REFINING OF NON-FERROUS METALS

J. G. BERRY*

Abstract

The fundamentals of refining of non-ferrous metals have been outlined. Examples of removal of impurities by selective oxidation, electrolysis, distillation, volatilization, etc., have been given. Refining of copper, lead, zinc, tin, and some other metals have been described. The importance of economics and time involved in refining process has been stressed.

Introduction

IT will be my endeavour in this paper to indicate the fundamentals of refining as they are applied to the more common members of this group, with a description of some of the processes, and, in doing so, I hope to promote discussion which, after all, is the objective of this symposium.

Definition

What, then, is the definition of ' refining ' ? Strictly speaking, it is the metallurgical process for the removal of impurities which follows the reduction of an ore or concentrate to metal. It can also be applied to any process used for the purification of scrap.

The term ' refining ', for the purposes of this discussion, must, however, be expanded to include the removal of impurities from an ore or concentrate before the reduction stage, as, in some cases, if such impurities are allowed to enter the product of reduction, they are difficult to remove in the subsequent refining process.

Whether before or after smelting, the objective of the metallurgist is the removal of undesirable elements from a metal or alloy.

Fundamentals and Examples

How, then, is the objective achieved ? It may be achieved by using the affinity of an undesirable element for another element, thus forming a compound, which is insoluble in the metal to be refined and which can easily be removed. Selective oxidation, electrolysis, distillation or volatilization may be used, while flotation, magnetic separation or chemical reaction may be used to remove undesirable elements prior to the reduction stage.

One of the earliest attempts at refining would be the ' purification ' of gold by thermal methods, while the most recent development in this field is the solution and precipitation of metals under controlled pressures from ores and concentrates or scrap, such as brass.

In the fire-refining of copper, many impurities are oxidized and removed in the slag, these impurities being oxidized in preference to the copper itself. On the other hand, in the refining of metals in which copper is itself an impurity its affinity for sulphur may be used to bring about its elimination.

Zinc is refined by distillation, while impurities, such as arsenic, can be removed by volatilization. Electrolysis, as a method of refining, is used for copper and, of course, the treatment of bauxite is a well-known example of ' pre-extraction ' refining, assuming that the proposed expansion of the original definition of refining is permitted.

Outlines of Refining Procedures

Copper — By far the greater tonnage of copper is produced from sulphide ores which,

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after concentration, are smelted to produce a 'matte' which, in turn, is 'blown' to blister copper in a converter. The blister copper, which is sent to the refinery may contain varying amounts of sulphur, iron, arsenic, aluminium, selenium, tellurium, bismuth, nickel, cobalt, gold and silver.

The actual refining process starts in the converter where, if bismuth is present, this impurity can be reduced to 0·001 per cent or less by prolonging the blowing at the slagging stage, and a concentrate, with a percentage of iron higher than normal, is produced to enable this to be done. Bismuth, if allowed to remain in the blister copper, cannot be removed by fire-refining.

Fire-refining of the blister copper is carried out either to produce an ingot of relatively high purity, or as a preliminary to electrolytic refining, and even after electrolytic refining the cathode copper may be again fire-refined to give the correct pitch for the production of copper-wire bars. In the fire-refining process, air is used for oxidation and the 'end point' is noted by studying the 'set' of samples taken at intervals from the bath. It is a feature of this process that the oxidation of the impurities is more rapid than that of the copper, thus enabling the impurities to be removed with comparative ease.

Of the impurities which have been noted, sulphur is eliminated almost at once. Iron is readily removed in the slag, as also is aluminium. Arsenic and antimony, if present, are removed by using soda-ash and lime, the lime being added to reduce the wear and tear on the furnace lining. These latter elements are, of course, removed after the normal slagging process has been completed.

Selenium and tellurium cannot be removed by fire-refining, although there are possibilities of some success using soda-ash under reducing conditions. However, these elements are normally removed by electrolysis, together with the precious metals which, if present, as would be expected, do not oxidize and, therefore, cannot be removed by fire-refining.

