H2S REMOVAL BY DIRECT LIQUID PHASE OXIDATION PROCESSES

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INTRODUCTION

Direct Liquid Phase Oxidation Processes (DLPOP's) are a group of processes that remove hydrogen sulfide (H2S) from gas streams by absorption in an alkaline aqueous solution. The absorbed H2S is converted to elemental sulfur through the action of a metal catalyst complex contained in the solution. These processes are very effective, being able to remove H2S to below the limits of detectability when required. They are almost totally selective for H2S, with respect to carbon dioxide (CO2). They are used to treat hydrocarbon streams directly, to recover sulfur from amine acid gas streams, and as tail gas cleanup following Claus sulfur recovery systems. Because they can remove and recover H2S to below detectable limits, these processes have become more important to oil and gas producers as environmental regulations have lowered emission levels for H2S, and its combustion product Sulfur Dioxide (S02).

New or modified DLPOP's are being developed very rapidly. Each new process announced has some claim to reduced side reaction products, reduced operating costs, reduced capital costs, improved sulfur quality, or to improved operability. Each process is protected from full disclosure of design and operating information by secrecy agreements with the company that holds the patent.

BASIC CHEMISTRY

All of the DLPOP's have the same three basic steps: (1) Absorption of the H2S in a aqueous alkaline solution; (2) Reaction of absorbed H2S with a metal complex, forming elemental sulfur; (3) Re-oxidation of the metal complex by air sparging. Before reaction with H2S the metal will be in either a +5 or a +3 oxidation state, and will be reduced to +4 or +2 respectively by the reaction. The re-oxidation step will return the metal to the higher oxidation state completing the process cycle. The alkalinity of the solution is required for effective absorption, and is usually provided by either sodium or potassium based chemicals. Details on reaction mechanisms are difficult to determine, and often are subject to secrecy restrictions if they are known.

The speed and degree of completion of each of these three steps is different for each process. These differences largely determine the equipment design required for each process. They also determine the amount of side reaction interference that will occur in each process.

Of particular importance is the reaction rate between the metal complex and the absorbed H2S. If the reaction is very fast, the amount of H2S actually present in the solution will be very low. This will allow a lower solution circulation rate and less contact stages to achieve the same removal efficiency. If the reaction rate is fairly slow, side reactions will have longer to take place. Many of the current commercial processes exist because someone has found an additive that increases the speed of the primary reaction, or decreases the speed of the side reactions.

PROCESSES

There are two types of DLPOP's commonly available in the U.S., vanadium based and iron based. Other types of DLPOP's, such as arsenic or quinone based systems, have been and are being used in other parts of the world. There is also a group of DLPOP's that were early developments but are not commonly used today. Several of the DLPOP's available in the U.S. incorporate components of these other types of DLPOP's, particularly the quinone systems.

Below is a listing and brief discussion of DLPOP's that are commercially available in the U.S. (See Table I for a condensed listing). This listing is not a recommendation, and failure to appear on this list does not imply that a particular DLPOP is not viable. New DLPOP's are being developed rapidly and some may not have been mentioned. Also, each potential application is different, and care should be taken to evaluate all of the DLPOP's before making a selection.

VANADIUM BASED DLPOP's

All of the vanadium based systems circulate solutions that contain significant levels of vanadium. The solutions used in vanadium based DLPOP's may or may not be considered hazardous, depending on the particular compound of vanadium used, the other compounds used, and the location of the plant being considered. In California, the levels of vanadium often make any solution being disposed of a hazardous waste.

Stretford

Developed by the British Gas Board, Stretford is one of the first DLPOP's, though several improvements have been made to the original process. There are a large number of U.S. plants that use this process, many have operating experiences similar to those described later in this paper for the ARCO Elwood Stretford unit in California. The principal components of the solution, as used in the U.S., are water, sodium vanadate, anthraquinone disulfonic acid (ADA), sodium hydroxide, and biocides.

