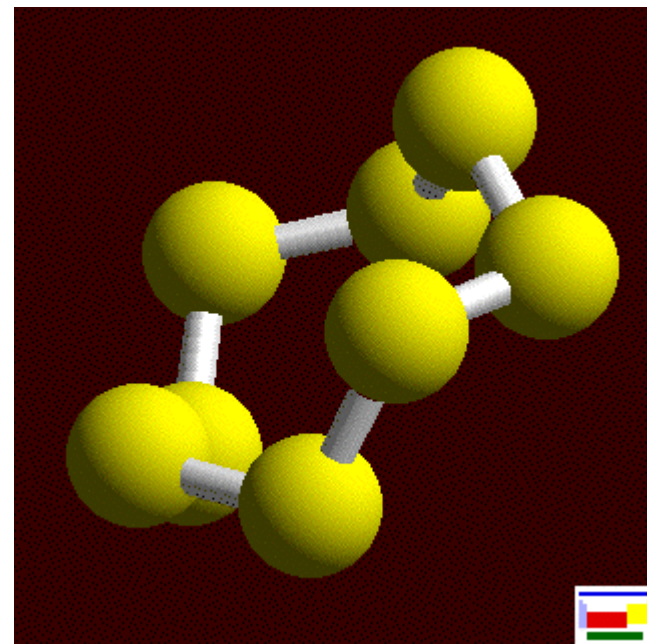


# Sulfur oxides



Presented by : TAHA 塔哈

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- ❖ Introduction.
- ❖ sources of sulfur oxides.
- ❖ Physical properties of atmospheric sulfur oxides.
- ❖ Characteristics of sulfur oxides.
- ❖ Chemistry of sulfur oxide formation.
- ❖ Acid Rain.
- ❖ Effects of acidic rain.
  
- ❖ Anthropogenic effects of  $\text{SO}_2$  .
- ❖ Coal Combustion.
- ❖ Sulfur in Coal Formation.
- ❖ Sulfur Oxides,  $\text{SO}_x$  As An Air Pollutants.
- ❖ Control of Sulfur Oxides.

# Sulphur Oxides

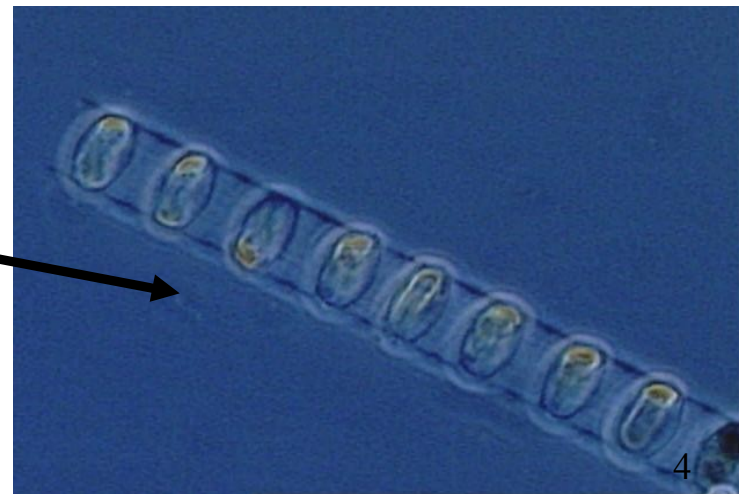
## Introduction:-

- Oxides of Sulphur, especially sulphur dioxide, a chemical compound with the formula  $\text{SO}_2$  are common pollutants of the air.  $\text{SO}_2$  is produced by volcanoes and in various industrial processes.
- Since coal and petroleum often contain sulphur compounds, their combustion generates sulphur dioxide. Further oxidation of  $\text{SO}_2$ , usually in the presence of a catalyst such as  $\text{NO}_2$ , forms  $\text{H}_2\text{SO}_4$ , and thus acid rain.



# Natural sources of sulfur oxides

- **Volcanic action.**
  - A volcanic gases: 90% water and  $\text{CO}_2$ ,  
 $\text{SO}_2$  content 1-10 % .
- **Sulfur compounds from biological activity**
  - $(\text{CH}_3\text{SCH}_3, \text{H}_2\text{S}, \text{CS}_2, \text{COS})$  will be oxidized in the atmosphere.
  - Sulfur emission in highest amount: dimethyl-sulfide from the oceans → biological activity of **fitoplankton**.



# Sulfur oxides from human activity

Atmospheric sulfur content **is mainly anthropogenic** (Human impact on the environment) origin.

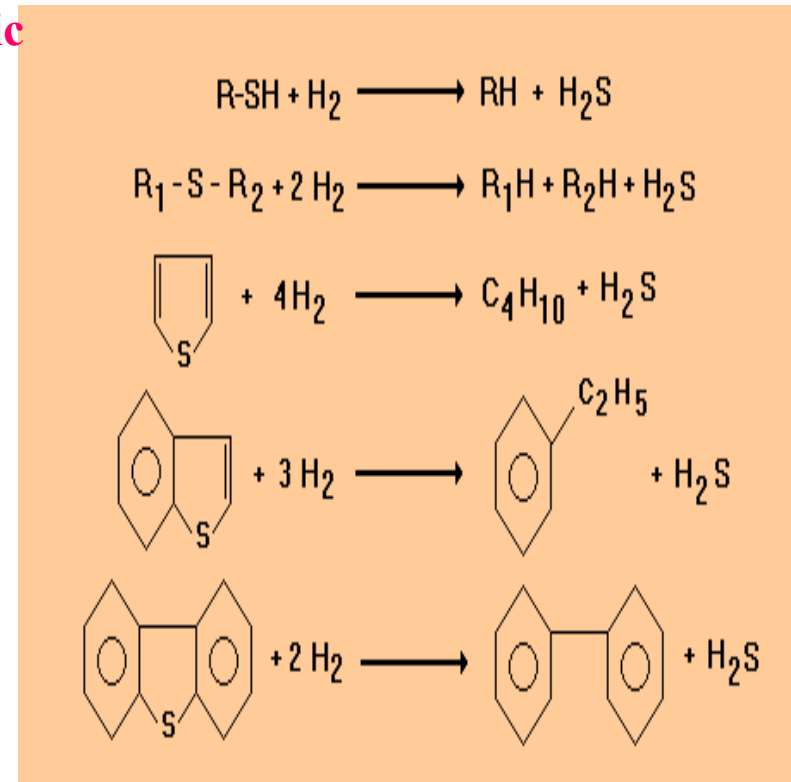
**Main source: combustion of fossil fuels**

• **Sulfur content of coal and crude oil differs:-**

**Crude oil:** mainly organic, (sulfides, mercaptanes, bisulfides, thiophenes) => can be removed by simple technology.

**Coal:**

- pyritic (FeS), removable by physical method,
- sulfates (CaSO<sub>4</sub>, FeSO<sub>4</sub>) removable by physical method (no decay at combustion temperature to SO<sub>2</sub>)



# Sulfur dioxide from human activity

smelter operation : far from built-up area.

**Not a solution due to the global character of sulfur oxide pollution !**



# Physical properties of atmospheric sulfur oxides

## Sulfur dioxide:

- colorless
- irritating odor (odor threshold 0,3-1 ppm (part(s) per million))
- soluble in water
- natural background~1 ppb

## Sulfur trioxide:

- highly reactive => short lifetime in the atmosphere, sulfuric acid formation with water.

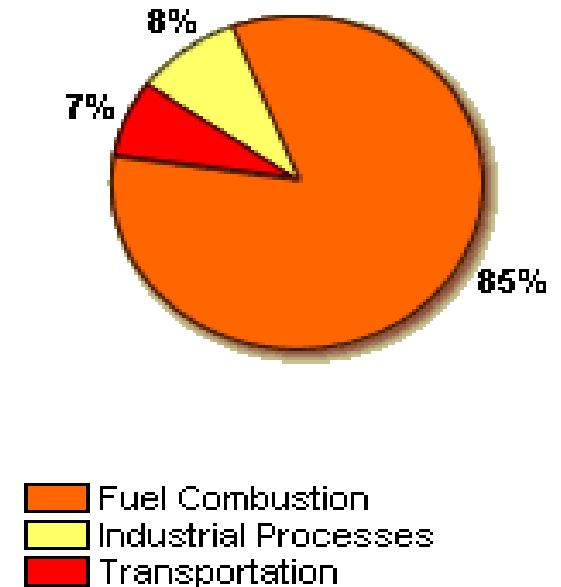
	Sulfur dioxide SO <sub>2</sub>	Sulfur trioxide SO <sub>3</sub>
Molecular mass	64	80
Melting point °C	-75	16,8
Boiling point °C	-10	43,7
density 0 °C, 101.3 kPa 20 °C, 101.3 kPa	1.250 g/dm <sup>3</sup> 2.93 g/dm <sup>3</sup>	2.052 g/dm <sup>3</sup> 1,916 g/dm <sup>3</sup>
Solubility in water 0 °C 101.3 kPa	80 dm <sup>3</sup> / dm <sup>3</sup> (97.7 ppmm)**	decay
Conversion factors 0 °C, 101.3 kPa	1 mg/m <sup>3</sup> = 2.663 ppmv*** 1 ppmv = 0.376 mg/m <sup>3</sup>	

Direct emission is mainly sulfur dioxide, only some percent of sulfur trioxide

# Characteristics I

- Sulfur oxides include sulfur dioxide ( $\text{SO}_2$ ), sulfur trioxide ( $\text{SO}_3$ ), and sulfuric acid ( $\text{H}_2\text{SO}_4$ ).
- The major sources of sulfur oxides are shown in Figure 1.
- Combustion of fossil fuels for generation of electric power is clearly the primary contributor of sulfur dioxide emissions.
- Industrial processes, such as nonferrous metals melting, also contribute to sulfur dioxide emissions.
- It is formed primarily during the combustion of sulfur-containing fuel or waste.
- Once released to the atmosphere, sulfur dioxide reacts slowly to form sulfuric acid ( $\text{H}_2\text{SO}_4$ ).
- Some of the sulfur dioxide in high temperature processes is oxidized to form sulfur trioxide.