Care must be taken in fire-refining and a balance struck between the amount of impurities removed and the time taken, as the longer the oxidation, the more copper goes into the slag which must be re-treated to recover that copper. This recovery is achieved by utilizing the affinity of copper for sulphur and the slags, resulting from the converting and refining operations, when added to the reverberatory furnace, react with and enter the matte.

Depending on the residual impurities, 'oxidation' is followed by 'poling' with green poles to reduce the dissolved copper oxide, after which the metal can be ingotted and sold for many purposes. If, however, high conductivity copper is required, and if the copper is suitable from the point of view of impurities, the fire-refining process can be continued, and it is interesting to note that some 6 or 7 per cent of the world's production is high conductivity fire-refined copper.

Electrolytic methods of refining remove the difficult elements, such as nickel, cobalt, selenium and tellurium, together with the gold and silver; and, as already stated, after the electrolytic process, the cathodes are melted and the copper subjected to a short fire-refining process by which the correct pitch or oxygen content is obtained before casting into wire-bars.

Lead — Lead, which may contain any of the following impurities, viz. copper, antimony, arsenic, bismuth and silver, has a very interesting course to follow from the blast furnace to the refined product, and at Port Pirie, South Australia, Dr. G. K. Williams, the then Chief Metallurgist at the Broken Hill Associated Smelter (Proprietary) Ltd., worked out a scheme for the continuous flow of metal from the bullion storage kettles to the finished product.

Copper is the first impurity to be removed, and this is done by drossing and by the utilization of the affinity of copper for sulphur. The blast furnace product is received in kettles, where it is allowed to cool. As the temperature drops, the dross formation reduces the copper to under 0·1 per cent. At this stage, sulphur is added and the final drossing carried out at as near to the freezing point as possible.

I remember, as a young man, watching this process being carried out on a very small scale in a solder pot, and the operator, quite a character, called the process ' cold burnin '. I have never heard the term before or since, but it aptly describes the process. The dross from this section is smelted to recover the copper, while the lead is pumped to the bullion storage kettles.

The lead is now ready for the continuous refining process. The first stage is ' softening ', in which, as is indicated by the name, the hardening elements, namely arsenic and antimony, are removed. The molten metal is agitated with compressed air and the oxidation of antimony and arsenic takes place together with a proportion of the lead. The concentration of antimony in the bath has a pronounced effect on the rate of oxidation and the blowers are controlled so that the antimony is oxidized quickly and the bath maintained within the critical range (0·02-0·04 per cent). The slag and softened metal are removed continuously, the slag being retreated to produce antimonial lead as well as to be used in the dezincing process mentioned later.

From the softened metal, steps must be taken to remove the dissolved oxygen, as this could upset the desilverizing process and increase zinc consumption. The molten metal is cooled and then re-heated to desilverizing temperature (650°C.) before feeding to the desilverizing kettles through a launder under a charcoal cover.

A desilverizing kettle is egg-shaped, being made in three sections bolted together, 23 ft. deep with a maximum diameter of 10 ft. These kettles are set in brickwork with six independent heating zones. A layer of zinc is kept on top of the charge and molten metal from the deoxidizing section flows in passing through the zinc layer and on into the main bulk of lead below. As the lead passes through the zinc layer, the zinc takes up the gold and silver, while the lead dissolves some of the zinc. When the zinc is sufficiently enriched, it is removed by ladles and fresh zinc added. The lead is discharged from the kettle by a syphon, the mouth of which is set some 18 in. from the bottom. Thus the incoming lead having passed through the zinc layer is displaced downward into the cooler zones, where the zinc alloy crystallizes out and rises back into the upper sections. The temperature of the lead, as it is displaced downward, falls nearly to the freezing point and the desilverized lead, rising up in the syphon, is re-heated by the metal in the upper sections.

The desilverized lead still contains a little zinc, and the final refining takes place in a furnace similar to that in which the ' softening ' was carried out, the same principle, namely oxidation, being involved. Here trouble was experienced owing to lack of fluidity of the slag, but by adding some antimonial slag from the softening furnace, this trouble was overcome without upsetting the refining process.

