Acid deposition phenomena

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Abstract

Acid deposition, commonly known as acid rain, occurs when emissions from the combustion of fossil fuels and other industrial processes undergo complex chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). Rain and snow are already naturally acidic, but are only considered problematic when less than a pH of 5.0

The main chemical precursors leading to acidic conditions are atmospheric concentrations of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). When these two compounds react with water, oxygen, and sunlight in the atmosphere, the result is sulfuric (H_2SO_4) and nitric acids (HNO_3), the primary agents of acid deposition which mainly produced from the combustion of fossil fuel and from petroleum refinery.

Airborne chemicals can travel long distances from their sources and can therefore affect ecosystems over broad regional scales and in locations far from the sources of emissions.

According to the concern of petroleum ministry with the environment and occupational health, in this paper we will discussed the acid deposition phenomena through the following.

- Types of acidic deposition and its components in the atmosphere
- Natural and man-made sources of compounds causing the acidic deposition.
- Chemical reactions causing the acidic deposition phenomenon in the atmosphere.
- Factors affecting level of acidic deposition in the atmosphere.
- Impact of acid deposition.
- Procedures for acidic deposition control in petroleum industry.

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Introduction

Acid rain is a serious environmental problem that affects large parts of the world Scientists discovered and have confirmed that sulfur dioxide and nitrogen oxides are the primary causes of acid rain.

Acid rain occurs when these gases react in the atmosphere with water, oxygen and other chemicals to form various acidic compounds sunlight increases the rate of most of these reactions the result is a mild solution of sulfuric acid and nitric acid This paper provide information about types of acid deposition, what causes acid deposition, effects of acid deposition, sources of acid deposition and what is being done to solve this problem.

1- Types of acid deposition and its components in the atmosphere

Acid rain is a broad term used to describe several ways that acids fall out of the atmosphere a more precise term is acid deposition which has two parts wet and dry

- **Wet deposition**

  Wet deposition refers to acidic rain ,fog and snow as this acidic water flows over and through the ground it affects a variety of plants and animals the strength of the effects depend on many factors, including how acidity of water, the chemistry and buffering capacity of the soils involved and the types of fish, trees, and other living things that rely on the water.

- **Dry deposition**

  Dry deposition refers to acidic gases and particles about half of the acidity in the atmosphere falls back to earth through dry deposition the wind blows these acidic particles and gases onto building, cars, homes, and trees dry deposition gases and particles can also be washed from trees and other surfaces by rain storms.

When that happens in the runoff water adds those acids to the acid rain making the combination more acidic than the falling rain alone.

Natural rain water is already slightly acidic because carbon dioxide dissolved into the rain water and produce carbonic acid. The two principal acids in acid rain are sulfuric acid and nitric acid their sources are sulfur dioxide and nitrogen oxides.Other emissions that affect acidity are free chlorine, ammonia, volatile organic compounds and alkaline dust.

