AN EFFECTIVE ONE-STEP PROCESS FOR SELECTIVELY REMOVING HYDROGEN SULFIDE FROM SOUR GAS

James B. Dobbs

NL TREATING CHEMICALS

ABSTRACT:

A variety of sour gas sweetening processes have been commercially available for a number of years, and reports of new processes appear regularly. Many of these processes present severe problems in economics and operating consistency for selectively removing hydrogen sulfide from sour gas, especially in the presence of high concentrations of carbon dioxide. This presentation describes a new one-step process which selectively removes H_2S, even in the presence of CO_2, and converts it directly to elemental sulfur. Only one vessel is used and this operates unattended or with minimum manpower. No recirculating pump, regenerating vessels, or reboilers are required. And perhaps most important, the spent slurry produced has been declared non-hazardous by most regulatory agencies.

Field operations have shown this one-step process to be safe and reliable. Experience has shown that existing available process equipment can often be adapted to use the process. Guidelines for equipment design are given and field applications for this type of process are suggested. Specific field installations are cited to illustrate the safe and simple operation of this new system which requires comparatively low capital investment.

INTRODUCTION

Hydrogen sulfide is a toxic, noxious, corrosive gas frequently found in untreated hydrocarbon gas mixtures (sour gas). The increasing concern for environmental pollution control, the health hazards associated with gases containing hydrogen sulfide in the work place, and the high costs associated with maintaining equipment needed to produce, process, and transport sour gas dictate that attention be given to sweetening sour gas.

A wide variety of sour gas sweetening processes have been used commercially for many years and the technology continues to grow as new demands are placed on applications such as CO_2

enhanced oil recovery methods. The established commercial processes frequently encounter problems in economics and operability for selectively removing low concentrations of H_2S, especially in the presence of high concentrations of CO_2. The development of new sour gas sweetening processes can be justified, especially when the operating parameters can be defined by the following factors:

- improved economics for hydrogen sulfide removal based on cost performance evaluations
- simplicity of operation
- low capital cost of the gas processing unit
- non-hazardous by-products of the hydrogen sulfide reaction which are environmentally acceptable for safe disposal
- a process adaptable to existing pieces of process equipment.

This paper describes a new process for sweetening sour gas that fulfills the above justifications. Since this new process falls into the category of a one step batch process that is a direct conversion mechanism, further references to this process will be called the One-Step Process.

DISCUSSION

There are seven major categories of processes by which sour gas can be sweetened:

1. Chemical solvent processes
2. Physical solvent processes
3. Direct conversion processes
4. Dry bed processes
5. Specialty solvent processes
6. Metallic sulfide processes
7. Formaldehyde process

Except for the formaldehyde, the dry bed and the metallic sulfide processes, all of the processes listed employ more than one vessel and are regenerative (See Table 1). Hydrogen sulfide is removed in the reaction vessel, and when the reactant is exhausted, the saturated reactant is transferred to a regeneration vessel. There heat may be applied to break an H_2S organo complex, or air is blown through the liquid to oxidize an organic reactant which has previously converted H_2S into sulfur. In the processes where heat is applied, the H_2S is released unchanged and must subsequently be further processed to convert it to sulfur, or it must be flared.

The One-Step process is a member of category number 3: it is a direct conversion process where H_2S is converted directly to sulfur. The One-Step process is different from all other commercial direct conversion processes in that it is the only one which operates in only one vessel and requires no auxiliary processing equipment.

It is not a regenerative process. When the oxidizing solution is spent it cannot be regenerated.

THE ONE-STEP PROCESS

The One-Step process is an engineered system optimized to selectively remove hydrogen sulfide from sour gas mixtures. As a simple description of the process, sour gas is bubbled through a fluid column of an aqueous solution of inorganic oxidizing agents where hydrogen sulfide is converted to elemental sulfur--in one step, even in the presence of high concentrations of CO_2. Since this reaction takes place in a one-step conversion it is defined as a batch process. Like any batch process, this process has a finite life expectancy and the reactants are eventually spent. At this point, the by-product slurry must be removed from the vessel and replaced by a fresh charge of oxidizing sweetener. One the most attractive attributes of the One-Step process is the non-hazardous nature of the spent slurry. This not only reduces the handling problems, but can also effect cost savings for by-product disposal.

