

LABORATORY SCALE INVESTIGATION INTO THE CORROSION OF COPPER IN A SULPHUR-CONTAINING ENVIRONMENT

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Abstract

The effect of temperature and gas composition on the corrosion rate and corrosion by-product of copper foil was studied by exposing it to sulphur (S₂), S₂ + hydrochloric acid (HCl) and hydrogen sulphide. The temperature was varied from 80 to 140 °C. Copper foil reacted with S₂ to form CuS, Cu₉S₈ and Cu_{1.8}S. Corrosion rates ranged from 9.6 µm/h at 110 °C to 0.5 µm/h at 140 °C. The presence of HCl caused pitting and enhanced the corrosion rate above 112 °C. Cu₂S formed when copper was exposed to hydrogen sulphide gas. Sulphide scale that formed was friable and non-adherent.

Keywords: A-copper, C-sulphidation, C-corrosion

1. Introduction

PGM (platinum group metal) smelters typically use copper waffle coolers to extract heat from the refractory wall. Corrosion of these copper coolers is a major concern in all PGM smelters that treat sulphide concentrates, as corrosion rates of greater than 60 mm/y have been observed at the slag-charge interface level in the smelter [1, 2, 3]. During the smelting of PGM-containing sulphide ores gases such as sulphur vapour, sulphur dioxide, water vapour and chlorine gas are given off [4, 5]. The source of the sulphur vapour is sulphides and labile sulphur contained in the feed [4]. Chlorine gas originates from the dissociation of halides such as KClMg(SO₄) and KMgCl₃ which can potentially be present in the feed [5]. Water vapour comes from the moisture [6] and chemically bound water in the feed material [7]. Water vapour dissociates to oxygen and hydrogen at high temperatures. The hydrogen can then react with other gases such as sulphur and chlorine to form hydrogen sulphide and hydrogen chloride gas [8]. High temperatures associated with the smelting process drive these gases towards a cooler place, which is in front of the copper coolers [5]. Reaction between these gases and the copper coolers result in the corrosion and subsequent consumption of the copper coolers.

A post-mortem analysis of refractory samples that were in contact with a corroded copper cooler indicated that elemental sulphur, base metal sulphides and CuS are associated with the copper cooler [9]. Wear of the copper cooler proceeded through reaction between the copper and base metal sulphides, as well as gaseous attack of copper mainly by sulphur gas.

Virtually no published data is available on the mechanism by which copper coolers corrode in PGM smelters. A number of authors have however, studied phase relations between copper and sulphur, chlorine and H₂S at low temperatures [10-22]. Bartkowicz and Stoklosa established that the sulphidation of copper between 97 °C and 150 °C is complex, with the formation of hexagonal chalcocite (Cu₂S), monoclinic chalcocite (Cu₂S) and covellite (CuS) [12]. Blachnik and Muller reported that covellite and Cu_{1.1}S form below 128 °C, while between 128 °C and 150 °C covellite (outer layer) and Cu_{1.8}S (inner layer) form when a copper foil is exposed to sulphur [13]. They also observed that the layer of sulphide scale that formed is porous and poorly adhered to the metallic core [13]. Covellite is in equilibrium with sulphur below 507°C, while Cu₂S is in equilibrium with copper according to the phase diagram by Vaughan and Craig (Figure 1, [18]). It can therefore be expected that when a copper foil is exposed to sulphur at temperatures below 150 °C, an outer layer of covellite (CuS) will form, while an inner layer of chalcocite (Cu₂S) will form on the metal surface. Covellite and chalcocite are therefore the sulphide phases that are expected to be associated with copper coolers when sulphide ores are smelted.

Figure 1: Temperature-composition diagram of condensed phases in the Copper-Sulphur system [18].

There is general agreement that chalcocite forms by the outward diffusion of copper ions when copper is exposed to hydrogen sulphide gas [10, 14-16], and that the rate of growth of chalcocite is enhanced by an increase in temperature [17].

CuCl is reported to be the main phase that forms when copper is exposed to hydrogen chloride gas [19, 20]. Chlorine has the ability to diffuse through the corrosion layer, providing a path for metal ion diffusion to the reaction surface. Chlorine therefore increases the corrosion rate by physically disrupting the protective scale [20-22].

The objective of this study was to determine how the surface temperature of copper and the composition of the corrosive gases affect the corrosion rate of copper, as well as the phase compositions and morphologies of the corrosion products. Laboratory scale corrosion tests were executed where the conditions that prevail on the surface of the copper cooler were simulated. Copper foil was exposed to sulphur vapour, sulphur vapour with hydrogen chloride gas, sulphur vapour with water vapour, and hydrogen sulphide gas. The laboratory scale corrosion tests were performed from 80 °C to 140 °C. This temperature range was chosen based on heat flux calculations through the wall of a PGM smelter [9].

2. Material and methods

2.1. Apparatus

Annealed 99.7 % copper foil* (thickness of 0.05 mm, width of 2.5 mm and length of 60 mm) was cut out of a copper sheet and used as the substrate. The samples were

* Supplied by Industrial Analytical, with typical analysis (ppm): Ag<100, Al<100, B<10, Ca 30, Fe<500, Mg<10, Ni<300, Pb<100, Si 10, Sn<100, Zn 100.

subsequently abraded mechanically using a silicone carbide paper to size 400 μm . Fibre glass tinned copper wires were soldered to each end of the copper foil for electrical connections. A Goodwill power supply (GPR 1850) was used as a current source. Shielded cables were used to complete the electrical circuit between the electrical instruments and the tinned copper wires from the foil. The foil was attached to a heat sink (hollow copper block of dimensions 70 mm x 20 mm x 20 mm with a 10 cm inner diameter, which was connected to a Labcon CPM 200 silicone oil bath). The silicone oil was circulated through the heat sink in order to regulate the temperature of the copper foil. A type K thermocouple was fitted onto the heat sink to measure the temperature of the copper foil. A sealable glass jar was used as a reaction chamber, through which different gaseous species were purged. A Heidolph MR2002 hot plate was used to heat a sublimed sulphur powder (Merck Chemicals) to above 200 $^{\circ}\text{C}$, to ensure the reaction chamber remained saturated with sulphur vapour. Argon (carrier gas) was bubbled through concentrated (32 %v/v) hydrochloric acid to generate hydrogen chloride gas. Hydrogen sulphide gas was produced by reacting 124 ml of 0.15 mol/L sulphuric acid with 10 g of iron sulphide (FeS) which theoretically produced 19.35 g of hydrogen sulphide gas according to the reaction model of FactSage [9]. Redox titrations were performed to confirm the amount of hydrogen sulphide gas that formed [23].

2.2. Experimental procedure

A copper foil mounted onto the heat sink was heated to the operating temperature under an argon atmosphere to avoid pre-sulphidation and oxidation of the foil. Upon reaching the operating temperature the copper foil was suspended in a sealed 3 L glass reactor containing the corrosive gas. Argon (99.9 %) at a flowrate of 0.25 L/min was used as a carrier gas. All the corrosion tests were performed in triplicate.

