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AN ANALYSIS ON THE BIOX PROCESS TO HYDROGEN SULFIDE ABATEMENT

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ABSTRACT

Few years ago a new method to solve the problem of hydrogen sulfide emission from geothermal plants has been developed. This method is based on the liquid phase oxidation of the hydrogen sulfide, that is carried out in the cooling tower using an oxidizing biocide as catalyst. This process called "BIOX"(BIocide-assisted OXidation) has been developed by Darrell L. Gallup /1/2/3/4/ that suggests to use Trichloroisocyanuric acid as oxidizing biocide. According to this author, using this agent it is possible to reduce secondary emission of hydrogen sulfide from cooling tower and if the lay out of the plant is modified, sending the turbine offgases to the liquid loop of the cooling tower, it is also possible to prevent primary emission. In this work an analysis of the process has been developed to verify the limits of the process.

INTRODUCTION

Hydrogen sulfide emission is one of the most important problem that have to be solved in the exploitation of geothermal fields. This product is the main contributor to air pollution of this type of power plants. Until now it has been discharged directly into the atmosphere but new regulations adopted in many countries oblige to a strictly reduction in the hydrogen sulfide emission. In some countries the abatement of hydrogen sulfide is required by law as necessary condition of their permission for working (Weres /5/).

The hydrogen sulfide can be eliminated with an incineration of the sulfur recovered in the liquid phase (Dalrymple et al. /6/) or with a treatment of the gas stream coming out of the turbine. This treatment can be an incineration, an oxidation over catalysts or an absorption in solutions. The Biox process has the goal to oxidize the hydrogen sulfide contents in the liquid phase, that flows between the direct contact condenser and the cooling tower, to sulfur or higher oxidation state. At the first time, by pure chance, this process has been tested at the Salton Sea geothermal fields and at Bulalo (Philippines). Gallup showed that the quantity of trichloroisocyanuric acid that is necessary to oxidize all sulfides is lower of the quantity that derives from the stechiometry of the reaction

$$3H_2S + 4C_3N_3O_3Cl_3 + 12H_2O =$$
$$3H_2SO_4 + 4C_3H_3N_3O_3 + 12HCl$$

If this reaction occurs a weight ratio of 9.11 kg of trichloroisocyanuric (TCCA in the following) acid for 1 kg of hydrogen sulfide is necessary. Gallup suggested that TCCA works as a catalyst and using a quantity of TCCA that is at maximum 10% of the previous quantity but very often 1% of the stechiometry it is possible to oxidize practically all the hydrogen sulfide to sulfate. This process is interesting because if it works it is possible not only to avoid hydrogen sulfide emission but also the deposit of colloidal sulfur on the cooling tower packing.

Interesting results develop from this new process but the limits of application are not really clear. In particular because the mechanism of oxidation is unknown it is important to look for if this is a general process or if it can be applied only for particular applications.

DESCRIPTION OF THE EXPERIMENTAL LOOP AND TEST EXECUTION

A schematic diagram of the experimental loop is showed in Fig. 1. As can be seen, the pilot plant consists of column, with 100 mm as inner diameter, equipped with 1.5 meter of static mixers. This loop is equipped with two probes, on the liquid inlet and on the liquid outlet, that allow the pH measurements and the sampling of liquid that have to be analyzed with spettrophotometer

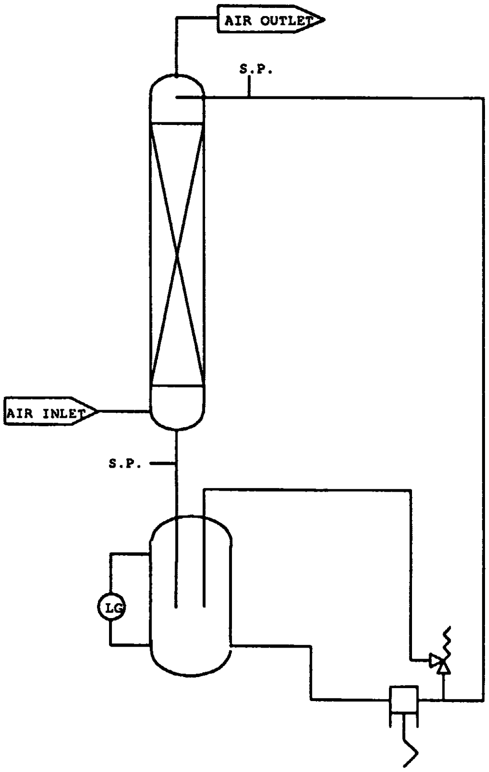

Fig. 1 Schematic diagram of experimental loop

This loop simulates what happens in a cooling tower, the results are interesting, not for the absolute value of the abatement, but only for the qualitative effect that the use of TCCA can induce.
The time test changes between 2 and 3 hours and during this time a continuos measurement of the pH has been performed. The measurements of sulfur concentration in the liquid phase have been performed every 10 minute and the analysis adopted, based on the use of spettrophotometer, allows a sensibility of 0-0.6 mg/l with an accuracy of +-0.003 mg/l.

