Theory and Practice of Cupellation at Port Pirie Pasminco Smelter

Dr. Douglas Swinbourne
RMIT University
PO Box 2476V
Melbourne, 3001, Australia

Andrea Winters, Michael Giunti
Pasminco Port Pirie Smelter
PO Box 219
Port Pirie, 5540, Australia

Abstract

The Port Pirie site has been a significant world producer of silver and gold as byproducts of lead smelting from Broken Hill lead concentrates since 1889. The technology used has changed over the years to maintain competitiveness and to meet increasingly stringent environmental and hygiene requirements. The current technology utilises vacuum induction furnace retorting to remove zinc from Parkes crusts, followed by a bottom blown oxygen cupel (BBOC) for oxidising lead to produce silver doré suitable for electrorefining. The BBOC has displayed superior oxygen utilisation and greatly improved hygiene compared to previous technology. In this paper the theoretical basis of cupellation is reviewed and a computational thermodynamics model developed to predict the affect of operating variables on the final doré composition. The composition of the doré anodes affects the operation of the subsequent electroparting of silver and gold, especially the cost of electrolyte purification, so the model can be used as an aid in optimising the silver production process.

1 Introduction

Silver production, as a byproduct of lead smelting utilising ore from the famous Broken Hill mine, commenced at Port Pirie, South Australia, in 1889. In that year the Broken Hill Proprietary Company Limited built a lead refinery at Port Pirie to refine lead from its own smelter at Broken Hill and from the British Broken Hill Proprietary Company Limited's blast furnaces at Port Pirie. In 1915 the smelter-refinery complex was purchased by the Broken Hill Associated Smelters Proprietary Limited and operated as such until 1988 when Pasminco Metals was formed [1].

Silver was refined from lead using the Parkes process, later becoming a continuous process developed by Williams in the 1920's [1]. Zinc was retorted from the silver crust in Faber de Faur retorts, then lead was removed in traditional reverberatory cupellation. The first stage involved a stream of air flowing over a very shallow bath of molten metal, with slag running continuously from the furnace to minimise the barrier between the air and the metal. The „rough doré" alloy produced was transferred to another cupel for oxidation using sodium nitrate to yield an doré containing typically

0.04 wt% Pb and 0.2 wt% Cu. The process suffered from low recoveries (80 – 83%), a long cycle time (4 –5 days) which caused large in-process inventories, inefficient use of labour and energy and poor hygiene [2].

In 1989 the reverberatory furnaces were replaced by a top submerged lancing Sirosmelt system to reduce the inventory of precious metals due to the high oxidation rates achieved and reduce operating costs [3]. Oxygen utilisation was found to exceed 95 % and cycle time was reduced to a little under 8 hours, but the grade of the doré which could be economically produced was poor, 0.8 wt% Pb and 0.4 wt% Cu. It was also found impractical to cast anode plates directly from the furnace, so the Sirosmelt doré was final-refined with sodium nitrate in a reverberatory furnace [2]. In 1993 it was decided to upgrade the lead and silver refineries to allow increases in production and a more flexible feed regime [4]. Batch desilvering of lead was reintroduced, the retorts were replaced by two vacuum induction retorts and the Sirosmelt reactor was replaced by a BRM-designed bottom blown oxygen cupel (BBOC) [5]. Commissioning commenced in 1997 and was completed in 1999, increasing lead throughput by 11% and, most significantly, doubling the silver production capacity of the smelter to over 400 tonnes per annum [6].

The BBOC process has proven to be generally successful, although lance jamming can be a problem in that it increases cycle time and refractory wear. Doré impurity levels can be reduced to 0.01 wt% Pb and 0.1 wt% Cu, but tapping to anode plates was found to be impossible so the doré needs to be heated to 1100–1150 °C to provide enough superheat. Impurity levels have been found to then rise to 0.2 wt% Pb and 0.6 wt% Cu. This puts an increased purification duty in the electrorefining plant [6].

This study was undertaken to provide a greater understanding of the cupellation process in the BBOC, with the intention of developing ways to maintain the low impurity levels initially achieved while at the same time allowing satisfactory anode plate casting.

2 The Silver Refinery

2.1 General Description

The Precious Metals Refinery (PMR) consists of two Junker Gmbh vacuum induction retorts (VIR's) using the Union Miniere licensed process [7], a bottom-blown oxygen cupel (BBOC) and a conventional parting plant using Balbach-Thum cells. Liquation of Parkes crust from the desilvering pan is carried out in the lead refinery in four cast iron kettles at 650°C. The upgraded alloy contains approximately 25 % Ag, 10 % Pb and 65 % Zn and is tapped into 350 kg moulds for delivery to the PMR [6]. This alloy then undergoes zinc distillation in a VIR, leaving a bullion which contains approximately 65-70 % Ag, 25 % Pb, less than 4 % Zn and a little copper. The distilled zinc is tapped from the condenser into 250 kg moulds and returned to the desilvering process. The bullion is charged to the BBOC, where zinc, lead and copper are oxidised by submerged injection of oxygen at 1000 °C. The slag, almost entirely litharge (PbO), is returned to the lead blast furnace and the doré is cast into 10 kg anode plates for electrorefining. Electrorefining takes place in 80 Balbach-Thum cells to produce 99.99 wt% silver at the cathode, which is then melted and cast into 30 kg ingots or granulated, according to customer demands. The cloths in the cells are periodically removed to recover anode slimes, which are further leached to produce a 98 wt% gold product. The PMR is operated by only three personnel. The Balbach-Thum cells are currently the production bottleneck and Pasminco are seeking an alternative technology.