The process produces sodium thiosulfate (thiosulfate) in a side reaction, which builds up in the circulating solution and interferes with the conversion of H2S to sulfur. The degree of thiosulfate production depends on equipment design and on the presence of compounds that act as inhibitors of the thiosulfate reaction. In order to maintain treating efficiency, a purge of solution must be taken. This purge must be adequate to maintain a constant thiosulfate concentration. Before selecting this process, careful consideration should be given to disposal of purged and replaced solution.

Unisulf^{TM}

This process was developed by the UNOCAL Corporation, and is very similar to the Stretford process. The additive system includes a thiocyanate and an aromatic sulfonate complexing agent not contained in Stretford. Improvements claimed are reduced side reaction products, resistance to biological contamination, reduced corrosivity, and higher temperature tolerance. The reduced formation of side reaction products eliminates the need for a continuous purge. Several commercial installations are using this process in the U.S.

Shafer Process^{TM}

This process was developed by Purtec Systems Incorporated, through a research project intended to find solutions to the problems associated with the Stretford process chemistry. The problems of particular interest were side reaction product formation and chemical, consumption. The process claims to have been successful at reducing both of these problems with the use of an additive system including boric acid, WDQ, and biocides. WDQ is proprietary compound of PURTEC Systems Inc. Other solution components are similar to those used in the Stretford process.

Sulfolin^{TM}

The Sulfolin process was developed by Linde TVT for use in the Sasol (South Africa) coal gasification plant. The first commercial test was conducted in 1985. The process has also been selected as the replacement for the Stretford process, by the ANG Coal Gasification Company. The additive system is similar to Stretford and includes sodium carbonate, vanadium and an organic nitrogen compound. The exact composition is proprietary. Primary benefits claimed are reduced operating costs due to lower chemical consumption and reduced side reaction products. This process is new and little is known about its operating problems or its applicability to situations other than coal gasification.

IRON-BASED DLPOP's

The iron-based DLPOP's probably originated from efforts to duplicate the reactions of the iron sponge in a reversible, liquid phase process. The original iron based processes were the Ferrox, Gluud, and Manchester processes. These processes all had some difficulty in keeping the iron complex in solution, thus the sulfur produced often contained a fairly high percentage of solid iron compounds. Although once used on a wide scale, when the vanadium and arsenic systems were developed, the original iron based systems fell into disuse. The modern iron based systems generally do not suffer from the same problems as these original processes, and in fact offer some benefits over the vanadium and arsenic processes. One of the primary differences is that the speed of the reaction between H2S and the iron compounds is much faster than the reaction of H2S with the vanadium and arsenic compounds. The other benefit is that the iron based systems seem to present less of an environmental problem when disposing of solution.

LO-CAT®

LO-CAT is a registered trade mark of ARI Technologies, Inc. The process uses a combination of organic chelating agents to keep the iron in solution. This process also uses a biostat to control biological infestations. There are a large number of U.S. plants that use this process. The primary benefits claimed are reduced equipment requirements, non-toxic solution and large turn down (and up) ratios.

Hiperion™

This process is marketed in the U.S. by ULTRA SYSTEMS Incorporated. The process appears similar to the Takahax process, which was developed in Japan about the same time Stretford was developed in Britain. The Hiperion process uses a sulfate and a metal salt of dicarboxylic acid in the solution. In operation, peroxides are formed that act as biocides. The exact system operation is proprietary. There is one known location using the process in the U.S., and several others under development.

Sulferox™

This process was developed by Shell Development Company. There is one known field location in the U.S. The process uses a chelating system to keep iron oxides in solution. The circulating solution can contain as much as 4% iron by weight. Benefits claimed are low circulation rates, low chelate consumption, and compact process design.