**Figure 1. Major Sources of Sulfur Dioxide (1997)**



Data source: U.S. EPA, 1998.

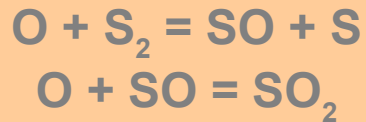


## Characteristics II

- Below 500 to 600°F, most of the sulfur trioxide, which is extremely hygroscopic, reacts with water molecules to form sulfuric acid.
- Sulfuric acid is a strong acid.
- Sulfuric acid can also be released from plants that manufacture batteries.
- Sulfuric acid vapor in moderate concentrations (2 to 8 ppm) is very beneficial to electrostatic precipitators because it adsorbs onto particle surfaces and creates a moderate resistivity.
- High concentrations can be detrimental to precipitator performance.
- High sulfuric acid levels can also cause significant corrosion problems for precipitators, fabric filters, and other control devices.
- The temperature of flue gases should be kept well above the dew point for sulfuric acid to prevent condensation on ductwork surfaces and components in the air pollution control system

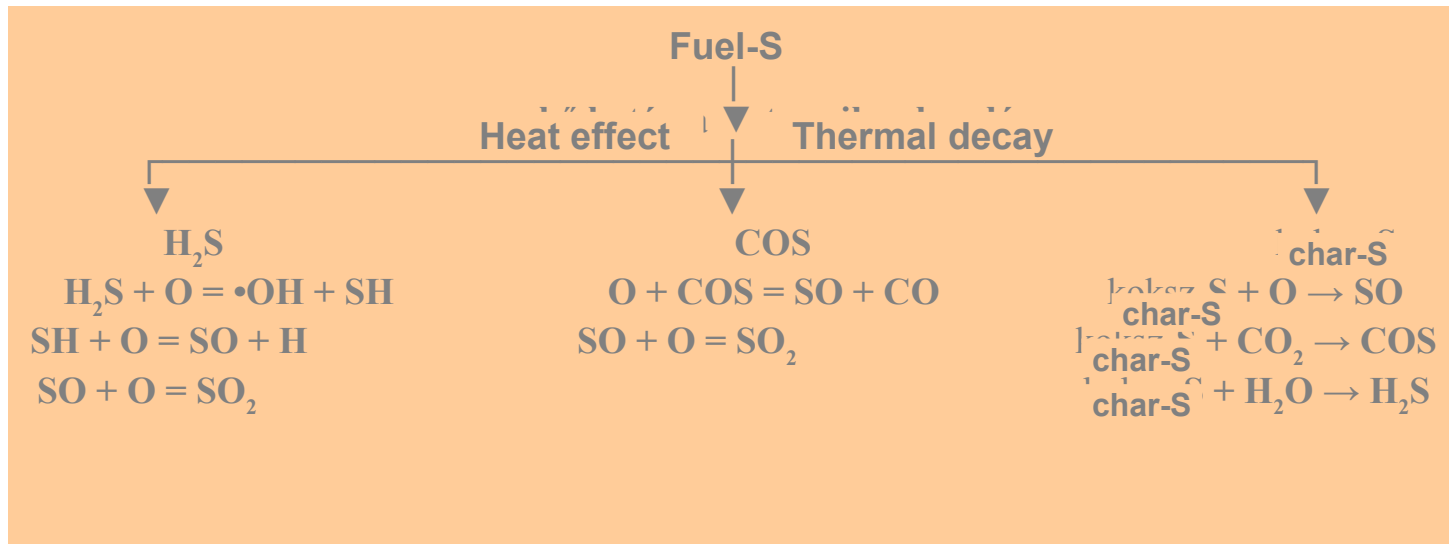
# Chemistry of sulfur oxides formation I

**Burning of elemental sulfur: oxygen atom starts the reaction transition compound: sulfur monoxide.**



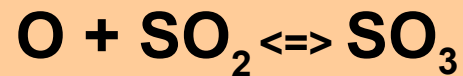
**Combustion of sulfur containing materials (fuel-S) :**

**thermal decay  $\rightarrow$  char-S, (shrunken solid fuel) hydrogen sulfide ( $\text{H}_2\text{S}$ ) and carbonyl sulfide (COS) form. All of the three products is oxidized to sulfur dioxide**



# Chemistry of sulfur oxides formation II

**Further oxidation of sulfur dioxide → sulfur trioxide:**



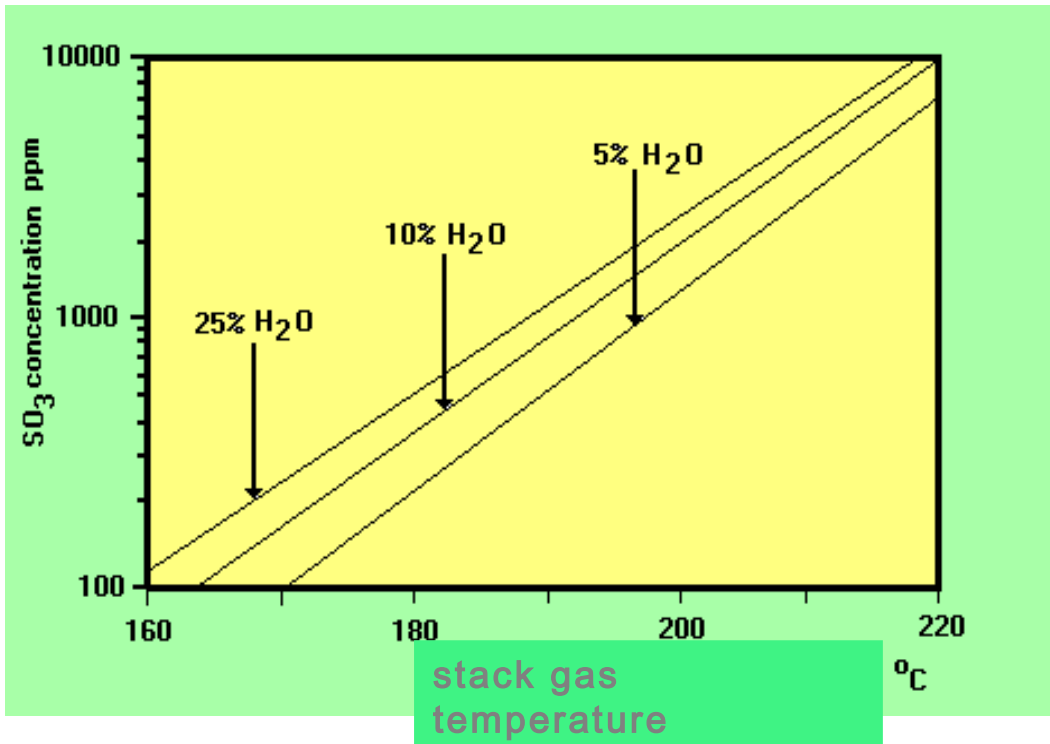
- oxygen atoms and hydroxyl radicals play a significant role.
- equilibrium shifts left with temperature increase
- the reaction rate is slow
- only 0.5-2.5% of  $\text{SO}_2$  is converted to  $\text{SO}_3$
- the time to reach the equilibrium depends of the catalytic effect of the metal content (W, Mo, V, Cr, Ni, Fe oxides) in ash

# Chemistry of sulfur oxides formation III

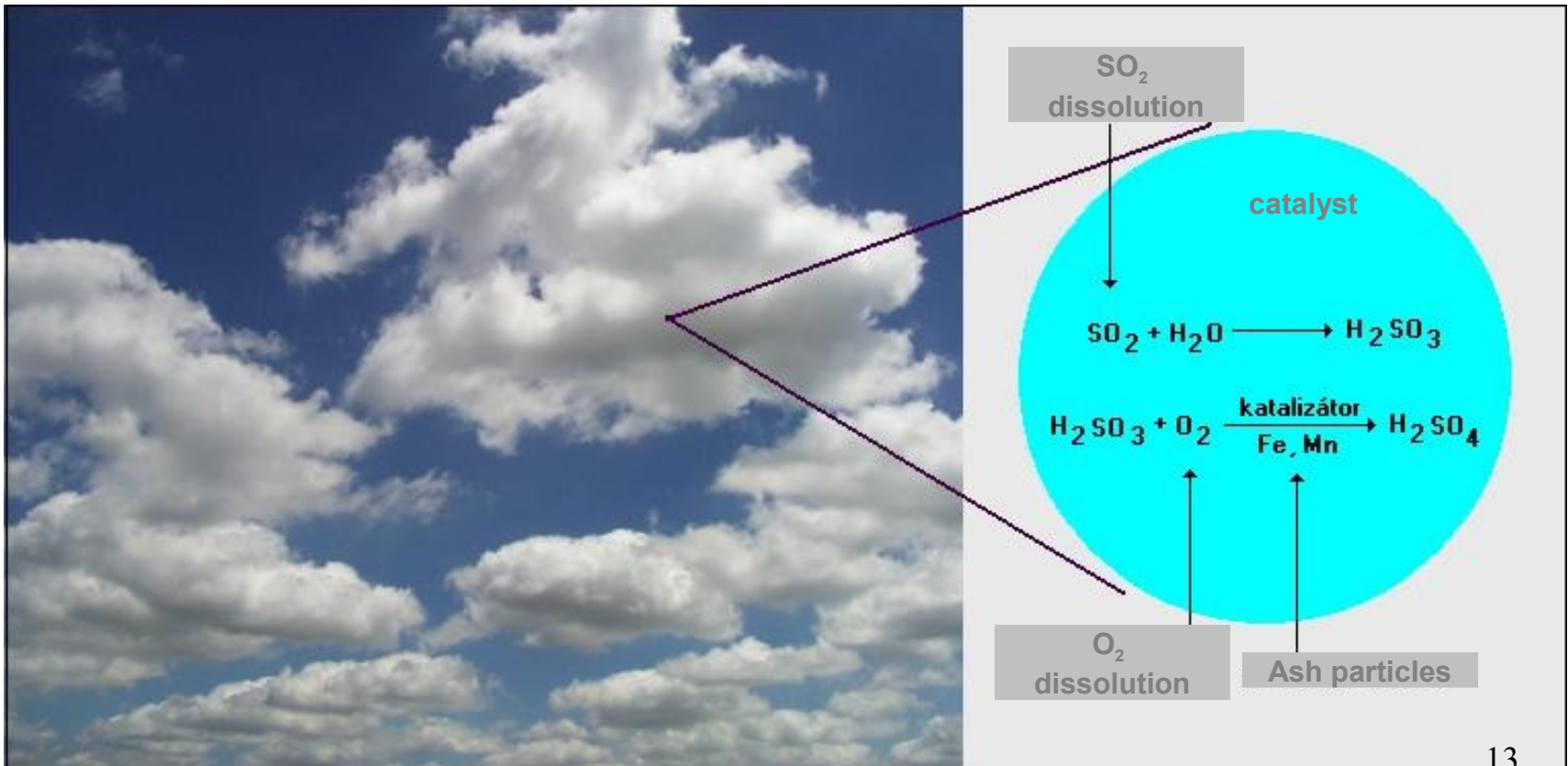
- Sulfur trioxide at **482 °C** transforms to sulfuric acid. Under the dew point **sulfuric acid** condensates on the structure materials (heat exchanger, stack wall ).