At Port Pirie, a specially pure lead has been produced; the material used as a basis for the process is not, as would be expected, refined lead as bismuth, an impurity difficult to remove, is often present. To overcome this, the antimonial slag from the softening furnace is used as a starting-point owing to the fact that bismuth remains with the lead at this stage and does not enter the slag. After reducing the slag, the arsenic and antimony are removed by combination with caustic soda; copper and silver by using zinc; and the zinc and final traces of antimony by using caustic soda and nitre, the resultant metal giving lead by a difference of 99·9992 per cent, which clearly illustrates the extent to which refining can be taken if so required.

Zinc — Turning now to zinc, the refining of which involves distillation as distinct from the direct production of zinc by electrolysis which cannot be strictly classified as a refining process.

However, a certain amount of refining is accomplished by liquation or segregation, where the 'end product' is spelter, an impure class of zinc containing a small quantity of lead. This is carried out in a simple furnace consisting of two sections. In the first, the metal is melted under reducing conditions at a temperature slightly above freezing, the excess lead separates out and collects at the bottom, whence it can be tapped off periodically. The refined metal, i.e. the alloy which has the lowest melting point and which contains about 1 per cent of lead, overflows into the second section, where an adequate temperature is maintained to permit pouring into ingots.

The New Jersey Zinc Company has patented a process for the refining of zinc by distillation, the first stage of which is to distil off the volatiles, namely zinc and cadmium, and then to distil off the cadmium from the zinc.

Tin — The refining of tin is another interesting study, as it involves pre-smelting treatment to remove certain impurities in addition to the post-smelting refining process. For example, at the ore-dressing stage, sulphides of iron and arsenic are removed by flotation, or, alternatively, for the removal of arsenic, the concentrate may be roasted. Acid leaching is often used to remove other impurities, including copper, while magnetic separation is used to remove wolfram.

The smelting is in two stages, a primary smelt producing relatively pure metal and a high tin-content slag, and a secondary smelting of the slag, producing an 'irony' tin and a low tin-content slag, the 'irony' tin being returned to the primary smelting charge.

The tin, depending upon its purity, is sent either to a liquating furnace, or to a refining kettle which has a capacity of some 60 tons of metal. In the kettle the temperature is allowed to drop and impurities to solidify, forming a crust which can be skimmed off. This crust and impure tin from other sources are treated in a liquating furnace.

The process of liquating or, as it is sometimes called, draining merely consists of holding the charge at the top of the sloping hearth of a liquating furnace at a temperature just above the melting point of the metal concerned. The lowest melting point and, therefore, purest metal which melts out, drains away down to the slope, where it can be collected for subsequent treatment. The residues which remain behind in the liquating furnace are returned to the reverberatory furnace.

The metal in the kettle is 'poled' or, perhaps, we should say, boiled, because poles are no longer used and air or steam is now the medium for agitation of the metal producing the oxidation of impurities. Copper, as in the case of lead, is removed by the use of sulphur. Antimony and arsenic, if not removed as already described, can be removed by the addition of aluminium, the compounds of aluminium with these two metals being insoluble. The aluminium additions are followed by further boiling to remove the dross and the excess aluminium.

Other metals — Let us now turn to some of the lesser known refining processes. Take, for example, the platinum metals which are to be recovered from sweepings etc. The sweepings are treated in a reverberatory furnace with litharge and the products are slag, matte and lead, but owing to the difference in affinity for matte and lead, the metals of this group are divided between the products. Platinum and palladium will be found in the lead, while osmium, iridium and ruthenium will be found in the matte.

The mechanics of the refining of magnesium are apparently still under discussion, but the process used is one of fluxing. There are several fluxes under various trade names, but it would appear that all contain magnesium chloride which reacts with the oxide suspended in the melt, and as it absorbs the oxide the flux thickens and drops to the bottom of the crucible.

