Operation of the bottom blown oxygen cupel at Britannia Refined Metals, Ltd.

K. R. Barrett
MIM Technology Marketing, Ltd., Northfleet, England

Synopsis

The cupellation of silver/lead bullion to recover precious metals is one of the oldest metallurgical processes known to man. In recent times this has been carried out in small reverberatory furnaces but the process suffers from a number of disadvantages. A new process has been developed at the Northfleet refinery of Britannia Refined Metals Ltd which gives much improved performance. The process depends upon the injection of oxygen through a nitrogen shrouded lance at the bottom of the furnace. The lance is consumable and of unique design. Reaction rates are high giving short process time, fuel consumption is low, oxygen efficiency is high and silver recirculation is low. The new process has resulted in substantially lower operation costs.

Introduction

The recovery of silver and gold from lead bullion is an important part of the lead refining process absorbing a major part of the total cost. Considerable work has been carried out at Britannia Refined Metals Ltd (BRM), to improve the efficiences of processes used (1). In the first stage silver is removed from the lead bullion by the Parkes Process. Zinc is added to the molten bullion contained in hemispherical steel kettles. A rich zinc/silver crust is formed which floats on the surface of the bath and is removed by a mechanical skimming machine. The rich crust contains excessive lead, which must be removed by pressing in Howard presses or by liquation. At Britannia Refined Metals Ltd the crust is liquated under a chloride flux cover to produce a rich silver/zinc alloy (triple alloy). The pressed crust or triple alloy is then retorted to recover zinc leaving a rich silver/lead bullion for recovery of silver. Pressed crust is usually retorted in Faber du Faur retorts but the triple alloy is retorted in electric furnaces under vacuum. At Britannia Refined Metals the Hoboken Vacuum Induction retort is used. The silver/lead bullion produced would typically contain 15% silver from pressed crust or 70% silver from liquated triple alloy. Both types of bullion can be effectively cupelled in the Bottom Blown Oxygen Cupel.

Cupellation

The final stage in the recovery of silver is the cupellation of the retort bullion. Cupellation is one of the oldest metallurgical processes known to man and records of its use to recover silver from silver/lead bullion go back to at least 500 B.C. The process is described by Agricola in De Re Metallica (A.D. 1613), was used and well known to the Romans and was described by Pliny(A.D.33). Cupellation depends upon on the selective oxidation of lead, when air is blown across the surface of the molten bullion allowing silver to concentrate in the bath.

In modern times cupellation has been carried out in reverberatory furnaces of up to 15-20 tonnes capacity. The furnaces are fired by oil or gas burners and air blown across the surface of the bath through tuyeres. The furnace can be tilted to allow litharge to flow out over the water cooled breast. Three furnaces of this type were used at BRM to produce up to 450 tonnes of silver per annum. The process suffers from a number of serious disadvantages.

On melting, an infusible zinc oxide rich dross is formed, which must be raked off and carries with it entrained silver rich bullion. This dross must be fed back to the furnace and fluxed with litharge but even so a viscous slag is produced carrying excessive silver.

In order to allow contact of the air with the bath it is necessary to run off the thin layer of litharge more or less continuously as it is formed. A skilled operator can minimise the amount of silver bullion run off with the litharge but even so the recirculation of silver is high at about 8%.

Fuel efficiency is low due to the need to maintain high excess air in the furnace atmosphere and heat transfer is poor. Process gas volume is high resulting in high gas handling costs and in excessive carry-over of precious metals in fume. Reaction rate is low due to poor contact between oxygen in the tuyere air and the lead in the bath. Precious metals in process is high due to the relatively high furnace volume. When fully charged the furnace silver inventory can be as high as 7000 kg. Interest charges on such stocks are substantial

Because of these disadvantages a research programme was undertaken at BRM to find a more effective way of cupelling silver lead bullion. A more intense reaction using oxygen rather than air was required and the available technology was reviewed. The Top Blown Rotary Converter (TBRC) was an obvious choice and the work of Volker Jung(2) and others was revived and test work commissioned.

Significant improvement in rate of reaction was achieved but acute refractory wear was experienced due to the washing action of the slag caused by rotation of the furnace. Oxygen utilisation was found to be low at 60% during the trial period. A further disadvantage was the inabilty to cast the silver produced directly into bars or anodes and the need to provide a holding furnace with the resulting added capital and operating costs from that.

The BRM research was therefore directed at the bottom blowing of oxygen in a non-rotating refractory lined furnace. Small scale tests were carried out at Imperial College and these showed such promise that a pilot plant was built at BRM to prove the process. After three years of development and pilot plant work a plant scale furnace was built and commissioned in Oct 1986. Patents have now been granted for the Bottom Blown Oxygen Cupel (BBOC).

