The effects of slag and gold bullion composition on the removal of copper from mine bullion by oxygen injection

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INTRODUCTION

The Miller chlorination process has assumed a pre-eminent position in the refining of gold bullion, a position it has maintained for over half a century. In the early sixties considerable interest was aroused by the idea of producing a consistently high grade bullion at the mine smelthouses themselves. However, as the use of chlorine in industrial plants is associated with considerable hazards, oxygen was considered a natural alternative, apart from bing less expensive than chlorine. Partial refining at the mine smelthouses would considerably decrease the requirements made on Rand Refinery Limited as well as indicating the possibility of reducing final refining costs. An added factor would be the purer silver chloride obtainable, after prior removal of the base metals by oxygen injection, which would facilitate the production of high-purity silver.

The free energies of formation of the oxides of the metals:- silver, copper, lead, zinc, iron and bismuth indicate that, with the exception of silver, these metals should be capable of removal as oxides by oxygen injection. Rose[1] had shown that during injection of gold bullion, considerable loss of silver to the borax-silver slag occurred and, furthermore, that copper removal was not effivient and oxide attack on the refractories was severe. Plant test work[2] had confirmed the difficulty of copper removal, but had shown that zinc and lead were almost completely removed. The difficulty of copper removal by oxygen injection warranted further investigation. Also, the high decomposition pressure of silver oxide suggested that by suitable control of the slag composition it might be possible to reduce to very small proportions the silver carried into the slag as oxide.

The oxidation of copper by oxygen injection and subsequent dissolution of the oxide in a slag may occur according to the following reactions:
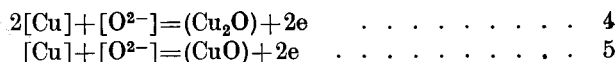
$$4[Cu] + O_2 = 2(Cu_2O) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$
$$2[Cu] + O_2 = 2(CuO) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$
$$2(Cu_2O) + O_2 = 4(CuO) \quad \ldots\ldots\ldots\ldots\ldots \quad 3$$

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$$2[Cu] + [O^{2-}] = (Cu_2O) + 2e \quad \ldots\ldots\ldots\ldots \quad 4$$
$$[Cu] + [O^{2-}] = (CuO) + 2e \quad \ldots\ldots\ldots\ldots \quad 5$$

Reactions 4 and 5 were considered because of the relatively high solubility of oxygen in molten silver and silver alloys. Thermodynamic data indicate that there is little possibility of any reaction involving the formation of CuO occurring at temperatures above 1 000 °C.

To ensure that the operative reactions 1 and 4 take place to the maximum extent, the following factors are significant.

(a) an increase in the activity of the copper in the bullion,

(b) an increase in the partial pressure of oxygen in the system,

(c) an increase in the activity of the oxygen in solution in the metal,

(d) a decrease in the activity of cuprous oxide in the slag.

From practical considerations, the operative variable most easily susceptible to control is the composition of the slag.

SOLUBILITY OF COPPER OXIDES IN BOROSILICATE SLAGS

Very scanty information exists on systems containing copper oxides but the indications are that slags containing considerable amounts of boric oxide would possibly prove to be the best solvents for cuprous and cupric oxides. This is attributed to the fact that the activities of copper oxides are much lower in boric oxide slags than in slags in which silica is the main network former. The number of possible slags containing boric oxide was limited by consideration of liquidus temperature, viscosity, corrosive action on refractories, volatilization, and ultimately cost (for industrial application). Slags in the systems soda-boric oxide-silica and lime-boric oxide-silica were selected paying due attention to the above limitations.

Additions of 5, 10 and 15 per cent cupric oxide were made to the finely ground, premelted slags. These mixtures were then reground and 2g quantities held in recrystallized alumina crucibles at temperatures of 1 150 °C and 1 250 °C respectively for 30 minutes. The crucibles were removed from the furnace, rapidly cooled, cut in half longitudinally, and a thin section taken from one half was subjected to microscopic examination.

When the copper oxides had not been completely dissolved in a particular slag, they were found to constitute the disperse phase of a two-liquid system while slag (presumably saturated with copper oxides) was the disperse medium. X-ray diffraction analysis of the disperse phase showed the presence only of cuprous and cupric oxides, the former predominating, particularly in the higher temperature tests. The remainder of the slag was in the glassy state due to the rapid cooling.

The solubility of the copper oxides was estimated using a combination of the intensity of the colour of the clear blue-green slag and the quantity and intensity of the yellow-brown disperse phase. The results are presented in Table I.

