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FACTORS INFLUENCING PLUME VISIBILITY

Report to Pasminco Metals - EZ Ltd

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SUMMARY

Factors influencing the visibility of the plumes from the Pasminco - EZ smelter at Risdon were investigated during two brief measurement campaigns during October 1990. The first campaign was disrupted by an industrial dispute so that a second campaign was instigated.

The parameters investigated were:

(i) Characterisation of the aerosol at either 'A' or 'B' stack and ahead of the foreshore treater by filtration and subsequent analysis.

(ii) the NO content of 'A' stack gases monitored continuously, whilst grab samples taken from other locations were periodically determined.

(iii) aerosol loadings of both the stack gases and upstream of one of the treaters monitored continuously with nephelometers.

Time-lapse photographic surveillance of the plumes from the foreshore stacks was also carried out.

It was concluded that the aerosol consisted of H_2SO_4 and the amount was strongly correlated with the levels of NO, the latter varying between 15 - 30 ppm before dilution with ingress air at the base of the stacks. The correlation was emphatically reinforced by the addition of ammonia to the roaster feed which resulted in very visible plumes.

Aerosol was produced by the exit gases from the new (#6) as well as the old (#3 and #4) acid plants as demonstrated on start-up after shutdown for maintenance.

No strong correlations were observed between roaster bed temperature, use of contaminated water (CW) or other operating conditions. However, there was little N content in the CW at the time of the observations.

The major source of NO would appear to be recycled dross from Casting Division which contains about 0.2% NH_3 .

It is deduced that plume visibility depends on the level of NO which catalyses the oxidation of SO_2 to H_2SO_4 and that the rate determining step for the formation of aerosol probably occurs in the liquid phase. Thus the presence of both NO and liquid (H_2SO_4) are needed to produce extra aerosol.

Keeping NO concentrations below about 15 ppm in the flues will result in low visibility plumes.

1. INTRODUCTION

The plumes from the Pasmaenco-EZ zinc smelter at Risdon vary considerably in visibility giving rise to adverse comments. The reasons for the variability are unknown. There is, however, anecdotal evidence that (i) the use of contaminated water (which contains ammonium ion) to cool the roasters produces increased plume visibility and (ii) the tail gas from the old acid plants (#3 and #4) is involved in some way with more visible plumes, whereas the new acid plant, which has candle filters, is not.

The implication of NH_3 received possible confirmation when the plumes became dramatically more visible on adding NH_4OH to the feed to the roaster during an appraisal visit to the site in August. A possible mechanism might lie in the chemistry of the chamber process for sulphuric acid whereby SO_2 is catalytically oxidised by NO_2 .

The investigation undertaken by CSIRO Division of Coal and Energy Technology, which is the subject of this report, was designed to provide a better understanding of the smelter process variables that affect plume visibility.

Two visits were undertaken to Risdon, the second being necessitated by an industrial dispute that occurred during the first period. As no detailed records were kept during the dispute, this report concentrates on results from the second measurement period.

2. METHODOLOGY

The approach taken for this study has been to monitor the potential visibility of the plumes whilst at the same time taking samples of the particulate burden by filtration and also measuring the nitrogen oxide (NO) concentrations at various parts of the plant. The filter samples were analysed back in the laboratory as were samples of contaminated water which were taken periodically. The measured parameters were then correlated with detailed records of plant operation.

2.1 Visibility

Visibility of the flue gas entering the forestacks 'A' and 'B' was monitored with nephelometers. These instruments measure the optical integrated (Mie) scattering coefficient, B_{scat} , at 550 nm wavelength of the flue gases by continuously withdrawing a sample of flue gas and measuring the intensity of the scattered light when the sample is illuminated with a pulsed xenon arc lamp. The instruments are calibrated by measuring the intensity of (Rayleigh) scattered light when filled with Freon 12, a gas whose scattering cross-section is known. For the second measurement period, a third nephelometer was installed ahead of either of the foreshore treaters. The output from the instruments were recorded on a strip chart recorder.