2.2 Cupellation in the BBOC

The BBOC is a 3 tonne capacity, non-rotating refractory lined furnace, fired with a natural gas/air burner. The key feature of the furnace is a consumable, nitrogen shrouded lance inserted through the bottom of the furnace, through which oxygen is blown directly into the molten alloy. There is little turbulence on the surface of the charge, which is advantageous both for refractory life and a low rate of fume emissions. Only one person is needed to operate the BBOC through its 15-20 hour cycle to produce "clean" silver doré (0.01 wt% Pb, 0.30 wt% Cu) ready for casting. A typical cycle comprises the following steps, where the times given are approximate;

[1] melting: metal butts with a composition in the range 60-75 wt% Ag, 25-40 wt% Pb, 0.3-2.5 wt% Zn and 1- 4 wt% Cu, are charged to the BBOC and melted over 4 hours.

[2] blowing and slagging: oxygen blowing commences and after 1.5 hours slag is skimmed off, taking 0.5 hours to remove 250-280 kg of slag. This is repeated four times, to give a total time of 8 hours. At this point the alloy contains approx. 0.1 wt% Pb.

[3] final blowing: oxygen blowing is used to reduce the lead content to the target of 0.01 wt%. Marble chips are periodically added to aid the raking off of the small amounts of slag formed.

[4] casting: the melt is super heated to 1100-1150 °C to avoid freezing during casting. Casting takes from 2 ½ to 4 hours and requires 3 operators to cast 2200 kg of silver into 10 kg anode plates. The impurity reversion increases as a function of casting temperature and the doré can reach 0.2 wt%Pb and 0.6 wt%Cu.

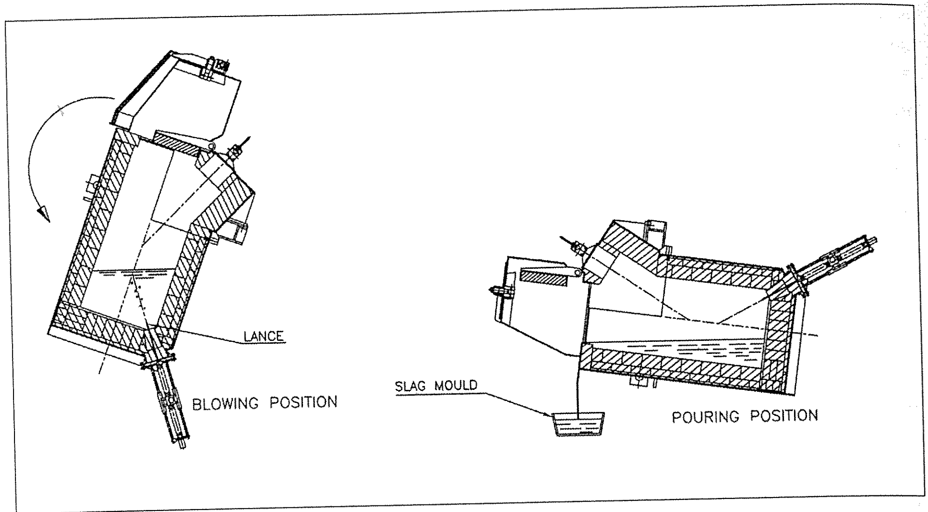

Figure 1: The BBOC reactor [5], reproduced with permission of the Instititution of Mining and Metallurgy.

3 Thermodynamic Modelling

3.1 Basic Analysis

Cupellation is a high temperature oxidation process which takes advantage of the large difference in stability of silver and lead oxides, as shown by the following equations for 1000 °C;

$$2Pb_{(l)} + O_{2(g)} = 2PbO_{(l)} \qquad \Delta G^{o} = -190.32\ \text{kJ} \tag{1}$$

$$4Ag_{(l)} + O_{2(g)} = 4AgO_{0.5(l)} \qquad \Delta G^{o} = 92.80\ \text{kJ} \tag{2}$$

The Gibbs free energy data was taken from the database of the Outokumpu Oy HSC Chemistry for Windows version 4.0 software package [8]. Contacting a silver-lead alloy with oxygen will result in preferential oxidation of the lead, eventually producing silver containing very low levels of lead. The slag produced will be almost pure PbO.

Expressing the Gibbs free energy data on a modified form of the Ellingham diagram yields a much more informative analysis of cupellation. Individual lines are drawn for the reactions at particular values of activity of the various components, chosen to be relevant to industrial practice. For the case of the lead oxidation reaction, the Gibbs free energy change as a function of species activities is;

$$\Delta G_{Pb} = \Delta G^{o}{}_{Pb} + 2RT\ln(a_{PbO}) - 2RT\ln(a_{Pb}) - RT\ln(p_{O_2}) \tag{3}$$

The activity of PbO can be taken as unity and if pure oxygen is used as the oxidant gas then its partial pressure is also unity, and so;

$$\Delta G_{Pb} = \Delta G^{o}{}_{Pb} - 2RT\ln(a_{Pb}) \tag{4}$$

Lines can be drawn on an Ellingham diagram for various values of lead activity in silver, as is shown by the solid lines on Figure 1. They are not parallel, but radiate from the value of the standard Gibbs free energy change for the reaction at a temperature of 0 K.