Evidently the solubility of the copper oxides decreases with increase in soda or lime and with increase in silica content. Having established that copper oxides were reasonably soluble, particularly in some of the slags tested, it was apparent that the cause of poor removal of copper from bullion by oxygen injection could not be attributable solely to the slags used in previous plant test-work.

OXYGEN INJECTION OF SILVER-COPPER ALLOYS

Alloys of silver and copper were selected for these tests as this should simulate the conditions of copper removal from precious metal-copper alloys. Use of these alloys would also provide information relating to the loss of silver to the slags. Two slags were selected for these tests, namely 10 per cent soda, 54 per cent boric oxide, 36 per cent silica and 38.3 per cent lime, 31,5 per cent boric oxide, 30,2 per cent silica. Similar slags had exhibited superior copper oxide solubility and were characterised by suitable liquidus temperature, viscosity, volatilization and refractory attack characteristics.

The oxygen injection tests were conducted in fireclay pots containing 100g of alloy and 100 g of slag. The oxygen lance was a four-bore thermocouple insulating rod made from sintered alumina cut back 1 mm at the tip to expose the bores when the rod rested on the bottom of the crucible. Oxygen injection was commenced 10 minutes after the contents of the crucible had reached the temperature of $1\,150\,°C$. The oxygen flow-rate was maintained at 150 ml per minute (S.T.P.) and injection times were, 5, 15, 30, 60, and 90 minutes. At the completion of each test the contents of the crucible were poured into a large round-bottomed conical iron mould. The resulting silver button was cleaned, weighed, and assayed for copper while the slag was ground and analysed for silver and copper.

The results for the silver-2 per cent copper alloys are presented in Figures 1 and 2. These results indicate that equilibrium with respect to copper removal was attained within 90 minutes of oxygen injection. The final copper content in the silver is lower with the soda slag than with the lime slag but less silver was lost to the lime slag. This indicates that the activities of the oxides of copper and silver are higher in the lime slags. Apart from the poorer copper removal using the lime slag, this slag also
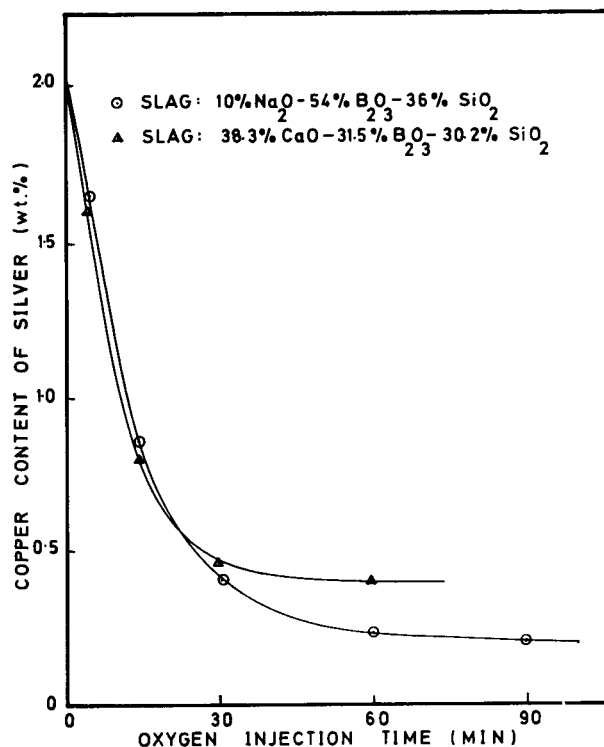

Fig. 1—Copper content of Ag-2% Cu alloys after oxygen injection under soda- and lime-borosilicate slags.
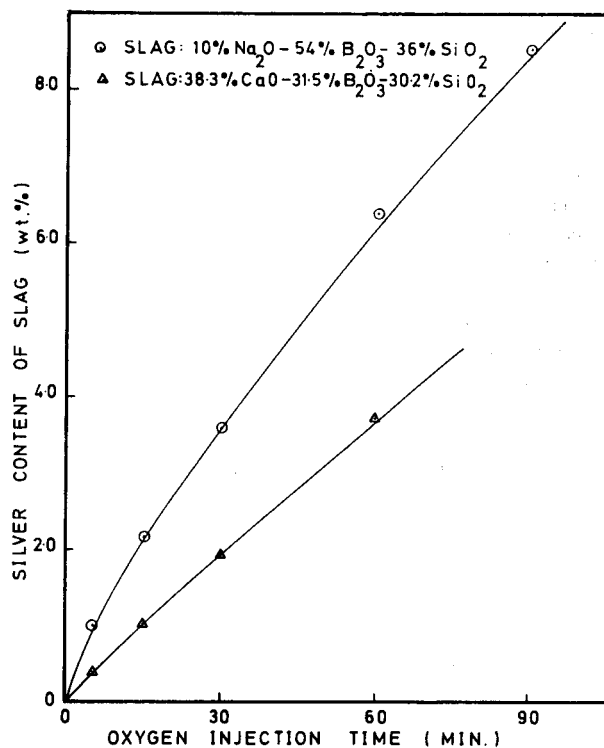

