Tikrit University

College of Petroleum Processes Engineering

Department of Petroleum and Gas Refining Engineering

Gas Technology

Forth Class

Lecture 12

By

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ACID GAS TREATING

1. Batch Type Processes

The most common type of process for acid gas removal is the batch type process and may involve a chemical process in which the acid gas reacts chemically with the cleaning agent, usually a metal oxide. These processes are not merely physical separation processes in which the acid gas is removed by a physical phenomenon, such as adsorption. Thus, the batch-type processes have the common requirement that the process be operated as a batch system where, at the end of the cycle, the chemical agent must be changed or regenerated in order to continue treating. Batch processes are limited to removing small amounts of sulfur, i.e., low gas flow rates and/or small concentrations of hydrogen sulfide.

1.1. Metal Oxide Processes

These processes scavenge hydrogen sulfide and organic sulfur compounds (mercaptans) from gas streams through reactions with solid-based media. They are typically nonregenerable, although some are partially regenerable, losing activity upon each regeneration cycle. Most dry sorption processes are governed by the reaction of a metal oxide with H2S to form a metal sulfide compound. For regenerable reactions, the metal sulfide compound can then react with oxygen to produce elemental sulfur and a regenerated metal oxide. The primary metal oxides used for dry sorption processes are iron oxide and zinc oxide.

1.1.1.   Iron Sponge Process

The iron sponge process is usually best applied to gases containing low to medium concentrations (300 ppm) of hydrogen sulfide or mercaptans. This process tends to be highly selective and does not normally remove significant quantities of carbon dioxide. As a result, the hydrogen sulfide stream from the process is usually high purity. Use of the iron sponge process for sweetening sour gas is based on adsorption of the acid gases on the surface of the solid sweetening agent followed by chemical reaction of ferric oxide (Fe_2O_3) with hydrogen sulfide:

$$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O$$

The reaction requires the presence of slightly alkaline water and a temperature below 43°C (110°F). A pH level on the order of 8–10 should be maintained through the injection of caustic soda with the water. The ferric sulfide produced by the reaction of hydrogen sulfide with ferric oxide can be oxidized with air to produce sulfur and regenerate the ferric oxide:

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S$$
$$S_2 + 2O_2 \rightarrow 2SO_2$$
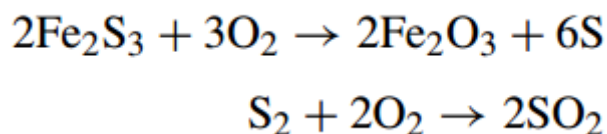
The regeneration step, i.e., the reaction with oxygen, is exothermic and air must be introduced slowly so the heat of reaction can be dissipated. If air is introduced quickly, the heat of reaction may ignite the bed. Some of the elemental sulfur produced in the regeneration step remains in the bed. After several cycles this sulfur will cake over the ferric oxide, decreasing the reactivity of the bed. Typically, after 10 cycles the bed must be removed and a new bed introduced into the vessel.

In the process as shown in Figure 1, the sour gas should pass down through the bed. In the case where continuous regeneration is to be utilized, a small concentration of air is added to the sour gas before it is processed. The number of vessels containing iron oxide can vary from one to four. In a two-vessel process, one of the vessels would be on stream removing hydrogen sulfide from the sour gas while the second vessel would either be in the regeneration cycle or having the iron sponge bed replaced.
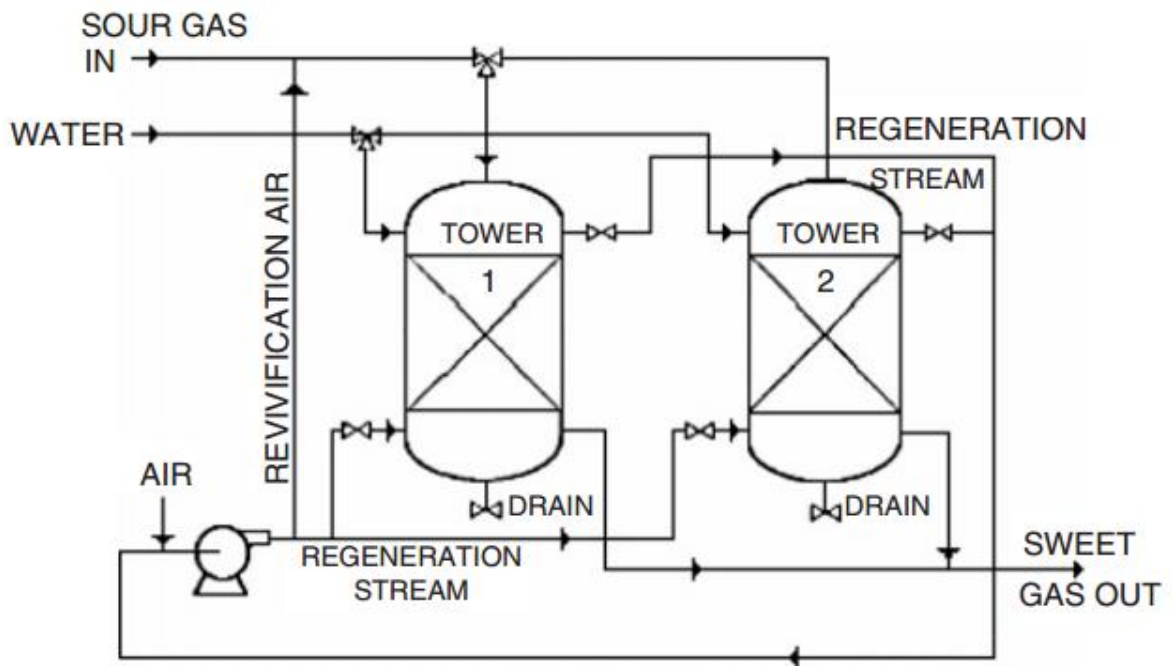
Figure 1: Typical iron oxide process flow sheet