2.3. Calculation of corrosion rates

An electrical resistance technique was employed to determine the corrosion rate of the copper foil. The change in foil resistance was measured using a four wire resistance measurement in which a wire of known resistance (shunt resistor) was connected in series with the copper foil and a current supply. The voltage drop across the shunt resistor was used to calculate the current flow through the circuit. The calculated current and the voltage drop across the copper foil was then used to calculate the resistance of the copper using Ohm's law ($V=IR$) [24].

A digital multimeter (Datataker DT80) with built-in sensors and data logger was used for data acquisition (voltage and temperature). The change in foil thickness was calculated from Equation 1, where R is the electrical resistance, ρ is the electrical resistivity, L is the electrical length, A is the cross-sectional area, t is the thickness and w is the width of the foil [25]:

$$R = \frac{\rho L}{A} = \frac{\rho L}{tw} \quad \text{Equation 1}$$

The length and width of the foil was assumed to be constant and the resistivity was calculated using Equation 2, where alpha (α) is the temperature coefficient of resistivity which accounts for the change in resistivity due to temperature [24, 25]:

$$\rho = \rho_{25^{\circ}\text{C}} [1 + \alpha(T - 25^{\circ}\text{C})]$$

Equation 2

Alpha (α) of the copper foil was determined by heating foil from 25°C to 140°C in an argon atmosphere. The slope of R/R_0 vs. dT gave an alpha value of 0.0031 K^{-1} . The change in foil thickness was plotted against time at constant temperature to determine the corrosion rate.

2.4. Determination of morphology and phase composition of the corrosion products

Upon completion of each experiment the copper foil was allowed to cool to room temperature under an argon atmosphere. The cooled copper foil residue and corrosion scale were subsequently analysed to determine the effect of temperature and gas composition on the morphology and phase composition of the corrosion product. This was done by performing XRD and SEM-EDS analyses, using a PANalytical X'pert Pro powder diffractometer with X'celerator detector and Fe filtered Co-K α radiation, and a Jeol JSM 6300 scanning electron microscope.

3. Results and Discussion

3.1. Corrosion of copper by sulphur vapour

3.1.1. Effect of temperature

Copper foil samples were exposed to sulphur vapour for 1 hour at temperatures in the range 65 °C to 140 °C to investigate the effect of temperature on the corrosion rate. The observed average corrosion rates of copper foil exposed to sulphur vapour were 3.1 $\mu\text{m/h}$ at 65 °C, 6.2 $\mu\text{m/h}$ at 80 °C, 6.5 $\mu\text{m/h}$ at 90 °C, 8.5 $\mu\text{m/h}$ at 100 °C, 9.2 $\mu\text{m/h}$ at 110 °C and 0.3 $\mu\text{m/h}$ from 120 °C to 140 °C (Figures 2 and 3).

Figure 2: Average corrosion rate as a function of temperature when copper was exposed to sulphur vapour in the temperature range 65 °C to 140 °C for 1 hour.

Figure 3: Thickness loss on copper foil as a function of exposure time for temperatures ranging from 65 °C to 140 °C (sulphidation by sulphur vapour).

The corrosion rate of copper exposed to sulphur vapour for 1 hour increased as the exposure temperature increased from 65 °C to 110 °C, while above 110 °C the corrosion rate decreased significantly. The decrease in corrosion rate could be attributed to the formation of a porous layer on the metal surface, similar to what was observed by Blachnik et al. [13]. Linear corrosion rate behaviour was observed in short exposure times (Figure 3), although there were minor variations during the initial 20 minutes of the test, which could have been caused by physical disruptions of the scale. To determine the transition temperature from high corrosion rates (below 110 °C) to low corrosion rates (above 110 °C) three experiments were performed where the substrate temperature was increased from 80 °C to 140 °C at 20 °C per hour. The aim of this test was to determine how fluctuating operating temperatures in the smelter would affect the corrosion of the copper coolers. Thickness loss versus exposure time for the first test is depicted in Figure 4. The transition temperature from fast to slow corrosion rates was 112 °C in the first and second test, while in the third test the transition occurred at 113 °C. The total thickness loss of the copper foil at the corrosion rate transition point was respectively 14.5 μm , 20.2 μm and 11.45 μm for the first, second and third tests. Transition from high to low corrosion rates could therefore be linked to temperature.

Figure 4: Thickness loss of copper foil as a function of exposure time in the temperature range 80 °C to 140 °C in sulphur vapour.

The change in corrosion rate observed between 112 °C and 114 °C coincides with the melting point of sulphur (which varies from 110 °C to 112 °C for α -sulphur, and is reported to be 114 °C for β -sulphur [18]). A slower corrosion rate can also be attributed to the porous sulphide layer that formed on the metal-scale interface, which poorly adhered to the metal. Poorly adhered corrosion scale can retard the diffusion of copper species to the surface for the reaction to proceed, leading to slower corrosion rates [12, 26]. Dravnieks et al. [26] explained that when a metal is covered with an oxide layer which is in contact with an oxidising gas, the oxidation of the metal will proceed by diffusion of metal through the oxide layer. With decreasing direct contact between the metal and oxide the supply of metal to the bulk of the scale is slowed down, and corrosion rates decrease. The porous sulphide layer underneath the thick solid layer of sulphur can therefore hamper the diffusion of copper to the reaction site where sulphidation takes place.

The high corrosion rates observed below 110 °C demonstrate that the sulphide scale that formed was not protective.

3.1.2. Effect of exposure time at 140 °C

Copper foil at 140 °C was exposed to sulphur vapour for 8 hours to ascertain the effect of long exposure times on the corrosion rate (Figure 5). An initial average corrosion rate of 0.11 $\mu\text{m}/\text{h}$ was observed in the first five hours of exposure of the first corrosion test. A sudden increase in corrosion rate was observed between the 294th minute and 356th minute while the temperature remained constant (indicated by arrows in Figure 5). During this period a total of 1.22 micron was lost in an hour which was about 10 times higher than the initial corrosion rate. The corrosion rate decreased sharply to 0.09 $\mu\text{m}/\text{h}$ for the remainder of the test. After the test a crack was observed in the corrosion product. The sudden increase in corrosion rate could therefore be attributed to the crack which exposed fresh copper to the corrosive gases. The two other replicates of this test depicted parabolic rate behaviour, and no cracks were observed in the corrosion product. Each of the three tests would display unique effects which is typical of what might happen with long exposure times, as in the PGM smelter.

Figure 5: Thickness loss of a copper foil as a function of exposure time at 140 °C in sulphur vapour.

