

Borates in lead recycling



1. General review of non-ferrous metallurgy

1.1 Dissolving metal oxide impurities

This application discusses the recovery of metals, (i.e. brass, bronze, copper, lead, zinc, etc.) The recovery can come from scrap or from slag left over from a primary smelting operation. In order to produce a product as pure as primary metal it is necessary to remove all oxides and extraneous impurities. Borates act as fluxes during melting, combining with metallic oxides at relatively low temperatures to bring them to the surface of the melt as a slag which can be decanted or skimmed off. These other metallic oxides are thus considered contaminants.

1.2 Cover flux to prevent air oxidation:

During melting, borates will protect metal from the oxidizing atmosphere of the furnace. Borates near the bottom of the furnace will melt last and float up to the surface of the molten metal dissolving oxides, silica (sand) and other non-metallic impurities. If the metal is to be refined at this stage any special additives or alloying fluxes should be introduced under the borate cover. The borate slag can usually be skimmed from the metal easily before pouring. If the slag is too thin, it may be thickened by addition of a small quantity of sand.

1.3 General advantages of the borates as cover fluxes are:

- High solvent action on metal oxides and siliceous material present
- Formation of highly fluid slags with only mild attack on refractories
- Ease with which slag can be thickened if necessary, and skimmed
- Ease and safety of handling
- Non-combustibility with minimum fuming tendency

Purification is performed by adding borates to the furnace, placing the scrap or dross on top and turning on the heat. Usually the surface is also covered with borates to provide a molten cover to prevent oxidation during heating. The borate at the bottom melts and rises

through the molten and/or partially molten metal dissolving the oxides and extraneous impurities and brings them to the surface forming a slag. This operation applies to cupola type furnaces while in reverberatory furnaces the borate is charged into the furnace directly with the scrap.

1.4 Smelting operation

In smelting non-ferrous scrap, *Dehybor*[®] (anhydrous borax) is recommended. Anhydrous forms are preferred to avoid puffing and intumescence (with possible steam explosions) as occurs when hydrated borates are heated vigorously. Anhydrous borates form an excellent liquid flux for most bronzes, brasses, and similar alloys, and also serve as scavengers to dissolve and carry out oxides, dirt, and sand which so often contaminate non-ferrous scrap.

While quantities will naturally vary somewhat with types of furnace and quality of the metal to be melted, from 0.006% to 0.01 wt% will generally purify the metal and serve as a cover. Sufficient *Dehybor* (anhydrous borax) should be used to form a cover about 0.25 inches thick. About half of the borate should be distributed over the bottom of the furnace before the metal is charged. The remainder should be added evenly over the metal. Some examples of metal refining are given as follows:

1.5 Other metallurgical applications

1.5a Nickel

Nickel ores usually contain large amounts of iron, copper sulfide, nickel sulfide, and sodium sulfide and varying amounts of precious metals. The ore is smelted and then blown in a basic converter to remove the iron. The remaining matter is then re-melted and the major portion of the copper sulfide and sodium sulfide form an upper layer while the nickel sulfide still contaminated with some iron, precious metals, copper sulfide, etc. remains in the lower level. The two layers are separated and the contaminated nickel sulfide layer is formed into impure anodes. These anodes are then placed in an electrolytic

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cell containing a nearly neutral solution of nickel sulfate. When an electric current is passed through the electrolyte, the impure anode slowly dissolves and the pure nickel deposits on the cathode. The cells are specially constructed to keep the cathodes away from any contaminants and the contaminants are recovered from the impure electrolyte.

The neutral condition noted above is maintained by the addition of a borate and other chemicals to control pH. Borates used to control pH include *Optibor*[®] (boric acid), boric oxide (anhydrous boric acid), and *Dehybor* (anhydrous borax).

1.5b Aluminum

Borates can be used in the actual process of preparing bauxite ore into aluminum. Low-grade fluoboric acid (HBF_4), produced from hydrofluoric acid and boric acid or boric oxide, is used in the manufacture of cryolite (Na_3AlF_6) for the electrolytic production of aluminum. The Alcoa Alzak process of electro polishing of aluminum also requires fluoboric acid. Ammonium fluoborates can also be used as fluxes for aluminum reduction. Boron is a grain refiner and hardening agent for aluminum.

It can be added to the crucible melt in the form of aluminum-boron master alloy prepared from KBF_4 or directly as boric oxide (anhydrous boric acid) to the electric furnaces where alumina and B_2O_3 are reduced to aluminum and elemental B. The presence of boron in aluminum can improve appearance and reduce tearing on rolling into thin sheets. A small amount of borate is used in the preparation of activated alumina catalysts.