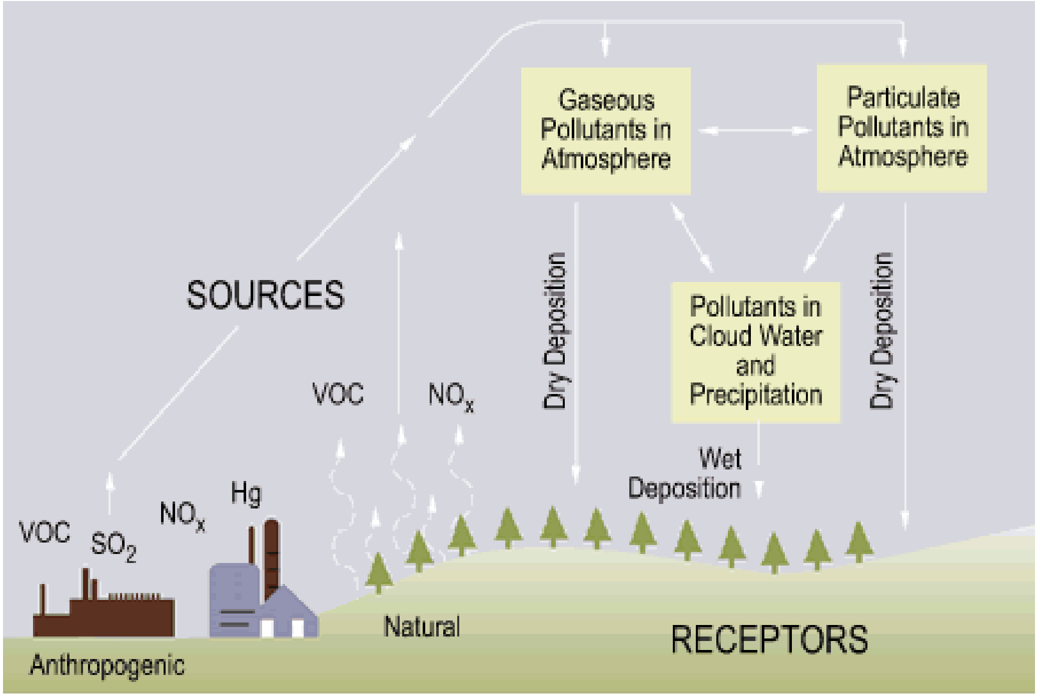

Gaseous Pollutants in Atmosphere
Particulate Pollutants in Atmosphere
SOURCES
Dry Deposition
Pollutants in Cloud Water and Precipitation
Dry Deposition
VOC
NO_x
Wet Deposition
VOC
SO_2
NO_x
Hg
Natural
RECEPTORS
Anthropogenic

Fig 1

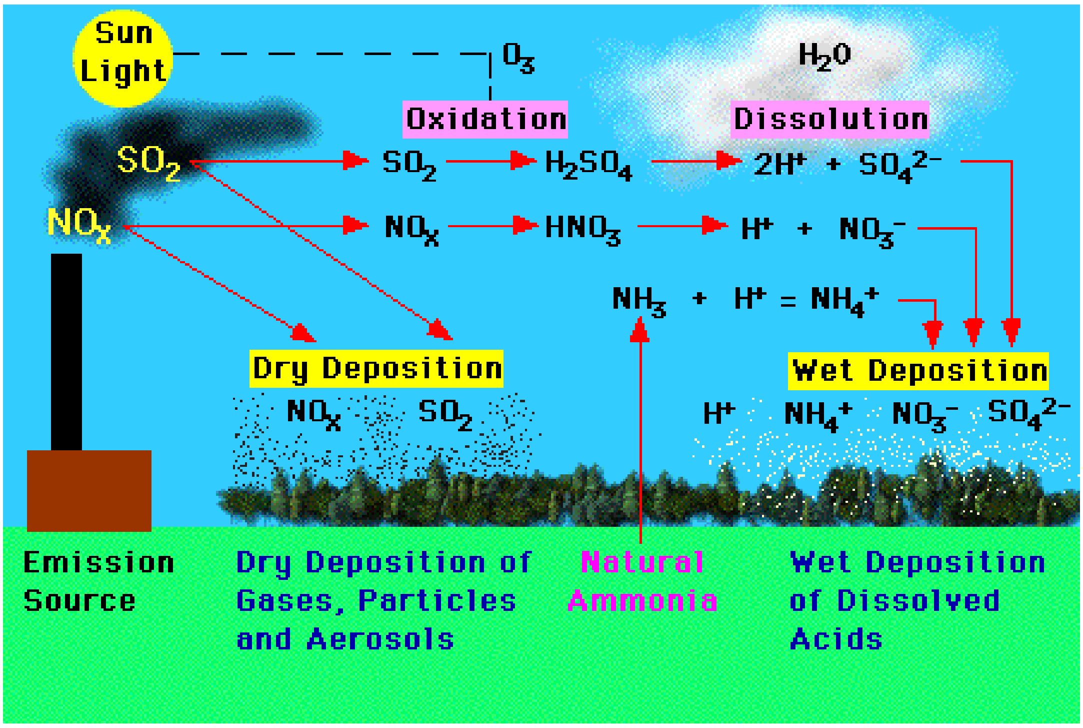

Sun Light
O_3
H_2O
Oxidation
Dissolution
SO_2
SO_2
H_2SO_4
$2H^+ + SO_4^{2-}$
NO_x
NO_x
HNO_3
$H^+ + NO_3^-$
$NH_3 + H^+ = NH_4^+$
Dry Deposition
Wet Deposition
NO_x SO_2
H^+ NH_4^+ NO_3^- SO_4^{2-}
Emission Source
Dry Deposition of Gases, Particles and Aerosols
Natural Ammonia
Wet Deposition of Dissolved Acids

Fig 2

2- Natural and man made sources of compounds causing the acidic deposition.