- The dew point of sulfuric acid depends on the  $\text{SO}_3$  and water content of the stack gas.

Dew point of sulfuric acid in function of  $\text{SO}_3$  and water concentration in stack gas

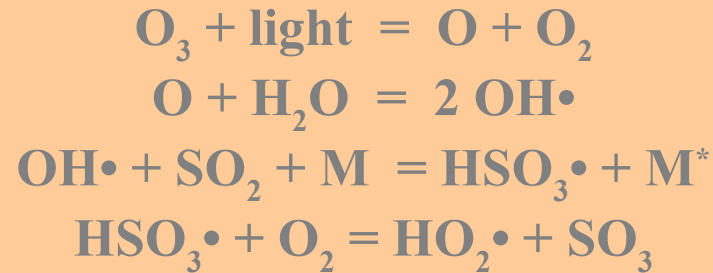


# Catalytic transformation of sulfur dioxide to sulfuric acid



# Photochemical transformation of sulfur dioxide to sulfuric acid

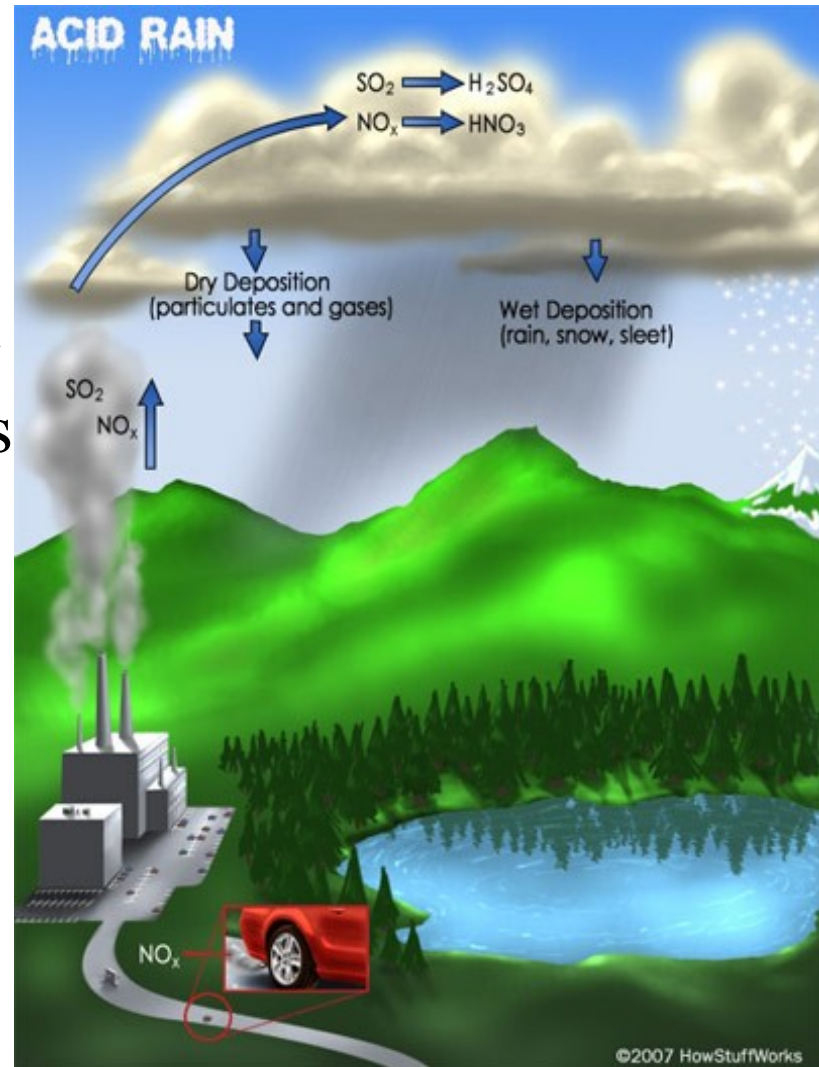
- **Hydroxyl radicals oxidize the sulfur dioxide to sulfur trioxide.**



**Acidic rain**

# Acid Rain

- This phenomenon results when sulphur dioxide dissolves in moisture in the air, forming sulphur acids, which eventually fall to the surface of the earth as acid rain.
- Acid rain directly attacks the protective coating of plants, acidifies lakes and soils which may result in the formation of substances that are toxic to plants and animals.



# Effects of acidic rain

- **pH of rain:** adjusted by the rate of natural acidic and basic materials
- **Usually acidic:** solution of carbon dioxide (pH=5.56)
- **Generally accepted:** pH under 5 is due to **human activity** .

The acidity surplus :

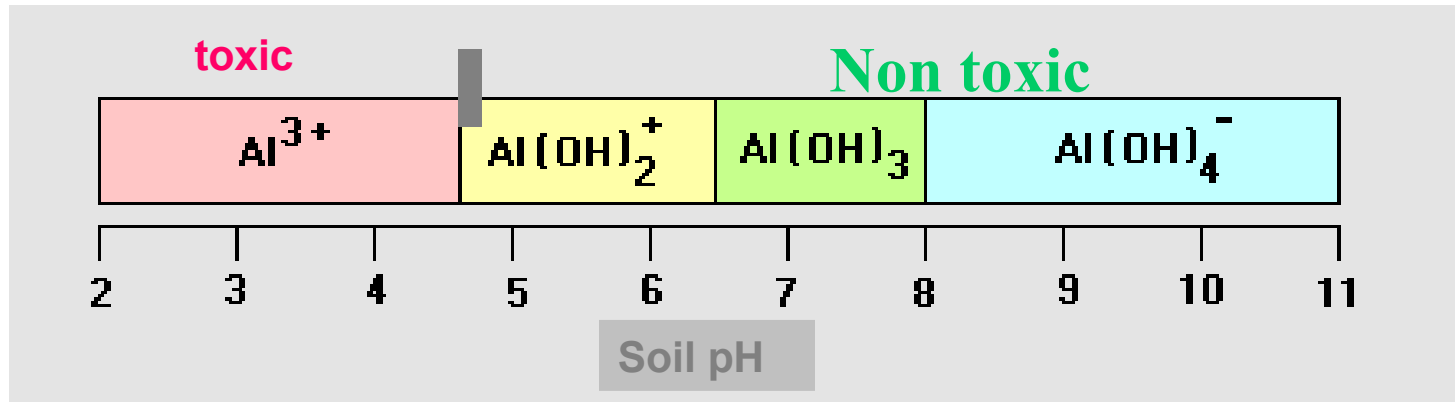
- 60-70% **sulfuric acid** from sulfur dioxide
- The rest comes from **nitric acid** formed from nitric oxide
- Some percent **hydrochloric acid**
- pH of rain > pH of fog particles



# Effects of acidic rain on plants

Three stages can be distinguished

1. Mobilization of soluble plant nutrients, e.g. nitrogen compounds
2. Nutrient wash out by the rain water → nutrient shortage
3.  $\text{Al}^{3+}$  ion liberation from the clay minerals due to the decreasing pH in the soil.
  - **The free aluminum ion is toxic to the roots, weakens the immunizing system → secondary infections**



