A SULPHUR BUDGET FOR SOUR GAS PLANTS

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ABSTRACT

The principal aim of this project is to produce a mass balance for the SO_2 that is emitted into the atmosphere from sour gas plants in various localities in Alberta. Partial sulphur budgets for two plants at dissimilar locations are shown to exhibit major differences.

The rise and dispersion of sour gas plant plumes have been investigated in detail. In order to investigate the chemical transformation of SO_2 within these plumes, the use of a conserved tracer that can be detected by neutron activation is discussed.

1. INTRODUCTION

There are certain peculiarities about sour gas plant plumes and the climate of Alberta which may enable us to shed a different light on the seemingly intractable problem of atmospheric sulphur budgets. The effluent from a sour gas plant sulphur recovery unit can be considered to be relatively "clean" in the sense that the only pollutant emitted is SO_2 without a significant loading of particulates or other contaminants. The water content has a high value of approximately 25 mole per cent, but the effluent is emitted from the stack at temperatures in excess of 800K so that the plume is normally invisible, except when the ambient winter temperature is below -15°C (Havlena et al., 1975). Thus this effluent is markedly different from that emitted from a coal-burning power plant, a smelter or an oil sands coke-burning power plant, and may have a greater potential to acidify soils and water, because there appears to be less opportunity to form neutral sulphates.

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Over 80% of the natural gas produced in Canada comes from Alberta, about one half of which is exported to the U.S.A. Over 50% of these gas fields are sour, i.e. they contain an appreciable percentage of H_2S. The sour gas processing plants are mainly located alongside the Rocky Mountains in the so-called sour gas corridor; see Figure 1. The H_2S is

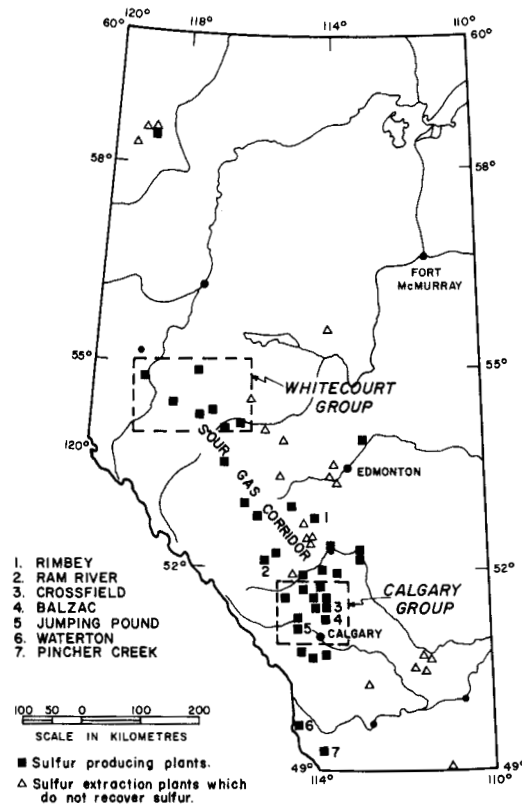

Figure 1. Location of Sulfur Extraction Gas Plants in Alberta (Reproduced from a report by Klemm, 1972)

removed from the natural gas and is then converted to elemental sulphur by the Claus process, but a small percentage (approximately 10^6 kg of SO_2/day in total) has to be incinerated and released to the atmosphere as SO_2. There are a few large sulphur recovery units which emit about 10^5kg of SO_2/day.

Public hearings were held in October, 1972 by the Alberta Environment Conservation Authority (1973) on "The Environmental Effects of the

Operation of Sulphur Extraction Gas Plants in Alberta." One result of these hearings was that it became much more widely appreciated that only a few per cent of the SO_2 emitted from these plants is accounted for by sulphation monitors (lead candles) within a 10 km radius of each plant. The project reported in this paper was established in order to attempt to answer the question: "Where does the rest of the SO_2 go to?" This is not to say that no experiments have been performed prior to this paper or even prior to 1972.

2. PREVIOUS WORK

A pioneering effort to determine the fate of SO_2 from sour gas plants is described by Summers and Hitchon (1973). They inferred that approximately 40% of the SO_2 emitted from the Rimbey sour gas plant (Figure 1) during a summer was returned by convective storms in the near vicinity of this plant. This is a somewhat surprising result as it does not rain for more than 10% of the time! This paradox, which was not discussed in their paper, can perhaps be explained by the normal diurnal wind pattern next to a mountain range on relatively calm days. Soon after sunrise an upslope wind sets in which could entrain the Rimbey plume into the convective storm cells that form for most of the day over the mountains. In the late afternoon the storm clouds move away from the mountains and heavy rain and/or hail often occurs at approximately the same distance from the mountains as that of the Rimbey plant.

