

REMOVAL OF H₂S FROM COAL-DERIVED GASES

by

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Introduction

When coal is gasified most of the sulfur is converted to H₂S and must be removed before the gas can be used either as a fuel or as synthesis gas. The UCB Sulfur Recovery Process (UCBSRP) is being developed as a general method for removing H₂S from gases. The H₂S is absorbed in a polyglycol ether, then reacted in the liquid phase with SO₂ to form marketable elemental sulfur and water. The process allows high specificity and flexibility; H₂S can be reduced to the part-per-million level or below in the presence of CO₂ and the other components of gasified coal. The CO₂ may be left in the original gas stream or it may be co-absorbed and recovered as a separate, sulfur-free product. The process thus has application both to syngas and hydrogen production from O₂-blown gasifiers and to power production using an air-blown gasifier.

Process Configurations

Figure 1 shows a flowsheet for the UCBSRP in a configuration that gives maximum selectivity for H₂S removal. In the primary absorber H₂S is removed primarily by physical absorption. The stream of solvent leaving the absorber is nearly saturated with all of the components of the gas being treated. A water wash at the top of the primary absorber prevents loss of solvent vapor in the treated gas.

Most of the solvent stream leaving the primary absorber then enters a reactor/crystallizer that operates at the pressure of the primary absorber. A second solvent stream containing SO₂ is metered into the same reactor at a rate that keeps the SO₂ content within the reactor a few percent above stoichiometric relative to the H₂S. (It is necessary to have an excess of one reactant or the other in each reactor to avoid excessive reactor volumes and the need for highly precise reactor control.) A clarified overflow from the SO₂-rich reactor is pumped back to the primary absorber. This solvent stream has been completely freed of its H₂S content but is still saturated with respect to the other components in the gas being treated in the primary absorber. The net co-absorption of these other gas components (such as CO₂) is thus kept quite small and the effective selectivity for H₂S is of the order of 50 to 100. The SO₂ content of this solvent stream, although low, provides a chemical enhancement for the absorption of the H₂S on the upper trays of the primary absorber to facilitate meeting very stringent H₂S specifications in the treated gas. (The temperature in the primary absorber is high enough to prevent precipitation of the sulfur formed by this reaction. Not shown in
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Figure 1, to avoid clutter, is provision for cooling both reactor/crystallizers with cooling water so that the solvent is sub-saturated in sulfur at all other points in the system.)

The underflow from the SO₂-rich reactor carries the sulfur and water formed in the reaction between H₂S and SO₂. The flow of this stream is sized to keep the water content of the solvent from exceeding 5% and is directly proportional to the rate of H₂S removal - - the flow will typically be about 10% of the total flow of solvent through the primary absorber. Sufficient H₂S-rich solvent, from the primary absorber, is added to the stream to leave a small excess of H₂S after all of the residual SO₂ has reacted. This stream is then flashed to atmospheric pressure in the settler/surge tank.

The sulfur made in the process forms a slurry in the underflow from the surge tank. The sulfur is recovered and washed in a centrifuge. In most cases about one-third of the sulfur will be burned in the furnace to make the SO₂ needed in the process. The energy recovered in the waste-heat boiler will usually supply and perhaps exceed the energy required by the process.

The overflow streams from the surge tank and the centrifuge are combined and sent to the solvent stripper. Boiling most of the water out of the solvent provides a stripping vapor that also removes unreacted H₂S and co-absorbed gases such as CO₂ from the solvent. Most of the solvent leaving the solvent stripper is used in the SO₂ scrubber where it absorbs the SO₂ from the combustion gas leaving the furnace. The SO₂ content of this solvent is nil, and hence the SO₂ content of the stack gas leaving the scrubber can readily be reduced to the part-per-million level. The remainder of the solvent from the stripper is sent to the primary absorber, where it prevents loss of SO₂ in the treated gas.