SELECTION GUIDELINES

Every case where H2S is present and needs to be removed is different, and requires individual analysis to select the best process or group of processes for the job being considered. There are several conditions under which one of the DLPOP's is likely to be an economical choice. The limits mentioned below are not hard and fast rules for application of these processes. They can only serve as guide posts to indicate that this class of processes should be considered. When more than one of these limits apply, these processes will be particularly strong candidates. The selection of a particular DLPOP is the job of the user.

Low Sulfur Rate

Consider using one of these processes if the total amount of H2S that must be removed is equivalent to less that 5 tons per day of elemental sulfur. As the total amount of sulfur that must be removed and recovered decreases, the advantage of these processes increases. This advantage is a result of two things; (1) the high cost of a minimum sized Claus type process, which is the normal recovery alternative, and (2) the fact that these processes can be used to remove the H2S directly from the hydrocarbon gas stream. The ability to remove and recover H2S in one step can often eliminate the need for an amine treating system.

High CO2 to H2S Ratio

If the volume of CO2 to be removed is more than twenty times the volume of H2S to be removed, the DLPOP's should be considered for the sulfur recovery step. As the ratio of CO2 to H2S2 in the removed acid gas increases, the Claus processes become more difficult and expensive to operate. When H2S makes up less that 30% of the removed acid gas, straight Claus sulfur recovery systems are not practical and one of the modified Claus or Selectox processes must be used. At some point the CO2 to H2S ratio will be high enough to make one or more of the DLPOP's economically attractive. This point is usually below 5% H2S in the removed acid gas. The exact point at which these processes become economic is strongly influenced by the H2S recovery efficiency required by the environmental regulations in force at the plant site.

High Removal Efficiencies Required

The DLPOP's are commonly used where environmental regulations or operating conditions require that the overall H2S recovery efficiency be in excess of 97%. Where the total sulfur flow is high, a DLPOP can serve as a tail gas cleanup to one of the a Claus sulfur recovery process. Where the total H2S rate is low, a DLPOP might serve as a combination removal and recovery process.

Low Processing Pressures

Processing pressures below 100 psig indicate that these processes should be considered. Low pressures make the amine treating systems more expensive to operate due to low loading, resulting high circulation rates, and high regeneration power cost. Very low pressures can make it impossible for an amine based system to adequately remove H2S to meet sales gas specifications. The DLPOP systems operate cost effectively at low pressures because they are not heat regenerated.

Contamination Problems

The presence of compounds that adversely react with amine based systems can make the DLPOP's the only viable processing solution. Cyanides, ammonia, and oxygen are the most often mentioned. For natural gas processing, cyanides and ammonia are not normally present, but high oxygen concentrations are sometimes encountered.

PROBLEMS

There are several problems that are quite common in DLPOP's when used in the oil and gas industry. Most notable are sulfur plugging, off color sulfur, biological infestation, and odors.

Sulfur Plugging

All DLPOP's produce solid sulfur in a liquid circulating fluid, and this sulfur tends to plug the processing equipment. Careful attention to mechanical design, sulfur removal, and operating conditions can minimize this problem, but expect some plugging when operating a DLPOP. The plugging problems seem to be more common when heavy hydrocarbon compounds or biological infestation are present.

Sulfur Color

Sulfur color seems to depend on how the solid sulfur is removed from the circulating liquid, and on the amount of hydrocarbon contamination. It is possible to get "bright yellow" sulfur from a DLPOP by using a sulfur melter, but not guaranteed. Other removal methods usually yield an off color-sulfur product. Sulfur color is usually not critical when the produced sulfur is used in agriculture. When the sulfur is used in other processes, poor color will reduce the price paid for the sulfur, and may make the sulfur unacceptable to the purchase. Before using a DLPOP, serious consideration should be given to the available sulfur market, and/or sulfur disposal.

