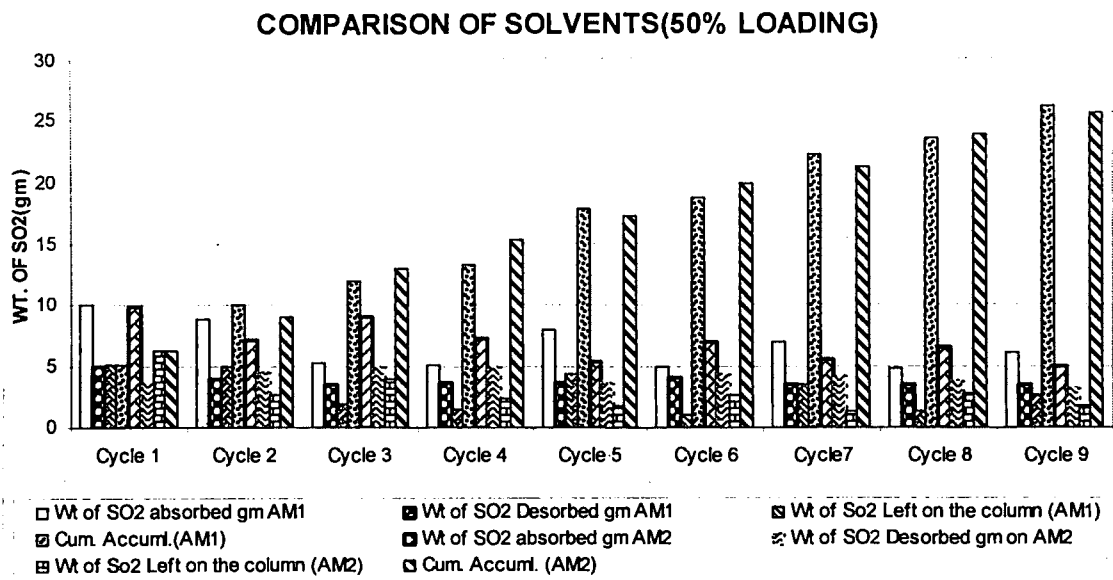


Fig 26: Comparison of Effect of Solvent

The two solvents used are compared in Fig 26 for their performance in adsorption and regeneration studies based on the 9 cycle data. As a general observation, it is found that AM2 works slightly better than AM1 in its adsorption performance. Whereas it gives definitely better results when regeneration is carried out. AM2 gives repeatable and reproducible regeneration.

12. CONCLUSION

The experimental study of separation of SO₂ (from gaseous mixture) was carried out on Supported Liquid Phase. The experiments were carried out with different extent of loading the solid support with two different solvents, and regeneration was done with N₂ stripping under different conditions of temperatures and with vacuum stripping.

The observations discussed above show that the amount of SO₂ absorbed/desorbed is affected by the extent of loading on the support. It appears that there exists some optimum loading between 25% and 50% loading of solvents. The regeneration of SO₂ remained practically the same, irrespective of the extent of adsorption amount. The various rates of nitrogen stripping produced the different rates of desorption.

The experiments of SO₂ absorption over the supported liquid phase were carried out under day-to-day prevailing temperatures ranging (15-33) °C. The effect of temperature on the absorption was not considered in this work. Moreover, the experiments are to be carried out with gaseous mixture to find the real behaviour of the supported liquid phase.

In addition, the observation by gravimetric methods revealed no accumulation of SO₂ over the support, after the experiments and requires to be traced.

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