

Mt Isa's smelter chimneys put out about 1000 tonnes of sulphur dioxide a day.

Cutting down on sulphur dioxide

When metals are extracted by smelting, sulphur dioxide pours off.

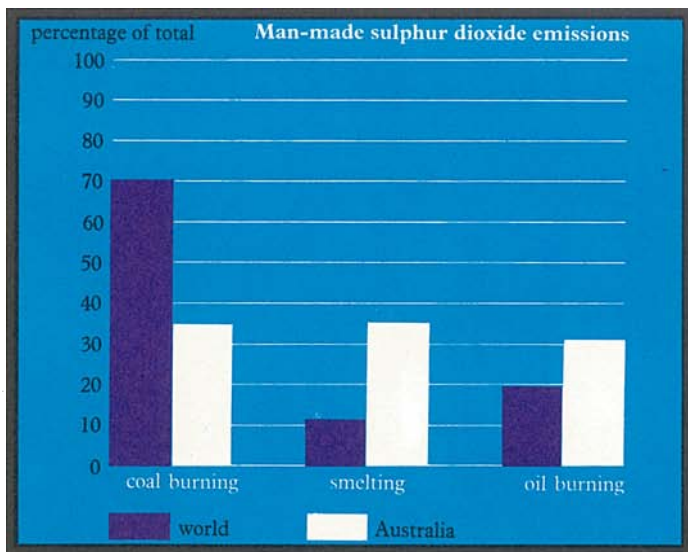
Sulphur dioxide is a traditional air pollutant, not a Johnny-come-lately like the photochemical pollutants that the motor car has brought to cities. Ever since people started burning coal and smelting ores to make bronze, they have been putting it into the air.

High concentrations have been recorded during pollution disasters, such as the great London smog of 1952 that killed about 4000 people. But so have high concentrations of other things, particularly soot and other airborne particles, and some evidence suggests that sulphur dioxide has not been the main culprit. Much remains to be learnt about its effects on people—on its own, mixed with other pollutants, and before and after it undergoes chemical change in the atmosphere.

Australia's output is about 1 400 000 tonnes a year, close to 1% of the world total. Although our population is only about 0.3% of the world's, we are well endowed with copper, lead, zinc, and nickel ores, and when the metals are

extracted by smelting, sulphur dioxide pours off. A lot is caught and used to make sulphuric acid, but about 500 000 tonnes go up smelter chimneys each year. Burning coal and coke give out nearly as much, and fuel-oil combustion is the next largest source.

Sulphur dioxide pollution is mainly a problem of cities and smelting towns, although the gas can remain airborne for several days and come down hundreds of miles from its source. A typical average concentration in inner areas of Sydney or Melbourne is a fairly low 0.02 parts per million. The highest average recorded in the Sydney area in 1973 was about 0.05 p.p.m.—at Redfern, an inner industrial suburb. By comparison, New York has



an average concentration of about 0.24 p.p.m.—more than ten times as high as most Sydney and Melbourne readings.

A large part of the reason for Australia's comparatively low levels is our good fortune in having fuels with low sulphur contents. Most Australian coal contains 0.5–1% sulphur, compared with several per cent overseas. Bass Strait oil contains about 0.1% or less, compared with 1–2% or more in most overseas oils. However, most fuel oil used here is imported, and can have a sulphur content as high as 3%. Australia's natural gas contains no sulphur, so sulphur dioxide levels should fall in our cities as industry makes more use of it.

Smelting towns

Smelting towns tend to show much greater variation between normal and peak sulphur dioxide concentrations, and much higher maximums. For example, a monitor at Port Kembla, N.S.W., recorded an average concentration for 1973 of about 0.05 p.p.m., similar to Redfern's. However, the highest average over a day at Port Kembla was nearly ten times as high, about 0.44 p.p.m., while at Redfern it was only about 0.13 p.p.m. Peak short-term concentrations of more than 1 p.p.m. were recorded four times at Port Kembla that year. At Port Pirie, S.A., peaks of more than 0.9 p.p.m. have been recorded in recent years.

What these figures mean in terms of human health is far from clear. In London's 1952 disaster the sulphur dioxide level reached 1.34 p.p.m., but clinical tests with bronchial patients—a group likely to be particularly susceptible—have shown no adverse effects from concentrations of 2 p.p.m. It seems that a sulphur dioxide-particle combination is consider-

ably more harmful than either the gas or soot on its own. The World Health Organization has recommended just over 0.02 p.p.m. (60 micrograms per cubic metre) as a long-term goal for annual average concentrations, but it says this figure applies only in conjunction with its recommended limit for particles. It also stresses that the figure is put forward tentatively and could be changed if more data on dose-response relations become available.