Biological Infestation

Biological infestation is fairly common for DLPOP's used in the oil and gas industry. The infesting organisms are usually sulfur reducing bacteria or one of the pseudomonas strains that eat one of the compounds in the solution. Infestation may or may not cause operational problems, depending on the type of infestation, the particular DLPOP involved, and the level of infestation. Infestation level is measured in organisms per liter, org/l. An infestation level greater than 10^6 org/l is considered cause for concern. Infestations below this level are normally tolerated.

Most of the DLPOP's have one or more biological control agents recommended for regular use. Some DLPOP's are free of infestation because compounds used in that DLPOP are toxic to infesting organisms. The likelihood of infestation and the operating problems that result should be considered carefully when selecting a particular DLPOP.

Odors

Objectionable odors are emitted by DLPOP's in some situations. They are usually attributed to the minor sulfur compounds, particularly mercaptans, present in the gas being treated. The severity of the problem depends on the particular compound(s) causing the odor, and on the location of the plant. Odors can be successfully handled by enclosing the process tanks and sending vapors through a charcoal canister system. DLPOP's treating amine acid gas and in tail gas cleanup tend to have fewer odor problems.

ARCO EXPERIENCE

ARCO has operating experience with two DLPOP's, Stretford and LO-CAT®. The Stretford process is located at our onshore facilities in Santa Barbara County, California. The LO-CAT process is located at the Sable Unit Gas Plant in Plains, Texas. In both cases, we are treating the hydrocarbon stream directly, accomplishing H2S removal and recovery in a single process step.

STRETFORD

The Stretford process unit was built in 1971 by the Ralph M. Parsons Co. (See Figure 1) The unit required higher solution circulation rates and lower gas rates than originally anticipated in order to achieve the required H2S recovery efficiency. Today, lack of available gas limits the unit's flowrate.

As originally built, the unit had a severe odor problem. We believe this problem was due to mercaptans absorbed from the gas stream, being released in the oxidizers. This problem was solved by covering the atmospheric vessels and blowing collected vapors through a charcoal canister system.

Side reaction products have been particularly bothersome in this plant. Since we are located in California, any waste solution is classed as hazardous waste, due to the vanadium content. The disposal cost for purged solution, required to limit the concentration of sodium thiosulfate, is very high.

We have experienced significant corrosion problems in our Stretford unit, which was constructed of carbon steel. While the exact corrosion mechanism has not been defined, we believe that sulfur reducing bacteria convert sodium thiosulfate to sodium sulfate and sulfuric acid. Some relief has been found by internally coating replacement piping with coal tar epoxy.

We have been able to correlate periods of plugging problems and high chemical consumption to high biological count. That is, these symptoms all tend to appear at the same time. We have not been able to determine why a relatively stable biological count will suddenly raise, thus we do not know if high biological infestation causes plugging and high chemical consumption, or if these problems are caused by the same thing that caused the biological count to increase.

LO-CAT®

The LO-CAT process unit was built in 1984 by ARI. (See Figure 2) The process has been effective at removing and recovering H2S. The process has also been adaptable. Though the start-up sulfur rate was twice the design basis, and this unit was able to handle the actual rates by increasing the catalyst concentration and the air sparging rate. The Sable Plant processes gas from a CO2 flood project. The drastic changes in inlet gas composition and flow rate have been handled without significant problems.

We have experienced some plugging problems, which we have attributed to a combination of mechanical design and liquid hydrocarbon in the feed gas. These problems have been greatly improved by installation of a coalescing separator on the inlet gas and by numerous minor mechanical changes.

To date, we have not detected biological contamination to any significant degree. The unit is constructed of 304 stainless steel and CPVC, and has had no corrosion problems. Chemical consumption has been somewhat higher than design, even when considering the increased sulfur production rate.

We have significantly revised our method of removing sulfur from the circulating solution, at substantial capital cost.

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Table 1
Direct Liquid Phase Oxidation Processes Available in the U.S.

