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LEAD/ACID BATTERY RECYCLING AND THE NEW ISASMELT PROCESS

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Abstract

The recovery of lead/acid batteries has long been practised for economic reasons. More recently, battery recovery has also been influenced by environmental concerns, both in the general community and within the recycling plants. These influences will probably increase in the future. With these factors in mind, Britannia Refined Metals Ltd. introduced new technology for battery recycling at its Northfleet, UK operations in 1991.

A process description of the Britannia Refined Metals Secondary Lead Operation, the reasons for selecting an Engitec CX battery breaking plant in combination with an Isasmelt Paste Smelting Furnace, and commissioning and current operation of the plant are discussed.

Introduction

Britannia Refined Metals (BRM) opened its new recycling facility at Northfleet, UK, in September 1991. The plant is designed to treat traditional lead/acid battery scrap through the use of state-of-the-art technology.

The plant incorporates automated materials-handling systems, together with process technology, to achieve reduced emissions and effluent discharges of the lowest levels by practicable means.

Commercial aspects

During the last twenty years, the demand for lead on the part of the battery industry has grown by an average of 4% per annum from about 1.1 million tonnes to about 2.35 million tonnes at present (1). Here, the battery share of the total lead consumption rose from 38% in 1969 to 62% today (Fig. 1).

It is very likely that the battery industry will consume 75% of the lead produced by the year 2000. It can be assumed, for the foreseeable future, that lead still has a good growth potential in this area because of it: (i) metallurgical properties; (ii) reliable availability, and (iii) comparatively low price, which accounts for only about 25% of the value of a new battery.

In 1990, the Western world had a lead-refining capacity of around 5.3 million tonnes per annum. Of this capacity, about 3 million tonnes were attributed to primary lead smelters and 2.3 million tonnes to recycling, or secondary, lead smelters (Fig. 2).

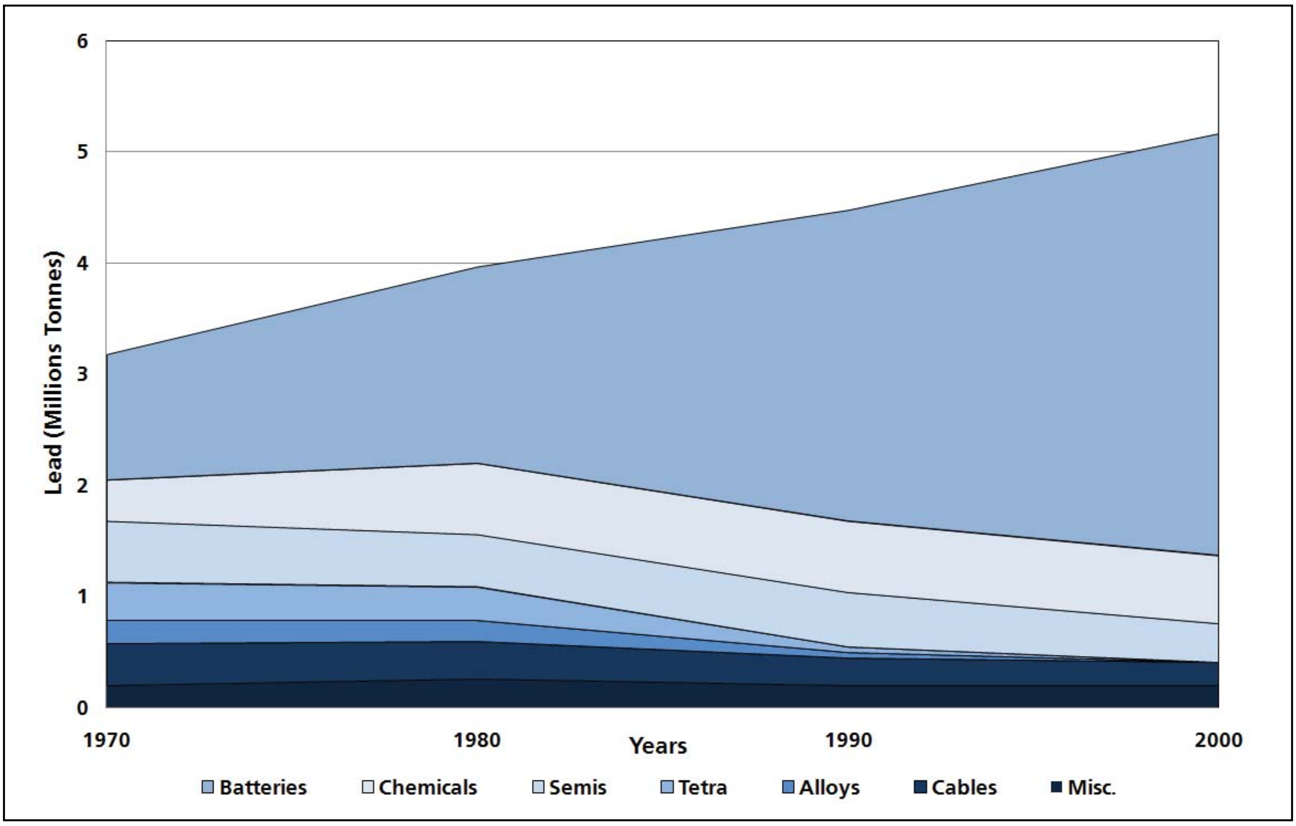

Figure 1 Recent and expected development of lead consumption in the Western world by end uses.