ANALYSIS OF THE EXPERIMENTAL RESULTS

In this paragraph will be shown experimental results obtained in this work.
First of all some tests have been performed to verify the reproducibility of the experimental results. Fig 2 shows the conversion of hydrogen sulfide in two different tests performed with a solution containing 55 ppm of hydrogen sulfide and air as oxidizing phase.

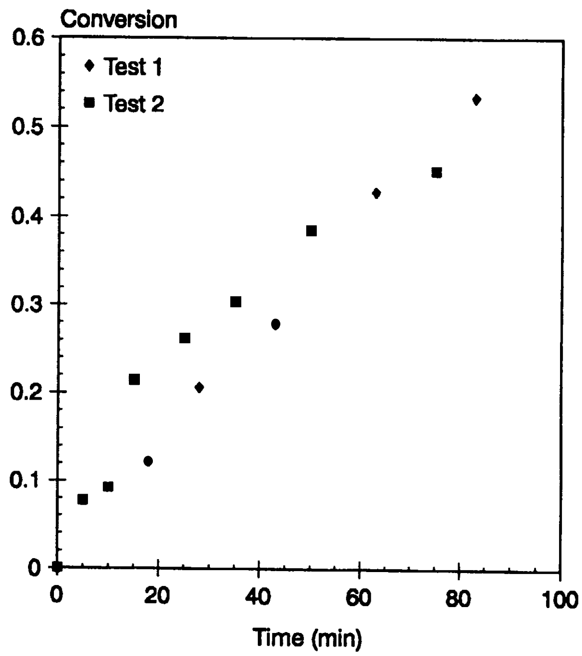

Fig. 2 Reproducibility tests. Conversion Vs Time (Oxidation of Hydrogen sulfide with air)

Fig. 2 shows the good reproducibility of the experimental results performed in this work. This figure shows that, using air as oxidant 80 minutes are sufficient to convert about 60% of the starting sulfides content.
The aim of the work is to evaluate if BIOX process can be applied in all the geothermal plants. For this reason some experiments have been performed and the results have been plotted in the next figures. In these figures square symbols indicate the results obtained if oxidation of sulfides have been performed using only air, triangles indicate the experimental results obtained using little quantity of TCCA in the liquid phase

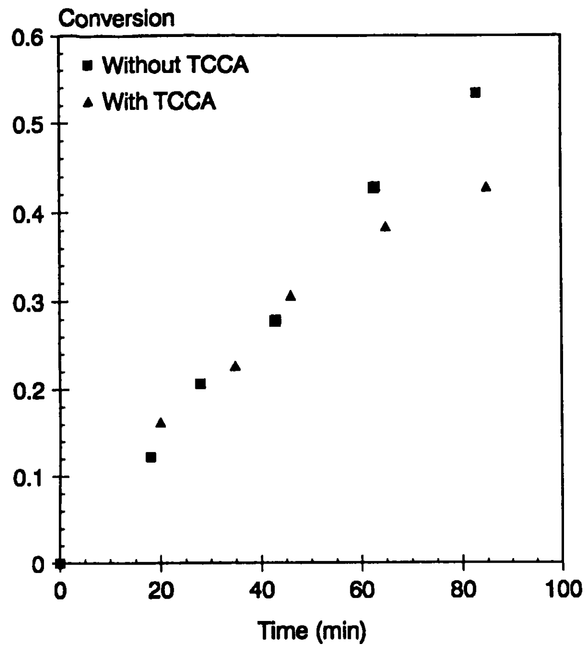

Fig. 3 Test 1. Conversion Vs Time (Oxidation of Hydrogen sulfide with air and using TCCA as catalyst)