Fig. 2—Loss of silver to the soda- and lime-borosilicate slags during oxygen injection into Ag-2% Cu alloys.
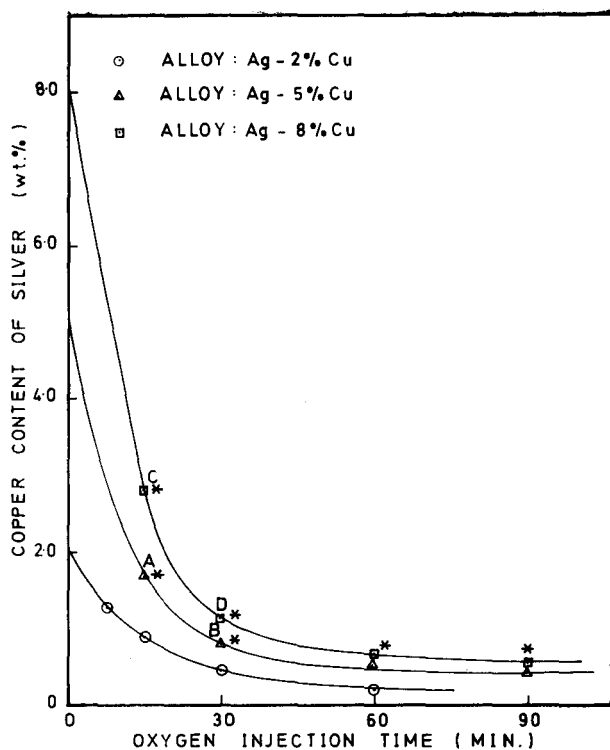
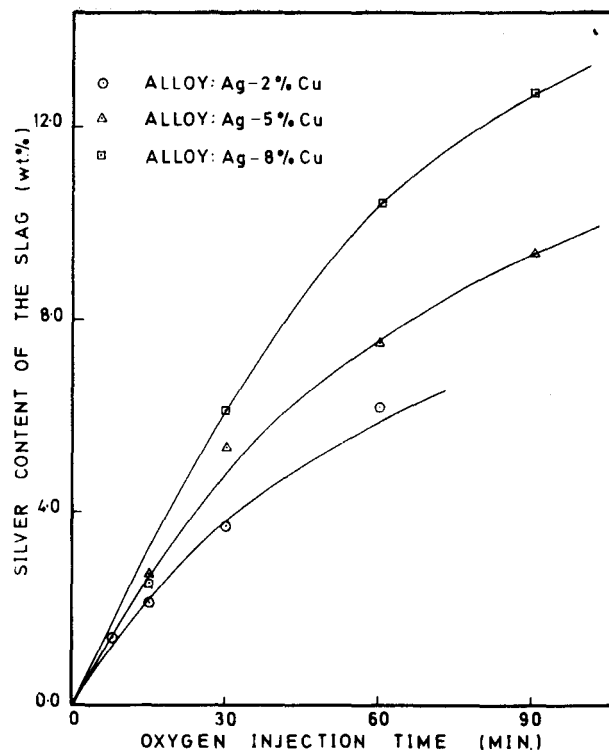Fig. 3—Copper content of Ag-2, 5 and 8% Cu alloys after oxygen injection under a 10% NaO₂, 54% B₂O₃, 36% SiO₂ slag.

Fig. 4—Silver loss to a 10% Na₂0, 54% B₂0₃, 36% Si0₂ slag during oxygen injection into Ag-2, 5, and 8% Cu alloys.

was rather viscous and very corrosive towards the refractories. It was, therefore, decided to discontinue investigations on the lime-boric oxide-silica slag system.

A second series of tests was then conducted on silver-copper alloys in which the copper contents were 2, 5 and 8 per cent respectively — the slag used contained 10 per cent soda, 54 per cent boric oxide and 36 per cent silica. The results obtained are presented in Figures 3 and 4. Duplicate oxygen injection tests showed that the precision of the values for the final copper content in the alloy is ±5 per cent and of the silver lost to the slag is ±3 per cent.