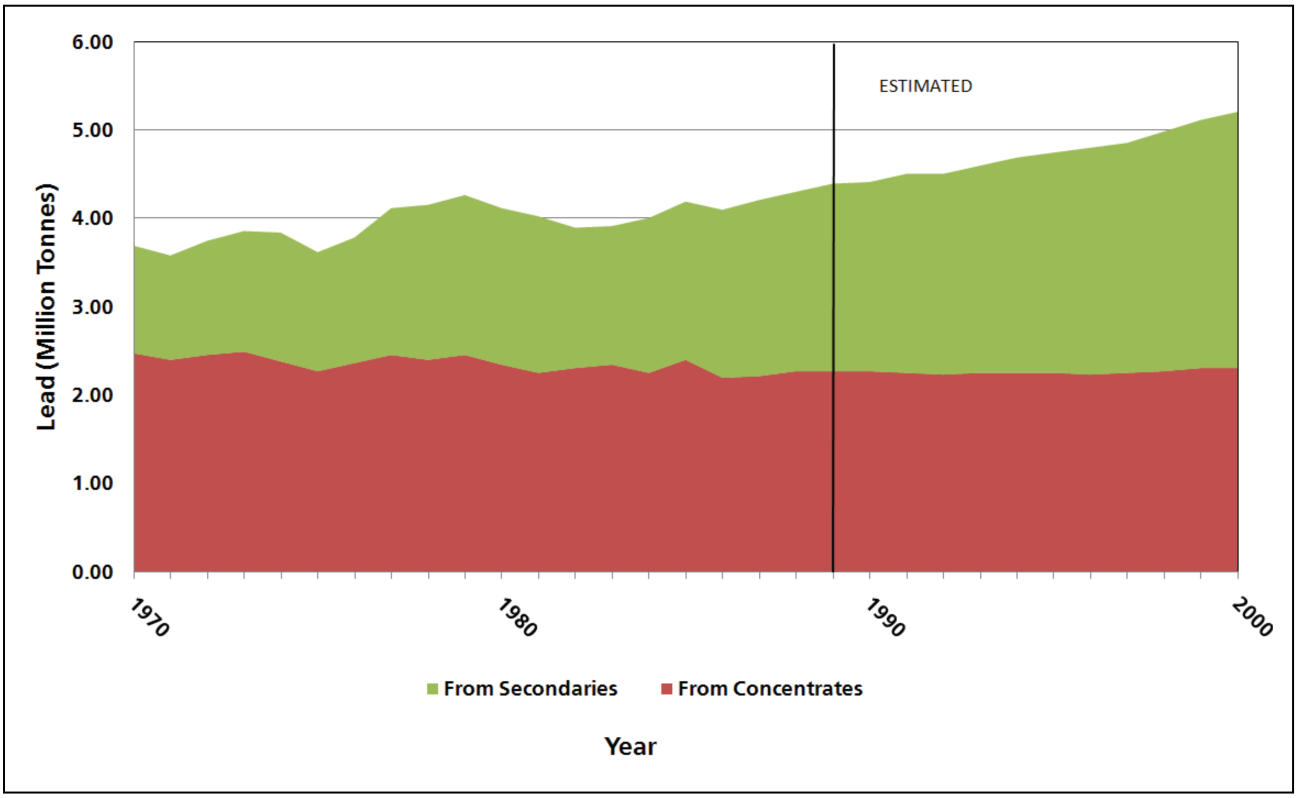

Figure 2 **Development of lead production from primary and secondary raw material sources**

In this decade there is a belief that secondary-lead production will have to increase by over 200 000 tonnes per annum, both in Europe and in the USA, because of continued growth in the generation of battery scrap and because governments are committed to increasing battery recycling rates to as close to 100% as possible.

In Europe and the USA, which together account for 75% of world secondary lead output, many producers are currently making operating losses due to low end prices. In addition, smelters are facing a rise in costs because of ever increasing environmental imposts. Additional costs could cause the closure of plants producing 200 000 tonnes per annum in the USA. A similar amount in Europe is vulnerable. The most vulnerable operation are small-to-medium sized plants, owned either by independent companies or by companies with no other lead interests. While smaller operations face problems, large greenfield secondary smelters are competitive. Upgrading larger operations and major expansions should also enable competitiveness to be maintained.

The initial objectives set up for the BRM project at its commencement in May 1989 were twofold: (i) to identify any opportunities in the lead business that would complement BRM's existing lead-refining business, and (ii) to identify opportunities to strengthen the economy and competitive position of BRM's existing lead-recycling business in the UK.

A broad spectrum of lead-based businesses were screened for industry attractiveness and financial returns. Expanded lead-recycling emerged as an attractive proposition. The installation of the CX battery breaking and paste desulfurization system, together with Lead Isasmelt, conforms with BRM's aims to be technically advanced and competitive by world standards. Further, approval for the project was based on the increasing need to demonstrate a commitment to improving the workplace and community environment.