No nation-wide standards have yet been adopted in Australia. The U.S. Environmental Protection Agency's recommendations are a maximum annual average of 0.03 p.p.m. and a maximum average over 24 hours of 0.14 p.p.m. We start smelling it when the concentration reaches about 0.5 p.p.m.

Smelters produce Australia's highest concentrations of the gas. In CSIRO, a considerable research effort is being put into examining alternative methods of metal recovery. Nearly all Australia's copper, lead, zinc, and nickel ores contain large amounts of sulphur, and the aim is to work out ways of removing this without converting it to sulphur dioxide.

The smelting process

Take copper as an example. By far the most common ore is chalcopyrite, which contains copper, iron, and sulphur. Conventional processing involves three steps—roasting, smelting, and converting.

► In roasting, hot air is blown through the ore; oxygen in it combines with the iron, while the copper remains as a sulphur compound. Oxygen also combines with sulphur that was linked with the iron, producing sulphur dioxide.

► In smelting, the products of roasting are melted in a furnace with 'slagging' material that encourages the iron-oxygen compound to settle above the copper-sulphur compound. The top layer is tapped off, leaving the copper compound.

► In converting, hot air is blown through the molten product of smelting. The sulphur forsakes the copper for the oxygen, and the products are sulphur dioxide and impure copper, which is then refined for use.

Well-established technology exists for turning the sulphur dioxide from smelting plants into sulphuric acid, but economics demand a use for large amounts of the acid nearby. The fertilizer industry is by far the biggest user. As it depends heavily on imports, such as the rock phosphate that it treats with sulphuric acid to produce superphosphate, it is mainly a seaboard industry. There is very little demand for sulphuric acid inland, and there are at present no sulphuric acid plants associated with Australia's inland smelters.

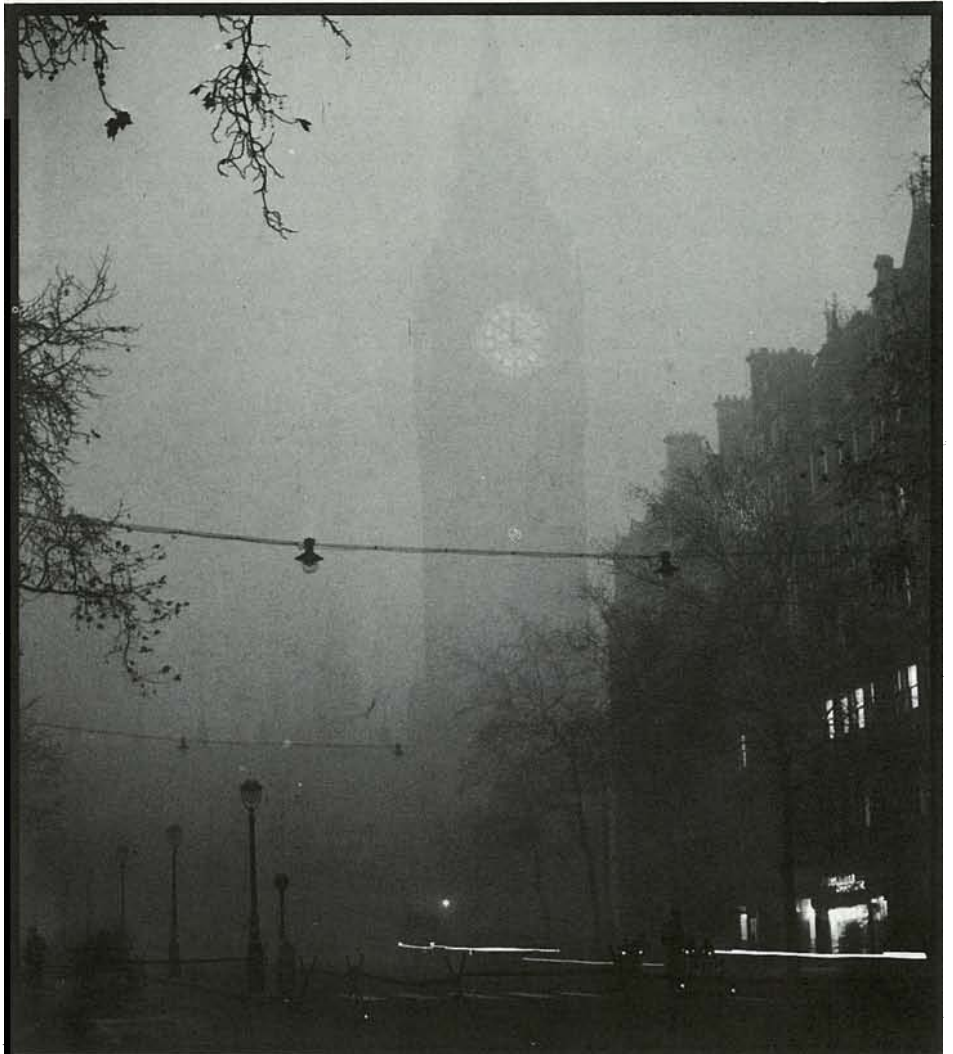
About 98% of the sulphur dioxide produced by lead and zinc smelting at Cockle Creek, N.S.W., is used to make sulphuric acid. About 60–70% of that from the lead smelter at Port Pirie, S.A., is put to the same use. The rest of Australia's smelters put all their sulphur dioxide into the air; these smelters produce nickel at Kalgoorlie, W.A., copper and lead at Mt Isa, Qld, and copper at Mt Morgan, Qld, and at Port Kembla, N.S.W.