Figure 2 shows a process configuration suitable for removing and recovering one or more components (in addition to the H₂S) from the gas being treated, such as removing CO₂ from a synthesis gas ahead of a shift reactor in a process for producing hydrogen. The operation of this process is identical to that described above in many respects. It differs as follows:

At the bottom of the primary absorber is a short section in which much of the H₂ and CO are stripped from the solvent. The stripping gas is obtained by a partial flash of the solvent immediately downstream of the primary absorber. Most of the H₂S-rich solvent stream leaving the flash drum, together with a controlled flow of SO₂ solution, enters an SO₂-rich reactor. The pressure of the SO₂-rich solvent stream is reduced in stages (only two are shown) to about one atmosphere. The off-gas from each stage is recompressed to the pressure desired for the CO₂ product and is contacted with neat solvent to remove traces of SO₂, then washed with water to recover solvent vapor. For the case shown, in which a high degree of CO₂ removal is not required, clarified H₂S-free solvent from the atmospheric flash can be pumped directly back to the primary absorber.

As in the flow configuration designed for high H₂S selectivity, the sulfur and water formed in the reaction are conveyed out of the last SO₂-rich reactor in a stream that is rendered H₂S-rich with by-passed H₂S solution. As before, the flow of this stream is proportional to the rate of sulfur production.

Lynn, et al. (1987) compared conventional technology to the UCBSRP for removing H₂S from the recycle gas of a crude oil residuum hydrodesulfurization unit. The UCBSRP has the potential for significantly reducing both the capital and operating costs because of the reduction in the number of processing steps and in utilities consumption. Lynn and Sciamanna (1988c) found a similar advantage for the UCBSRP for treating natural gas to remove H₂S, water and C₃₊ hydrocarbons.

Gas and Sulfur Solubilities in Process Solvents

The solubilities of H₂S, SO₂, CO₂, propane, butane and sulfur in a variety of glycol ethers have been measured as a function of temperature. Water, a product of the reaction, reduces these solubilities. These results have been reported by Demyanovich and Lynn (1987) and by Sciamanna and Lynn (1988a and 1988b).

Reaction Kinetics

The reaction between H₂S and SO₂ in glycol ethers is relatively slow when uncatalyzed. However, as reported by Neumann and Lynn (1986), tertiary aromatic amines are effective catalysts and reduce the time required for nearly complete reaction to a few seconds.

Corrosion Studies

Corrosion studies were performed by submerging metal coupons half way in a solution of H₂S or SO₂ in a glycol ether. To make the system as corrosive as possible, the solvent was a mono-ether (which is also an alcohol) and sulfur and water were added in concentrations twice (or greater) those encountered in the process. The exposure was carried out for three successive 20 to 30-day periods at each temperature. Table 1 shows the corrosion rates observed.

Table 1: Corrosion Rates of Steels in Process Solutions.

MEASURED RATES AND CONDITIONS *				
Metal	SO ₂ : @ 100°C	@ 120°C	H ₂ S: @ 150°C	
Carbon Steel	0.6	1.7	0.05	
304 Stainless	0.7	1.5	0.02	
316 Stainless	1.3	4.8	0.01	

* Mils/year in diethylene glycol methyl ether, 5% H₂O, saturated with sulfur, 50 - 100 psi gas pressure.

Since 60°C is the maximum temperature at which SO₂ is present (outlet of the SO₂ absorber), carbon steel and 304 and 316 stainless steels should corrode at rates much less than 1 mil/year (0.02 mm/yr) under all process conditions.

Sulfur Crystallization

A major potential advantage of the UCB Sulfur Recovery Process is the purity of the crystalline sulfur that is produced. The sulfur crystallizes from solution both as a result of cooling and as a result of chemical reaction between H₂S and SO₂. In the former case the degree of supersaturation is relatively low because the solubility of sulfur in the solvent varies only a few grams per liter over the temperature range of interest. A substantially higher concentration of sulfur can result from the chemical reaction.

The crystallizer consists of a well-stirred 2-liter vessel. Hot saturated feed enters at the top, and the vessel walls are cooled. Cold effluent exits at the bottom of the vessel as a sulfur/solvent slurry. A sample of the effluent slurry is collected when the system is at steady-state and the size distribution of the sulfur crystals is determined. analysis.

Gas Absorption with Chemical Reaction

Tray efficiency data are needed for two process situations. In one, H₂S at very low concentration is being absorbed by a chemically reactive solution of SO₂. In the other, gaseous SO₂ in the low parts-per-million concentration range is absorbed by lean process solvent. Both are of interest because one wishes to effect very stringent sulfur removal with the UCBSRP. The equipment consists of a single sieve tray (or section of packed column) placed in a test section through which gas and liquid streams pass. Murphree tray efficiencies are determined from the mass balances and previously obtained solubility data.

