A PRACTICAL HYDROGEN SULFIDE ABATEMENT PROCESS FOR AIR DRILLING AND VENTING GEOTHERMAL STEAM WELLS

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ABSTRACT

A simple, economic process has been developed and applied to full scale operations for the abatement of hydrogen sulfide emissions while air drilling and venting geothermal steam wells. The process consists of blooie line injection of sodium hydroxide and hydrogen peroxide. 91-98% of hydrogen sulfide emissions can be abated during the drilling of a typical geothermal steam well for a cost of less than $10,000.

INTRODUCTION

Hydrogen sulfide is an odorous gaseous pollutant generally present in geothermal steam. When the first geothermal steam well was drilled at the Geysers in 1922, the presence of hydrogen sulfide odor was accepted as a naturally occurring phenomena associated with fumarolic activity. Most of the fumarolic activity has declined during the ensuing years due to man's modifications to harness this natural energy source for electrical power generation.

The majority of today's hydrogen sulfide emissions entering the atmosphere from the Geysers are from man-made devices. Increased environmental awareness in recent years has resulted in a legislative standard for hydrogen sulfide based on the threshold of smell. This standard of 30 ppb has been exceeded on occasion as a result of Geysers emissions. New source review rules promulgated by the California Air Resources Board were recently adopted as regulation in Lake County, CA. The rule requires that the respective air pollution control officer review any proposed new source of pollutant in excess of 20 pounds/hour and deny a construction permit if there is substantial evidence that the new source will prevent attainment of the ambient hydrogen sulfide standard.

Some geothermal well drilling activity, even though it constitutes a minor transitory source of emission, has been constrained as a result of these new regulations. The response has been the development of a process - using blooie line injection of hydrogen peroxide and sodium hydroxide to abate the hydrogen sulfide emissions during drilling, plant gathering line venting and well bleeding operations in order to prevent future violations of point source emission rules or the ambient air quality standard. From preliminary laboratory work performed by FMC Corporation, a manufacturer of hydrogen peroxide, at the request of Dr. R. W. Rex, it was determined that field drilling conditions could not, economically, be lab simulated. Republic Geothermal, in August of 1976, then designed and constructed a pilot sized geothermal muffler unit for use in California's high pressure steam field, the Geysers. The muffler unit was designed to dynamically simulate flow conditions present in conventional mufflers used to suppress noise and control particulates. Steam for the field trial was supplied by Magma Power Company and at Magma's request, field and technical assistance was furnished by their operator, Union Oil's Geothermal Division.

The process involves the continuous injection of aqueous hydrogen peroxide and sodium hydroxide solutions into the geothermal steam. Injection is made into the blooie line upstream from the muffler. The principal product of the oxidation is sodium sulfate, a neutral salt. During preliminary testing, sulfide abatement of 91% was achieved at a 4:1 weight ratio of hydrogen peroxide to hydrogen sulfide and 2.8:1 weight ratio of sodium hydroxide to hydrogen sulfide.

CHEMISTRY

The products of sulfide oxidation are controlled by pH and the chemical reactions that take place with hydrogen peroxide are illustrated by the simplified equations:

$$H_2S + H_2O_2 \xrightarrow[\text{solution}]{\text{acid or neutral}} \frac{1}{X} S_x + 2H_2O$$

$$S^{--} + 4H_2O_2 \xrightarrow[\text{solution}]{\text{alkaline}} SO_4^{--} + 4H_2O$$

At ambient temperatures a period of 5 to 20 minutes is generally needed for hydrogen peroxide to completely react with sulfide in aqueous solution. This range has led some investigators to conclude that indigenous catalysts are operating. At 122°F the reaction is complete in 15 seconds. Rates in water solutions at still higher temperatures should be extremely fast. The presence of heavy metal ions will increase reaction rates even further. Reactions in the pilot system proceeded to completion in less than 4 seconds.