Similarly, the expression for the silver oxidation reaction, where the silver activity and the oxygen partial pressure are both unity and the variable activity is that of $AgO_{0.5}$ is;

$$\Delta G_{Ag} = \Delta G^{o}{}_{Ag} + 2RT\ln(a_{AgO_{0.5}}) \tag{5}$$

Another set of lines on the same Ellingham diagram for various values of silver oxide activity in the PbO slag can be drawn, as shown by the dashed lines on Figure 2.

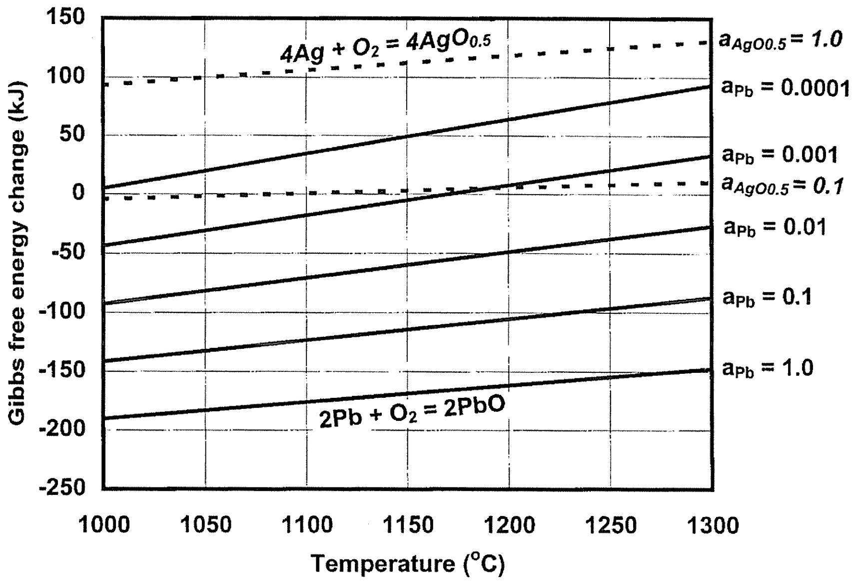

Figure 2: Modified Ellingham diagram for cupellation using pure oxygen.

The equilibrium position for either reaction lies along the Gibbs free energy change value of zero. Some useful conclusions can be drawn from the diagram;

[1] the activity of lead in molten silver varies from about 0.0001 at 1000 °C to a little over 0.001 at 1200 °C. The lead content of the silver is thus a strong function of temperature.

[2] the activity of $AgO_{0.5}$ in the molten PbO slag is very close to 0.1 and is quite insensitive to temperature.

Assuming $AgO_{0.5}$ is ideal in PbO, this is equivalent to 5.1 wt% Ag. It is important to appreciate that silver is co-oxidised with lead, so there would significant silver losses during cupellation if all slag formed remained in the furnace until equilibrium.

The actual oxygen partial pressure in the injected gas in the BBOC is only 0.83 atm. due to the presence of a small quantity of nitrogen used to shield the lance. The equilibrium lead content of the silver under this oxygen partial pressure, calculated using activity coefficient data discussed later, is given in Figure 3.

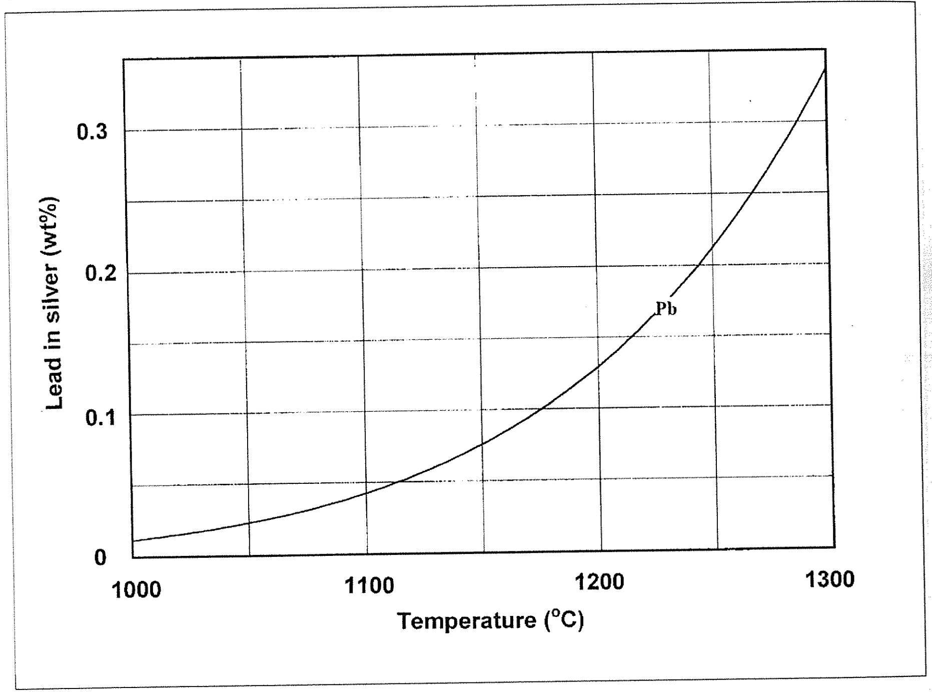

Figure 3: The equilibrium lead content of silver as a function of temperature at an oxygen partial pressure of 0.83 atm. and at a PbO activity of unity.