1.1.2.   Zinc Oxide Process

Zinc oxide is also used for hydrogen sulfide removal from the gas stream. The zinc oxide media particles are extruded cylinders 3–4 mm in diameter and 4–8 mm in length. The general reaction of zinc oxide with hydrogen sulfide is

$$ZnO + H_2S \rightarrow ZnS + H_2O$$
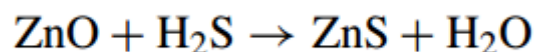
At increased temperatures (400 to 700°F), zinc oxide has a rapid reaction rate, therefore providing a short mass transfer zone, resulting in a short length of
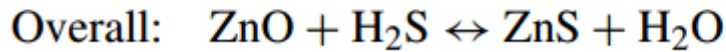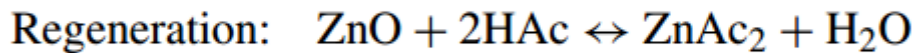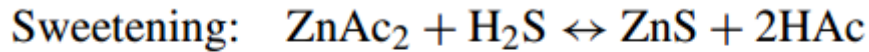
unused bed and improved efficiency. Generally, the iron oxide process is suitable only for small to moderate quantities of hydrogen sulfide. Approximately 90% of the hydrogen sulfide can be removed per bed, but bed clogging by elemental sulfur occurs and the bed must be discarded, and the use of several beds in series is not usually economical. Removal of larger amounts of hydrogen sulfide from gas streams requires a continuous process, such as the **ferrox process** or the **Stretford process**. The **ferrox process** is based on the same chemistry as the iron oxide process except that it is fluid and continuous. The **Stretford process** employs a solution containing vanadium salts and anthraquinone disulfonic acid.

1.2. Slurry Processes

Slurry processes were developed as alternatives to iron sponge. Slurries of iron oxide have been used to selectively absorb hydrogen sulfide. The results have been inconsistent; problems include obtaining stoichiometric use, premature hydrogen sulfide breakthrough, and foaming. Also, high corrosion rates have been reported. This has been circumvented by coating the contact vessels with phenolic or epoxy resins. The chemical cost for these processes is higher than that for iron sponge process. Also, because liquids freeze and foam, antifreeze must be added in winter and an antifoamant agent should be available.

1.2.1.   Chemsweet Process

In this process, Chemicals used are a mixture of zinc oxide, zinc acetate, water, and a dispersant to keep the zinc oxide particles in suspension. The following reactions are performed in a Chemsweet process.

$$\text{Sweetening:} \quad ZnAc_2 + H_2S \leftrightarrow ZnS + 2HAc$$

$$\text{Regeneration:} \quad ZnO + 2HAc \leftrightarrow ZnAc_2 + H_2O$$

$$\text{Overall:} \quad ZnO + H_2S \leftrightarrow ZnS + H_2O$$

The Chemsweet process can treat gas streams with a high hydrogen sulfide concentration and has been operated between pressures of 89 and 1415 psia.

1.2.2. Sulfa-Check Process

The Sulfa-Check process selectively removes hydrogen sulfide and mercaptans from natural gas in the presence of carbon dioxide. The process uses sodium nitrite (NaNO2). Sodium hydroxide and sodium nitrite are consumables in the processes and cannot be regenerated. This process is accomplished in a one-step single vessel design using an aqueous solution of sodium nitrite buffered to stabilize the pH above 8. Also, there is enough strong base to raise the pH of the fresh material to 12.5. The claimed reaction with hydrogen sulfide forms elemental sulfur, ammonia, and caustic soda as follows:

$$NaNO_2 + 3H_2S \leftrightarrow NaOH + NH_3 + 3S + H_2O$$
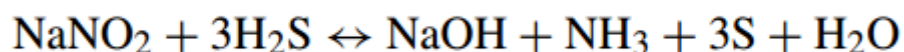
Other reactions forming the oxides of nitrogen do occur (, and carbon dioxide in the gas reacts with the sodium hydroxide to form sodium carbonate and sodium bicarbonate.