

Corrosion of copper coolers in PGM smelters

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Corrosion of copper coolers is a major problem in platinum group metal (PGM) smelting furnaces. This study describes an investigation into the wear mechanism(s) of copper coolers through two post-mortem analyses of the freeze lining and refractory bricks of a PGM smelter, as well as laboratory-scale experiments whereby copper was corroded under controlled conditions.

The post-mortem analyses on freeze lining and refractory samples were performed using scanning electron microscopy—energy dispersive spectrometry (SEM-EDS), X-ray fluorescence spectroscopy (XRF) and X-ray powder diffraction (XRD). On visual inspection of the furnace wall it was observed that at the slag-feed interface the front magnesia-chrome refractory brick was completely corroded and only the freeze lining separated the copper cooler from the furnace contents. At the bottom section of the slag zone the front refractory brick was still intact. Base metal sulphides and elemental sulphur were the major phases observed at the copper cooler-freeze lining interface, whereas at the copper cooler-front brick interface only CuS and element sulphur were observed. Wear of the copper cooler proceeded through reaction between the copper and base metal sulphides, as well as gaseous attack of copper by sulphur.

In the latest furnace wall designs the magnesia-chrome refractory bricks are replaced by graphite blocks. A post-mortem analysis of a graphite block, which was removed from the same PGM smelter, was performed using XRD, SEM-EDS and inductively coupled plasma analysis (ICP). It was confirmed that graphite plays a significant role in reducing the extent of reaction of corrosive gases and base metal sulphides with the copper cooler.

Laboratory-scale experiments were carried out to determine the effect of corrosive gas composition and copper surface temperature on the corrosion rate and morphology of the corrosion products. Tests were performed on copper foils at temperatures from 80°C to 140°C. Corrosive gases included S₂, S₂ with HCl, and H₂S. It was found that when a copper foil is exposed to sulphur the sulphides that form are CuS at 80°C, CuS and Cu₉S₈ at 110°C, Cu₉S₈ and Cu₁₁S₈ at 140°C. Linear corrosion rate behaviour is observed between 80°C and 110°C since the sulphide scales are not passivating and they poorly adhere to the copper foil. Additions of HCl enhance the corrosion rate at temperatures above the melting point of sulphur. Cu₂S forms when copper is exposed to H₂S gas. Average corrosion rates of copper foil by sulphur vapour were 54 mm/y at 80°C and 80 mm/y at 110°C, whereas above 112°C the corrosion rate decreased to 5 mm/y. The corrosion rate and morphology of the corrosion product are functions of temperature and the corrosive gas composition.

Keywords: PGM smelter, copper cooler, sulphidation, corrosion, freeze lining, refractory, graphite block.

Introduction

Corrosion problems are associated with copper coolers in all platinum group metal (PGM) smelting furnaces that treat uncalcined concentrates¹. Corrosion rates of copper coolers in excess of 60 mm/y were observed on the slag-charge interface level of a PGM smelter^{1,2,3}. Sulphidation of copper coolers by sulphur gas, coupled with chlorination by HCl gas, was characterized as the main cause of copper cooler corrosion from the analysis of post-mortem refractory samples and thermodynamic calculations^{1,2}. Prolonging the life of the furnace refractory walls through copper cooling technology remains a challenge;^{1,2} however, great benefits have been reported through the use of graphite blocks in current smelter designs⁴.

There are virtually no published data on the mechanism involved in the corrosion of copper coolers in PGM smelters. Data on the phenomenon of corrosion are vital in understanding the wear mechanism of copper coolers and in shaping future cooling system designs. The objective of this project was to determine the wear mechanism of copper waffle coolers in PGM smelters through post-mortem analyses of refractory samples that were taken from the refractory wall of a primary PGM smelter, as well as through laboratory-scale sulphidation experiments on copper foils. The objective of the laboratory tests was to determine how the surface temperature of the copper cooler and the composition of the corrosive gas affect the corrosion rate of the copper, the types of phases that form in the corrosion product, as well as the morphology of the corrosion product.

Calculation of interfacial temperatures in the refractory wall

The post-mortem analysis was performed on the refractory wall of a PGM smelter that was lined with plate coolers in the free board zone, waffle copper coolers with magnesia-chrome bricks in the slag zone and magnesia-chrome bricks in the matte zone (hearth). Alumina-chrome based rammable refractory material filled the gaps between the waffle cooler knobs, forming the rammable-copper cooler composite (Figure 1).

The thermal energy flux through the refractory wall was calculated by implementing Fourier's law of one dimensional heat transfer (Equation [1]):

$$Q = -kA \left(\frac{\Delta T}{\Delta X} \right) \quad [1]$$

In this calculation it was assumed that $T_{cold\ face} = 40^\circ\text{C}$, $T_{hot\ face} = 1\ 550^\circ\text{C}$, the thermal conductivity of the magnesia-chrome brick at $1\ 550^\circ\text{C}$, $k_{brick} = 2.8\ \text{W/mK}$, the thickness of the rammable was 5 mm, and that the copper-rammable composite ratio was 1:1. From the energy flux the interface temperatures in the refractory wall were calculated using Equation [2]:

$$T_x = T_{x-1} \left(\frac{T_{cold} - T_{hot}}{R} \right) R_x \quad [2]$$

where T_x = interface temperature ($^\circ\text{C}$), T_{x-1} = hot face temperature of the previous layer ($^\circ\text{C}$), R_x = thermal resistance of layer x (thickness of the layer/thermal conductivity through the layer), R = total thermal resistance through the wall.

