H_2S OXIDATION IN AEROSOLS

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SUMMARY - Hydrogen Sulphide is often released into the atmosphere when deep geothermal fields are exploited for energy recovery. The oxidation products of H_2S are SO_2 and H_2SO_4, both of which *can* cause environmental problems. The effect of H_2S emissions cannot be quantified however, because the rate of atmospheric oxidation is unknown. It was assumed that the oxidation would take place primarily in the aqueous phase in aerosols and therefore a laboratory apparatus was designed and built to study the rate of oxidation of H_2S in aerosols. For aerosols in the 5 - 25 μm range, the rate of oxidation in neutral to acidic pH was found to be less than the residence time in the apparatus.

1.0 INTRODUCTION

Hydrogen sulphide is released to the atmosphere when deep geothermal fluids are exposed to lower pressures either naturally or artificially for energy recovery. The Ohaaki power station, for example, emits about 1800 tonnes/year H_2S to the atmosphere. Ultimate exploitation of the central North Island's geothermal resource could release 10,000 tonnes/year. A recent review of emissions identified a risk to "ecologically vital" wetlands along the Waikato River from sulphur dioxide (SO_2) produced by the oxidation of H_2S. SO_2 is directly toxic to vegetation (Economic Commission for Europe Report, 1984) and is further oxidised to sulphate ion (SO_4) in the atmospheric aerosols (Charlson et al., 1978) which is a major component of acid rain.

However, the effect of H_2S emissions can not be quantified because the rate of atmospheric oxidation is unknown. It may be assumed that the oxidation of H_2S will proceed primarily in aerosols, and will be particularly important in the mists or fog which occur in humid regions of geothermal activity. The large surface area presented by the water aerosol should facilitate H_2S gas adsorption and oxidation through-increased contact with atmospheric oxygen. As well, the very small radius of curvature in droplets can promote high surface energies in aerosol particles, which can further enhance chemical reaction times. Consequently, it was felt that the chemical reaction of H_2S oxidation would be very fast, and the apparatus designed allowed for these fast reaction times. The purpose of this project was to measure the rate of H_2S oxidation under simulated "fog" conditions and so allow prediction of the rate of SO_2 production in cooling tower plumes.

The oxidation of H_2S gas dissolved in water normally proceeds by one of two reaction paths, depending upon pH. At 25°C and pH <7, H_2S is may be oxidised to elemental sulphur or to S_2O_3 and SO_3 by the reactions:

$$H_2S + 0.5O_2 = S^\circ + H_2O \quad (1)$$

or: $$2H_2S + 2O_2 = S_2O_3^{-2} + H20 + 2H' \quad (2)$$

followed by $$S_2O_3^{-2} + O_2 + H_2O = 2HSO_3^- \quad (3)$$

and $$HSO_3^- + 0.5O_2 = SO_4^{-2} + H^+ \quad (4)$$

At pH values greater than 7, H_2S dissociates to HS^- which may oxidise to form $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}. The sulphur oxyanions $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} were therefore the species of interest in the aerosols.

2.0 EXPERIMENTAL APPARATUS

The initial apparatus is shown diagrammatically in Figure 1, with an inset showing an enlargement of the nebuliser. The reaction chamber was made of 100 mm perspex tubing, with a nebuliser fitted at one end, and the spinning aerosol collector at the other. The nebuliser creates an aerosol suspension or "fog" by passing pressurised, humidified air or N_2 over a fine venturi connected to a supply of distilled or distilled, deoxygenated water. The nebuliser was constructed from a modified atomic absorption atomizer. Flow rates of the nebulising gas and the H_2S were measured with flowmeters. The reaction chamber was held at an angle of ca. 30° to the horizontal plane. Under these conditions, the very large aerosol particles fall under the influence of gravity and can be purged from the apparatus through the drain shown in the figure. H_2S gas is introduced around the nebuliser and interacts with the fog as it ascends towards the collection apparatus at the higher end. Initial attempts using a reaction chamber without bends were run both vertically and horizontally. Residence times for the fog in the chamber, at the maximum gas flows used, vaned from 18-20 seconds in a vertical chamber to 25-30 secs in a horizontal chamber.

