ELECTRO-FENTON AND ELECTROCOAGULATION FOR SMALL SCALE REMOVAL OF H_2S FROM GEOTHERMAL GAS STREAMS

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ABSTRACT

Field experiments are being undertaken to trial the effectiveness of the electro-fenton and electrocoagulation processes to remove H_2S from condensed steam at Wairakei. The cooled condensate and accompanying gas (~0.4wt% gas in total of which 97wt% is CO_2 and 1.5wt% H_2S) is passed through the electrochemical cell at 450 ml/min. Preliminary experimental results show that H_2S is easily removed at >97% efficiency from the gas stream. The aim is to collect sufficient data across a range of experimental conditions to determine the factors which affect removal efficiency of H_2S which would help design a larger scale reactor.

1. INTRODUCTION

One of the potential uses of a geothermal gas stream that is free from H_2S is for carbon dioxide (CO_2) enrichment for enhanced plant growth in a glasshouse. Although effective chemical technologies exist for removal of poisonous and corrosive hydrogen sulphide (H_2S) from geothermal gas, these are expensive and only economic for electricity production in a strict regulatory environment (Padilla, 2007; Rodríguez et al., 2014). Also the residual H_2S concentrations achieved or desired in many of the industrial abatement processes, would still be too high to be able to be used for horticultural purposes.

We are trialling electrocoagulation (EC) and electro-fenton (EF) processes to remove H_2S from condensed steam at Wairakei. Using aerated power station offgas would have been preferable but such an effluent stream was not readily accessible.

2. EF AND EC PROCESSES

These processes are used for the remediation of industrial waste waters containing a wide variety of toxic and hazardous pollutants (Akyol et al., 2013; Nidheesh and Gandhimathi, 2012; Emamjomeh and Sivakumar, 2009). They are simple and efficient methods, environmentally friendly and do not generate secondary pollutants. Other advantages include ease of operation, uncomplicated equipment, absence of adding additional chemicals (in EC), rapid sedimentation and less sludge production. Disadvantages include the possible need to dispose of the sludge.

In EC, generation of coagulants is in situ by dissolving of sacrificial anodes by application of a direct current. In this application cast iron electrodes are used which generates iron (Fe^{2+}) monomeric and polymeric hydrolysis products which react with the H_2S.

In the conventional Fenton process both Fe^{2+} and hydrogen peroxide (H_2O_2) are added externally while in EF the Fe^{2+} is added by the sacrificial anode and the H_2O_2 is added either externally or generated electrochemically by oxygen reduction at acid pH. The oxidation of H_2S by H_2O_2 is greatly accelerated by the addition of Fe^{2+} due to the formation of highly reactive hydroxyl radicals. In these experiments the H_2O_2 was added externally but air was also injected into the condensate-gas stream.

2. EXPERIMENTS

Steam from the “S” steam line at the Wairakei Power Station is cooled in a ¼” stainless steel coil to between 65°C to 70°C. Past the reactor the condensate cooled to <40°C (typically ~ 35°C).

The composition of the gas in steam varied between experiments due to power station operations but was typically ~0.4wt% gas in total of which 97wt% was CO_2, 1.5wt% H_2S and remainder insoluble residual gas but negligible ammonia).

A saturated solution of NaCl is injected in the condensate-gas stream at ~ 8 ml/min to increase solution conductivity. At this point 1% H_2O_2 could also be injected, at 2 or 4 ml/min as well as air between 200 and 400 ml/min.

The stream flows through the electrochemical cell at a mass flow rate ~ 430 ml/min. The cell consists of a 1 m long 25 mm diameter titanium tubular reactor which acts as the cathode and which is packed with 1mm iron wire which acts as the anode. The power supply was a Statron type 2224.1.

The mixture then flows via a holding vessel and pipe to a sump. At this point the liquid and gas are separated and can be individually sampled without additional air contamination. Sampling was undertaken 40 minutes after any change in experimental conditions as it took this long to fill the vessel with liquid. Past the reactor the gas is segregated from the condensate, flowing as discrete bubbles on top of the liquid at a faster rate than the water flow.

Gas samples were collected into evacuated glass ampoules containing 4N caustic and cadmium acetate (or 4N caustic alone). Water samples were collected into rubber sealed bottles for total bicarbonate and also 100 ml filtered samples were preserved with either zinc acetate or cadmium chloride for total sulphide.

3. RESULTS

3.1 Data

The gas composition and condensate flow rate for five experiments is given in Table 1. The H_2S removal percentages, $(1\text{-}H_2S_{vapour}/H_2S_{incoming})$x100, on passing the condensate and gas streams through the reactor and piping with and without current are shown in Tables 2 and 3 respectively. Table 4 lists the theoretical moles of H_2S (assuming sulphur as reaction product) that reacts by injecting 2 and 4 ml/min of 1% H_2O_2 and 9 and 16 mmoles/min of air.

All the results are summarized in Figure 1.

