FURTHER APPLICATIONS OF THE BOTTOM BLOWN OXYGEN CONVERTER

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Abstract

The BBOC was developed by Britannia Refined Metals Ltd. for the cupellation of silver-lead bullion produced in the Parkes Process. A production scale furnace was installed in 1986 and has operated successfully since that time producing some 400 tonnes per annum of silver. The process depends upon the injection of oxygen at the bottom of the furnace through a nitrogen-shrouded consumable lance. This principle has resulted in a number of advantages over the old reverberatory type cupellation furnace.

Several other applications have been identified for this lance system and test work has been conducted on a pilot scale to obtain process data. One particularly attractive application is in the pyro refining of precious metal doré produced from copper refinery slimes. In test work on a 250 Kg furnace, selenide matte produced from slimes smelting was refined using sodium carbonate flux. The test results are summarised and the requirements for a production scale plant are discussed. Work has also been carried out to evaluate the lance system in a higher temperature application for the refining of black copper. Other applications investigated include electrolytic lead refinery slimes processing and softening of lead bullion. Work is also projected on the injection of hydrocarbon gases to provide reducing conditions and submerged combustion heating of the melt.

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Introduction

Work began at Britannia Refined Metals Ltd. (BRM) in the early 80's to find a more effective way of cupelling lead-silver bullion produced in the Parkes Process. The classical reverberatory-type cupel in use at BRM at that time suffered from a number of disadvantages mainly resulting from the fundamentally poor thermal efficiency coupled with low oxygen utilisation efficiency. These in turn lead to long process times, excessive fuel consumption, high precious metal inventory and relatively high process gas volumes.

One area investigated was the use of oxygen and oxygen-enriched air in the cupel. Enrichment of the air blast supplied to the surface of the melt was found to be of marginal benefit and was not economically viable. In order to improve gas/metal contacting a series of submerged lance designs were tested in the cupel furnace. Although some improvements were indicated, the wear rate of lance materials was excessive and also it became evident that the basic design of the furnace, having a shallow bath with large surface area, was unsuited for the development of a high intensity reactor.

Subsequently experiments were carried out using submerged injection of oxygen into a deep bath furnace. Initial pilot plant work was carried out on a 1.5 tonne capacity tilting furnace. The original concept of a fixed tuyere device eventually gave way to the development of a consumable lance system. Fig 1 shows the principal of operation of the lance. The lance consists of two concentric stainless steel tubes with

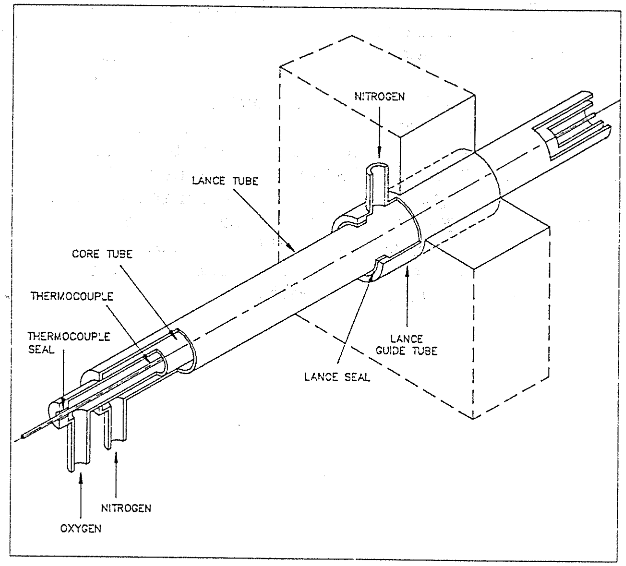

Figure 1 - BBOC Lance System

a small annular gap between them. Commercially pure oxygen is passed through the central tube and cooling nitrogen through the annulus. The lance passes through a third tube which is fixed through the refractory wall of the furnace with its own supply of nitrogen for sealing the lance. Wear of the tip is sensed by a fixed thermocouple passing down the centre of the lance and this causes it to be advanced to compensate for wear. The operation of the 3 tonne production unit, which has been in use at Britannia since 1986 for cupellation of lead-silver, bullion has been described previously (1)(2).