The Bottom Blown Oxygen Cupel

The furnace at BRM is a refractory lined cylindrical furnace with a capacity of 3.0 tonnes and is hydraulically tilted. It is equipped with a charge door and hygiene hood at the top. The furnace is fired with a natural gas/air burner. A key feature of the furnace is the lance, designed by BRM engineers. The lance is nitrogen shrouded and located at the bottom of the furnace as illustrated in Fig 1. The lance is consumable and as wear takes place it is automatically advanced to maintain a constant position in relation to the furnace. This is achieved by means of a temperature sensing thermocouple at the tip of the lance. When the temperature reaches a predetermined point the lance is advanced by means of a small hydraulic motor. Due to the nitrogen shroud, the rate of consumption is low and one lance lasts for several charges. The lance drive assembly is shown in fig.2. The design of the furnace allows for tilting to the optimum positions for blowing and slag removal. For blowing, the furnace is tilted to position 'A' Fig 3, so that there is no washing of the furnace lining with slag. Oxygen is virtually totally absorbed and there is little turbulence of the surface of the charge. Slag removal, or casting silver, is carried out in the 'B' position, where slag pots or an ingot casting machine can be located. On the BRM furnace oxygen and nitrogen are stored in liquid tanks and fed directly to the furnace via evaporators. The use of oxygen in place of air results in substantially reduced process gas volume, reduced precious metal carry-over in fume and reduced gas handling costs. Due to the perfect contact between oxygen and the bath, the oxidation rate is very high and the lead in the charge is eliminated in three hours. The rate of elimination is illustrated in fig.4. Zinc oxide is readily fluxed and entrainment of metal in the slag is low due to the minimal turbulence and the ability of metallics to settle from the slag prior to tapping. Recirculation of silver has been shown to be as low as 3% in by-products. The intense reaction allows a much smaller furnace to be used making possible a substantial reduction in inventory. Energy consumption is low as, during the oxidation period due to the exothermic oxidation of lead, the process is autogenous and the burner is not required during this period. Copper is removed at BRM by means of additions of lead in the final stages. The quality of silver produced is >997 and can be cast directly into ingots or anodes for electrolytic refining. At BRM due to the absence of gold or platinium group metals, market 999 silver is produced by fire refining in a further stage, Fine Cupellation.

Process chemistry.

The chemistry of the cupellation process is easily understood and relies on the relative oxidation potentials of the impurity metals, with respect to silver. The thermodynamic stability of the oxides within the operating temperature regime is given by the free energy of oxide formation. This data shows that the sequence of oxidation is zinc-lead-copper.

The free energy of formation of silver oxide is positive at the operating temperature , indicating that it is unstable and that silver cannot be oxidised in the process.

The selectivity of the oxidation reactions is indicated by the equilibrium constants for the reactions as follows.

1) $PbO + Zn = Pb + ZnO$

The equilibrium constant k at 1000°C (Where $\ln k = -\frac{\Delta G}{RT}$)

$= 3.7 \times 10^5$ indicating that zinc removal will be highly selective with respect to lead.

2) $Cu_2O + Pb = 2Cu + PbO$

$k = 2.3$ indicating that copper removal will accompany lead oxidation over a wide range of lead content.

These predictions are observed in practice, where the majority of the residual zinc in the input bullion is removed in the early stages of oxidation with relatively little lead. Only when the zinc content has been reduced to a very low level does the rate of lead oxidation increase. Zinc oxide has a melting point in excess of 1800°C and will therefore remain solid until fluxed with lead oxide.

Copper is removed together with lead throughout cupellation but the rate of removal increases as the lead content is reduced to low levels at the end of the process. At BRM copper is removed in the final stages by means of small additions of lead.

Each of the oxidation reactions is exothermic and the heat of reaction is given as follows:-

	K.Cal/Kg	Therms/1000 Kg
Copper	281	11.2
Lead	235	9.3
Zinc	1041	41.3

For typical lead oxidation rates of 400 - 500 Kg/hr the heat release is approx 100,000 K.Cal (or 4 Therms)/hr which is greater than heat losses from the furnace and an increase in bath temperature results.

Operating procedure.

By means of an electric hoist, 3 tonnes of Vacuum Retort bullion blocks are added to the furnace in the vertical position and melted by means of the natural gas/air burner. The furnace is then tilted to the 'A' position and blowing commenced. Blowing is continued with oxygen at up to 9.0 l/sec (nitrogen 1.0 l/sec) and the burner turned off. Zinc contained in the retort bullion is first oxidised and forms a viscous slag but as blowing is continued the litharge formed dilutes the zinc content and produces a fluid liquid slag. This allows prills of metal to settle and separate from the slag. After 1 1/2 hours the furnace temperature will have stabilised at about 900°C and the first slag can be tapped. The furnace is tilted hydraulically and the liquid slag poured to moulds.

Oxygen blowing is continued at the same rate for a similar period to remove the remainder of the lead. During this period it is necessary to turn on the burner to a low fire position, as the lead concentration is reduced and the heat of reaction is insufficient to maintain the bath temperature. Litharge is again tapped and the bath sampled to determine the residual lead and copper contents. Blowing is continued until the silver concentration is >990, when copper removal is commenced.