The plumes were also subject to timelapse photography from the roof of Purification Division and from Limekiln Pt.

2.2 Measurement of NO

A NO detector was installed at the base of 'A' stack. The detector measures NO by its chemiluminescent reaction with O_3 . The instrument generally measured the concentration of NO continuously in the flue gas at the base of the 'A' stack, but was also used to measure NO in grab samples of flue gas taken from various parts of the process downstream of the roasters.

When NO concentrations exceeded the dynamic range of the instrument, the flue gas was diluted by a measured amount with nitrogen from a compressed gas cylinder

2.3 Filter Samples

Samples of flue gas aerosol were collected on weighed 21 x 14 cm washed quartz fibre filters. The filters were mounted in a polypropylene holder attached to the flues through 13mm dia. polypropylene tubing. At 'A' stack and upstream of the foreshore treaters, there was sufficient positive pressure at the sampling ports to obviate the need for a pump, but for 'B' stack a pump had to be used. The volume of filtered flue gas was measured with a dry gas meter.

2.4 Bag Samples

Grab samples of flue gas in 20 L Teflon bags were obtained periodically from different parts of the process such as roaster and acid plant tail gases and ahead of the foreshore scrubbers. The samples were analysed for NO and sometimes NH₃. The NO was measured as in section 2.2, whilst the NH₃ was either determined by converting it to NO using a stainless steel converter at 800°C and then determining NO as in 2.2 or alternatively by bubbling 1L of the sample through 0.1N HCl and thence measuring any NH₃ present in an aliquot of the absorbate with an ion selective electrode at pH 10 - 11.

2.5 Filter and CW analysis

After drying and weighing the filters, a 47 mm dia circle was cut from selected ones and sonified in 2 x 10 ml distilled water. After making up the extracts to 25 ml, the pH of each of the extracts was measured before analysis for major anions by ion chromatography and for cations and S by inductively-coupled plasma atomic emission spectroscopy.

2.6 Time-lapse photography

Two Super-8 time lapse cameras were deployed, one on the roof of Purification Division, the other at Limekiln Pt. Exposure rates were one frame every 40 s.

3. RESULTS AND DISCUSSION

3.1 Measurement results

3.1.1 Aerosol loading and Visibility

The weights of aerosol collected on the quartz filters are presented in Table 1 along with the times and locations of their exposure. It can be seen that, at the base of the stacks, the levels of particulate matter were quite low and about two orders of magnitude less than before the foreshore scrubbers. The accuracy of the weights is about ± 1.5 mg. Analysis of the collected material is presented in Table 2. This shows that the aerosol is H_2SO_4 as only SO_4^{2-} and H^+ could be detected in significant quantities. The acidity of the aqueous extracts was roughly equivalent to the amount of SO_4^{2-} , certainly within the limits of accuracy achievable from measuring the pH of filter extracts. As only H_2SO_4 was encountered on the filters, it was decided not to proceed with analysis of all filters.

The low collection weights make it difficult to develop correlations between them and the nephelometric data. However, on one day (October 17) a filter was exposed for about 6 h. A plot of filter weights v B_{scat} integrated over the collection time is shown in Figure 1a. It is, of course, heavily weighted by the long exposure filter.

Although the aerosol loading upstream of the scrubbers was roughly 100 fold greater than downstream, B_{scat} was only a factor of 10 higher. However, it should be borne in mind that the nephelometer has an optimum sensitivity towards particles of about 0.5 μm in diameter, ie about the same wavelength of the illuminating light. The sensitivity of the instrument decreases significantly to particles > 2 μm in diameter. The aerosol remaining after the scrubbers is heavily hydrated which increases the particle size and results in less response from the nephelometer. In contrast, the filters are dried before weighing so hydration water goes unrecorded.

There was a strong correlation between B_{scat} reading for each stack (Figure 1b).