The brick-rammable interface temperature can range from 48°C to 109°C as the thickness of the rammable varies respectively from 0.1 mm to 5 mm. The interface temperatures in the refractory wall increase with decreasing brick thickness, but the change in brick thickness was not considered in these calculations. The thermal energy flux through the refractory wall was also calculated for the scenario of a freeze lining at the hot face instead of the magnesia-chrome brick. The cold face of the freeze lining was calculated to be 153°C when the rammable has a thickness of 5mm in front of the waffle knob.

Post-mortem analysis of the furnace wall that was lined with magnesia-chrome bricks

Post-mortem refractory samples were collected from a PGM smelter after 12 months in operation, samples were analysed with X-ray fluorescence, X-ray powder diffraction

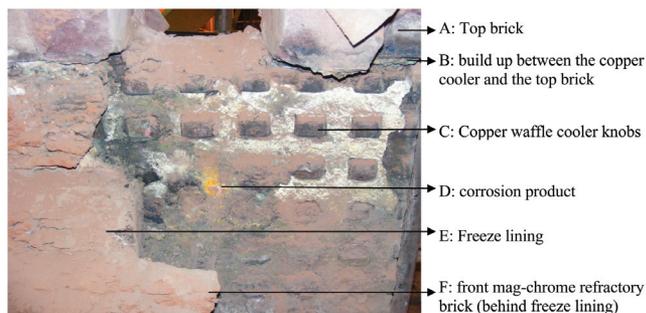


Figure 1. Front view of the furnace refractory wall, showing the top brick, copper waffle cooler knobs covered with corrosion product and the freeze lining

and scanning electron microscopy (using energy dispersive spectrometry). Samples were collected from the following areas:

- Between the top brick and the cooler
- Between the front brick and the cooler
- Between the freeze lining and the cooler
- The freeze lining.

Sample taken between the cooler and top brick

A mixture of blue crystals with white and black soft material formed the bulk of the corrosion product collected on top of the cooler. The top brick seemed to have been pushed upward as this layer formed. The blue crystals formed adjacent to the cooler while the black layer with white inclusions was in contact with the top brick.

Copper sulphate (with different degrees of hydration) and Al_2O_3 were the most abundant phases detected by XRD between the cooler and top brick. CuCl and elemental sulphur were detected as minor phases.

Copper and sulphur trioxide were detected by XRF with no elemental sulphur, which confirmed the presence of sulphates and not sulphides. This sample was friable which made it a challenge to prepare a polished section for EDS analysis.

Freeze lining

The morphology of the freeze lining varied from a very porous cracked hot face to a dense cold face. A gap of approximately 2 cm (parallel to the copper cooler) was observed between the copper cooler and front brick as well as between the copper cooler and freeze lining. The gap could have formed during operation or due to refractory wall contraction during furnace shutdown. If this gap formed during operation, a channel through which oxygen and off-gas from the free board could reach the surface of the copper coolers was provided. Gaps can lead to contact resistance between the coolers and the refractory, which results in a decrease in cooling efficiency⁵.

$\text{CaFe}(\text{Si}_2\text{O}_6)$, $\text{CaMgFe}(\text{Si}_2\text{O}_6)$ and $(\text{MgFe})_2(\text{SiO}_4)$ were major phases detected by XRD in the freeze lining, with minor amounts of $\text{MgFe}(\text{Cr}_2\text{O}_4)$, Cr_2O_3 , Al_2O_3 and NiS . BSE images of the freeze lining are depicted in Figure 3. Sub-samples were taken from the hot face, middle portion and cold face of the sampled freeze lining. $\text{CaMgFe}(\text{Si}_2\text{O}_6)$ (Figure 3 no.1), $\text{CaFe}(\text{Si}_2\text{O}_6)$ (Figure 3 no.2) and $(\text{MgFe})_2(\text{SiO}_4)$ (Figure 3 no.3) were identified by EDS as main constituents of the hot face and middle portion of the sample of freeze lining. $\text{MgFe}(\text{Cr}_2\text{O}_4)$ (Figure 3 no.4), iron sulphide (FeS) (Figure 3 no.5), $(\text{CuFeNi})\text{S}_x$ (Figure 3 no.5), $\text{Cu}_{1.8}\text{S}$ (Figure 3 no.5) and CuFeS_2 (Figure 3 no.6) were