The points in Figure 3 marked with an asterisk indicate that these slags, at the completion of the test, were heterogeneous, i.e., they contained undissolved oxide together with silver metal. Points A, B, C and D in Figure 3 exhibited pseudo liquid immiscibility, the upper liquid being a clear dark green glass while the lower, in contact with the alloy was found to be a disperse system of cuprous oxide, silver metal and slag saturated with cuprous and silver oxides. The silver metal was apparently entrained as fine droplets in the very viscous disperse system. It is of practical significance that a ·higher initial copper content of the silver-copper alloy produces a higher final copper content in the alloy and higher silver losses to the slag.

Oxygen injection into pure silver metal yielded the results presented in Figure 5. Also plotted on this graph, for comparison purposes, are silver contents of slags from the tests carried out on the silver-2 per cent

copper and silver-8 per cent copper alloys. The silver losses to the slag are considerably increased when the silver alloy contains copper and the magnitude of this loss is related to the copper content of the alloy. It is thought that this may be attributed to the mechanical entrainment of silver metal in the viscous cuprous oxide phase formed initially in the interfacial zone and that this silver, due to the increased surface area, may be more readily oxidised than that in the molten alloy phase.

EFFECT OF VARIATIONS IN THE COMPOSITIONS OF SODA-BORIC OXIDE-SILICA SLAGS ON COPPER REMOVAL FROM SILVER-COPPER ALLOYS

The tests described had indicated that slag composition appeared to have a significant influence on removal of copper from silver-8 per cent copper alloys when oxygen was injected into the molten alloys for 90 minutes. To confirm these indications and in an attempt to provide some basis for the determination of optimum slag composition a further series of tests was carried out using the range of slag compositions shown in Table II. All the compositions used had liquidus temperatures low enough for practical use and the conditions of the test were as previously described, the temperature chosen being 1 150°C. The results obtained are included in Table II and presented pictorially in Figure 6.
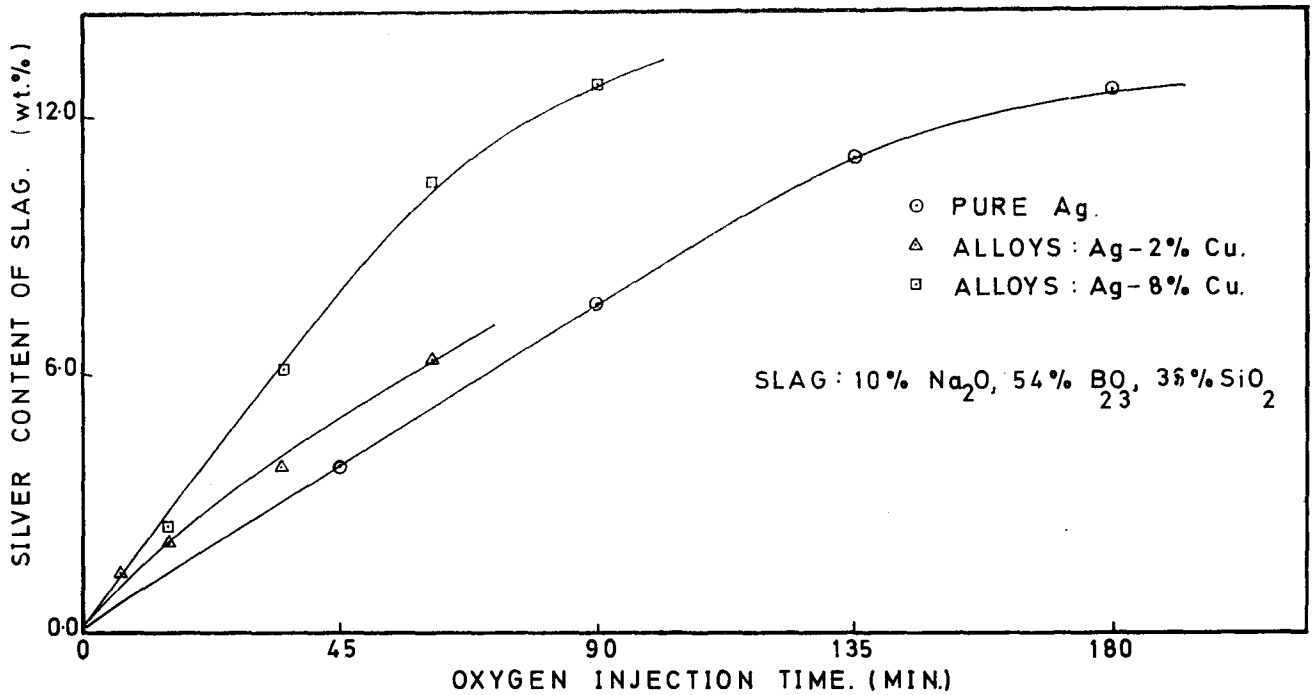
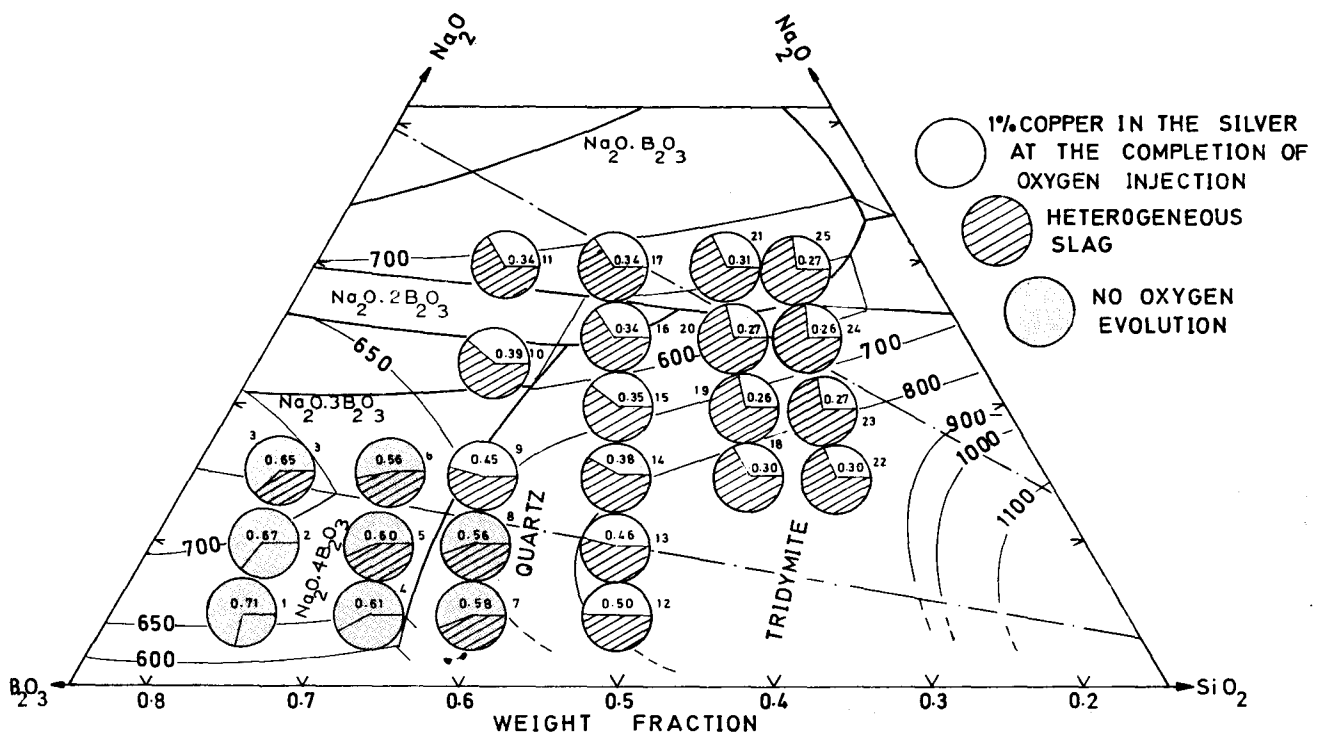Fig. 5—Silver loss to slag during oxygen injection

Fig. 6—Copper contents of Ag-8% Cu alloys after 90 minutes of oxygen injection.

