RECOVERY OF COPPER AND COBALT FROM INDUSTRIAL SLAG BY TOP-SUBMERGED INJECTION OF GASEOUS REDUCTANTS

Xun An, Nan Li and Eric J Grimsey

Department of Minerals Engineering and Extractive Metallurgy
Western Australian School of Mines
Private Mail Bag 22
Kalgoorlie, Western Australia 6430

Abstract

Slag from an electric slag cleaning furnace was injected with methane and air mixtures to facilitate the recovery of copper and cobalt. The effects of methane-to-air ratio, gas flow rate and temperature on the reduction and metal separation were investigated. The results showed that over 90 percent copper and up to 60 percent cobalt could be recovered from the slag with a gas utilisation of around 70 percent, as calculated by thermodynamic simulation. Methane-to-air ratio was a major factor affecting the rate of reduction under the present experimental conditions. Further, injection of gaseous reductants greatly enhanced the coalescence and settling of entrained metal droplets. A reduction mechanism is proposed and the factors influencing the coalescence of copper droplets are discussed.

Introduction

Direct-to-Blister flash smelting technology has been used to treat high grade copper concentrate at the Olympic Dam Operations of WMC Resources Ltd in South Australia. The process is operated at oxygen pressures of around $10^{-5.5}$ atm, higher than a conventional flash furnace, in order to eliminate the majority of sulphur from the concentrate. As a result, metal loss in slag can exceed 20 percent copper, with up to 12 percent as cuprous oxide and the remainder as entrained metallic copper prills [1].

The recovery of metal from slag is undertaken in a conventional electric furnace in which a surface layer of coke is used to reduce metal oxides, with metal being recovered after settling through the slag layer. These processes are relatively slow because reduction is inhibited by the limited area of contact between coke and slag, and because settling is not enhanced through the forced coalescence of fine droplets. Thus, conventional electric slag cleaning can represent a bottleneck when coupled with a high intensity smelting process such as that used by WMC Resources Ltd at Olympic Dam.

The opportunities for accelerating the existing slag cleaning process lie firstly with increasing the rate of chemical reduction and secondly with increasing the coalescence of metal droplets in the slag [2-4]. There have been a number of attempts to develop more efficient slag cleaning processes [5-10], with one of the most effective methods being the injection of gaseous or solid reductants into the molten slag bath. During injection, the reduction kinetics are increased significantly by the intense mixing of the reductants with slag [11-12]. Such injection processes may be carried out using a top-submerged lance in an existing slag cleaning furnace or in a purpose-designed intense smelting furnace, as used in the Sirosmelt/Ausmelt process [13-16].

Top-submerged injection of methane and air mixtures has been used in the experimental reduction of a commercial nickel slag [17]. The results showed that very effective reductions for nickel (90%), cobalt (70%) and copper (55%) were achieved within 30 minutes. The same method was used in the present work to investigate the chemical reduction of cuprous and cobalt oxides from the Direct-to-Blister copper slag of WMC Resources Ltd. A high level of physically entrained copper in the test slag (around 5%) also provided a good opportunity for observing droplet coalescence in a turbulent slag bath. Parameters studied included the total gas flow rate, methane-to-air ratio and temperature.

Experimental

<u>Materials</u>

The test slag was obtained by water granulation directly from the slag launder of the electric furnace at Olympic Dam, and was analysed by standard wet chemical methods for total iron, silica, magnesia, alumina, calcia, and total copper and cobalt. A selective dissolution phase analysis was carried out also to distinguish between dissolved oxides and entrained metals for both copper and cobalt. The slag contained 5.25 percent cuprous oxide plus entrained metal, with total copper being 10.0 percent. A valuable, but minor amount of cobalt oxide was present at 0.24 percent. The complete analysis of the slag is given in Table I.

Dried air and industrial grade methane (99.1 vol% CH_4 with 0.6 vol% N_2 as a major impurity) were injected into the slag through a lance. Methane was burned with oxygen in the lance to

form carbon monoxide and hydrogen gases prior to reduction according to the reaction:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad (1)$$

The stoichiometric ratio of methane-to-oxygen is 2:1 which represents a methane-to-air ratio of 0.43:1. Ratios greater than 0.43:1 will produce fine carbon from the cracking of methane.

Table I Composition of the slag used in reduction tests (in wt%)

Fe as FeO$_x$	SiO$_2$	MgO	Al$_2$O$_3$	CaO	CuO$_{0.5}$	Cu (total)	CoO	Co*	S
44.5	23.0	1.0	3.2	0.3	5.25	10.0	0.24	0.19	<0.02

* All cobalt present as oxide.

Apparatus

The experiments were carried out in a laboratory furnace with silicon carbide elements, as shown in Figure 1. The furnace temperature was controlled by a CAL9900 temperature controller within ± 2 °C. The slag was held in a magnesia crucible (64 mm O.D. × 58 mm I.D. × 142 mm high) which was covered by an alumina dish (78 mm I.D.). There were three holes in the dish and an alumina tube (15 mm O.D. × 11 mm I.D. × 30 mm high) was cemented into each hole to minimise slag spillage during the injection. A lance was introduced through the central hole of the dish and immersed in the slag. Other holes were used for temperature measurement and sampling. During a test the slag temperature was measured continuously using a type R thermocouple.
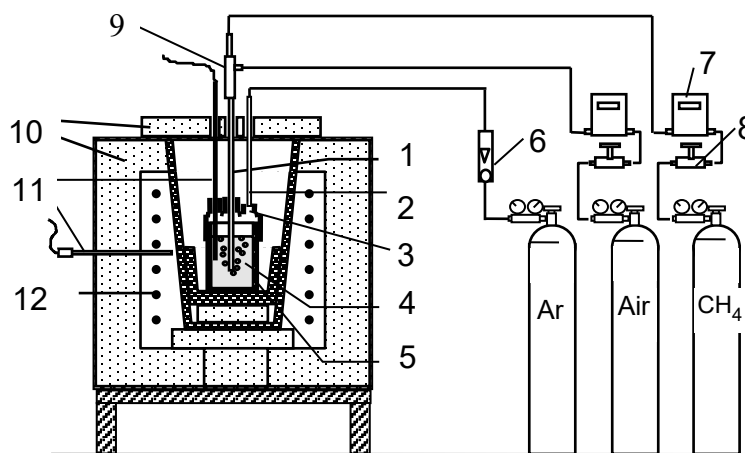