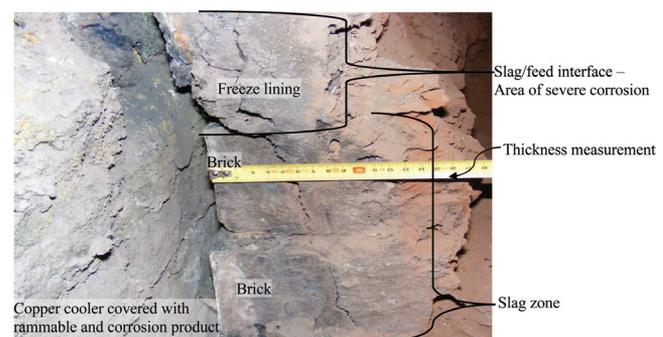


Figure 2. Side view of the refractory lining

Cu, Fe and Ni sulphides

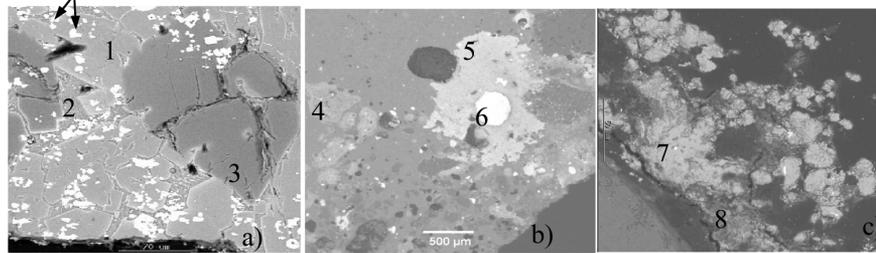


Figure 3. BSE images of a freeze lining sample: (a) hot face (b) middle portion, and (c) cold face of the freeze lining. [1 = $\text{CaMgFe}(\text{Si}_2\text{O}_6)$; 2 = $\text{CaFe}(\text{Si}_2\text{O}_6)$; 3 = $(\text{MgFe})_2(\text{SiO}_4)$; 4 = $(\text{FeMg}(\text{Cr,Al})_2\text{O}_4)$; 5 = $(\text{CuFe})_9\text{S}_5$, $\text{Fe}_{1.2}\text{S}$ (area analysis); 6 = CuFeS_2 ; 7 = CuCl ; 8 = (Ca,Cu,Cl,S,Fe) mixture]

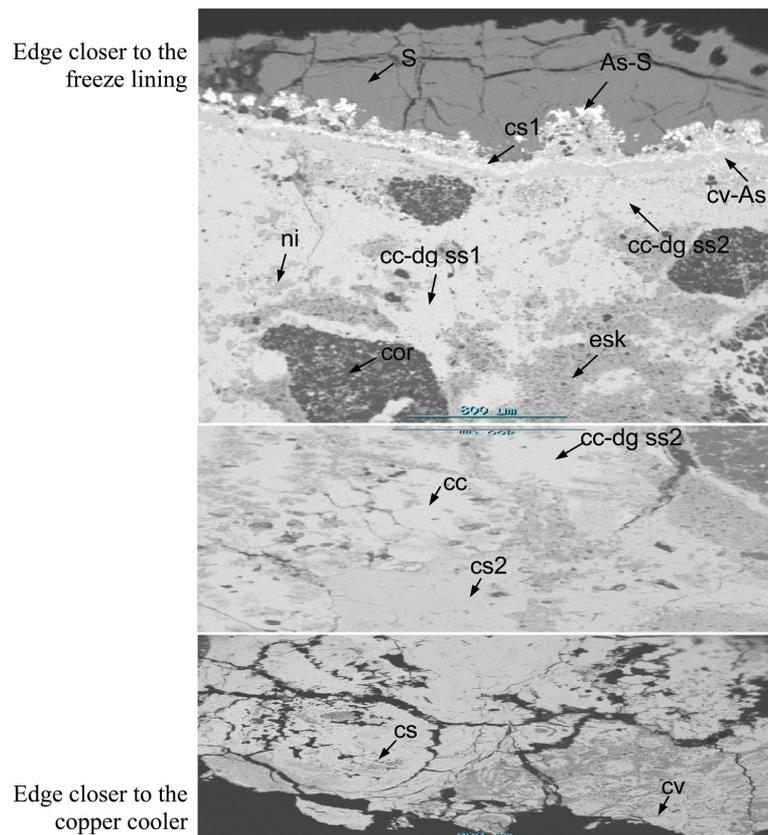


Figure 4. Profile across the corrosion product from the cold face of the freeze lining up to 20 mm towards the copper cooler surface. [S = sulphur, As = arsenic, cv_As = CuS and arsenic, cv = CuS , cc = Cu_2S , ni = NiS , esk = Cr_2O_3 , cor = Al_2O_3 , cc-dg-ss = $\text{Cu}_2\text{S}-(\text{CuFe})_9\text{S}_5$ solid solution, cs = copper sulphide]

minor phases in the hot face and middle portion of the freeze lining sample. $\text{CaMgFe}(\text{Si}_2\text{O}_6)$ was detected by EDS as the main phase in the cold face sample of the freeze lining, with a mixture of copper chloride (CuCl), calcium (Ca), sulphur (S) and iron (Fe) (Figure 3 nos.7 and 8) at the edge of the sample.

