

西南交通大学
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Control of Sulfur Oxides

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15.1 Introduction

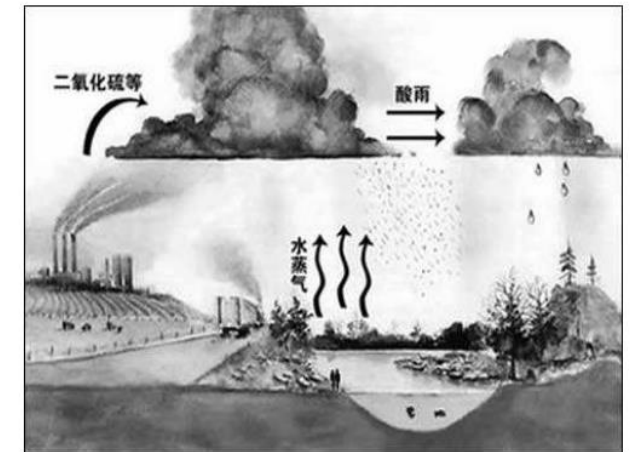
◆ Sulfur Oxides (SO_x) : SO_2 and SO_3

◆ Serious effects of emissions of SO_x to the atmosphere:

- Respiratory illnesses
- Loss of chlorophyll in green plants
- Acidic deposition

◆ Emission sources in the U. S.

- Coal-fired power Plants
- Industrial fuel combustion (petroleum refining)
- Industrial processes (H_2SO_4 manufacturing, and smelting of nonferrous metals)



15.1 Introduction

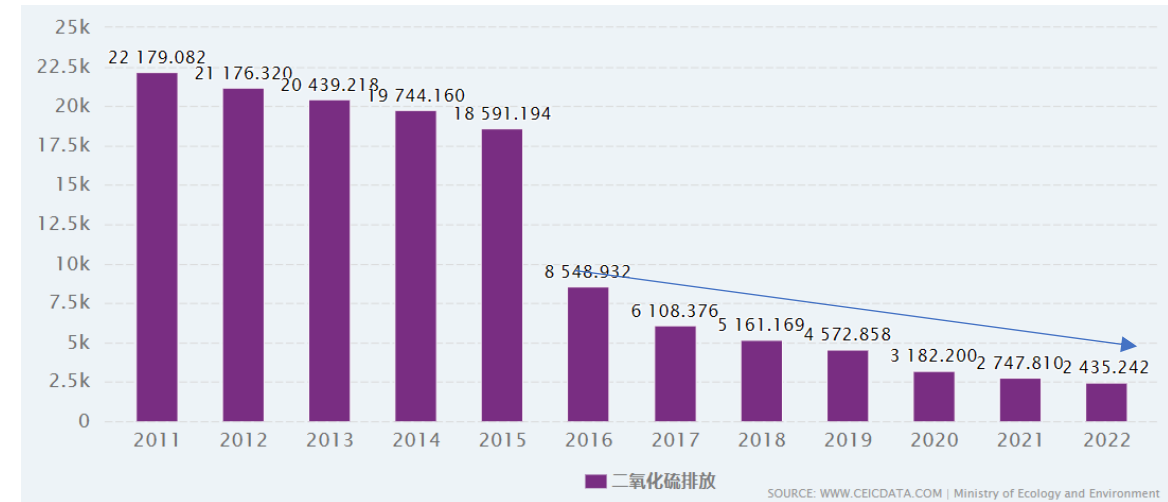
◆ Reductions in SO_x emissions

Trend in USA Emissions of SO₂
(1970-2023)

| Source Category | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| FUEL COMB. ELEC. UTIL. | 4,636 | 3,412 | 3,297 | 3,253 | 2,304 | 1,562 | 1,382 | 1,310 | 1,015 | 836 | 990 | 903 |
| FUEL COMB. INDUSTRIAL | 682 | 658 | 614 | 520 | 441 | 433 | 376 | 357 | 331 | 248 | 247 | 236 |
| FUEL COMB. OTHER | 219 | 210 | 196 | 120 | 112 | 52 | 44 | 43 | 44 | 28 | 29 | 29 |
| CHEMICAL & ALLIED PRODUCT MFG | 126 | 126 | 122 | 123 | 113 | 111 | 111 | 106 | 96 | 82 | 81 | 72 |
| METALS PROCESSING | 144 | 144 | 114 | 105 | 99 | 85 | 85 | 74 | 64 | 50 | 51 | 53 |
| PETROLEUM & RELATED INDUSTRIES | 122 | 120 | 94 | 86 | 84 | 101 | 86 | 95 | 91 | 189 | 195 | 194 |
| OTHER INDUSTRIAL PROCESSES | 188 | 188 | 186 | 167 | 153 | 139 | 146 | 145 | 136 | 125 | 131 | 127 |
| SOLVENT UTILIZATION | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| STORAGE & TRANSPORT | 9 | 9 | 7 | 3 | 1 | 4 | 1 | 1 | 1 | 1 | 1 | 1 |
| WASTE DISPOSAL & RECYCLING | 25 | 25 | 25 | 25 | 25 | 24 | 25 | 25 | 25 | 36 | 36 | 35 |
| HIGHWAY VEHICLES | 27 | 28 | 27 | 28 | 27 | 26 | 24 | 23 | 17 | 10 | 9 | 10 |
| OFF-HIGHWAY | 119 | 83 | 83 | 84 | 26 | 24 | 27 | 27 | 27 | 15 | 18 | 18 |
| MISCELLANEOUS | 130 | 112 | 85 | 85 | 117 | 135 | 201 | 205 | 118 | 224 | 281 | 176 |
| Total | 6,428 | 5,117 | 4,850 | 4,598 | 3,502 | 2,696 | 2,508 | 2,411 | 1,965 | 1,845 | 2,068 | 1,853 |
| Wildfires | 45 | 44 | 21 | 24 | 66 | 72 | 102 | 104 | 26 | 141 | 174 | 67 |
| Total without wildfires | 6,383 | 5,073 | 4,830 | 4,575 | 3,437 | 2,624 | 2,407 | 2,307 | 1,939 | 1,704 | 1,894 | 1,786 |
| Miscellaneous without wildfires | 85 | 67 | 64 | 61 | 52 | 63 | 100 | 101 | 92 | 83 | 107 | 109 |

Source: Air Pollutant Emissions Trends Data | US EPA

Trend in CHN Emissions of SO₂
(2011-2022)



Source: <https://www.ceicdata.com.cn/zh-hans/china/industrial-waste-air-emission/cn-sulphur-dioxide-emission>

15.2 Overview of Control Strategies

◆ Two basic approaches to controlling SO_x emissions

(1) Remove sulfur from fuel before it is burned →

(2) Remove SO_2 from the exhaust gases

| Main Option | Suboption | Examples of Processes |
|---|---|--|
| Do not create SO_2 | Switch to a low-sulfur fuel Desulfurize the fuel | Convert to natural gas Oil desulfurization Coal cleaning |
| SO ₂ scrubbing: Throwaway | Wet scrubbing | Lime Limestone Forced oxidation Inhibited oxidation Dual alkali Magnesium Enhanced Lime (MEL) Seawater |
| | Dry scrubbing | Lime spray drying Lime injection Trona Nahcolite Circulating fluidized bed |
| | Regenerative | Absorption with water (smelters) Wellman-Lord MgO Citrate Carbonate Sulfite Forced oxidation (with gypsum sales) |
| | Dry processes | Activated carbon adsorption Copper oxide adsorption |



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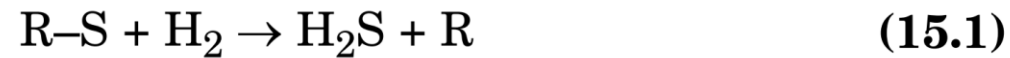
02 | Fuel Desulfurization



15.2.1 Fuel Desulfurization

◆ Oil desulfurization: diesel and gasoline for motor vehicle fuels (1-3% S)

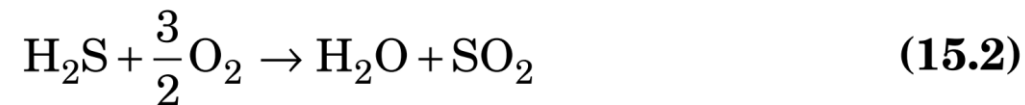
- **Desulfurization units:** remove organic sulfur from oil via a catalytic reaction with hydrogen



where R represents any organic group.