It has been reported that the silver content of the PbO slag is strongly temperature dependent during Sirosmelt cupellation, and that the silver content is typically 0.6 wt% [2]. The lower silver content than predicted is expected since the Sirosmelt process never reached equilibrium as evidenced by the reported high lead and copper levels in silver. However, the strong temperature dependence can only be explained by a corresponding strong dependence of the activity coefficient of $AgO_{0.5}$ in molten PbO, yet it is difficult to believe that this could be the case. A possible explanation is that silver in the Sirosmelt slag was mostly entrained metal and the observed temperature dependence is a consequence of changes in the viscosity of the slag, and thus the settling rate of the metal droplets.

Small amounts of zinc and copper are also present in the alloy charged to the cupellation furnace. The standard Gibbs free energy changes, also taken from the database of the Outokumpu Oy HSC Chemistry for Windows version 4.0 software package [7], for these reactions at 1000 °C are;

$$2Zn_{(l)} + O_{2(g)} = ZnO_{(s)} \qquad \Delta G^{o} = -437.45\ \text{kJ} \tag{6}$$

$$4Cu_{(l)} + O_{2(g)} = 4CuO_{0.5(s)} \qquad \Delta G^{o} = -151.76\ \text{kJ} \tag{7}$$

Zinc would be expected to be oxidised to a solid ZnO dross very early in the cupellation process, while copper would be a little less effectively oxidised than lead. High levels of zinc in the feed to cupellation, due to inadequate removal in the previous dezincing stage, causes several process problems. Zinc oxide in the PbO slag raises its viscosity and increases silver entrainment losses, while the very exothermic zinc oxidation reaction leads to increased refractory wear and excessive lance consumption [6].

3.2 Computer Modelling

The computational thermodynamics package "HSC Chemistry for Windows" version 4.0 was used for the modelling. This program takes as inputs the species involved and the phases within which they occur, their initial amounts and their activity coefficients. Any one species can be assigned to multiple phases. The single-atom cation-base formalism for species was used so that composition-independent values of activity coefficients could be applied. The program often experiences convergence difficulties if expressions relating activity coefficient to composition are used. The database in the package requires modification to enable the use of the single-atom cation-base formalism. Values of H°, S° and C_p coefficients for the conventionally represented species were halved to convert the data from, for example, Ag_2O to $AgO_{0.5}$, etc., and these data were then stored in the "own database".

The initial amount of alloy charged to the BBOC is typically 3000 kg and has a representative composition of 26 wt% Pb, 2 wt% Zn, 2 wt% Cu, balance Ag. The flowrates of oxygen and nitrogen through the lance are 21.3 and 2.4 Nm^3/hour respectively, and for the purposes of the model these were converted to the amounts of these gases injected over a 5 minute period. The amounts of oxygen and nitrogen were increased in steps by these amounts.

The activity coefficients used for the species in the alloy were based on data taken from the compilation of HULTGREN [9]. The data was modelled according to the quadratic formalism introduced by Darken [10] where, in a binary alloy 1-2 in which 1 is the solvent;

$$\log(\gamma_2) = \alpha_{12}(-2N_2 + N_2^2) + \log(\gamma^o_2) \tag{8}$$

where γ_2 is the activity coefficient of 2, γ^o_2 is the limiting activity coefficient of 2, α_{12} is a constant and N_2 is the mole fraction of 2. The expression for lead in silver at 727 °C, the temperature at which the data was available, was found to be;

$$\log(\gamma_{Pb}) = 0.107(-2N_{Pb} + N_{Pb}^2) + 0.303 \tag{9}$$

From this expression it was determined that the activity coefficient of lead in silver only varied from 1.8 to 2.0 over the full range of compositions expected. Since interest was focussed on the final lead content, the value of the activity coefficient of lead in silver at 727 °C was taken to be 2.0. It was corrected to the temperatures of interest in this work using the following relationship, which assumes that the silver-lead system is a regular solution;

$$(\log\gamma^o_i)_{T_2} = (\log\gamma^o_i)_{T_1}(T_1/T_2) \tag{10}$$

where γ^o_i is the limiting activity coefficient of "i" and T is in degrees Kelvin. From this relationship the values of the limiting activity coefficients of lead in silver at 1000 °C (1273 K) and 1100 °C (1373K) are both 1.7 to the accuracy justified by the data. Similarly the activity coefficient of copper in silver at 990 °C was found to be given by the expression;

$$\log(\gamma_{Cu}) = 0.812(-2N_{Cu} + N_{Cu}^2) + 0.521 \tag{11}$$

and a value of 3.3 was found to apply to very dilute solutions of copper in silver at 990 °C. The corresponding value at 1100 °C is 3.0, found using expression 10. The ternary formalism of DARKEN for the system Ag-Cu-Pb was used to show that dilute lead and copper in silver interacted with each other so little that the activity coefficients of each could be taken as constant. Finally, the activity coefficient of zinc in silver was taken as 1, simply because zinc is oxidised from silver to very low levels early in the BBOC blow and the actual value of the activity coefficient for zinc in silver is unimportant to a consideration of the final composition of the alloy.

Regarding the slag, no information could be found in the literature on the activity coefficients of $AgO_{0.5}$, $CuO_{0.5}$ and ZnO in molten PbO, so the slag was taken to be an ideal solution. The activity coefficients of all gaseous species were set to unity.

4 Results and Discussion

4.1 Cupellation at 1000 °C.

The composition of the alloy as a function of the amount of oxygen injected is given in Figure 4. It can be seen that the first element to oxidise is, as expected, zinc and it is reduced to insignificant levels after the addition of only approx. 15 kg of oxygen. Over this period the lead content of the alloy slightly increases as a result of the removal of zinc, but thereafter decreases almost linearly, while the copper content steadily decreases. The alloy composition changes very slowly after 110 kg oxygen addition when the target lead content of 0.01 wt% has been achieved, with a corresponding copper content of approximately 0.07 wt%. This is close to the 0.1 wt% Cu claimed in practice [6]. At this point the direct silver recovery can be shown to be 96.95 %. Little change occurs with further oxygen addition because the system is very close to equilibrium with the injected gas.