Table 1: Experimental conditions

Expt. #	Condensate	CO_2	H_2S	CH_4	Others (incl. CH_4)	CO_2/H_2S	H_2S/CH_4
	ml/min		mmoles/min				
1	425	16.5	0.78		73.8	21.2	
2	433	32.7	0.63		12.0	52.3	
3	418	35.3	1.2		0.7	30.4	
4	440	40.6	1.0	0.27	1.0	43.0	3.5
5	440	42.5	0.83	0.20	6.8	51.2	4.2

Table 2: %H_2S Removed, no current

Expt. #	No treatment	H_2O_2	H_2O_2	Air	Air
	%	ml/min	%	mmoles /min	%
2	48			16	24
3	70	2	84		
3		4	92		
4	50	4	84	9	49
5	52				

Table 3: %H_2S Removed, with current

Expt. #	I	EC	H_2O_2	H_2O_2 + EC	Air mmoles /min	Air +EC
	amps	%	ml/min	%		%
1	2.3	81				
1	5.5	92				
2	5.1	77				
2	5.1				16	86
2	5.1				16	95§
3	5.5	96				
3	3.9		2	95		
3	3.9		4	97		
4	5.0		4	98		
4	5.0				9	95
4	5.0	92				
5	4.0		4	97		
5	4.0	90				

§ temperature increased to 96°C

Table 4: Theoretical moles of H_2S that can react with with air or H_2O_2.

1% H_2O_2 ml/min	1% H_2O_2 mmoles/min	% H_2S reacted[1] mmoles/min
2	0.6	0.6
4	1.2	1.2
Air mmoles/min	O_2 mmoles/min	% H_2S reacted[2] mmoles/min
16	3.4	6.7
9	1.9	3.8

[1] molar ratio $1O_2{:}1H_2S$; [2] molar ratio $0.5O_2{:}\ 1H_2S$ assuming elemental S is the reaction product

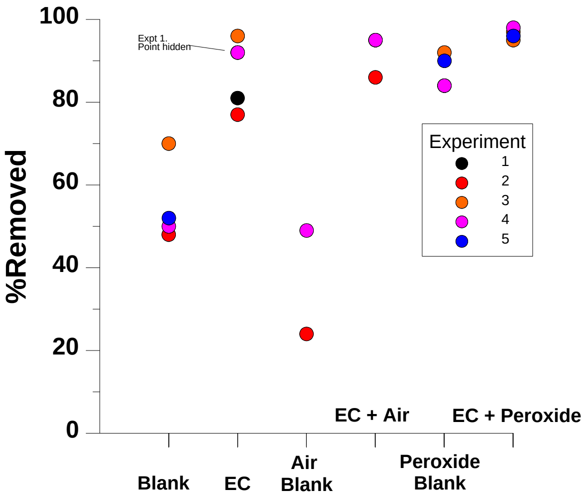

Figure 1: %H_2S Removed, all data

3.2 Data Trends

3.2.1 No treatment

About 50% of the total incoming H_2S was removed from the gas phase without any treatment, other than passing the condensate and gas stream through the reactor and piping. This is because of the relatively high solubility and lower concentration of H_2S compared to CO_2 (Henry's law constants 12.4 and 37.8 bar/molal at 35°C respectively). Experiment 3 had a higher removal of 70% (and also higher relatively for subsequent EC). This could not be accounted for by any different experimental conditions between this experiment and the other 3 where blank samples were collected and is seen as an anomalous result.

3.2.2 Air only

Air was injected at two different flow rates, 9 and 16 mmoles/min (experiments 4 and 2 respectively). At the lower air flow rate there was essentially no change to the removal percentage of H_2S compared to no air injection. The inference being that removal was due to scrubbing by condensate without any additional oxidation by aeration. At the higher flow rate the removal was worse and halved to 24% (Table 2). At the higher flow the air strips out the dissolved gas into the vapour phase which accounts for the reduction in the apparent decrease in removal of H_2S from the vapour phase.

3.2.3 H_2O_2 Only

The H_2O_2 injection rate was set by prior steam line sampling which determined the likely H_2S mass flow. However subsequently during these experiments, the gas concentration in steam was lower than expected. This meant that the H_2O_2 rate was higher than would have been ideal to clearly see the effect on removal with changes in injection rate and treatment. H_2O_2 was injected in experiments 3, 4 and 5 at 4 ml/min and at 2 ml/min in experiment 3 only. An injection rate of 4 ml/min should have been theoretically sufficient to react with all the incoming H_2S (Table 4). In experiment 3 at 2 ml/min the removal percentage rate increased over no treatment to 84%. Increasing the injection rate to 4 ml/min further increased the removal to 92%. In experiments 4 and 5 an injection rate of 4 ml/min gave removal rates of 92% and 84% respectively (Table 2).

In the no treatment option discussed above, the total fraction of H_2S (vapour + liquid) is unchanged at the exit, as removal of H_2S from the vapour phase is by scrubbing into the liquid phase. The difference with addition of H_2O_2 (and also EC) is that almost all of the total H_2S is removed by reaction. In experiment 5, analysis of the condensate showed less than 3% of the total incoming H_2S remained in the liquid with either H_2O_2 addition or EC, whereas 37% of the H_2S was carried in the liquid phase with no treatment. Total dissolved carbonate (as CO_2) in the condensate measured in experiments 4 & 5, varied between 6 to 11%, of the total, depending on pH.