Sample taken between the cooler and the freeze lining

The sample behind the freeze lining consisted of yellow, grey, white, black and green material which was attached to the copper cooler. $\text{Cu}_{1.8}\text{S}$, Cu_3FeS_4 , CuS , Al_2O_3 , Cr_2O_3 and $\text{Cu}_2(\text{OH})_3\text{Cl}$ were major phases detected by XRD with $(\text{CuFe})_4\text{S}_4$ and sulphur (S) as minor phases.

EDS analyses were performed on this sample from the side which was in contact with the freeze lining up to 20 mm towards copper cooler (Figure 4, Table I). It was observed that sulphur (S) formed an outer layer of the corrosion product followed by arsenic sulphide (As+S) (which also contains some tellurium (Te)). Adjacent to the arsenic sulphide was a thin layer of a non-stoichiometric copper sulphide ($\text{Cu}_{1.3}\text{S}$) which was followed by a thicker layer of CuS with arsenic (As) and tellurium (Te) inclusions. Adjacent to CuS was a $\text{Cu}_2\text{S}-(\text{CuFe})_9\text{S}_5$ solid solution, which formed the bulk of the corrosion product which extended towards the copper cooler, with nickel sulphide (NiS) dispersed in this solid solution. The

Table I
EDS analyses of the sample collected between the freeze lining and copper cooler (atom %)

Name of phase	Description of phase	*Al	As	Cl	Co	*Cr	Cu	Fe	Ni	*Si	S	Te	Total	Stoichiometry	Mineral name
S	Dark grey	0.0	0.0	0.2	0.0	0.0	0.1	0.0	0.0	0.5	99.2	0.0	100.0	S	Sulphur
As	White	0.2	22.3	0.0	0.1	0.0	0.4	0.0	0.1	0.7	71.6	4.8	100.2	Mixture of AsS, S	Arsenic sulphide, sulphur
cv-As	Grey-white	0.2	4.9	0.0	0.0	0.1	44.5	0.0	0.0	0.5	40.6	9.3	100.1	Mixture of CuS, As, Te	Covellite, arsenic, tellurium
cs1	Light grey	0.0	0.0	0.9	0.0	0.0	55.9	0.0	0.1	0.4	42.8	0.0	100.1	Cu _{1.3} S	Copper sulphide
esk-1	Grey	0.8	0.0	0.0	0.0	47.0	30.6	0.0	0.0	0.3	21.1	0.0	99.8	Mixture of Cr ₂ O ₃ , Cu _{1.5} S	Eskolaite, copper sulphide
cor	Dark	98.4	0.0	0.0	0.0	0.0	1.4	0.0	0.1	0.0	0.0	0.0	99.9	Al ₂ O ₃	Corundum
Ni	Small grey spots	0.0	0.1	0.0	1.1	0.2	0.9	4.5	46.4	0.5	46.4	0.0	100.1	NiS	Millerite
cc-dg ss1	Light grey	0.0	0.0	0.0	0.0	0.0	64.0	2.9	0.0	0.4	32.7	0.0	100.0	Cu ₂ Fe _{0.1} S	Chalcocite-digenite ss1
cc-dg ss2	Light grey	0.0	0.0	0.0	0.0	0.0	59.3	6.7	0.1	0.3	33.7	0.0	100.1	Cu _{1.8} Fe _{0.2} S	Chalcocite-digenite ss2
cs2	Light grey	0.0	0.0	0.0	0.0	0.0	61.1	0.0	0.0	0.3	38.6	0.0	100	Cu _{1.6} S	Copper sulphide
cs	Light grey	0.4	0.1	0.1	0.0	0.0	54.5	0.0	0.0	0.4	44.6	0.0	100.1	Cu _{1.2} S	Copper sulphide
cc	Light grey	0.0	0.0	0.0	0.2	0.0	67.0	0.8	0.1	0.4	31.2	0.1	99.8	Cu _{2.1} S	Chalcocite
cv	Light grey	0.0	0.0	2.1	0.0	0.0	47.0	0.0	0.0	3.1	47.8	0.0	100	CuS	Covellite

!*Al, Cr and Si were taken as oxides, i.e. Al as Al₂O₃, Cr as Cr₂O₃ and Si as SiO₂.

(Cu+Fe):S atomic ratio of this solid solution phase ranged from 2:1 to 2.1:1. The Cu:S atomic ratio of the copper sulphide ranged from 1.26:1 to 2.11:1, which included Cu₂S. Ramming material, Al₂O₃ and Cr₂O₃ were interspersed with this solid solution phase. Closer to the copper cooler was a non-stoichiometric copper sulphide with Cu:S atomic ratio ranging from 1.2 to 1.6, and also minor amounts of CuS.