Initially, BRM would invest £22.5 million in creating a £20-30 million per annum lead-recycling plant. This would exploit the advantages of the BRM site and Isasmelt technology and would also acquire the recycling business of Chloride Metals Limited.

Reasons for selection of technology

Based on an operating experience of the existing rotary-furnace-based plant and an awareness of the pressures facing the secondary-lead industry, a number of key areas were identified, where any new selected process had to offer improvements.

These were:

1) minimise sulphur emissions to atmosphere;
2) eliminate soda addition and produce a discard slag that met the TCLP leach test;
3) minimise low-level emissions of lead, through effective containment of lead oxide and paste during storage and handling and

4) select a process with low operating costs.

After careful consideration of the alternative technologies, BEM chose a process route based on the following principal process steps:

1) mechanical battery breaking and separation using the Engitec CX process for paste desulfurization;
2) Isasmelt to treat paste and grid metal to produce soft lead, antimonial alloy and an environmentally-acceptable discard slag; and
3) pyrometallurgical refining for final processing to alloys.

The capital costs of upgrading to CX type systems are more than twice that of less extensive changes to a conventional plant, but other savings offset the additional capital costs, particularly for larger plants. The cost of operating and slag-dumping are lower. Furthermore, there could be revenue from by-product sodium sulfate.

The CX System was developed by Engitec Impianti S.P.A., Milan, Italy. The Isasmelt technology was developed by Mount Isa Mines Limited, Australia, in association with CSIRO. The process was originally developed for the treatment of lead concentrates and the technology has now been extended to the treatment of copper and nickel concentrated and to battery-past smelting.

The innovative feature of the Isasmelt technology is the submerged top entry lance, inside of which are helical vanes to impart a swirling motion to the process gas stream. This design causes an increased rate of heat transfer from the lance to the process gas, as well as the formation of a frozen slag layer on the outer surface of the lance. This slag coating protects the lance so that it can be immersed in the bath for extended periods without excessive wear.

Submerged gas injection via the special lance provides an alternative to tuyeres in metallurgical processes. This technique greatly simplifies vessel design and eliminates refractory problems that are associated with tuyeres.

Process description

Materials' handling

The materials' handing system has been designed to minimise spillages around the plant. Deliveries of fluxes and reductant are discharged into covered storage bays from where they are moved to feed hoppers by a front-end loader. Subsequent transfer to the furnace is via a computer-controlled conveyer system with a local exhaust ventilation to all transfer points.

Battery storage

Incoming deliveries of batteries are discharged into a bay area after a thorough physical inspection. The batteries are stored ready for charging to the feed hopper that supplies the hammer mill. Acid drained from the batteries is collected in a sump at the rear of the bay; it is filtered and pumped to storage.

Battery breaking

Battery breaking technology is based on the Engitec CX process. The CX plant is designed to treat 16 tonnes per hour of scrap batteries. The hammer mill reduces the feed size to a maximum of 50 mm and deposits it onto a vibrating washing screen.

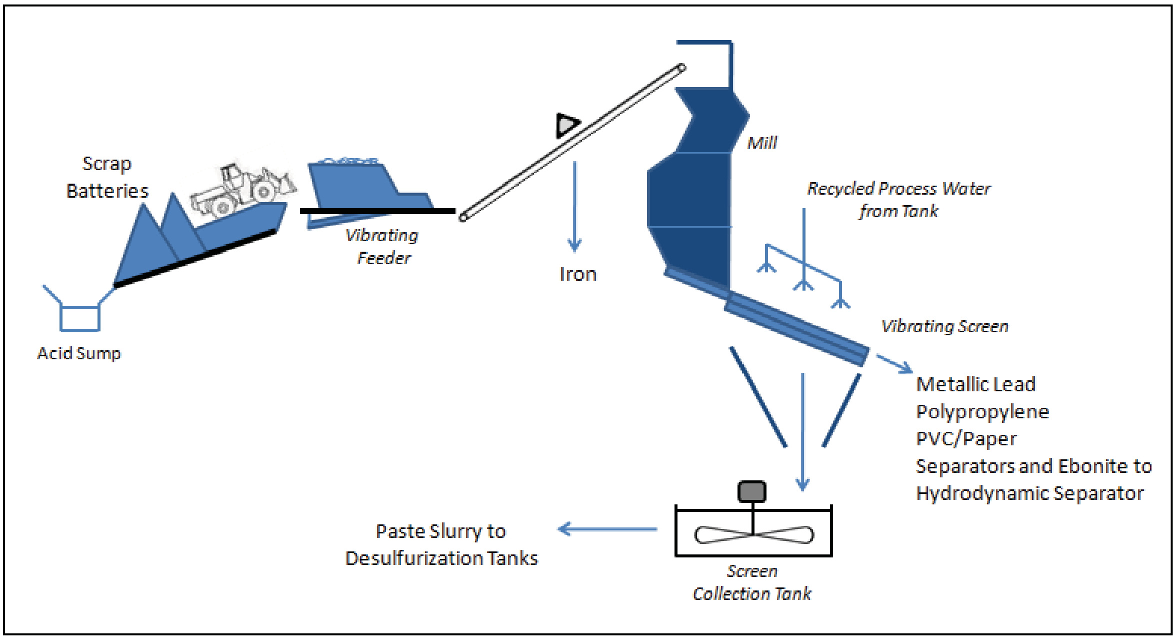

Figure 3 Battery crushing and screenings

The latter has a 0.8 mm mesh aperture that allows the fine lead paste to pass through and be collected in a stirred tank prior to desulfurization. Overside from the screen is fed to a hydrodynamic classification system that separates the component part, namely: polypropylene, metallic grids and poles, ebonite, and separator (see Figs. 3, 4).