🗨️ When the H_2S was burned as part of the fuel gas, it produced SO_2

- **Recovery units (Claus process):** part of the H_2S is burned to SO_2 , and then the two compounds are combined over a catalyst to simultaneously oxidize and reduce each other.



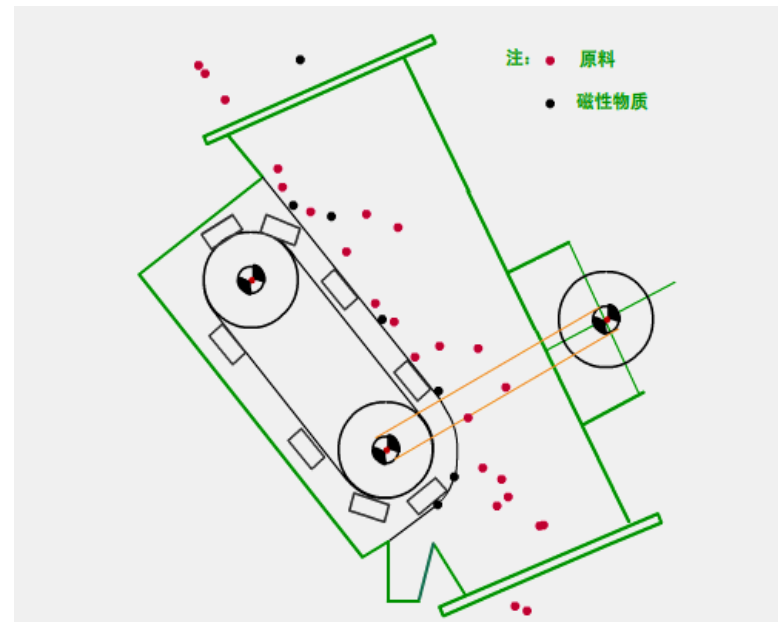
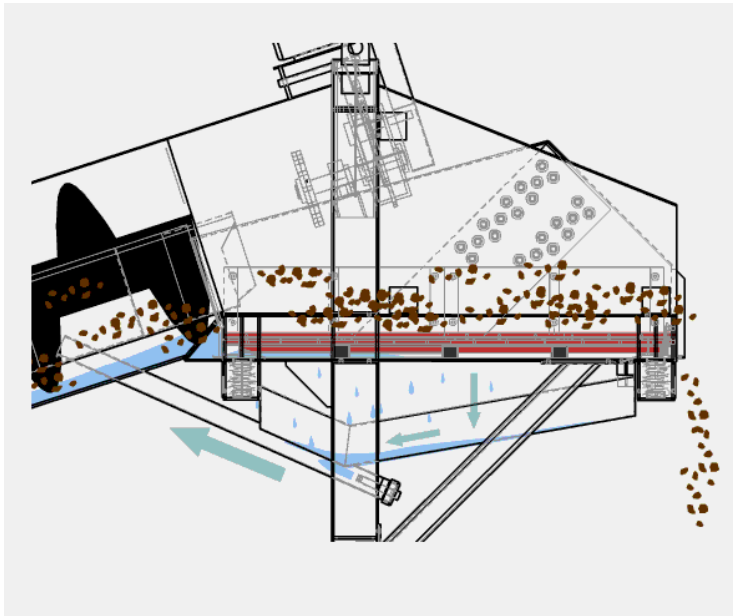
- Also for **Natural gas** (before the gas is admitted to pipelines)

👍 The elemental sulfur is separated in the molten state and sold as a by-product, and the emissions of either H_2S or SO_2 from a refinery are reduced substantially.

15.2.1 Fuel Desulfurization

◆ Coal cleaning (2%+ S)

- **Sulfur in mineral form (pyrites (FeS_2) or mineral sulfates):**
removed relatively easily by washing or other physical cleaning processes



- **Organic sulfur:** Coal gasification and liquefaction processes



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04 | Flue Gas Desulfurization



15.2.2 SO₂ Removal Techniques

(1) Remove sulfur from fuel before it is burned

(2) Remove SO₂ from the exhaust gases

- **Flue Gas Desulfurization**

A stream of gas that is dilute in SO₂ (about 0.2% or 2000 ppm SO₂).

- **Absorption of smelter off-gases:**

Oxidize the SO₂ to SO₃ gas, and then absorb the SO₃ in water to make H₂SO₄, which can be sold as a by-product.

A concentrated stream of SO₂ (about 10% or 100,000 ppm SO₂)

| Main Option | Suboption | Examples of Processes |
|---|---|--|
| Do not create SO ₂ | Switch to a low-sulfur fuel Desulfurize the fuel | Convert to natural gas Oil desulfurization Coal cleaning |
| SO ₂ scrubbing: Throwaway | Wet scrubbing | Lime Limestone Forced oxidation Inhibited oxidation Dual alkali Magnesium Enhanced Lime (MEL) Seawater |
| | Dry scrubbing | Lime spray drying Lime injection Trona Nahcolite Circulating fluidized bed |
| | Regenerative | Absorption with water (smelters) Wellman-Lord MgO Citrate Carbonate Sulfite Forced oxidation (with gypsum sales) |
| | Dry processes | Activated carbon adsorption Copper oxide adsorption |

15.2.2 Flue Gas Desulfurization

The phase in which the main reactions occur

wet

- Limestone scrubbing
- Lime scrubbing
- Forced oxidation/inhibited oxidation
- Dual alkali

dry

- Lime-spray drying
- Dry injection

◆ Throwaway Processes

The sulfur removed from the exhaust gas is discarded.

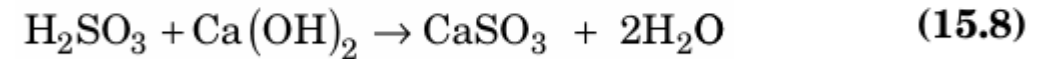
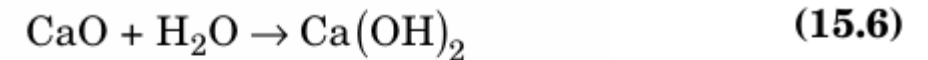
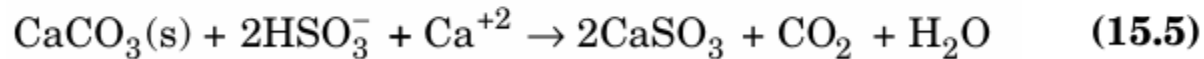
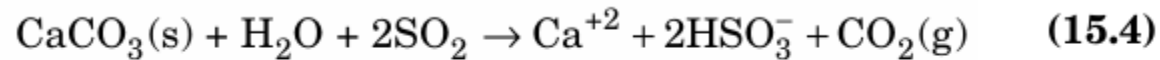
◆ Regenerative Processes

The sulfur is recovered in a usable form.