A limited comparison of the visibility of the plume from 'B' stack, as measured by B_{scat} , with the readings of the obscrometer fitted to that stack was carried out. The data are shown in Figure 2 and display considerable scatter. This is not surprising because of the complex nature of the interaction of small particles and light. It is generally recognised that measurements of the amount of scattered light rather than obscuration give better correlations with visibility. Obscuration is a better measure of large particles. For further discussion see eg Middleton (1968).

3.1.2 Flue gas NO concentrations

The NO concentrations in the flue gas at a number of locations in the roaster - acid plant -foreshore stack system, as determined by analysis of grab samples, are listed for each of the measurement periods in Tables 3a and 3b respectively.

Volume concentrations of 20 - 25 parts per million (ppm) were typical throughout the plant downstream of the roasters to ahead of the foreshore scrubbers. Dilution by ingress air induced by the stack fans reduces the stack concentrations to 6 - 12 ppm. There were, however, occasions when the amount of NO in the flue gas was significantly lower or higher than usual and these variations will be discussed later.

3.1.3 The influence of NO concentrations

The NO concentrations and the values of B_{scat} were generally highly correlated. This is shown in Figures 3a and 3b, in which the 10 min average values of B_{scat} for the 'A' stack and 'A' prescrubbers respectively are plotted against the 'A' stack NO concentration. The data are for for the period 0800 -1700 on October 16, 1990.

A portion of the chart record for October 16, presented in Figure 4, illustrates the correlation well. This is because there were periodic variations in the levels of NO and the aerosol loading as measured by B_{scat} . The possible cause of these will be discussed later. A more dramatic illustration at a different period on that day is shown in Figure 5. On this occasion the aerosol loading exhibited a greater degree of variation for a given change in NO concentration. The data for this day (October 16) in the form of 2 min

average values are presented in Figure 6. The high degree of scatter implies that there is another factor influencing the amount of aerosol other than NO. However, it does seem that plume visibility is a function of NO concentration. When NO concentrations are down to 15 ppm, the plumes are hard to detect visually.

3.1.4 Time lapse photography

Inspection of the films showed that fume from the lead sulphate dryers and smoke/dust apparently from near the wharf area were dominant features during the October 16 - 18. (The wharf area was partly obscured by a headland on the NE side of the Derwent). Both stacks had plumes visible from both sites in the latter half of the afternoon on October 17. This coincides with elevated NO and B_{scat} readings. Also, a brief pulse was noted at 1300 h from Limekiln Pt, which coincided with the start up of #6 acid plant. (The Purification site was frequently obscured by the PbSO_4 dryer fume, also visibility depends on viewing angle, background and illumination characteristics so that one site may get a better view than another at any one time).

The plumes caused by the ammonia addition (see later) was also quite evident from both sites.

3.2 Influence of process variables on NO concentration

3.2.1 Acid plant operation

The #6 acid plant was closed down about 0400 h on October 17, due to a failure of the D/T pump and came back on stream just before 1300 h. On restart, increases in NO and B_{scat} were recorded as shown in Figure 7. Note the pulse of NO which did not produce an immediate corresponding pulse in any of the B_{scat} signals, but seemed to give rise to a slower increase in B_{scat} .

The #4 acid plant was also shutdown for maintenance on October 3. During this period, there was almost no aerosol going up 'A' stack stream whilst 'B' stack seemed

normal. The acid plant came back on stream around 1640 h with concomitant increases in NO concentrations and B_{scat} for both 'A' and 'B' flues.

3.2.2 Roaster bed temperature

On October 18, the bed temperature of #6 roaster was varied between 920 and 980 °C. On cool down from 980 °C, contaminated water (CW) was used at a rate of 6 m³/h. Grab sampling of the exit gases during this period showed no significant changes in NO concentrations, indicating that production of NO from atmospheric nitrogen in the roaster operation is negligible. No effect of increased roaster temperature was apparent on NO and B_{scat} levels. However, the application of CW resulted in 0.5 - 1 ppm rise in the NO at 'A' stack, and small (circa 20%) rises in B_{scat} at all three locations.