PROCESS NAME	TYPE	COMMENTS
Stretford	Vanadium	One of the earlier processes. Purge often required. Many U.S. plants. SOLUTION: water, sodium vanadate, ADA, NaOH, biocides
Unisulf™	Vanadium	UNOCAL Corp. Similar to Stretford with reduced side reaction. Purge not required. Several U.S. plants. SOLUTION: as Stretford plus thiocyanate and aromatic sulfonate .
Shafer™	Vanadium	Puretec Systems Inc. Similar to Stretford with reduced side reaction and chemical consumption. Purge not required. SOLUTION: as Stretford plus boric acid, WDQ, biocides.
Sulfolin™	Vanadium	Linde TVT Similar to Stretford with increased H2S reaction rate and lower chemical cost. No Purge. One known U.S. coal gasification plant. SOLUTION: water, sodium carbonate,vanadium, organic nitrogen compound.
LO-CAT®	Iron	ARI Technologies, Inc. Based on early iron systems with an improved chelate system to keep iron in solution. Normally no purge. Many U.S. plants. Fast H2S reaction. SOLUTION: water, iron, chelates, pH control, biostat
Hiperion™	Iron	ULTRA SYSTEMS Inc. Similar to Takahax process. One plant in U.S., others being developed. Fast H2S reaction SOLUTION: water, sulfate, metal salt of dicarboxylic acid
Sulferox™	Iron	Shell Development Co. Uses a chelating system to keep up to 4 % iron in solution. Fast H2S reaction. One known U.S. plant.