15.2.2 Flue Gas Desulfurization (wet)

◆ Limestone/lime Scrubbing

- **Principle:** a limestone/lime slurry is contacted with the flue gas in a spray tower. The sulfur dioxide is **absorbed, neutralized, and partially oxidized** to calcium sulfite and calcium sulfate.



👍 Absorbent is abundant and inexpensive.

👎 Scaling inside the tower, equipment plugging, and corrosion.

*lime is a much more reactive reagent than limestone

👍 Better utilization of the reagent and more flexibility in operations.

👎 High cost of lime relative to limestone.

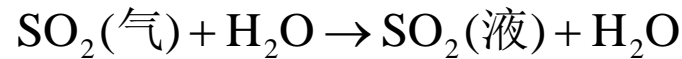
Now, both lime and limestone systems can achieve **efficiencies of 98–99%**.

15.2.2 Limestone/lime Scrubbing

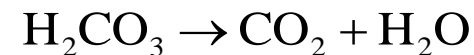
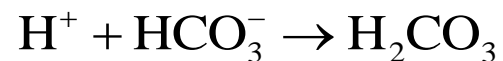
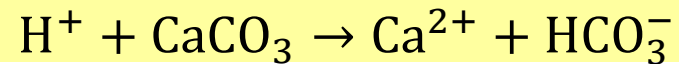
➤ Net reaction



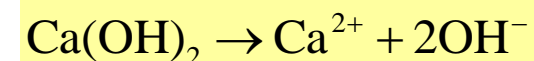
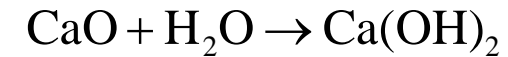
1. Dissolution of SO_2 (slow)



2. Dissociation of limestone/lime (key)

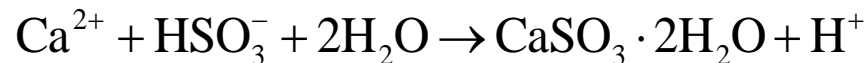


Influenced by
pH (5.8-6.2)

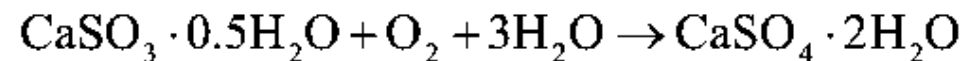


Lime dissociates
more easily,
regardless of pH

3. Absorption

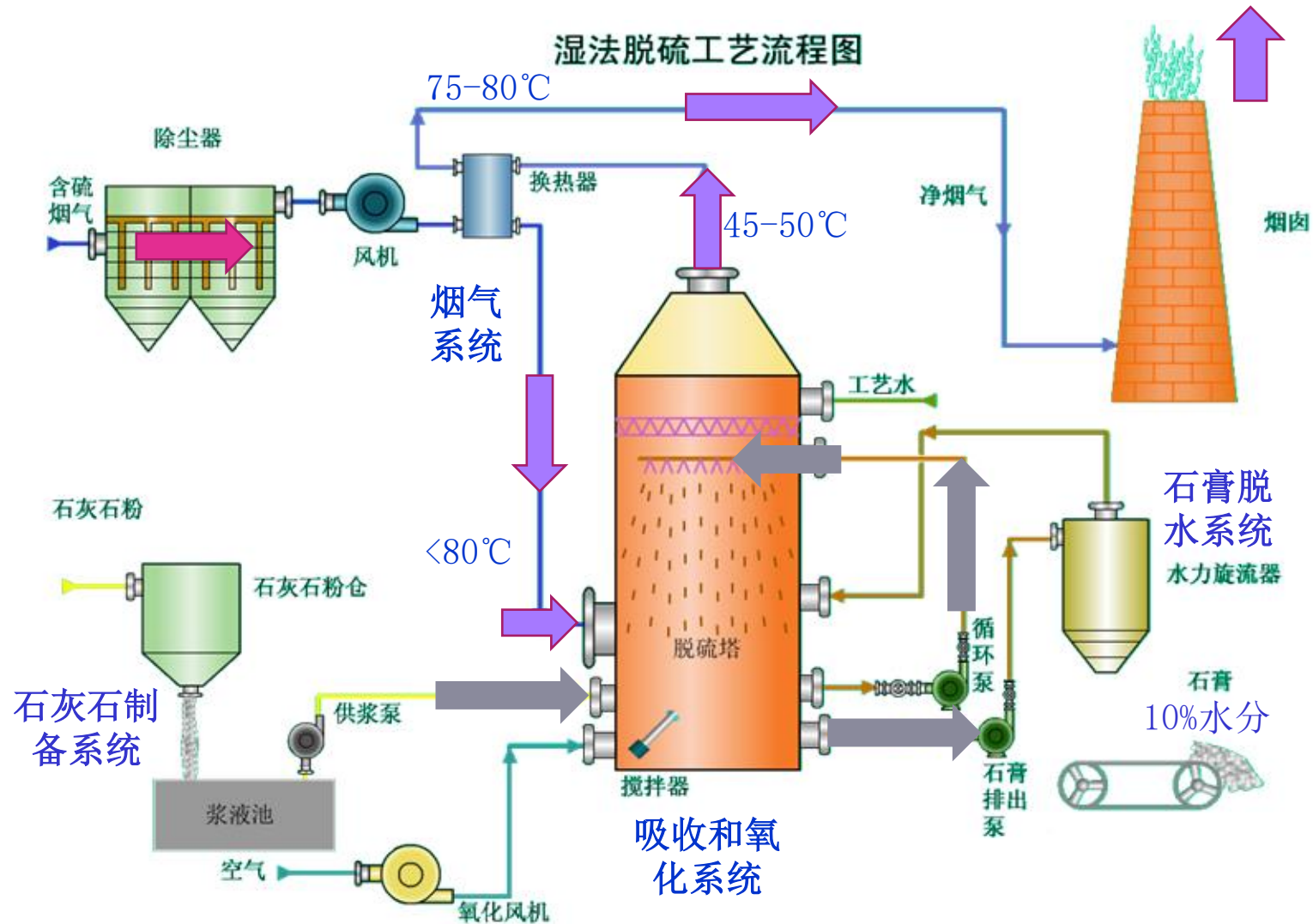


4. Partially oxidization (Excess oxygen)



15.2.2 Limestone Scrubbing (wet)

Widely accepted by the coal-fired power industry: lower cost and simpler to operate



