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ENVIRONMENTAL CHARACTERISTICS AND OCCUPATIONAL HAZARDS ASSOCIATED
WITH ABATEMENT OF NON-CONDENSABLE GASES AT THE GEYSERS

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ABSTRACT

Environmental restrictions on hydrogen sulfide gas emissions from geothermal operations in the Geysers steam field has led to the application of Stretford process for abatement of this gas. This process treats the non-condensable gases by taking the feedgas from the gas ejectors which are down stream from the turbine and condenser. The Venturi-absorber, which uses a non-volatile liquor, is designed to accomplish near total hydrogen sulfide removal. The origins and characteristics of potential streams from the Stretford process such as air emissions, aqueous effluents, and solid wastes are described. The occupational hazards potentially associated with operation of Stretford units and toxicity and regulatory information about hazardous chemicals involved in this process is presented.

INTRODUCTION

The non-condensable gases generally contain high proportion of carbon dioxide, hydrogen sulfide, ammonia, and traces of other gases. It is interesting to note that the hydrogen sulfide content of geothermal steam at the Geysers varies considerably with location--from about 50 to 800 ppm. Earlier units at the Geysers utilize a mix of alkali, hydrogen peroxide, and ferric ion as the hydrogen sulfide abatement system but these systems created a problem of becoming plugged in the cooling tower and in other associated systems.

The Stretford process was developed in the early 1950's by the Western Gas Board, now a part of the British Gas Corporation and the Clayton Aniline Company. This process remains the world's leading liquid redox sulfur recovery process with over 100 plants currently in operation today, and has been applied to a broad range of industrial process effluents, including:

- Geothermal Power Production
- Natural Gas Production
- Coal Gasification
- Coke Oven Gas
- Refinery Fuel Gas
- Claus Tail Gas

Since the Stretford process has demonstrated its unique ability to remove hydrogen sulfide efficiently from a variety of gas streams in several applications, this is the process that has been adopted by most of the newer operators at the Geysers for the abatement of non-condensable gases from geothermal steam.

In this paper we describe the origin and characteristics of potential waste streams and emissions from the Stretford system. However, there is no evidence that Stretford units pose a substantial threat to either health or safety if the proper precautions are taken, but employees may be exposed to hazardous chemicals from two process streams: (a) hydrogen sulfide (H_2S), ammonia (NH_3), carbon disulfide (CS_2), carbonyl sulfide (COS), mercaptans and thiophenes in the process gas entering the Stretford unit; and (b) materials in the Stretford solution itself: vanadium salts, anthraquinone disulfonic acid (ADA), and miscellaneous additives.

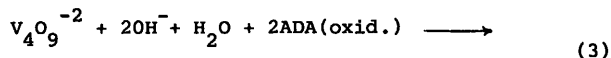
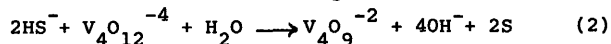
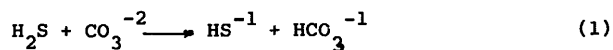
ENVIRONMENTAL CHARACTERISTICS

The chemical impurities associated with non-condensable gas present a risk of environmental contamination. Much of the technical evolution of geothermal electric technology has been motivated by the need to control the release of these impurities to the environment. The Stretford process has been successfully used in the near total removal of hydrogen sulfide from the non-condensable gas in the geothermal steam by taking the feedgas from the gas ejectors which are downstream from the steam turbine and condensers.

The original Stretford process used an aqueous solution containing sodium carbonate and bicarbonate and the weak salts of the 2:6 and 2:7 isomers of anthraquinone disulfonic acid (ADA). A major drawback of the original process was due, in part, to the rate of the reaction to form elemental sulfur. The slow reaction rate required large tank volumes and working solution inventories. Also, the amount of sulfur produced was set by the amount of dissolved oxygen in the wash liquor. Research efforts were initiated by the Northwestern Gas Board to increase the sulfur-producing reaction rate by testing various additives in the working solution. The addition of sodium vanadate was found to be the most successful. It changed the

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reaction mechanism by which elemental sulfur was formed during the process. The modified Stretford process chemistry has been described by numerous authors (3-6,8,12). The chemistry of the Stretford process is typically described as occurring in the four sequential stages as shown below.



First, H_2S reacts with alkali (Equation 1) to form bisulfide ion. Second, bisulfide is oxidized by metavanadate to form elemental sulfur (Equation 2). Third, reduced vanadium is reoxidized by ADA (Equation 3). And finally, ADA is reoxidized by oxygen (Equation 4).

These reactions are simplistic representations of the overall Stretford process chemistry. Each reaction probably consists of a series of reactions which may contain intermediate species. A possible alternative reaction pathway which has been proposed involves the reaction of molecular oxygen with ADA to produce O_2 and/or H_2O_2 oxygen species. These chemically active oxygen species then oxidizes the reduced vanadium completing the redox cycle.