Copper smelting—by far the biggest source—contributes about two-thirds of the total.

Port Kembla—the smelter chimney is the tall one.



Midday in a London smog in the early 1950s. Implementation of the *Clean Air Act, 1956*, has since greatly reduced smogs in the city.



Research on alternatives

Research has been going on for a long time in many countries on alternative separating processes, but smelting remains the almost universally used technology. In Australia, an electrolytic process is used at Risdon, Tas., to recover zinc, but it also produces sulphur dioxide, which is used to make sulphuric acid. The only process in operation here that doesn't produce the gas is a Canadian-developed one used at Kwinana, W.A., to separate nickel. This gets rid of the sulphur in the ore as ammonium sulphate, which finds a ready market as fertilizer. With additional steps, this process could be applied to copper processing, but not to the recovery of lead or zinc.

The CSIRO research on alternatives has concentrated on the area with the greatest potential for reducing emissions here, copper recovery.

At the Sydney laboratories of the Division of Mineral Chemistry, Mr

David Williams has looked closely at the possibility of modifying existing smelting techniques to produce solid sulphur instead of sulphur dioxide. The method he has examined involves removing some of the sulphur in the ore as hydrogen sulphide and the rest as sulphur dioxide, and then mixing the two gas streams together. They react to produce sulphur and water; and, if the proportions are right—twice as much hydrogen sulphide as sulphur dioxide—no sulphur compounds are left in the final gases.

Mr Williams has found in laboratory experiments that the copper ore, chalcopyrite, reacts with steam at about 680°C to produce copper-sulphur and iron-oxygen compounds and the gas he wants, hydrogen sulphide. This reaction can convert about 60% of the sulphur in the ore to hydrogen sulphide, enough to reduce sulphur dioxide emissions from the complete process by at least 80%.

In the Melbourne laboratories of the

Division, Dr Keith Cathro has shown that copper can be readily separated from the product of the steam reaction by chemical means. Then sulphur dioxide is not produced. The foul-smelling and very poisonous hydrogen sulphide given off in the first part of the process can be easily converted to harmless substances.

Three-stage method

Dr Cathro is investigating a totally different three-stage method of copper recovery. It disposes of the sulphur from the ore in the form of the iron-sulphur compound, pyrite.

First the chalcopyrite ore is mixed with sulphur and heated to 350–400°C. This produces pyrite and compounds of copper, sulphur, and small amounts of iron that are more soluble than the original ore. Next, these are mixed with a copper chloride solution, which dissolves the copper compounds forming a more copper-rich chloride solution. Sulphur, which can be recycled and used

There's lots of sulphur

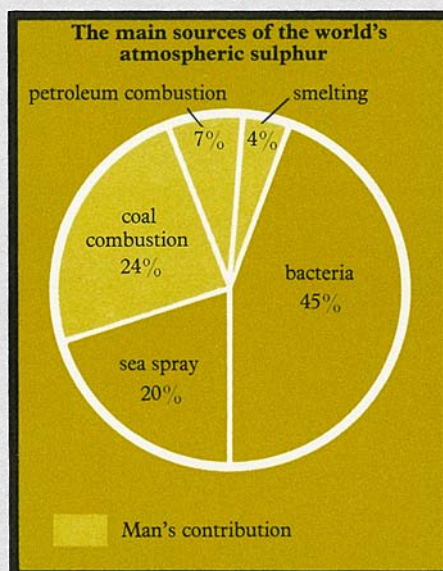
Sulphur dioxide pollution is a man-made problem, but most of the sulphur in the air finds its way there without human help. The trouble is that people live near their smelters and fuel-burning factories.

Bacteria that live in mud and produce hydrogen sulphide gas from decomposing animal and vegetable matter put ten times more sulphur into the air than all the world's smelters. The hydrogen sulphide is quickly converted to sulphur dioxide. Sea spray contributes more than five times as much as smelting—about the same amount, in fact, as the world output from coal combustion. The other important natural source is volcanic fumes.

But we're catching up. Human activity is now contributing about a third of the sulphur content of the atmosphere and, if output continues to grow at rates similar to those of recent years, we are likely to raise the proportion to half by the end of the century. However, studies of old glacier ice indicate that the background sulphur dioxide concentration in the atmosphere is not changing, despite the increasing output. It remains between 0.001 and 0.01 p.p.m.