Other factors affecting corrosion behaviour of a scale includes morphology of the corrosion product (porosity, grain size and permeability), loss of the protective layer due to poor adherence [15], defects [22] and internal stresses which lead to crack formation [11]. These factors may induce linear rate growth of the corrosion layer at long exposure times. Tests performed under synthetic conditions can therefore not be extrapolated to longer reaction times (as under plant conditions) since sulphidation kinetics can change over time, depending on the morphology of the sulphide scale, and the disruption thereof [11].

3.2. Corrosion of copper by sulphur vapour and hydrogen chloride gas

Copper foil was exposed to both sulphur vapour and hydrogen chloride gas at 80 °C, 110 °C and 140 °C, to determine the effect of hydrogen chloride gas addition on

sulphidation. At 80 °C parabolic rate behaviour was observed, with a thickness loss rate that decreased from 0.07 $\mu\text{m}/\text{min}$ in the first hour to 0.02 $\mu\text{m}/\text{min}$ at the end of the second hour. This parabolic rate behaviour observed at 80 °C can presumably be attributed to the critical thickness effect observed by Reid and co-workers [22]. According to these authors the rate of film growth becomes parabolic when the corrosion product reaches a critical thickness, which indicates that diffusion of copper through the corrosion layer becomes rate-limiting as the corrosion scale becomes thicker.

A linear corrosion rate of 0.07 $\mu\text{m}/\text{min}$ was observed at 115 °C in the initial 90 minutes after which the slope increased to 0.16 $\mu\text{m}/\text{min}$. The cause of the increase in corrosion rate is not clear. An average corrosion rate of 0.19 $\mu\text{m}/\text{min}$ was observed when the temperature of the copper foil was 140 °C.

Faster corrosion rates at 140 °C compared to 80 °C and 115 °C can be attributed to the ability of the hydrogen chloride gas to penetrate through the corrosion layer at higher temperatures [21, 22]. Differences in morphology of the corrosion products that form at these temperatures (80 °C to 140 °C), may also influence the corrosion behaviour of the copper foil since chlorine diffuse faster in chalcocite than in covellite [27]. Copper foils were also exposed to a mixture of sulphur vapour and hydrogen chloride gas where the copper foil temperature was gradually raised from 80 °C to 140 °C at 20 °C intervals to determine the transition temperature from a slow corrosion rate (at 80 °C and 110 °C) to a fast corrosion rate (at 140 °C). The thickness loss versus time graph for the first test is depicted in Figure 6. The transition temperature was 112 °C in both the first and the second test. The total thickness loss was respectively 10.74 μm and 19.8 μm at this transition temperature. It was again observed that temperature strongly influences the corrosion rate. In the presence of hydrogen chloride gas the corrosion changed from a slow rate to a high rate at 112 °C, while in sulphur vapour the corrosion rate changed from a high rate to a low rate at 112 °C.

Figure 6: Thickness loss as a function of exposure time at varying temperatures (80 °C to 140 °C) when copper foil was exposed to both sulphur vapour and hydrogen chloride gas.

It is presumed that the sulphide layer that forms above 110 °C is passivating to sulphur, but the presence of chlorine enables the corrosive gases and metal ions to diffuse to the reaction site, thereby enhancing corrosion. In the presence of hydrogen chloride gas the corrosion rate of copper by sulphur can be enhanced to above 100 mm/y if the copper surface temperature is above 110 °C. This agrees with the work of Tran et al. [11], who reported that foil cleaned with hydrogen chloride reacted faster at temperatures above the melting point of sulphur, compared to foil cleaned with alcohol. It can therefore be concluded that the transition from a slower to a faster corrosion rate is associated with the melting of the sulphur, and the ability of chlorine to permeate through a thick layer of molten sulphur and sulphide phases. The observed increase in corrosion rate at 142 °C was presumably caused by cracks and defects in the foil since they could not be attributed to any phase transformations or the formation of any additional phases.

3.3. Corrosion of copper by hydrogen sulphide gas

Copper foil was also exposed to hydrogen sulphide gas at 80 °C, 110 °C, and 140 °C for 110 minutes. Average corrosion rates at these temperatures were respectively 0.003 $\mu\text{m}/\text{min}$, 0.01 $\mu\text{m}/\text{min}$ and 0.08 $\mu\text{m}/\text{min}$. The corrosion rate of copper by

hydrogen sulphide gas therefore increases with temperature, similar to what Tran and co-workers observed [17].

3.4. Morphology and phase composition of the corrosion products

3.4.1. Copper exposed to sulphur vapour

BSE images of the corrosion products that formed when copper foil was exposed to sulphur vapour at different temperatures are depicted in Figure 7. A black corrosion product formed at 80 °C (Fig. 7a), which contained fine yellow particles at the gas-scale interface. Covellite and synthetic sulphur were detected by XRD as major phases in this corrosion product. This phase composition was confirmed by EDS analysis.

Figure 7: BSE images of the cross section of the corrosion product formed during sulphidation with sulphur vapour at a) 80 °C, b) 110 °C, c) 140 °C and d) 80 °C-140 °C.

A black non-adherent layer was formed after exposing the copper foil to sulphur at 110 °C (Fig. 7b). Covellite and digenite (Cu_9S_5) were detected by XRD as major phases. A dense uniform copper sulphide with a Cu:S atomic ratio of 1 (covellite) was detected by EDS at the gas-scale interface. Meaningful EDS analysis of a porous copper rich sulphide layer adjacent to the copper foil could not be determined due to the high porosity of this layer. However, the stoichiometry of this phase is close to that of yarrowite (Cu_9S_8).

The corrosion product after exposure of a copper foil to sulphur vapour at 140 °C consisted of a thick deep red layer at the gas-scale interface (Fig. 7c). Yarrowite, covellite and sulphur were detected by XRD as major phases with digenite as a minor phase. EDS detected the outer layer to be sulphur, followed by a porous non-adherent copper sulphide layer in between the sulphur and copper layers, with a stoichiometry close to that of yarrowite.

It is assumed that the apparent deviation from stoichiometry when the sulphide layers that formed at 110 °C and 140 °C were analysed by EDS, is due to a mixture of very finely divided and intergrown sulphides such as digenite, covellite and yarrowite, similar to what was reported by Blachnik et al. [13].

The effect of temperature variation on the morphology of the corrosion products was examined by exposing a copper foil to sulphur and increasing its temperature from 80 °C to 140 °C. A poorly adherent corrosion product formed under these conditions, with a thick red layer at the gas-scale interface (Fig. 7d). Covellite and sulphur were detected by XRD as the major phases. According to the EDS analysis a sulphur layer formed at the gas-scale interface. A dendritic copper sulphide with the stoichiometry of covellite could be distinguished adjacent to this sulphur layer, followed by a smooth, dense and uniform layer of covellite with cracks parallel to the foil surface, adjacent to the copper foil. Varying the copper foil surface temperature from 80 °C to 140 °C therefore affects the morphology and phase composition of the corrosion product, and favours the formation of covellite.