# Effect of acidic rain on natural water I

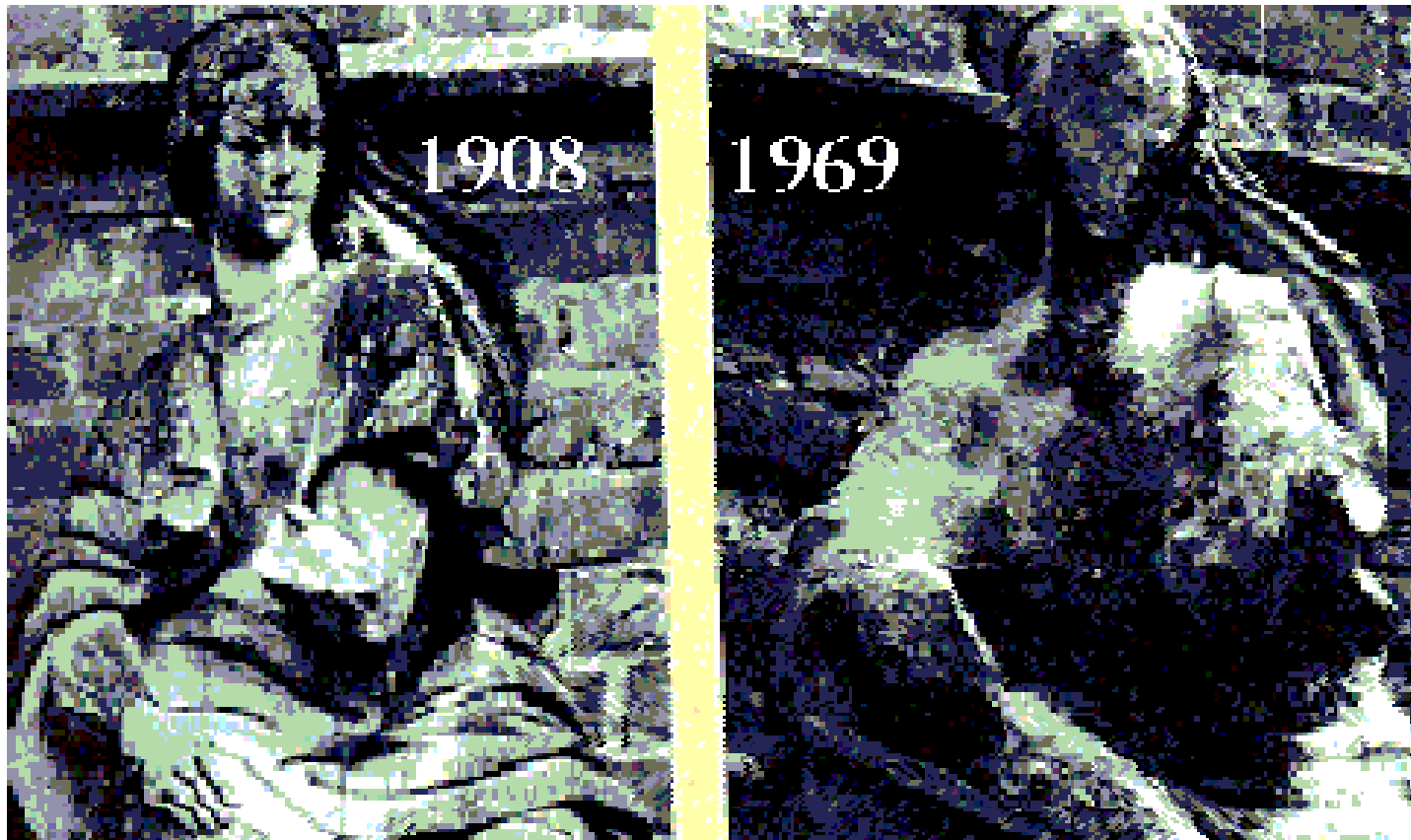
- The excess of  $H^+$  ion in rain water shifts the hydro carbonate equilibrium towards the formation of free carbon dioxide.



- The physically dissolved  $CO_2$  inhibit the  $O_2 \leftrightarrow CO_2$  exchange in living organisms : e.g. fish).
- occurs at spring when the melted acidic snow flows suddenly into the rivers of catchments area.
- If natural water is in contact with limestone, dolomite, the pH does not change → buffer effect. The living organisms are killed by the increased  $CO_2$  content
- In case of weak buffer effect (small Ca- and Mg-hydro carbonate content) the living organisms are killed by the decreased pH

# Effect of acidic rain on calcium carbonate containing materials I.

- calcium carbonate containing materials: marble, limestone, plaster, concrete → sensitive to acidic rain
- in the last fifty year the weathering of open air ancient monuments speeded up



# Effect of acidic rain on **calcium carbonate containing materials II.**

- **Effect: The infiltrating acidic rainwater contaminated by sulfuric acid changes the crystals of calcium carbonate to calcium sulfate**



- **The solubility of calcium sulfate > solubility of calcium carbonate.**
- **Crystal volume of CaSO<sub>4</sub> > crystal volume of CaCO<sub>3</sub>**  
**stress in the material structure → crack**

# Effect of acidic rain on metal constructions I

## Preliminary conditions of the electrochemical corrosion:

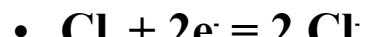
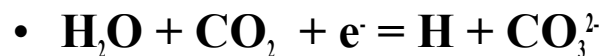
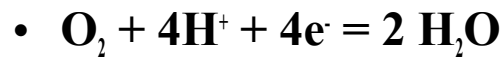
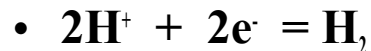
- 1. two metallic material with different electrochemical potential in metallic contact.
- 2. electrolyte cover on the metallic contact, (e.g.. water solutions of acids, salts)
- 3. presence of electron uptake material ( $\text{H}^+$   $\text{O}_2$   $\text{Cl}_2$  )

## Electrochemical corrosion of metal:

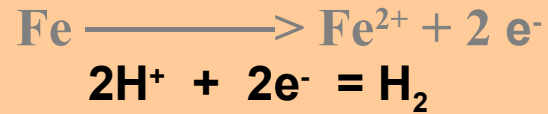
- **Oxidation:** the metal transform to ion and free electrons release.



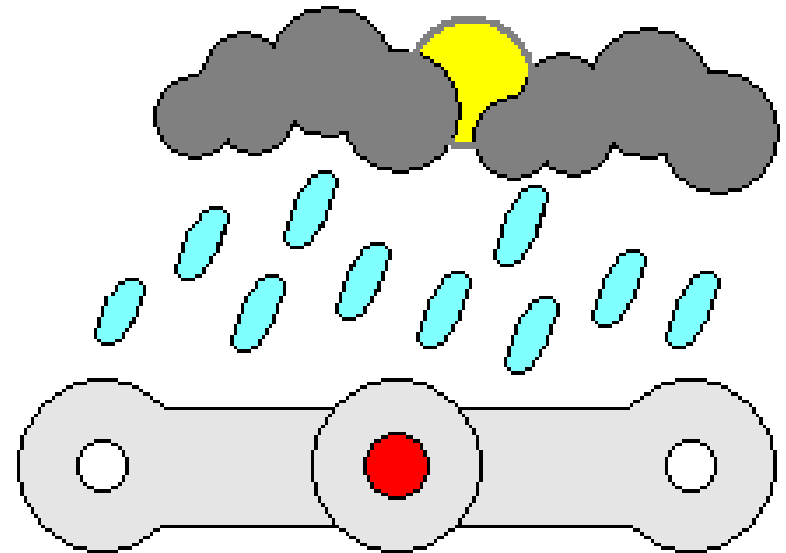
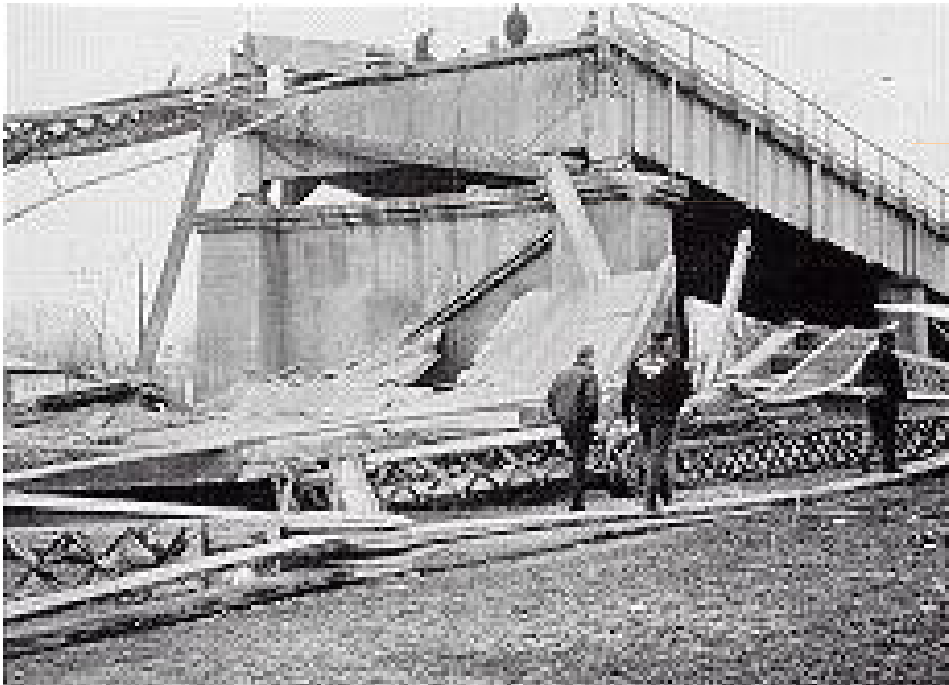
- **Reduction:** uptake of free electrons by



# Effect of acidic rain on metal constructions II



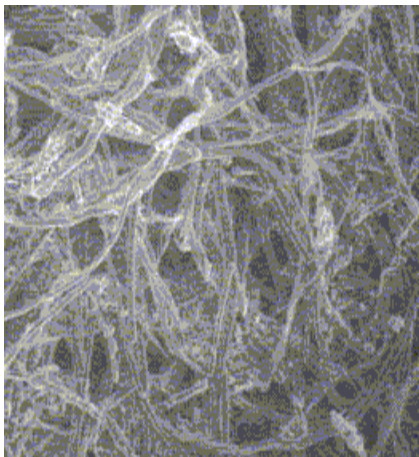
Acid rain: electrolyte and the hydrogen ion serves the reduction (electron uptake)