The production of soluble sulfur species is one of the most undesirable side reactions frequently encountered when operating Stretford plants. Some of the possible reaction pathways for aqueous production of soluble sulfur species in the Stretford process are discussed by Trofe (9). Although these reactions may not be specifically confined to the oxidizer, the high oxidation potential in the oxidizer favors the specific reactions which produce soluble sulfur species. These unwanted side reactions add additional operating costs to the process in the form of:

- *Higher chemical consumption; and
- *Increased costs associated with treating and for disposal of Stretford blowdown streams.

The origins of potential waste streams from the Stretford process may be distinguished into three categories: (1) air emissions; (2) aqueous effluents; and (3) solid wastes.

Air Emissions

The air used in the oxidizer is usually vented to the atmosphere either directly as in the case of an open oxidizer or through a vent pipe if the vessel is enclosed. The vent gas will consist primarily of nitrogen and oxygen along with water vapor picked up from the solution. It can also contain small amounts of COS, CS_2 , mercaptans, ammonia, and hydrocarbons (2,11). If the concentration of contaminants in the oxidizer vent

gas is large enough to pose environmental health, or safety risks, then the gases may either be absorbed by an activated carbon bed or combusted.

In order to remove excess water from Stretford solution, the liquor is sent to an evaporator. The evaporator off-gas stream is normally small but it may contain small concentrations of Stretford solution compounds and/or volatile gases remaining in the solution after the oxidizer. The volatile gases present in the evaporator off-gas should be negligible since they would be expected to be driven off in the oxidizer.

Odor problems emanating from the sulfur pit can be an additional air quality problem. The predominant odor-causing compounds are mercaptans, sulfides, COS and H_2S . An analysis of the head space over the sulfur shows well over 100 specific sulfur compounds, not all of which have been identified (7).

No data are available on the fugitive emissions from Stretford plants, but the concerns are not expected to be major. Hydrogen sulfide, the most toxic gas in the system, does not exist to any significant extent beyond the inlet gas piping. COS is present in the absorber inlet and outlet gas piping, but in much lower concentrations in the inlet gas. COS produces toxic effects similar to that of H_2S but of a lesser magnitude. Carbon dioxide and other gases such as CO and CH_4 may be present in the inlet gas piping to the absorber and the absorber vent gas.

Aqueous Effluents

Stretford liquor is considered a toxic hazardous waste in California by the CAM (California Assessment Manual), primarily because of vanadium, arsenic, and mercury content. Thiosulfate is a contributor to the chemical oxygen demand of the effluents, but is not particularly toxic.

Autoclave or melter effluent is a solution purge stream which is decanted from direct, continuous sulfur melters or autoclaves. It may contain higher concentrations of salts and other contaminants than solution purge streams.

Process leaks and spills are another potential source of effluent discharges. The primary concern is related to worker health and safety due to exposures in the immediate area of the leak or spill. Many new plants recover all process leaks and spill internally via a small sump tank and finally disposed of as a hazardous waste.

Solid Waste

Sulfur is produced from Stretford plants in the form of a sulfur cake which can either be disposed of or purified to elemental sulfur. The sulfur cake is made of about 50% sulfur and 50% interstitial fluid, which contains dissolved a variety of sodium salts, process chemicals, and heavy metals. Basically for this heavy waste and its disposal must meet the criteria set forth by the

Department of Health Services (DOHS) and Division of Waste Evaluation. A waste is defined as hazardous under RCRA based on tests for corrosivity, flammability, reactivity, or toxicity, or hazardous wastes. In the case of sulfur cake, the primary concern would be toxicity as determined by application of the EPA Extraction Procedure.

An alternative to disposing of the sulfur cake is to purify the sulfur and sell it as a by-product. Sulfur is usually sold either for agricultural use as a soil amendment or as a feedstock for sulfuric acid plants, although there are other industrial uses (1). Sulfur purification is accomplished in many plants by either filtration or by decanting of the liquid followed by washing and then melting in an autoclave or similar device. The feasibility of producing salable sulfur depends upon both economics and the purity demands of the buyer.

Impurities which can be found in the sulfur include ash, carbon, salts, and metals, especially vanadium. The varying contents of ash and other impurities in the sulfur are due to different filtering, washing, and melting techniques.

Molten sulfur from autoclaves and sulfur pits can cause severe burns if accidentally splashed on the human skin (10). Incidents of flashing and fires have become more frequent and have sparked concern over the transportation of sulfur. Because of a recent expressway accident and ensuing fire in Benicia, California, molten sulfur may soon be regulated as a hazardous material by the Department of Transportation. A notice of proposed rule-making appeared in the November 21, 1986 issue of the Federal Register. This regulation, if promulgated, would have the effect of requiring shipping papers, making, labeling, and transport vehicle placarding, but would not prevent or significantly raise the cost of transporting molten sulfur.