In view of the many advantages of this system over the conventional cupellation process, discussions were initiated with other companies employing oxidative refining technology to explore other possible applications of the lance technology.

Features of the BBOC Process

The injection of oxygen directly into the base of the furnace, away from the refractory, means that the region of high reaction rate is projected into the centre of the metal bath. Oxygen efficiencies of around 100% are achievable using this system which also provides vigorous mixing of the bath as a result of the nitrogen flow. By conducting the oxidation in a small, intensive reactor, with very little cooling by nitrogen, effective use is made of the exothermic heat of reaction and in many cases the process becomes thermally autogenous during much of the refining cycle. Reaction rates per unit of furnace volume have been found to be 10-20 times greater than the conventional reverberatory cupel.

Fig 2 shows the operating sequence of the BBOC. Solid charge is added by overhead hoist with the furnace in an upright position or alternatively liquid charging may be used. Melting takes place in the forward tilted position following which the furnace is tilted back into the blowing position. Periodically slag is removed by tilting the furnace forward and if necessary further solid charge may be added. On completion of refining the doré metal is cast directly to moulds. The lance may be replaced at any time during the cycle by tilting the furnace into the forward position.

Oxygen efficiency is maximised by the submerged injection system and is not influenced by the presence of surface slag layers. This is a major advantage over top blown furnaces, (which require oxygen penetration through the slag layer) and in turn this has been shown to give reproducible results in terms of the progress of refining against quantity of oxygen injected. Process control and in particular end point determination is thus facilitated.

In metal refining applications, the ability to accumulate a thick layer of slag is beneficial in that it facilitates the removal of slag with the minimum of metal entrainment. For example in the cupellation process at BRM, the change to the BBOC from the old reverberatory type cupel, reduced silver in slag by approx. 50%.

Refractory wear in the BBOC is mainly confined to the slag line where litharge attack is greatest. An ongoing programme of refractory investigations has been carried out since the process began operation and lining life has been progressively improved. Currently up to four months operation is possible using dry jointed refractories of fused grain direct bonded magnesite-chrome. The slag line is water-jacketed using a simple jacket external to the furnace shell. Further trials are planned using a refractory of ultra-low silica content which is believed will minimise litharge attack.