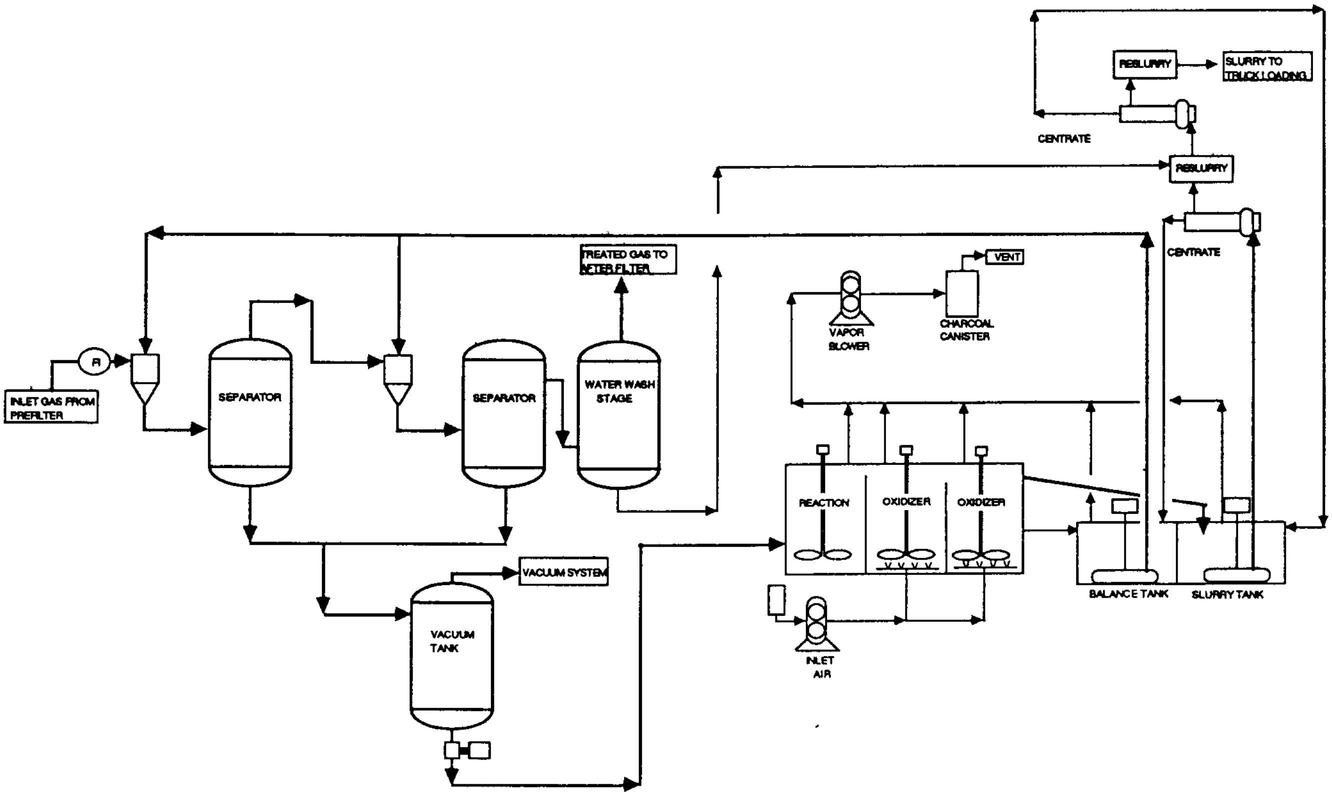

Figure 1 - Ellwood Stretford Unit

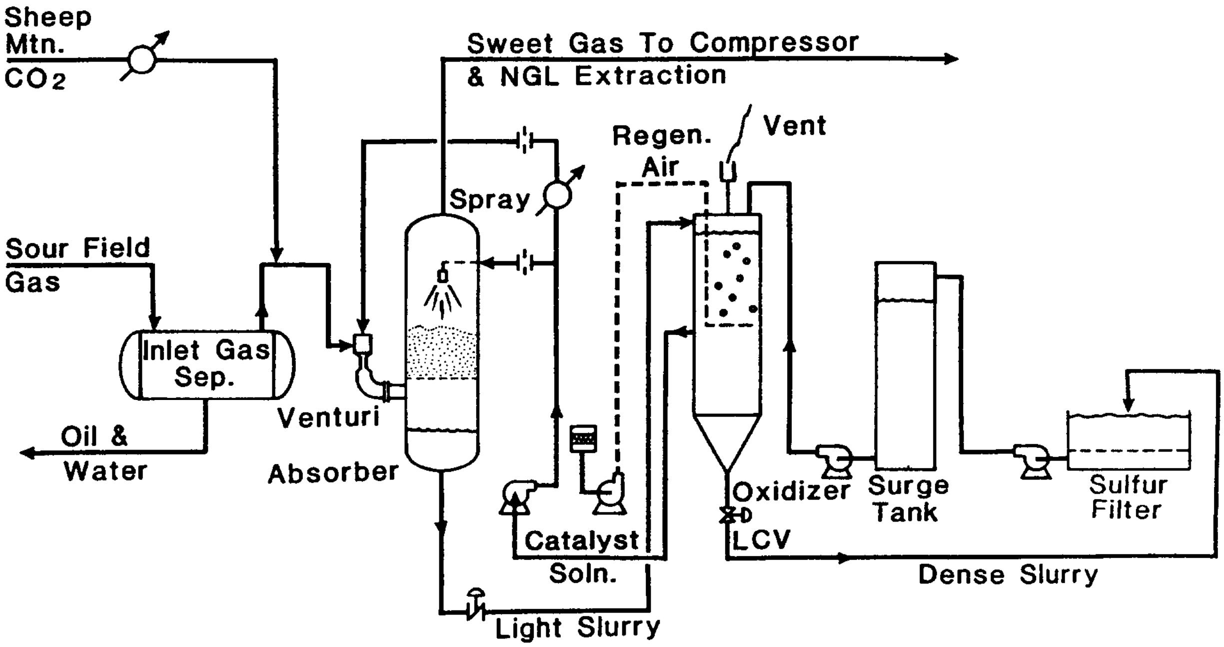

Figure 2 - Sable CO_2 recovery plant — simplified LO-CAT® process scheme