



Factors influencing base metal recovery from waste reverberatory furnace slags in a 50 kVA laboratory DC plasma arc furnace

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Synopsis

The recovery of cobalt and copper from waste slag was studied in a plasma DC-arc furnace in reducing conditions. Three fluxes, CaO, CaF₂, and TiO₂, were investigated for their influence on selective recovery of cobalt into an iron-rich alloy. A further investigation on the influence of furnace power on the reduction of slag to recover cobalt to the alloy showed that a change in power setting had an unexpected effect on the recovery of metals to the alloy, in that selectivity of base metal recovery over iron recovery decreased at an increased power level.

Keywords: DC-furnace, reduction, nonferrous, slags

Introduction

The pyrometallurgical recovery of cobalt from waste copper slags is one of the recent advancements in nonferrous extractive metallurgy. The most recent technologies apply DC Plasma arc furnace technology to recover nonferrous metals. This technology has come with its challenges in both equipment configuration and the optimization for maximum recovery of valuable metals, as reported by Jones *et al.*, (1997). The main feature of this study is the application of this type of technology at laboratory scale to investigate the selective recovery of cobalt under three different flux types. It is an extension of the work conducted in a tube furnace and reported elsewhere (Banda *et al.*, 2002).

Mechanisms of reduction of slag by carbon have been investigated and have shown that the limiting reaction is probably the Boudouard reaction. From tube furnace studies on the carbothermic reduction of Zambian copper-dump slags, it was concluded that carbon-based reduction is only effective up to a certain level, after which excessive amounts would be required for complete recovery of the pay-metals. The selective recovery was found to be dependent on the chemistry modification of the slag (Banda *et al.*, 2002). The effects of MgO and Al₂O₃ on fayalitic slags that have been investigated have focused on the liquidus

temperature of the slag (Zhao *et al.*, 1999a, 1999b).

The fluxes used in this study are, however, focused on selectively influencing the activity of FeO_x, SiO₂ and CoO in the slag. It has been shown that activity coefficient of CoO increases when CaO substitutes SiO₂ and it decreases with an increase in SiO₂. The amount of SiO₂ in the fayalitic slag from the reverberatory furnace is very high, and further addition of silica to the slag would not have much influence on the activity of CoO or FeO_x. However, since the molten slag would contain free ions of Fe and Co, it is thought that a good slag modifier (from a selectivity perspective) should be one that would selectively reduce the activity of FeO in the slag and consequently reduced the Fe content in the alloy, and will not be reduced significantly itself.

Published research on the behaviour of TiO₂ in slags may help to predict its effect in the molten fayalitic slags under reducing conditions. According to Tranell *et al.* (2002), the Raman spectroscopic shows that Ti⁴⁺ has a tetrahedral coordination and can be assumed to be a network-forming ion. The findings by Tranell *et al.* (2002) are supported by the thermodynamic studies of Martin *et al.* (1975), which showed that silica and titania generally compete for coordination with basic components such as CaO, MnO, and FeO. Further studies show the addition of titania to silicate slags show that it decreases its viscosity and increases electrical conductivity and sulphide capacity, which can be interpreted as a weakening of the silicate network. Increased conductivity would imply that for a similar power dissipation, a longer arc length at the same operating current would be required to inject more energy in the furnace.

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Titania is also classified as an amphoteric oxide, depending on its concentration in the slag and the ratio of other network formers and network modifiers in the slag.

CaO has a higher affinity for SiO_2 than FeO has, according to Sommerville *et al.* (1982). Therefore, when it is added to the silicate slags, it lowers the activity of the SiO_2 but is likely to raise the activity of FeO (and other transition metal oxides).

The complete interaction of CaF_2 with highly siliceous slags is not well understood, except for its impact on slag viscosity, in that it significantly reduces the slag viscosity to make it very fluid. Depending on whether additional fluidity is required, it may be desirable or problematic. Its influence on recovery selectivity was investigated, despite the low probability of it being used industrially. CaF_2 poses an additional problem in that environmentally unstable slags are formed, and the potential presence of SiF_4 in the off-gas may pose a problem when it comes into contact with moisture.

The dump slag in this study is an old reverberatory furnace slag with a liquidus temperature in the range of 1100 to 1200°C. On the other hand, the reduced alloy is an iron-rich, low carbon alloy with a liquidus close to 1500°C. This would imply that, if a slag is at a similar or higher (as is normal for DC plasma arc furnace) operating temperature, it would have 400–500°C superheat, which would make it extremely fluid. Additional fluidity through fluorspar addition may therefore aggravate the situation and cause problems with the maintenance of furnace integrity.

