

separating sulfur

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explores H₂S removal with liquid redox processes.

Liquid redox is a process used to remove hydrogen sulfide (H₂S) from sour natural gas and other gas streams by converting it to solid elemental sulfur for sale or disposal. It is based on a reduction-oxidation reaction carried out in an aqueous solution and catalysed by iron which is held in solution by organic chelating agents. The spent solution is then circulated to an oxidiser to be regenerated with air and reused. This process forms solid sulfur particles that can be easily filtered from the solution. As shown in Figure 1, the typical applications are streams where the total amount of sulfur removed is greater than 0.5 tpd and less than 20 tpd. Liquid redox processes are not usually economical for streams that contain very small amounts of sulfur, where the total amount is less than several hundred pounds per day.

The niche for liquid redox processes can be found between two extremes – sour gas streams with high concentrations of H₂S and a constant throughput near the design point, where the Claus process is utilised, and those with very dilute H₂S concentrations, where non-regenerable scavengers are applied in towers or by direct injection.

Liquid redox can process virtually any kind of gas stream and, as a result, the technology has been applied in a wide variety of applications to achieve 99.9%+ H₂S removal in a single stage.

How it works

H₂S contacts the liquid redox solution inside the absorber and is converted to elemental sulfur and water. The solution is then routed to the oxidiser where the catalyst is regenerated using air. Regenerated solution is pumped back to the absorber. A slip stream of solution from the oxidiser is routed to a sulfur filter to produce sulfur cake. Depending upon the type of sulfur filter chosen, a settler may be employed to concentrate the solution into a slurry with higher solids content. This can improve the operation of the sulfur filter.

The redox process utilises an aqueous solution of iron, whose solubility in water and catalytic performance is enhanced by a proprietary blend of chemicals. The H₂S is

converted to elemental sulfur by redox chemistry according to the following overall reaction:



Equation 1 is the same (overall) as the Claus reaction, but the mechanisms are very different. The redox reaction is carried out in separate sections of the process as summarised in equations 2 and 3:



The exothermic absorber reaction represents the oxidation of H₂S to elemental sulfur and the accompanying reduction of the ferric iron state (active) to the ferrous iron state (inactive). This reaction is irreversible and not equilibrium dependent. The oxidiser reaction (also exothermic) represents the oxidation of the ferrous iron back to the ferric iron state.

All reactions take place in solution at near ambient temperature, making the process inherently safe. The working solution operates at a pH between 8 and 9. NaOH or KOH is used to control the pH.

There are no known contaminants that will completely inhibit the reaction of H₂S to elemental sulfur. However, it is undesirable to contaminate the solution with liquid hydrocarbons or amine, both of which can cause foaming that leads to operational problems.

Liquid redox systems can be used in multiple locations when treating natural gas and other sour gas streams. The most used applications are direct treating the gas at the available pressure and as the sulfur recovery unit (SRU) behind an acid gas removal unit (AGRU). Within these two applications, several system configurations are possible.

The process can also be used as a tail gas treating unit (TGTU) or integrated into a TGTU downstream of a Claus SRU. The benefits of this include the ability to:

- Send dilute acid gas to the TGTU, avoiding dilution of the Claus feed.

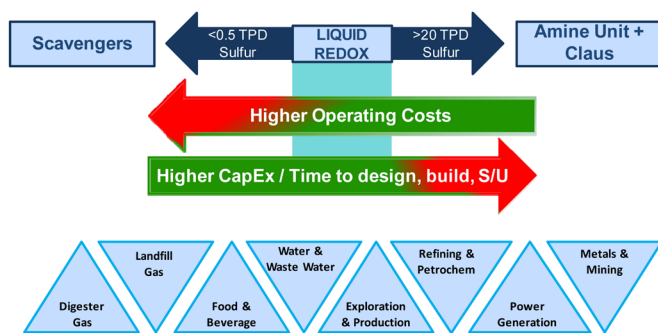


Figure 1. The application niche for liquid redox technology.

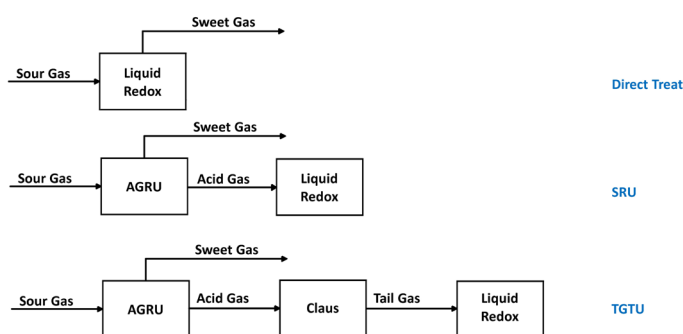


Figure 2. Common schemes using liquid redox in natural gas processing.