According to figures compiled by Dr

Davey of the Division of Chemical Engineering, something like 85 million tonnes of sulphur are transferred from land to the oceans each year—most of it in addition that Man's activities make



to normal river run-off. However, no sulphur shortage will arise in the foreseeable future; the situation is one of extreme glut. Canada is the biggest producer. Its natural gas contains sulphur, which has to be removed to prevent

pipeline corrosion. The quantities are so great that 12 million tonnes had been stockpiled by the end of 1973 and its price in Alberta, where it is produced, had fallen from about \$A25 to \$4 per tonne.

The low price has encouraged Australian fertilizer manufacturers to produce their sulphuric acid requirements from imported sulphur rather than sulphur dioxide from smelters. However recent large increases in shipping freights may encourage a move in the other direction. The landed price of Canadian sulphur in Australia is now about \$45 a tonne.

At present Australian industry imports a little more than half the sulphur it uses. The rest, except for a small amount from oil refineries, comes from smelter gases that are treated to produce sulphuric acid instead of being emitted to the atmosphere. Dr Davey calculates that Australia could achieve more than self-sufficiency in sulphur production if it needed to. If 90% of the sulphur available in the fossil fuels consumed and the metal concentrates treated in Australia in 1971 had been recovered, supply would have exceeded demand by 42%. However the sulphur would have cost many times more than imported sulphur.

again in the first step, is also formed. It and the pyrite are filtered out. Finally, the copper is separated out by electrolysis.

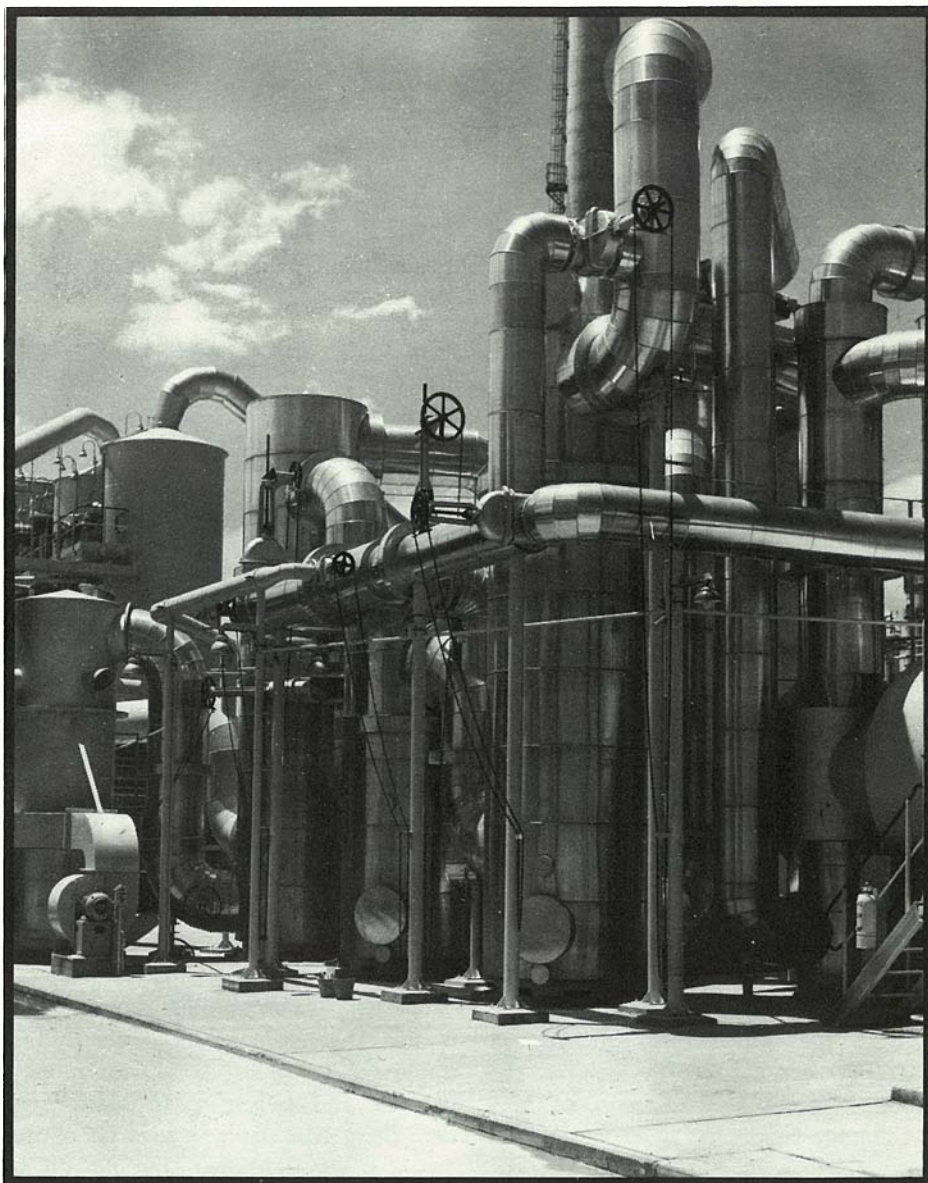
Dr Cathro has been able to achieve a 98% extraction rate of copper from ore—a good result. He has also shown that the electrolysis stage uses much less power than other electrolytic methods of copper recovery. He has tested the method with ores from Mt Lyell (Tas.), Bougainville (Papua New Guinea), Mt Isa, and Mt Morgan, and achieved satisfactory results with all of them. But it is a big step up from laboratory experiments to a plant, and his conclusion so far is only that the process is 'probably technically feasible'. The reactions will be scaled up and the commercial prospects fully assessed only if industry becomes interested.