Figure 1: A schematic diagram of the experimental set-up used in the gaseous injection tests. 1 - Alumina lance; 2 - Argon inlet; 3 - Slag sampling hole; 4 - Molten slag; 5 - Magnesia crucible (enlarged); 6 - Rotameter; 7 - Mass flow meter; 8 - Metering valve; 9 - Three-way connector; 10 - Insulation bricks; 11 – Thermocouples; 12 - Furnace heating elements.

The required methane-to-air ratios were established by adjusting the individual gas flow rates using micro-metering valves and the flow rates were monitored with calibrated digital mass

flow meters. The injection lance consisted of an outside alumina sheath (8 mm O.D. × 5 mm I.D.) and an inside alumina tube (4 mm O.D. × 2 mm I.D.), as shown in Figure 2. A 1.2 mm hole was diamond drilled in the sheath to form a nozzle 10 mm above the base.
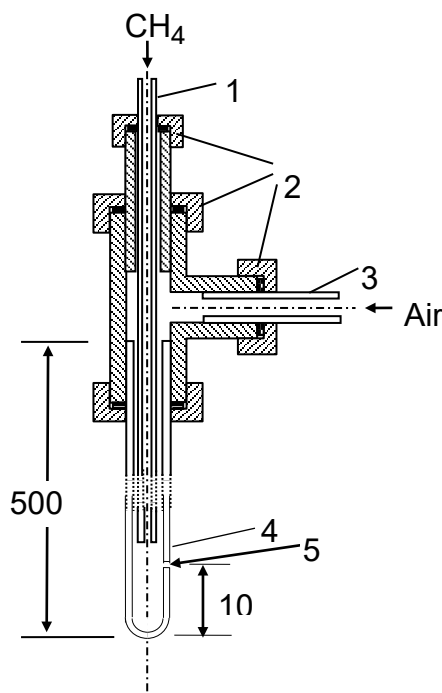

Figure 2: Cross section of the double lance used in the tests.
1 - Inside alumina lance for methane (1.5 mm I.D.);
2 - Lock nuts with Teflon seals; 3 - Alumina tube;
4 - Outside alumina lance for air flow (5 mm I.D.);
5 - Hole: 1 mm diameter.

Methane was delivered through the inside tube and air through the annulus. Both were pre-heated when they flowed through the hot lance. The methane was mixed with air and burned at around 10 mm below the opening of the inside tube. The best position for the opening of the inside tube was determined experimentally to be 100 mm above the bottom of the sheath. This provided sufficient space inside the lance for pre-combustion of methane prior to contact with slag. The depth of lance immersion in slag was around 40 mm below the slag surface.

Procedure

The crucible was charged with 500 grams of slag and heated in the furnace under a cover of high purity argon. When the desirable temperature was reached, the molten slag was homogenised by bubbling argon through an alumina lance for ten minutes. The methane and air then were adjusted to provide the desired gas ratio and total flow rate before the lance was lowered into the molten slag to start the injection. The reduction of cuprous and cobalt oxides during the injection was traced by slag sampling at intervals. Dip samples were taken on a stainless steel rod which was quenched into water. The samples then were dried and ground for chemical analysis. The injection lasted 50 minutes followed by settling for 60 minutes. During the first 30 minutes of settling, the slag was stirred by bubbling with high purity argon at 2

L/min. The copper which separated from slag formed a metal button at the bottom of the crucible. This was cleaned, weighed and chemically analysed after each test.

Results

Effect of methane-to-air ratio on reduction

Figure 3 shows the effect of methane-to-air ratio on the reduction of cuprous oxide at 1573 K. The ratios of 0.43:1, 0.6:1, 0.8:1 (at a total flow rate of 1 L/min) and 0.2:1 (at a total flow rate of 2 L/min) were used in the tests. It can be seen that the rate of reduction increased with an increase in methane-to-air ratio from 0.2:1 to 0.8:1. The injection generally was very effective for the reduction of cuprous oxide at all methane-to-air ratios. Around 81 percent cuprous oxide was reduced at a ratio of 0.2:1, and over 90 percent at higher ratios.
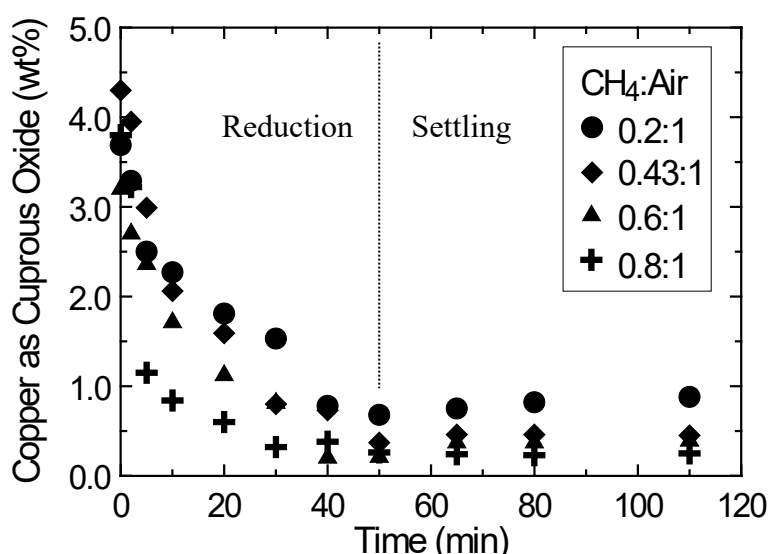
Figure 3: Effect of methane-to-air ratio on the cuprous oxide reduction. Total gas flow rate: 1 L/min for methane-to-air ratios of 0.43, 0.6, 0.8; Total gas flow rate: 2 L/min for methane-to-air ratio of 0.2; Temperature: 1573 K.