3.4.2. Copper exposed to sulphur vapour with hydrogen chloride gas at 140 °C

The copper foil residue was perforated and heavily pitted after exposure to a mixture of sulphur vapour and hydrogen chloride gas at 140 °C (Figure 8). Covellite (CuS) and elemental sulphur (S) were detected by XRD analysis in this corrosion product. A

copper sulphide layer with a Cu:S atomic ratio of 1 (covellite) was detected by EDS. Hydrogen chloride gas addition at 140 °C changed the phase composition of the sulphide from a mixture of yarrowite, covellite and digenite to only covellite. The presence of hydrogen chloride therefore increased the average sulphur content of the sulphide scale that formed.

When varying the temperature from 80 °C to 140 °C two layers were identified by EDS: A sulphur layer at the gas-scale interface and covellite with small amounts of chlorine on the metal-scale interface. XRD detected α -sulphur, covellite and minor amounts of tolbachite (CuCl_2). The phase composition of the corrosion product at 80 °C to 140 °C is different to that observed at 140 °C in that chloride phases were not detected at 140 °C.

Figure 8: BSE image of the cross-section of the copper foil after exposure to both sulphur vapour and hydrogen chloride gas at 140 °C.

3.4.3. Copper exposed to sulphur vapour with water vapour at 80 °C to 140 °C
Covellite, α -sulphur and dolerophane ($\text{Cu}_2\text{O}(\text{SO}_4)$) were detected by XRD as major phases that formed when copper was exposed to both sulphur vapour and water vapour. Two layers with non-stoichiometric compositions could be distinguished by EDS: a porous inner layer and a dendrite-structured layer at the gas-scale interface. The inner layer consisted of a non-stoichiometric copper oxysulphate phase. The dendrites are Cu-S-O-based with a Cu:S atomic ratio of 1, and contains 13 wt% oxygen (Figure 9). Copper oxide did not form. This presumably is due to the sulphur that absorbed onto the copper surface and limited the sites for hydroxyl ions, which are required for metal oxide formation when water vapour is present [28].

Figure 9: BSE image of the corrosion product which formed when copper was reacted from 80 °C to 140 °C in a sulphur vapour and water vapour atmosphere.

3.4.4. Copper exposed to hydrogen sulphide gas

An adherent sulphide scale was observed when copper foil was exposed to hydrogen sulphide gas at 140°C. The foil was pitted adjacent to the sulphide scale (Figure 10). The sulphide scale consisted of high and low chalcocite according to the XRD analysis. The stoichiometry of the sulphide was confirmed by EDS to be Cu_2S . These findings are in agreement with the observation reported in the literature that chalcocite is the sulphide phase which forms when copper reacts with hydrogen sulphide gas [11, 12, 14, 15].

The temperature of the copper foil was varied from 80 °C to 140 °C to examine the effect of varying temperature on the phase composition of the corrosion product. Low and high chalcocite were major phases detected by XRD with minor amounts of covellite. A mixture of CuS and Cu_9S_8 was detected by EDS as the constituent of this corrosion product. The significant difference in phase composition is that only Cu_2S was detected in the sample produced at 140°C, while CuS and Cu_9S_8 were also detected in copper foil that was heated from 80 °C to 140 °C.

Figure 10: BSE image of a cross-section of the copper foil after exposure to hydrogen sulphide gas at 140 °C.

4. Conclusions

A summary of the phases that were detected in the corrosion products are listed in Table 1.

CuS was the main sulphide phase that formed when copper foil and sulphur reacted at 80 °C, 110 °C and 140 °C. The amount of CuS that formed decreased as the sulphidation temperature increased from 80 °C to 140 °C. CuS was the major phase at 80°C with sulphur powder at the gas-scale interface. CuS was observed together with Cu₉S₅ adjacent to the foil at 110°C, while no sulphur was associated with this corrosion product. Cu₉S₈ was the major phase observed at 140 °C, together with a layer of molten sulphur at the gas-scale interface. Below the melting point of sulphur (112 °C) sulphur gas reacted with copper to form CuS and sulphur powder at the gas-scale interface. Above the melting point of sulphur a porous copper rich sulphide layer formed adjacent to the copper foil, with a layer of molten sulphur at the gas-scale interface.

When copper foil at 140 °C was exposed to sulphur and either hydrogen chloride gas or water vapour, CuS was the main phase associated with the corrosion product.

The presence of chlorine induced pitting corrosion and perforation of the copper foil.

Only minor amounts of CuCl₂ were detected after the copper foil was exposed to sulphur vapour and hydrogen chloride gas at 80 °C to 140 °C.

The exposure of copper foil to water vapour together with S₂ resulted in the formation of a dendrite structured CuS with minor amounts of a copper oxysulphate phase (dolerophane). The reaction of both water vapour and sulphur vapour with copper at 140 °C changed the morphology of the corrosion product from Cu₉S₈ to dendrites of covellite and dolerophane.

Cu₂S was only observed when copper foil at 140°C was exposed to hydrogen sulphide gas. The reaction between copper foil and hydrogen sulphide gas at low gas concentrations did not seem to have a strong effect on the corrosion rate compared to reactions of copper by sulphur vapour.

Corrosion rates ranging from 3.1 µm/h to as high as 9.2 µm/h were observed when copper foil was reacted with sulphur vapour between 65 °C and 110 °C. Sulphidation of copper by sulphur vapour can therefore cause severe corrosion even at moderate temperatures. The corrosion rate decreased significantly above the melting point of sulphur (112 °C), while above 112 °C chlorine enhanced the corrosion rate significantly.

Sulphides that formed when copper foil reacted with sulphur vapour were friable and non-adherent to the copper. This had the consequence that the reproducibility of the corrosion experiments was good at short reaction times, but substantially poorer with longer exposure times as a result of crack formation and loss of the protective layer due to poor adherence of the scale.

It can be inferred from these laboratory scale experiments that the corrosion of copper coolers mainly proceeds through the reaction with S₂, whereby a friable and non-adherent sulphide scale forms. This scale is prone to cracking and peeling off, which implies that corrosion of the copper cooler will proceed as long as the furnace remains in operation. Any chlorides in the feed to the furnace are potentially harmful to the cooler, as chlorine enhances the corrosion rate of copper with S₂. Hydrogen sulphide

does not seem to play a major role in the corrosion of copper coolers in PGM smelters.

5. Acknowledgements

The authors would like to thank Mintek for financial support.