In bismuth refining, an alloy of bismuth and lead is formed, and to remove the lead, bismuth sulphide is added to the melt. The reaction between the bismuth sulphide and the lead gives bismuth and lead sulphide which is removed — another example of utilizing the affinity of certain metals for sulphur.

Aluminium, which has a strong affinity for oxygen, cannot be refined by normal methods, and any refining process must be based on electrolysis. Even so, there are still limits in respect of the purity of the material to be refined if this process is to be carried out economically. The electrolytic refining, or 'three-layer' process, as it is called, is used for this particular metal. A lower layer of impure aluminium, which has been alloyed with copper, rests on the carbon block furnace bottom of the cell; the electrolyte is a mixture of sodium fluoride, aluminium fluoride and barium fluoride, and the pure aluminium is ladled off from the surface of the bath.

The latest proposal for the refining of aluminium scrap is to use the property of the solubility of aluminium in mercury. However, it can be well imagined that the mechanical difficulties of such a method are extremely great, especially when it is remembered that the solubility of aluminium in mercury is best at temperatures of the order of 650°C.

In concluding this rather general survey of non-ferrous metal refining, there is one point which must be stressed and which must be borne in mind when one is devising methods for the refining of any particular metal, namely the economics of the process which must be carefully assessed. Scrap metal is cheap, and the more impure it is, the cheaper, but even so it has a value, and to that value must be added the treatment charges, so that it is quite obvious that expensive and complicated procedures cannot be considered for the lower-valued metals.

Another point, especially in the case of precious metals, is the time factor and the 'lock-up' of the metal in process, and this, of course, is most important where prices in the bullion markets may rise or fall within the time the refiner has his customer's metal in hand.

Discussions

MR. S. SARKAR (Metal Corporation of India Limited)

The different processes leading to the production of refined lead as practised in the Tundoo Smelter of Metal Corpn. of India Ltd. produce lead as high as 99·993 per cent which is perhaps the same or better than the Broken-Hill smelter in Australia.

MR. J. G. BERRY (Copper Corporation, Ghatsila)

In clarification of a point raised by Mr. Sarkar, it is pointed out that the assay quoted in the paper of 99·9992 per cent lead was a metal refined to a super purity and not to the standard 'Broken-Hill' brand.

MR. S. VISWANATHAN (Tata Iron & Steel Co. Ltd.)

(a) The definition of refining should not include pre-smelting work; (b) as impurities are known to modify the physical properties, one would, therefore, be interested to know the effect of impurities on some non-ferrous metals; and (c) what are the difficulties for the utilization of SO_2 obtained from the copper smelter at Ghatsila ?

MR. J. G. BERRY (*Author's Reply*)

In reply to (a) it is my opinion, as stated in the paper, that pre-smelting work is necessary in some cases to remove certain undesirable elements and as such should be included. (b) In non-ferrous work the processes as described are for the most part common commercial practices. The effect of impurities on non-ferrous metals is a different subject and would not come within the purview of refining. (c) Regarding the utilization of SO_2 the problem has been under examination for some time, but there are two points which are the stumbling blocks — (i) lack of market in the near vicinity and (ii) technical difficulties arising out of the use of one converter at a time. Cost of transport of acid precludes the Calcutta market. Jamshedpur users have their own plants and have not shown any enthusiasm for the acid if produced at Ghatsila.

The large overseas producers have several converters in operation at the same time and they do not attempt to collect all the sulphur dioxide from a single converter as would be necessary in our case. They can pick and choose and take the gas from the second blow and ignore the slagging blow which produces a low gas strength. After some experimentation we think we can overcome this difficulty.

MR. A. K. GUPTA [Sepulchre Brothers (India) Ltd.]

Mr. J. G. Berry has pointed out various difficulties experienced at the Copper Corpn. for carrying out the recovery of sulphur from the smelter gases, one of which is its low strength.

It may be mentioned that at the Copper Smelter Works at Harjavalta, Sweden, two sulphuric acid plants are working starting with smelter gases containing varying percentages of SO_2 of 1·7 to 7 per cent, with a conversion efficiency of 98 per cent.