It is evident that matte and gases penetrated the freeze lining and diffused through the rammable refractory material since base metal sulphides and solid sulphur were detected between the freeze lining and the copper cooler.

Corrosion of the copper cooler at the slag-feed interface when magnesia-chrome bricks were used in the furnace lining therefore progressed through two wear mechanisms: (1) the reaction of the copper cooler with sulphur, which resulted in the formation of CuS and deposition of sulphur; and (2) reaction of the copper cooler with the base metal sulphides such as NiS and (CuFe)_xS, which diffused through the porous freeze lining.

Sample taken between the cooler and the front brick

CuS, elemental sulphur, Al₂O₃ and Cr₂O₃ were identified as the major phases in this sample with minor amounts of Cu₂(OH)₃Cl. The presence of small amounts of SiO₂, Te, Tl and As were confirmed by XRF analysis.

No Cu_{1.8}S, nickel sulphide or Cu₂S were detected in this sample, which suggests that the corrosion mechanism that occurs behind the brick is different from the corrosion mechanism that occurs behind the freeze lining when the brick is totally consumed. Wear of the copper cooler behind the front brick proceeded through chemical reactions between the copper cooler and off gases such as sulphur which resulted in sulphur deposition and consequently the formation of CuS. This was preceded by the penetration of furnace off-gas through the refractory brick and rammable material.

Post mortem analysis of the furnace wall that was lined with graphite blocks

To address corrosion problems associated with copper coolers, a new design was adopted in which the upper

waffle cooler is lined with graphite blocks⁴. A graphite block which was six months in production was received from the same smelter for a comprehensive post mortem analysis.

The phases in the hot face and the cold face of the graphite block were determined using SEM-EDS, XRD and ICP. These phases were then compared to the phases observed in the post-mortem sample that was collected when magnesia-chrome bricks were used in the lining.

Phase chemical analysis

Backscattered electron images of the top portion of the graphite block are shown in Figure 5. The hot face at the slag-feed interface had a 2 mm thick freeze lining. The infiltration depth of sulphides into the graphite block was less than 1 mm. The freeze lining was composed of FeS, CuFeS₂, (Fe,Ni)₉S₈, NiS, with minor amounts of MgFeSi₂O₆, CaMgFeSi₂O₆ and Mg₂SiO₄. The top edge of the graphite block at the graphite-graphite interface contained Cu₉Fe₉S₁₆, FeS, CuFeS₂ and (Fe,Ni)₉S₈. The cold face of the top edge of the graphite block consisted of Cu₂S (1 in Figure 5) and (Cu,Fe,Ni)_xS_x (2 in Figure 5). These phases could be found up to a depth of more than 2 mm into the graphite block.

The hot face of the bottom portion of the graphite block had a freeze lining which consisted of CuFeS₂, FeS, (FeNi)₉S₈ and slag. The cold face of this bottom sample had CuFeS₂, (CuFe)₉S₅ and CuSO_{4.5}H₂O. FeS, (Fe,Ni)₉S₈ and slag could be distinguished at the graphite-castable interface, at the bottom edge of the graphite block.

Laboratory-scale sulphidation tests

Experimental

An annealed 99.7% copper foil, 50 μm thick, 2.5 mm in width and 60 mm in length was cut out of a copper sheet and used as the substrate. This copper foil was mounted on a heat sink and heated to the operating temperature by circulating hot silicone oil through the heat sink. Upon reaching the operating temperature the copper foil was suspended in a sealed 3ℓ glass reactor containing molten sulphur such that the sulphur vapour reacted with the

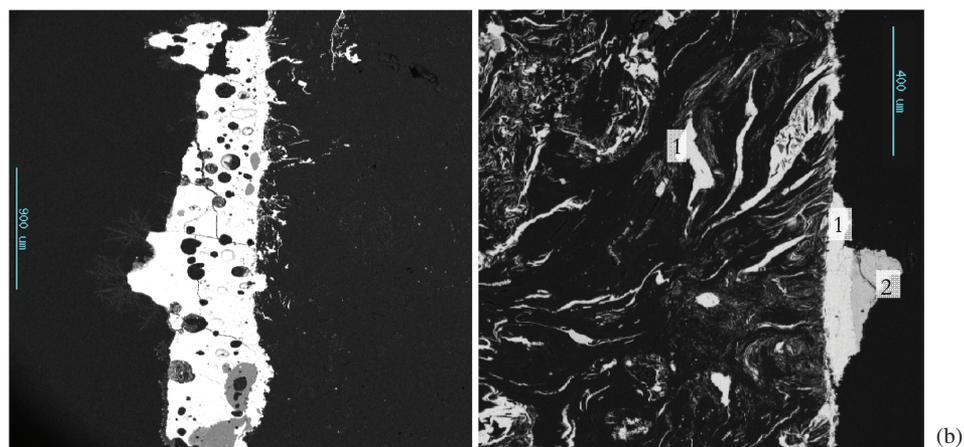


Figure 5. BSE images of the top sample from the graphite block: (a) = hot face; (b) = cold face. 1 = Cu_{2+x}S ; 2 = $(\text{Cu},\text{Fe},\text{Ni})$ sulphide