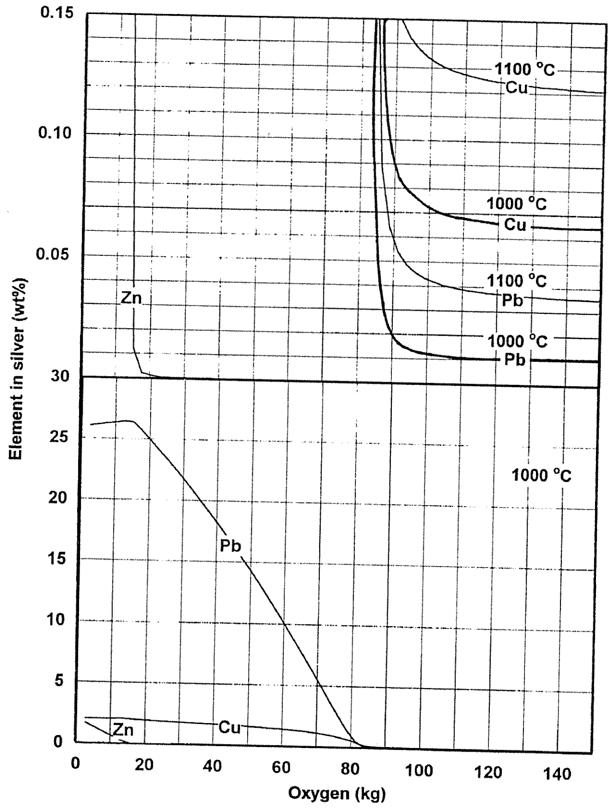

Figure 4: Alloy composition during progressive oxidation in the BBOC at 1000 °C, except where otherwise noted.

It was noted that in the earlier Sirosmelt process the alloy was oxidised to 0.8 wt% Pb and 0.4 wt% Cu, the copper content being less than the lead content [2]. The model confirmed that at these poor levels of lead removal, copper is oxidised more than lead and that the levels quoted are in accord with the model predictions.

Figure 5 shows the evolution of the slag composition. Initially only ZnO is formed and it will appear as a solid dross on the alloy surface, as has been reported [2]. As the addition of oxygen increases PbO is formed and fluxes the ZnO, although the ZnO solubility in PbO at 1000 °C is only approximately 8.5 wt% [11]. If the initial alloy contains much more than 2 wt%Zn, complete fluxing of ZnO will not be achieved and this will cause process problems. The copper content of the slag rises steadily after approx. 20 kg of oxygen addition. The silver content of the slag is the most important operational issue and is seen to remain very low until approx. 80 kg oxygen addition, but thereafter rises rapidly. With further oxygen addition past 100 kg it continues to rise but very much more slowly as equilibrium is approached. When the alloy has achieved the target lead content of 0.1 wt%, the $AgO_{0.5}$ content of the slag is equivalent to approx. 6 wt% Ag. In practice the silver content of the slag could be much higher due to entrainment of silver droplets.

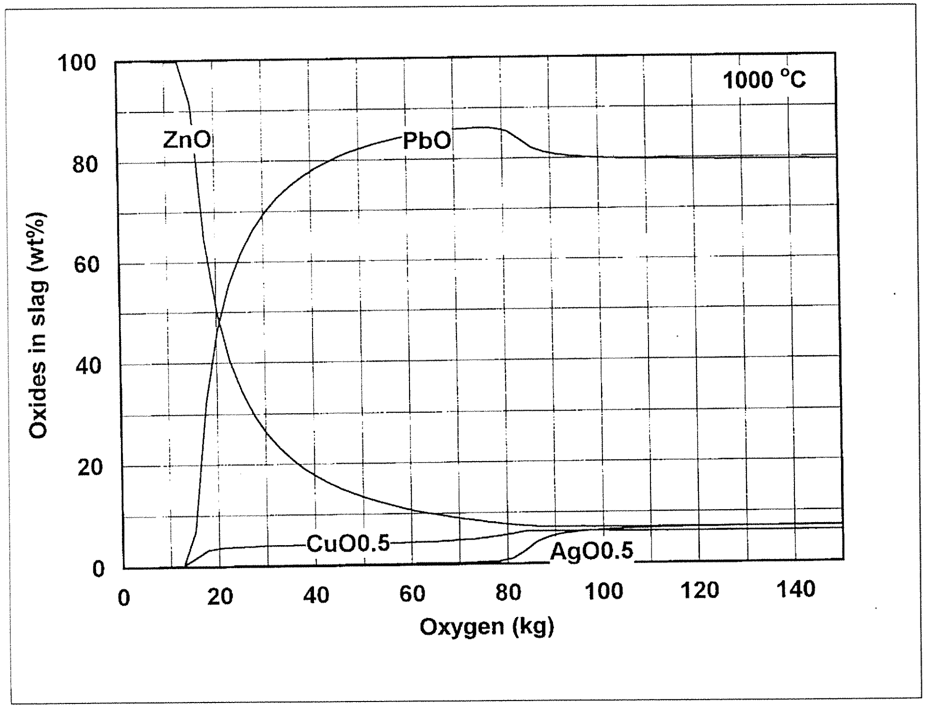

Figure 5: Slag composition during progressive oxidation in the BBOC at 1000 °C.