Experimental method

Experiments were conducted in a laboratory plasma arc furnace. This furnace is an in-house construction used for academic research. The experiments presented in this study are part of the work carried out to characterize the furnace performance. Features of the furnace are illustrated in Figure 1.

A Messer Griesheim LG1100–1 plasma cutting torch power supply, rated at 50kVA supplied power to the furnace. Values of voltage across the anode and cathode were measured with a DC multimeter and the current read from the power supply unit. These values were used to calculate the power generated and supplied for smelting the slag.

Electrode length before and after the experiment was measured to obtain the electrode consumption rate. This enabled the measurement of the arc length by recording the position of the electrode arm relative to the crucible bottom, depth of the crucible, and height of the melt in the crucible. The final height of the melt in the crucible was typically between 50 and 60 mm. A variable speed electric motor was used to drive a rack-and-pinion hoisting mechanism for the cathode. This enabled the control of arc length and electrode position. Graphite crucibles (with a male-female connection into a graphite cylindrical anode) were used inside the furnace and were removed with tongs after completion of the experiment. A variable frequency vibratory feeder was used to feed the premixed charge into the furnace via a feed chute. Figure 2 shows a photo of the furnace with its vibratory feeder, gas cooler and dust knock-out drum (behind the furnace). The furnace is equipped with sight-glasses, which can either be clear or tinted (to observe the arc). Argon is used to purge the furnace before and during the experimental run.

Furnace charge comprised reverb dump slag, anthracite, and the flux, premixed in appropriate proportions. It was fed at an average rate of 1.36 kg/h and at the end of every batch of feeding, an idling time of five to ten minutes was allowed so that complete melting of furnace charge could be achieved. The flux was added in three doses at 20, 40, and 60 g, to a reverb dump slag weight of 1000 g, while the reductant addition was kept constant at 96 g, a pre-determined amount that yielded maximum metal recovery in the absence of fluxes. The theoretical energy requirement for the total feed

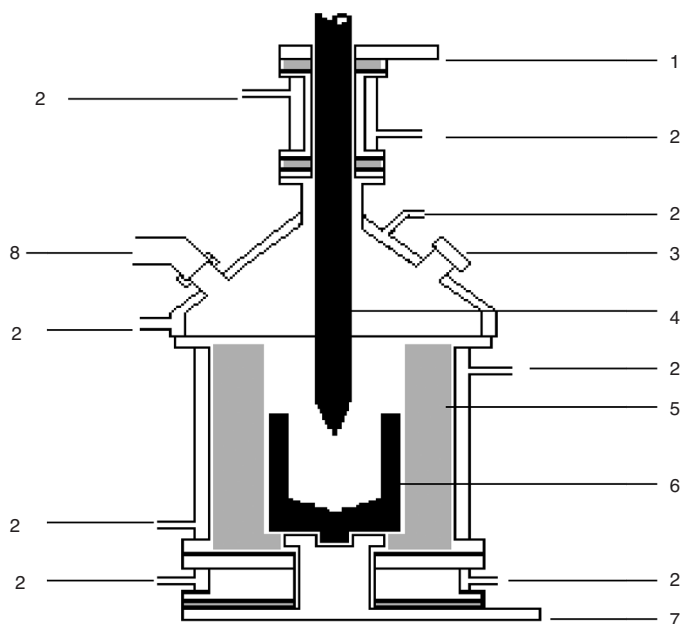


Figure 1—Schematic diagram of the DC plasma furnace used in the extraction of cobalt from slag. 1. Cathode terminal, 2. Cooling water channel, 3. Feed port, 4. Graphite electrode, 5. Refractory thermal blanket, 6. Graphite crucible, 7. Anode terminal, 8. Off-gas outlet to the scrubbing box

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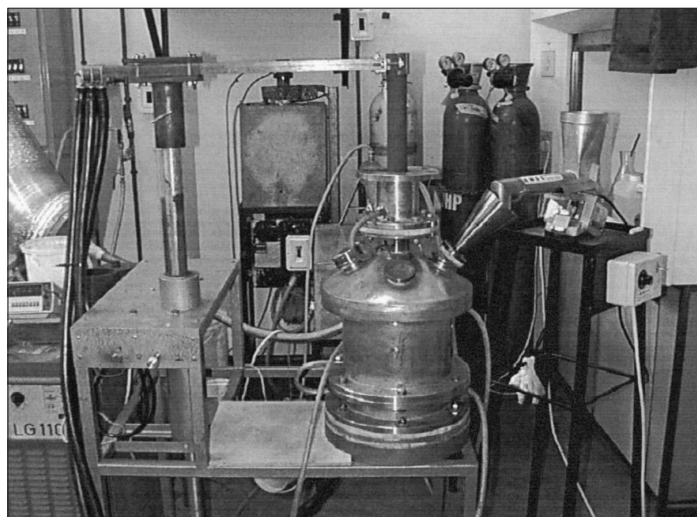