Also at the Melbourne laboratories of the Division of Mineral Chemistry, Dr Tom Biegler is working on a novel electrolytic method of turning chalcopyrite ore into compounds from which the copper can be more readily extracted by chemical means. The products are copper-sulphur compounds. By-products are hydrogen sulphide gas and an iron compound that can be converted to another from which the metal can be extracted in ordinary steel-plant blast furnaces. Dr Biegler has found that his process consistently changes more than 90% of the ore into more reactive compounds. He is continuing his experiments to find out how to achieve maximum conversion with minimum energy use.

Energy use

Greater consumption of energy seems to be an inevitable drawback of methods that don't produce sulphur dioxide, because when sulphur burns and gives off the gas it also contributes heat energy. The prospects don't seem bright at present of developing methods cheaper than smelting for large-scale copper production, but conditions may change in ways that will make alternatives more attractive. Apart from eliminating sulphur dioxide, probably their main attraction now is that, unlike smelting, they should be suitable for low-capacity plants.

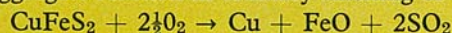
An attack on sulphur dioxide emissions from another direction may result from recent research done by Dr Jim Blackwood and colleagues at the CSIRO Division of Chemical Engineering in Melbourne. They have found that brown coal char and charcoal have large appetites for the gas, converting it (depending on



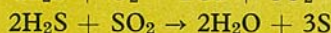
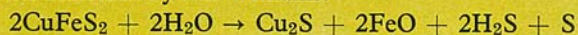
A sulphuric acid plant.

The chemistry of copper separation

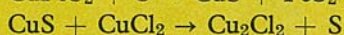
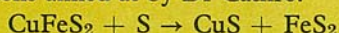
The aggregate reaction in ordinary smelting of chalcopyrite:



Reactions aimed at by Mr Williams:

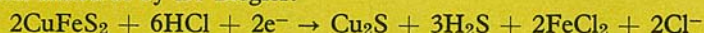


Reactions aimed at by Dr Cathro:



Copper is then separated from the Cu_2Cl_2 electrolytically.

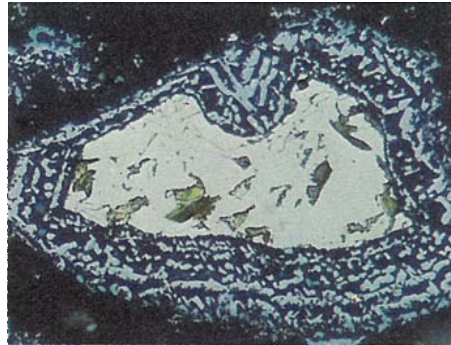
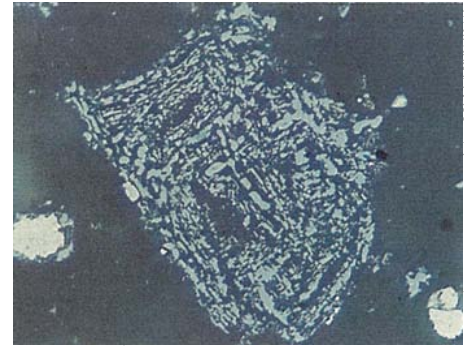
Reaction aimed at by Dr Biegler:





A magnified view of chalcopyrite before, during, and at the end of treatment by Dr Biegler's process.

Greater consumption of energy seems to be an inevitable drawback of methods that don't produce sulphur dioxide . . .



the conditions) to either pure sulphur or carbon disulphide, a liquid used to make fungicides and rayon. If the right conditions are provided, the sulphur dioxide will turn the char into activated carbon, valuable as an industrial filter.

The discovery could be applied to sulphur dioxide removal from electricity plant, factory, and smelter emissions. However, any application seems improbable in the near future, certainly in Australia, because of the cost of the process and the need to transport char.