Paste desulfurization

The paste slurry that contains lead oxide and lead sulfate is partially dewatered and pumped into the reaction vessels with collected battery acid and liquid caustic soda.

During this operation the following reactions take place:

$$H_2SO_4+2NaOH \rightarrow Na_2SO_4+2H_2O \qquad (1)$$

$$PbSO_4+2NaOH \rightarrow Na_2SO_4+PbO+H_2O \qquad (2)$$

Lead oxide is maintained in suspension and, upon completion of the reaction, is pumped to a pressure filter. The filter cake is washed before discharge (to reduce the sodium sulfate content) and then conveyed to storage ready for smelting. The sodium sulfate solution is further filtered and pumped to storage prior to further treatment in the effluent plant (Fig. 5).

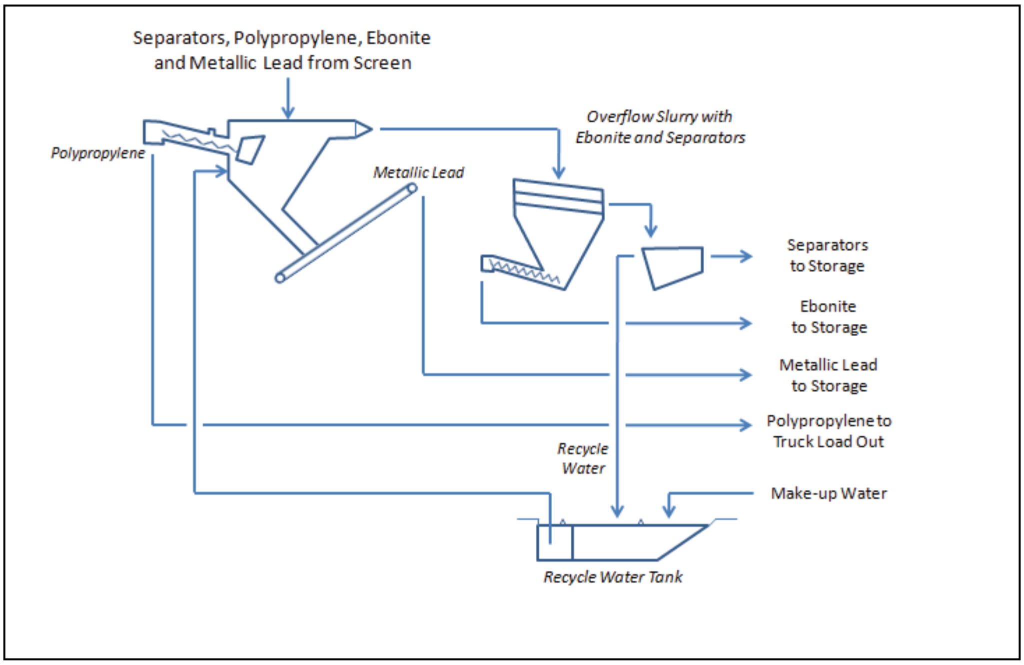

Figure 4 Hydrodynamic separation system

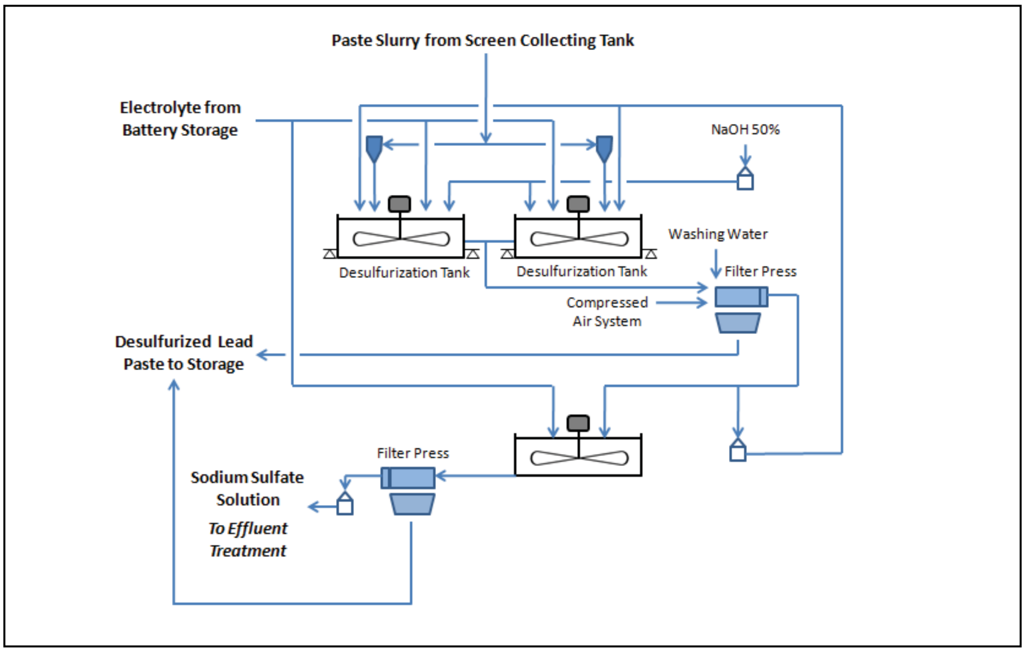

Figure 5 Paste desulfurization

Effluent-treatment plant

The effluent treatment plant has been designed to treat up to a maximum of 200 m^3 per day of raw effluent from the CX plant. The raw effluent is pumped into the reception tank of the Exxflow unit. By careful control of the pH and pumping through a series of fabric membrane, the treated effluent meets quality standards of both current and pending legislation. The treated effluent is then pumped into storage prior to discharge (see Table 1 for discharge limits).

TABLE 1

Maximum allowable effluent discharge limits

pH value	6.0 to 9.0
Volume of discharge (m^3/day)	200 m^3/day
Biochemical oxygen demand 10mg/l in 5 days at 20°C	
Dissolved antimony (mg/l)	5
Dissolved lead (mg/l)	1
Dissolved zinc (mg/l)	1
Dissolved arsenic (mg/l)	0.2
Dissolved silver (mg/l)	0.1
Dissolved copper (mg/l)	0.1