15.3 Process Chemistry

◆ Maximize SO₂ removal

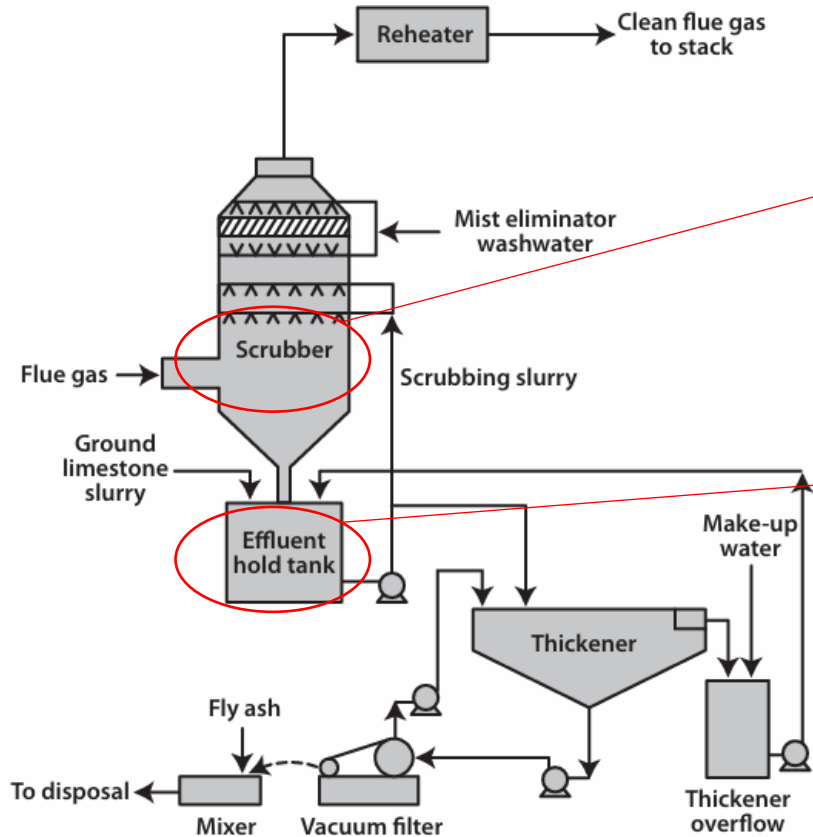


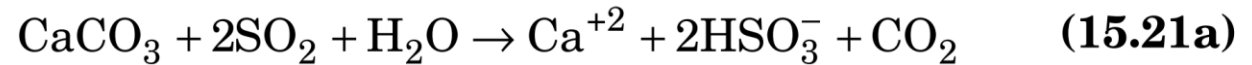
Figure 15.1

Schematic process flow diagram for a limestone-based SO₂ scrubbing system.

(Adapted from Henzel et al., 1981.)

➤ Avoid scaling

- Providing two separate working areas within the same vessel: the scrubber and the effluent hold tank



If an excessive amount of CaCO₃ is input, the bisulfite ion will not be stable, and **CaSO₃ will precipitate** inside the scrubber (forming scale). If the pH is too low (less than about 4.5), **SO₂ absorption** will be adversely affected.



➤ Maximize the utilization of the limestone

- Proper pH control
- Using finely ground limestone
- A sufficiently high liquid/gas ratio

Excess oxygen results in CaSO₄ (gypsum). Maintain a high liquid/gas ratio can **prevent Gypsum precipitation** in the scrubber

15.2.2 Flue Gas Desulfurization (wet)

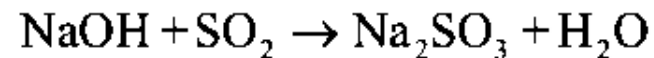
◆ Dual Alkali System (wet)



Use **two reagents** and two process loops to **eliminate scaling and plugging** inside the scrubbing tower encountered with limestone/lime scrubbing

Principle:

1. A solution of sodium sulfite (Na_2SO_3)/sodium hydroxide (NaOH) provides the **absorption**/neutralization of SO_2 inside the tower.



Both sodium sulfite (Na_2SO_3) and sodium sulfate (Na_2SO_4) are soluble in water, no precipitation occurs inside the scrubber.

👍 Reduce scaling and plugging and lower maintenance costs.

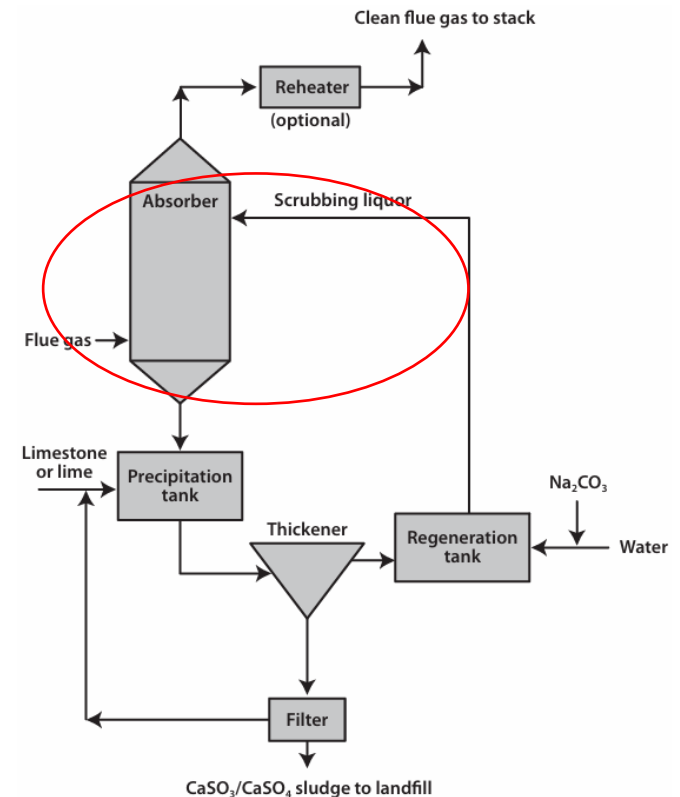
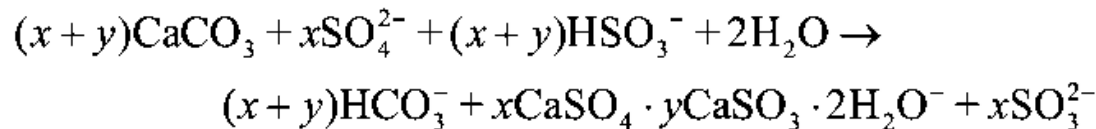
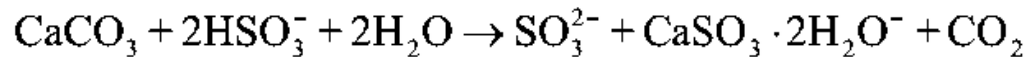
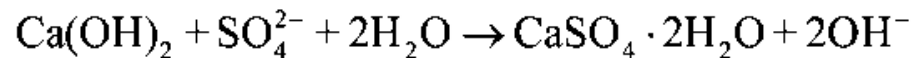
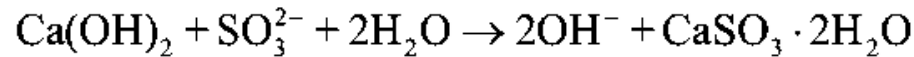
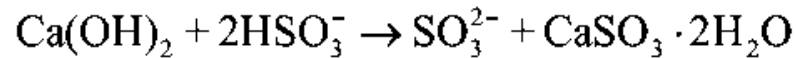


Figure 15.2
Schematic process flow diagram for a dual alkali FGD system.