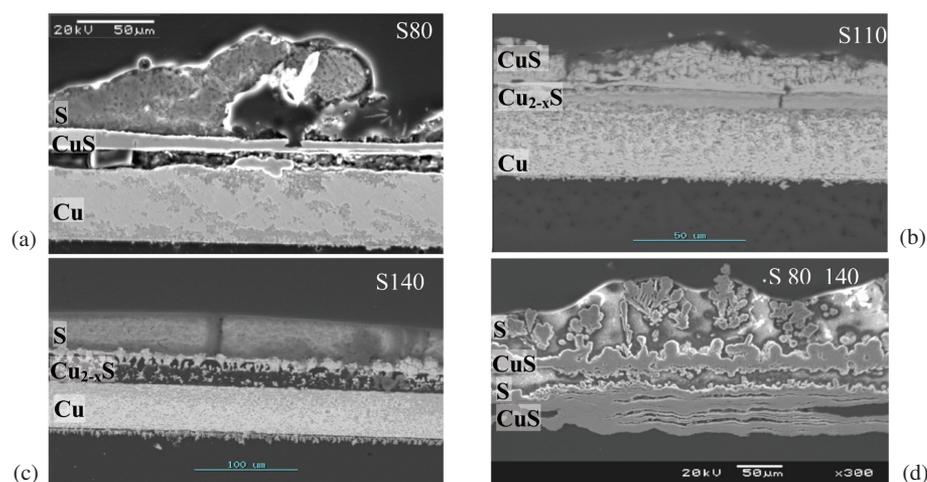


Figure 6. BSE images of the cross-sections of the corrosion products formed during sulphidation with S_2 at (a) 80°C , (b) 110°C , (c) 140°C and (d) 80°C – 140°C

copper foil before exiting through a reactor lid. The reactor remained on the hot stove for the duration of the experiment to ensure that the sulphur remained molten. Argon (technical grade) at a flow rate of 0.25 l/min was used as a carrier gas.

Copper foil samples were respectively exposed to sulphur vapour, a mixture of sulphur and HCl, and H_2S . The copper foil samples that were exposed to sulphur vapour were reacted for a duration of 1 hour at different temperatures in the range 65°C to 140°C to investigate the effect of temperature on the corrosion rate. These experiments were repeated at 80°C , 115°C and 140°C with HCl addition at 0.01 l/min (0.04 atm) to investigate the role of HCl on sulphidation. HCl was introduced to the reactor by bubbling argon through concentrated 32% v/v HCl acid. Copper was exposed to H_2S for 2 hours at 80°C , 110°C and 140°C to determine the corrosion rate of copper by H_2S as a function of temperature. H_2S was synthesized by reacting 124 ml of 0.15 mol/l sulphuric acid with 10 g of FeS which theoretically produced 19.35 g of H_2S according to the reaction model of FactSage software. Redox titrations were used to determine the amount of H_2S formed⁶. Each of the corrosion experiments was repeated three times to verify repeatability.

The thickness loss of the foil due to corrosion was determined by measuring the change in foil resistance with time. The slope of thickness loss versus exposure time was determined by fitting a straight line through the curve.

Upon completion of the experiments the copper foil was allowed to cool to room temperature under an argon atmosphere. The copper foil residue with corrosion product was submitted for analysis to investigate the effect of temperature and gas composition on the morphology and phase composition of the corrosion product. Phase compositions and morphologies of the corrosion products were characterized by SEM (Jeol JSM 6300) using energy-dispersive spectrometry (EDS). Crystalline phases were determined by powder X-ray diffraction (XRD) using Fe filtered $\text{Co-K}\alpha$ radiation on a PANanalytical X'pert Pro powder diffractometer with X'celerator detector.

Results and discussion

According to the laboratory tests performed, reaction products between copper and sulphur include CuS and sulphur powder at 80°C (Figure 6a), CuS and (Cu_9S_8) at 110°C (Figure 6b), Cu_9S_8 and $\text{Cu}_{1.8}\text{S}$ at 140°C (Figure 6c). The BSE images of these corrosion products at different temperatures are shown in Figure 6. Sulphur formed the outer layer followed by CuS and the copper-rich sulphide

formed adjacent to the copper foil exhibiting high porosity and non-adherent properties. The effect of temperature variation on morphology was examined by exposing copper foil to sulphur and increasing its temperature gradually from 80°C to 140°C. Sulphur formed an outer layer at the gas-scale interface and CuS formed adjacent to the foil (Figure 6d). A sulphide phase with a dendritic structure could be distinguished between the sulphur layer and CuS layer. This sulphide phase has a Cu:S atomic ratio of 1, which is the stoichiometry of CuS.

The presence of chlorine induces pitting corrosion which was confirmed by the perforation observed in the residue of the copper foil. CuS and minor amounts of CuCl₂ were observed after exposure of copper to sulphur and HCl, but no CuCl was observed. C₂S was the major phase associated with the corrosion product which formed when copper was exposed to hydrogen sulphide gas at 140°C.