The decrease in total copper (oxide plus entrained metal) in the slag in the above tests is shown in Figure 4. Again, the rate increased as the methane-to-air ratio increased from 0.2:1 to 0.8:1. No metal was produced when pure argon was injected at 1573 K for 45 minutes, although there was around 5 percent metallic copper entrained in the original slag. It appears that the settling of metal droplets is enhanced by gaseous agitation only under reducing conditions.

Cobalt oxide began to reduce after 30 minutes of injection (Figure 5). An increase in the methane-to-air ratio from 0.43:1 to 0.8:1 significantly enhanced the extent of cobalt reduction with more than 50 percent of cobalt in slag being reduced at a ratio of 0.8:1.

Effect of total gas flow rate on reduction

Figures 5 and 6 show that the reductions of cobalt and cuprous oxides were almost unaffected by variation of the total gas flow rate from 1 to 2 L/min at a methane-to-air ratio of 0.43:1. A

flow rate of less than 1 L/min was difficult to control using the present equipment and there was little increase in reduction rate at a flow rate higher than 2 L/min.
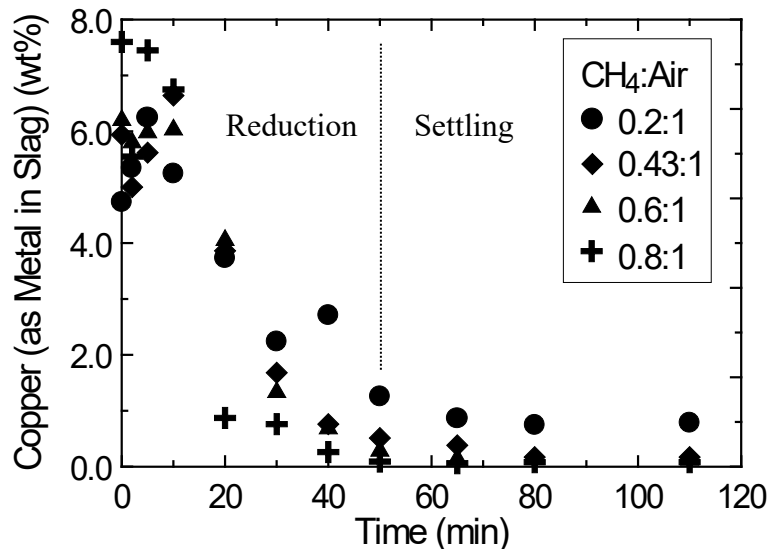

Figure 4: Effect of methane-to-air ratio on the total copper content (oxidised plus entrained). Total gas flow rate: 1 L/min for methane-to-air ratios of 0.43, 0.6, 0.8; Total gas flow rate: 2 L/min for methane-to-air ratio of 0.2; Temperature: 1573 K.
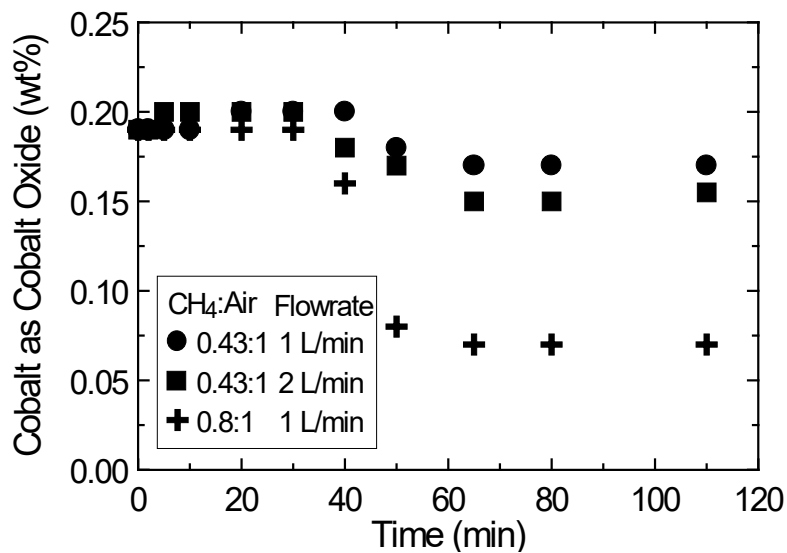

Figure 5: Effects of methane-to-air ratio and total gas flow rate on the cobalt oxide reduction. Temperature: 1573 K.

Figure 7 shows the decrease in total copper content in the slag at the total flow rates of 1 and 2 L/min and at a methane-to-air ratio of 0.43:1. The higher flow rate slightly enhanced copper separation from slag during the injection. This is presumably because of enhanced droplet

coalescence, since the same degree enhancement was achieved simply by blowing with argon at 2 L/min, for 30 minutes, after the end of reduction.
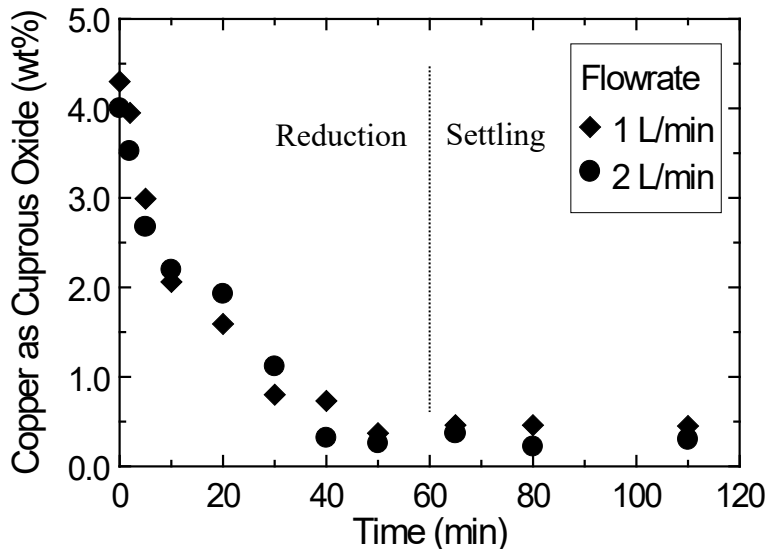