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Figure 1: Temperature-composition diagram of condensed phases in the Copper-Sulphur system

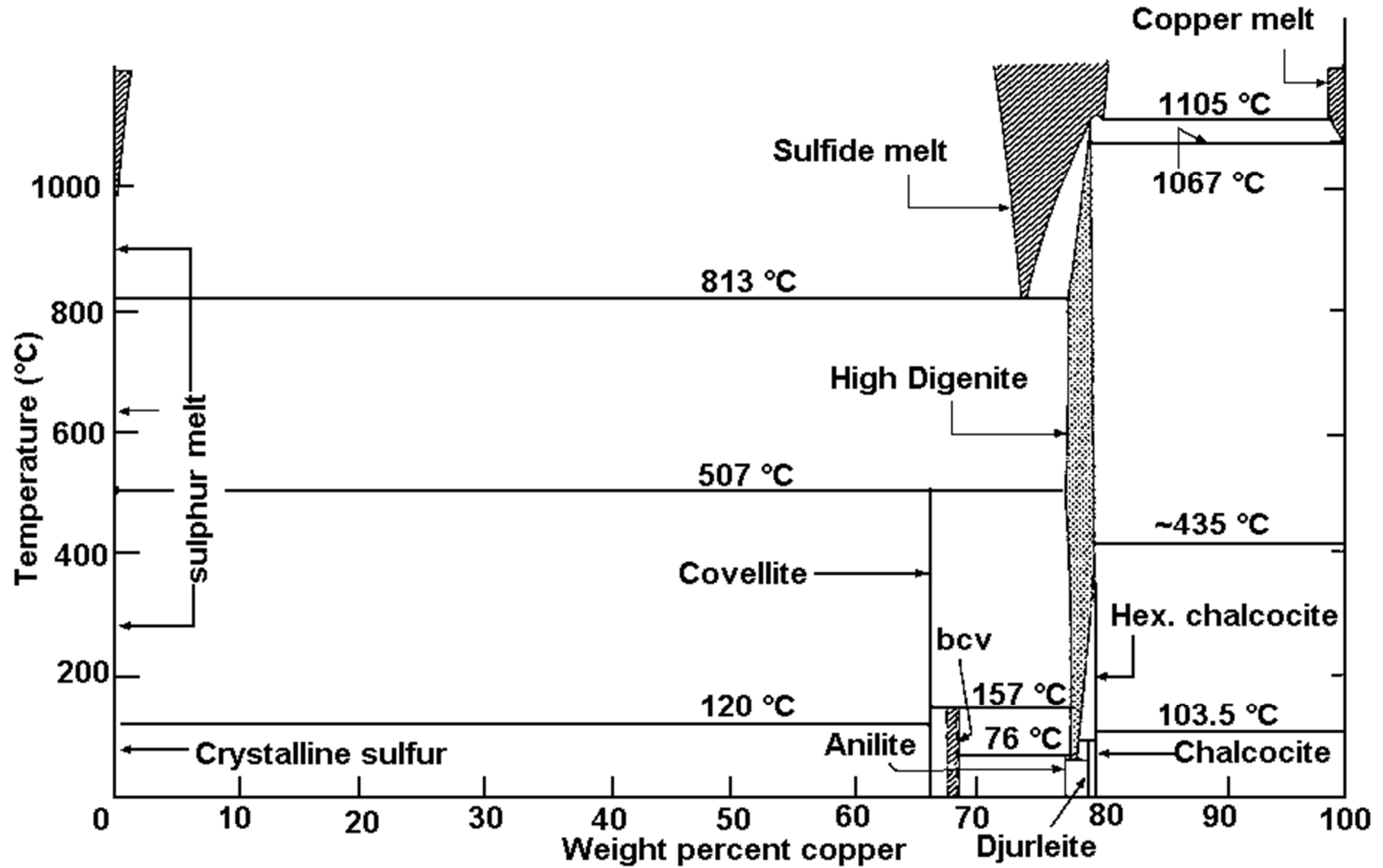


Figure 1: Average corrosion rate as a function of temperature when copper was exposed to sulphur vapour in the temperature range 65 °C to 140 °C for 1 hour.

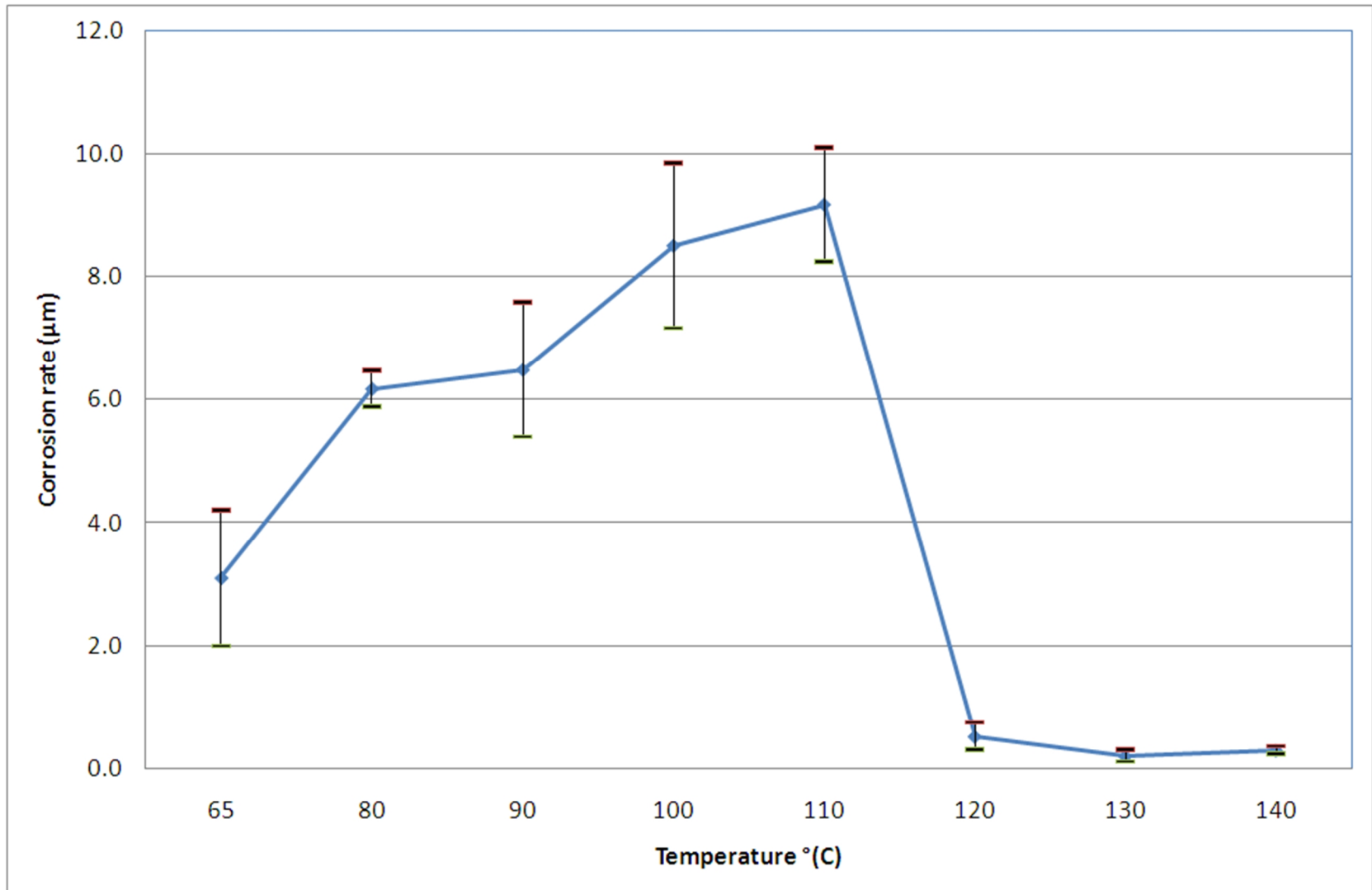


Figure 2: Thickness loss on copper foil as a function of exposure time for temperatures ranging from 65 °C to 140 °C (sulphidation by sulphur vapour).