Corrosion rates ranging from 27 mm/y to as high as 80 mm/y were observed when copper foil was reacted with sulphur vapour respectively between 65°C and 110°C (Table II). The corrosion rate decreased significantly between 110°C and 120°C. In order to determine the transition temperature at which corrosion rates change, tests were run where the temperature was gradually raised from 80°C to 140°C at 20°C intervals every hour. It was observed that the transition temperature is 112°C which coincides with the melting point of α -sulphur⁷. The transition in corrosion rate behaviour could therefore be attributed to the phase transition of sulphur from solid to liquid. The presence of chlorine induces a transition from linear to parabolic rate behaviour below 112°C. Above 112°C the chlorine enhances the corrosion rate significantly. At temperatures below 140°C the corrosion rate of a copper foil by hydrogen sulphide is very low, the highest corrosion rate observed at 140°C was 0.08 $\mu\text{m}/\text{min}$. The reaction of copper with hydrogen sulphide gas therefore does not have a strong effect on copper corrosion compared to reactions of copper with sulphur.

Copper foil was exposed to sulphur vapour at 140°C for 8 hours to ascertain the effect of long exposure time on corrosion rate behaviour. The thickness loss versus time relationship is shown in Figure 7. An initial average corrosion rate of 0.11 $\mu\text{m}/\text{h}$ was observed in the first five hours. A sudden increase in corrosion rate was observed from 294.25 minutes to 356.5 minutes (indicated by arrows in Figure 7), while the temperature remained constant. During this period a total of 1.22 micron was lost in an hour, which was about 10 times the initial rate.

After 1 hour a sharp decrease in thickness loss rate was observed although the slope of the graph remained higher than the initial slope. After the test a crack was observed in the corrosion product. A sudden increase in corrosion rate could be attributed to the crack which exposed fresh metal to the corrosive gases. Each test would display unique effects but this was a noteworthy example of what might happen with long exposure times. Other factors which affect corrosion rates include morphology of the corrosion product (porosity, grain size and permeability), loss of the

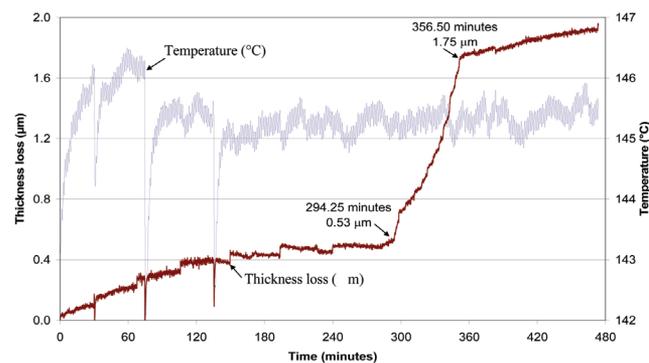


Figure 7. Thickness loss of a copper foil as a function of exposure time at 140°C in sulphur vapour

protective layer due to density differences and poor adherence⁸, defects⁹ and internal stresses which lead to cracks¹⁰. These factors may induce linear rate growth of the corrosion layer at long exposure times. Due to these uncontrollable variables that affect the corrosion behaviour of copper foil, it would be inaccurate to apply the parabolic rate law to estimate corrosion rates during long exposure times as in the smelter; hence linear corrosion rates were assumed in estimating the corrosion rates. Tests performed under synthetic conditions cannot be extrapolated to longer times to predict plant conditions, since different sulphidation phases are observed over time¹⁰.

Conclusions

The following observations were made when comparing the post-mortem analyses of the furnace wall lined with magnesia-chrome bricks with the scenario where graphite blocks were used in the lining:

- Graphite plays a significant role in inhibiting corrosive gases and base metal sulphides from reaching the copper cooler surface. Very little corrosion of copper coolers was observed at the slag-feed interface when the graphite block was used compared to when mag-chrome bricks were used.
- The graphite block was virtually uncorroded at the slag - feed interface, while the magnesia-chrome brick was totally consumed at the slag-feed interface.
- No elemental sulphur was detected in any of the graphite samples.
- The freeze lining on the graphite block was thin (2 mm), and consisted mostly of matte, whereas the freeze lining that was observed on the magnesia-chrome bricks was 10 cm thick and consisted mainly of oxide phases. The freeze lining on the graphite block was not as porous and full of cracks as the freeze lining on the mag-chrome bricks.
- Similar phases could be identified on both the graphite block and in the freeze lining attached to the magnesia-chrome brick, which confirms that base metal sulphides do get deposited on the sidewalls of the furnace at the

Table II
Average corrosion rates of copper foil exposed to sulphur vapour at different temperatures

Average temperature °C	62.6	80.1	89.8	99.1	108.9	120.8	127.8	140.0
$\mu\text{m}/\text{h}$	3.1	6.2	6.5	8.5	9.2	0.5	0.2	0.3
mm/y	27.2	54.1	56.8	74.5	80.3	4.6	1.8	2.6

slag-feed interface, where dissolution of the feed takes place. In the case of the graphite block, the base metal sulphides mostly remain on the hot face or penetrate along the graphite-graphite interface, whereas where magnesia-chrome bricks are used the base metal sulphides can diffuse through the freeze lining to the cold face of the refractory wall.