OPERATING REQUIREMENTS FOR THE ONE-STEP PROCESS

The One-Step process has a requirement for four basic parameters as follows:

- Pressure rated H_2S Scrubber (bubble tower)
- Efficient Sparger
- Efficient Mist Eliminator
- Control of flow rates and/or pressures

The scrubbing vessel should be a simple unit without internal plates, trays or baffles. (Figure 1) It is important that vessel pressure ratings are consistent with the operating pressures. At the bottom of the scrubber an efficient sparger should be installed in a manner to evenly distribute the flow of gas across the diameter of the vessel. An effective mist eliminator at the top of the vessel will prevent chemical and fluid carry over into the effluent gas. A flow regulator and/or pressure regulator should be employed to control gas flow through the vessel and to dampen pressure surges. Like other gas treating systems, these controls will reduce the tendency of mechanical carryover problems.

Other minor periphery equipment such as check valves, sampling valves, thermometer well, U-tube, etc., facilitate minimum manpower demands for operation. When these are in place, the tower is charged to a predetermined fluid level with a special buffered oxidizing solution for treatment of the sour gas.

ONE-STEP PROCESS SWEETENING SOLUTION

The sweetening solution used by the One-Step process can be described as an aqueous solution of inorganic oxidizing agents in a specially buffered system. The solution is non-flamable and non-corrosive as defined by the U.S. Department of Transportation. Thus the chemical is considered safe for handling. The chemical solution is stable indefinitely in storage and therefore does not have a shelf-life problem. The chemical solution acts as a metal passivator and will not corrode mild steel. Therefore capital costs are saved because expensive alloy construction is not required. Field experience has shown that the chemical system can frequently be used in existing equipment with minor modification.

SPENT SLURRY COMPOSITION

As the One-Step sweetening process progresses, the oxidants react with H_2S and produce finely divided particles of elemental sulfur. At the point in time when all of the oxidants have been consumed, the vessel contains a slurry which must be replaced with a fresh charge of reactants.

This slurry is composed of approximately 60% liquid and 40% solids. The solids are made up of elemental sulfur and the sodium salts of carbonate and bicarbonate. The density of the solids are not greatly different to the liquid portion. Since the solids do not readily stick together, they are well dispersed in the fluid while the gas is bubbling through the tower. This also aids in ease of cleaning at turn around time.

The by-product slurry has been examined and classified by several environmental agencies. Samples of the slurry have been taken from operating towers and analyzed by independent laboratories. (See Table II for a typical analysis of the spent slurry.) Based upon this data, The United States Environmental Protection Agency has declared the slurry is not a RCRA listed waste. As defined by 40 CFR 262.11 the slurry is considered non-hazardous.

The United Kingdom, Department of Energy has placed the One-Step spent slurry into Category 5 which allows up to 1000 tons per installation per year to be discharged overboard into the sea.

The State of California-Department of Health Services has ruled that the slurry complies with Section 66305, Title 22 of the California Administrative Code and is therefore a Class II non-hazardous waste.

The requirements for a Class II waste are as follows:

non-corrosive

non-flamable

non-reactive

no heavy metals

no chlorinated hydrocarbons

no hazardous components from the EPA list of hazardous materials.

The non-hazardous classification of the spent slurry not only reduces handling risks, but it can also reduce the cost of disposal. In some areas local environmental agencies require that all wastes must be disposed in approved dump sites. In other areas only hazardous materials must go to the approved hazardous dump sites. Table III shows some typical costs for disposal of waste materials.

GUIDELINES FOR THE ONE-STEP PROCESS EQUIPMENT DESIGN

Four general parameters are required to size a scrubbing vessel for this one-step process:

- gas flow rates to be processed
- hydrogen sulfide content of the gas to be treated
- operating pressure of the system

- gas temperature at the point of treatment.