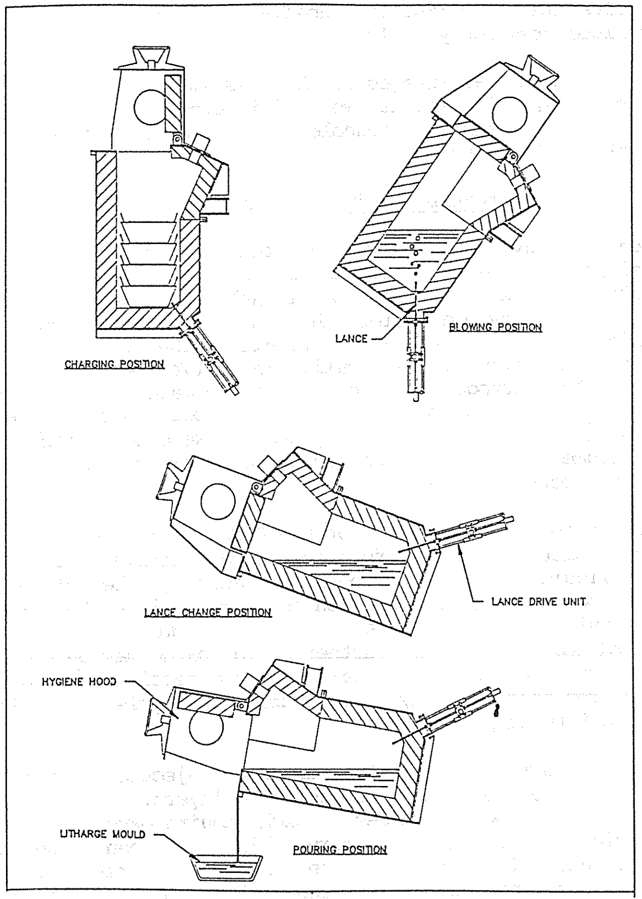

Figure 2 - BBOC Operating Positions

The use of a top blown rotary converter (TBRC) for the cupellation of lead-doré bullion at Rand Refinery Ltd. has been described recently (3). Here it has been necessary to limit the extent of refining to about 12% PM's in order to avoid refractory problems due to litharge attack at elevated temperatures and difficulties in control of the operation as the end-point is approached. These problems are not observed in the BBOC which is used at BRM to achieve a purity of

greater than 99% silver prior to further refining treatment in another furnace. If the bath temperature is too low in the final stages it is possible to freeze metal on the lance but this is readily remelted by tilting into a holding position.

Black Copper

The smelting of copper scrap in a blast furnace results in the production of an impure bullion known as 'Black Copper' which typically contains about 80% copper with varying amounts of iron, zinc, tin, lead and nickel. Traditionally this metal is refined to anode grade copper by air blowing in a converter followed by final refining and deoxidation in an anode furnace.

One proposal for increasing the intensity of both the smelting and refining processes is the use of the TBRC. The BBOC offers an alternative method of introducing oxygen for the refining process. In order to evaluate the performance of the bottom blown system in this more demanding environment, a testwork programme was carried out at Warren Spring Laboratory (WSL) which at the same time compared the top and bottom blown systems directly using the same basic furnace arrangement. Results of this work have been presented (4) and are briefly summarised below.

In total, seven bottom blown and six top blown tests were conducted in which the mode of operation was basically as follows:

- Charge between 200-250Kg of black copper with flux
- Melt and sample the metal bath
- Blow with oxygen once a temperature of 110-1150°C had been reached using the burner to provide ancillary heat when necessary.
- Remove the first slag (iron-based)
- Add more flux
- Blow with oxygen to remove the remainder of the tin and lead.
- Pour the furnace contents (1250-1350°C), cool, separate slag and metal
- Analyse products

Two different batches of black copper were used for the tests. These had the following composition:

	BATCH 2	BATCH 3
Cu	82%	78%
Fe	3.1%	5.2%
Zn	2.7%	3.4%
Sn	3.5%	4.4%
Pb	3.7%	3.8%
Ni	4.7%	4.3%

As anticipated, the melting time in the top blown tests was shorter as a result of the improved heat distribution resulting from rotation of the furnace. About 50% extra melting time was required in the bottom blown furnace.

It was found that in the bottom blowing tests, oxygen flowrates had to be limited to 100-150 $Nl.min.^{-1}$ to avoid excessive splashing. This limitation is due both to the small furnace size and the fact that the same lance size was used as on the 3 tonne production BBOC.

During the initial iron blow, in which the iron was reduced to about 0.5% using a silica flux, the maximum rate of exothermic heating is obtained and the bath temperature increased rapidly to about 1300°C. After removal of this slag blowing was continued with more flux for tin and lead removal.

One of the main conclusions of these tests was that the bottom blowing technique was at least 3 times as efficient in the use of oxygen. Comparison of the data for top and bottom blowing tests in which a copper grade of approx. 98% was achieved in each case (Test 4 in each case) illustrates this clearly (Table I). The charge weight in each case was 250 Kg.