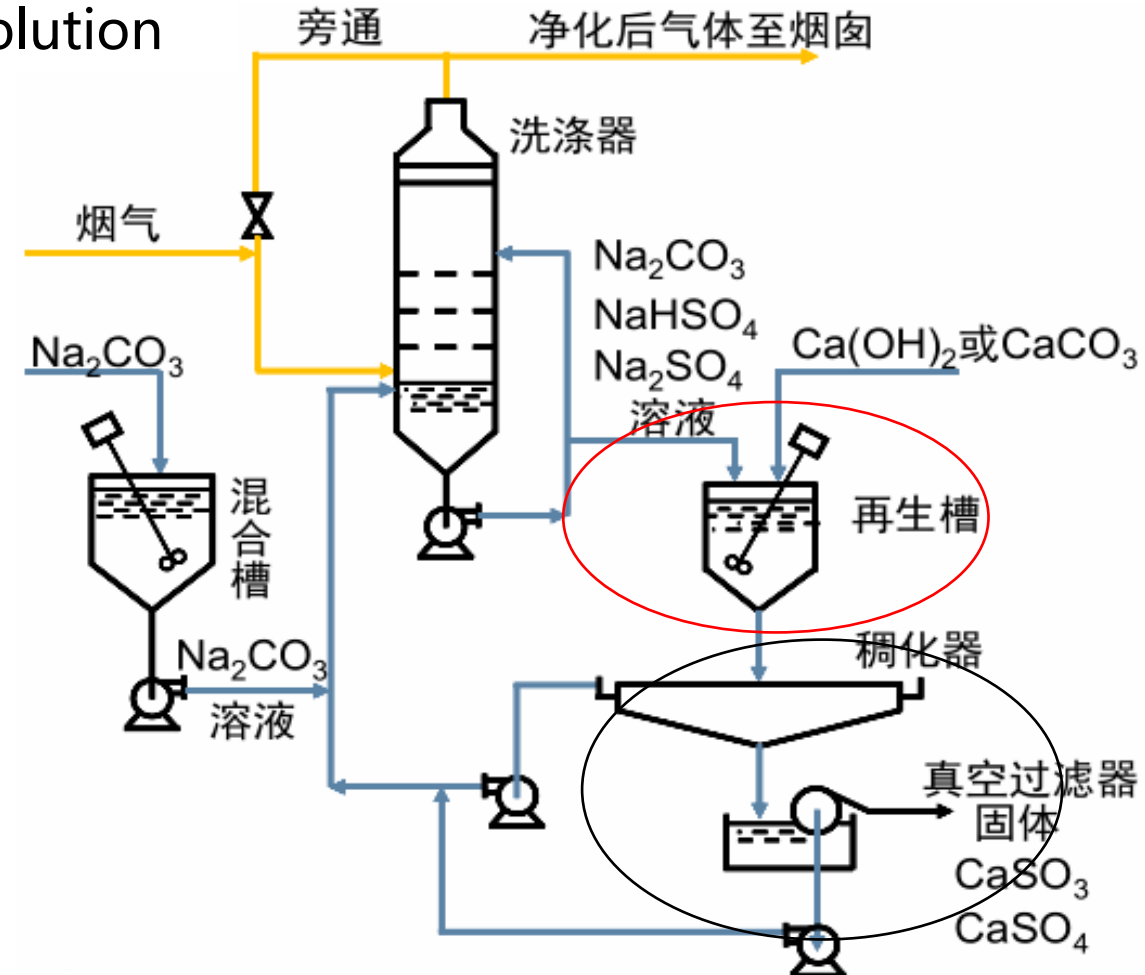
15.2.2 Dual Alkali System (wet)

Disposal of large volumes of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ solution would pose a water pollution problem.

- Lime or limestone is added to the scrubber effluent to simultaneously **precipitates** the sulfite/sulfate ions and **regenerates** the sodium hydroxide in a separate vessel.



👎 Need an elaborate treatment or disposal system for the soluble sodium salts; great sodium consumption.



15.2.2 Flue Gas Desulfurization (wet)

◆ Forced Oxidation (external) System

- **Principle:** Conventional limestone + $\text{CaSO}_3/\text{SO}_4$ waste slurry is **oxidized (via excess air contact)** in a separate tank) to a gypsum sludge.
- 👍 The oxidized waste is more easily de-watered and is more stable in sludge disposal ponds.
- 👎 high pumping costs and is prone to plugging and scaling.

◆ Inhibited Oxidation System

- **Principle:** Adding a fine water emulsion of elemental sulfur/a small amount of EDTA to **inhibit the oxidation of SO_2 to sulfate**.
- 👍 Prevents scaling, requires less operating power/maintenance, and uses less fresh water than forced oxidation.

15.3 Operational Factors

➤ Chemical Parameters

$$\frac{N}{A} = K_g (\bar{P}_{\text{SO}_2} - H_{\text{SO}_2} C_{\text{SO}_2}) \quad (15.26)$$

where K_g = overall gas phase transfer coefficient

In Eq. (15.26), K_g is given by

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{H_{\text{SO}_2}}{\phi k_l} \quad (15.27)$$

$$\frac{N}{A} = \text{flux of SO}_2, \text{ mol/s-cm}^2$$

$$k_g = \text{local mass transfer coefficient, mol/(s-cm}^2\text{-atm)}$$

$$\bar{P}_{\text{SO}_2} = \text{partial pressure of SO}_2 \text{ in the bulk gas, atm}$$

$$H_{\text{SO}_2} = \text{Henry's law constant, atm/(mol/L)}$$

$$k_l = \text{local mass transfer coefficient, mol/(s-cm}^2\text{-mol/L)}$$

$$C_{\text{SO}_2} = \text{concentration of SO}_2 \text{ in the bulk liquid, mol/L}$$

ϕ = an enhancement factor to account for chemical reactions that permit SO_2 to diffuse through the liquid film as bisulfite or sulfite species as well as SO_2



Table 15.4 SO_2 Scrubber Chemical Parameters and Their Effects on the Enhancement Factor, ϕ

| Parameter | Effect on ϕ | | | | | | | | |
|--|--|-------------------------------|--------|-----|----|------|-----|------|-----|
| Gas composition | ϕ decreases as SO_2 concentration increases; for example, at pH 5.8, | | | | | | | | |
| | <table> <tr> <th>\bar{P}_{SO_2}, ppm</th><th>ϕ</th></tr> <tr> <td>500</td><td>10</td></tr> <tr> <td>1000</td><td>7.5</td></tr> <tr> <td>2000</td><td>5.8</td></tr> </table> | \bar{P}_{SO_2} , ppm | ϕ | 500 | 10 | 1000 | 7.5 | 2000 | 5.8 |
| \bar{P}_{SO_2} , ppm | ϕ | | | | | | | | |
| 500 | 10 | | | | | | | | |
| 1000 | 7.5 | | | | | | | | |
| 2000 | 5.8 | | | | | | | | |
| Bulk liquid sulfite and bisulfite concentrations | ϕ increases as $C_{\text{SO}_3^{2-}}$ increases; ϕ decreases as $C_{\text{HSO}_3^-}$ increases | | | | | | | | |
| pH | ϕ increases as pH increases. (Note: because the solution tends to be in equilibrium with CaSO_3 solids, $C_{\text{HSO}_3^-}$ decreases as pH increases; thus, the effect of pH is essentially that of $C_{\text{HSO}_3^-}$) | | | | | | | | |
| Alkali additives | ϕ increases as alkali species increase | | | | | | | | |
| Buffer additives (organic acids) | ϕ increases as buffer additives increase (ϕ values of 20–30 are achieved with as little as 10–15 mmol/L of adipic acid) | | | | | | | | |