The design of the spinning aerosol collector relied on centrifugal force to impact the aerosols on to the periphery of the collector where they would coalesce and then could be collected. To this end, a circular plate with

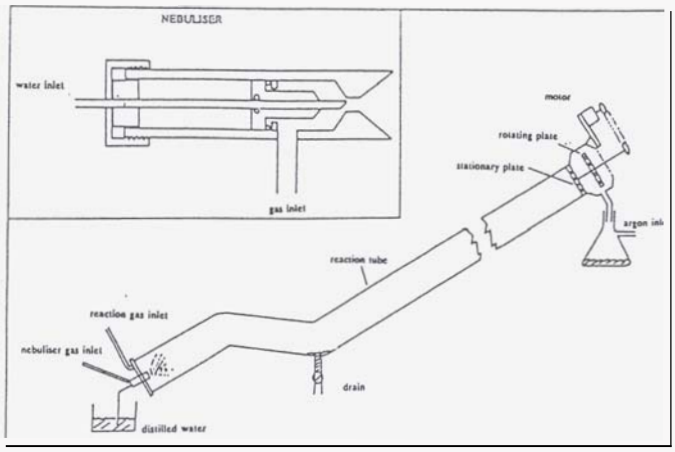

Figure 1. Initial apparatus configuration with inset showing nebuliser.

various sized holes was rotated using a small electric motor. It was found necessary to include a stationary plate with small holes just prior to the collector to minimise the formation of a vortex within the reaction tube. It was found that the centrifugal force created by the spinning plate caused the gas stream to be directed into the aerosol collection tube. This forced a large amount of H_2S gas into the NaOH solution where the coalesced aerosols were being collected, and therefore gave very erroneous results. This was remedied by maintaining a positive argon pressure within the collection bottle, however, it was felt that the whole collector design needed to be changed to give reliable **sampling.**

A second configuration of the apparatus was therefore constructed and this is shown diagrammatically in Figure 2. In this ***case,*** the nebuliser design was identical to the initial apparatus, but a completely new design of aerosol collector (Figure **3)** was employed. This was a jet impactor, based on that reported by Berner (1988). The aerosol is forced through a jet where the velocity is increased. The jet then impacts on to a flat surface where the aerosol's greater momentum forces it on to the surface and it then coalesces with other aerosol particles to form a liquid drop. This drop is then forced to the edge of the impaction plate where it falls under gravity. The collection device was made from a specially dense HDPE, the impaction plate was fabricated from TEFLON, and three different accelerating jets were constructed to allow for differing flow rates. The liquid sample was collected into a syringe and injected immediately into the HPIC, eliminating the need for a sample collection medium and delays in the analytical procedure. *Also,* there is minimal contact of the sample with the H_2S stream, and so post-coalescent interaction is avoided. The H_2S was added to the aerosol stream in the angled section of the reaction tube, where the larger particles had already coalesced. The new design incorporated a drain to collect these very heavy aerosols, and the exhaust gas stream exiting from the aerosol collector was now passed through a NaOH solution to absorb the excess H_2S for safety reasons. The flow rates

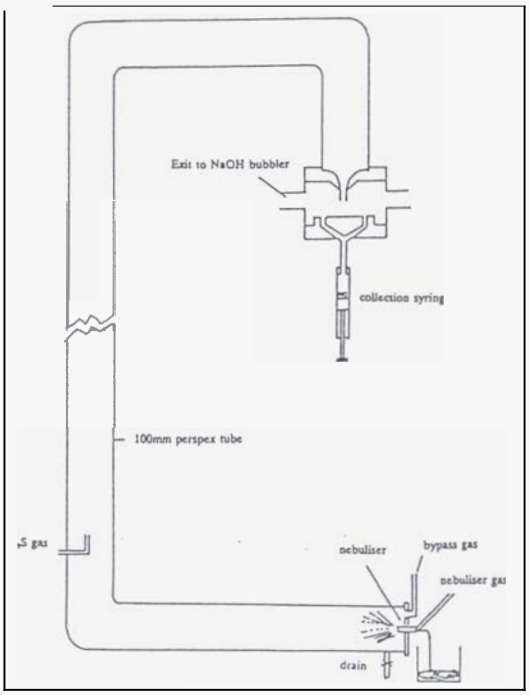

Figure 2. Final design utilising existing nebuliser and new aerosol impaction collector