3.2.4 EC Only

For experiments 1, 3, 4 & 5 the removal at 5A was typically just over 90%, although in experiment 2 the removal unaccountably was lower at 77%. Halving the current to 2.3A in experiment 1 only reduced the removal by 10% to 81%. The reactor sediment was determined by XRD to be greigite (Fe_3S_4) and amorphous iron sulfides. After exposure to air lepidocrocite (FeO(OH) and elemental sulfur were also detected.

3.2.5 EC and Air

In experiment 2 injection of 16 mmoles/min of air increased the removal over EC alone by 9%, from 77% to 86% and subsequently to 95% by increasing the condensate temperature to 96°C (although there is no comparison with EC alone at such a high temperature). Recall that in experiment 2, air only (no EC), the removal rate was 24% due to the sparging of H_2S from the condensate into the vapour phase. In experiment 4, at an air injection rate of 9 mmoles/min, the changes over EC alone was negligible; an increase from 92% to 95%. The experiment was not repeated and the small increase could be within experimental error.

3.2.6 EC and H_2O_2

EC and H_2O_2 together only increased the removal by minor amounts over EC alone. In experiment 3 EC at 5.5A gave a similar result (~95%) as EC at 3.9 A and 2 ml/min H_2O_2 injection. In the latter increasing the injection rate to 4 ml/min only further increased the removal to 98%. In experiments 4 and 5 at 4 ml/min H_2O_2 injection, the increase over EC alone was only 7% respectively to 97%. However the amount of H_2S dissolved in the condensate as a percentage of the total, with EC only and EC with H_2O_2 was essentially the same (3% and 2% respectively in experiment 5). Unlike air, with H_2O_2 alone (no EC) the removal was substantially higher than with no treatment, up to 92% in experiment 3 at 4 ml/min injection rate.

4. DISCUSSION

The aim of these experiments is to collect sufficient data across a range of experimental conditions to determine the factors which affect removal efficiency of H_2S which would help design a larger scale reactor. These preliminary experiments showed that given the experimental conditions in Table 1, EC alone can remove over 90% of the incoming H_2S. Additional injection of H_2O_2 only increased the removal by another ~7%. However H_2O_2 injection by itself was about as efficient at EC alone, so both together should perhaps have been highly efficient at removing the H_2S.

H_2O_2 stability is affected by both temperature and pH. In these experiments the condensate temperature in the reactor was relatively constant (between 65-70°C) for most experiments (with and without current) while the pH typically increased by ~ 1 pH unit to pH 6 with EC. The pH difference cannot account for relative ineffectiveness of H_2O_2 with EC.

The most likely explanation is that reactor voltages were too high resulting in large excess of production of Fe^{2+}, more than sufficient to remove most of the H_2S from solution (viz. essentially the same amount of H_2S remaining in solution for EC and EC+H_2O_2 in experiment 5). The problem then becomes one of better mixing of the gas and liquid phases in the outlet piping. This may also account for the relatively little effect observed of injecting air where the H_2O_2 is produced in situ from the electrochemical reduction of oxygen.

Scrubbing alone could remove about half of the incoming H_2S and could constitute the first step in the process. However loss of dissolved CO_2 limits the effectiveness of scrubbing as would having a gas stream higher in H_2S. Increasing the pH increases the solubility of H_2S but also increases the solubility of CO_2.

5. FUTURE WORK

1. The experiments will be repeated with conditions which will better reflect those required for the EF process rather than the present which favored EC. The dose rates and voltages will be lowered to attempt to the better differentiate between the treatment options rather than working at near maximum removal rates.

2. The design of the piping past the reactor will be modified to increase the gas-liquid mixing.

3. The iron sludges appeared to oxidize relatively quickly and recirculating these may improve efficiency of the process requiring less energy expenditure.

4. The experiments will also be conducted on much higher total gas and higher H_2S content than in the present experiments.

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REFERENCES

Akyol, A., Can, O.T., Demirbas, E. and Kobya, M.: A comparative study of electrocoagulation and electro-Fenton for treatment of wastewater from liquid organic fertilizer plant. *Separation and Purification Technology, 112, 11-19.* (2013).

Emamjomeh, M.M., Sivakumar, M.: Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *Journal of Environmental Management, 90(5), 1663-1679.* (2009).

Nidheesh, P.V. and Gandhimathi, R. Trends in electro-Fenton process for water and wastewater treatment: An overview. *Desalination, 299, 1-15.* (2012)

Rodríguez E.; Harvey W.S.; Ásbjörnsson E.J.: Review of H_2S Abatement Methods in Geothermal Plants. *Proceedings 38th Workshop on Geothermal Reservoir Engineering*, (2014).

Padilla, E.K.: Preliminary Study on Emission Abatement and use of Gas from Geothermal Power Plants in El Salvador. *United Nations University, Geothermal Training Programme, Iceland,* Reports 2007, Number 18. (2007).