Figure 6: Effect of total gas flow rate on the cuprous oxide reduction. Methane-to-air: 0.43:1; Temperature: 1573 K.
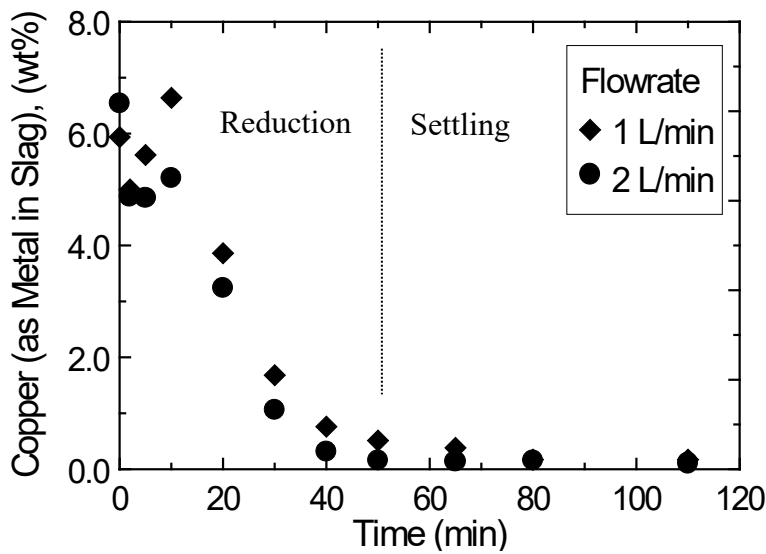

Figure 7: Effect of total gas flow rate on the total copper content (oxidised plus entrained). Methane-to-air ratio: 0.43:1; Temperature: 1573 K.

Effect of temperature on reduction

Figure 8 shows that, within experimental error, the rate of cuprous oxide reduction was independent of change in temperature from 1523 to 1623 K, at a methane-to-air ratio of 0.43:1 and total gas flow rate of 1 L/min.
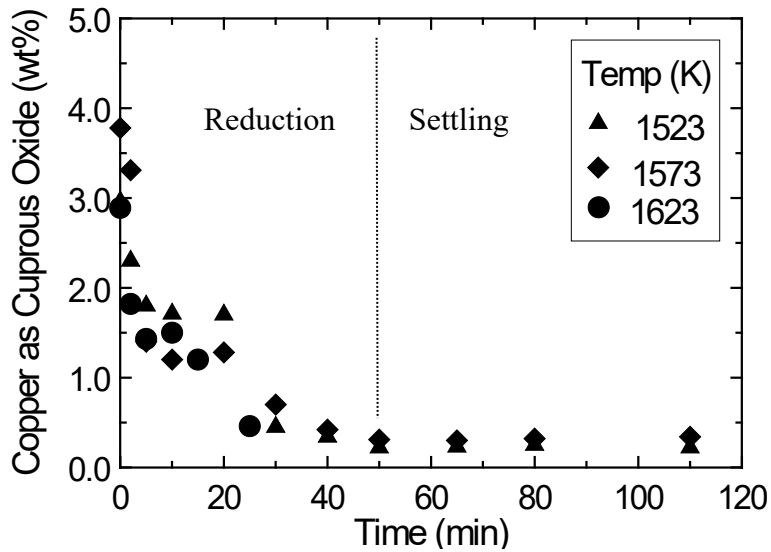
Figure 8: Effect of temperature on the cuprous oxide reduction. Total gas flow rate: 1 L/min: Methane-to-air ratio: 0.43:1.

Effects of methane-to-air ratio and gas flow rate on metal recovery

A copper alloy button was found at the bottom of the crucible after each test when the reducing gas was used. No metal button was formed where only pure argon was injected into the slag, for example, at 1 L/min for 30 minutes.

Figure 9 shows that the final weight of the metal button reduced from 500 grams of slag increased significantly with an increase in methane-to-air ratio from 0.2:1 to 0.8:1. A higher gas flow rate (2 L/min) also increased the mass of the metal button as a result of contamination with iron and cobalt, as discussed below.
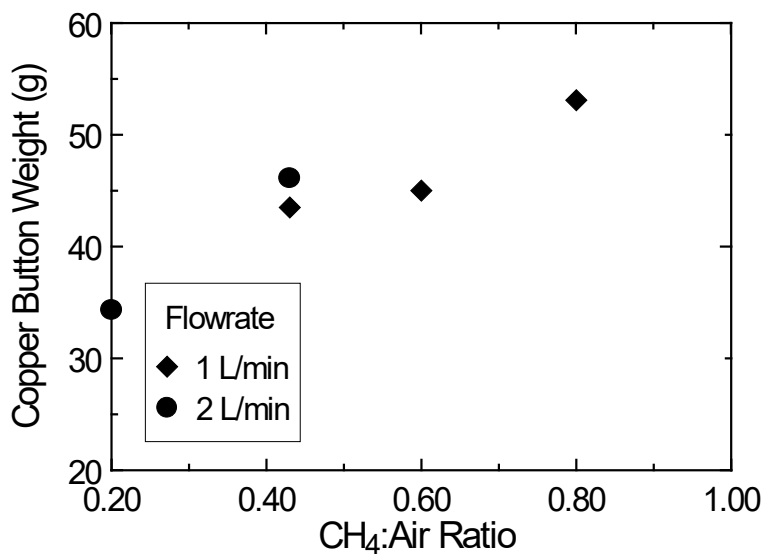

Figure 9: Weight of copper alloy button produced from reduction of 500

grams of slag.