The gas composition is given in Figure 6. The oxygen partial pressure in the reacting bubbles rising through the alloy varies over a very wide range as blowing proceeds. It remains below 10^{-2} atm. until the addition of 2.6 kmol (83 kg) of oxygen, representing almost 100% oxygen utilisation until then. However, as the lead content of the silver approaches the target level, the oxygen partial pressure rises to approach the initial oxygen content of the injected gas i.e. the oxygen utilisation decreases quickly towards zero. As noted earlier, Port Pirie practice is to skim slag every 1 to 1.5 hours, with the amount of slag removed being 250-280 kg. The model predicts that after 1 hour of blowing the slag mass would be 285 kg, and after 1.5 hours it would be 495 kg. This shows that in practice, even in the first hour of blowing, the oxygen utilisation of the process is less than 100 %.

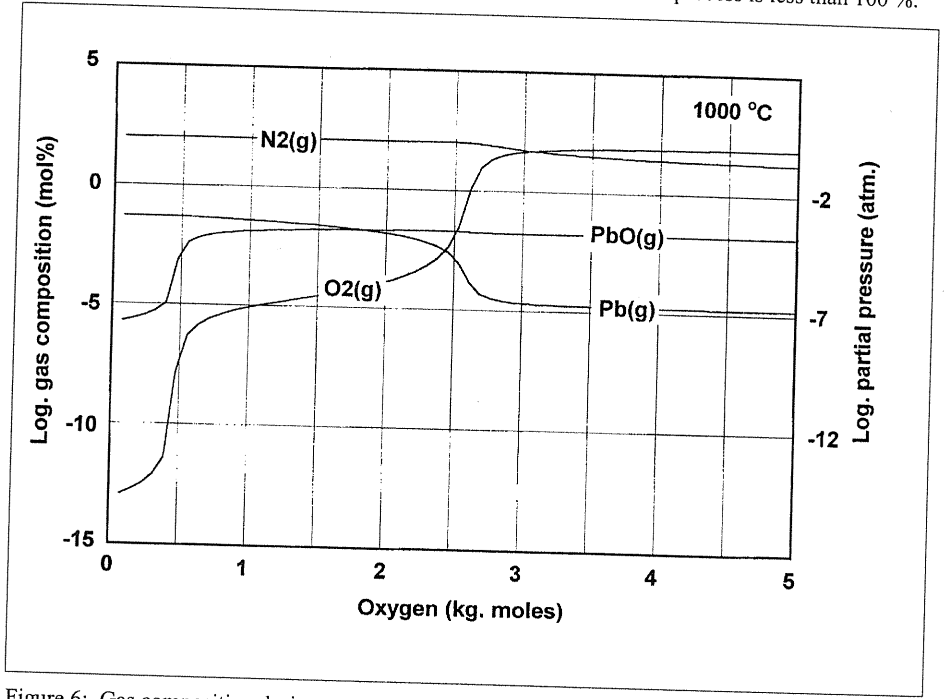

Figure 6: Gas composition during progressive oxidation in the BBOC at 1000 °C.

The lead vapour partial pressure in the offgases is an important occupational hygiene issue. Figure 6 shows that the lead content of the gas is initially accounted for by elemental lead, but that the contribution of PbO becomes predominant after approx. 2.0 kmol (80 kg) of oxygen addition. This can be seen more clearly on Figure 7, which also shows the total lead vapour pressure. While the total vapour pressure is always small, below approx. 5 x 10^{-4} atm., it is highest during the first half of the blowing cycle so this period presents the greatest occupational hygiene risk to the operators.

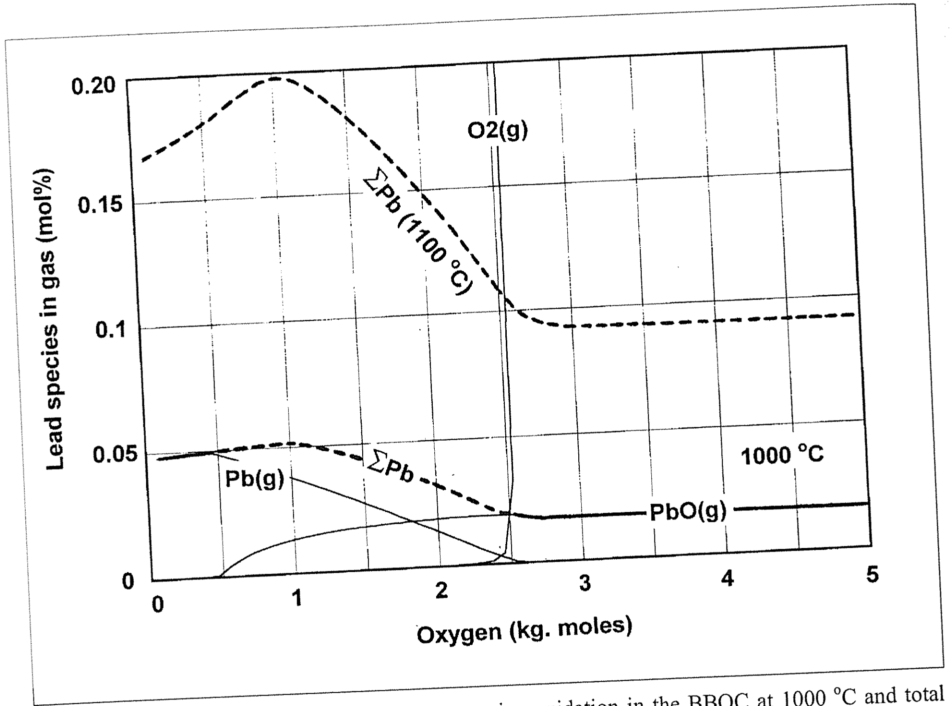

Figure 7: Lead species in the gas during progressive oxidation in the BBOC at 1000 °C and total lead at 1100 °C.