An investigation of wind statistics by Benjamin (1975), using the technique of Paterson and Benjamin (1975), supports the idea of air currents moving to and fro within the sour gas corridor. Similar diurnal variation of the wind direction has also been reported for Calgary by Longley (1969). These air movements may well lead to a build up of pollutant concentration as well as explaining the observations of Summers and Hitchon (1973).

The ground level SO_2 concentrations recorded by 7 continuous monitors around the Balzac plant have been investigated (Mohtadi and Rowe, 1973) to test the applicability of various dispersion correlations for sour gas plant plumes and to ascertain the meteorological conditions which cause pollution episodes. An episode was defined as an hourly average ground level SO_2 concentration of 0.15 ppm or greater. Twenty-eight pollution episodes occurred during the twelve month period of this investigation. Twenty of these episodes can be definitively classified into the following categories:

(a) uniform atmosphere - 5 cases;
(b) inversion breakdown - 6 cases;
(c) plume trapping - 9 cases.

Inversion breakdowns and plume trapping, which are associated with clear

skies and low winds, are by no means rare or unusual east of the Rocky Mountains and are part of the normal variation in the meteorological dispersion conditions of Alberta.

Sour gas plant plume rise and diffusion has been investigated in detail, using airborne rapid response SO_2 monitors, by many workers; see, for example, Lee et al. (1973) and ERA Sciences (1974). All of these investigations have been carried out over relatively flat terrain, and have shown that sour gas plant plumes disperse in a manner similar to any other industrial stack plume. However, the problem of plume dispersion in complex mountainous terrain still requires much further study. Plume flow across a long ridge has been studied at the Jumping Pound plant (Figure 1), and an acceptable engineering model for this distinct topographical feature, involving the concept of potential flow, has been developed (Leahey and Rowe, 1974). Computer dispersion models for complex terrain have been applied to sour gas plant plumes by Lantz et al. (1972) and Wallis et al. (1975).

A number of plume marking techniques, e.g. the incomplete combustion of a hydraulic cluid, have been used in order to visualize the rise stage of these plumes. A novel technique for photographing SO_2 plumes using the ultraviolet light from the sun and exploiting the UV absorption properties of SO_2 has been under development for some time, and this method appears to be an almost ideal way to photograph sour gas plant plumes (Havlena et al., 1975).

H_2S from different sour gas pools varies considerably in its S^{34}/S^{32} abundance ratios. Krouse (1974) has investigated whether sulphur isotope abundances can be used to monitor gas industry emissions of sulphur compounds and their effects on the environment. He examined the sulphur isotope abundances of lead candle sulphation monitors, and found that he could readily identify the major source of emission in a neighborhood but the "background" isotopic composition appears to vary significantly from site to site and with season.

The fate of SO_2 in the atmosphere has to be experimentally determined, in part, by monitoring what arrives at the ground. For the past three years, Nyborg (1975) has been investigating the pH and SO_4-S content of: rainfall, snowfall, dryfall (particulates), water (protected), soils, grasses and barks. These data are being taken at over 70 sites, which are concentrated just north of Calgary, and around the Ram River and Waterton sour gas plants, and scattered throughout the southern half of the Province (Figure 1). These observations (Nyborg, 1975) suggest that direct absorption of sulphur gases is more important than deposition in rain and snow.

Nyborg's sites are mainly located on agricultural lands. An investigation of the uptake of sulphur gases by pine trees is being undertaken by Legge et al. (1975), their data are quite fascinating because they indicate that the concentration of a sulphur compound can

be an order of magnitude lower within a forest canopy than above it; see, also, ERA Sciences (1974).

3. FATE OF SO_2

Examination of the data collected to date reveals that the sulphur budget for an individual sour gas plant is very dependent on its particular location and on the climatology of that area. For example, Nyborg (1974) conducted experiments around the Waterton plant, where he placed pots of soil with barley plants at distances up to 40 km downwind from the stack. His findings show that during a three month summer period the soil and barley gained at least an order of magnitude more sulphur by absorption than that deposited by rain, which contrasts markedly with the findings of Summers and Hitchon (1973) at the Rimbey plant.

Besides the drier climate, Nyborg's data are determined in part by the topography of the Rocky Mountains to the west of the Waterton plant (Figure 1), which is shaped like vanes and gives rise to extremely persistent westerly winds. A high level of mechanical turbulence is generated by these mountain vanes, which reduces the rise and increases the diffusion of the plume bringing it rapidly to the ground, with resultant high levels of absorption in a narrow downwind sector (Wallis et al., 1975).

The effect of wind directional persistence at the Waterton plant is also clearly evident in the total sulphation monthly averages taken by lead candles. Oval shaped isopleths can be readily drawn for these sulphation data on the downwind (easterly) side of the Waterton plant, and also for those of the much smaller nearby Pincher Creek plant. Interestingly enough, this information was used to resolve the division between the gas plant operators of the settlement of damages awarded to ranchers as a result of emissions from these two plants. At all other plants investigated the lead candle data do not yield such definitive trends; in fact the values indicate that the contribution from the background is of the same order of magnitude as that due to the stack; see, for example, Rowe (1974). Although the airborne background concentrations are normally much lower than those due to the stack, the plume is infrequently carried by the wind to the monitor.