Figure 2—Photograph of the laboratory furnace setup

Table I Composition of the slag used in plasma furnace experiments											
Component	SiO ₂	TiO ₂	Al ₂ O ₃	Fe _x O	MnO	MgO	CaO	K ₂ O	P ₂ O ₅	CuO	CoO
Wt%	42.25	0.49	7.94	33.74	0.10	3.20	6.96	3.46	0.25	1.06	1.83

was 0.76 kWh/kg total feed. Titania is also classified as an amphoteric oxide, depending on its own concentration in the slag and the ratio of other network formers and network modifiers in the slag. Experiments were conducted at two power settings for each flux type and amount used. Power settings were controlled by changing the current to the cathode electrode, and for this study two settings were set at 0.25 kA and 0.40 kA. These power levels may be higher than the theoretically required (up to 10 times) to melt the total charge from ambient to about 1550°C. High specific energies were necessary to compensate for the heat losses that occurred during the smelting process. The temperatures produced at these power settings were in the order of 1450 to 1550°C, as measured by a Mikron 90H infrared pyrometer mounted on a tripod. The material balance of the furnace showed a loss of about 30% of the initial charge to the flue dust. Analysis of the flue dust was not carried out. Therefore the results presented in this paper are based on the material that was contained in the crucibles at the end of the smelting run. The analysis of the slag used in the experiments is given in Table I.

Alloy and slag were separated from the crucible after the crucible had cooled down. Analysis of the slag was by X-ray fluorescence for the total compositions the major elements and the amount of iron, copper and cobalt present. Samples were analysed for major elements on a Philips PW 1410 wavelength dispersive XRF-spectrometer using an Rh-tube at the University of Stellenbosch. Major elements were analysed on fusion discs using the Norrish and Hutton (1969) fusion technique. Crushed and milled samples were analysed by means of X-ray diffraction techniques. Powder preparations

were produced and subjected to Co(K α) radiation. Semi-quantitative mineral proportions were determined from the peak heights of X-ray diffraction patterns, and peak identification was done in correspondence with the JCPDS database.

Each alloy sample was separated from the slag and weighed. The alloy was analysed for iron, cobalt, copper, silicon and titanium by using the ICP-MS (inductively coupled plasma) technique. Prior to the analysis, the alloy was pulverized in a tungsten carbide ring mill to a fine powder.

Results and discussion

The results of the analyses of the slag and alloy are shown in Tables II and III. It can be seen from these results that modification of the slag chemistry has a significant influence on the recovery of cobalt and copper from the waste slag, although the outcomes were not consistent throughout. The base-metal to iron recovery ratio in the alloy varied with the addition of the flux as well as the power level used. The effects of additions of the various slag modifiers are presented graphically in Figures 3–10.

It is generally thought that higher specific power input into the furnace would lead to higher recoveries because of the lower viscosity of the slag plus the increased stirring effect of the arc (increased impinging force) on the slag. However, the findings of the study indicate that this is not necessarily the case.

Figures 3 and 4 show that Fe and Co show basically similar behaviour at the lower and higher power levels for the addition of lime as chemistry modifier. In both cases optimal cobalt recovery occurred at the maximum amount

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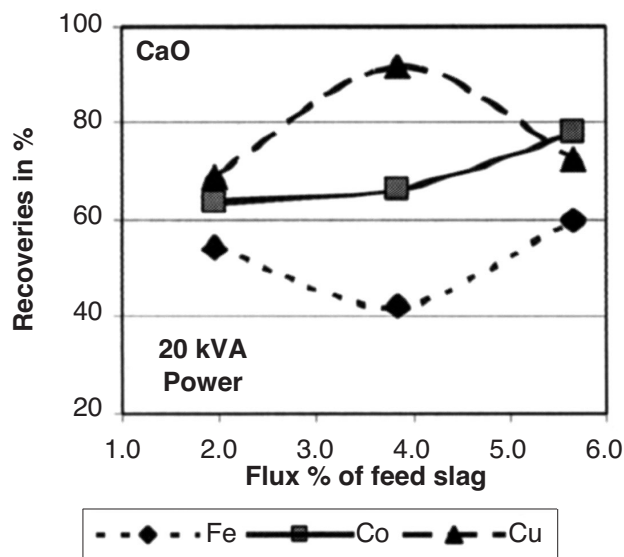