Table I

	Time of Iron Blow Mins.	O2 flowrate $Nl.min.^{-1}$ Mins.	Time of 2nd Blow Mins.	O2 flowrate 2nd blow Mins.	O2 Passed Nl./100Kg.
Bottom Blown	8	75	29.5	150	2000
Top Blown	12.5	275	50	275	6875

Copper Refinery Slimes

The slimes produced in copper electrorefining vary widely in composition from one plant to another. In general they will contain the impurities which are insoluble in the electrolyte, particularly the precious metals, selenium and tellurium together with others such as arsenic, antimony and lead which are anodically dissolved and subsequently precipitated from solution. In addition there is likely to be refractory material originating from any mould wash adhering to the anodes. The chemical compounds likely to be present in slimes are numerous and complex but in general the silver is largely combined with selenium and tellurium as Ag_2Se and Ag_2Te, lead is present as $PbSO_4$ and arsenic and antimony exist in complex oxide form. Copper may be present not only in metallic form but also as selenide, telluride, sulphide and other compounds.

Due to the large compositional variations in slimes produced at different refineries, processing flowsheets in use are also varied and have been adapted to suit the particular requirements. The first step is normally the removal of copper by sulphuric acid leach with air sparging.

The classical system for pyrometallurgical processing of the leached slimes consists of smelting to a bullion or matte followed by oxidative refining to product doré bullion suitable for electrorefining. The selenium may be recovered by roasting prior to smelting or alternatively it may be removed by fuming or slagging during the refining process.

Reverberatory-type doré furnaces have traditionally been used for this smelting and refining duty but their well-known disadvantages have led to their replacement in a number of plants by other more efficient processes. One factor which is nowadays of paramount importance is the precious metals inventory held up in process. Large doré furnaces can hold up many tonnes of precious metals, the financing costs for which make up one of the most significant operating costs. Diversions of precious metals into slag and fume requiring recycling also add to the overall lockup.

Small, intensive reactors are capable of rapidly processing smaller batch quantities with a consequent reduction of inventory levels and with significant reduction in gas cleaning volumes. At present, most of this process intensification has centred on the top blown rotary furnace (TBRC) which is capable of combining the smelting and refining duties. For the oxidative refining of the bullion phase the bottom blown system has been shown to be more attractive in that a higher oxygen efficiency is obtained, better process control is possible and other operational advantages are obtained.

At ASARCO's Amarillo copper refinery, slimes produced are high in silver and selenium After leaching for copper removal followed by filtration, the filter cake is smelted with fluxes in a short rotary furnace. The products are a recycle slag and a matte phase consisting predominately of silver selenide. A fume of high selenium content is also produced which is processed for selenium recovery.

Processing of the matte, which contains approx. 60% Ag, 20% Se and 6% Te with 8% Cu and less than 1.5% Pb and Sb, is carried out in doré furnaces of about 15 tonnes capacity. Lancing using oxygen-enriched air with a soda ash flux is used for the removal of selenium and tellurium into the slag. The final stage of the cycle involves removal of copper to the required level of about 0.5% by further oxidation using nitre as a reagent. A typical refining cycle in this furnace is of the order of 7-10 days with a final doré production of 8 tonnes.

The use of the BBOC for this refining duty offered the possibility of replacing the doré furnaces with a single unit in order to give a reduction in inventory level and other operational benefits. In order to obtain performance data for such a system the BBOC pilot installation at Warren Spring Laboratory in the UK was used to run a series of tests on the Amarillo matte. This furnace has a working volume of about 25l and is equipped with an oxy-gas burner and a bottom lance system. A more detailed description of the pilot plant has been given (4).

The main chemical reactions taking place involve the oxidation of silver selenide and telluride and their reaction with the soda ash flux.

$$Ag_2Se + O_2 \rightarrow 2Ag + SeO_2 \quad (1)$$
$$Na_2CO_3 \rightarrow Na_2O + CO_2 \quad (2)$$
$$SeO_2 + Na_2O \rightarrow Na_2SeO_3 \quad (3)$$

Similar reactions are involved in the conversion of Ag_2Te to Na_2TeO_3 and Ag. The standard procedure involves the injection of oxygen-enriched air into the bath using blowing pipes of special colbalt-based alloy. A layer of soda slag on the furnace helps to capture the SeO_2 but volatilisation is so rapid initially that much of it passes to the gas cleaning system. Tellurium oxidation increases later in the refining cycle but its lower volatility allows it to be more readily captured in the slag.