TABLE II

THE EFFECT OF SLAG COMPOSITION ON THE FINAL COPPER CONTENT
OF Ag — 8% Cu ALLOYS
AFTER OXYGEN INJECTION FOR 90 MINUTES

Slag number	Na$_2$O Wt. %	Ratio B$_2$O$_3$/SiO$_2$	Final copper content of silver Wt. %	Oxygen evolution from alloy
1	5	3,0	0,71 (D)	None
2	10	3,0	0,67 (D)	,,
3	15	3,0	0,65	,,
4	5	2,0	0,61 (D)	,,
5	10	2,0	0,60	,,
6	15	2,0	0,56	,,
7	5	1,5	0,58	,,
8	10	1,5	0,56	,,
9	15	1,5	0,45	Positive
10	22,5	1,5	0,39	,,
11	30	1,5	0,34	,,
12	5	1,0	0,50	Very little
13	10	1,0	0,46	Positive
14	15	1,0	0,38	,,
15	20	1,0	0,35	,,
16	27	1,0	0,34	,,
17	30	1,0	0,34	,,
18	15	0,67	0,30	,,
19	20	0,67	0,26	,,
20	25	0,67	0,27	,,
21	30	0,67	0,31	,,
22	15	0,50	0,30	,,
23	20	0,50	0,26	,,
24	25	0,50	0,26	,,
25	30	0,50	0,27	,,

Only slags 1, 2, and 4 were capable of dissolving all the oxides formed during the actual period of oxygen injection. All the other slags were heterogeneous at the conclusion of the test and showed undissolved cuprous oxide evenly distributed throughout the mass.

A phenomenon occurred which had not been observed previously, viz., the evolution of oxygen on solidification of several of the alloys after completion of the test. For such evolution of oxygen to occur it would appear that the slags used in these particular tests have greater oxygen ion activities and hence cause the silver to dissolve a greater amount of oxygen. This, in turn, increases the activity of oxygen in the alloy and facilitates the oxidation of a greater amount of copper. It would appear that the oxygen ion activity in the slag is the dominant factor in determining the equilibrium of the reaction of copper with oxygen to form cuprous oxide, the solubility of the oxide in the slag being relatively less important. This is illustrated by the high final copper content in the alloys under those slags with higher cuprous oxide solubility such as 2, 5, 8, 13 (Table II) whereas the lowest final copper content, 19, 20, 23, 24, 25 (Table II) was found under slags which certainly do not have a very high solubility for cuprous oxide but presumably a higher oxygen ion activity.

OXYGEN INJECTION OF GOLD-COPPER AND GOLD-SILVER-COPPER ALLOYS

The above tests had shown that contrary to expectation a considerable proportion of the copper could be removed from silver-copper alloys by oxygen injection under soda-boric oxide-silica slags.

In an attempt to throw further light on the relative effects of the solubility of copper oxide in the slag and the variation in oxygen ion activities, tests were carried out using slags of various characteristics but using molten alloys with a high gold content. Injection of oxygen into molten gold-copper alloys held under such slags would supply information on the effect of the slag composition on copper removal in the absence of silver, i.e., the system would be sensitive to copper oxide solubility in the slag. The additions of silver to the alloys would then indicate the effect of dissolved oxygen in the alloy, i.e., the system would be sensitive to the oxygen ion activity of the slag.

The slags selected for these tests had compositions corresponding with slags 1, 8, and 19, as given in Table II. From the previous tests it had been shown that slag 1 had a high solubility for cuprous oxide and a low oxygen ion activity, slag 19 had a high oxygen ion activity but low solubility for cuprous oxide, while slag 8 was intermediate in character.

The oxygen injection tests were conducted for periods of 90 minutes on charges containing 100 g of alloy and 100 g of slag. The first series of tests was carried out using a gold-8 per cent copper alloy and in a subsequent series of tests the gold alloy contained 8 per cent copper and 10, 20, and 30 per cent silver respectively. The results are presented in Figures 7 and 8.

Evidently changes in slag composition, and hence changes in cuprous oxide solubility and oxygen ion activity, have little effect on copper removal in the absence of silver in the alloys. Figure 7 also shows clearly that the removal of copper from gold bullion increases with the increase in the silver content of the
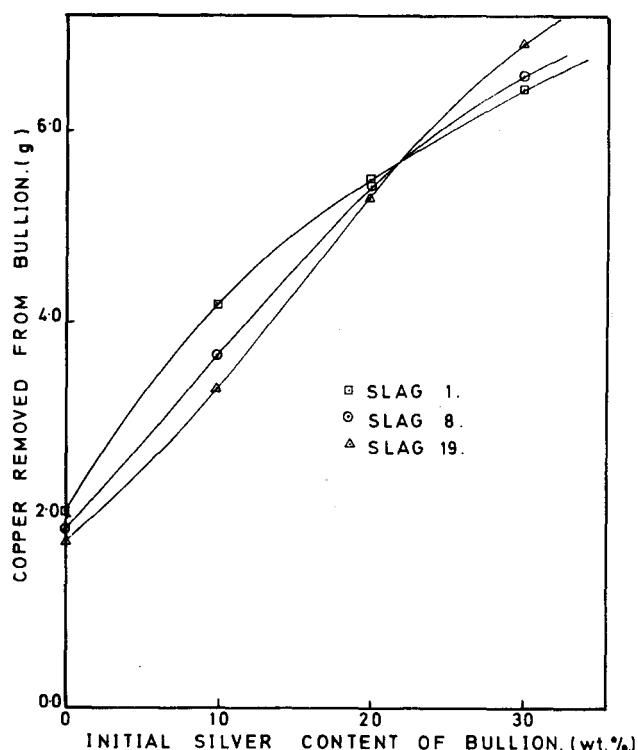