Chimney height has a lot to do with concentrations of sulphur dioxide—the higher the chimney, the lower is the

concentration at ground level. State governments specify minimum heights for chimneys when they approve proposals for new industries. These vary with topography, climate, and the presence or absence nearby of other air pollution sources, as well as with emission volumes.

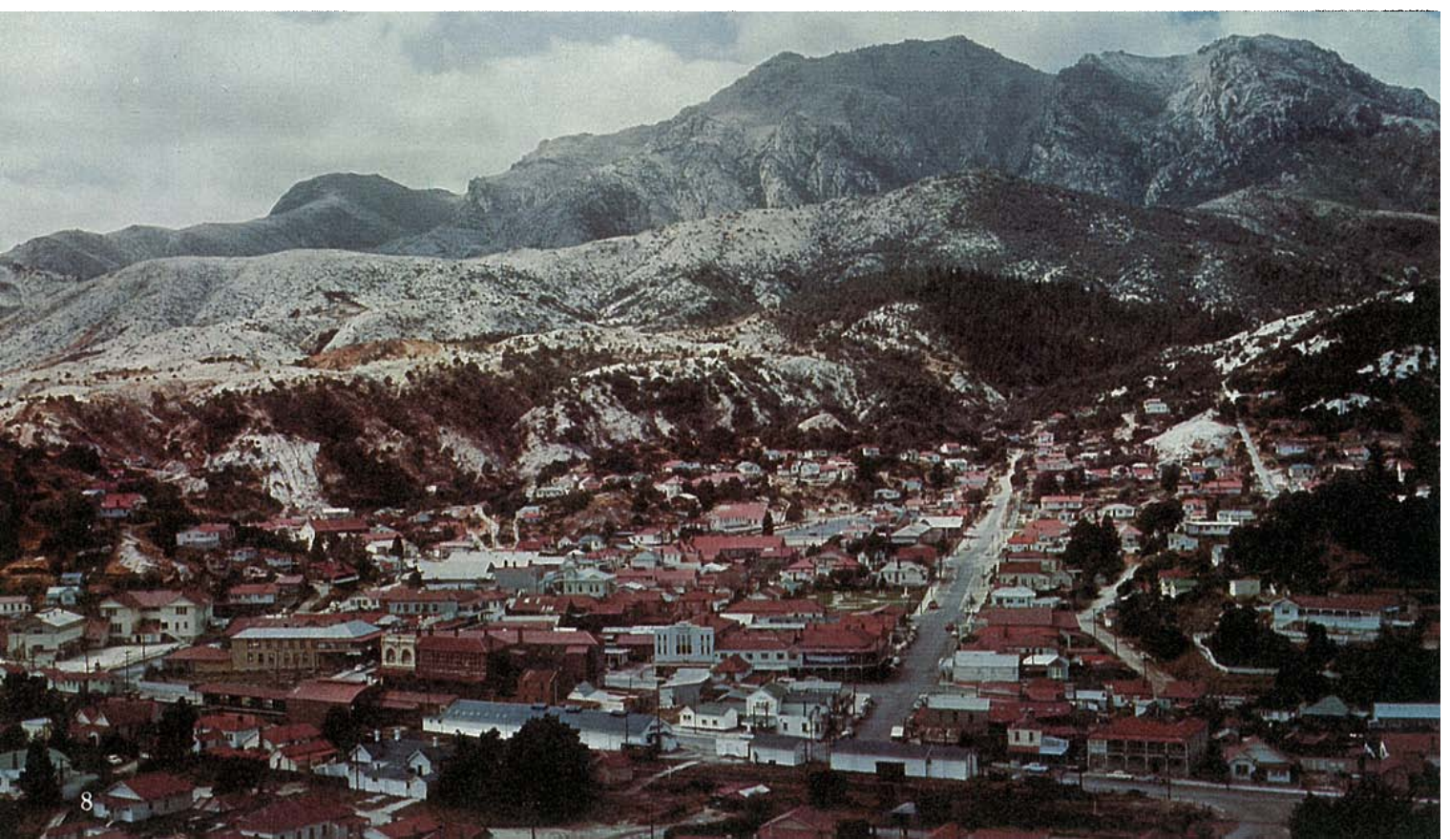
In the atmosphere

What happens to sulphur dioxide after it leaves a chimney is obviously an important question. It is also a very difficult and largely unanswered one. One thing that happens to a lot of the gas, if it stays airborne long enough, is conversion to sulphuric acid and other

sulphates. It can turn rain-water into a mild acid. And the sulphuric acid can attach itself to particles, making them corrosive.