The volume of gas to be treated and the operating pressure dictate the diameter of the vessel. The diameter of the vessel should be chosen such that the maximum linear or superficial velocity in the unit will be below .16 ft./sec. Gas velocities below this range will assure a homogeneous flow regime of the gas through the fluid column. This will allow maximum gas-to-liquid contact time and complete transfer of the hydrogen sulfide from the gaseous state to hydrogen sulfide in solution.

When the velocity of the gas is controlled in the proper range, then the gas-to-liquid contact time can be regulated by adjusting the fluid column height in the vessel. Figure 2 defines the minimum fluid column height required to completely remove all hydrogen sulfide. (In Figure 2 for example, a gas stream carrying 1000 ppm of H_2S would require a 7 1/2' fluid column to sweeten the gas.) By balancing a convenient vessel diameter size and the fluid column height, a tower design can usually be produced such that the run times between recharging the vessel will be at least 30 days and sometimes longer. However recharging the one-step vessel is not a major problem as it is with some systems. In most locations complete turnaround can be accomplished in two to three hours. This includes cleaning the vessel, recharging with fresh solution and returning the system to operation.

Operating temperatures need to be somewhat controlled to obtain maximum operating efficiency. The transfer mechanism of moving hydrogen sulfide from the gaseous state to the solution state is controlled by temperature. Optimum efficiency appears to lie between 75°F and 110°F. Therefore some temperature maintenance may be desirable.

OPERATING FIELD APPLICATIONS

In a little over one year, approximately 150 operating units have been put into service. The systems have involved gas volumes from a few MCF/D up to 34 MMCF/D. Hydrogen sulfide concentrations have ranged from a few parts per million up to 7.5% This process is not adaptable to all gas treating systems. Since it is not regenerative it becomes uneconomical for high gas volumes at high concentrations of H_2S. However even this may be feasible if circumstances preclude other large regenerative systems.

Table IV is a tabulation of some examples of units in service. They are located in most geographical areas of the U.S. where gas is produced.

CONCLUSIONS

This one-step process for sweetening sour gas is simple to install and operate. The operating cost is low because no reboilers are needed and there are no pumps or other moving parts to be maintained. The capital investment is low since only one vessel is required and that can be constructed of mild steel. This process requires minimum space, which may be at a premium on an off-shore platform or on a location in a residential area. The system requires minimum manpower for periodic inspections and for recharging the vessel. And last, but not least, the by-product slurry is non-hazardous, reducing handling and disposal problems. This process certainly warrants inspection and comparison where gas treating is required.

ACKNOWLEDGEMENT

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REFERENCES

1. Dow Chemical Co., Gas Conditioning Fact Book, 1962, pp 145-228

2. United States Patent No. 4,515,759

3. Bhatia, K., W. Georgie, G. McFarland, "A New Process for Sweetening Sour Gas," paper presented at Chemicals in the Oil Industry at the University of Manchester, Manchester, England

4. Union Carbide Corporation, Gas Treating Chemicals Bulletin, 1969

Table I
Sweetening Processes

PROCESS TYPE	REGENERABLE	REGENERANT	VESSELS	SUBSEQUENT PROCESSING
Chemical Solvent	Yes	Heat	Multi	Yes
Physical Solvent	Yes	Heat	Multi	Yes
Direct Conversion	Yes	Air	Multi	No
Dry Bed	Yes/No	None	Single/ Multi	Yes/No
Specialty Solvent	Yes	Heat/Air	Multi	Yes/No
Metallic Sulfide	No	None	Single	No
Formaldehyde	No	None	Single	No

Table II
Typical Spent Slurry of the One-Step Process

COMPONENT	COMPOSITION; % WEIGHT LIQUID	SOLID
WATER	36.8	
NITRITE	1.0	
NITRATE	.9	
BICARBONATE	8.2	
CARBONATE	1.2	
SULFATE	1.7	
TETRATHIONATE	2.5	
AMMONIUM	.3	
SODIUM	7.3	
SULFUR		20.2
SODIUM BICARBONATE		17.7
SODIUM SULFATE		0.7
SODIUM TETRATHIONATE		1.6
TOTAL	59.8	40.2

The spent slurry had a pH of 8.0 and did not contain heavy metals, cyanides, sulfides, or chloronated organic compounds.