3.2.3 Cell Feed addition to #6 roaster feed belt

On October 17, 140 L cell feed solution was added to the concentrate being fed to #6 roaster over the period 1520 - 1550 h. From 1550 - 1625 h, a further 140 L of cell feed solution, fortified with ammonium sulphate, was added. It was difficult to discern the effects on plume visibility or NO concentrations due to changing background levels of NO and B_{scat} during this period. There may have been an increase in NO at 'A' stack of about 1 - 2 ppm in a background fluctuating between 8 and 10 ppm during the second addition whilst 'A' stack B_{scat} increased from 0.08 to 0.1 m⁻¹ and that for 'B' stack went from 0.01 to 0.015 m⁻¹.

The two additions mean that N was added at about 8 and 16 g/min respectively. If all this N was converted to NO then NO concentrations should have risen by approximately 3 and 6 ppm in the flues (assuming a flow of 2400 m³/m) or 1 and 2 ppm in the stack gases for the two additions. This is consistent with observation.

3.2.4 Addition of ammonia to #6 roaster feed belt

Between 1509 and 1539 h on October 18, 40 L of strong (23.4%) NH_4OH were added to the feed to #6 roaster. The rate of addition was equivalent to 230 g/min N translating to an extra 80 ppm of NO in the flue gases or 25 ppm at the stacks. As there was obvious loss of NH_3 from the feed on the conveyer belt before entering the roaster, smaller increases in NO would be anticipated. Inspection of Table 3b shows NO concentrations reaching 40 - 60 ppm in a grab sample from the roaster. The uncertainty is due to the excessive dilution of the sample required to bring the concentrations within the dynamic range of the NO detector. The data are presented in Figure 8. Over the period of the NH_3 addition, NO went from 6 to an average of 25 ppm at 'A' stack, whilst B_{scat} from 0.01 to 0.04 m^{-1} at 'A' stack, from 0.15 to 0.6 m^{-1} ahead of the scrubbers and from 0.003 to 0.014 m^{-1} at 'B' stack. Thus the NO increased much in line with expectations, and was associated with roughly proportional increases in the aerosol in the flue gases. This observation lends further support to the connection between visibility and the levels of NO.

3.3 The sources of NO

The only obvious source of NO brought to our attention was the NH_3 in the contaminated cooling water applied to the roasters. Analyses were performed on a number of samples of CW collected during our visits. The results are listed in Table 4. NH_3 was present at 0.1 - 0.15 g/L. Typically, about $4 \text{ m}^3/\text{h}$ are applied to each roaster, thus producing 4 - 6 ppm NO in the flue gases (assuming a gas flow rate of $2400 \text{ m}^3/\text{min}$). This accounts for only about 25% of that observed. It should be noted, however, that for the year ended June 1990, average NH_4 ion concentrations in CW were 0.3 g/L (B.A. Richardson summary report 11/07/90). Such concentrations would obviously yield twice as much NO.

Subsequent to our measurement periods, we were informed of another source of NH_3 , viz the dross, from Casting Division, recycled into the roasters. The dross contains circa 0.3% N (an assay spot check gave 0.28% N/ NH_3) and is recycled irregularly, but at a rate averaging 20 tonnes per day. A further 15 ppm NO would be expected from this

particular source though actual values may be rather different due to the uncontrolled method of addition to the roaster feed.

These two sources can account for the bulk of the NO to be found in the flues.

3.4 The source of the aerosol

It seems certain that the extra H_2SO_4 aerosol is generated downstream of the acid plants otherwise it would have been scrubbed out in these plants.