Dissolved nickel (mg/l)	0.1
Dissolved cadmium (mg/l)	0.05
Dissolved mercury (mg/l)	0.05

The Isasmelt furnace

The Isasmelt furnace consists of a refractory-lined cylindrical vessel (1.8m internal diameter) and is designed to produce 35 000 tonnes per annum of bullion (Fig. 6).

Desulfurized paste from the CX plant, together with reductant, is continuously fed into a bath of molten battery paste. The submerged combustion lance agitates the bath and produces a soft bullion that is intermittently tapped into a launder and pot system. At the end of each complete cycle, the furnace slag is conditioned and reduced to produce a high-antimony bullion and a discard slag [2]. The compositions of the furnace feed materials and the resulting products are given in Tables 2 and 3, respectively.

TABLE 2

Composition of furnace feed materials

Material	Battery Paste	Grid metal	Flue dust
Pb (wt.%)	66.20	90.8	60.00
Sb (wt.%)	0.45	2.5	2.00
S (wt.%)	1.00		

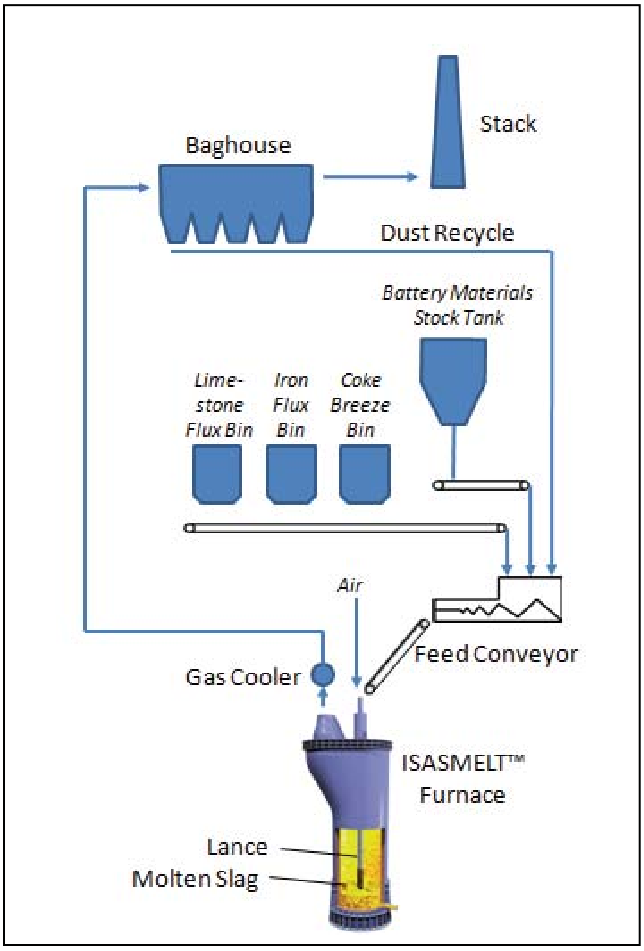

Figure 6 Schematic illustration of the Isasmelt plant

TABLE 3

Composition of products

Material	Soft Lead	Hard Lead	Slag	Flue Dust
Pb (wt.%)	99.8	79.2	0.5	60.0
Sb (wt.%)	<0.1	20.6		2.0
Cu (wt.%)	0.1	0.1		
FeO (wt.%)			50.0	
SiO_2 (wt.%)			25.0	
CaO (wt.%)			15.0	

The process is operated on a semicontinuous basis. When smelting paste, soft lead is tapped every 3 h. This allows slag to accumulate in the furnace. Antimony oxide becomes concentrated in the slag so that the metal tapped is relatively low in antimony. When about 250 tonnes of material has been charged, metal is again tapped and additions of lime and iron are made to give the required final slag composition. Similar procedures are adopted for grid metal smelting.