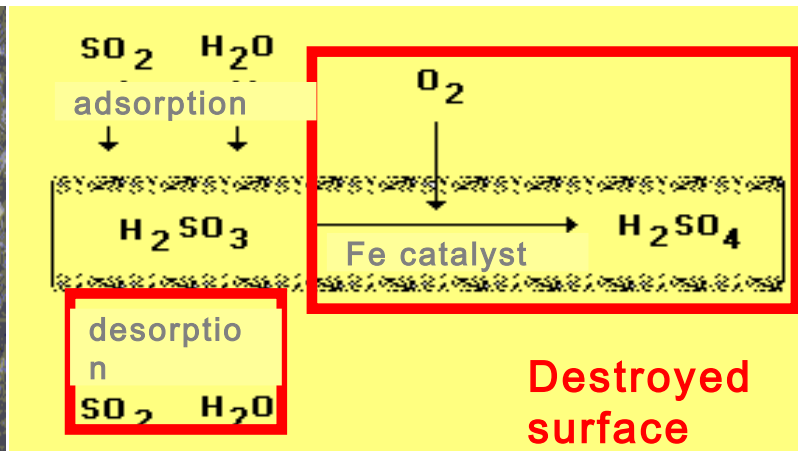
**Air pollution induced electrochemical corrosion resulted in the collapse of Silver bridge over Ohio river on 15-th. Dec. 1967.**

# Effect of atmospheric SO<sub>2</sub> on papers

Paper surface



H<sub>2</sub>SO<sub>4</sub> formation on the surface



The result



No  
damage

# Anthropogenic effects of SO<sub>2</sub>

**Anthropogenic**:- (chiefly of environmental pollution and pollutants)

- **Good solubility in water → the effect on the upper part of the respiratory system.**
  - **Irritating effect over 10 ppm**
- **Nonstop irritation of mucous lining in urban air results in frequent colds, flu.**



# *Coal Combustion*



# Coal



# Coal – what is it?

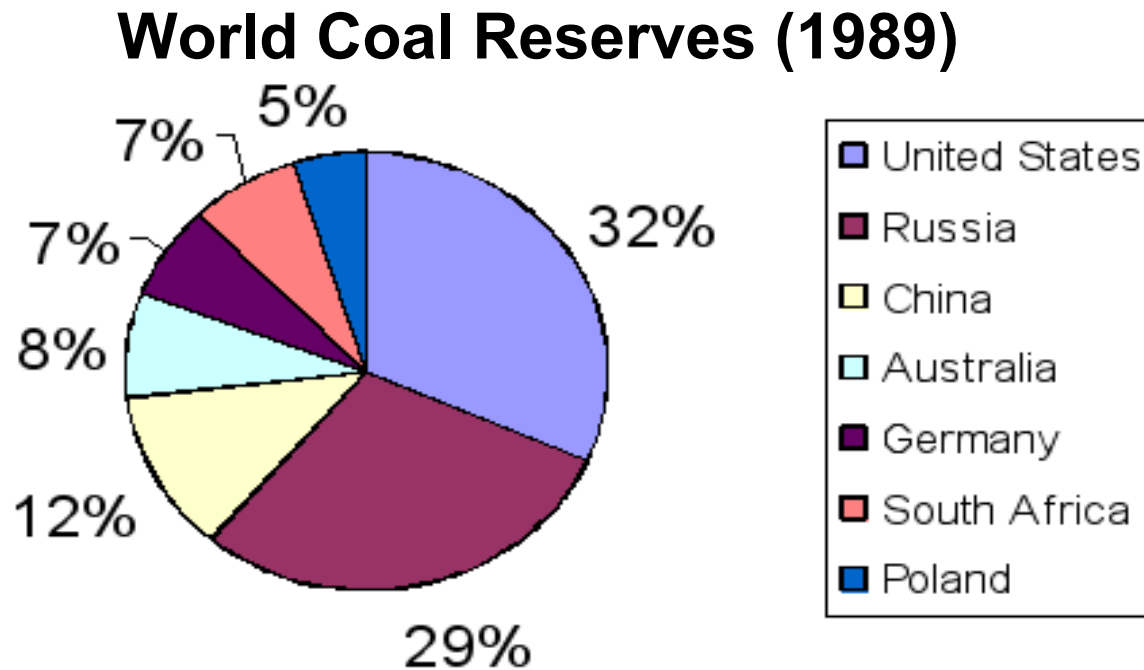
Proximate Analysis Elemental Composition

C	65-95%
H	2-7%
O	<25%
S	<10%
N	1-2%
Char	20-70%
Ash	5-15%
H <sub>2</sub> O	2-20%
VM	20-45%

- Inhomogeneous organic fuel formed mainly from decomposed plant matter.
- Over 1200 coals have been classified.

# Coal Sources

- Coal is the world's most plentiful fossil fuel.
- Recoverable world coal reserves are estimated at about  $1 \times 10^{12}$  tons.



# Coal Applications

- Homes – heat and cooking
- Transportation – steam engines
- Industry – metal works
- **Electricity – power plants**



# Coal Formation

Like other fossil fuels, including petroleum (a liquid) and natural gas, coal (a solid) is formed from dead plant matter under millions of years of high temperature and pressure. The energy that we get from burning fossil fuels is the energy that plants get from the sun via photosynthesis, which is why fossil fuel is sometimes called “buried sunshine”.

During the Carboniferous period, which spanned from about 360 to 290 million years ago, the Earth was covered by large, swampy forests in many areas. Thus, many of the plants fell into swamps when they died; as time passed, sedimentation and tectonic movements buried the swamps and peat bogs deeply into the Earth’s crust. This prevented oxygen from oxidizing the plants’ organic material (like cellulose) – in other words, bacteria that break down organic matter by aerobic decomposition did not have oxygen to do so. Furthermore, the deep burial and compression by sedimentary rocks squeezed water out of the plant matter, and the high temperature and pressure converted the organic material to fossil fuels.

# Sulfur in Coal Formation

**Sulfur** entered coal formation from a variety of sources in a variety of forms. Much of it came from **marine water** in the form of **sulfate** ( $\text{SO}_4^{2-}$ ), but it also came from the plant matter itself in various forms of organic sulfur. Some sulfur also came from **fresh water** and **minerals**.

Sulfur exists in coal as sulfides, organic sulfur, sulfate, and elemental sulfur. A common and notable sulfur-containing compound in coal is pyrite, or iron (II) sulfide ( $\text{FeS}_2$ ); its nickname is Fool's Gold, characterizing its resemblance to gold. Sulfate-reducing bacteria (yes, there is a phylogenetic group based on this trait) reduced sulfates from marine water (especially brackish water) to make hydrogen sulfide ( $\text{H}_2\text{S}$ ), which then reacted with iron in water to form pyrite.

(Since these bacteria live and operate in low-oxygen environments, they undergo anaerobic respiration – essentially, they “breathe” sulfur instead of oxygen.) In the coal industry, coal with high amounts of sulfur (or any other impurities) is considered to be of low grade, because less energy can be obtained from it.

# Sulfur in coal (<10%)

## Organic sulfur (40%)

Chemically bonded to the hydrocarbon matrix in the forms of thiophene, thiopyrone, sulfides and thiol.

## Inorganic sulfur (60%)

Imbedded in the coal, as loose pyrite -  $\text{FeS}_2$  or marcasite, and calcium/iron/barium sulfates.

Sources of sulfur in coal: Seawater sulfates, Limestone



# Coal Combustion Air Pollutants

- $\text{CO}_2$
- $\text{CO}$
- $\text{NO}_x$
- $\text{SO}_x$
- Particulate matter
- Trace metals
- Organic compounds





## Sulfur Oxides, SO<sub>x</sub> As An Air Pollutants



# Air Pollution I

- **Air pollution** is the “introduction of chemicals, particulate matter or biological materials that cause harm or discomfort to humans or other living organisms, or cause damage to the natural or built environment, into the atmosphere.”
- There is great concern over deteriorating air quality as it can contribute to many health problems in our community, especially for the very young, the elderly and those who already have respiratory problems.



# Air Pollution II

- Cancers and premature death can also be attributed to poor air quality.
- Air pollution not only has a real health cost, it also has an economic and environmental cost.
- Economic effects include the increased use of the health system and reduced activity of affected people, while environmental effects include damage to plants, animals and man-made structures, such as buildings and monuments.