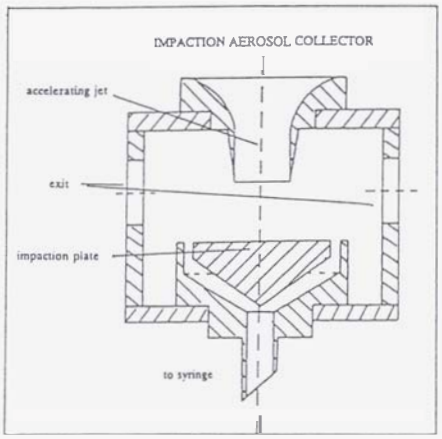

Figure 3. Design of the jet impactor aerosol collector

of the input gas streams were measured and as well, the outlet gas stream was monitored. Two inlet gas streams were used besides the H_2S inlet. Correct operation of the nebuliser required a certain flow, but the impact collector required a greater flow. Consequently a bypass gas flow was introduced beside the nebuliser to increase the total flow to that required for correct operation of the impact collector.

3.0 ANALYTICAL PROCEDURES

3.1 *Chemical Analysis*

Initially, the analytical techniques were as follows for:

1. H_2S - the methylene-blue colorimetric method as set out in Greenberg (1992)

2. S_2O_3, SO_3 and SO_4 - HPIC using a tetraborate/ mannitol eluent, an AS4A anion column and a conductivity detector.

Later, another **DIONEX HPIC** was used for the analysis of all sulphur species that were measured. **A** method had been developed to measure HS^- as well as the oxygenated sulphur species. **This** used a **NaOH** eluent, **an** AS4 column and both conductivity (SO_3,S_2O_3 and SO_4) and UV/Vis spectrophotometric (HS^-, SO_3 and S_2O_3) detectors. This system requires meticulous attention to clean eluents due to the possibility of HCO_3^- being formed on contact with air. This detail was advantageous in the analysis of H_2S, where contact with air also needed to be avoided. Results are reported in mg/kg unless otherwise stated.

The **HPIC** system was not able to detect polythionate ions, although some considerable effort was expended in testing various procedures, and various pure polythionate species.

3.2 *Measurement of Aerosol Particle Size*

A method for the optical measurement of aerosol particle size was developed, based on the method of D.J. Schaefer. This uses a "Formvar" gel to preserve the impact craters of *the* aerosol when it is accelerated in a jet. The gel is coated on to a microscope slide from a 2-**3%** solution of "Formvar" in $CHCl_3$, then exposed to aerosols travelling at >20m/sec. The size of the impact craters are then measured under a microscope. Two examples are shown in Figure **4.**

4.0 RESULTS

4.1 *Aerosol Particle Size*

For the nebuliser settings used in this study, aerosol sizes vaned from *5* - 10μm *(see* Table **1).** Often, there appeared to be a bimodal distribution, which may reflect both the true aerosol size (2.5-10 μm) and the size of agglomerated droplets falling from the nebulizer (>20 μm). The latter are a natural consequence of condensation and agglomeration in the jet design used for accelerating the aerosols. It was found that very small aerosols could not be produced with the very limited equipment available.

Smaller aerosol particles of 0.1 - 5.0 μm **can** only be produced by condensation processes. A high pressure gas atomizer such as we were using, has a particle size range of about 1 - 100 pm. Liquid pressure sprays produce particle sizes of around 100-5000 μm. For comparison, mists are normally in the range of 0.1 - 10 μm, while clouds and fog are in the 1- 100 μm range. Raindrops vary from about 100 μm upwards.

Table **1:** Aerosol sizes for varying nebulizer conditions.