It is well known that NO will catalyse the oxidation of SO_2 by O_2 . This is the basis for the lead chamber process for the manufacture of H_2SO_4 . The process proceeds via



In the gas phase, reaction 2 is fast and reaction 1 is rate controlling (Wendt and Sterling, 1973). (SO_3 normally rapidly hydrates to form H_2SO_4). In the Chamber process, the oxidation of SO_2 (ie reaction 2) actually takes place in acid solution via nitrosyl sulphuric acid, NOHSO_4 .

At low NO concentrations, such as are present in the Pasmenco operation, reaction 1 becomes insignificant as the rate is second order in NO. Wendt and Sterling (loc. cit.) suggest that:



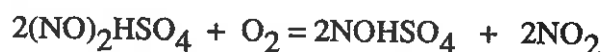
then become important, with reaction 3 being rate controlling. However, reaction 3 has an activation energy of 100 - 150 kJ/mole (Armitage and Cullis, 1971, Wendt and

Sternling, loc. cit.), so that at ambient temperatures, it does not proceed, the rate coefficient being around 10^{-19} L/mole-sec.

Assuming that the extra aerosol is generated by reactions involving NO, we conclude, therefore, that the oxidation of SO_2 cannot be accounted for by homogeneous gas phase reactions, but must involve heterogeneous processes. These would, in effect, provide the mechanism for the oxidation of NO. Further, it may provide an explanation as to the variability in the relationship between the concentrations of NO and B_{scat} displayed in Figure 2c.

The interaction of nitrogen oxides and SO_2 in aqueous solution is well known, though not necessarily well quantified (eg Martin et al, 1981, Lyon and Cole, 1989). Most of the work has involved dilute solutions rather than strong acids. Despite the widespread use of the Chamber process for H_2SO_4 manufacture up until the mid twentieth century, detailed knowledge of the liquid phase reactions involved is both complex and incomplete. (see eg Gmelin, 1963)

Conceptually, a reaction such as:



would provide the required oxidation of NO. (The oxidation of NO in solution by O_2 is alluded to in the oxidation of SO_2 in fog, Hoffman and Jacob, 1984). The production of extra aerosol in the flue gases requires that the ' SO_3 ' desorbs from the liquid phase. This is well established for strong H_2SO_4 .

The need for a liquid phase to carry out the necessary chemistry may be the reason for the belief that the #6 acid plant is immune with regard to influencing plume visibility. This plant is fitted with candle filters which would remove residual acid aerosol and thereby reduce the scope for SO_2 oxidation down stream. However, as is shown in Figure 6, aerosol does appear to be produced by this unit. The candle filters may not be 100% efficient and the flue walls probably accumulate an acid coating.

To minimise oxidation of SO_2 in the flues or, rather, to reduce visibility, would necessitate keeping NO concentrations in the tail gases to less than about 15 ppm. Alternatively, reducing the reaction time (ie shorter flues) would also have the desired effect.

4. CONCLUSIONS

The results of the investigations clearly showed

- (i) the aerosol giving rise to visible plume from 'A' and 'B' stacks consisted of H_2SO_4 .
- (ii) the NO concentrations in the stack gases was comparable to that in the roaster tail gases after allowing for dilution by ingress air.
- (iii) a strong correlation between the concentration of NO in the stack gases and the response of the nephelometers, B_{scat} , sampling both the stack gases and upstream of the foreshore treaters.
- (iv) little evidence of influence of process variables such as roaster bed temperature and use of contaminated water. (There was, however, little N in the contaminated water during the measurement periods).
- (v) The visibility of the plumes increased when the #4 and #6 acid plants came back on line after shutdowns.

It appears that, based on the respective N contents, CW and the recycled dross are the major sources of NO.

It is deduced, on the basis of the above observations that SO_2 is being oxidised in the flues by NO via a heterogeneous mechanism. Thus, it is necessary for liquid to be present in the flues, either as aerosol or surface coating of the flue interiors.

To keep plumes barely visible would require NO concentrations in the flues below 15 ppm or the current operating conditions. Better removal of aerosol from the acid plant tail