- Bypass the Claus unit to handle extreme turndown of acid gas flow.
- Routinely achieve <10 ppm H_2S in the treated stream, eliminating recycle to the front of the Claus plant.

System configurations

Direct treat

Liquid redox has been used successfully in low and medium pressure applications up to 500 psig for direct gas treatment, including the sweetening of associated natural gas and gas withdrawn from storage fields. The liquid redox process also offers great potential for direct treatment of natural gas in high pressure applications. Significant economic advantages can be achieved over amine-based sulfur recovery approaches because the amine, Claus, and tail gas systems are replaced with a single step liquid redox system. The operability of direct treat liquid redox systems works well below 500 psig but has not yet been proven at pressures exceeding 500 psig.

Before reaching the redox unit, raw sour gas stream passes through a knock-out drum or coalescing filter to remove any entrained liquids or solids. The feed gas is then routed to an absorber where it encounters an aqueous solution of chelated iron. H_2S is absorbed into the solution and then reacts with the iron to form solid elemental sulfur.

Treated gas exits the absorber vessel and passes through a knockout pot with an optional water wash to recover any entrained solution and protect downstream processes.

Solution exiting the bottom of the absorber is routed to the oxidiser vessel for regeneration of the iron catalyst

using air. In high-pressure applications, a flash drum is used to flash methane or other combustible components from the solution prior to entering the oxidiser. In low-pressure applications, a pump may be required to route solution to the oxidiser.

The air exiting the oxidiser may be routed to a knock-out pot to recover any entrained solution. This stream contains <1 ppm of H_2S so it is directly vented to the atmosphere in most cases. If harmful or undesirable components have been absorbed from the raw feed gas (RSH, COS, NH_3 , hydrocarbons), the vent stream is routed to a seal pot and then a thermal oxidation unit.

Removal of sulfur from the unit is accomplished by directing a slip stream of circulating solution to a sulfur filter system. The sulfur filter may be configured in several ways, but the objective is always the same: recover as much chelated iron solution as possible while concentrating the sulfur into a solid cake. Not all of the solution is recovered. Some catalyst, chemicals and salts formed in side-reactions (e.g. sulfates, thiosulfates, carbonates and bicarbonates), and some products of chemical degradation will be lost in the sulfur cake. As solution is lost, some catalyst is also lost, which will be replaced with fresh catalyst addition.

If an incident of extreme contamination occurs, operators would perform a bleed and replacement procedure until the solution recovers within an acceptable range.

Autocirculation

An alternative processing scheme has been developed and implemented for Merichem Company's LO-CAT[®] process for non-combustible gas streams.

When processing a non-combustible gas stream such as an amine acid gas, either the direct treat configuration or a lower energy consumption processing option called autocirculation may be used. Autocirculation units employ a unique design that incorporates an absorber and oxidiser within a single vessel. The motive force for solution circulation is caused by sparging gases into the solution. The addition of non-combustible gas vapours in the absorber section(s) lowers the specific gravity of the chelated iron solution, causing it to rise. In the oxidiser section(s), the addition of air creates the same motion. Autocirculation equipment can be designed in either a round or box configuration.

Performance

Turndown

Liquid redox processes do not suffer performance declines with reduced flow or fluctuating flows and compositions; this is one of the strong advantages of this class of processes. In contrast, the Claus process may lose conversion efficiency when there are fluctuations in inlet flowrate and composition. Note that unit flowrates of solution and air for regeneration are generally kept at or near design levels, regardless of the sulfur load. This is done so that circulation patterns are constant and to help prevent sulfur particle settling.