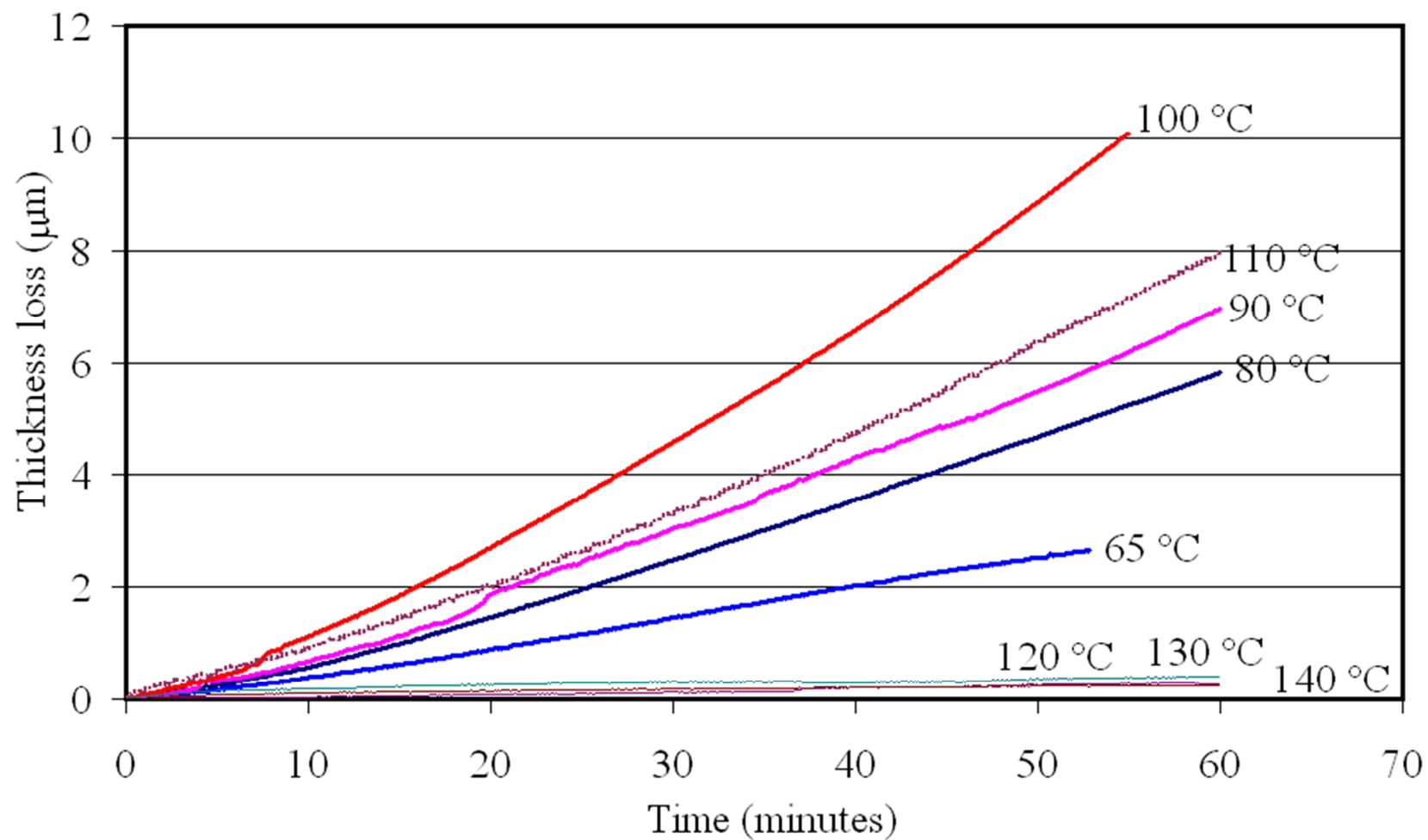


Figure 3: Thickness loss of copper foil as a function of exposure time in the temperature range 80 °C to 140 °C in sulphur vapour.