Figure 3—Effect of CaO as modifier on metal recoveries to alloy at a power level of 25 kVA

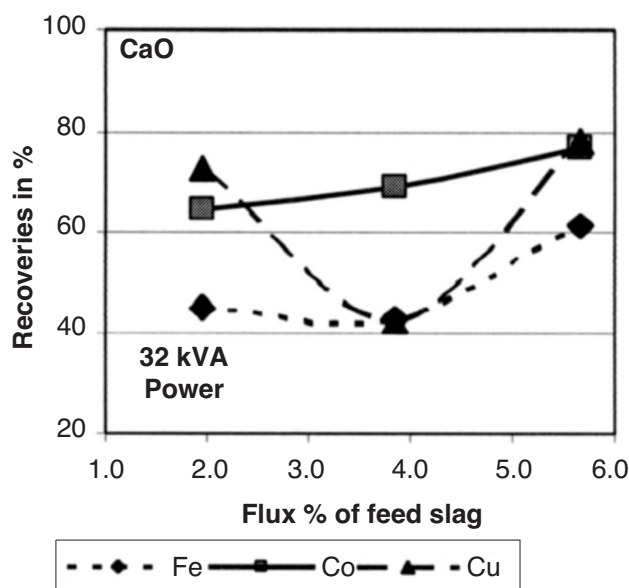


Figure 4—Effect of CaO as modifier on metal recoveries to alloy at a power level of 32 kVA

studied. Copper shifted its recovery-flux concentration curve from an upward to a downward curve.

Figures 5 and 6 show that the effect of addition of fluorspar is significantly dependent on the power level, higher power levels leading to higher recoveries of all metals. Cu and Fe were the most sensitive to flux addition (both increasing with increasing flux addition), while Co showed the least sensitivity to additional flux.

Figures 7 and 8 indicate that operating at higher power increased the recovery of all metals in the case where rutile was added as a chemistry modifier. While maxima were noted for Co and Fe and a minima for Cu, all the curves became monotonically decreasing at the higher power level.

The cobalt/iron recovery ratio in the alloy decreased when the current/power to the furnace was increased, as shown in

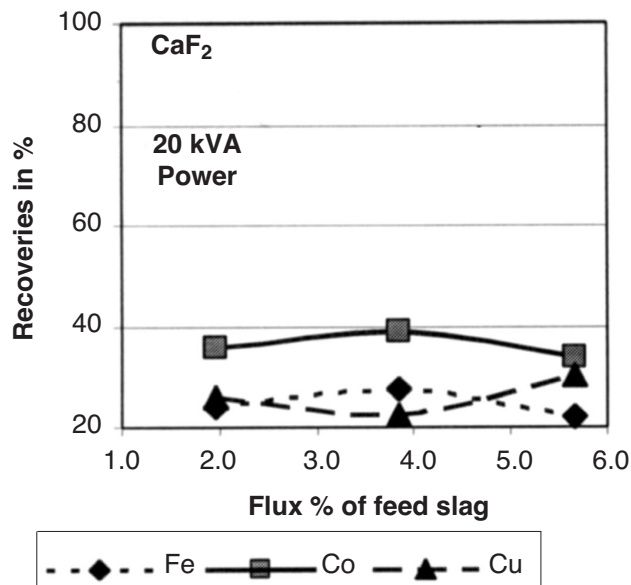


Figure 5—Effect of CaF₂ as modifier on metal recoveries to alloy at a power level of 25 kVA

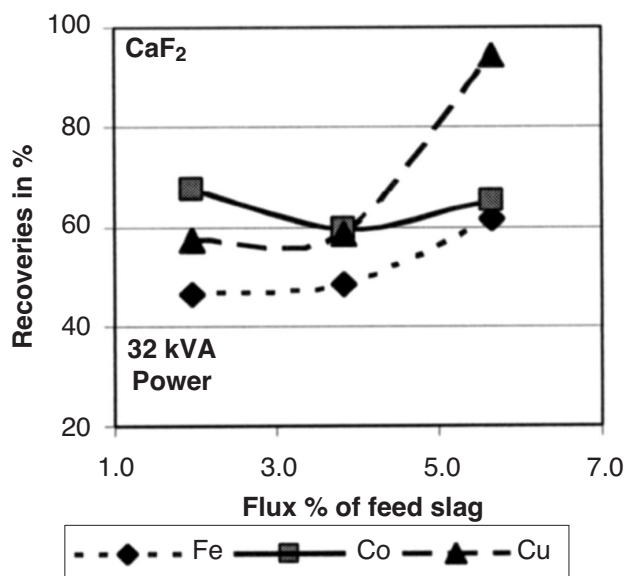


Figure 6—Effect of CaF₂ as modifier on metal recoveries to alloy at a power level of 32 kVA