4.2 Cupellation at 1100 °C

The effect of increasing temperature by 100 °C was modelled to determine how sensitive the operating parameters of cupellation are to temperature. After the addition of 100 kg of oxygen it was noted that;

- the lead content of the silver increased from 0.01 wt% to 0.04 wt% (Figure 4), a very significant increase and well above the target. Further blowing to a total of 150 kg of oxygen only dropped the lead level to 0.035 wt%, a minor improvement for such a large increase in oxygen usage.
- the silver content of the slag decreased a little, from 6.5 to 5.8 wt% $AgO_{0.5}$, and this accounts for a small improvement in silver recovery from 96.95 % at 1000 °C to 97.38 % at 1100 °C.
- the copper content of the silver increased from 0.08 wt% to 0.13 wt% (Figure 4), again a significant increase. Blowing to 150 kg of oxygen only reduced this to 0.12 wt%.
- the maximum total partial pressure of lead in the offgas increased from 0.05 vol% to 0.2 vol% (Figure 7). The occupational hygiene risk to the operators has increased significantly.

It was reported [6] that when the metal in the BBOC is heated to 1100-1150 °C to provide enough superheat for anode casting, the lead and copper levels rise to 0.2 wt% and 0.6 wt% respectively. Even though slag is skimmed prior to heating, there still remains a significant amount of PbO absorbed into the furnace refractories so lead reversion via the following reaction is possible;

$2Ag + PbO = Pb + 2AgO_{0.5}$

These impurity levels are higher than predicted by this model and suggest that lead reversion may not be a simple thermodynamic process.

The kinetics of lead reversion was examined by heating 10 g of pure silver in one magnesia crucible and 7 g of PbO in another at 1200 °C in contact with air in a muffle furnace. The silver was then poured into the crucible containing the PbO. At various time intervals the crucible was removed and the PbO quenched using a cold steel rod. A portion of the silver button was analysed for lead, first confirming by optical microscopy that there was no PbO entrainment in the sample. The results are shown in Figure 8. It can be seen that the lead content of the silver rose rapidly within 5 minutes of contact, before slowly falling to the equilibrium value appropriate to these conditions. As yet no explanation can be offered for these observations, however they provide support for the unusually high lead contents found in practice when the silver in the BBOC is heated prior to casting.

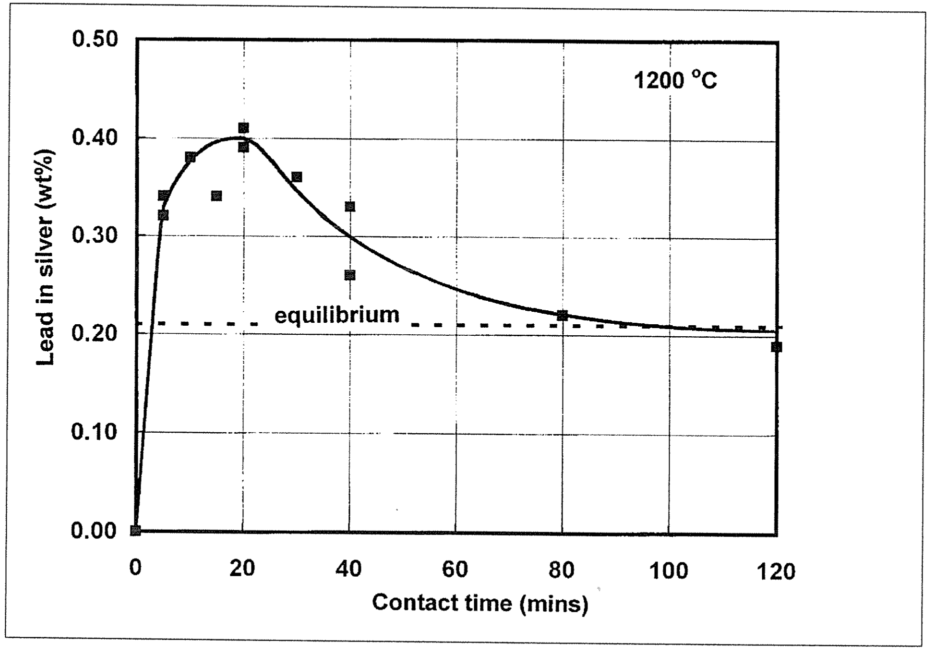

Figure 8: The lead content of silver in contact with molten PbO and air at 1200 °C for increasing contact time.

It can be concluded that an increased cupellation temperature has a significant deleterious impact on silver quality and will necessitate more frequent purification of the electrolyte in the electroparting process. This has a very negative impact on the economics of silver recovery. Means for allowing heating of the silver while limiting the opportunity for lead reversion are currently being considered. One possible option is to granulate the silver rather than cast anode plates, because this will be a much quicker process and require less superheating. Refractories that absorb less PbO are also being sought.

4.3 Multiple Slag Skims

In practice slag is not left on the metal until the completion of the blowing cycle, being skimmed approximately 4 times at equal time intervals. The incentive for doing this is apparent from Figure 5 - only at the later stages of the blow does the silver content of the slag become high, leading to a reducing recovery of silver to the bullion. By removing the slag prior to this increase, the volume of slag present during the final stages of blowing is greatly reduced so the extent of silver loss is correspondingly decreased.