Copper removal is carried out by the addition of lead "shots". Each shot is 150 kg of lead and three or four are required to reduce copper content from 0.5% to <0.04%. The procedure is to maintain the bath temperature close to the melting point at 960°C during this treatment. The lead ingots are added and blowing continued until all the lead has been oxidised. The lead oxide carries copper oxide with it and the bath is sampled after the litharge from each shot is tapped. When the copper content is reduced to the target level the oxygen is turned off the lance and the bath purged with nitrogen to reduce the oxygen content of the silver before casting.

Casting of silver at BRM is carried out by tilting the furnace to the pouring position and pouring the 1.8-2.0 tonnes directly to 450 kg blocks for final treatment in the Fine Cupel. For plants where electrolytic refining is necessary the anodes can be conveniently cast in the same way. A materials balance is given in Table 1 and typical furnace performance in Table 2.

Other applications of the BBOC.

The use of the bottom blowing technology, using the consumable nitrogen shrouded lance has led to investigations into other applications, for which such a furnace is suitable. Test work has been carried out at the Warren Springs Laboratory of the United Kingdom Department of Trade and Industry on the treatment of black copper (3). Black copper typically contains Cu 75 - 85%, Fe 5%, Zn 3%, Sn 1.5 - 4.5%, Pb 4% and Ni 1.5 - 4.5%. The impurities must be removed by oxidation to produce fire refined copper. This is traditionally carried out in a reverberatory furnace or more recently in the TBRC. The pilot scale tests carried out gave very encouraging results, when compared with the TBRC. The conclusions of this work were as follows.

1) The consumable lance assembly, developed for the cupellation of lead silver bullion can operate at the higher temperature experienced in the refining of black copper.

2) Oxygen efficiency is as much as three times greater when using the BBOC, than when using

Table 1.
BBOC Materials Balance

	Weight Kg	Ag	Pb	Zn	Ag	Pb	Zn
		Percent			Content		
Charge:							
Retort Bullion	3000	76	17	2	2280	510	60
Retort Slag	159	30	35	30	48	56	48
Lead	450		100			450	
		Percent			Content		
Product:							
Silver	2249	99.7			2249		
Litharge	1235	6	76	6	74	939	74
Fume	154	3	50	30	5	77	46

Table 2.
BBOC Operating Performance

	Classical Cupel*	BBOC
Ave PbO production rate kg/hr/tonne furnace capacity	21.5	42.3
Peak PbO prod rate kg/hour	375	850
Silver production/ day kg	919	4106
Oxygen used M^3/tonne Ag		30
Nitrogen used M^3/tonne Ag		5
Fuel used Therms/ tonne Ag	992	61
Silver Recirculation %	8	3.4
Ag in process kg (max)	7000	2328

* Based on cupellation of 15% silver retort bullion at Britannia Refined Metals Ltd.

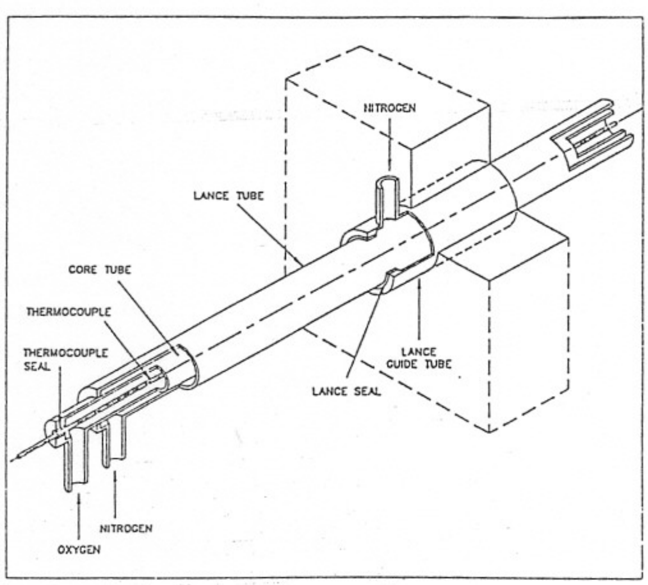

Fig.1 BBOC Shrouded Lance

top blowing.

3) Because of the greater efficiency, refining times can be reduced when bottom blowing. However the heat release on bottom blowing is more evenly distributed and slag temperature is lower.

4) Both top and bottom blowing are low fuming processes.

5) The high efficiency of oxygen use in in bottom blowing offers greater potential for process control.

The successful application of the BBOC to other processes will be extended to other materials. Test work is planned for the treatment of copper matte, rich in precious metals and for the treatment, including cupellation, of slimes from copper and lead electrolytic plants.

Conclusions

The BBOC at Britannia Refined Metals has proved to be an outstanding success and the process is now an established part of the flow sheet. The process has resulted in considerable interest in applications other than cupellation of silver/lead bullion. As a result research is currently in hand or planned for the use of the BBOC for the treatment of copper and lead electrolytic refinery slimes and for the treatment of black copper and matte rich in precious metals. It is clear that the process has many potential applications where an intense reactor using bottom blown oxygen can be used.

References.

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