The reduction stage to produce the final slag is then commenced. Coal is added through the charge port and the oil flow on the lance is increased to raise a slag temperature in the final stages to between 1150 and 1250 °C. A ferrosilicate slag is produced with a low content of lead. The furnace is then tapped for metal and discard slag. The operational parameters of the furnace are summarised in Table 4.

The flow sheet for the smelting past and grid metal is shown in Figs. 6 and 7. This shows the two stages of smelting in which soft lead is tapped at intervals to allow antimony to accumulate in the slag, and then is reduced to produce a hard lead and low lead discard slag.

TABLE 4

Details of Isasmelt furnace operation

Operation parameter	Smelting		Reduction
	Paste	Grid metal	
Bath temperature (°C)	800-900	800-900	1200-1250
Feed rate (t/h)	10	18	
Air flow (N m^3/s)	1.4	0.9	2.1
Oil flow (kg/h)	500	390	570
Coal rate (t/h)	0.5.		0.5

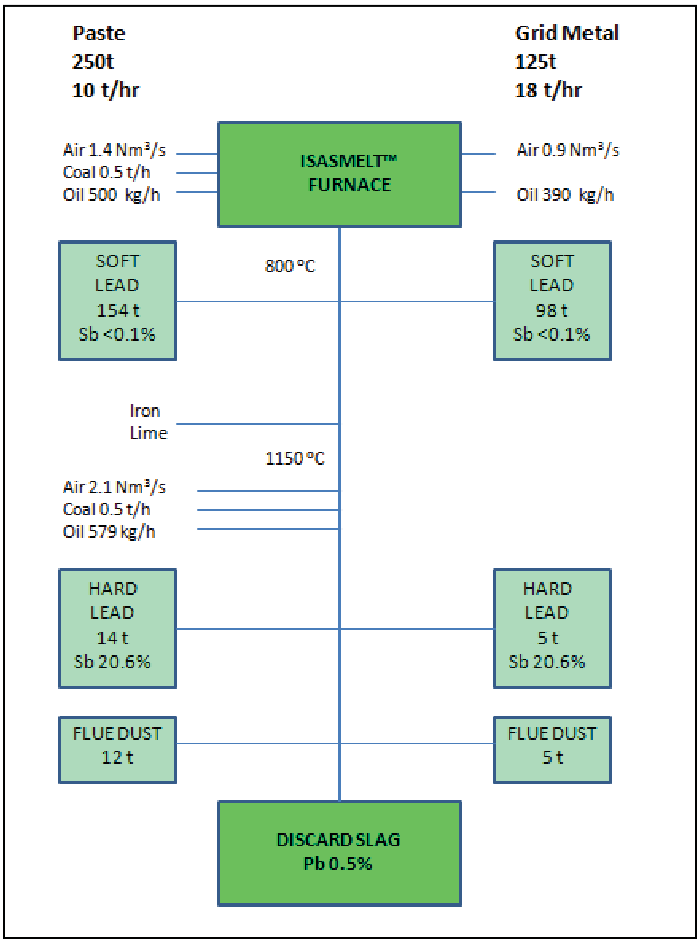

Figure 7 Flowsheet of Isasmelt process

Antimony distribution

The antimony distribution between the slag and lead metal is dependent upon the oxygen potential of the system or, in practical terms, upon the lead content of the slag. Thus: (i) under oxidizing conditions, i.e., high lead in the slag, the antimony is mainly in the oxide form Sb_2O_3 and therefore goes preferentially to the slag, and (ii) under reducing conditions, i.e., low lead in slag, the antimony is reduced to metallic form and dissolves in the lead.

During soft-lead production, oxidizing conditions are maintain, and results indicate that soft lead (<0.1wt.%Sb) will be produced down to 40to 50wt.% Pb in slag. This gives 10wt.% Sb in the slag generated per 200 tonnes cycle.

Slag reduction/hard lead production

During the soft-lead stage, the lead in slag is gradually reduced from 90% down to between 40 and 50% as the paste residuals and coal ash concentrate in the slag. As discussed above, this will be the limit of soft-lead production, and a full reduction and final slag stripping is required to produce a discard slag.

Final stripping of the slag to produce a low-lead discard slag will not be a problem as it is a batch process and, therefore, the reduction and fuming times can be extended. There is, however, one aspect of the reduction that requires special attention, namely fluxing/temperature control. As the lead is reduced, iron and lime are required to flux the slag. Optimum flux targets will require some plant testwork. As the lead contents drop, higher temperatures will be necessary to maintain slag fluidity, as discussed below.

Furnace Temperature

The furnace-operating temperature is dependent upon the lead in slag: low lead contents require high temperatures to maintain slag fluidity. There temperatures will also depend upon the soda content.

The upper operating temperature is limited in order to:

- enable the taphole to be closed on slag
- maintain a protective slag coating
- minimize fuel consumption

The lower operating temperature is limited in order to:

- prevent furnace accretions
- maintain slag with sufficient fluidity for high heat and mass transfer rates and for rapid settling of lead prills

During normal operations, the temperature is varied between 800 and 1200 °C. The temperature depends on the stage in the operating cycle.