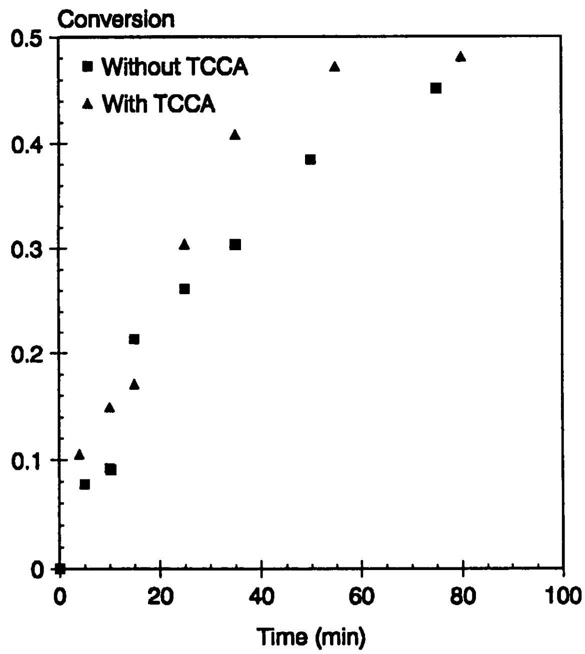

Fig. 4 Test 2. Conversion Vs Time (Oxidation of Hydrogen sulfide with air and using TCCA as catalyst)

In these two tests the starting concentration of sulfides was about 55 ppm and the weight ratio between the TCCA and sulfide ions was about 0.14. These figures show that the presence of TCCA doesn't seem to introduce any changes in the sulfides oxidation process.

Fig 5 shows test performed with different working conditions. In this case the starting sulfides concentration was about 20 ppm and the weight ratio between TCCA and sulfides ions was 0.046.

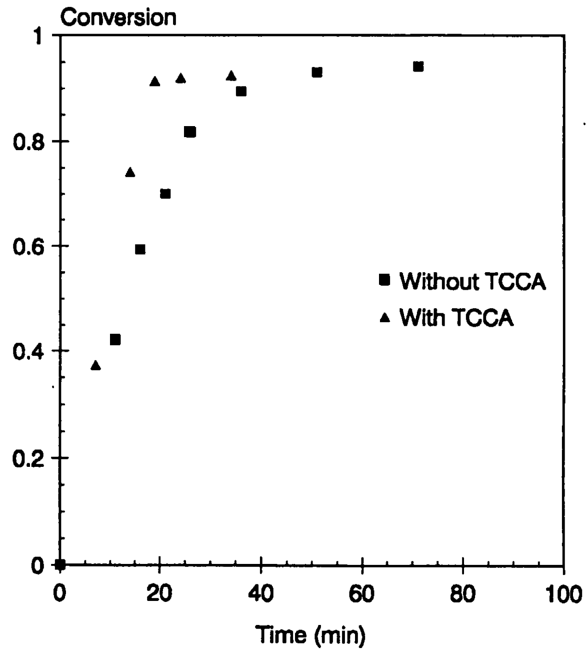

Fig. 5 Test 3. Conversion Vs Time (Oxidation of Hydrogen sulfide with air and using TCCA as catalyst)

Also in this case no appreciably changes are induced by the use of TCCA. In table 1 working conditions for the different tests have been reported

Test	Air Flowrate m3/h	Liquid Flowrate l/h	pH	Starting Sulfides ppm
1	75	54	10	55
2	50	75	10	55
3	50	75	10	20

The results obtained in the first part of the work indicate that sulfides in water and sulfides in a solution containing TCCA are oxidized by air with the same velocity.

For this reason if a catalyst action is present this is associated to a formation of a complex between some metal and TCCA.

In the second part of the work some experiments have been performed to verify if some complex between TCCA and Iron, Copper or Nickel can induce a catalyst action.
To verify if the catalyst action induced by the complexes of TCCA and Iron, Nickel or Copper is due to the complexes or is due to the presence of the metals two different acquisitions have been performed. For each metal the first acquisition is relative to the use of the complex whereas the second is relative to the metal without the TCCA.
Fig. 6 shows the effect of Nickel complex.

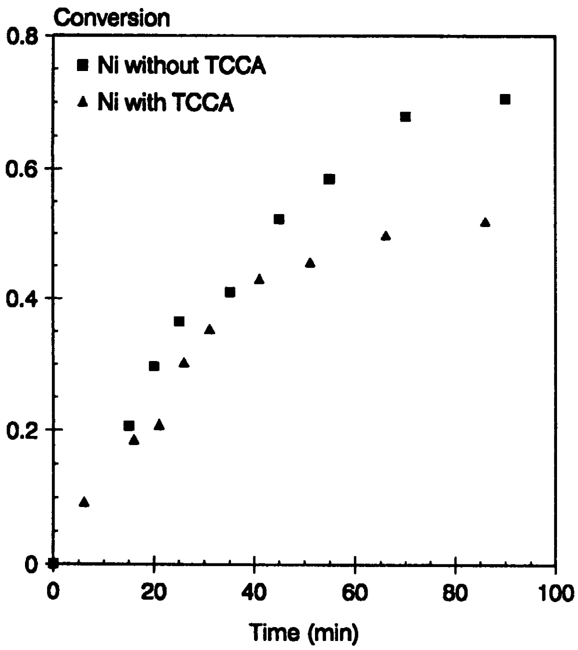

Fig. 6 Nickel effect. Conversion Vs Time (Oxidation of Hydrogen sulfide with air and using as catalyst complex Ni-TCCA and Ni alone)