Figures 9 and 10. This finding is in agreement with the findings by Yücel *et al.*, (1992) who also found a decrease in the recovery of copper and cobalt with increased power levels. An explanation of this behaviour is attributed to the influence that the metal-slag equilibrium has on the partitioning of metal to the slag at elevated temperatures. This behaviour was investigated by Kor (1984) and it was found that cobalt and copper metals have a tendency to partition to the slag at higher temperatures. With this view in mind, Açma (1997) concluded that it is possible to enrich metallic matte (Fe, Co, Cu₂S.FeS) in cobalt with high efficiency by 'low temperature' carbothermic reduction (1400°C) of copper slags. However, operating at these temperatures is still problematic. The amount of heat required

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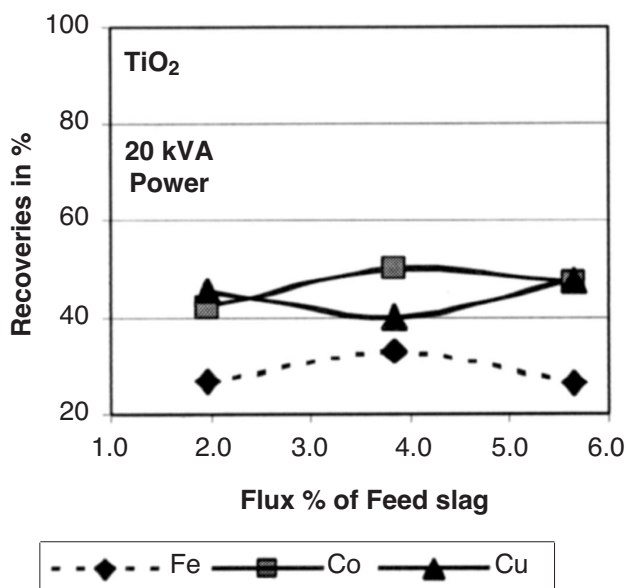


Figure 7—Effect of TiO₂ as modifier on metal recoveries to alloy at a power level of 25 kVA

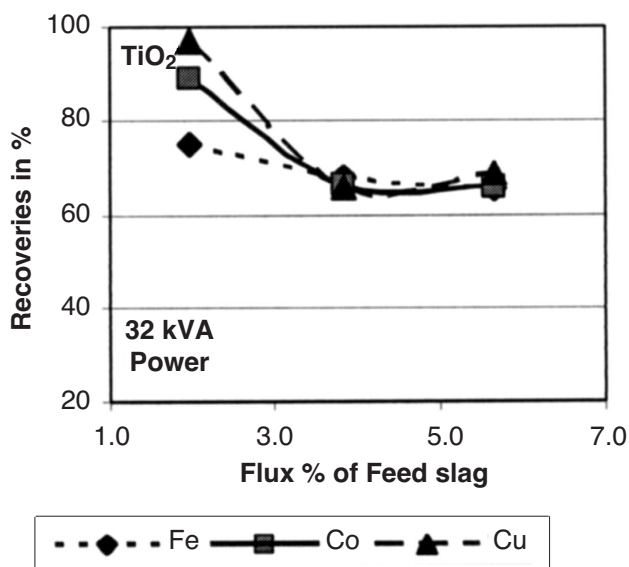


Figure 8—Effect of TiO₂ as modifier on metal recoveries to alloy at a power level of 32 kVA

to maintain the metallic melt above its liquidus temperature would be enormous, resulting in superheating the slag to several hundreds of degrees Celsius above the slag liquidus temperature (which is at traditional matte smelting temperatures). This would create an operational challenge as far as 'freeze-lining' of the refractory wall in the slag zone is concerned.