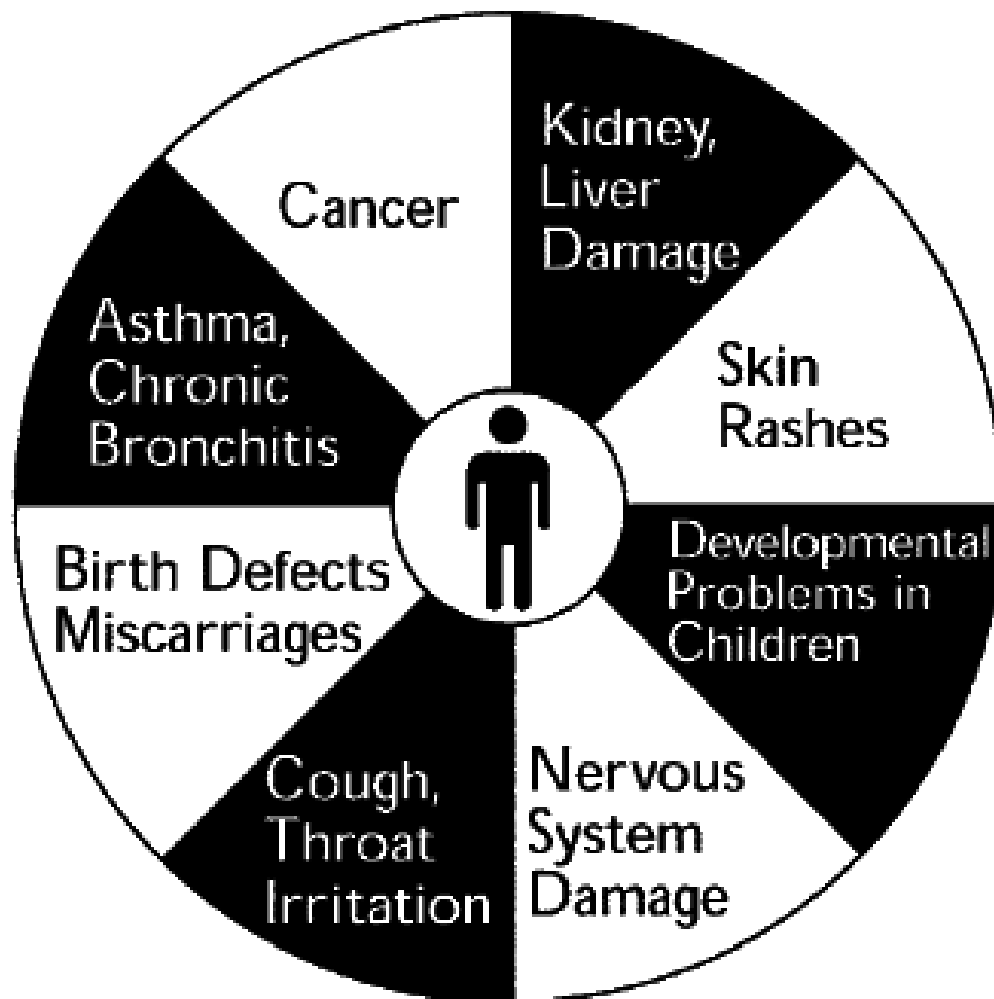
# Air Pollutants

- Carbon monoxide and CO<sub>2</sub>
- Nitrogen oxides (esp. NO<sub>2</sub>)
- CFC's
- Volatile Organic Compounds
- Ammonia
- Odours
- Particulate matter
- Pollen, dust-mites and other allergens
- Radioactive compounds
- Oxides of Sulphur (esp. SO<sub>2</sub>)

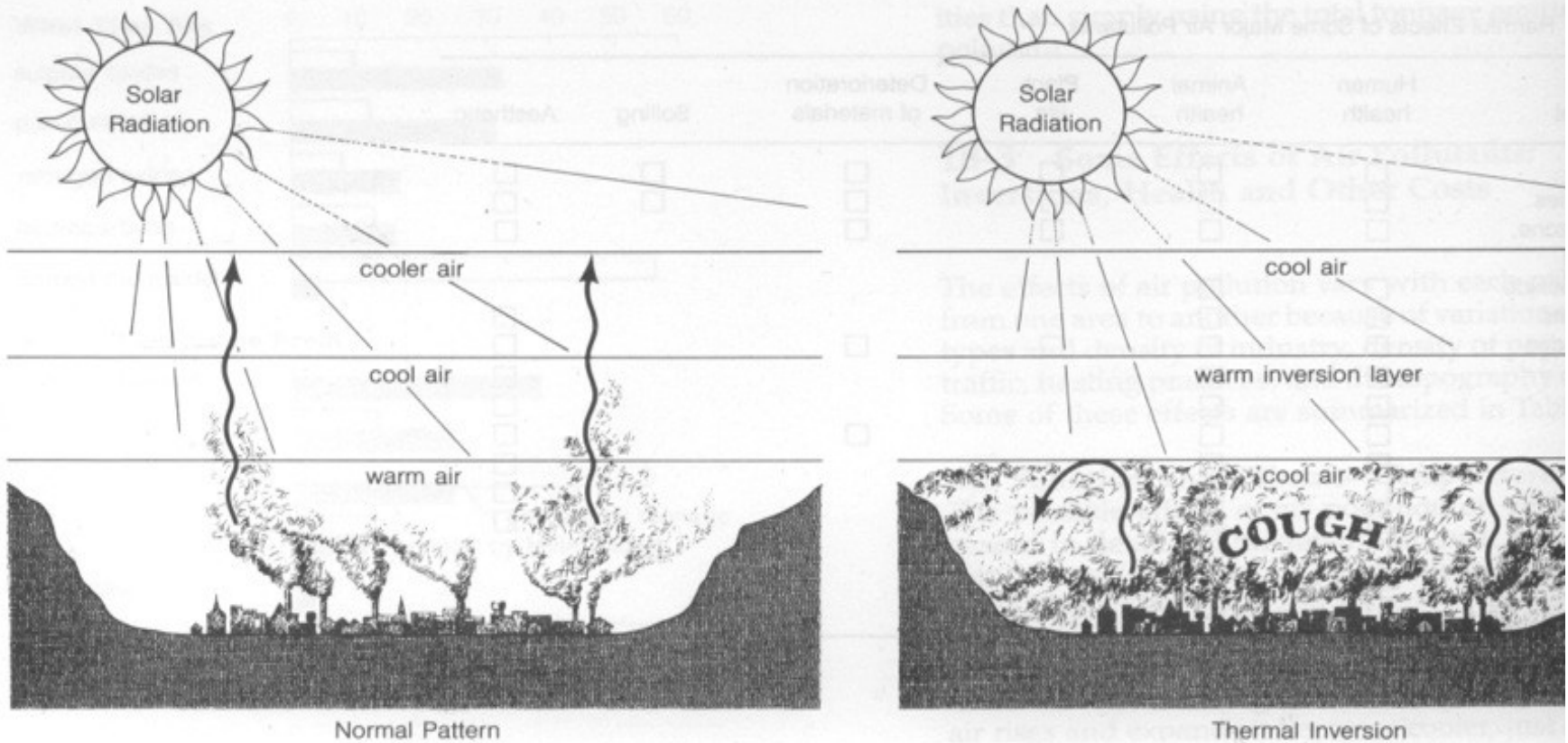
What do you think the most common source of air pollution is?

- A. Industrial sources
- B. Electricity generation
- C. Transport emissions
- D. All of the above

# WHAT HEALTH PROBLEMS ARE CAUSED BY TOXIC AIR POLLUTANTS?



# Temperature Inversion

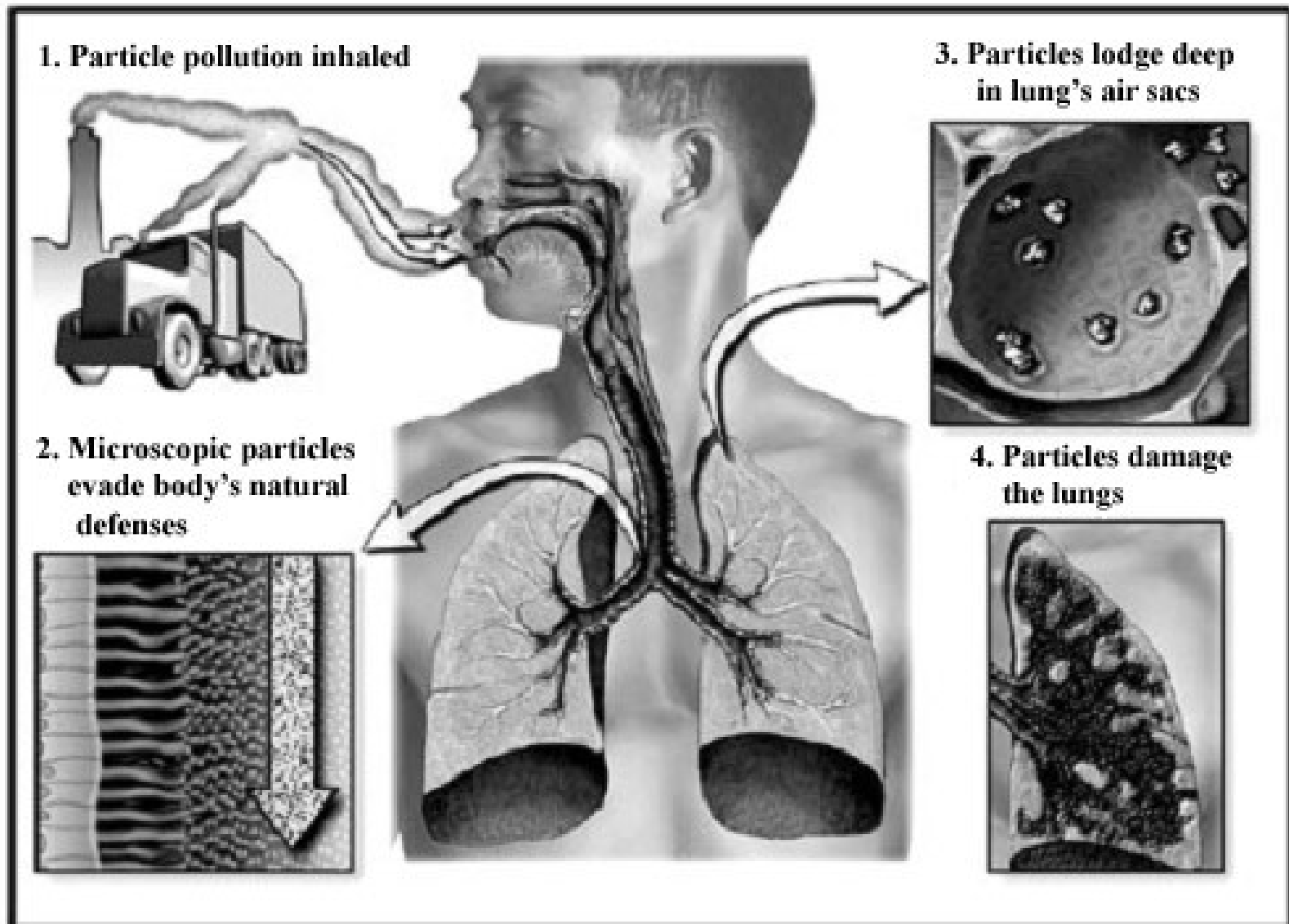


**Figure 18-4** Temperature inversions cause pollutants to build up because trapped cool air cannot rise to carry pollutants away.



