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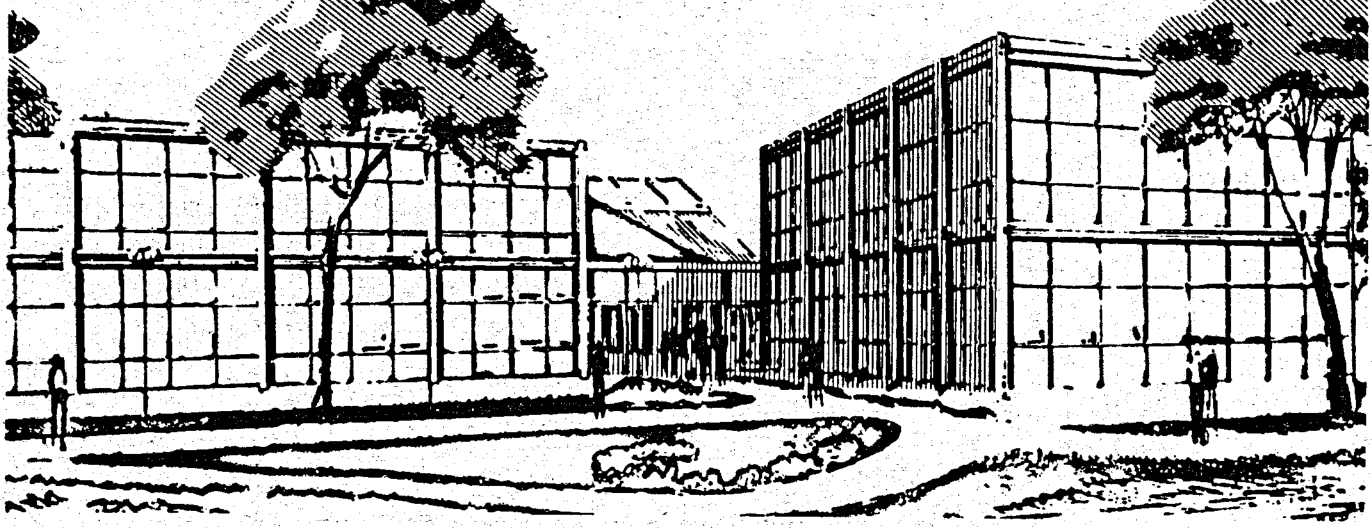

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DISCLAIMER

AN EFFECTIVE H_2S ABATEMENT PROCESS USING GEOTHERMAL BRINE EFFLUENTS

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ABSTRACT

A simple and potentially inexpensive method for removal of H_2S from noncondensible gases evolved in geothermal flash processes has been successfully tested on a small scale in the field. The method consists of scrubbing the noncondensible gases of H_2S with brine effluents which contain relatively high concentrations of Pb, Zn, and Fe such as those of the Salton Sea and Brawley Geothermal Fields in the Imperial Valley, California. For plant applications, noncondensibles including H_2S would be ejected from a surface steam condenser (necessary to minimize the volume of liquid in contact with H_2S) and scrubbed with effluent brine just prior to preinjection clarification. The metal sulfide precipitates are removed in the clarification step and the noncondensibles, less H_2S, are vented as usual.

INTRODUCTION

The removal of H_2S from noncondensible emmissions from geothermal power plants continues to be a major engineering consideration in the overall design and operation of a plant. Commercialization of the SSGF in the Imperial Valley, California, will be no exception. Operating data at the 2-stage flash Geothermal Loop Experimental Facility (GLEF), a joint SDG&E/DOE project, indicate H_2S concentrations on the order of 1000-2500 ppm (by volume) in the vented noncondensibles. The rate and length of time of well production appear to influence the amount of noncondensible gases produced. When Magmamax 1 was initially produced, the noncondensible gas content, primarily CO_2, was as high as 3 wt% (SDG&E 1974). This led to the design and the initial operation of the GLEF as a flash binary process. However, with prolonged well production, the noncondensible gas concentration has declined to ~0.3 wt% (Jacobson 1979) and as a result, the GLEF was modified to operate in the flash steam mode. Nonetheless, the H_2S concentration in the noncondensibles remains high, although the absolute quantity appears to have declined along with the CO_2. It is clear that some form of H_2S abatement will be necessary to satisfy air quality standards.