Cyanide forms as a result of a reaction between carbon, sodium and nitrogen in the lining of Hall-Heroult cells during the aluminum production. This has led to the classification of spent pot liner as hazardous waste. Attempts to suppress cyanide formation by sealing cells to avoid the penetration of air have brought at best partial success. On the other hand, adding suitable reactants to the pot lining shows considerable promise. In laboratory tests, boric oxide was

found to suppress cyanide formation almost completely, at conditions generally favoring the reaction of sodium, carbon and nitrogen to form sodium cyanide. The resulting cyanide levels in the pot lining were reduced to as low as a few ppm.

1.5c Precious metal recovery

The gold and silver refining industry and assaying laboratories use *Dehybor* as part of their flux formulations. The other ingredients in the flux formulation will vary depending on whether the gangue associated with the ore is acidic, basic or reducing in character. The major reason for using a form of borate is that it readily associates with the metallic oxide contaminants at a sufficiently low temperature to minimize the loss of precious metal and to give longevity to the melting equipment.

2. Lead recovery

2.1 Introduction

The secondary production of lead begins with the recovery of old scrap from worn-out, damaged, or obsolete products and with new scrap. The main source is lead-acid batteries but could include pipes, sheets, cable coverings and other lead containing metals.

With batteries, the lead can only be obtained by breaking open the case. This is commonly done using a battery breaking machine which, in addition to crushing the case, separates out the different components of the battery and collects them in hoppers. Thus, the pastes (oxide and sulphate), grids, separators and fragmented cases are all separated from one another. The battery acid is drained, neutralized, and disposed of carefully.

The case material is separated by the battery breaker into hard rubber and polypropylene fractions, the latter being the more common today. The hard rubber fraction is either washed and discarded or can be utilized as a reductant in the smelting process. The polypropylene is subjected to a cleaning and reprocessing operation to make a good

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quality recycled material. In view of the diverse range of colors found in battery case materials, the polypropylene is normally reprocessed to black or other dark shades. Typical applications for the reprocessed plastic are new battery cases, water tanks, video cassette boxes or flower pots. The sorted materials are collected in bays to await make-up of the feed to the smelting furnace.

2.2 Secondary smelting

The blast furnace was used to provide a low grade antimonial lead, which would be softened - either in a refining kettle or a reverberatory furnace. The high antimony slags would be accumulated for a subsequent blast furnace campaign to produce high antimony bullion for blending into alloys of the desired composition.

Most companies now use rotary furnaces which can be either oil or gas fired. The charge can either be tailored to give a lead of approximately the desired composition or a two stage smelting procedure can be employed which can yield crude soft lead and crude antimonial lead. In stage one, the furnace conditions are held oxidizing for antimony but neutral to lead, thus forming antimony oxides which are insoluble in molten lead. In the second stage, conditions reducing to both lead and antimony are used which reduces any metallic oxides to the metal and liberates carbon monoxide and carbon dioxide.

For example:

Stage one

Battery plates are charged using little or no reducing agent and crude soft lead is tapped off after a few hours with the antimonial slag and lead oxide and sulphate being retained in the furnace. Further plates are charged and more soft lead withdrawn until sufficient slag has accumulated for the slag reduction stage.

Stage two

Coke or anthracite fines and soda ash are now charged, both lead and antimony oxides and lead sulphate are reduced and the cycle ends. Some companies make use of hard rubber battery cases as co-reductants because of their high carbon content and because of

the high cost of metallurgical coke. Iron may be added to the charge in moderate amounts to matte any sulphides produced from the reduction of sulphates and to prevent any sulphurous fumes from leaving the furnace.

As with primary smelting, large volumes of gas are produced, carrying with them substantial quantities of dust. On leaving the smelter, the gas is cooled from about 900°C to about 100°C using air and/or water cooling. The gases pass into a bag house which contains hundreds of woven cloth bags. The gases pass through the bags and the dust remains on the surface. Periodically, there is a negative back pressure and the flow to a particular bag is cut. The dust-cake cracks and the dust tails to the bottom of the bag chamber. It is collected, agglomerated and fed back into the smelter. The gases pass out of the stack and into the atmosphere, dust free. In the course of processing one ton of lead, as much as 100 tones of air have to be cleaned in this way.

2.3 Secondary refining

Once smelting is complete, the molten lead is removed from the smelting furnace and can be cast into large blocks (called pigs) weighing 1.5 to 2.5 tons. These are transferred to the refining kettles which are top-access pots sunk into the refinery floor. Alternatively, in more modern plants, the molten lead is pumped directly from the smelting furnace to the refinery pots thus saving on time and energy in re-melting.