# Air Pollution and allergies

- The increased rates of allergy and asthma in city environments and in those living close to highways has drawn attention to the role of outdoor pollution.
- Common air pollutants, such as ozone, sulfur dioxide, and nitrogen dioxide probably act more as irritants than as promoters of sensitization.
- These pollutants have been shown to be hazardous to adults and children with asthma. Recent studies suggest that prematurely born children are more sensitive to the respiratory effects of outdoor pollution.
- There may also be an association with diesel exhaust particles and the worldwide increase in respiratory allergies. Diesel exhaust has been shown to enhance the ability to make the allergy antibody in response to exposure to allergens.



[http://www.mde.state.md.us/programs/ResearchCenter/Report sandPublications/Pages/ResearchCenter/publications/general\\_mde/vol1no12/particlepollution\\_photo.aspx](http://www.mde.state.md.us/programs/ResearchCenter/Report%20sandPublications/Pages/ResearchCenter/publications/general_mde/vol1no12/particlepollution_photo.aspx)

# Control of Sulfur Oxides

# Control Techniques

## Introduction

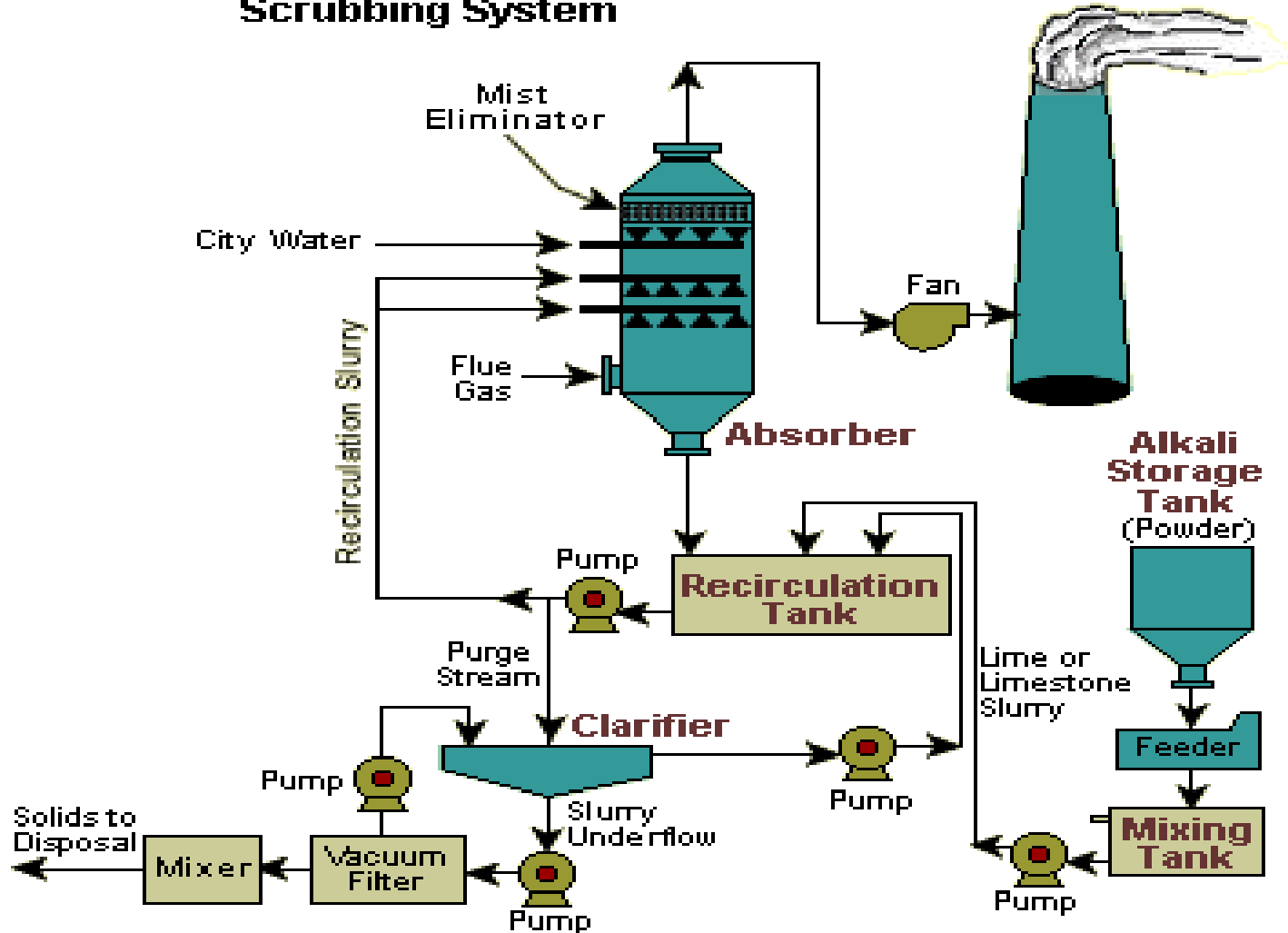
- Air pollution control systems for sulfur dioxide removal are large and sophisticated. Sulfur dioxide is controlled by three different techniques: absorption, adsorption, and the use of low-sulfur fuels.
- The control systems used for sulfur dioxide are usually not designed to remove sulfuric acid.
- The sulfuric acid concentrations are usually below the levels where it is not economically feasible or environmentally necessary to install control systems.

# Absorption

- Absorption processes use the solubility of sulfur dioxide in aqueous solutions to remove it from the gas stream.
- Once sulfur dioxide has dissolved in solution to form sulfurous acid ( $\text{H}_2\text{SO}_3$ ), it reacts with oxidizers to form inorganic sulfites ( $\text{SO}_3$ ) and sulfates ( $\text{SO}_4$ ).
- This process prevents the dissolved sulfur dioxide from diffusing out of solution and being re-emitted.
- The most common type of sulfur dioxide absorber is the limestone ( $\text{CaCO}_3$ ) wet scrubber.

- An example flowchart is shown in the figure.

**Figure 1. Example Flowchart of a Limestone-Based SO<sub>2</sub> Scrubbing System**



- Limestone is the alkali most often used to react with the dissolved sulfur dioxide.
- Limestone slurry is sprayed into the sulfur dioxide-containing gas stream.
- The chemical reactions in the recirculating limestone slurry and reaction products must be carefully controlled in order to maintain the desired sulfur dioxide removal efficiency and to prevent operating problems.

## Wet scrubbers used for sulfur dioxide control

- Wet scrubbers used for sulfur dioxide control usually operate at liquid pH levels between 5 to 9 to maintain high efficiency removal.
- Typical removal efficiencies for sulfur dioxide in wet scrubbers range from 80 to 95%.
- The wet scrubber (absorber) vessels do not efficiently remove particulate matter smaller than approximately 5 micrometers.
- In the case with low-efficiency particulate wet scrubbers, the particulate removal efficiency increases rapidly with particle size above 5 micrometers
- A moderate-to-high efficiency particulate control system is used upstream from the sulfur dioxide absorber to reduce the particulate matter emissions in the less than 3 micrometer size range.
- These upstream collectors also reduce the quantity of particulate matter that is captured in the absorber.

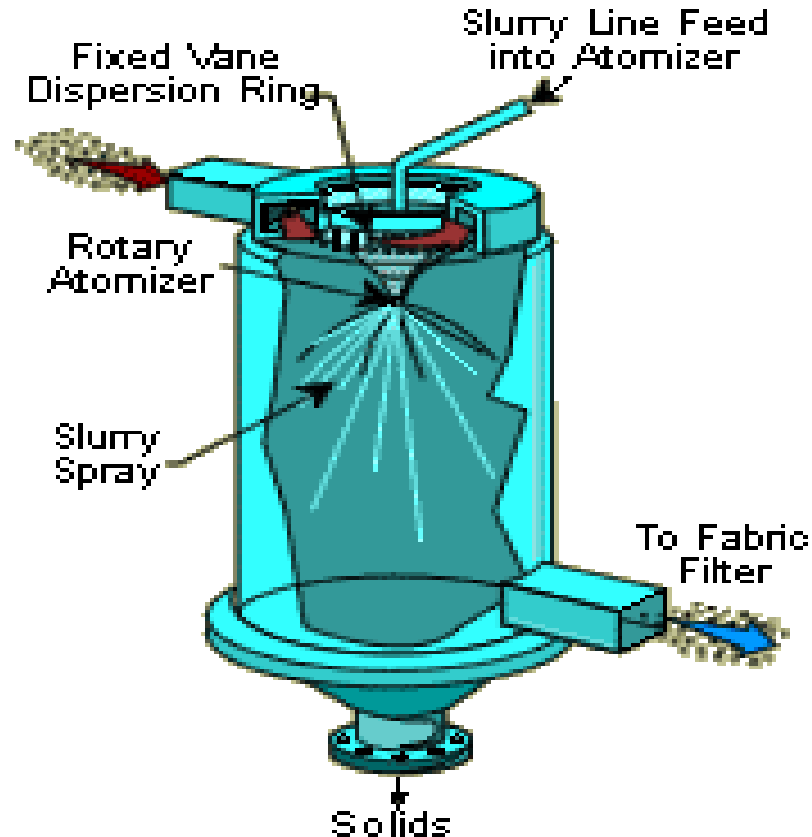


## spray atomizer dry scrubber

- Another type of absorption system is called a spray atomizer dry scrubber (see Figure 2), which belongs to a group of scrubbers called spray-dryer-type dry scrubbers.