Rain made acid by sulphur dioxide emitted in central Europe has been blamed for the acidification of rivers and lakes in southern Norway, resulting in the death of large numbers of salmon and trout. Products of sulphur dioxide are believed to be responsible for the acceleration that has occurred this century in the rate of deterioration of many old paintings, statues, and buildings like the Parthenon and the Colosseum. Cleopatra's Needle, the huge stone obelisk

Queenstown, Tas.—vegetation is slowly returning to the denuded landscape.



carved in Egypt about 1475 BC and brought to England in 1878, is said to have corroded more in 100 years in London's air than in more than 3000 years in Egypt's.

To find out more about what happens to the gas, a team from the Sydney laboratories of the Division of Mineral Chemistry, led by Mr Williams, is taking a close look at the plume from the smelters at Mt Isa. The town's two smelter chimneys put out something like 1000 tonnes of sulphur dioxide per day. They are close together and can be regarded as virtually one source. As no other major sources of air pollution exist in the district, it should be possible to find out how a plume behaves in an otherwise clean atmosphere.

The scientists made preliminary observations last September and will be back in Mt Isa next April for a big measuring effort. They are doing their field work in late autumn, winter, and early spring, because in that middle part of the year atmospheric conditions—low-level temperature inversions lasting from about 10 p.m. to 10 a.m.—regularly prevent the emissions rising more than about 350 m. As a result, the plume takes the form of a gradually widening and thickening line extending perhaps 200 km from the chimneys.

The plan is to measure sulphur dioxide concentrations at various distances out along this type of plume, using a sensing instrument pointing upwards from a four-wheel-drive vehicle. Also, a specially

Some sulphur dioxide levels in air

p.p.m.	
3000	Half the hamsters in an experiment died after 1½ hours
40	No bronchitic effects in test rats after 3 months
5	Limit recommended by World Health Organization for inside factories where people spend 8 hours a day 5 days a week
2	No adverse effects on bronchial patients in clinical tests
1.34	Maximum in 1952 London disaster
1	Peaks above this measured at Port Kembla, 1973
0.5–1.0	Limit for conscious detection by humans
0.44	Highest 24-hour average, Port Kembla, 1973
0.24	New York annual average
0.15	Visible damage to some plants
0.14	Maximum 24-hour average—not to be exceeded more than once a year—recommended by U.S. Environmental Protection Agency
0.13	Highest 24-hour average, Redfern, 1973
0.05	Highest year's average in Sydney area, 1973—at Redfern
0.021	W.H.O. long-term goal for annual average concentrations
0.02	Typical annual average in inner Sydney or Melbourne

A little sulphur is good for plants

The country around Queenstown, western Tasmania, is sometimes likened to the surface of the moon. The description was more appropriate earlier this century than it is now; in sheltered areas trees and other plants are growing again. But the landscape is still mainly bare bedrock.

Smelting started there in 1896. The process used for the next 25 years sent clouds of unburnt sulphur as well as sulphur dioxide up the chimneys.

Historian Geoffrey Blainey describes what happened:

'Sulphur, rain and fire swiftly painted a new landscape. Fogs heavily charged with sulphur made green grass and

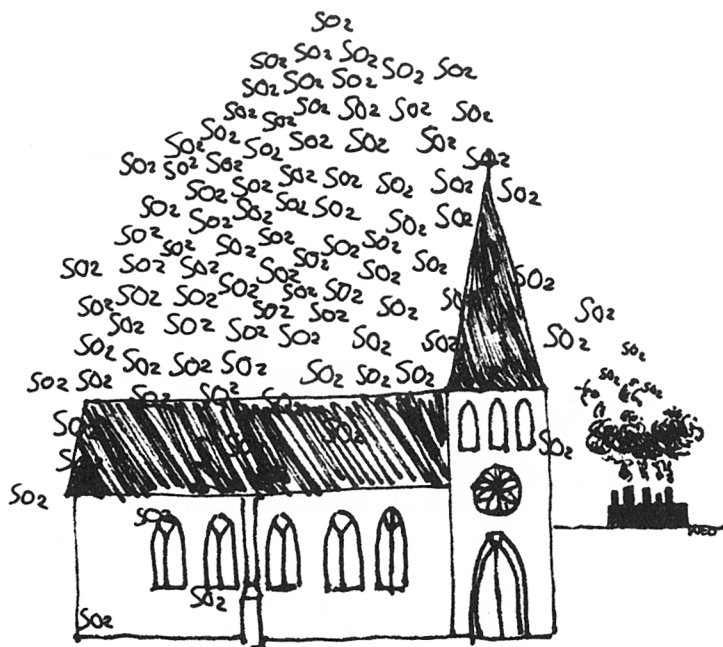
plants yellow in a day. Bushfires raced through the scrub in successive summers and left blackened hillsides. No fresh vegetation grew, for the sulphur fumes killed almost all the plant life within miles of the smelters. Heavy rain began to erode the top soil . . .'