The principal impurities which are removed in secondary lead refining are copper, tin, antimony and arsenic. Copper can be removed in a similar fashion to that outlined for primary lead. Some companies use iron pyrites and sulphur which works at a higher temperature and can also remove any nickel present. The other elements are removed by a modified Harris process. Bismuth and silver levels tend to be slightly higher than in primary lead but are rarely removed.

When scrap lead is supplied in clean metallic form e.g. sheet or pipe, this may be re-melted in the refinery kettle without having to undergo

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smelting. The common impurities in scrap lead are copper, tin and antimony, whilst occasionally zinc, iron or arsenic may be present. The material is often contaminated with dirt and other materials. These impurities are removed using the same basic techniques as have been previously described. Lead smelters are normally run at 1100 to 1200°C; when they smelt recycled lead.

2.4 Typical profile of fluxing compounds

- Borate (*Dehybor*, *Neobor*[®], and *Optibor*[®])
- Carbonate – Lead carbonate process from lead acid batteries
- Lime
- Scrap lead and lead wastes
- Soda ash
- Silica and scrap iron
- And combinations of these

2.5 Borate value as a flux

- High solvent action on metal oxides and siliceous materials producing a purer metal
- Formation of highly fluid slags due to the reduction of the liquidus temperature allowing for the extraction of more lead and leaving less in the slag
- Ease with which slags can be thickened and skimmed if necessary based on metal chemistry
- Reduction in energy costs due to the lowering of the melting point in the furnace
- Anticipated improvements in the cooled more solidified slag due to reduction in the leaching effect of lead sulfate from the slag
- Ease and safety of handling a inorganic borate compound
- Non-combustibility with minimum fuming tendency

2.5a Borate functionalities

The effect of the B_2O_3 will depend on the composition of slag, and how close it is to a eutectic. In most cases, it should lower the liquidus temperature.

Optibor[®] (Boric acid)

As boric acid heats up, it dehydrates slowly, forms a melt; the melt bubbles as it loses additional moisture. The melting point of *Optibor* begins at 176°C (348.8°F). As for the effect of an addition rate of 5% boric acid (2.8% B_2O_3), we estimate that the melting point of the slag might decrease by 50 to 100 degrees Celsius.

Judging by the effect of B_2O_3 on the melting point of PbO, you should expect a more dramatic effect with 10% boric acid (5.6% B_2O_3).

During smelting of lead, a layer of molten Na_2SO_4 is generally separated from the slag layer. The solubility of molten B_2O_3 is very low in molten Na_2SO_4 (0.2-0.3%); and molten B_2O_3 is completely miscible with molten PbO. It is expected that most of the B_2O_3 will be in the PbO slag layer, and very little in the molten Na_2SO_4 layer.

Neobor or *Dehybor* (boric acid)

As Sodium borates heats up, it dehydrates slowly, forms a melt; in the case of *Neobor* the melt bubbles as it loses additional moisture. The melting point of *Neobor*[®] is < 200°C (392°F). The melting point of *Dehybor* is 742°C (1368°F). The effect of *Neobor* or *Dehybor* on the liquidus temperature of the slag from lead smelting is expected to be similar to that of boric acid for equivalent amounts of B_2O_3 . *Neobor* tends to bubble and sputter during initial heating of the charge in the smelter as it dehydrates. *Dehybor* behaves better during melting, as it is the dehydrated product.

2.6 Testing protocols

2.6a Proposed customer test procedures – lab

A lab-based furnace test is recommended to determine the melting regimes and yield characteristics that borates bring to recovering lead and the removal of metal oxides. It is suggested that lab tests be carried out with typical plant slag samples in crucibles with 0%, 2%, 5% and 10% of the borate compound. Based on the observed reduction of liquidus temperature of the slag, plant tests can be carried out with the desired concentrations of the boron compound.



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U.S. Borax, part of Rio Tinto, is a global leader in the supply and science of borates—naturally-occurring minerals containing boron and other elements. We are 1,000 people serving 500 customers with more than 1,700 delivery locations globally. We supply 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles east of Los Angeles. We pioneer the elements of modern living, including:

- **Minerals that make a difference:** Consistent product quality secured by ISO 9000:2001 registration of its integrated quality management systems
- **People who make a difference:** Experts in borate chemistry, technical support, and customer service
- **Solutions that make a difference:** Strategic inventory placement and long-term contracts with shippers to ensure supply reliability

About 20 Mule Team® products

20 Mule Team borates are produced from naturally occurring minerals and have an excellent reputation for safety when used as directed. Borates are essential nutrients for plants and key ingredients in fiberglass, glass, ceramics, detergents, fertilizers, wood preservatives, flame retardants, and personal care products.

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