Acid deposition can form as a result of the oxidation of nitrogen oxides (NOx) or sulphur dioxide (SO2) gases that are released into the atmosphere the process of altering these gases into their acid counterparts can take several days, and during this time these pollutants can be transferred hundreds of kilometers from their original source. Acid precipitation formation can also take place at the Earth's surface when nitrogen oxides and sulphur dioxide settle on the landscape and interact with dew or frost.

Emission of sulfur dioxide

Emission of sulfur dioxide are responsible for 60-70 % of the acid deposition that occurs globally. More than 90 % of the sulphur in the atmosphere is of human origin as shown below.

- Coal burning - coal typically contains 2-3 % sulphur so when it is burned sulphur dioxide is liberated.
- The smelting of metal sulfide ores to obtain the pure metals. Metals such as zinc, nickel, and copper are all commonly obtained in this manner.
- 69.4 % of sulfur dioxide is produced by industrial combustion.
- 3.7 % of sulfur dioxide is produced by transportation

The 10% remain is from anthropogenic sources as shown below

- Volcanic eruptions - although this is not a widespread problem, a volcanic eruption can add a lot of sulphur to the atmosphere in a regional area.
- Organic decay.
- Sea spray
- Plankton
- Rotting vegetation

Emission of Some nitrogen oxides

Emission of some nitrogen oxides in the atmosphere come from human activities and anthropogenic sources. 95 % of the elevated levels of nitrogen oxides in the atmosphere are the result of human activities as shown below.

- Firing process of extreme high temperature (automobiles, utility plants)
- Chemical industries (Fertilizer production)

The remaining 5 % comes from several natural processes. The major sources of nitrogen oxides include:

- Bacterial action in soil.
- Forest fires.
- Volcanic action
- Lightning

3- Chemical reactions causing the acidic deposition phenomenon in the atmosphere

The acidity of acid deposition dose not only depending on level of emission but also depending on the chemical reaction both sulfur dioxide and nitrogen oxides are released and rise to the upper atmosphere to react with oxygen and water in the presence of sunlight to form acids through many steps which broken into two phases (gas phase – liquid phase)

Chemical reactions of oxidation of sulfur dioxide to form sulfuric acid

- Oxidation by ozone this process is more fastly than photo-oxidation by 108-109 times and dose not need to catalyst

- Oxidation by photo-oxidation process which use UV light from electromagnetic spectrum then react with moisture to form sulfuric acid.

But in aqueous phase sulfur dioxide will oxidizing by oxygen molecules but need metal catalyst as iron and manganese this oxidation unlike others because it use hydrogen peroxide as oxidation agent and this reaction will produce intermediate product peroxy-mono-sulfuroeus acid

- **Chemicals reaction in gas phase for SO_2**

Sulfur in coal burns in oxygen to form sulfur dioxide

$$S\ (\text{from coal})_{(g)} + O_{2\ (g)} \longrightarrow SO_{2\ (g)}$$

Sulfur dioxide reacts with oxygen in atmosphere to form sulfur trioxide

$$2SO_{2\ (g)} + O_{2\ (g)} \longrightarrow SO_{3\ (g)}$$

Sun light and hydroxide radical combine to form sulfuric acid

$$SO_{2\ (g)} + 2(OH)_{(g)} \longrightarrow H_2SO_{4(g)}$$

- **Chemicals reaction in liquid phase for SO_2**

Sulfur trioxide react with moisture in the atmosphere to form sulfuric acid

$$SO_{3\ (g)} + H_2O_{\ (L)} \longrightarrow H_2SO_{4\ (L)}$$

- **Chemicals reaction in gas phase for NO_x**

Combustion engines mix oxygen and nitrogen together

$$N_{2\,(g)} + O_{2\,(g)} + \text{energy} \longrightarrow 2NO_{(g)}$$

Nitrous oxide react with oxygen diatomic molecule to produce nitrous dioxide

$$2NO_{(g)} + O_{2\,(g)} \longrightarrow 2NO_{2(g)}$$

Sun light and hydroxide radical combine to form nitric acid

$$NO_{2(g)} + OH_{(g)} \longrightarrow HNO_{3(g)}$$

- **Chemicals reaction in liquid phase for NO_x**

Nitrogen dioxide react with moisture in the atmosphere to form nitric acid

$$NO_{2(g)} + H_2O_{\,(L)} \longrightarrow HNO_{3(L)}$$

There are other gasses to form acid such as carbon dioxide

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow H^+ + HCO_3$$

4- Factors affecting level of acidic deposition in the atmosphere.