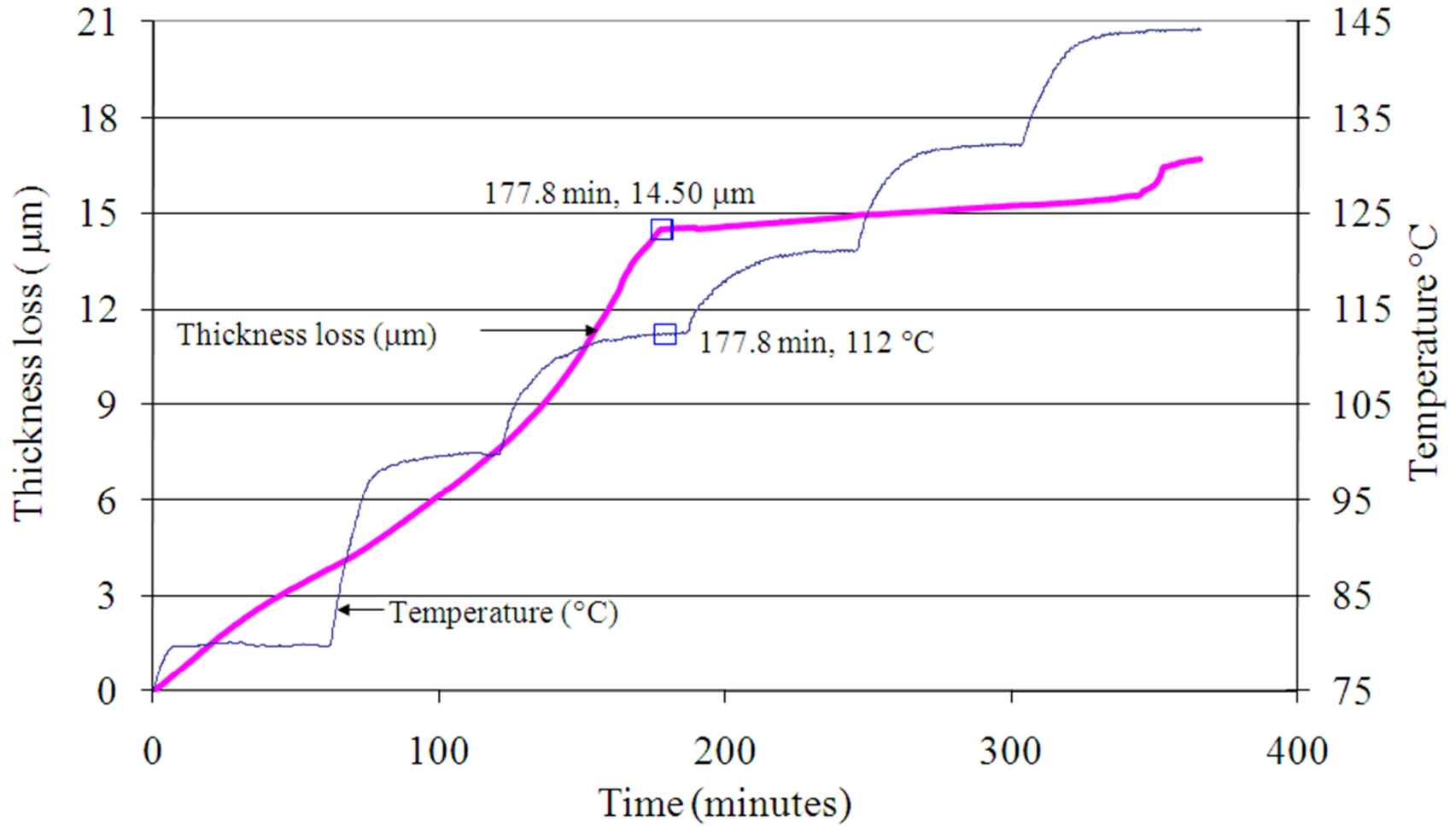


Figure 4: Thickness loss of a copper foil as a function of exposure time at 140 °C in sulphur vapour.

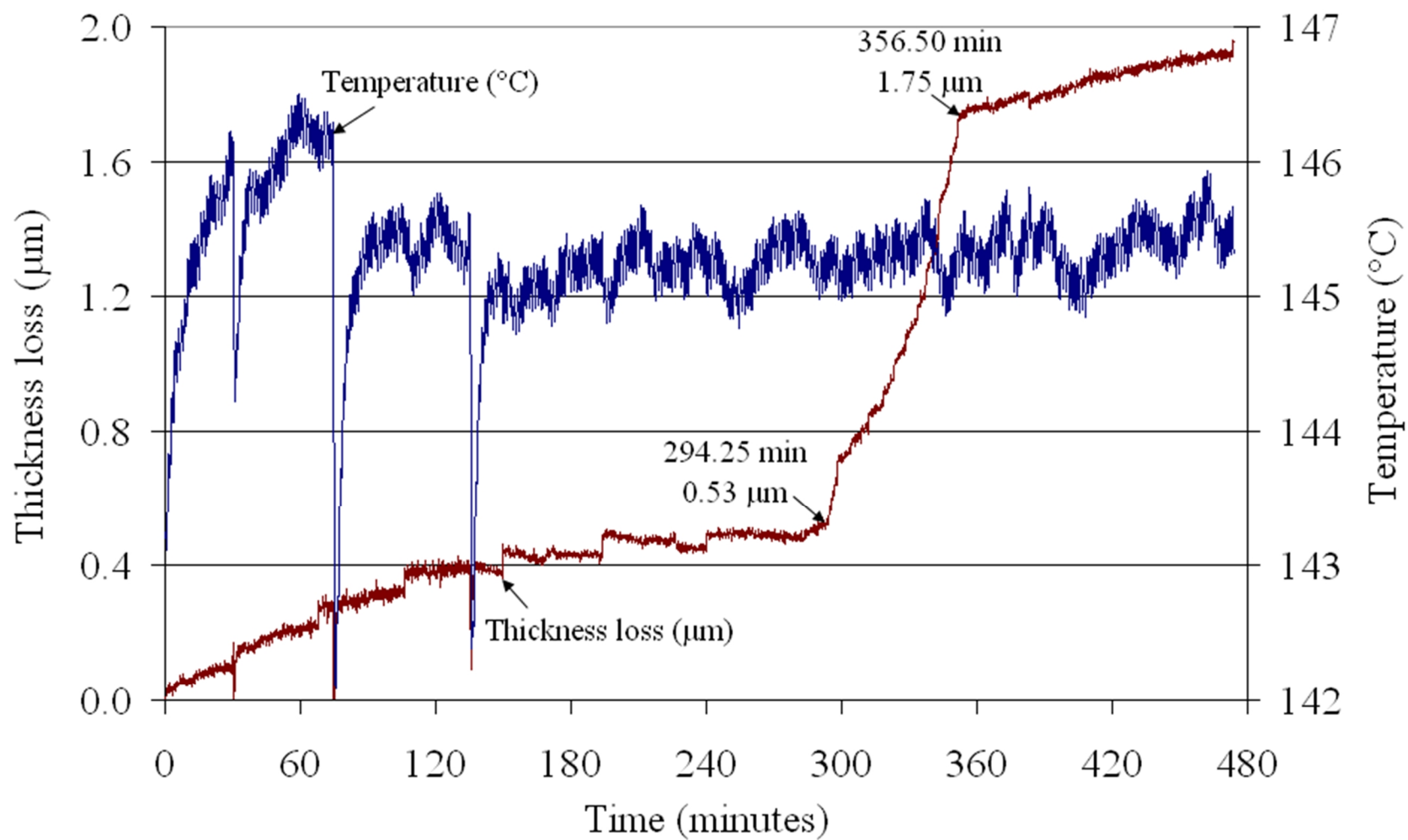


Figure 5: Thickness loss as a function of exposure time at varying temperatures (80 °C to 140 °C) when copper foil was exposed to both sulphur vapour and hydrogen chloride gas.