Figures 10 and 11 show the respective cobalt and iron levels in the copper button as a function of methane-to-air ratio at total flow rate of 1 L/min. The data for one test at 2 L/min are included also. The figures show that the cobalt and iron contents increase slightly with increase in methane-to-air ratio from 0.43:1 to 0.6:1, and significantly with increase in the ratio from 0.6:1 to 0.8:1. The one test at 2 L/min shows that the contamination of cobalt and iron is enhanced significantly with an increase in the total gas flow.
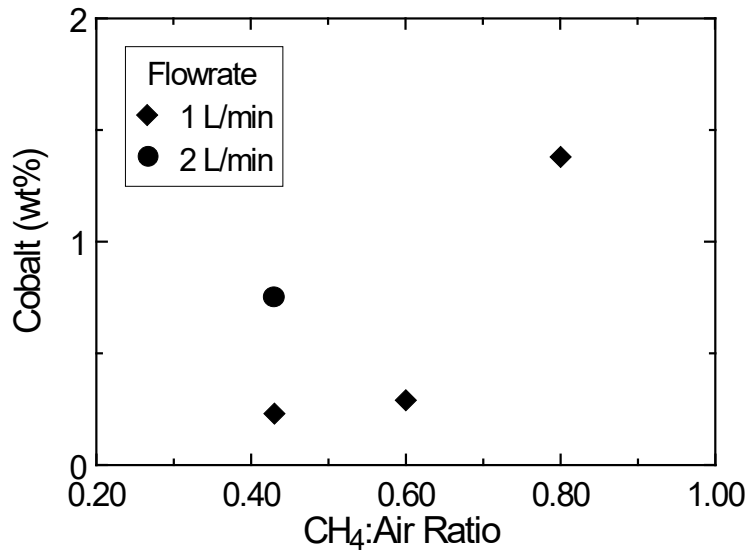

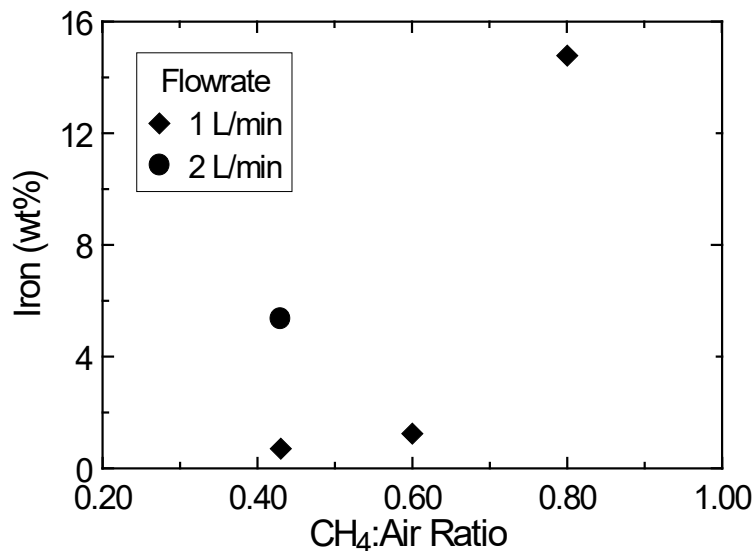Figure 10: Cobalt content in the copper alloy button produced from reduction of 500 grams of slag.

Figure 11: Iron content in the copper alloy button produced from reduction of 500 grams of slag.

Discussion

Reduction of metal oxides

The process was characterised by the reduction of cuprous oxide prior to cobalt oxide (Figure 5). This may be expected since not only is cuprous oxide less thermodynamically stable than cobalt oxide [18], the concentration of cuprous oxide in slag was more than 20 times higher than that for cobalt oxide. It is possible that the reduction proceeds in two stages with different mechanisms, and the reduction of iron oxides plays an important role in both stages of reduction.

In the first stage, cuprous and iron oxides are co-reduced. Since there is more than 4 percent copper (as cuprous oxide) in the slag, cuprous oxide should have a chance to be reduced by CO and H_2 at the gas-slag boundary. However, the reduction of ferric to ferrous ions could dominate because the iron content in the slag is much higher than copper (Cu/Fe ratio is 1:9). As the ferric/ferrous ratio falls, the oxygen potential of the slag is lowered. Under these conditions, cuprous oxide could be reduced by ferrous ions as a secondary reductant in the bulk slag [2], namely:

$$Cu^+ + Fe^{2+} \rightarrow Cu + Fe^{3+} \tag{2}$$

This would occur at any nucleation sites, such as on the surface of copper droplets. The reduction of cuprous oxide by CO and H_2 may be significant initially, but the secondary reduction with ferrous ions will become dominant as the copper content decreases. The oxygen potential in the first stage is not low enough for cobalt oxide reduction.

When the copper content in the slag falls below around 0.5 percent, the second stage of reduction begins. Because both copper and cobalt levels are low in the slag, the reduction of iron oxides by CO and H_2 again dominate. It is possible that the reduction of ferrous oxide to metallic iron at the gas-slag boundary begins to occur, as the slag becomes more reducing. The metallic iron then is released as small particles when the bubbles leave the slag surface. These iron particles are mixed into the bulk slag and act as secondary reductant for cobalt and copper via the reactions:

$$Co^{2+} + Fe \rightarrow Co + Fe^{2+} \tag{3}$$

$$2Cu^+ + Fe \rightarrow 2Cu + Fe^{2+} \tag{4}$$

The above reactions presumably occur at the surface of the particles. This results in iron-cobalt-copper alloy particles in the bulk slag. A thermodynamic simulation (details are given later) was carried out for the reduction with the methane-to-air ratio of 0.43 at 1 L/min (presented in Figure 5 as full circles) and predicted that the oxygen pressure should be 1.15×10^{-11} atm and

the ferric/ferrous ion ratio should be around 0.032 at the beginning of the second stage (after 30 min reduction). The reduction of pay metals with metallic iron in the bulk was observed also in the electric furnace reduction of a commercial nickel slag [19]. Here it was found that the significant reduction of pay metal oxides occurred only when the ferric/ferrous ion ratio fell to 0.04 or below. This is consistent with the above predictions.