A variety of ecological, chemical, physical, and human factors determine the vulnerability of an ecosystem to acid deposition:

• Watershed **bedrock composition:**

Certain rocks, such as granite, weather slowly and do not produce neutralizing chemicals. Watersheds that contain these rocks are more vulnerable to acidification.

• **Land use history**:

Various management techniques, such as clear cutting, can change a forest ecosystem's capacity to neutralize acid inputs.

• **Disturbances***:*

Insect defoliation, fires, and other types of disturbances can stress ecosystems making them less resilient to acidification.

• **Vegetation type:**

Different plant species respond in different ways to acid deposition and also contribute differently to ecological processes that regulate acidification.

• **Landscape features**:

Elevation, edges (e.g., the edge between a forest and field), the presence or absence of vegetation, and the steepness and directional face of a slope all affect acidification.

• **Soil depth:**

Shallow soils are often more sensitive to acidification than deep soils.

• **Base nutrient reserves:**

Elements such as calcium, potassium, and magnesium are base nutrients that help buffer acid inputs. Higher amounts of these nutrients increase an ecosystem's capacity to neutralize acids.

5-Impact of acid deposition

Most importantly, acid deposition can affect health of a human being it can harm us through the soil and leaks or through the atmosphere or through man-made materials and structures

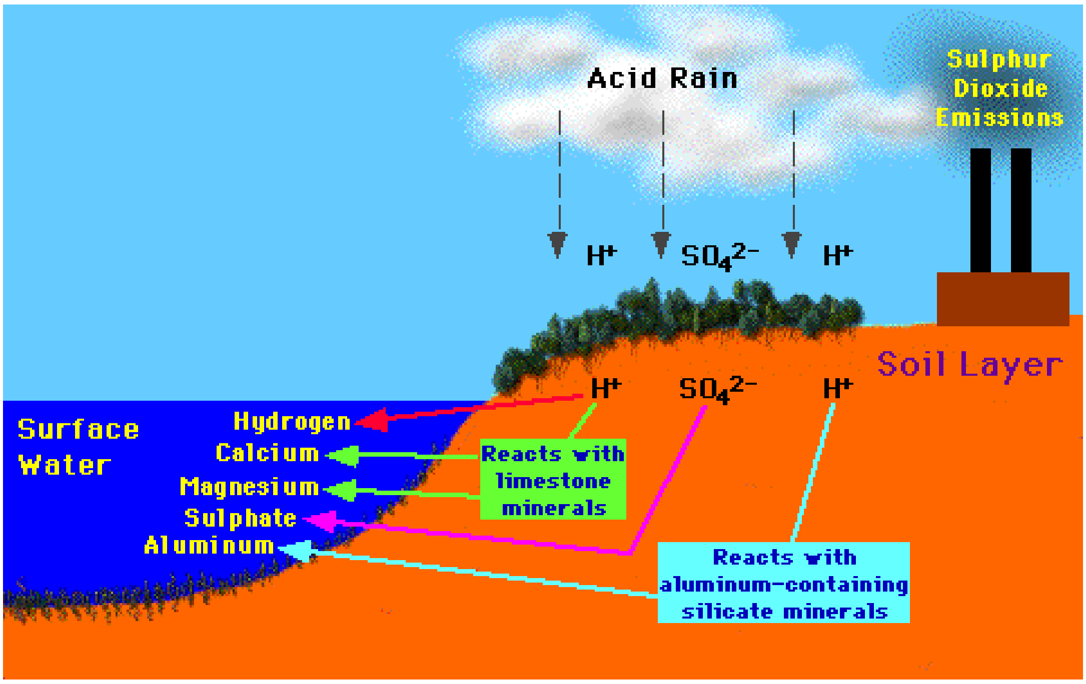
Affect on forest

Water run-off enters nearby streams, rivers, or lakes. That soil may have neutralized some or all of the acidity of the acid rainwater. This ability of neutralization is call buffering capacity. Without buffering capacity, soil pH would change rapidly.

High pH levels in the soil help accelerate soil weathering and remove nutrients. It also makes some toxic elements, for example aluminum, more soluble .acid rain can seep into the ground, poisoning the trees with toxic substances that are slowly being absorbed through the roots. When acid rain falls, the acidic rainwater dissolves the nutrients and helpful minerals from the soil.