The testwork programme was aimed at achieving removal of impurities into a soda phase as in the current process but with a minimum of volatilisation of selenium. The tests were designed to provide an operating procedure suitable for refining the matte through to doré grade metal and to provide process and metallurgical data for the design of production scale plant.

The basic procedure adopted in all the tests was as follows:-

1. 250 Kg of matte was charged
2. The charge was melted using an oxy-fuel burner whilst feeding the lance with a flow of nitrogen
3. Soda ash flux was added and allowed to melt
4. The furnace was tilted into the blowing position and oxygen blown into the melt at a rate of up to 200 Nl.min.$^{-1}$
5. The slag was poured and more flux charged
6. Steps 3-5 were repeated until refining was complete.
7. The doré was cast out.

Metal samples were taken from the melt periodically after first stopping the blowing and tilting the furnace into the holding position.

Test Results

Charge melting was accomplished within 90-110 mins. using 260-275 Nl.min.$^{-1}$ natural gas and 380-455 Nl.min.$^{-1}$ of oxygen. A flux addition of 20-25 Kg of soda ash was made with the initial charge. The contents were completely fluid at a temperature of 900°C and the furnace was then tilted into the blowing position. It was found that an oxygen blowing rate much in excess of 200 Nl.min.$^{-1}$ gave rise to excessive splash and in subsequent testwork this was maintained as close as possible to 200 Nl.min.$^{-1}$. This is a phenomenon associated with the small scale and is not a limiting factor on large units.

The change in both silver and selenium contents with volume of oxygen passed is shown in Fig 3 in which the results of three separate tests are plotted. It can be seen that good reproducibility was obtained between tests although temperature control proved to be somewhat difficult due to the small furnace size and the high rates of heating and cooling. Temperatures were in general maintained between 1000°C and 1200°C during refining.

During the limited number of tests carried out it was not possible to optimise the flux additions and slag removal times so as to obtain the best separation of impurities. The selenium contents of the slags averaged 28.5% whilst the maximum value obtained averaged 38% over three tests. Selenium recovery in the doré furnace process is difficult to evaluate accurately and often involves large unaccounted losses. In the testwork, sampling of the off-gas showed very low fuming rates for selenium with a recovery into the slag of more than 90%. General visual observation of the off-gas above the furnace suggested that very little fume was produced. The lance operation during the tests was satisfactory and the wear rate was not excessive.

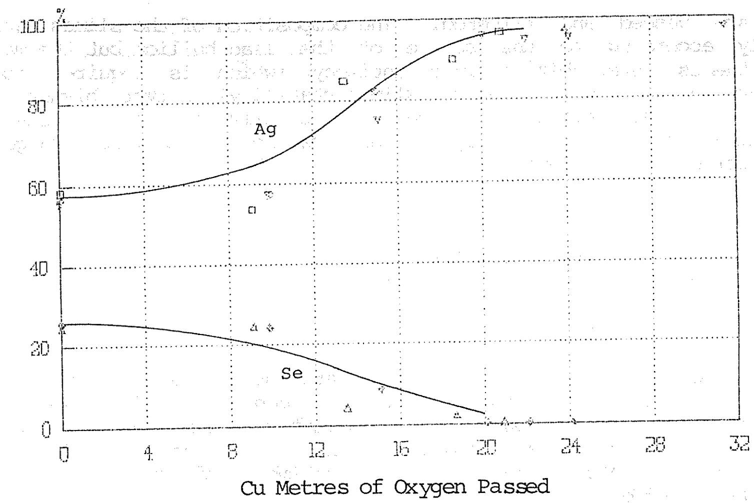

Figure 3 - Selenide Matte Refining

All the slags were fluid and were readily removed from the furnace. As was expected, the process chemistry was found to be essentially the same as in the existing process and copper removal below about 1.1% was not possible using only soda ash as flux. Sodium nitrate flux is commonly used for copper removal below this limit.