Multiple slag skimming was simulated by a simplified two stage skimming cycle. The composition of the alloy after 70 kg of oxygen addition was taken as the input to a new HSC file in which the masses of the slag components were set to zero. A further 30 kg of oxygen were then progressively added, to bring the total oxygen addition to 100 kg, as before. The following changes in performance parameters in changing from a single final slag skim to two slag skims were noted;

- silver recovery rose from 96.95 % to 99.36 %. In a single cycle this is equivalent to the mass of silver lost to the slag dropping from 64 kg to only 13.5 kg. This is a significant increase in direct recovery and a substantial reduction in the in-process inventory of silver.
- the final lead content of the silver dropped from 0.01 wt% to 0.006 wt%. This is the result of a reduced activity of PbO in the slag since the $CuO_{0.5}$ and $AgO_{0.5}$, which are mostly formed in the latter stage of the blow, reduce the PbO content of the slag.
- the copper content of the silver doubled from 0.08 wt% to 0.175 wt% as a result of a higher activity of $CuO_{0.5}$ in the slag since the volume of diluting PbO is much reduced.

In summary, direct silver recovery is very significantly improved by two stage slag skimming and lead removal was enhanced, but copper removal was much poorer. A higher copper content in the silver anodes is the price that must be paid for the improvement in direct silver recovery.

4.4 Kinetic Considerations

The kinetics of cupellation in the BBOC have not been examined experimentally in this work, but a consideration of the mechanism of cupellation leads to some interesting conclusions. A schematic of a bubble in the silver alloy is shown in Figure 9. The presence of a molten film of PbO within the bubble has an important influence of the kinetics of oxidation.

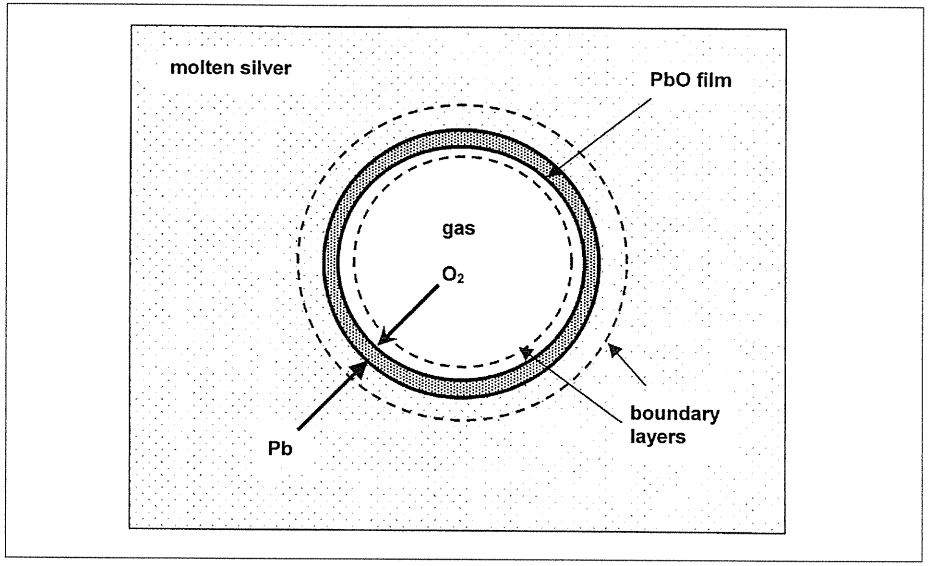

Figure 9: A schematic of an oxygen gas bubble within the molten alloy in the BBOC.

For all of the blowing period the bubbles initially contain almost pure oxygen, so gas phase mass transfer (of oxygen) control of the reaction rate is very unlikely. While the lead content of the alloy is relatively high for much of the blowing period, liquid phase mass transfer (of lead) control is also unlikely so the reaction rate must be controlled by either the rate of the chemical reaction at the alloy interface or the diffusion of reactants through the PbO film. Given the relatively high process temperature, it can be speculated that diffusion of oxygen through the PbO film is rate controlling. This diffusion rate may be slow enough that even early in the blow all of the oxygen in the bubbles is not consumed before the bubble breaks the surface of the molten pool in the BBOC. Towards the end of the blow, when the lead content of the silver is approaching 0.01 wt%, the liquid phase mass transfer rate of lead to the bubble interface will also become very slow and the overall oxidation rate will decrease very rapidly.

It is not surprising then that the thermodynamic model predicts that the target lead content of the silver will be reached in approximately 3.5 hours of blowing, while in practice the time taken is approximately 10 hours. It is not likely that changes to BBOC practice would influence the rate of oxidation much, and in fact there is little incentive to attempt this since the cycle time in the BBOC is not a process bottleneck in the silver refinery.

5 Conclusions

Over the 112 years of producing silver at the Port Pirie site, the technology used has evolved with the changing needs for higher production rates and much greater environmental cleanliness. Currently the BBOC is used for cupellation and has proved successful, although there is still an issue involved with the need to superheat the metal prior to anode casting. This has been found to increase the lead content of the silver above desirable limits. Thermodynamic modelling and kinetic experiments have provided a deeper understanding of the cupellation process and confirmed the role of increased temperature in degrading the quality of the metal product. Means are being explored for limiting the extent of lead reversion while still allowing heating of the metal for improved anode castability.

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