These minerals are then washed away before trees and other plants can use them to grow when acid rain is frequent, leaves tend to lose their protective waxy coating, when leaves lose their coating, the plant itself is open to any possible disease. Acid rain does not only affect organisms on land, but also effect organisms in aquatic biomes. For example, frogs may tolerate relatively high levels of acidity, while snails are more sensitive to pH changes.

Fig 3



Affect on fish

Sulfuric acid in polluted precipitation interferes with the fish's proficiency to take in oxygen, salt, and nutrients. For freshwater fish, maintaining osmo-regulation (the ability to maintain a state of balance between salt and minerals in the organism's tissue) is essential to stay alive. Acid molecules cause mucus to form in their gills preventing the fish to absorb oxygen well. Also, a low pH level will throw off the balance of salt in the fish's tissue. Calcium levels of some fish cannot be maintained due to the changes in pH level. This causes a problem in reproduction: the eggs are too brittle or weak. Lacking calcium causes weak spines and deformities in bones. Sometimes when acid rainfall runs off the land, it carries fertilizers with it. Fertilizer helps stimulate the growth of algae because of the amount of nitrogen in it. However, because of the increase in the death of fish the decomposition takes up even more oxygen. This takes away from surviving fish. In other terms, acid rain does not help aquatic ecosystems in anyway.

Affect on manmade materials

Acid rain does not only damage the natural ecosystems, but also man-made materials and structures. Marble, limestone, and sandstone can easily be dissolved by acid rain. Metals, paints, textiles, and ceramic can effortlessly be corroded. Acid rain can downgrade leather and rubber. Man-made materials slowly deteriorate even when exposed to unpolluted rain, but acid rain helps speed up the process. Acid rain causes carvings and monuments in stones to lose their features.

In limestone, acidic water reacts with calcium to form calcium sulfate.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + 2H^+ + CO_3^{-2}$$

For iron, the acidic water produces an additional proton giving iron a positive charge.

$$4Fe_{(s)} + 2O_{2(g)} + 8H^+_{(aq)} \longrightarrow 4Fe^{+2}(aq) + 4H_2O_{(l)}$$

When iron reacts with more oxygen it forms iron oxide (rust).

$$4Fe^{+2} + O_{2(g)} + 4H_2O_{(l)} \longrightarrow 2Fe_2O_{3(s)} + 8H^+$$

Affect on human

Most importantly, acid rain can affect health of a human being. It can harm us through the atmosphere or through the soil from which our food is grown and eaten from ,One of the serious side effects of acid rain on human is respiratory problems. The sulfur dioxide and nitrogen oxide emission gives risk to respiratory problems such as dry coughs, asthma, headaches, eye, nose, and throat irritation.

6-Procedures for acidic deposition control in petroleum industry.

Until we reduce air pollution acid rain will continue to be a problem, activities to resolve this problem include cleaning up the smokestacks and exhaust pipes that pour pollutants into the air finding alternative sources of energy, repairing the damage already done by acid rain and conserving our resources

a- The national goal to reduce current levels of sulfur dioxide and nitrogen oxide production by

- Implement and enforce tough regulations to limit any credit for the height of tall stacks
- Adopt and implement penalties for major polluters violating emission standards
- Establish a National Air Quality standard for fine particles, such as sulfates and nitrates

b- Clean up smokestacks and exhaust pipes by installing "Scrubbers" in smokestacks

- For sulfur dioxides three of main technologies for controlling SO_x emissions from utility boilers, large industrial boilers, and large industrial furnaces and kilns all involve the injection of sulfur absorbing substance into the exhaust gases (flue gases) from the boilers.

1. Duct injection

Flue gases are cooled typically using water as a coolant to an appropriate then routed to an absorber unit then a solution of calcium hydroxide ($Ca(OH)_2$) is sprayed into the flue gases this calcium sorbent reacts with SO_x in the gases to form calcium sulfate ($CaSO_4$) and calcium chloride ($CaCl_2$) these reaction products together with fly ash (particulate matter from the gas stream) and un-reacted sorbent are removed from the flue gases by settling and by the use of a fabric filter the reaction products are disposed of and un-reacted sorbent can be recycled back to the absorber

