

Making a residue pay

The Electrolytic Refining and Smelting Company is located at Port Kembla, N.S.W. During its copper-smelting operations, metallic impurities in the copper ore pass as fumes, along with sulphur dioxide gas, up the flue. At present, the 5000 tonnes of these impurities that each year are caught in bags are mixed with water to make a slurry and then stockpiled in ponds, where they have become something of a nuisance.

On the face of it, the accumulating 'fume' is worth a great deal of money, which is why it has been stockpiled. It is rich in zinc and lead, and may contain valuable amounts of copper and tin. Even at today's depressed prices, the metals in each year's accumulation should be worth more than \$1 million. The snag is that at present there's no economic way available to extract them.

In the past, Hardman Chemicals Pty Limited (a Sydney firm) bought all the fume as feedstock for producing zinc sulphate. The firm then resold the leadrich tailings that remained after this treatment. But rising costs and variations in the metallic content of the fume have made this operation unprofitable. Hardman Chemicals and Electrolytic Refining and Smelting are therefore looking around for alternative ways of extracting the metals. Meanwhile the stockpile grows.

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Copper refinery and smelter complex of Electrolytic Refining and Smelting, Port Kembla.

ber of years she has been looking at ways of separating lead and silver from metals like zinc and tin. She began this research as part of a program to try to find a way of economically separating lead from other metals in ore from the McArthur River lead and zinc deposits in the Northern Territory.

Separating copper

It has been known for some years that copper can be separated from other contaminant metals by roasting its ore with carbon and salt. Indeed the TORCO process for extracting copper uses just this method. Metallic copper becomes attached to the carbon particles, leaving the other metal impurities behind. The copper is then obtained by roasting the mixture of copper and carbon in a smelter.

Unfortunately, this technique cannot be used for extracting lead, since that metal is molten at the temperatures needed and will not stick to the carbon.

However, Miss Bear discovered, if the ore is roasted with salt and coal char in the presence of sulphur dioxide (a common waste gas in a smelting works, which

is often considered a pollutant) then a similar process takes place in which the metal is deposited on the char as the sulphide. (Lead sulphide has a much higher melting point than metallic lead, and is still solid at the temperatures required.) Once the sulphide has become attached to the char, it can be fed into existing smelting processes to obtain the metal.

Miss Bear tried the process out on concentrated McArthur River ore and on a number of ore-processing residues that contained high levels of lead, zinc, and iron, and smaller amounts of silver. As she had expected, with the right conditions more than 90% of the lead did indeed finish up as the sulphide on the char—as also did most of the silver. (These two metals can easily be separated by existing processes.) Much of the zinc and iron combined into a chemical complex, and remained behind in the residue.

At about this time Hardman Chemicals approached the Division of Mineral Chemistry about ways of separating metals in the smelter fume of Electrolytic Refining and Smelting. Miss Bear thought that it might be possible to treat it in a similar way to McArthur River ore.

Like this ore, the stockpiled fume at Port Kembla contains large amounts of lead and zinc. But unlike the ore it contains little iron. Unfortunately, if the fume is roasted with salt, char, and sulphur dioxide, the zinc appears along with the lead on the char.

Iron needed

Miss Bear therefore tried adding iron to the fume. As expected, zinc then combined with the iron to form a chemically unreactive complex. So, when salt and char were subsequently added to the hot roast, both metals remained behind as a residue while lead, silver, and one or two other precious metal contaminants moved onto the char. Once there, they could be extracted by existing commercial processes.

Obviously, one of the keys to economical separation of lead from the Port Kembla fume by this method will be a cheap source of iron. Pyrite (iron sulphide) seems one likely source. Being a sulphide of iron, this ore will burn to

The stockpiled fume at Port Kembla contains large amounts of lead and zinc. give both heat and sulphur dioxide — both items that can be used to reduce running costs when roasting the fume.

Wastes a source?

Iron-rich wastes could provide another source. Two companies in Tasmania — the Electrolytic Zinc Company of Australasia, and Tioxide Limited — produce such wastes. However, neither of these residues contain their iron in the form of a sulphide. Thus, if used, heat for roasting and sulphur dioxide would have to come from outside.

In separate experiments, Miss Bear tried roasting the Port Kembla smelter fume with several sources of iron. These included high-quality laboratory ferrous oxide, pyrite, copperas (Tioxide Ltd's waste from Burnie, Tas.), pure ammonium jarosite, and ammonium jarosite residue from the Electrolytic Zinc Company's plant at Risdon near Hobart. (In copperas the iron is mainly in the form of ferrous sulphate, while in ammonium jarosite it's mainly present as basic sulphates.)

In all these experiments, at an optimum pre-roast temperature of about 800° C and with an adequate supply of sulphur dioxide present, between 85% and 90% of the lead in the fume turned up as lead sulphide on the char after it was added. Practically all of the zinc and most of the copper impurities in the fume

Copper smelting at ER&S: ponds of stockpiled metallic impurities given off during this operation by the copper ore have become something of a nuisance.

remained behind as a residue containing a mixture of zinc and copper ferrites.