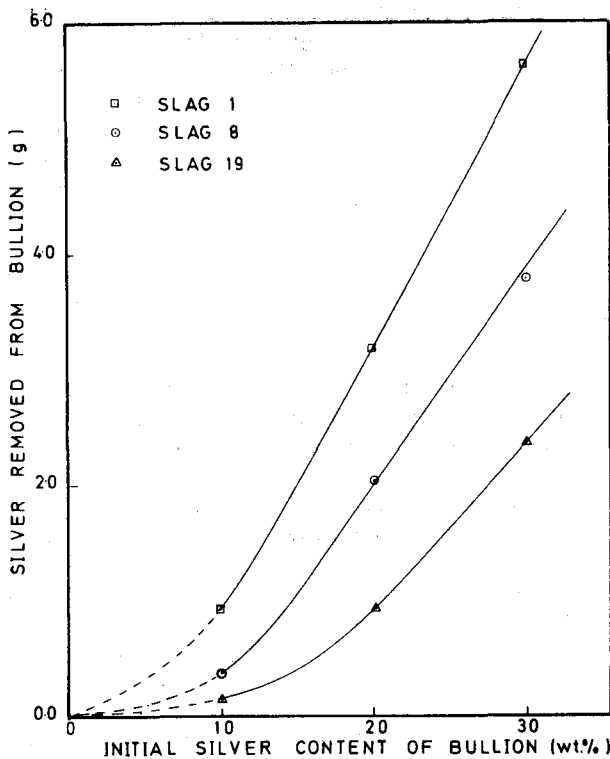Fig. 7—Copper removal by oxygen injection of Au- O to 30% Ag-8% Cu alloys under soda-borosilicate slags.

Fig. 8—Silver loss to soda-borosilicate slags during oxygen injection into Au-O to 30% Ag-8% Cu alloys.

bullion. The position of the curve for slag 19 indicates that the oxygen ion activity in the slag assumes greater importance in the removal of copper as the silver content of the bullion is increased. Using the slag with higher oxygen ion activity (slag 19), there is greater dissolution of oxygen in the bullion with increase in silver content of the bullion. Figure 8 illustrates the greater solubility of silver oxide in slag 1 which slag was shown earlier to a high solubility for cuprous oxide.

DISCUSSION

The structure of fused boric oxide (B_2O_3) proposed by Anderson et al[3], as a result of a study of infra red spectra, appears to be the most commonly accepted one. According to this study fused boric oxide consists of $(B_9O_{14})^-$ complexes held together by hydrogen bonds. One of the nine boron atoms in the complex is tetrahedrally coordinated; the other boron atoms are triangularly coordinated. Each tetrahedron shares a corner with BO_3 triangles in pairs. Each of the pairs of BO_3 triangles shares additional corners with another pair of BO_3 triangles.

When soda is added to a melt of boric oxide there is an increase in the number of BO_4 tetrahedra and B-O-B linkages and a continuous network is approached. Additions of soda up to 15 per cent change the coordination number of boron atoms from 3 to 4 and the spatial distribution results in the lowest energy structure
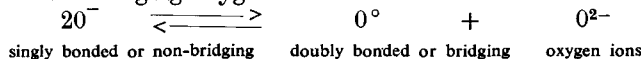
$$(BO_3)^{3-} + O^{2-} \qquad = \qquad (BO_4)^{5-} \quad . \quad . \quad 6$$

triangular coordination   tetrahedral coordination
As the soda content is increased above 15 per cent by

weight, the energy requirements change and non-bridging oxygen ions occur.