In detail the reactions proceed at more rapid rate in the liquid phase and H_2S assimilation into the liquid phase is accelerated by an increased liquid phase pH as follows:

$$2\ NaOH + H_2S \rightleftharpoons Na_2S + H_2O$$

$$\text{or } NaOH + H_2S \rightleftharpoons NaHS + H_2O$$

plus Peroxide

$$Na_2S + 4H_2O_2 \rightarrow Na_2SO_4 + 4\ H_2O$$

$$\text{or } NaHS + 4H_2O_2 \rightarrow Na\ HSO_4 + 4\ H_2$$

The reaction products Na_2SO_4 and Na HSO_4 are stable salts and will not revert to hydrogen sulfide in the sump during neutralization activities upon completion of drilling.

Analysis of test muffler condensate reaction products performed for Republic by Quality Water Laboratory, Inc. identified trace amounts of SO_3, SO_2 and elemental sulphur, and it is probably due to the catalytic action of iron and trace heavy metals that the reaction does not proceed in precise stoichiometric proportions as displayed in the simplified equations above. Although not field tested, many other combinations of oxidents, and pH modifiers can be utilized to effect similar results. However, since hydrogen peroxide is a readily available, inexpensive industrial chemical and strong reagent solutions can be prepared with NaOH, sodium is the preferred cation for creating a strong alkaline environment for the practical disassociation and oxidation of H_2S.

Measurements made of the resultant steam emitted to the atmosphere indicate no caustic or peroxide carryover to the atmosphere.

OPERATING PROCEDURES

In field practice, implementation of the system is very straightforward. Caustic and peroxide injection points should be separate and located as closely as practical to the banjo box in order to provide maximum system residence time for the reaction to proceed to completion and maximum exposure to high Reynolds, Froude, & Webber number flow regimes for optimal mixing. Vacuum sampling points should be provided both upstream of the injection point and on the muffler stack in order to control abatement levels and optimize process efficiencies.

Hydrogen peroxide storage and transfer lines should be 304 or 316 passified stanless steel using low volume positive displacement chemical metering pumps for injection such as Pulsa Feeder Model 7120 4.2 to 42 GPH electric driven pumps. Care should be taken that storage tanks are protected by anti-siphon valves and that all hydrogen peroxide handling equipment has been passified with 68% Nitric Acid for $\pm$ 24 hours.

Caustic storage and handling facilities can be mild steel and require no special handling procedures other than adequate containment provisions for personnel safety and anti-siphon valves to avoid storage contamination. If the system is to be utilized during cold weather conditions, a 25% aqueous solution of sodium hydroxide is recommended in that its freezing point is 0°F where 50% solutions freeze at 50°F.

For a typical geysers production well $\pm$ 2000 gallons of storage should be provided for each chemical depending on delivery problems at the specific location.

Injection points should be provided with high energy spray nozzles for improved mixing and dispersion in the blooie line. In line strainers are recommended in that the nozzles will tend to plug with foreign material. Provisions should be made for removal and cleaning of spray nozzles which provide minimum down time and personnel exposure.

The scope of this presentation is necessarily limited to the initial development phases of the abatement process and the construction aspects of full scale facilities. Republic Geothermal has not had the occasion to implement the process on a full scale operational basis, however, this sulfide abatement process has been utilized by other operators with reported attainable field abatement levels of up to 95% with per well costs averaging $6500. An additional important advantage of this blooie line abatement process is that atmospheric pollution can be mitigated continuously, independent of drilling operations. Previously tested systems, relying on drill string injection, necessarily preclude abatement during all rig operations other than drilling. This new method results in significant reductions in abatement efficiencies and undesirable pollution of the atmosphere.

Republic currently has its hydrogen sulfide process equipment leased to Phillips Petroleum Co. and it is being operated for Phillips by the R. F. Smith Corporation. The R. F. Smith Corp., a geological services corp. specializing in the provision of well mud logging services, also provides rig floor compressor breathing equipment, Scott Air Packs, blooie line vacuum sampling devices, hydrogen sulfide monitering equipment and intends to provide and operate the hydrogen sulfide abatement process described in this paper as a service to operators in the Geysers area.