Work Required for Proof-of-Concept

The crystallizer is being modified to incorporate crystal size classification to retain smaller crystals and produce a product of larger size. Sulfur will be produced by chemical reaction. Data obtained for absorption of H₂S enhanced by the presence of SO₂ in the solvent will be used to develop a model that incorporates the reaction kinetics work done previously.

A computer model that simulates all of the unit operations in the process is operational and facilitates process synthesis for specific applications. It will be used to evaluate and further refine the process configurations shown in Figures 1 and 2 for the purification of hydrogen derived from gasified coal.

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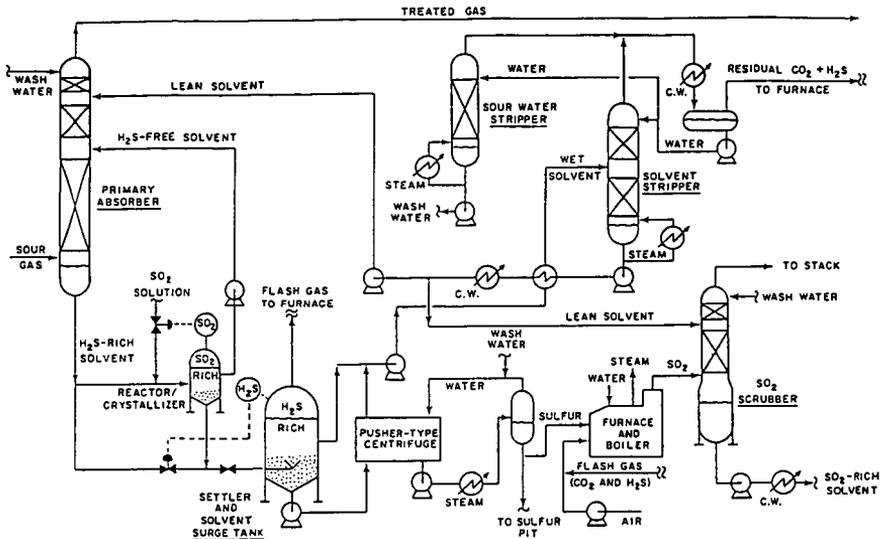


Figure 1 H₂S-Selective Process.

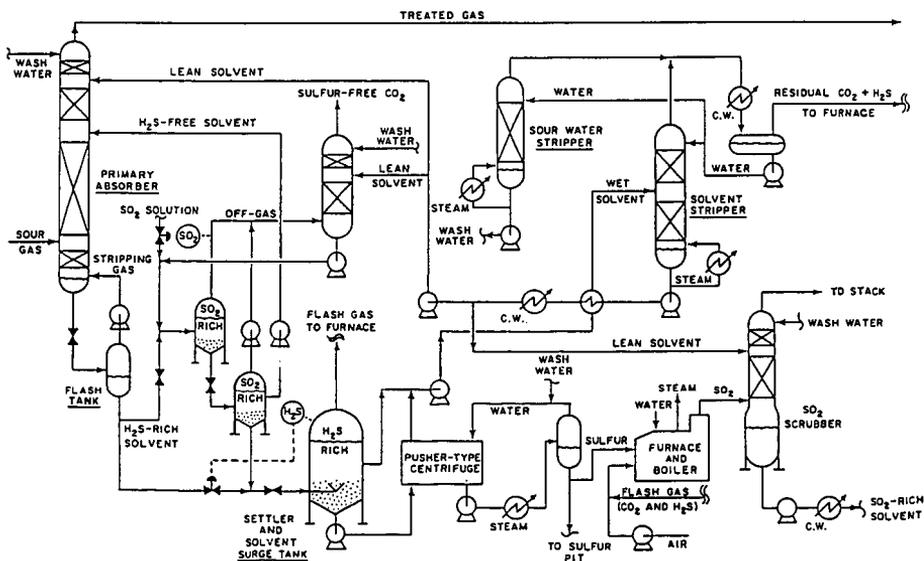


Figure 2 Co-Absorption Process.