One week's exposure to a sulphur dioxide concentration of 0.15 p.p.m. has been shown to cause visible damage to some plants, and it is suspected that chronic injury to a few sensitive plant species can occur at much lower annual average concentrations—even as low as 0.03 p.p.m.

But plants need sulphur. They take

it from the soil and the air, and sulphur dioxide added to the atmosphere reduces the requirement for sulphur in fertilizers. Scientists in Western Germany have estimated that their country's annual emissions of about 8 tonnes per square kilometre benefit agriculture to the extent of \$US 25 million.

Dr Davey calculates that Australia's emissions, averaged over the whole country, are enough to provide only about 2% of the requirements of farm crops. In Britain, by contrast, these needs are, on average, met and exceeded by half. Fortunately a sulphur input five or six times higher than the minimum requirement has been shown not to be harmful.



fitted-out aeroplane will be flown through the plume to collect air samples, which will be tested for sulphuric acid, other sulphates, and other gases and particles. Factors that affect the shape and composition of the plume, such as wind speed and air temperature, will be measured so that their effects can be worked out. The contents of smelter emissions before they leave the chimneys will be analysed, and so will samples of the atmosphere outside the visible plume.

Effects of the gas

The project should tell us a lot about what happens to sulphur dioxide in the atmosphere. It won't tell us anything about the biological or other environmental effects of the gas and the chemicals it changes to, but it should provide useful background information for researchers studying these.

At the CSIRO Division of Chemical Engineering in Melbourne, Dr Ron

Davey is drawing together information from around the world on the effects. He has published a general review of the sulphur situation in Australia, and is now examining existing information on the effects of sulphur compounds in the atmosphere on plants. He plans to follow this with a close look at the medical effects. His reports will help clarify what is known and what needs to be found out.

Australia doesn't appear to have any major sulphur dioxide pollution problems at present, although people living near smelters can experience discomfort when weather conditions lead to short-term build-ups near the ground. Levels in our cities are generally quite low, and should stay that way as long as low-sulphur fuels remain available. For some time still, economic rather than environmental considerations are likely to determine whether new metal recovery technologies are introduced and whether

power plants and factories remove sulphur dioxide from their emissions. However, with production and population constantly increasing, it is encouraging to know that it is possible to burn fuels and separate copper, lead, zinc, and nickel from their ores without pouring sulphur dioxide into the air.

More about the topic

Recovery of copper from chalcopyrite concentrate by means of sulphur activation, cupric chloride leach, and electrolysis. K. J. Cathro. *Proceedings of the Australasian Institute of Mining and Metallurgy*, 1974, 252, 1-11.

The conversion of sulphur dioxide by reaction with carbon. J. D. Blackwood and D. J. McCarthy. *Pace*, 175, 28, (in press).

The sulphur problem and the non-ferrous metal industries in Australia. T. R. A. Davey. *Pace*, 1973, 26, 20-27.

Methods of reducing or avoiding the generation of sulphur dioxide during sulphide mineral treatment. *CSIRO Minerals Research Laboratories, Research Review* No. 11, 1973.

Report from the Senate Select Committee on Air Pollution. The Parliament of the Commonwealth of Australia. *Parliamentary Paper* No. 91, 1970.

'Annual Results of Air Pollution Monitoring, 1973.' (Division of Occupational Health and Pollution Control, New South Wales: Sydney 1974.)

'The Peaks of Lyell.' Third Ed. G. Blainey. (Melbourne University Press: Melbourne 1967.)

'Introduction to the Scientific Study of Atmospheric Pollution.' Ed. B. M. McCormac. (D. Reidel Publishing Company: Dordrecht 1971.)

Sulphur and health

The difficulty of saying anything very definite about the medical effects of sulphur dioxide pollution is illustrated by the following quote from the report of the Senate Select Committee on Air Pollution:

'The Committee was unable to obtain any real evidence on the relationship between air pollution and health in the Australian environment, and material the Committee has read on overseas experiences is in many ways inconclusive and conflicting.'

The Committee was talking about the effects of air pollution in general. Attempting to separate out the effects of sulphur dioxide and other sulphur compounds only increases the problem.

A good deal of evidence exists correlating air pollution containing both minute particles and sulphur dioxide with interference to normal respiratory function, increased susceptibility to respiratory disease, and increased mortality from cardio-respiratory causes.

However, evidence also exists that sulphur dioxide and sulphuric acid mist

on their own, in concentrations well above those measured during the 1952 London smog disaster, do not cause respiratory problems. Sulphur dioxide appears not to penetrate further than the upper respiratory tract, but combined with particulate pollution it might penetrate further.

Dr Davey's conclusion from his study of the literature so far is that, in the absence of appreciable particulate pollution, the safe limit may be above 2 p.p.m. for long periods, whereas it is much lower in air heavily laden with particles.