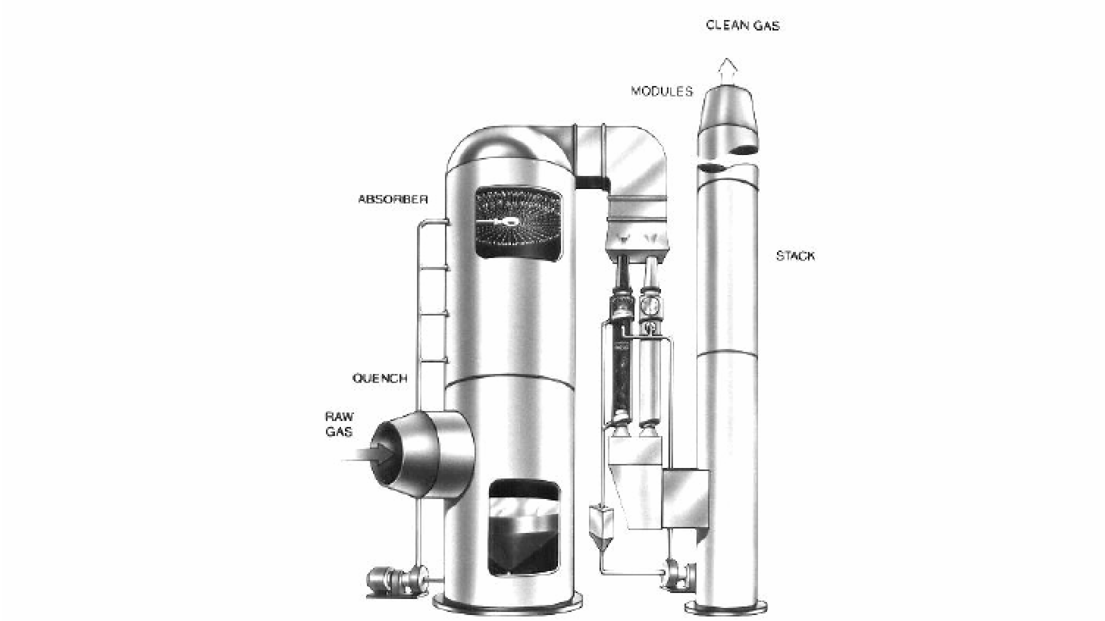
Pre- electrostatic precipitation sorbent injection can remove 30-70 % of SO_x im the flue gases.

Post- electrostatic precipitation sorbent injection in which Injection occurs after the exhaust gas has passed through the electrostatic precipitation can achieve 80- 90 % removal

2. Wet scrubber or flue gas desulphurization (FGD)

Flue gas enter a large reaction vessel where they are sprayed with a water slurry containing about 10% lime (calcium oxide CaO) or limestone the calcium compound react with the SO_x in the flue gas forming calcium sulfate and calcium sulfite which are collected thickened (by removing water and filtration) mixed with fly ash and stabilized with additional lime, and disposed of in landfills we reduce remove 80—90% of the SO_x in the flue gases, it are applicable to new plants and in retrofit installations, relatively costly.

Fig4



3. Dry scrubber or spray dryers

A slurry of quicklime mixed with water (calcium hydroxide) is atomized and sprayed into a tower where it mixes with hot exhaust gases the calcium hydroxide reacts with SO_x in the exhaust gases as the droplets dry resulting in the production of a dry calcium sulfate/sulfite by product which is collected in the bottom of the spray dryer and in equipment used to collect particulate matter

Dry scrubber can remove 70—90% of the SO_x in the flue gases, it can be used in retrofit as well as installations, cost slightly less than wet scrubbers and are somewhat simpler to operate.