15.3 Operational Factors

➤ Physical Factors

- **liquid/gas ratio (L/G):** the greater the L/G ratio, the greater the SO₂ absorption efficiency. (40 to 100 gal/1000 acf)
- **Proper gas and liquid flow distribution:** prevent scaling and promote good gas–liquid contact.
- **Finely ground limestone** (90% passing a 325-mesh screen)
- **Gas velocity:** mass transfer increases as gas velocity increases. But too high a flow rate will cause a decrease in contact time and incomplete absorption
-

15.2.2 Flue Gas Desulfurization

◆ Throwaway Processes

wet

- Limestone scrubbing
- Lime scrubbing
- Forced oxidation/inhibited oxidation
- Dual alkali

dry

- **Lime-spray drying**
- **Dry injection**

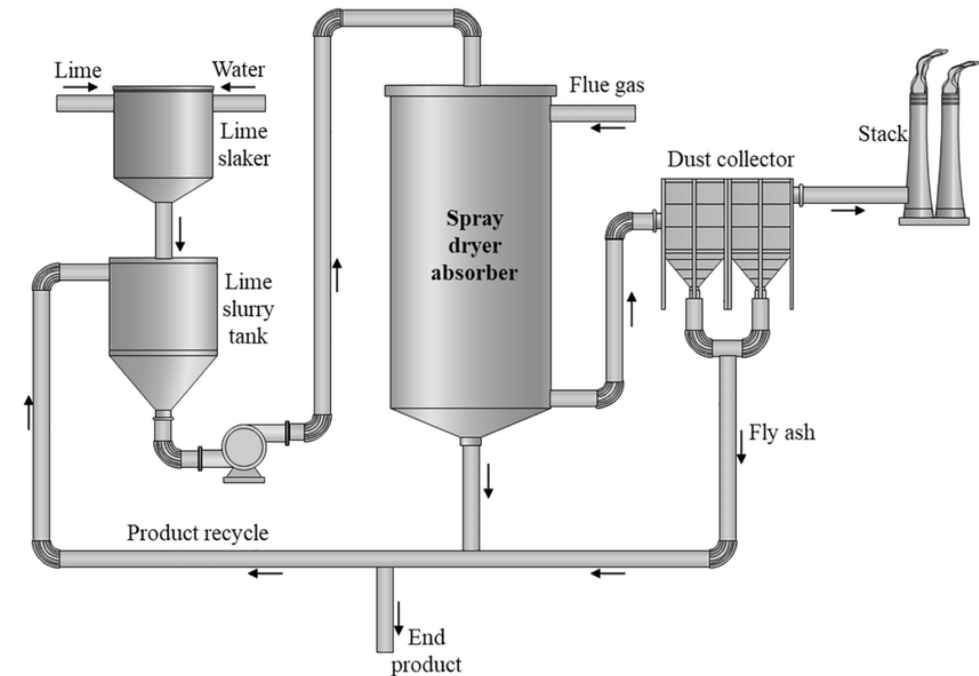
◆ Regenerative Processes

15.2.2 Flue Gas Desulfurization (wet/dry)

◆ Lime-Spray Drying

Principle:

- A lime slurry is sprayed into the absorption tower, and SO_2 is absorbed by the slurry, forming $\text{CaSO}_3/\text{CaSO}_4$.
- The water evaporates before the droplets reach the bottom of the tower.
- The dry solids are carried out with the gas and collected in a baghouse with the fly ash.



- 👍 Few maintenance problems, low energy usage, and low capital and operating costs.
- 👎 The potential to blind the fabric if the temperature of the flue gas approaches the dew point.

15.2.2 Flue Gas Desulfurization (dry)

◆ Dry Injection

Principle:

- The pulverized lime or limestone is injected into the flue gas.
- Dry sorption occurs and the solid particles are collected in a baghouse.
- Further SO₂ removal occurs as the flue gas flows through the filter cake on the bags.

👍 Low capital costs and low maintenance requirements, can collect mercury emissions.

👎 High reagent costs and possible waste disposal problems.

15.2.3 Flue Gas Desulfurization

◆ **Throwaway Processes**

◆ **Regenerative Processes**

wet

- **Wellman-lord (W-L) process**
- **Magnesium oxide**
- **Citrate scrubbing**

dry

- **Activated carbon adsorption**
- **Copper oxide adsorption**

15.2.3 Flue Gas Desulfurization (wet)

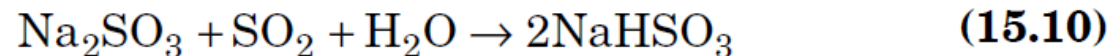
◆ Wellman-Lord (W-L) process

(1) Flue gas pretreatment

- remove most of the remaining particles as well as any existing SO₃ and HCl
- cool and humidifies the flue gas

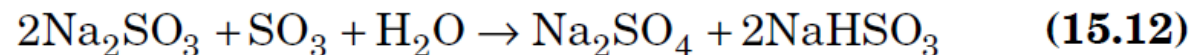
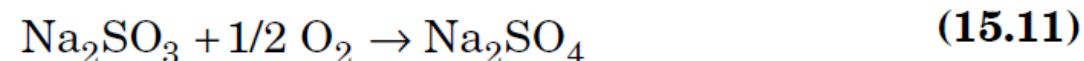
(2) SO₂ absorption

- The flue gas is contacted with aqueous sodium sulfite and the SO₂ is absorbed and reacted to form **sodium bisulfite**.



(3) Purge treatment

- Some of the sulfite is oxidized to sulfate by oxygen.
- SO₃ that passes through the prescrubber results in aqueous sulfate.

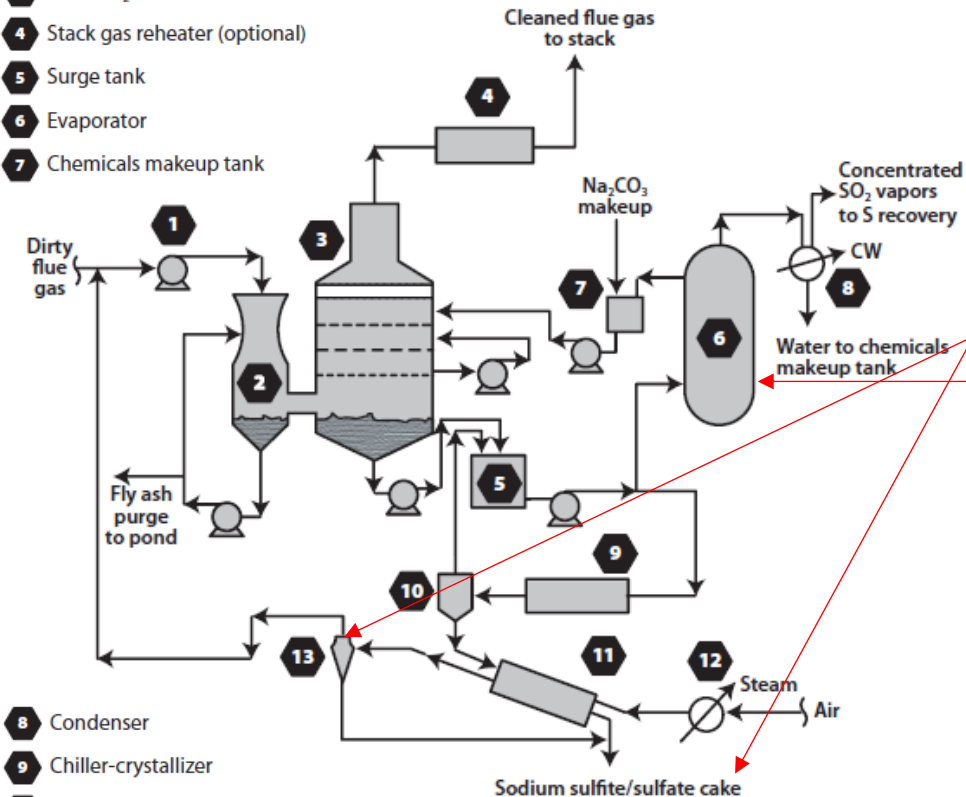


- The **sodium sulfate** does not contribute to further SO₂ absorption and must be removed.