The effect of modifying the slag with CaO, TiO₂, and CaF₂ on Co/Fe ratio is illustrated in Figures 9 and 10. The addition of CaO to the slag increased the recovery of cobalt metal but with a relatively high co-recovery of iron. This is as a result of CaO increasing the activity of both FeO and CoO in the slag. Literature on the effect of the addition of CaF₂ to the slag says that it tends to lower the liquidus temperature of

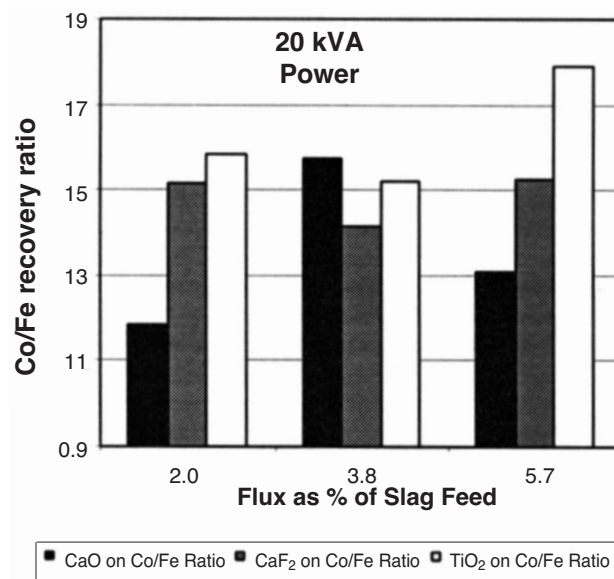


Figure 9—Effect of various modifiers on Co/Fe recovery ratios at a power level of 25 kVA

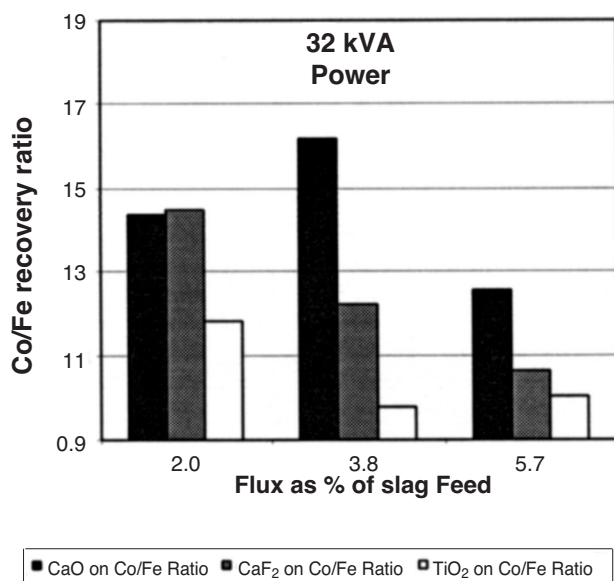


Figure 10—Effect of various modifiers on Co/Fe recovery ratios at a power level of 32 kVA

the slag (which needs no lowering in this case!). On the other hand, Rosenqvist (1983) claims that its main effect is that of a dilution, and that it does not seem to affect much of the activities of other components. The structural influence of CaF₂ on slag chemistry is still not well understood. It was observed in this study that the amount of iron in the slag increased with increased addition of this flux.

Table II provides the actual slag and alloys, compositions after the layers were allowed to separate and solidified. The solidified slag and alloy layers were separated, milled and analysed by XRF and ICP.

Table III gives the calculated recoveries used in the figures above, as well as the calculated cobalt to iron recovery ratios.

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Table II

Composition of the alloy from the furnace

Operating current Flux type Mass of flux added as % of slag Experiment no.	0.25 kA (20 kVA)								
	CaO			CaF ₂			TiO ₂		
	1.96	3.85	5.66	1.96	3.85	5.66	1.96	3.85	5.66
	1	2	3	4	5	6	7	8	9
Fe%	86.19	80.55	83.63	85.69	87.15	83.84	81.06	83.79	80.72
Co%	5.63	7.00	6.05	7.17	6.80	7.06	7.08	7.04	7.97
Cu%	7.37	11.82	9.63	6.26	4.72	7.71	9.18	6.82	9.72
Si %	0.75	0.53	0.62	0.88	1.30	1.39	2.65	2.22	1.57
Ti%	0.06	0.09	0.06	0.01	0.02	0.00	0.03	0.12	0.02
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Operating current Flux type Mass of flux added as % of slag Experiment no.	0.4 kA (32 kVA)								
	CaO			CaF ₂			TiO ₂		
	10	11	12	13	14	15	16	17	18
	10	11	12	13	14	15	16	17	18
Fe%	83.49	86.34	86.30	85.75	85.93	85.13	83.87	79.51	83.57
Co%	6.61	7.72	5.98	6.85	5.78	5.00	5.47	4.30	4.63
Cu%	9.07	5.71	7.34	7.05	6.94	8.74	9.47	7.52	5.86
Si%	0.69	0.19	0.27	0.25	1.21	0.95	0.63	8.31	5.27
Ti%	0.15	0.04	0.11	0.09	0.13	0.18	0.56	0.36	0.67
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table III