The rates of reduction of cobalt and cuprous oxides were found to be influenced little by an increase of the flow rate of reducing gases from 1 to 2 L/min (Figures 5, 6). This may be due to two factors, firstly the gas-slag interfacial area was not increased significantly as the gas flow rate was doubled, and secondly the reduction of these oxides was kinetically limited by mass transfer within the gas bubble. An increase of flow rate from 1 to 2 L/min may result in channelling effect and a low gas utilisation. Consequently, the increased amount of the reducing gases was not utilised in the process.

Since the interfacial chemical reaction would be relatively rapid at a high temperature, and the bulk slag would be well mixed by the action of injected gas bubbles, the transport of gas to the boundary within the bubble is most likely to be the rate controlling step. A similar conclusion was reached when a commercial nickel slag was subjected to gaseous reduction [17]. Here it was found that the reduction rate increased both with a decrease in nozzle size and an increase in depth of lance immersion. Both observations indicated that the gas bubbles and bulk slag had not achieved complete equilibrium before the bubbles left the surface.

Figure 8 showed that the reduction of cuprous oxide is independent of temperature increase within experimental error, as was observed also for the gaseous reduction of nickel oxide from slag [17]. This is consistent with transport control rather than chemical control.

Figures 10 shows that, in contrast to the reduction of cobalt oxide, the recovery of cobalt into the copper button is significantly enhanced by an increase in the gas flow rate. A simultaneous increase in iron content in the copper button (Figure 11) suggests that the copper button must act as a collector for the alloy particles (formed in the second stage of reduction) when it was moved through the slag by the action of gas injection. As the gas flow rate was increased, more alloy particles would be rounded up by the moving copper button due to a better contact between them. During this process, a small amount of copper (around 2% of the button weight) was recovered also.

A major factor affecting the process was the methane-to-air ratio. The reductions of metal oxides were enhanced as the methane-to-air ratio was increased beyond the stoichiometric value for combustion of 0.43:1 (Figures 3, 5). Under these conditions, the excess methane would be decomposed to fine carbon, which would drive the reduction through the regeneration of carbon monoxide via the Boudouard reaction, namely:

$$CO_2 + C \rightarrow 2CO \tag{5}$$

The recovery of both iron and cobalt into the copper button was increased also at higher ratios (Figures 10, 11) because more alloy particles was formed under stronger reducing conditions.

Thermodynamic simulation of reduction

A thermodynamic simulation was carried out to predict the behaviour of cuprous oxide during the reduction and to estimate the utilisation of the gaseous reductants. The simulation was based on a stepwise concept that has been used successfully by the present authors [17] and others [20-22] to simulate multiphase reaction kinetics.

If gas transport to the boundary within the bubble is assumed to be slow, a chemical equilibrium would be achieved only between the slag and an envelope of gas at the boundary within the bubble. Thus the amount of gas used in the reduction is a fraction of the total gas injected. This may be quantified by defining the degree of equilibrium attainment (D_e), namely:

$$D_e = \frac{\text{Moles of gas equilibrated with slag}}{\text{Total moles of gas injected into slag}} \qquad (6)$$

The value of D_e is assumed to be independent of slag composition. This parameter represents the gas utilisation in the process.

The equilibrium calculation was performed using STEPSOL [23], a public domain pyrometallurgical process modeller. The program uses the Solgasmix algorithm of Eriksson to find the equilibrium composition for a given mass balance. The thermodynamic data required for the calculation are the free energies of formation of each species in all phases and the parameters for the melt activity models. The details of the slag and alloy models used in this work are reported elsewhere [17, 23]. All gases were assumed to be ideal.

The simulation was performed in a series of steps. Small amounts of methane and air were allowed to enter the reaction system as input for each step and were removed after they reached equilibrium with the slag. STEPSOL automatically carried out the calculation for a specified number of steps and generated a data file containing the equilibrium compositions of all phases in each step.

Figures 12 and 13 show the simulated curves along with the experimental points for cuprous oxide reduction. They are in good agreement when a gas ultilisation of around 70 percent is assumed. The simulation predicted that the rate of cuprous reduction is affected significantly by the methane-to-air ratio, but not by temperature.

Coalescence and separation of copper droplets from slag

A microscopic examination of the slag samples showed that metallic copper existed as 10-100 μm droplets in the original slag. A significant number were surrounded by solid coatings of magnetite, probably arising from oxidation-reduction reactions of the type:

$$2CuO_{0.5} + 3FeO \rightarrow 2Cu + Fe_3O_4(s) \qquad (7)$$

Similar coatings have been observed by other workers [24].

The separation of fine droplets (<100 μm) from the slag would require their effective