The test work indicated several areas where the BBOC has significant benefits compared to the conventional process. These include:

- Reduced flux consumption of approx. 80%.
- Higher Se content of slag.
- Reduced fuel consumption.
- Lower gas cleaning volume.
- Reduction in working inventory of at least 8 tonnes (Ag+Au)
- Improved process control.

It is estimated that a single 3 tonne nominal capacity BBOC will be capable of replacing the existing cupel furnaces. An 18 hour cycle is proposed in which 2 tonnes of doré would be produced.

Projected savings by the use of this technology are considerable and as a result of the favourable economic analysis ASARCO is proceeding with the installation of a BBOC for this application at Amarillo during 1991.

Lead Refinery Slimes

In the Betts electrolytic lead refining process, impure lead anodes are electrolysed in an aqueous solution of lead fluosilicate and fluosilicic acid. Pure lead is deposited at the lead cathodes whilst the more electropositive impurities remain insoluble and are retained on the anode in the form of a slimes. Periodically during electrolysis the anodes are removed and the slime mechanically cleaned after which they are washed and filtered. The composition of the slimes varies greatly according to the source of the lead bullion but the major constituents invariably include antimony (which is required to be present in the anode to control slimes stability), silver, bismuth and lead. Other elements which are normally present in smaller concentrations are gold, copper and arsenic. A typical range of composition is as follows:-

Sb	40 - 50%
Ag	3 - 12%
Bi	4 - 15%
Pb	10 - 25%
Au	100 - 300 g/t
Cu	1 - 4%
As	1 - 16%

As with copper slimes, lead slimes are processed in a number of different ways at different plants, but in general the first step is a smelting operation followed by the oxidative refining of the bullion produced. Only silver and gold remain unoxidised, the lead and bismuth being oxidised into a slag phase whilst antimony and arsenic are mainly volatilised and collected as fume.

The smelting process is relatively difficult due to the low bulk density of the slimes and the low thermal conductivity. Static reverberatory furnaces, short rotary furnaces or electric furnaces are used for smelting and the products are a high antimony slag phase and metal bullion.

The next stage of processing is the removal of antimony from the bullion. This may be carried out in either reverberatory or rotary furnaces either by lancing, in which case slag formation is favoured, or by surface blowing where the volatilised oxide tends to be entrained and is collected as fume.

The final stage consists of the cupellation of the remaining bullion to produce a doré which is later processed by electrorefining. The litharge slag produced is rich in bismuth and is normally smelted to produce a high bismuth metal feed to the bismuth recovery section. If the lead content is high it is sometimes economical to remove both a high lead followed by a high bismuth slag. During cupellation it is sometimes necessary to add extra lead to the charge to assist copper removal.

In order to investigate the effectiveness of the BBOC for antimony and arsenic removal a test was carried out in the 1.5 tonne pilot plant. Initially 1075 Kg of alloy containing 9.8% Sb, 0.85% As was charged and melted. At a temperature of 450°C, oxygen blowing at a rate of 360 $Nl.min.^{-1}$ was commenced. After injecting 26.3 Nm^3 oxygen, 250 Kg slag was skimmed and an additional 475 Kg alloy was charged. Blowing then continued at the same rate with periodic slag removal until antimony removal was complete. During the test the temperature increased to a maximum of 1050°C due to the heat of reaction. Very little fume generation was observed and results indicated a high recovery of Sb into the slag. The Sb and As contents of the bath are plotted against volume of oxygen injected in Fig 4. Slags were removed at the points indicated and their compositions are given in Table II.