H_2S ABATEMENT PROCESS

A simple and inexpensive method for removing H_2S from noncondensible vent gases was identified and initially tested by LLL. The method involves scrubbing the noncondensibles with spent brine effluents which contain high concentrations of heavy metal ions such as Pb, Zn, and Fe. The H_2S is absorbed in the brine and reacts to form insoluble heavy metal sulfides which precipitate out and are removed prior to reinjection. The method is particularly applicable for use with Salton Sea and Brawley Geothermal Field brines which are known to contain high concentrations of heavy metal ions. At the Salton Sea Geothermal Field, the brines contain on the order of 65 ppm Pb, 280 ppm Zn, and 270 ppm Fe, far in excess of the stoichiometric quantity necessary to react with all the H_2S. The reabsorption of H_2S in the spent brine is favorable because of the new equilibrium established between the gas and liquid at lower temperature and higher pH.

The principal reactions are the absorption of H_2S and dissociation:

$$\begin{aligned} H_2S\ (g) &= H_2S\ (aq) \\ H_2S\ (aq) &= H^+ + HS^- \\ HS^- &= H^+ + S^= \end{aligned}$$

followed by precipitation of metal sulfides

$$\frac{2}{Z} = M^{Z+} + S^= \quad M_{2/Z}S(s),$$

where Z is the oxidation number.

The overall reaction is

$$\frac{2}{Z} M^{Z+} + H_2S\ (g) \quad M_{2/Z}S(s) + 2H^+$$

The precipitation of metal sulfides is also the sulfide eliminating step in the $CuSO_4$ process (Brown 1979, Coury 1977). But unlike the $CuSO_4$ process, use of effluents eliminates chemical feed costs, regeneration steps, and problems that may be associated with slurry pumping and recirculation.

INITIAL MEASUREMENTS

Initial measurements with a small, single stage contactor (see Figure 1) in which vent gas from the GLEF stack was contacted with cooled effluent at 25°C in a countercurrent flow mode gave high efficiencies. At a gas/liquid flow ratio, corresponding to 0.3 wt% noncondensible gas in the brine, > 98% removal of H_2S was attained. At a higher gas/liquid ratio, corresponding to 1 wt%, gas content, scrubbing efficiencies continued to be quite high at 95%. H_2S concentrations were measured with "Ecolyzer H_2S Analyzers" Series 2000 from Energetics Science Inc.

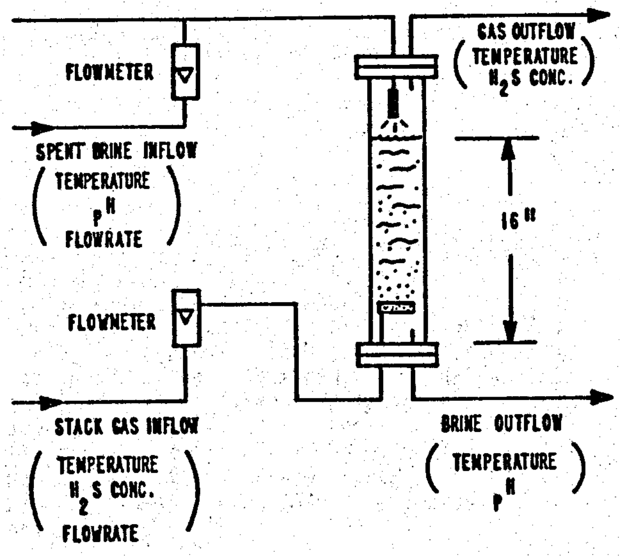

Figure 1. Shcematic diagram of test apparatus for generating data on H_2S removal by contact with brine effluents. Contactor consists of 2" dia. glass pipe. Gas distribution is produced by fritted glass sparger. ( ) indicates measurements made on flow streams. Brine samples are collected for metal ion and suspended solids analysis.