Process-gas treatment

Process gad from the Isasmelt furnace is first rapidly cooled from 1000 to 450 °C by air-atomised water sprays in the furnace off-take. The gas can be further cooled by air admixture in the gas cooler, if required. The cooled gas is filtered in a baghouse that is fitted with 504 Goretex coated fibreglass bags to remove the dust and fume.

Isasmelt baghouse capacity is 80 000 N m^3 per hour of process gas. Filtration efficiency is 99.98%. The cleaned gas is discharged from a 90-m tall chimney.

The original intention to recycle the baghouse fume to the Isasmelt feed preparation system did not succeed due to the unsuitability of conveying equipment. A revised scheme to pug the fume with water and add to the Isasmelt past feed is currently being designed.

Kettle Floor

The kettle floor consists of 2X120-tonne hemispherical steel kettles each with an integral hood, mixer and dedrossing unit. Firing is by a tangential burner beneath each kettle. The burner runs on landfill gas.

Traditional refining techniques are used to produce a range of alloys to meet the specific requirements of customers. A dedicated filter unit provides ventilation during refining operations.

Moulding

The moulding machine is of the in-line design and can cast up to 23 tonnes per hour of finished product. The simple design allows for low manning and reduced maintenance requirements. Each 25 kg ingot is automatically stamped with a bath number then stacked and banded in 1 tonne bundles ready for final inspection prior to shipment.

Plant commissioning

The Isasmelt furnace was commissioned in June 1991 and temporarily fed lead oxide paste produced at the Britannia Recycling Limited operation, Wakefield, UK, until the CX plant came on line in September 1991.

CX plant

Basically, this is a well-engineered plant, capable of achieving production targets. There were problems that needed to be solved with equipment items such as pump-shaft seals, the operators' computer interface with the plant PLC control system, handling of polypropylene chips and separator fibre build-up on the recirculation water collection tank. Such problems have been largely addressed, or solutions have been developed that are awaiting resources to be installed.

The plant is capable of operating at a battery-breaking design rate of 16 tonnes per hour. Current availability is about 80% on a normal operating day, but averages 60% on a monthly basis. At present, the major reasons for lost time centre on the following:

- filter press paste collection, i.e., collection screw reliability
- paste-cake storage bin feeder restrictions
- pump-shaft seals
- effluent treatment plant capacity and operator control
- various control valves, electrical solenoids, limit switches, and tank level measurement probes
- reliability of the lubricating oil supply to the hammer-mill bearings

It is important to state that these problems are the collective responsibility of BRM, Engitec and other suppliers of specific items of equipment, and have been accepted as such. Non-familiarity with the process technology also caused a critical lack of spare parts for some pieces of equipment, which has now been remedied. Several hours of automation have also been unsatisfactory and are currently running in semi-auto or manual control mode. For example: the filler press cycle; neutralisation of effluent and the effluent treatment plant cycles and pH adjustment.

Effluent-treatment plant

An understanding of, and control over, the chemical reactions and pH of solutions at various stages of the effluent-treatment process took considerable time to develop. In the early stages of CX plant commissioning, considerable production delays were caused by the need to recycle effluent up to several times before it was within discharge limits. The addition of ferric sulfate, rigorous control over solution pH and rigorous control over the methodology for liquor sampling were necessary before this particular piece of plant was eliminated as a major bottleneck. Accurate and reproducible checking of pH control by plant operators was, and still is, a major factor in controlling this plant to obtain the consistent results achieved within the discharge consent limits.

Isasmelt furnace

The Isasmelt furnace has demonstrated that it is capable of achieving design capacity for both paste smelting and grid melting. Feed rates of up to 20 tonnes per hour of paste have been achieved on soft lead production. The soft lead process is extremely robust, and steady operation has been achieved.

Operator skills are steadily improving and all crews are capable of running the soft-lead and grid-melting stages with minimum supervision. More experience is required however, to successfully carry out slag reductions. Slag reduction to produce a final discard slag and achieve the full, five-stage, operating cycle as originally envisaged has still to be implemented. Averaged production rate and plant availability are not yet at the desired levels; current availability is 60%.

Until furnace operating hours have reached the desired level, soft-lead production will be maximised. This means that Isasmelt intermediate slag will continue to be recycled through the rotary furnace for final treatment. Lance tip lives of several days have been achieved, and it is expected that this will be extended. The major cause of lance failure is high-temperature excursions. A build-up of soda slag (the residue of paste desulfurization) also reduces the thickness of the protective slag coating on the lance and contributes to lower lance life.

Feed handling

Basically, the paste-feed system consists of a 200-tonne live bottom storage bin with an internal screw that delivers paste onto a series of standard conveyer belts.

Soon after start-up it was clear that handling non-free flowing and very sticky material such as wet-battery paste was a major problem. Belt cleaning, maintaining correct belt tracking, keeping tail and head drums clean and free running and transfer chutes clear of blockages all require a major effort on the part of the operators. Substantial redesign is required in the conveyor belt area to overcome all of these problems.