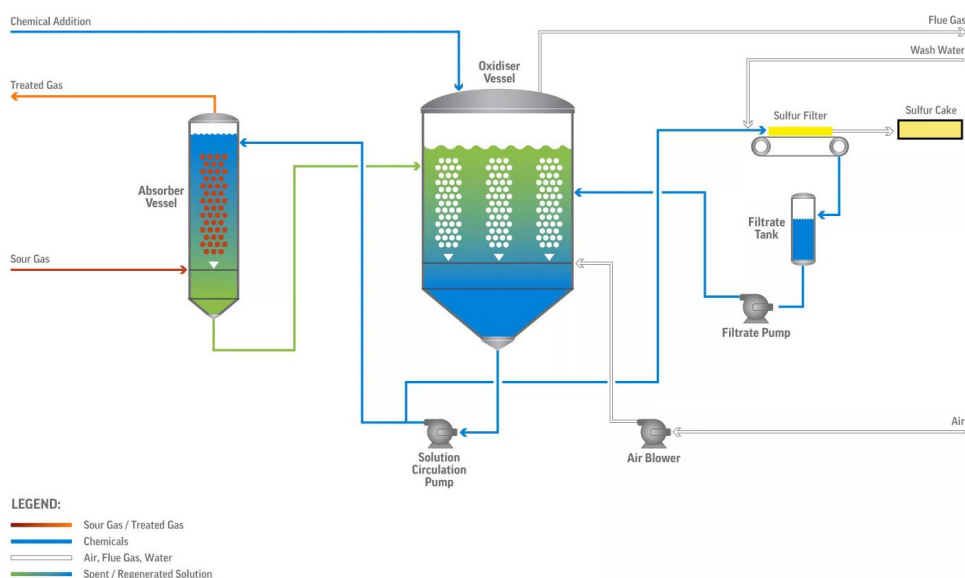


Figure 3. The liquid redox process as an acid gas removal unit (AGRU).

recommended over NaOH when CO₂ levels in the feed gas are high, e.g. in an amine acid gas.

Removal of other sulfur species

Removal rates of mercaptans, COS, CS₂ or other sulfur species are not significant in liquid redox units and these sulfur species usually end up in the treated gas stream. In some cases, small amounts of organic sulfur may be soluble in the solution and can be liberated in the oxidiser. In these cases, the oxidiser vent should be routed to a thermal oxidiser to prevent odour problems.

H₂S removal

Commercial liquid redox units can remove greater than 99% of H₂S from a wide range of inlet gas conditions. If proper solution properties (pH, catalyst concentration, etc.), flowrate and residence times are maintained, liquid redox units can meet pipeline specifications of 4 ppmv or less.

Sulfur quality

Sulfur produced by liquid redox processes is a slurry of relatively small sulfur crystallite sized particles also containing carbon, ash and iron. There is a market for the liquid redox sulfur cake as a fertilizer or 'soil amendment'. The distance of the redox unit producing the sulfur cake from the market is critical when determining the value of the sulfur cake. The sulfur cake is safe for transportation and it contains no entrained H₂S. Operators dispose of any sulfur cake not used as a fertilizer or soil amendment in local landfills.

Reliability/operability

Liquid redox processes generate a slurry of solid sulfur particles suspended in an aqueous solution. As such, plugging of lines and vessels is always a possibility. Monitoring a liquid redox unit requires regular measurement of parameters such as pH, redox potential, metal ion and salt concentrations, and gas conditions at the inlet and outlet. Like amine units, liquid redox units tend to foam when liquid hydrocarbons enter with the inlet gas. Properly designed and operated units minimise plugging and limit operator attention to as low as 1–3 hr/d.

Impact of high CO₂ on removal

Absorption of CO₂ into the redox solution has a minimal effect on the chemistry and does not produce situations where H₂S removal specifications cannot be met. However, high inlet CO₂ concentrations can lead to greater caustic requirements for pH control. Since potassium salts are more soluble in the solution compared to sodium salts, KOH is

Byproducts

Typical byproducts generated by liquid redox processes include thiosulfate and sulfate. High concentrations of any of these byproducts can lead to increased solution densities, higher pumping requirements, and salt precipitation. If byproduct concentrations reach critical levels, blowdown of liquid redox solution may be necessary. As noted previously, salt removal via the sulfur cake is common and generally avoids the need for any purge stream.

Environmental, health, and safety considerations

For the most part, liquid redox units do not pose any unusual environmental, health, or safety risks. Sulfur cake from liquid redox units is considered a mild health and safety risk. Sulfur cake is a skin and eye irritant. Prolonged exposure can cause dermatitis and may affect the respiratory system. The sulfur cake is usually moist (though not wet to touch), does not dust and is not likely to ignite. It does not require degassing and is safe for transport. Disposal in a local landfill is common.

Storm water or wastewater from liquid redox units should be routed to a closed drain system. Exposure to aqueous liquid redox solution poses minimal health and safety risks. However, some of the make-up chemicals (e.g. caustic) in their concentrated form may be a greater risk for dermal and eye irritation.

Conclusion

The liquid redox process provides a flexible, reliable and economical way to remove over 99.9% of the H₂S in sour gas streams when the total amount of sulfur removed is between 0.5 tpd and 20 tpd. The aqueous redox solution utilises a continually regenerated chelated iron catalyst to convert H₂S to elemental sulfur. The sulfur is filtered from the solution and can be used as fertilizer or disposed of in landfill. The process has minimal safety and environmental concerns and can be used to treat virtually any gas stream. 