- The amounts of base metal sulphides at the cold face of the graphite block were very low compared to the amounts detected behind the freeze lining and the magnesia-chrome brick.
- Chloride-containing phases were observed in the graphite block at the cold face of the sample collected halfway between the top sample and the bottom sample, and in the lid of the graphite block, which held the graphite block and the copper cooler together. In the post-mortem sample from the magnesia-chrome brick, chloride-containing phases were detected in the sample which was taken from top of the cooler and between the copper cooler and the front brick.
- $\text{Cu}_2\text{Cl}(\text{OH})_3$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were observed on the lid of the graphite block and the cold face of the top portion of the graphite block, after the sample had been stored for four months.

The phase composition of the corrosion product is a function of both the temperature and the corroding gas composition. When copper is exposed to sulphur, CuS forms at temperatures below 110°C , with Cu_9S_8 as a minor phase adjacent to the copper foil. Cu_9S_8 and $\text{Cu}_{1.8}\text{S}$ are predominant sulphide phases that form at 140°C . However, addition of HCl retards the formation of the copper-rich sulphides at 140°C , resulting in the formation of CuS and minor amounts of CuCl_2 . The sulphides that form from the reaction of copper and sulphur are friable and non-adherent which makes the sulphide prone to cracking and peeling off, exposing fresh metal surface for further reaction.

Corrosion rates as high as 80 mm/y can be observed when copper foil is exposed to sulphur at 110°C . This observation suggests that sulphur alone can cause severe corrosion to copper coolers even at moderate temperatures. Copper foil corrosion rate decreased from 80 mm/y at 110°C to 5 mm/y at 112°C which could be attributed to the melting of sulphur. Contrary to this observation when HCl was added, the corrosion rate was enhanced above 112°C , and pitting corrosion was observed.

The corrosion rate behaviour in short exposure times is linear and cannot be accurately extrapolated to long exposure times, as there are other factors that affect corrosion as reaction times increase, such as density, porosity, thickness, adhesion and physical disruption of the scale¹⁰.

References

1. NELSON, L.R., GELDENHUIS, J.M.A., EMERY, B., DE VRIES, M., JOINER, K., SARVINIS, J., STOBER F.A., SULLIVAN, R., VOERMANN, N., WALKER, C. and WASMUND, B. Hatch developments in furnace design in conjunction with smelting plants in Africa. *Southern African Pyrometallurgy 2006*, R.T. Jones (ed.), South African Institute of Mining and Metallurgy, Johannesburg, 5–8 March 2006. pp. 417–436.
2. HUNDERMARK, R., DE VILLIERS, B., and NDLOVU, J. Process description and short history of Polokwane smelter. *Southern African Pyrometallurgy 2006*, R.T. Jones (ed.), South African Institute of Mining and Metallurgy, Johannesburg, 5–8 March 2006. pp. 35–42.
3. PISTORIUS, C. Confidential Report, University of Pretoria, 2004.
4. VAN MANEN, P.K. Furnace energy efficiency at Polokwane smelter. *Third International Platinum Conference 'Platinum in Transformation'*, The Southern African Institute of Mining and Metallurgy, 2008. pp. 191–196.
5. PLASCENCIA, G., UTIGARD T.A., and JARAMILLO, D. Extending the life of water-cooled copper cooling fingers for furnace refractories. *Journal of Metals*, 2005. pp. 44–48.
6. LENAHAN, W.C. and MURRAY-SMITH, R. DE L. *Assay and analytical practice in the South African mining industry*. The Southern African Institute of Mining and Metallurgy, Monograph series M6, 2001. pp. 176–177.
7. VAUGHAN, D.J. and CRAIG, J.R. *Mineral chemistry of metal sulfides*. Cambridge University, 1978.
8. GESMUNDO, F., NIU, Y., CASTELLO, P., VIANI, F., HUNTZ, A.M., and WU, W.T. The sulphidation of two-phase Cu-Ag Alloys in H_2 - H_2S mixtures at 550 – 750°C . *Corrosion Science*, 1996. vol. 38, no. 8, pp. 1295–1317.
9. REID, M., PUNCH, J., GARFIAS-MESIAS, L.F., SHANNON, K., BELOCHAPKINE, S., and TANNER, D.A. Study of mixed flowing gas exposure of copper. *Journal of the Electrochemical Society*, 2008. vol. 155, no. 4, pp. C147–C153.
10. TRAN, T.T.M., FIAUD, C., and VILLANOVA, A. The atmospheric corrosion of copper by hydrogen sulphide in underground conditions. *Corrosion Science*, 2003. vol. 45, pp. 2787–2802.



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