Nebulise (l/min)	*Air* flow (l/min)	Aerosol size (μm)
Fine jet:		
14	37	5 - 10, > 20um (bimodal)
13	37	5-25
17	37	2.5-10 at side of jet 10-50 at centre of jet
Mid *size* jet:		
17	43	2.5-15um

The nebuliser pressure = 35-38 psi in all cases

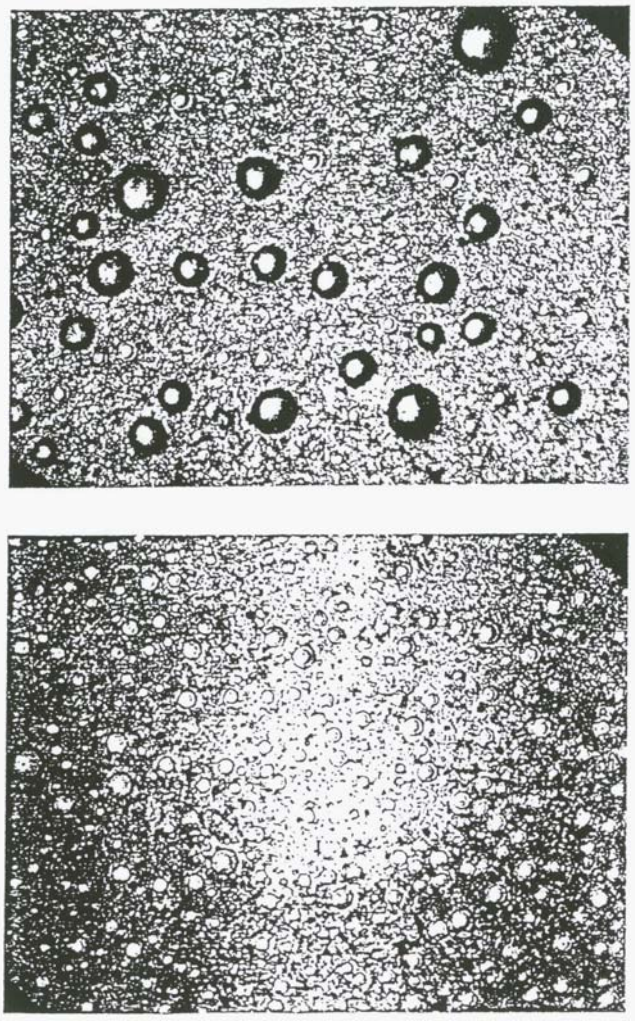

Figure **4.** Photomicrographs of impact craters in FORMVAR. The scale is approximately 1cm = 35μm.

4.2 *The absorption and oxidation of H_2S gas.*

The following gas flow and pressures are common to all results listed in Table 2 except S5 and S6:

Bypass air flow	31 l/min
Bypass N_2 flow	33 l/min
Total pressure	35-40 psi
Nebuliser	13-16 l/min

Samples S5 & S6 were collected into deoxygenated NaOH. *All* others were collected directly from the chamber using a syringe to avoid contact with the atmosphere. The H_2S flow results shown in Table 2 are also plotted in Figure 5.

Initially, the experiments were directed towards measuring the rate at which H_2S was dissolving into the aerosols. *As* might be expected, H_2S concentrations in the aerosol increase as a function of H_2S gas flow (Figure 5). The two highest H_2S flows correspond to samples S5 and S6 and it is clear that the rotating aerosol collector provides a greater opportunity for interaction with the H_2S inlet gas. However, it is also evident from the results in Table 2, that substituting 0,-free N_2 for air as a carrier gas in the reaction chamber made little difference to the apparent oxidation rate of H_2S in the chamber. The concentrations of oxyanions in aerosols in contact with air are similar to those of aerosols in contact with O_2-free N_2. The concentrations of S_2O_3 also appeared to be independent of H_2S concentrations although SO_3 and SO_4 concentrations showed a marginal correlation (Figures 6a-6c). Even when extreme lengths to omit atmosphere oxygen from the chamber were employed, the concentration of oxyanions remained the same (eg. sample KLB 4-8).

If oxidation is occurring in the reaction chamber this would appear to indicate that either the oxidation rate of H_2S is independent of both PO_2 and dissolved H_2S concentrations. As this is most unlikely, other possibilities were then examined.