The structure of fused silica on the other hand comprises a continuous network due to both the high cation field strength of the silicon cation and its four-fold coordination with oxygen. Additions of soda to this structure result immediately in the progressive formation of non-bridging oxygen ions

$$2O^- \quad \underset{<}{\overset{---->}{=\!=\!=}} \quad O^\circ \quad + \quad O^{2-}$$

singly bonded or non-bridging   doubly bonded or bridging   oxygen ions

The structure of borosilicate melts was deduced by Riebling[4]. At low concentrations of silica, the boric oxide exhibits normal solvent behaviour with the silicon atoms widely separated. When additions of silica reach 10 to 20 mole per cent the solution shows a departure from ideality and it would appear that microclusters of silica are formed, an effect which persists until the silica content reaches 60 mole per cent. Above 60 mole per cent silica the boron atoms remain clustered and/or are forced to accept a tetrahedral configuration with the silica approaching extensive network formation.

The addition of soda to borosilicate melts has the effect of decreasing the microclustering of the silica since the coordination of the boron atoms is changed to a tetrahedral type similar to that of silicon in silica. This change in coordination of the boron occurs in preference to the formation of non-bridging oxygen ions in the silica because of the lower energy requirements. However, as the silica content is increased the amount of soda reacting in this manner decreases from the maximum of 15 per cent for pure boric oxide and nonbridging ions occur with lower soda contents.

Hence, a slag with a high boric oxide content should have greater solubility for modifying oxides than one with a high soda and/or silica content. This is attributed to the lower energy requirements of the change in coordination of the boron from 3 to 4 as opposed to the formation of non-bridging oxygen ions when the content of silica or modifying oxide is high. The lower energy requirements lead to a lower activity of the modifying oxide in the melt with accompanying greater solubility. The results in Table I confirm the suggestion made above in that the solubility of the copper oxides in the slags decreased with increase in soda or lime and with increase in silica content.

Pearce[5, 6] established that the oxygen ion activity in a soda-boric oxide melt is lower than that of a similar soda-silica melt by a factor of six. This is verified by the results presented in Table II where oxygen evolution from the silver button occurred only if the slag used during the oxygen injection test was relatively low in boric oxide content. It would appear that slags of higher free oxygen ion activity increase the partial pressure of oxygen in the system. This results in a greater amount of oxygen being dissolved in the silver with a consequent increase in activity of the oxygen in the alloy. Therefore, a greater amount of copper is oxidised and removed from the alloy — the silver in the alloy acting as an oxygen carrier. The importance of the free oxygen ion activity of the slags was confirmed by tests in which the oxygen lance was immersed to only half the depth of the slag layer so that no direct contact occurred between

the oxygen gas and the bullion. Under these conditions the final copper content of silver-5 per cent copper alloys was reduced to 2,63 per cent, 4,50 per cent and 4,10 per cent when using slags 19, 1 and 8 respectively. The oxygen ion activity of slag 19, which is high in soda and silica content, therefore, permits it to transfer oxygen to the silver far more readily than do slags 1 and 8 which have higher boric oxide contents.

There is a striking parallel between the results obtained in these tests and the transfer of oxygen from the furnace atmosphere through the slag to the molten steel bath in the conventional open-hearth process for steel refining.

CONCLUSIONS

In the case of gold bullions containing up to 8 per cent copper the test work has shown that only 20 to 25 per cent of the copper may be removed by oxygen injection when no silver is present. Changes in the characteristics of the slags appear to have very little effect on the proportion of copper removed.

When silver is present in the gold bullion the removal of copper increases almost linearly with increase in the silver content reaching a maximum of over 80 per cent when the bullion contains 30 per cent silver. The maximum removal of copper occurs with the use of a slag characterised by a high oxygen ion activity, this property being apparently of greater significance than the ability of the slag to dissolve cuprous oxide.

Removal of copper from copper-silver alloys and from gold-silver-copper alloys is always accompanied by a loss of silver to the slag, the loss increasing proportionately with the silver content of the alloy. This loss of silver is however markedly dependent on the oxygen ion activity of the slag and to a lesser degree on the solubility of copper and silver oxides.

The results tabulated below show the effect on copper removal and loss of silver by using slags with different characteristics.

On a practical basis the loss of silver to the slag presents a serious problem, as one of the main objects of the oxygen injection process is to remove from the bullion all the impurity elements leaving the silver to be recovered as a high quality by-product either by chlorination or electrolysis of the bullion.

REMOVAL OF COPPER AND LOSS OF SILVER TO THE SLAG

WHEN TREATING A GOLD-COPPER-SILVER BULLION CONTAINING 30 PER CENT SILVER

No.	SLAG		REMOVAL OF COPPER FROM BULLION Per cent	LOSS OF SILVER TO SLAG Per cent
	Oxygen Ion Activity	Solubility for Cu_2O		
1	Low	High	80	19
8	Intermediate	Intermediate	81	12,5
19	High	Low	85	7,5

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