POTENTIAL OCCUPATIONAL HAZARDS

Employees assigned to Stretford recovery units may be exposed to a number of potentially toxic chemical substances via inhalation, dermal, or ingestion routes. The greatest health and safety risk associated with Stretford plant operation is the potential exposure to H₂S gas from piping leaks and other releases in the piping upstream of the absorber. Mercaptans, carbon disulfide, ammonia, and hydrocarbons can also be released from the oxidizer vent and impact the immediate workplace. The mixing of chemicals to produce make-up solution presents another opportunity for worker exposure to sodium metavanadate dust and other less toxic sodium salt particulates which constitute a nuisance-type dust hazard. Readily available toxicity and regulatory data about some of the Stretford hazardous chemical substances is presented in Table-1.

The Permissible Exposure Limits (PEL) shown in Table-1 are the legal standards for occupational exposure in establishments under Occupational Safety and Health Administration (OSHA) jurisdiction. The Threshold Limit Value (TLV) is a recom-

mended standard for occupational exposure published annually by the American Conference of Governmental Industrial Hygienists.

CONCLUSIONS

1. Using the Stretford process, the abatement and control of the non-condensable gases that will meet current pollution control standards can be adequately accomplished in an efficient manner.

2. The main sources of air emissions from Stretford process are absorber overhead gases, oxidizer vent gases, evaporator off gases, sulfur pit off gases and fugitive emissions.

3. The potential aqueous streams from Stretford process are purge solution, melter effluent and leaks and spills.

4. The sources of solid wastes from Stretford process are sulfur/sulfur cake and equipment cleaning wastes.

5. Actions to minimize the risks from potential exposures include housekeeping and maintenance activities to reduce fugitive emissions, spills and ambient air monitors to warn of H₂S leaks. Also, standard industry safety practices for operation and maintenance of piping containing H₂S gas should be followed.

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TABLE - 1 STRETFORD PROCESS AVAILABLE TOXICITY AND REGULATORY DATA SUMMARY

Compound	OSHA, PEL	OSHA, TLV	Toxicological Effects	
			Acute	Chronic
Ammonia	50 ppm	25 ppm	Temporary blindness and intolerable irritation of mucous membranes at concentrations above 200 ppm.	Irritation of eyes and mucous membranes; odor threshold of 20 ppm or less.
Anthraquinone disulfonic acid	None Established	None Established	Low acute and chronic toxicity.	
Carbon dioxide	5,000 ppm	5,000 ppm	At concentrations of 3% it has weak narcotic effects such as reduced acuity of hearing and increased blood pressure and pulse. Depth of respiration markedly increases. Signs of intoxication become apparent at concentrations of 4-5% after 30 minutes of exposure. At levels of 7-10% unconsciousness may occur within a few minutes. One minute of exposure to 10% CO ₂ (100,000 ppm) is the lowest concentration reported to cause death in humans.	Repeated daily exposure at 0.5 to 1.5% is well tolerated by normal individuals.
Carbon disulfide	20 ppm 30 ppm	10 ppm (skin)	Narcosis at high concentrations	Central and peripheral nervous system damage. Acceleration of coronary heart disease
Carbon monoxide CO	50 ppm	50 ppm	Headache, nausea, vertigo, mental symptoms at low concentrations (<400 ppm) after exposure for several hours. Prolonged exposure at higher concentrations causes severe headache, muscular incoordination, weakness, vomiting, dizziness, dimness of vision, fainting, coma, and death.	Headache, weakness, nausea dizziness
Hydrogen sulfide	20 ppm	10 ppm	Primarily a respiratory irritant at lower concentrations (50-500 ppm). At concentrations of 250-600 ppm pulmonary edema and bronchial pneumonia may ensue. Symptoms of headache, dizziness, excitement,	Prolonged exposure of 250-600 ppm has been reported to cause pulmonary edema and bronchial pneumonia. Chronic exposure to low levels (5-100 ppm) have caused eye

TABLE - 1 STRETFORD PROCESS AVAILABLE TOXICITY AND REGULATORY DATA SUMMARY

Compound	OSHA, PEL	OSHA, TLV	Toxicological Effects	
			Acute	Chronic
Hydrogen sulfide			nausea or gastrointestinal disturbances, dryness and sensation of pain in the nose and throat and chest, and coughing. At high concentrations (500-1000 ppm) acts as a systemic poison causing unconsciousness and death through respiratory paralysis. Odor threshold of 0.3 ppm or less.	effects of conjunctivitis (inflammation of the inner surface of the eyelids), Keratitis (inflammation of the cornea), itching and smarting of the eyes, cloudy cornea, destruction of epithelial layer with sealing resulting in blurring of vision. Other symptoms include nervousness, cough and insomnia.
Mercaptans	10 ppm	0.5 ppm	Severe eye irritation, depression of central nervous system, pulmonary edema, injury to the respiratory system causing death due to respiratory paralysis.	Headache, nausea, irritation of eyes and mucous membranes.
Sodium hydroxide	2mg/m ³	2mg/m ³	Irritation of nasal passages; pneumonitis; skin and eye burns.	Permanent lung damage and ulceration of nasal passages.
Sodium-m-Vanadate	None Established	None Established	Low acute and chronic toxicity.	
Thiophene	None Established	None Established	Toxicological effects under study by National Toxicology Program	