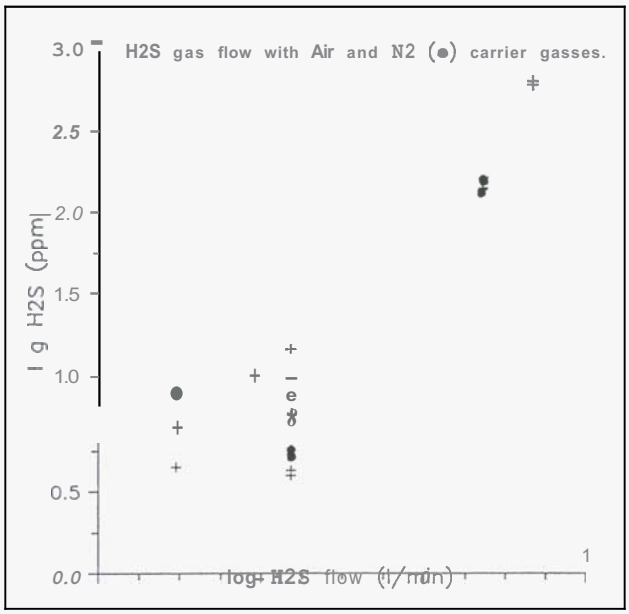

Figure 5. Dissolved H_2S concentrations as a function of H_2S flow into the reaction tube.

Table 2. Results of experimental runs using both distilled and deoxygenated water aerosols and air and N_2 carrier gasses.

Sample	H_2S flow	Aerosol	H_2S	S_2O_3	SO_3	SO_4
A. Air carrier gas						
S5	4.7	d H_2O	615	1.6	7.4	24.8
S6	4.7	d H20	625	5.6	7.6	24.1
KLB 14-4	0.13	d H_2O	9.39	0.07	0.3	0.3
KLB 15-4	0.22	deox H_2O	14.7	0.15	0.41	0.11
KLB 16-4	0.045	deox H_2O	4.5		0.12	
KLB 16-4(2)	3.3	deox H_2O	144	1.6	2.82	0.06
KLB 30-7	0.22	deox H_2O	4.31	11.43	5.53	0.21
KLB 30-7(2)	0.22	' "	4.00	6.47	3.70	0.20
B. O_2-free N_2 carrier gas						
KLB 23-4	3.3	deox H_2O	137	4.26	3.18	1.04
KLB 23-4(2)	2.3	deox H_2O	147	2.63	2.73	0.41
KLB 30-7(3)	0.15	deox H_2O	10.4	12.25	5.60	0.34
KLB 3-8	0.22	deox H_2O (s)	5.76	4.16	3.24	<dl
	(after 1 hour in syringe)		5.33	3.36	3.1	<dl
KLB 4-8*	0.22	deox H_2O	7.47	3.80	3.64	0.14
KLB 4-8(2)	0.03	deox H_2O	7.52	4.16	4.04	0.08
KLB 4-8(3)	0.03	deox H_2O	7.58	3.45	3.51	0.25

* Using glove bag around inlet system, and He and N_2 bubbled water in nebuliser and humidifier respectively.

4.3 *The effect of aerosol composition*

It is possible to vary the chemistry of the aerosol fluid by substituting different liquids into the nebuliser. Although the use of oxygenated water in the aerosol did not appear to affect H_2S oxidation, a brief examination of the effect of aerosol composition on H_2S absorption and oxidation confirmed that more alkaline solutions will take up more H_2S, with a proportional increase in the oxidation products (see Table 3).

Table 3. The effect of aerosol composition on H_2S dissolution and oxidation

Aerosol	H_2S	S_2O_3	SO_3	SO_4
deox H_2O	144	1.6	2.82	0.06
0.001 NaOH	178	2.49	4.03	0.09
0.01 NaOH	426	6.77	7.13	-

4.4 *Oxidation outside the reaction chamber*

It appears from all of the previous results that some oxidation is occurring in the system as a whole. One possibility is that the N_2 used (supposedly O_2 free) as an inert gas had traces of oxygen present. Consequently, an experiment was carried out using He gas followed by the N_2 in an effort to confirm the N_2 purity. It has been mentioned previously that the eluents for the HPIC had to be continually bubbled with helium to maintain an oxygen free solution by displacement of other gases initially and then by maintaining a positive pressure inside the eluent container. An H_2S sample was made up using helium bubbled water where it could be guaranteed that no oxygen was present in the solution. The sample was transferred to the HPIC using oxygen free techniques. Immediately following this, the solution was bubbled with the oxygen free nitrogen and a further sample transferred to the HPIC. The results are shown in Table 4. There is no significant difference between the two samples indicating that the N_2 contains no oxygen impurities.