Table III
Typical Waste Disposal Costs

STATE	CLASS I[1]	CLASS II[2]
CALIFORNIA	\$150-\$200/Ton	\$11-\$14/Ton
TEXAS	\$90-\$110/Ton	TBD*
LOUISIANA	\$67-\$81/Ton	\$24-\$32/Ton
OKLAHOMA	\$60-\$70/Ton	TBD*
WYOMING	\$130-\$145/Ton	TBD*

[1] Includes: Heavy metals
Caustic
Formaldehyde
Iron sponge on chips

[2] Includes One-Step Process

* To Be Determined

Table IV
One-Step Process Operating Units

LOCATION	GAS MCF/D	OPERATING PRESSURE psi	H_2S CONTENT ppm IN	H_2S CONTENT ppm OUT	TOWER SIZE	FLUID COLUMN HEIGHT	EST. RUN TIME DAYS
COLORADO	8000	90	12	0	10' X 17'	5.5'	180
WYOMING	3000	150	800	0	7' X 20'	10.0'	20
TEXAS	300	45	1000	0	2' X 20' (2)	10.0'	30
TEXAS	4000	850	200	0	4' X 24'	6.5'	29
OKLAHOMA	800	180	80	0	4' X 20'	8.0'	240
KANSAS	200	60	165	0	2.5' X 12'	6.0'	150
LOUISIANA	16000	1035	23	0	6' X 32'	5.0'	45
CALIFORNIA	300	60	2000	0	4' X 18'	7.0'	28
UTAH	1300	800	20	0	3' X 20'	5.0'	200

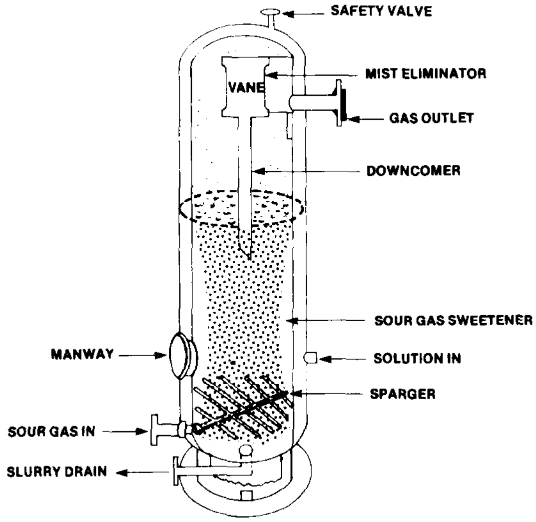

Figure 1 - Typical H_2S scrubber (bubble tower)

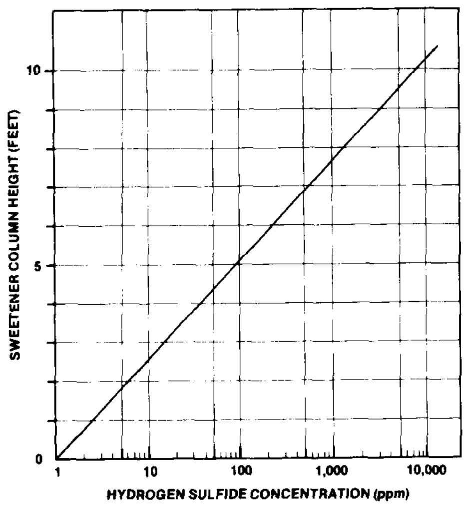

Figure 2 - The degree of hydrogen sulfide removal is controllable by adjusting process parameters