coalescence into larger drops. If the droplets are brought together by agitation, coalescence will occur if the film of slag between them is drained away before the agitation separates the droplets again [25]. Thus in the Vanyukov Process [26-27] it was found that injection was effective for coalescence within a certain range of mixing power input. Below this range the droplets would not coalesce, and above it they would shear into smaller droplets. Coalescence also is affected by the viscosity of slag and the interfacial tension of metal and slag phases since these affect the drainage rate of slag between contacting droplets. A decrease in slag viscosity and increase in interfacial tension will improve the conditions for drainage of slag film as well as for the collision of metal droplets [27].
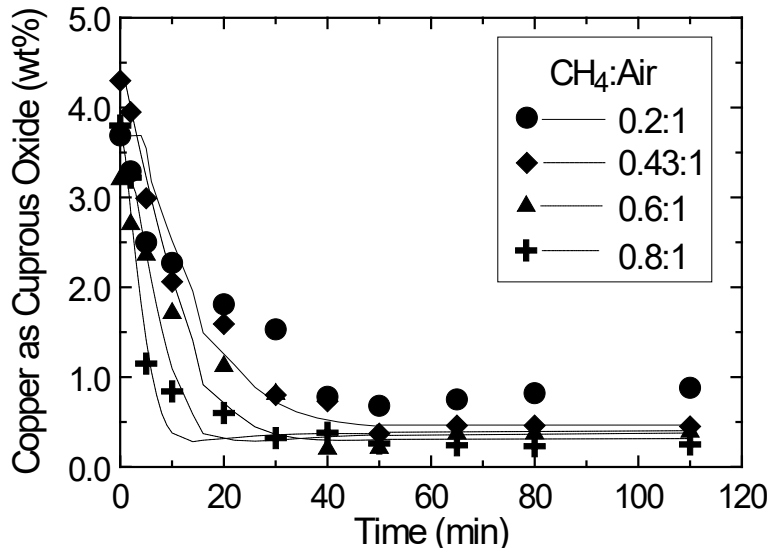

Figure 12: Experimental data versus simulated curves for various methane-to-air ratios. Total gas flow rate: 1 L/min for methane-to-air ratios of 0.43:1, 0.6:1, 0.8:1; Total gas flow rate: 2 L/min for methane-to-air ratio of 0.2:1; Temperature: 1573 K. 70 percent gas utilisation is assumed in the simulation.
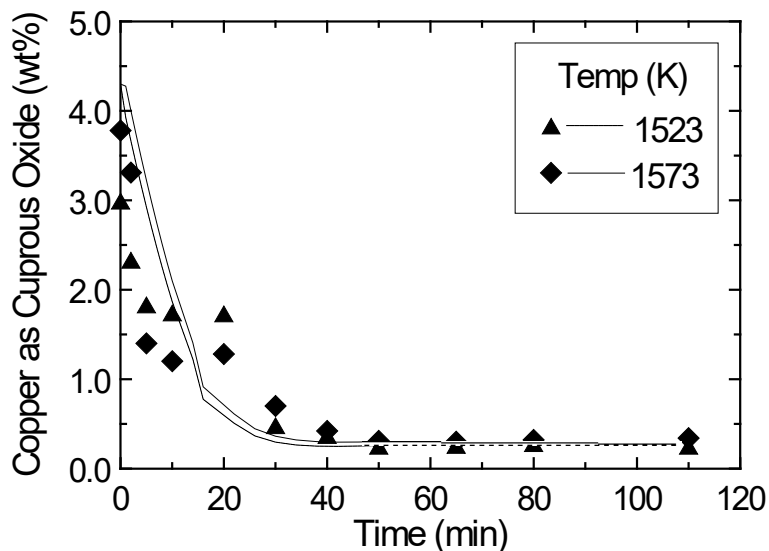

Figure 13: Experimental data versus simulated curves for different temperatures. Gas flow rate: 1 L/min; Methane-to-air ratio: 0.43:1. 70 percent gas utilisation is assumed in the simulation.

When the present melt was stirred by gaseous injection of inert argon, there was no coalescence and settling of the 5 percent of metallic copper known to be entrained in the slag. Coalescence was probably inhibited both by the presence the solid magnetite rims and also by the relatively high viscosity of the slag as a result of a high ferric oxide content.

When the reducing gas was injected into slag, the total copper content was found to decrease rapidly and the settling of metal droplets in slag apparently was not a limiting step for metal recovery. Figures 4 and 7 illustrates a rapid fall in the total copper content of the slag which implies both an effective settling of the primary entrained metal droplets, as well the secondary reduced metal droplets. The latter can form initially as fine metal dispersions if the metal films formed around gas bubbles by reduction, rupture within the slag bulk [28-29]. The present results indicate that the reduction of magnetite by injected gas facilitates metal droplet coalescence in the agitated melt. It is noteworthy that a significant drop in the slag viscosity was observed after the blowing of reducing gas for around 10 minutes, and this was accompanied by a significant drop in the ferric iron content of the slag, as determined by chemical analysis.

Conclusions

(1) The electric furnace slag from WMC Resources Ltd, Olympic Dam Operations in South Australia has been reduced by injection of methane and air mixtures and the effectiveness of this process has been investigated. A slag containing 5 percent cuprous oxide and 0.24 percent cobalt oxide was reduced at methane-to-air ratios from 0.2:1 to 0.8:1 and 1573 K. The results showed that over 90 percent cuprous oxide and up to 60 percent cobalt oxide were recovered from the slag after 30 minute reduction. Under the present experimental conditions, the process was affected mainly by the methane-to-air ratio. The effects of total gas flow rate and temperature were only minor.

(2) A thermodynamic simulation showed that gas utilisation for the reduction was around 70 percent.

(3) The coalescence of copper droplets was enhanced by injection of reductant, since the copper droplets entrained in a solid magnetite phase were liberated as the magnetite was reduced. The injection also increased the frequency of droplet collision and promoted coalescence. A significant decrease in slag viscosity due to the ferric ion reduction would enhance coalescence also.

Acknowledgements

References

1. A.K. Biswas and W.G. Davenport, Extractive Metallurgy of Copper (England: Pergamon Press, 1980).

2. J.M. Floyd and P.J. Mackey, "Developments in the Pyrometallurgical Treatment of Slag: A Review of Current Technology and Physical Chemistry", IMM Symp. Extractive Metall.'81, (London: IMM, 1981), 345-371.

3. P.J. Mackey, "The Physical Chemistry of Copper Smelting Slags - A Review", Can. Metall. Quarterly, 21 (1982), 221-260.

4. W.R.N. Snelgrove and J.C. Taylor, "The Recovery of Values from Non-Ferrous Smelter Slags", Can. Metall.Quarterly, 20 (1981), 231-240.