Table II

	Sb %	As %	Pb %
Slag A	9.47	3.71	48.86
Slag B	25.91	1.13	57.87
Slag C	13.89	.35	74.49
Slag D	13.19	.09	84.13

The lance system operated well under these conditions with virtually no consumption at temperatures below 750°C. The calculated oxygen efficiency during the test was close to 100%.

The BBOC is capable of carrying out both the deantimonising and cupelling operations in a single furnace with a high antimony recovery into the slag and low off-gas volumes.

A 3 tonne BBOC furnace is to be installed at the Onsan plant of Korea Zinc Ltd. for slimes processing duties. Initially the furnace will be used in the cupellation of deantimonised bullion it is planned to extend the use eventually to include deantimonising also.

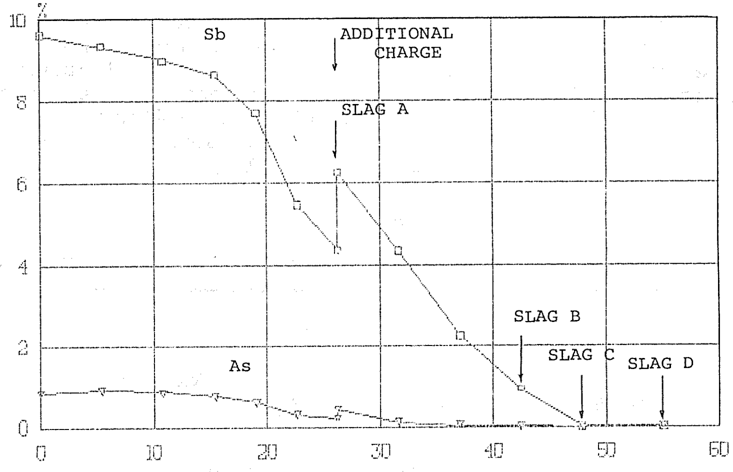

Figure 4 - Sb and As Removal in a 1.5 tonne BBOC

Future Developments

The use of the BBOC for smelting as well as refining offers the possibility of further reducing the precious metals inventory in slimes processing whilst at the same time minimising off-gas volumes and achieving substantial operating and capital cost savings. As in the doré furnace, it would be possible to charge slimes directly to the BBOC, where the turbulence created by the gas flow would assist the assimilation of the charge. The use of an oxy-fuel burner to replace the existing fuel-air burner would also be beneficial.

As a means of further improving the slimes smelting stage, test work is projected to replace the nitrogen flow in the lance shroud with a hydrocarbon fuel gas. It is anticipated that submerged combustion would allow efficient heat transfer to the charge of up to 25% of the total heat input, the remainder being provided by a fixed oxy-fuel burner. This system would allow the complete pyrometallurgical processing of the slimes to be carried out in a single intensive reactor capable of achieving the desired final purity level and allowing direct casting of the doré anodes.

Conclusion

Since its inception as a more efficient replacement for the conventional cupellation furnace, the BBOC has been shown to be capable of other oxidative refining applications. Bottom injection offers some inherent advantages over top jetting techniques, such as low fume production, high oxygen efficiency and good process control.

The BBOC lance system has now been successfully operated in a number of duties including the processing of Parkes crust, selenide matte, black copper and antimony/arsenic removal. The black copper work demonstrated the ability of the lance system to operate in severe operating environments up to 1350°C and achieve oxygen efficiencies three times that of the top blowing system.

The BBOC pilot plant processing of selenide matte from copper slimes has demonstrated the quick and effective refining of this material to a doré. The ability to develop a deep slag layer without hindering oxygen transport enables effective capture of volatile species in the slag. This can eliminate the need for costly fume scrubbing equipment to recover selenium. The BBOC technology will shortly be introduced to lead slimes processing at Korea Zinc's Onsan plant.

Acknowledgements

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