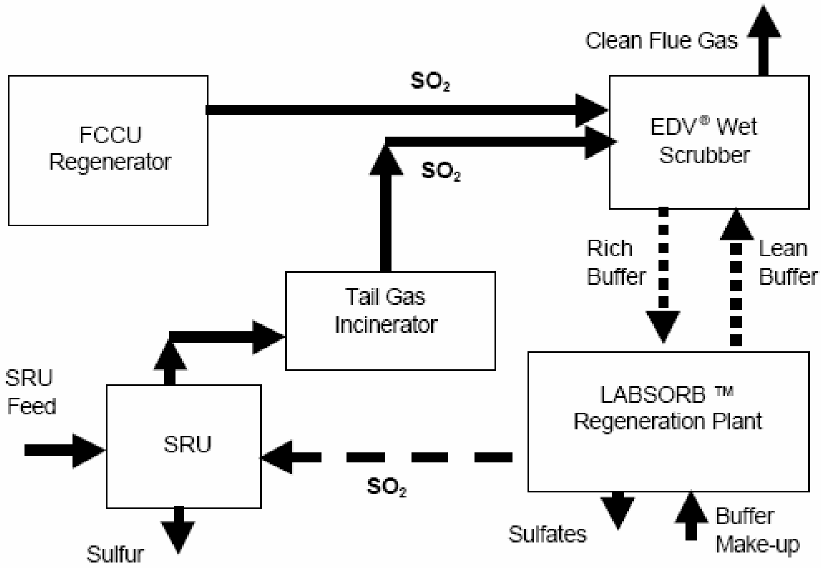


FIG. 5: LABSORB™ TREATING FCCU REGENERATOR GAS PLUS SRU GAS

- For nitrogen oxides two of main technologies for controlling NO_x emissions from utility boilers, industrial facilities include primarily selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) of NO_x to elemental nitrogen (N_2)

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1. Selective non- catalytic reduction (SNCR)

A nitrogen-based chemical reagent-most commonly urea (CH_2CONH_2) or ammonia (NH_3)-is injected just after the exhaust gases exit the boiler (that is, when the gases are still very hot).SNCR can reduce NO_x emissions by 35 to 60 percent, can be used in new and retrofit installations, and have relatively low capital costs. SNCR has mostly been used with gas and oil-fired boilers and turbines, but has been demonstrated on coal-fired boilers and has also been used on specific types of cement kilns. Concerns with the SNCR technology include possible ammonia contamination of fly ash (ammonia can cause odor problems), release of unreacted ammonia into the environment with treated flue gases, and production of (N_2O), a potent greenhouse gas, during the reaction of flue-gas NO_x with the injected reagents.

2. Selective catalytic reduction (SCR)

The SCR process is similar to SNCR, in that ammonia is reacted With the NO_x in the flue gas to yield (mostly) molecular nitrogen. The difference between the technologies, as their names imply, is That SCR makes use of a catalyst to accelerate the chemical reactions, and (thanks to the catalyst) can operate at lower flue gas temperatures than SNCR. The catalysts used in SCR are oxides of metals, typically vanadium and titanium. SCR has been widely used in low-sulfur coal and oil-fired power plants but its use with medium- and high-sulfur coals is still in the demonstration phase SCR can remove 70 to 90 % of the NO_x in the flue gas, but is significantly more expensive than SNCR systems. Issues such as the impact of alkalis and arsenic common coal contaminants) on catalyst life, the emissions of un-reacted ammonia, and the conversion of SO_2 to SO_3 by catalysts (and the impact of that process on NO_x removal) all may have an impact on the applicability of SCR.

c. The use of alternative ways of producing energy

- Hydroelectric power
- Nuclear power
- Solar power
- Wind power

d. The need to conserve resources

- Take action by individuals.
    1. Turn off lights, computers and other applications when you're not using them
    2. Use energy efficient appliances lighting, air conditions, heater, refrigerators, washing machines
    3. Insulate your home as best you can
    4. Use public transportation or better yet walk or bicycle whenever possible
    5. Buy vehicles with low NO_x emissions and maintain all vehicles well
- Corporations must conserve energy along the same guidelines

e. The need to restore a damaged environment

add powered limestone (a natural base) to the water in a process called liming

Summary

Recently, seriousness of the acidic deposition problem is recognized by a large number of world countries .Acidic deposition is the removal of sulfates and nitrates from the atmosphere by both wet and dry processes. Consequently, the overall process is more properly termed acid deposition.

Increased precipitation acidity appears to be due to sulfuric (65%) and nitric acids (30%). The apparent major sources of precursors, sulfur dioxides (SO_2) and nitrogen oxide (NO_x), for these strong acids include fossil-fuel-fired power plant, industrial boilers, metal smelters and automobiles

Most importantly, acid deposition can affect health of a human being. It can harm us through the soil and leaks, the atmosphere or man-made materials and structures. One of the serious effects of acid deposition on human is respiratory problems.

The sulphur dioxide and nitrogen oxide emissions give risk to respiratory problems such as dry coughs, asthma, nose, and throat irritation

The use of add-on control technologies is the likely solution that need to reduce particulate emissions for environmental compliance.

The use of electrostatic precipitators and wet scrubbers is specifically addressed in most regulations. Both technologies are in widespread use for controlling particulate emissions to levels well within the applicable regulations.

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