15.2.3 Wellman-Lord (W-L) process

The stream from the bottom of the absorber is **rich in bisulfite** and is routed for further processing.

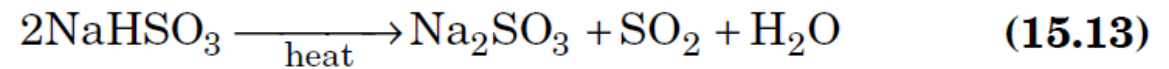
- 1 Blower (fan)
- 2 Venturi prescrubber
- 3 Main SO₂ scrubber
- 4 Stack gas reheater (optional)
- 5 Surge tank
- 6 Evaporator
- 7 Chemicals makeup tank



- 8 Condenser
- 9 Chiller-crystallizer
- 10 Centrifuge
- 11 Air dryer
- 12 Heater
- 13 Cyclone

(4) Sodium sulfite regeneration

- The slurry is centrifuged: the solids are dried and discarded, the centrifugate (rich in bisulfite) is returned to the process.
- **SO₂ is liberated and sodium sulfite crystals are regenerated.**



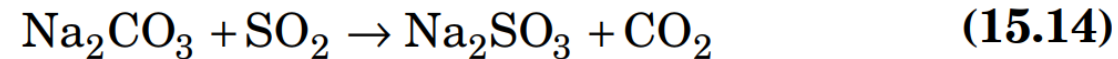
- The water vapor is condensed and recovered, producing a **concentrated stream of SO₂ gas**.

15.2.3 Wellman-Lord (W-L) process

(5) Processing to a marketable product

- The concentrated stream of SO₂ gas can be reduced to elemental sulfur or oxidized to sulfuric acid either on-site or at a nearby chemical plant.

***Make-up:** some of the sodium is removed from the process via the sodium sulfate purge, soda ash (Na₂CO₃) is added to provide make-up sodium.



15.2.3 Flue Gas Desulfurization (wet)

◆ Magnesium Oxide (MgO) Process

- **Principle:** a slurry of $\text{Mg}(\text{OH})_2$ produces $\text{MgSO}_3/\text{MgSO}_4$ solids. The solids are then calcined, generating SO_2 and regenerating MgO .

👍 Little solid waste, Flue gas pretreatment,

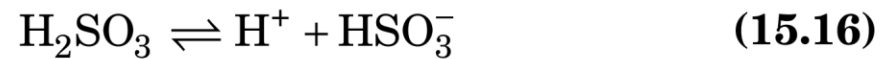
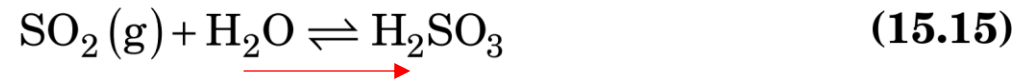
👎 A high-temperature calciner is needed.

15.2.3 Flue Gas Desulfurization (wet)

◆ Citrate-Scrubbing Processes

Principle:

- The citrate ions in solution increase the effective solubility of SO_2 by binding some of the hydronium ions created when SO_2 absorbs into water.



- As the citrate ions react with and remove hydronium ions in solution, the equilibria of Reactions are shifted to the right, promoting further SO_2 absorption.

15.2.3 Citrate-Scrubbing Processes

➤ Regenerating the solution/recovering the SO₂

□ **U.S. Bureau of Mines process:** the SO₂ is reduced with H₂S to elemental sulfur.

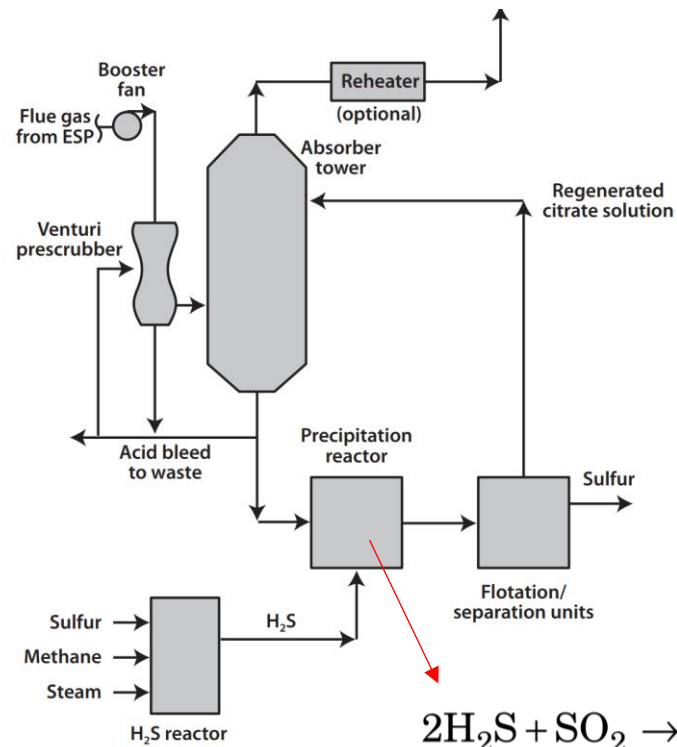
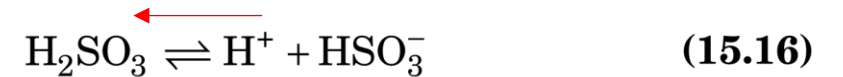


Figure 15.5
Simplified schematic diagram of the U.S. Bureau of Mines citrate FGD process.

□ **Flakt-Boliden process:** heating and steam-stripping the SO₂-loaded citrate solution, resulting SO₂-rich stream.



15.2.3 Flue Gas Desulfurization

◆ Throwaway Processes

◆ Regenerative Processes

wet

- Wellman-lord (W-L) process
- Magnesium oxide
- Citrate scrubbing

dry

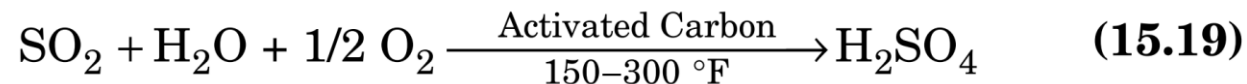
- **Activated carbon adsorption**
- **Copper oxide adsorption**

15.2.3 Flue Gas Desulfurization (dry)

◆ Activated Carbon Adsorption

Principle :

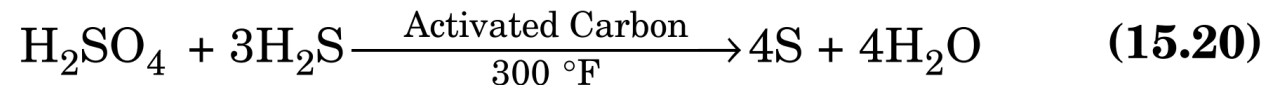
- The carbon **catalyzes the reaction of SO₂ to H₂SO₄**, thus preventing desorption of the SO₂.