The great advantage of this process is that all its products, including the residue, can be treated to extract their metals using well-established commercial processes.

Feed for the jarosite process?

Of interest in this regard is the fact that zinc ferrite is the material refined in the jarosite process used by the Electrolytic Zinc Company at Risdon to extract further quantities of zinc from the 'primary' residue produced during the process of separating zinc from its ore.

During this process the company first roasts the ore to convert the zinc it contains from the sulphide into the oxide. The ore is then treated with sulphuric acid, which leaches out much of the zinc as zinc sulphate. This is then treated electrolytically to obtain the zinc metal.

As well as producing zinc sulphate, the leaching process leaves a residue consisting of about 30% iron, 20% zinc, and lower levels of some other metallic impurities of which lead and silver are the most valuable. This 'primary' residue consists mainly of zinc ferrite, and the company produces about 80 000 tonnes each year.

That 20% of zinc in the primary residue is still valuable, and Electrolytic Zinc independently developed the 'jarosite' process as a way of separating the zinc from the iron.

By 1970, when this process came on stream, the stockpile of stored primary



Miss Joy Bear's technique for extracting metals from the Port Kembla smelter fume is but one of several attempts to find a profitable way of using the stockpile at the Electrolytic Refining and Smelting Company. An alternative treatment has, for example, been under investigation at the Australian Mineral Development Laboratories (AMDEL), Adelaide.

Dr Dion Giles of Murdoch University and Mr Alexander Boden of Hardman Chemicals have been following up yet another method, very different from Miss Bear's. Instead of roasting the fume to extract its valuable metals, they have extended Hardman Chemicals' current technique of treating the fume with sulphuric acid to extract its zinc content.

The company's present technique allows recovery of about two-thirds of the zinc in the fume as zinc sulphate. The remaining residue still contains valuable amounts of several metals — particularly lead, tin, copper, and of course, zinc. Being able to extract these could well tip the economic balance enough to allow the company to profitably treat all the Port Kembla fume once more.

Dr Giles and Mr Boden have added a further two stages to the existing treatment. Both stages involve treating the residue with hot hydrochloric acid. Consequently, the tin in the residue comes out as a precipitated concentrate, and the zinc as a mixed solution of zinc chloride and zinc sulphate. In addition, the treatment converts about 80% of the lead into lead chloride, which can be recovered pure.

As with the products of Miss Bear's technique, use of standard methods will allow extraction of the metals. Adoption of either of these two methods, or of any other, will depend on their running costs on an industrial scale, and on the market for their end-products.

Hydrometallurgical treatment of Port Kembla copper smelter fume. D.E. Giles and A. Boden. Proceedings of the Australian Institution of Mining and Metallurgy No. 262, 1977.

residue had reached 11/4 million tonnes.

Jarosite, the waste product resulting from processing of the primary residue, is currently dumped at sea just off the continental shelf south-east of Hobart (see $Ecos\ 1$). It could also be a source of iron for complexing the zinc and copper in the Port Kembla fume.

Recycling the iron

Miss Bear suggests that it should be possible for the Port Kembla fume to be

Jarosite waste could also be a source of iron.

treated first with jarosite to allow extraction of the lead, and then for the zinc ferrite residue to be treated by the jarosite process to extract the zinc.

The end product would of course once again be jarosite. Thus what the whole

process of roasting the Port Kembla fume with jarosite residue and then passing it through the jarosite process would really be doing is recycling the iron in the residue.

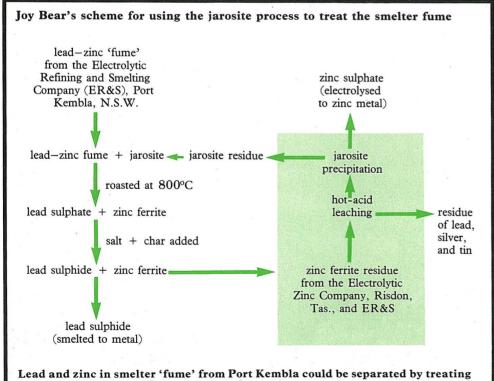
Such a solution to Electrolytic Smelting and Refining's fume problem has its obvious attractions. Nevertheless, Miss Bear's suggested method is only one of several being considered by the company at Port Kembla. It may not prove the most economic - for instance, transporting either the fume or jarosite residue over long distances is very expensive. At present the company is interested, but has yet to come to a decision. Certainly it has not entered into any agreements with the Electrolytic Zinc Company concerning either treating its fume or supplying jarosite waste for treating it at Port Kembla.

More about the topic

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Treatment of lead sulphate materials by the segregation process. I.J. Bear and R.R. Merritt. Transactions (Section C) of the Institution of Mining and Metallurgy, 1975, 84, 92-8.

Mechanism of segregation of lead sulphide from lead sulphate. I.J. Bear, R.R. Merritt, and A.G. Turnbull. Transactions (Section C) of the Institution of Mining and Metallurgy, 1976, 85, 637.



Lead and zinc in smelter 'fume' from Port Kembla could be separated by treating it first with jarosite residue and then passing the zinc ferrite produced back through the jarosite process (shaded on the chart) at Risdon, Tas.