5. C.C. Banks and D.A. Harrison, "The Recovery of Non-Ferrous Metals from Secondary Copper Smelter Discard Slags", Can. Metall. Quarterly, 14 (1975), 183-190.

6. S.C.C. Barnett and J.H.E. Jeffes, "Recovery of Nickel from Thompson Smelter Electric Furnace Slag", Trans.IMM (Section C: Min. Proc. Extr. Metall.), 86 (1977), 155-157.

7. P.R. Ammann, J.J. Kim and T.A. Loose, "The Kennecott Process for Nickel-Slag Cleaning", Journal of Metals, 1979, no. 2: 20-25.

8. O. Addemir, J. Steinhauser and W. Wuth, "Copper and Cobalt Recovery from Slags by Top-Injection of Different Solid Reductants", Trans. IMM (Section C: Min. Proc. Extr. Metall.), 95 (1986), 149-155.

9. Y. Mori and T. Kimura, "Cleaning of Copper Converter Slag by Coal Injection", Metall. Review MMIJ, 3 (3) (1986), 141-154.

10. W.R.N. Snelgrove and J.C. Taylor, "The Recovery of Values from Non-Ferrous Smelter Slags", Can. Metall.Quarterly, 20 (1981), 231-240.

11. J.M. Floyd and D.S. Conochie, "SIROSMELT - The First Ten Years", Symp. Extractive Metall. (Melbourne, Australia: AusIMM, 1984), 1-8.

12. J.M. Floyd, "Submerged Bath Smelting Applied to the Non-Ferrous Metal Industry", Paul E. Queneau Int. Symp. Extractive Metall. Copper, Nickel and Cobalt, vol. I (TMS, 1993), 473-487.

13. J.M. Floyd, "Nickel Slag Cleaning", Can. Patent, (1976), No. 998246.

14. J.M. Floyd, G.J. Leahy, R.L. Player, and D.J. Wright, "Submerged Combustion Technology Applied to Copper Slag Treatment", AusIMM Conf. (North Queensland, Australia, AusIMM, 1978), 323-327.

15. J.M. Floyd and D.S. Conochie, "Reduction of Liquid Tin Smelting Slags: 1 - Laboratory Investigations", Trans. IMM (Section C: Min. Proc. Extr. Metall.), 88 (1979), 114-122.

16. J.M. Floyd and D.S. Conochie, "Reduction of Liquid Tin Smelting Slags: 2 - Development of Submerged Combustion Process", Trans. IMM (Section C: Min. Proc. Extr. Metall.), 88 (1979), 123-128.

17. X.Y. Yan, N. Li and E.J. Grimsey, "Reduction of Waster Slags using Top-Submerged

Injection of Gaseous Reductants", 5th International Conference on Molten Slags, Fluxes and Salts'97 (Sydney, Australia: TMS-AIME, 1997), 135-145.

18. S.S. Wang, N.H. Santander and J.M. Toguri, "The Solubility of Nickel and Cobalt in Iron Silicate Slags", Metall. Trans., 5 (1974), 261-265.

19. I. Dal, N. Li and E.J. Grimsey, "The Reduction of Nickel Slag by Graphite Electrodes with AC and DC currents", Nickel and Cobalt'97, vol. II, ed. C.A. Levac and R.A. Berryman (Subary, Ontario: The Metallurgical Society of CIM, 1997), 77-92.

20. D.G.C. Robertson, B. Deo, and S. Ohguchi, "Multicomponent Mixed-Transport-Control theory for Kinetics of Coupled Slag/Metal and Slag/Metal/Gas Reactions: Application to Desulphurization of Molten Iron", Ironmaking and Steelmaking, 11 (1984), 41-55.

21. P.J. Mackey and M. Nagamori, "Stepwise Equilibrium Simulation of Zinc Fuming from Reverberatory Slag with CO Gas", H.H. Kellogg Int. Symp. Quantitative Description of Met. Extraction Processes (TMS, 1991), 111-125.

22. B.S. Terry and C.L. Harris, "Kinetics of Reduction of Metal Values from Fayalite-Based Slags - Part 2: Modelling of Idealised Slag-Cleaning Conditions", Trans. IMM (Section C: Min. Proc. Extr. Metall.), 104 (1995), 92-101.

23. E.J. Grimsey and A.E. Morris, "Activity Models for Pyrometallurgical Processes Using STEPSOL", AusIMM Extractive Metall. Conf. (Perth, Australia: 1991), 257-261.

24. E. Almendras, D. Cordero, C. Diaz, A. Luraschi, J. Manriquez, G. Sanchez and T. Utigard, "Reduction Kinetics of El Teniente Converter Slags", Proceedings of International Symposium: Challenges in Process Intensification, ed. C.A. Pickles (Toronto: The Metallurgical Society of CIM, 1996), 437.

25. G.V. Jeffreys and G.A. Davies, 1971. "Coalescence of Liquid Droplets and Liquid Dispersion", Recent Advances in Liquid-Liquid Extraction, ed. C. Hanson (Pregamon Press, 1971), 495.

26. A.G. Hunt, A.A. Komkov and M.L. Sorokin, "A Preliminary Comparison of the Vanyukov Process and Flash Smelting for the Smelting of Nickel Concentrate", Extractive Metallurgy of Gold and Base Metals (Kalgoorlie, Western Australia: AusIMM, 1992), 421-425.

27. A.D. Vaskevich, L.V. Schwartzer, N.A. Miklin and E.A. Pashkova, 1988. "The Patterns of Fragmentation and Coalescence of Matte Droplets in the Vanyukov Process" (in Russian), Tsvet Metally, 29 (1988), 29-32.

28. D.R. Poggi, R. Minto and W.G. Davenport, "Mechanisms of Metal Entrapment in Slags", Journal of Metals, 1969, no. 11: 40-45.

29. R. Minto and W.G. Davenport, "Entrapment and Flotation of Matte in Molten Slag", Trans. Inst. Min. Metall. (Section C: Min. Proc. Extr. Metall.), 81 (1972), 36-42.