The live bottom Storall bin performed very well during the first six months of operation during which the past was not desulfurized. Delivery rates of 15 tonnes per hour were readily achievable. After paste desulfurization was introduced, the performance of the Storall decline markedly to about 5 to 7 tonnes per hour. The obvious change was a hard build-up of paste on the internal discharge screw so that, in effect, the screw resembled a solid shaft with little of the flights exposed. This build-up is exceptionally hard and a cementing reaction by residual sodium sulfate in the paste is thought to be the cause. Cake-washing tests in the filter press prior to release and experimentation with the Storall bin screw design and surface finish are currently in progress. Obviously, this problem has affected throughout of the Isasmelt furnace but is somewhat compensated by operating the rudimentary and temporary BRL paste-feed system in parallel. This means extra labour cost and lowers overall control of the plant.

Gas handling

The process-gas handling system is satisfactory when all operating parameters are functioning correctly, e.g., baghouse bag-cleaning system, cell isolation damper movements, inducted draught fan control, feed moisture content, flue-pressure measurement. Problems with any of these can cause reduced draught and the feed rate to the furnace must be reduced in order to maintain acceptable hygiene conditions.

Basically, the size of all of the baghouse devoted to the Isasmelt furnace is not large enough to cater for all that can go wrong in an operating place. This has been recognised and an extension of baghouse capacity is due to be commissioned in December 2002.

Plant Future

CX plant

The major mechanical items of plant that affect availability have been mentioned. In most cases, solutions have been identified and will continue to be implemented. It is expected that plant availability will be confidently at the 80% level by mid-1993. The effectiveness of paste washing to remove residual sodium sulfate will also be tested in the near future.

Other areas requiring longer-term investigation include the following:

- rapid wear on the rotating hammers of the breaking mill
- dealing with power-supply interruptions that result in bogging of the mixers in the paste-holding tanks
- dissolution of caustic dross (a by-product of the primary-lead refinery) to produce an essentially free supply of liquid caustic

Isasmelt furnace

Rates of paste smelting and grid melting for soft-lead production have been demonstrated to exceed production budget requirements. As with the CX plant, however m the availability must be further improved, to this end, the feed-handling and process-gas handling systems need to be modified and/or expanded. Both of these issues are currently being redressed.

In addition, longer-term strategies are being developed to overcome soda slag build-up in the Isasmelt furnace and the production of the final discard slag. With respect to the build-up of soda slag on the bath and consequent lance attack, two approaches to control are being investigated, namely:

effective washing of the sodium sulfate from the filter press paste cake, and

any residual soda slag in the furnace may have to be treated through a separate higher level furnace taphole for periodic removal; such a taphole eliminates the need to drain the entire bath through the normal taphole in order to remove the soda slag.

In respect of production to final discard slag, there are two basic types of slag reduction procedures that have been investigated on a pilot scale since November 1991. The first type is the semicontinuous treatment of slag as it is produced at the end of the soft-lead production cycle (as wet out in the original operating concept). The slag will need to be cluxed with millscale (iron oxide), limestone and silica to produce a slag composition, at the end of reduction, that has a melting point between 1200 and 1250 °C and a viscosity that is sufficiently low to enable tapping from the vessel.

The main problem experienced with the reduction of high-lead slag (i.e., above 50wt.% Pb) is that such a slag has a propensity to foam, especially at the start of reduction. The other difficulties with the semicontinuous treatment of high lead slags are:

- the additions of fluxes are made to an estimated weight of slag in the furnace; this can lead to frequent additions with a corresponding delay for slag analysis
- there is a need to run deep slag baths of high-lead slag to enable a lance to operate on the lower volume of discard slag
- the wear on bricks is expected to increase due to the frequent thermal cycling

Although there are solutions to some of these difficulties, on balance, the campaign basis retreatment of soft-lead slags after size reduction and analysis may be more attractive.

The slag treatment procedure is simply the charging of high-lead slag with fluxes and reductant to a low-lead (30wt.%) slag bath. The lead in slag is maintained at between 30 and 40% and metal is tapped periodically. When the depth of slag has reached a certain level, a batch reduction is performed and a hard metal and discard slag are tapped. If needed, the slag can be fumed to very low levels of lead i.e., 0.5wt.% PB. This procedure has been demonstrated many times in the pilot plant and once on the commercial scale. The discard slags so produced have passed the TCLP leach tests. The main attractions of this procedure are:

- minimal foaming of the lower –lead slags
- more control of flux additions – the weight and composition of slags in known before treatment
- frequency of plant dislocations for slag treatment is less by running campaigns of slag reduction
- less thermal cycling of the refractories

There are clearly time and fuel penalties in reheating slag, as well as more materials handling than in the semicontinuous procedure. The lack of slag foaming and simpler operations of the retreatment route, however, make it the currently favoured process option.

Conclusions

The major aspects of commissioning, performance to data and future activities of the Isasmelt process have been discussed. As is usual where new technology is being advance, changes would have been made given the benefit of hindsight. Fortunately, the fundamentals of this new technology for secondary-lead operation r sound in both process and engineering. By mid-1993, it is confidently expected that both lead alloy output and the cost of production will be within forecast.

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