In this case, an alkaline slurry is sprayed into the hot gas stream at a point upstream from the particulate control device. As the slurry droplets are evaporating, sulfur dioxide absorbs into the droplet and reacts with the dissolved and suspended alkaline material.

**Figure 2. Spray Atomizer Dry Scrubber**

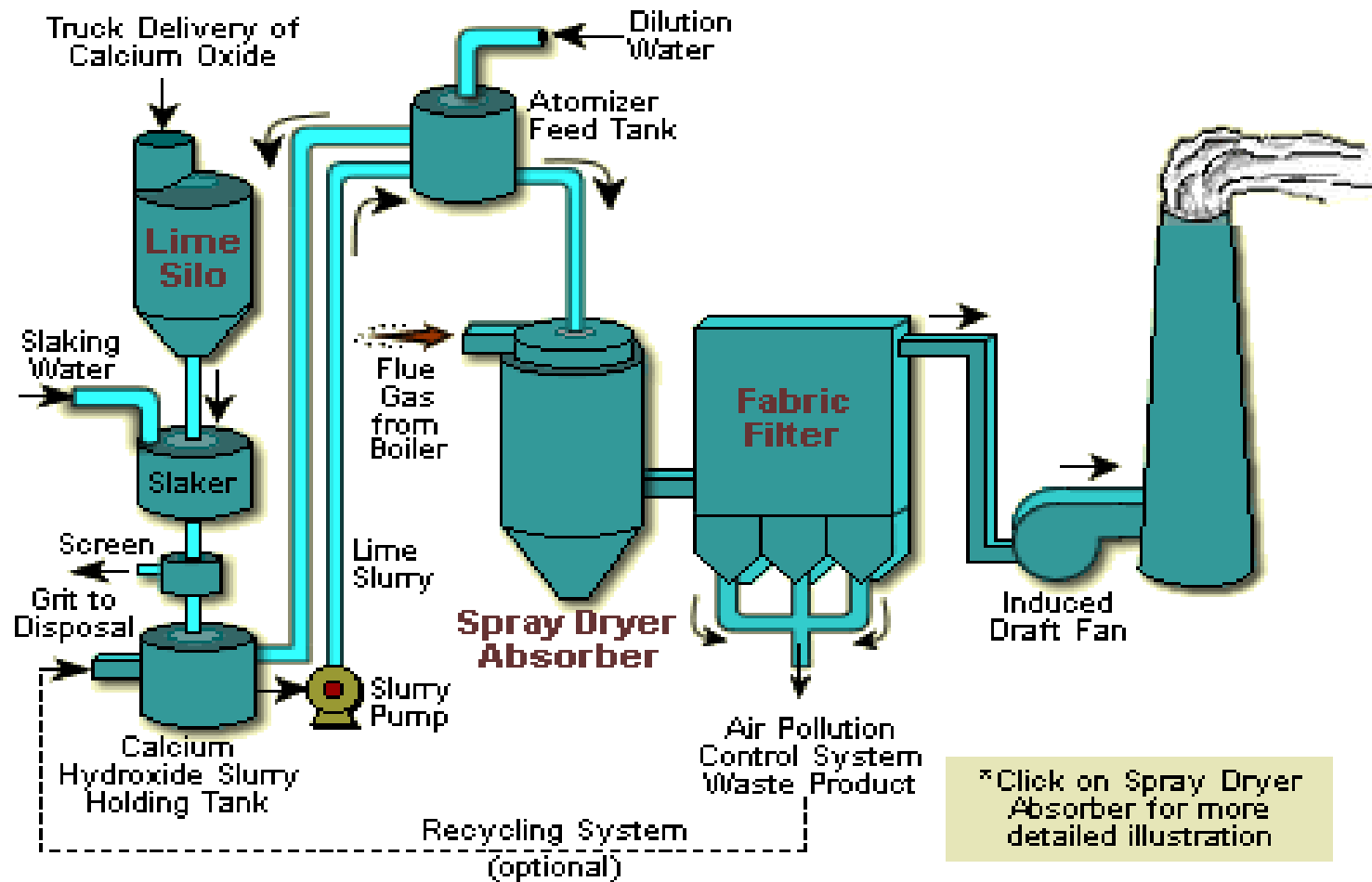


## spray atomizer dry scrubber II

- Large spray dryer chambers are used to ensure that all of the slurry droplets evaporate to dryness prior to going to a high efficiency particulate control system.
- The term "dry scrubber" refers to the condition of the dried particles approaching the particulate control system.
- Fabric filters or electrostatic precipitators are often used for high efficiency particulate control.
- The system shown in Figure 3 has a fabric filter.

# spray atomizer dry scrubber with a fabric filter

**Figure 3. Spray-Dryer-Type Dry Scrubber**



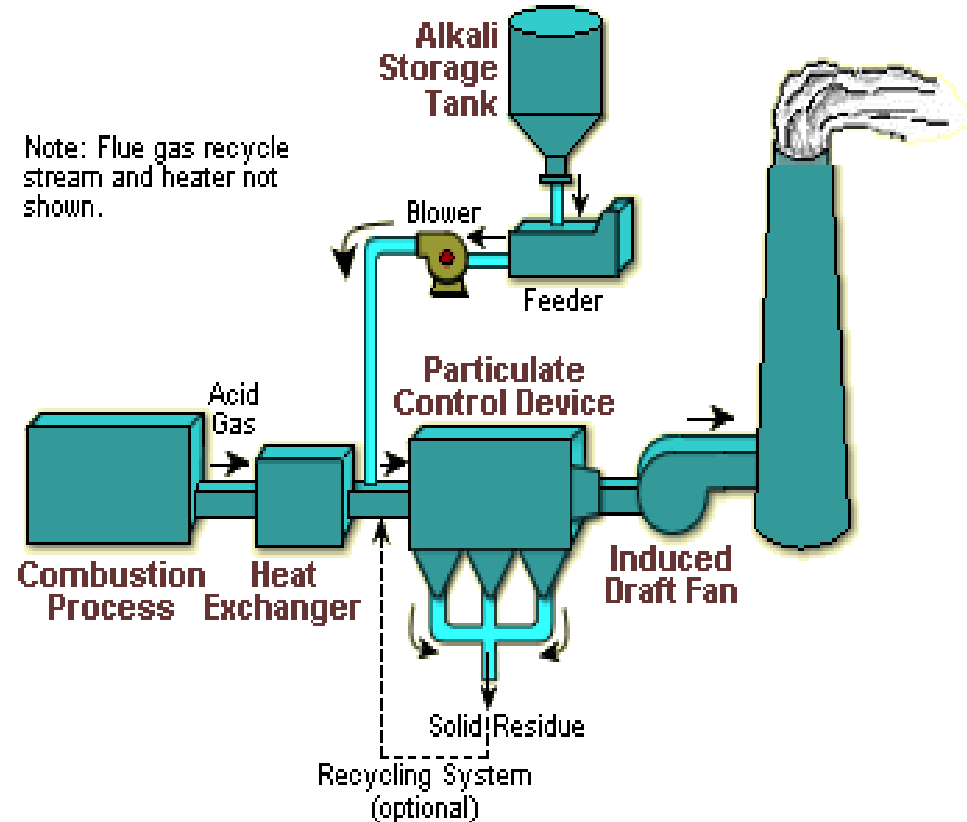
- Spray-dryer-type absorption systems have efficiencies that are similar to those for wet-scrubber-type absorption systems.
- These generate a waste stream that is dry and, therefore, easier to handle than the sludge generated in a wet scrubber.
- The equipment used to atomize the alkaline slurry is complicated and can require considerably more maintenance than the wet scrubber systems.
- Spray-dryer-type absorption systems operate at higher gas temperatures than wet scrubbers do and are less effective for the removal of other pollutants in the gas stream such as condensable particulate matter.
- The choice between a wet-scrubber absorption system and a spray-dryer absorption system depends primarily on site-specific costs.
- The options available for environmentally sound disposal of the waste products are also an important consideration in selecting the type of system for a specific application.
- Both types of systems are capable of providing high efficiency sulfur dioxide removal.

# Adsorption

- Sulfur dioxide can be collected by adsorption systems.

In this type of control system, a dry alkaline powder is injected into the gas stream. Sulfur dioxide adsorbs to the surface of the alkaline particles and reacts to form compounds that cannot be re-emitted to the gas stream. Hydrated lime (calcium hydroxide) is the most commonly used alkali.

Figure 4. Dry-Injection-Type Dry Scrubber



- However, a variety of alkalis can be used effectively.
- A flowchart for a dry-injection-type dry scrubber (adsorber) is shown in Figure 4.
- A dry-injection-type dry scrubber can be used on smaller systems as opposed to using the larger, more complicated spray-dryer-type dry scrubber.
- However, the dry injection system is slightly less efficient, and requires more alkali per unit of sulfur dioxide (or other acid gas) collected.
- Accordingly, the waste disposal requirements and costs are higher for adsorption systems than absorption systems.

# Alternative Fuels

- Other techniques used for limiting the emissions of sulfur dioxide are simply to switch to fuels that have less sulfur or to convert to synthetic (processed) fuels that have low sulfur levels.
- The sulfur dioxide emission rate is directly related to the sulfur levels in coal, oil, and synthetic fuels.
- Not all boilers can use these types of fuels.
- Each type of boiler has a number of very specific and important fuel characteristic requirements and not all low sulfur fuels meet these fuel-burning characteristics.

# References I

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