REFERENCES

1. Castrantas, H. M., Rex, R. W., Turner T. A., "Hydrogen Sulfide Abatement at Geothermal Wells" Proceedings, Lake County Geothermal Environmental Conf. (1976)

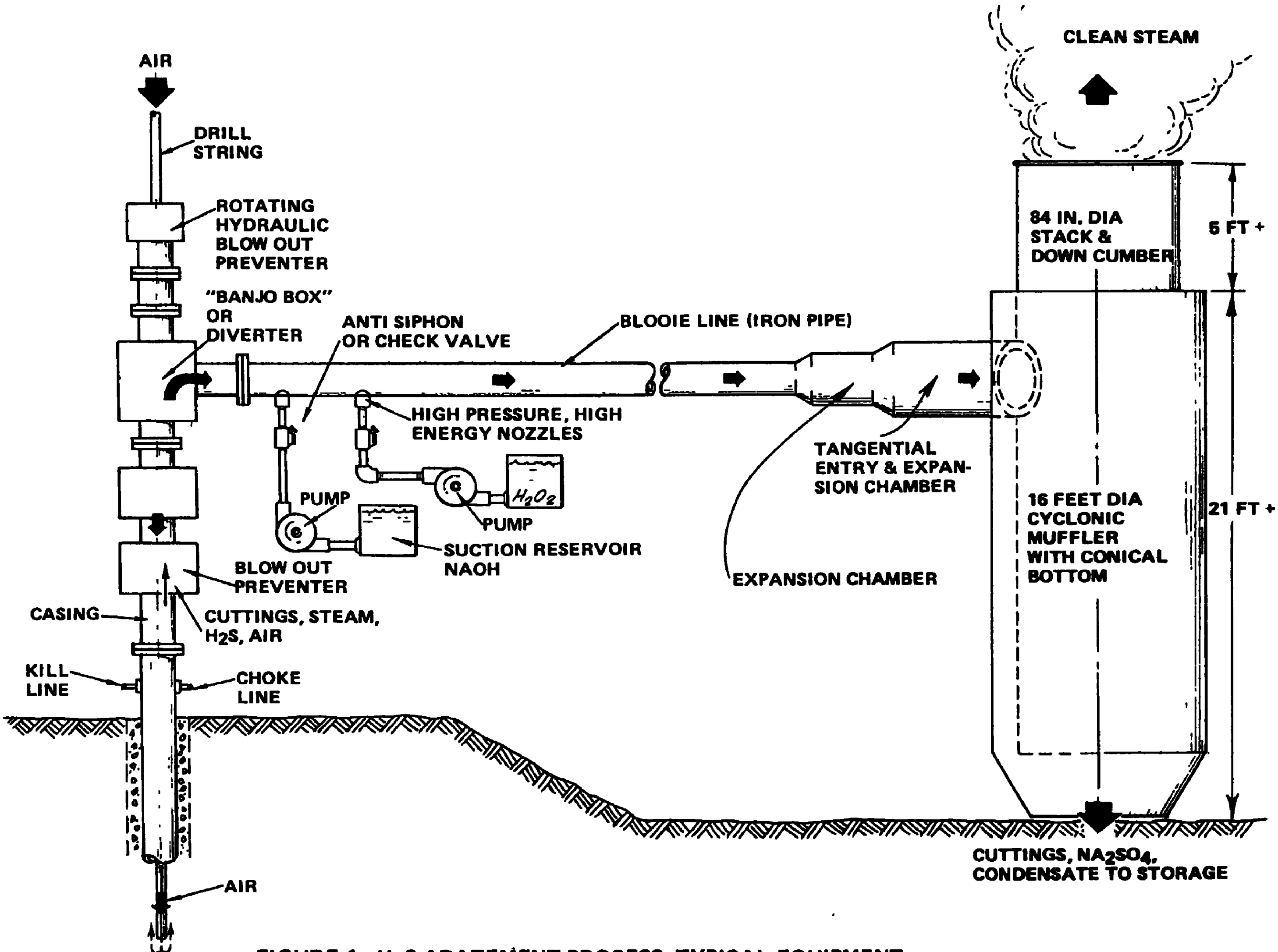

FIGURE 1. H_2S ABATEMENT PROCESS, TYPICAL EQUIPMENT