Calculation of the recovery of the metal from the slag

Operating current Experiment no.	0.25 kA											
	CaO				CaF ₂				TiO ₂			
	1	2	3	Average	4	5	6	Average	7	8	9	Average
Fe %	53.84	41.80	59.60	51.75	23.78	27.58	22.12	24.49	26.67	32.97	26.31	28.65
Co%	63.70	65.81	78.11	69.21	36.03	39.01	33.73	36.26	42.23	50.19	47.08	46.50
Cu%	68.93	91.82	72.56	77.77	25.98	22.36	30.43	26.26	45.21	40.17	47.43	44.27
Si%	0.56	0.33	0.54	0.48	0.29	0.50	0.44	0.41	1.05	1.05	0.62	0.91
Ti	4.24	5.24	4.59	4.69	0.32	0.84	0.14	0.43	0.92	5.29	0.62	2.28
Co/Cu	0.92	0.72	1.08	0.91	1.39	1.74	1.11	1.41	0.93	1.25	0.99	1.06
Co/Fe	1.18	1.57	1.31	1.36	1.52	1.41	1.52	1.48	1.58	1.52	1.79	1.63
Operating current Experiment no.	0.40 kA											
	CaO				CaF ₂				TiO ₂			
	10	11	12	Average	13	14	15	Average	16	17	18	Average
Fe %	44.91	42.55	61.33	49.59	46.51	48.60	61.31	52.14	75.22	67.63	65.35	69.40
Co%	64.40	68.94	76.97	70.10	67.36	59.27	65.25	63.96	88.89	66.30	65.59	73.59
Cu%	72.99	42.10	78.11	64.40	57.23	58.77	94.19	70.06	96.91	65.58	68.52	77.01
Si%	0.44	0.11	0.23	0.26	0.16	0.83	0.82	0.60	0.68	8.51	4.97	4.72
Ti	8.82	2.10	8.30	6.41	5.47	7.86	14.09	9.14	54.78	33.48	56.68	48.31
Co/Cu	0.88	1.64	0.99	1.17	1.18	1.01	0.69	0.96	0.92	1.01	0.96	0.96
Co/Fe	1.43	1.62	1.25	1.44	1.45	1.22	1.06	1.24	1.18	0.98	1.00	1.06

The addition of TiO₂ to silicate slags probably displaces SiO₂ partially in silicate compounds resulting in stabilization, of the FeO as titanate compounds. As mentioned earlier, it would compete for FeO, resulting in increased activity of SiO₂ in the slag. As a result, this flux also tends to increase the quantity of silicon in the alloy more than when CaO or CaF₂ was used.

Conclusion

In conclusion, it can be said that increased power and higher operating temperatures lead to increased recoveries of all three metals, Co, Cu and Cu, in all cases except during lime addition. While a significant enrichment effect of Co relative to Fe in the alloy was noted with rutile addition at the lower

power level, this effect became less noted at the higher power level.

Rutile had the deleterious effect of increasing the amount of Si reporting to the alloy, which may cause downstream problems during hydrometallurgical processing.

Fluorspar addition is viewed as problematic as it further reduces an already low slag liquidus temperature, while not improving the cobalt recovery significantly over that found with lime addition.

Lime addition proved to be the most advisable, from a cobalt recovery perspective as well from environmental and raw materials, availability viewpoints.

All the above-mentioned slag modifiers were considered at a stage during the process development of the industrial cobalt recovery from waste slag process.

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As the slag is highly acidic and has such a low liquidus temperature, the effect of magnesite instead of lime, or the addition of alumina may be considered in further research. However, the complex slag chemistry of the waste slags makes a-priori speculation of the effect of slag modifiers on the metallurgical behaviour of these slags difficult to quantify or qualify; empirical evaluation and validation would remain essential.

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New engineering service for mining industry*

Well-known mining contractor Cementation Mining Skanska has launched a new business unit to provide practically engineered solutions for the mining industry drawn from the group's worldwide expertise.

'This is a strategic and logical move based on the wealth of technical expertise available within our organization,' says Cementation Mining director Tim Wakefield. 'The new global venture focuses on a holistic approach to construction, development, toll mining, refurbishment and maintenance in hard rock mining, drawing on our other operational skills in exploration drilling, water sealing, raiseboring and underground support. It aims to assist mining companies in planning optimally designed, lower cost, reduced risk projects, from feasibility through design and construction to delivery.'

The new business unit is headed up by Fernando Guilherme, a mining engineering with 25 years' deep mining experience, who started in the industry as a learner official and was most recently a production manager with a major gold- mine operator.