Also in this case, as in the case of oxidation without metals, the effect of TCCA seems to be negligible. The conversion obtained using Ni alone even seems to be greater of the conversion obtained with TCCA and Ni.
In the following the effect of Iron has been tested also in this case the presence of TCCA did not induce any positive difference from the case of oxidation the Iron alone.
Fig 7 shows the experimental results obtained.

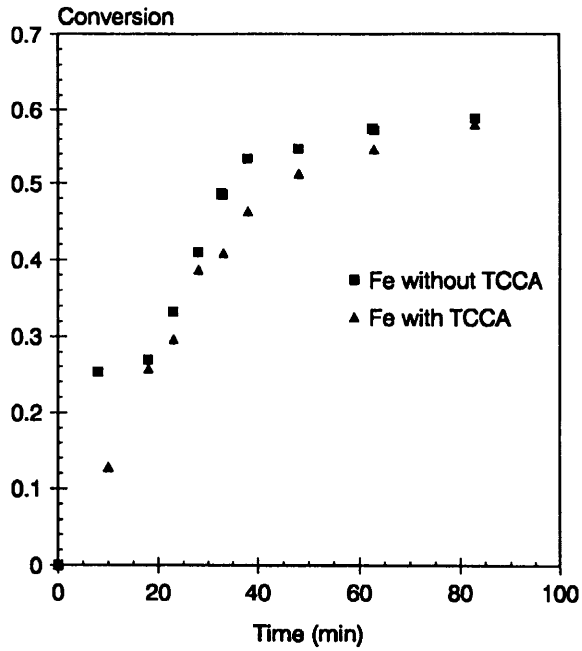

Fig. 7 Iron effect. Conversion Vs Time (Oxidation of Hydrogen sulfide with air and using as catalyst complex Fe-TCCA and Fe alone)

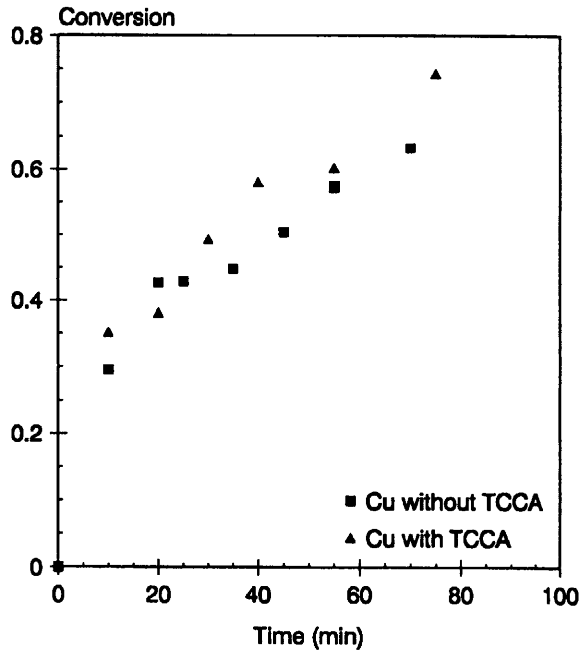

Fig. 8 Copper effect. Conversion Vs Time (Oxidation of Hydrogen sulfide with air and using as catalyst complex Cu-TCCA and Cu alone)

The last metal that has been analyzed is Copper, as for Iron and Nickel, the effect of the presence of TCCA seems to be negligible
Fig 8 shows the experimental results.

CONCLUSIONS

In this paper the BIOX process has been analyzed. This process developed to oxidize hydrogen sulfide to sulfite has been proposed few years ago. It has been applied at Salton Sea geothermal field and at Bulalo, Philippines, with good results. Because the range of application of this process is not clear in this paper some laboratory's experiments have been performed. These tests have evidenced that the presence of trichloroisocyanuric acid seems to have negligible effects both alone and if into a complex with Copper Iron or Nickel. The experimental results have showed that the catalytic action of trichloroisocyanuric acid not always is present. For this reason it seems to be necessary a more accurate analysis on the process to identify what is the mechanism that induced the oxidation of sulfur to sulfide at Salton Sea and at Bulalo. This research it is really important because otherwise the use of BIOX process in others geothermal fields can be absolutely useless.

ACKNOWLEDGMENTS

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