Table 4. Comparing H_2S oxidation in solutions purged with He and with 0,-free N_2.

Sample treatment	H_2S	S_2O_3	SO_3	SO_4
H_2O boiled, purged with He (25 mins) then H_2S.	116	86.2	18.5	0.76
As above, then bubbled with N_2	148	102	27.6	0.64

From all of the work to this point, it appeared that oxidation was occurring outside the sample chamber after sample collection. There were then just two possibilities:

a) oxidation occurring in the sample prior to analysis

b) oxidation occurring inside the HPIC system

The effect of oxidation reactions after collection and before analysis was examined by holding the samples in the syringe prior to injection into the HPIC (Table 5). Evidently, little oxidation of H_2S occurred over the time frames examined.

Table 5. Immediate and delayed analysis of collected samples

Medium	Time	H_2S	S_2O_3	SO_3	SO_4
0.005 NaOH	20hrs	615	1.6	7.4	24.8
" "	200hrs	625	5.6	7.6	24.1
syringe	5hrs	5.76	4.16	3.24	<dl
"	65hrs	5.33	3.36	3.1	<dl

It was then almost certain that oxidation was taking place after sample collection and after injection into the HPIC. The likely effect of H_2S oxidation in the eluent was tested in two separate ways. Initial work (Table 6) had indicated that oxidation in caustic solutions was possible and reasonably rapid:

Table 6: Oxidation rates in oxygen-bearing 0.005m NaOH medium after collection

Collection Medium	H_2S	S_2O_3	SO_3	SO_4
ox-NaOH	240	210	21.7	34.0
ox-NaOH	278	97.7	69.2	71.0

Consequently, the caustic soda eluent was deoxygenated and the oxidation rates tested before and after deoxygenation (Table 7). The same degree of oxidation occurred suggesting that if oxidation is occurring in the HPIC system, oxygen is available from sources other than the eluents.

Table 7: The effect of deoxygenating the NaOH eluent.

Sample treatment	H_2S	S_2O_3	SO_3	SO_4
H_2O boiled, bubbled with He (25 mins) then H_2S (0.15 l/min)	116	86.2	18.5	0.76
Bubbled eluents with He (20 min) then reran (1) above	177	56.3	22.6	0.65

At this stage, it was concluded that the oxidation was indeed taking place inside the DIONEX HPIC. Further investigation showed that the most probable explanation was that the flexible pressure tubing used within the instrument was permeable to oxygen, so that the eluent was receiving oxygen before encountering the very large surface area (and therefore very reactive component) of the HPIC column.

5.0 CONCLUSIONS

Reactions (1) - (4) given in the introduction, show the oxidation path of H_2S in acid and near-neutral solutions. The experimental runs using distilled or deoxygenated water as an aerosol developed a pH as low as 4.5 following contact with the H_2S gas. In this case, one would expect the formation of elemental sulphur and its absence in the collected samples or the reaction chamber is further evidence that the oxidation observed was not occurring in the reaction chamber.

Instead, the caustic eluent used in the HPIC provides a conducive environment for the oxidation of HS to S_2O_3 and SO_3. Together with the very large reactive surface area of the HPIC column, the very small amount of oxygen that is able to permeate the tubing in the HPIC is sufficient to give measurable oxidation products.

The amount of oxidation observed is the same regardless of whether *air* or an inert gas is used in the reaction chamber. This suggests that the reaction rate is greater than the residence time in the-reaction chamber. This residence time is of the order of 12-15 secs. No detectable oxidation was observed in this time when neutral aerosols were formed. It appears that oxidation in alkaline solutions is much faster, however this is probably not relevant for the geothermal situation.

6.0 REFERENCES

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