More recent measurement with GLEF brine effluents maintained at 80 ± 5°C, close to the temperature (100°C) at which the effluents are processed for injection also resulted in > 96% removal of H_2S at 0.3 wt% gas/liquid flow ratios. However, the efficiency of removal begins to decline steeply at a gas/liquid ratio above approximately 0.5 wt%. This drop off may be due to insufficient column height, since the highest gas/liquid ratios used were still well below maximum based on stoichiometry. Gas inlet temperatures were running about 43°C from the stack at the GLEF. We observed a significant drop in brine pH from pH 5.1-5.5 to pH 4.1-4.6 following contact with the noncondensibles gases. This is consistent with the reaction described above and with absorption of CO_2. Some adjustment in effluent clarification operation may be necessary to overcome the retardation of silica precipitation as a result of lowered pH. On the other hand, precipitation of metal sulfides could enhance overall clarifier operation by improving solids contact and sludge blanket characteristics. Figure 2 is a plot of overall scrubber efficiency for H_2S removal vs. gas/liquid ratios. The results demonstrate the high efficiency of H_2S removal using a simple, single-stage contactor without internal packing or baffling. Optimizing scrubber design should improve H_2S removal efficiency at the higher gas/liquid flow ratios. A brief test at the GLEF by Magma and SDG&E using the reaction chamber of a 30 gpm EIMCO clarifier as the contactor indicated scrubbing efficiencies on the order of 97% (Featherstone 1979). This adaptation of the process combines H_2S abatement with preinjection clarification with minimal added plant costs, and with potential beneficial effects with respect to clarifier efficiency and mineral recovery from the sludge.

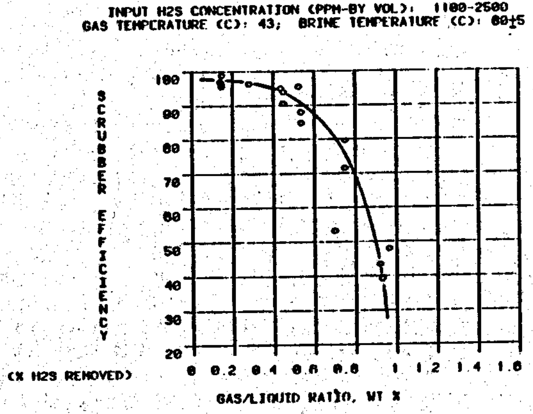

Figure 2. H_2S removal efficiencies over the potential range of noncondensible gas to brine ratios for SSGF brines.

IMPACT ON STEAM CONDENSATION

In order to achieve high overall abatement of H_2S, a surface type steam condenser will be required to minimize the volume of liquid in contact with H_2S in the gas phase and thereby maximize the amount of gaseous H_2S to be ultimately scrubbed.

The distribution of H_2S between the gas and liquid phases is not sensitive to the absolute quantity of H_2S, but depends largely on pH and temperature. The distribution is given by Henry's Law

$$\frac{H_2S(aq)}{H_2S(g)} = K = 10^{-1.15} (@40°C) \text{ (Helgeson 1969)}$$

where H_2S (aq) is the concentration of dissolved H_2S in moles/liter and H_2S (g) is the partial pressure of H_2S in atmospheres. At a 40°C condensing temperature and a mass ratio of condensate to brine of 0.2, about 98.8% of the H_2S would be partitioned in the noncondensible gas phase. At condensate pH's greater than ∿ 6.2, progressively more of the H_2S will be absorbed in the liquid and less H_2S ejected in the gas phase. Desorption and release of H_2S will then occur should the condensate be used for cooling water makeup. In previous measurements at the GLEF (LLL 1977), the 1st stage condensate pH was approximately 6.2. Lower stage steam condensates had much higher pH's (8.5-9.5) and would readily absorb H_2S. However, only a small fraction of H_2S is retained in the brine after the 1st stage flash. This amount, subsequently desorbed in the lower flash stages and evolved with the low pressure steam, may still pose a problem. For an accurate assessment of specific H_2S abatement requirements the actual amounts and distribution of H_2S in the various streams need to be precisely determined.

CONCLUSIONS

A highly efficient method for removal of H_2S from the noncondensible gases by scrubbing with spent brine effluents has been demonstrated in a small, single stage contactor operating in a countercurrent flow mode. The method is unique to those geothermal fluids such as the Salton Sea and Brawley Geothermal Field brines which contain relatively high concentrations of heavy metal ions such as Pb, Zn, Cu, and Fe. The process is simple, inexpensive, and is particularly adaptable to preinjection clarification.

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