Simple calculations (Benjamin, 1975) similar to those of Scriven and Fisher (1975), but using a Gaussian plume model rather than solving the diffusion equation (K theory), and using a constant deposition velocity of 1 $cm.s^{-1}$ and a mixing layer of limited depth show that as much as 30% of the sulphur emission from a sour gas plant could be accounted for by dry deposition within 100 km of the plant. The predictions of this model can be made to agree reasonably well with Nyborg's data for sites close to both the Waterton plant and the Calgary group of

plants. However, this model is not able to reconcile Nyborg's values at remote sites (greater than 100 km) as well as those near to the sour gas plants; the reason for this anomaly remains to be determined.

An interdisciplinary project at the University of Calgary has been established in order to attempt to solve the sulphur budget for sour gas plants. A schematic presentation of this project in the form of an SO_2 mass balance equation for the atmosphere showing the principal areas of interest of each of the (original) co-workers is given below:

$$\begin{bmatrix}SO_2 \text{ emitted from} \\ \text{local sources}\end{bmatrix} + \begin{bmatrix}\text{Background } SO_2 \\ \text{(Krouse)}\end{bmatrix}$$

$$= \begin{bmatrix}SO_2 \text{ transported by} \\ \text{convective diffusion} \\ \text{(Aziz and Rowe)}\end{bmatrix} + \begin{bmatrix}SO_2 \text{ transformed by} \\ \text{chemical reactions} \\ \text{(Mohtadi)}\end{bmatrix}$$

$$+ \begin{bmatrix}SO_2 \text{ absorption at} \\ \text{ground surfaces} \\ \text{(Hodgson)}\end{bmatrix} + \begin{bmatrix}SO_2 \text{ rainout and} \\ \text{washout}\end{bmatrix}$$

As reviewed above, much work has already been done on all aspects of the sulphur budget for sour gas plants except for the question of possible chemical transformations of the SO_2 within the plumes.

4. PLUME TRACERS

An extensive literature exists on the atmospheric chemistry of SO_2 and a survey of this information as it pertains to sour gas plant plumes has been completed by Mohtadi and Gyuse (1975). A few plume chemistry field experiments have been reported in the literature, almost entirely for power plants, which have yielded conflicting evidence about the rate of oxidation of SO_2; see, for example, Wilson (1975). Only the ratios of SO_2 to sulphates at various downwind distances have so far been reported, and the oxidation rate of SO_2 has then been inferred from these data. It is not possible to determine directly the mass flux of a plume component, such as SO_2, through a downwind cross-section by airborne sampling because of the turbulent nature of the atmosphere (Brown et al., 1972). A conserved tracer needs to be injected into the stack gases in order to obtain an additional check of the oxidation rate and to verify that the total sulphur mass flux is conserved, assuming that the sulphates do not fall out (Manowitz et al., 1972).

A review by Exall (1975) of conserved tracers that can be detected at extremely low concentrations (of order 10^{-12}) revealed two main contenders: SF_6 gas with electron-capture gas chromatography, or

elements with low natural abundance but high thermal neutron capture cross-sections. SF_6 has been rejected because of a variety of chemical reactions that appear likely to proceed with the high temperature sour gas plant stack gases. The high sensitivity obtainable by combining neutron activation with gamma-spectrometry in the determination of microquantities of elements suggests that this technique should be most suitable for plume chemistry experiments. The criteria governing the choice of element are: nuclear properties, natural abundance, price and suitability as a tracer of air movements. Gold, indium and lanthanum are among the more suitable elements. Due to its very short half-life, indium would have to be chemically separated soon after irradiation before counting. Atmospheric dust can contain significant quantities of lanthanum, which leaves gold as apparently the most suitable element for this conserved tracer technique.

Airborne high-volume filter samples have been obtained (Exall, 1975), both within a sour gas plant plume and upwind of the plant. This experiment was performed shortly after rain had fallen and the ambient air dust levels were presumably low at that time. After neutron activation, the only significant elements found on all filters were sodium and bromine. A nozzle apparatus to inject a fine spray of a solution of gold into the incinerator of a sour gas plant is currently being developed.

In conclusion, sour gas plant effluents in Alberta offer a unique opportunity to study SO_2 transformations in plumes that are almost completely devoid of particulates in a non-industrial clean air environment. Furthermore, a sulphur recovery unit could be used as an experimental reactor since the heat emission rate and particulate loading could be varied rapidly during a given meteorological event.

ACKNOWLEDGEMENT

This work is supported by a National Research Council of Canada Negotiated Development Grant to The University of Calgary Interdisciplinary Sulphur Research Group (UNISUL).

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