'In the South African mining industry, world-class expertise developed over decades tends to remain within the companies that provide the physical solutions in the development of mines and mining techniques,' says Wakefield. 'Our new venture, under a single global brand, provides the industry with access to the combined expertise of all our people, who have firsthand knowledge of what works and what does not work in mining development and contracting applications across the world.'

'The synergy derived from translating plans and estimates and then having done the work, is what makes the deliverable so unique and valuable. Designs incorporate in their detail the innovations that happen daily at the rock face.'

Cementation Mining currently offers the best in technical expertise from around the world. Canadian technology is

presently being tested by Cementation Mining on a mine in Namibia, for example, while a South African-developed cactus cleaning system is being used in a sinking application in Canada. Trials of a sonic 3D tomography technique, developed from Cementation's tunnelling in the UK have been conducted in the bottom of sinking shafts to forecast rock formations and to detect potholes and cooling domes in the UG2 platinum reef of the Bushveld Complex.

The new business unit boasts a total integrated engineering solutions capability, including specialist areas such as mechanized mining planning and methods, logistical aspects surrounding trackless equipment, shaft engineering—both vertical and decline—exploration drilling, and safety, health, environmental and quality systems. Cementation owns a substantial fleet of underground plant and has accumulated many years of experience in underground equipment maintenance.

Wakefield points out that for Cementation Mining's markets to be sustainable, mining development projects must be costeffective. 'The rand/US dollar exchange rate has put considerable pressure on local projects during 2003 and, as participants in the industry, it is up to us to assist in containing costs while at the same time focusing on yet further value enhancement.'

The new business unit, under the brand Cementation Skanska Engineering, has commenced trading. Initial projects have included the 3D tomography trials, a secondary muck handling study for horizontal development in Canada, and a shaft tonnage upgrade proposal in Zambia. ♦

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Platinum industry adopts uniform safety training*

The platinum industry has taken a major leap forward on the safety front by opting for universal Safety, Health and Environmental (SHE) induction training.

Impala Plats and Anglo Plats are party to the universal safety approach, having agreed, after in-depth investigations, to select KBC whose core offering is generic induction, legal and environmental outcomes-based SHE training programmes.

The decision to go the generic route was taken by the platinum industry's Bushveld Safety Forum, established two years ago to provide a platform for discussion and management of safety challenges in this key sector.

The rationale behind the joint training initiative was fourfold. Firstly, as a key industry, the platinum industry has SHE obligations to workers, trade unions, shareholders, investors and the international market.

Secondly, the contractors and suppliers involved in the platinum industry are fundamentally the same. It therefore made economic, as well as practical business, sense to avoid duplication of effort, cost and time in providing generic safety training services to the industry.

Thirdly, in terms of outside contractors, the platinum industry's management is responsible for the legal and safety liabilities of contractors allowed on site at a platinum facility. This scenario is unique to the platinum sector.

Finally it's necessary to ensure that South African platinum producers comply with international safety legislation, and the Mine Health and Safety Act and the Occupational Health and Safety Act have been couched in overall compliance with international norms and are broadly recognized as being among the world's best.

The generic approach ensures a single standard using training content, co-developed with detailed input by the stakeholders, says KBC MD Michael Kruger.

Having been essentially designed by the industry itself in a collaborative process, the resultant courses are tailor-made to the industry's technical and legal needs.

They comply with international standards and all applicable local legislation and are premised on the principle of good practice and a flexible approach to

managing accident and incident exposure and risk.

Certification in terms of the induction courses is transferable from site to site and remains valid for a year. The courses are constantly reviewed in conjunction with the Bushveld Safety Forum, taking into account practical experience as the needs of the industry evolve in safety terms.

While training has traditionally been one of the most conservative, change-resistant fields, the courses recognize the emphasis on learner participation and 'edutainment' in the interests of better results and greater effectiveness.

The active involvement of the learner is encouraged through guided discovery.

High-level training is provided by cost-effective, self-paced, interactive Computer Based Training (CBT) programmes, accessible anywhere and at anytime. In a sense, this is 'just in time' learning.

KBC has also developed mobile training centres for the platinum industry on the premise that training should be available wherever the need arises.

The courses are aligned with SAQA requirements and can be used for credits of SAQA qualifications, ultimately embracing the highest level of such qualifications. Clients have access to an interactive, SAQA aligned database on their learners that is either standalone or web enabled.

Benefits flowing from the generic approach include access to appropriate, in-depth expertise, which could not justifiably have been created in-house, accurate management of SHE related budgets, and the delegation of most day-to-day responsibilities in terms of SHE compliance.

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