- The carbon can be regenerated by **water washing**, producing a dilute sulfuric acid stream that often is neutralized and discarded.

Westvaco process:

- SO₂ is adsorbed onto carbon.
- The carbon flows to the next vessel, where the sulfuric acid is **reacted with hydrogen sulfide**, resulting in adsorbed elemental sulfur.



- ¼ Sulfur is vaporized and recovered. The remainder reacted with H₂ to generate the H₂S needed by Reaction (15.20) to regenerate the carbon.
- The regenerated carbon is then recycled back to the start.

15.2.3 Flue Gas Desulfurization (dry)

◆ Copper Oxide Adsorption

Principle :

- SO_x adsorption and reaction occurs at 750 °F to form copper sulfate.
- The bed is regenerated with a reducing gas (H_2 or $\text{H}_2 + \text{CO}$) to form a concentrated stream of SO_2 .
- The bed is reduced to copper, but is later oxidized to copper oxide when in the adsorption mode.



One of the few processes that can control both SO_2 and NO_x .

15.4 Mercury control

- **Wet flue gas desulfurization** has been shown to be able to remove some of the mercury.
 - The actual removal percentage depends on the percent of the mercury that is in **the oxidized state**: 50 to 80% of the oxidized mercury, none of the elemental mercury.
 - The total removal percentage for FGD systems: **20 to 60%** as the percent of oxidized mercury at the scrubber inlet goes from 15% to about 80%
- **Activated carbon** injected into the flue gas upstream of a baghouse achieves a higher mercury removal percentage

Cost Estimates

❑ Factors have affected the costs of FGD systems

- Size of plant
- Type of FGD process
- Type of project (new or retrofit)
- Percentage of sulfur in the coal
- Degree of removal required
- Access to and costs of raw materials(e.g., trona, limestone, steel, concrete, etc.)

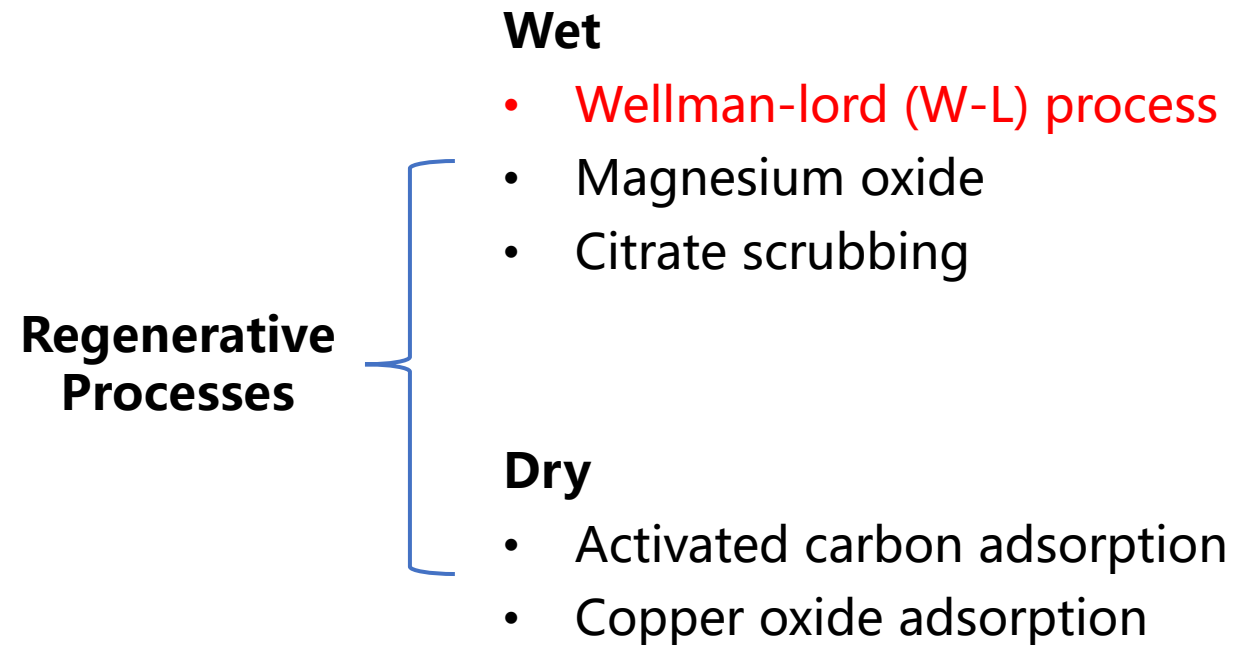
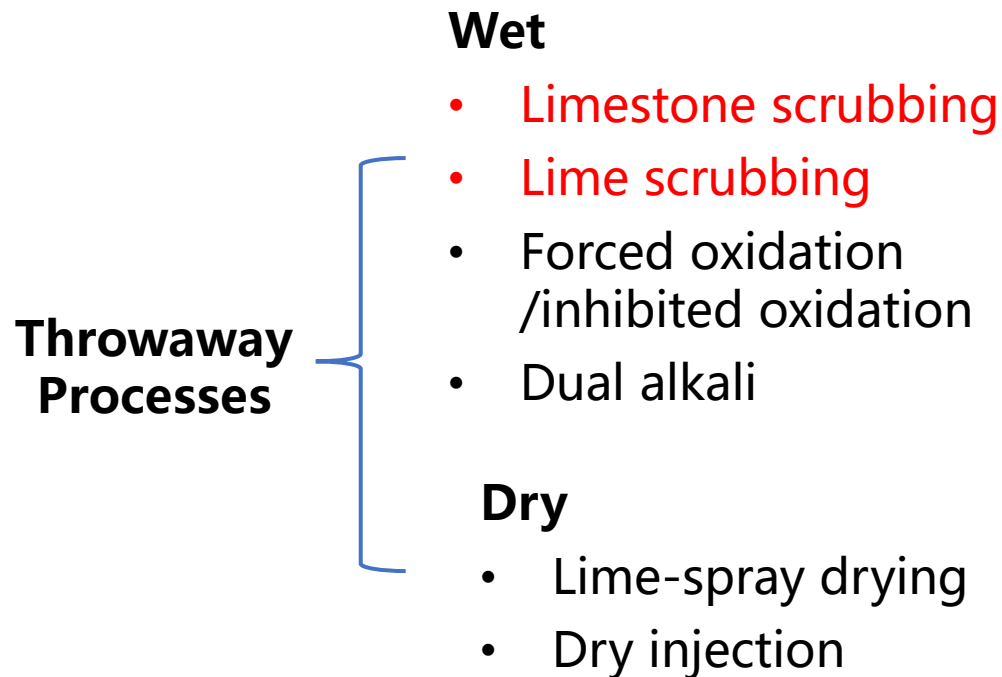
❑ An FGD scrubber represents a huge investment for a coal-fired power plant: as much as 20% of the total capital investment of the power plant.

Conclusions

□ Flue Desulfurization

- Convert to natural gas
- Oil desulfurization
- Coal cleaning

□ Flue Gas Desulfurization



Quiz

| | Principle | Advantages | Disadvantages |
|---------------------|-----------|------------|---------------|
| Limestone/ lime | | | |
| Dual Alkali | | | |
| Dry Injection | | | |
| Wellman- Lord | | | |
| Activated Carbon | | | |