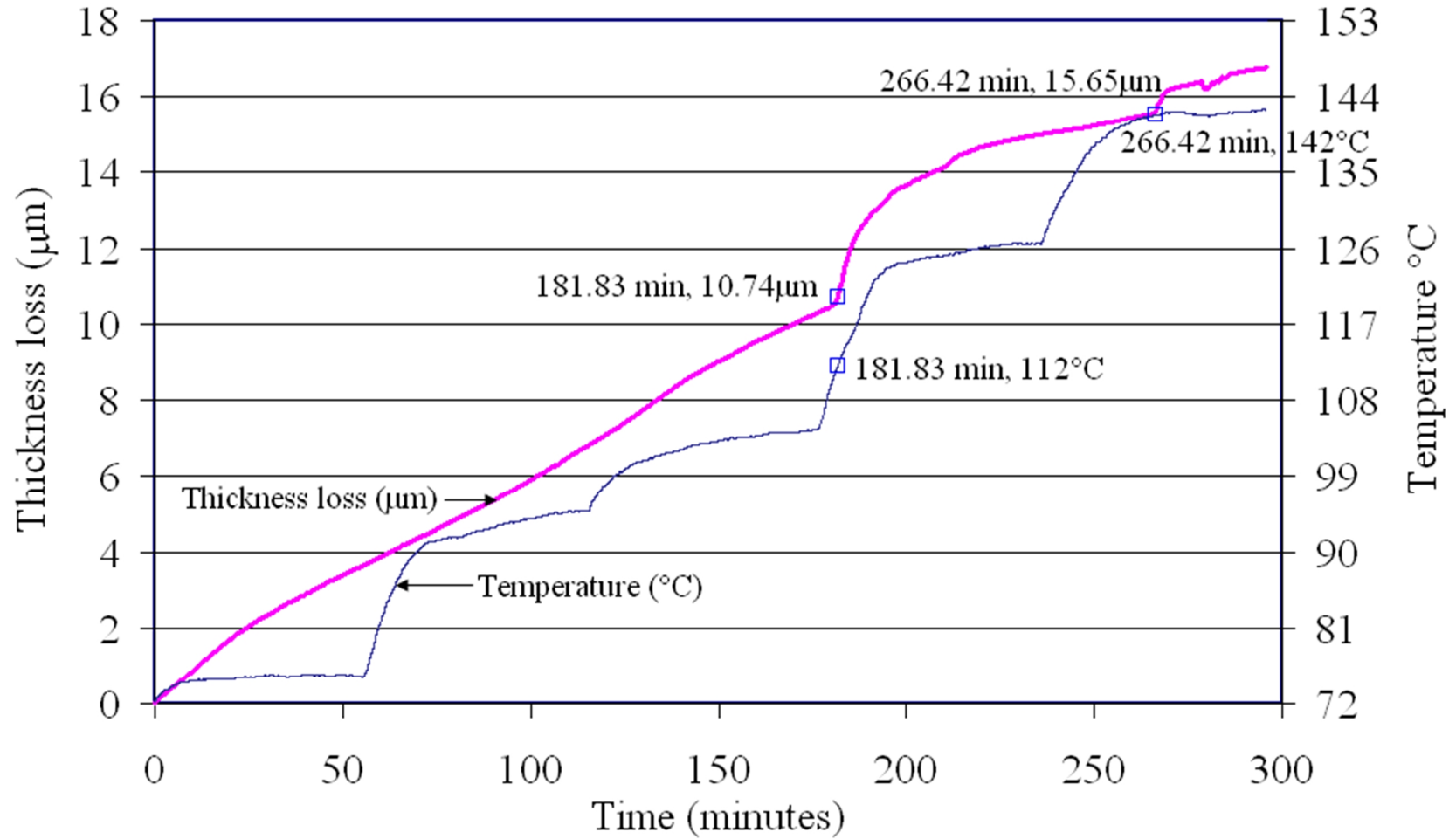


Figure 6: BSE images of the cross section of the corrosion product formed during sulphidation with sulphur vapour at a) 80 °C, b) 110 °C, c) 140 °C and d) 80 °C-140 °C.

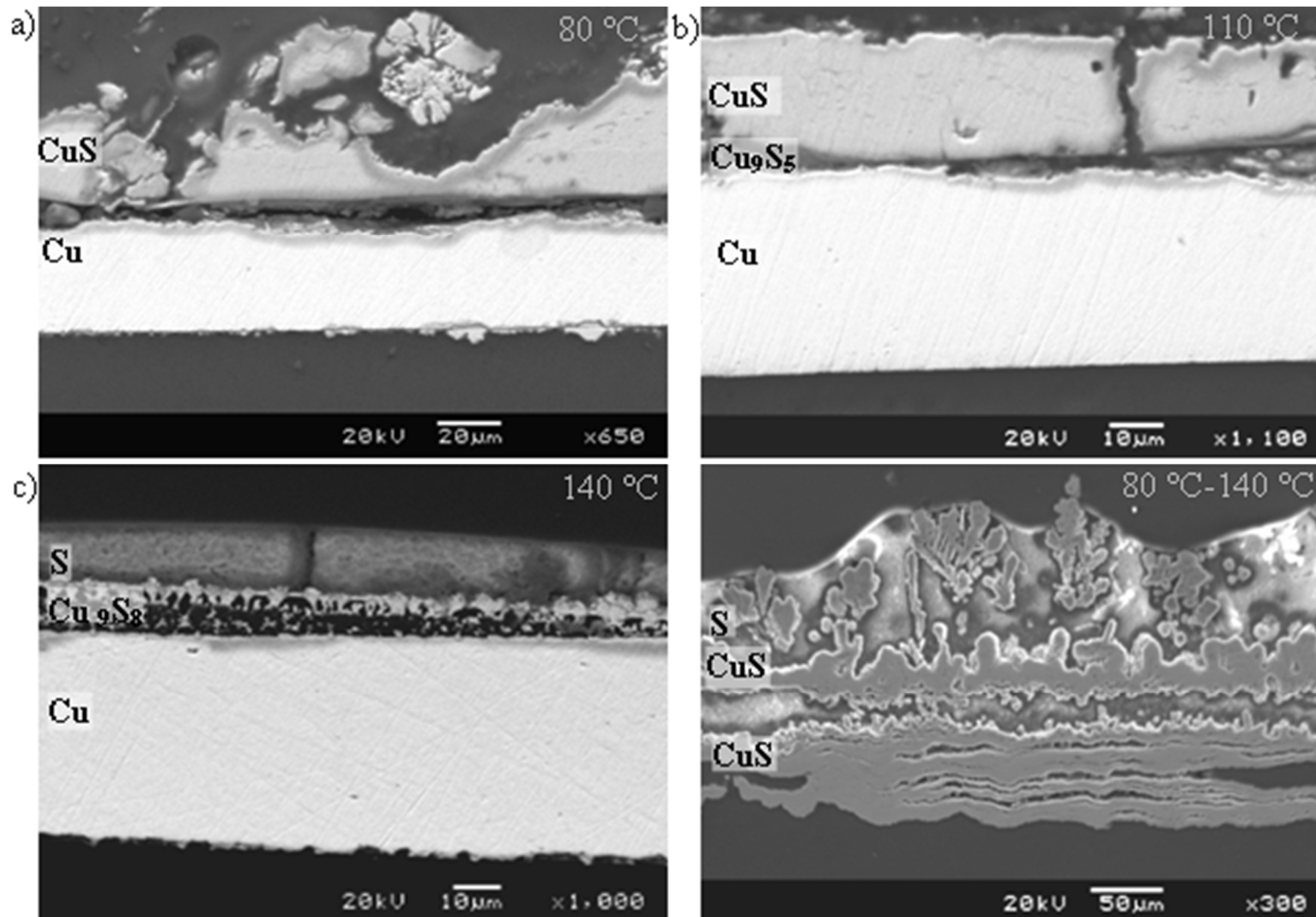


Figure 7: BSE image of the cross-section of the copper foil after exposure to both sulphur vapour and hydrogen chloride gas at 140 °C.

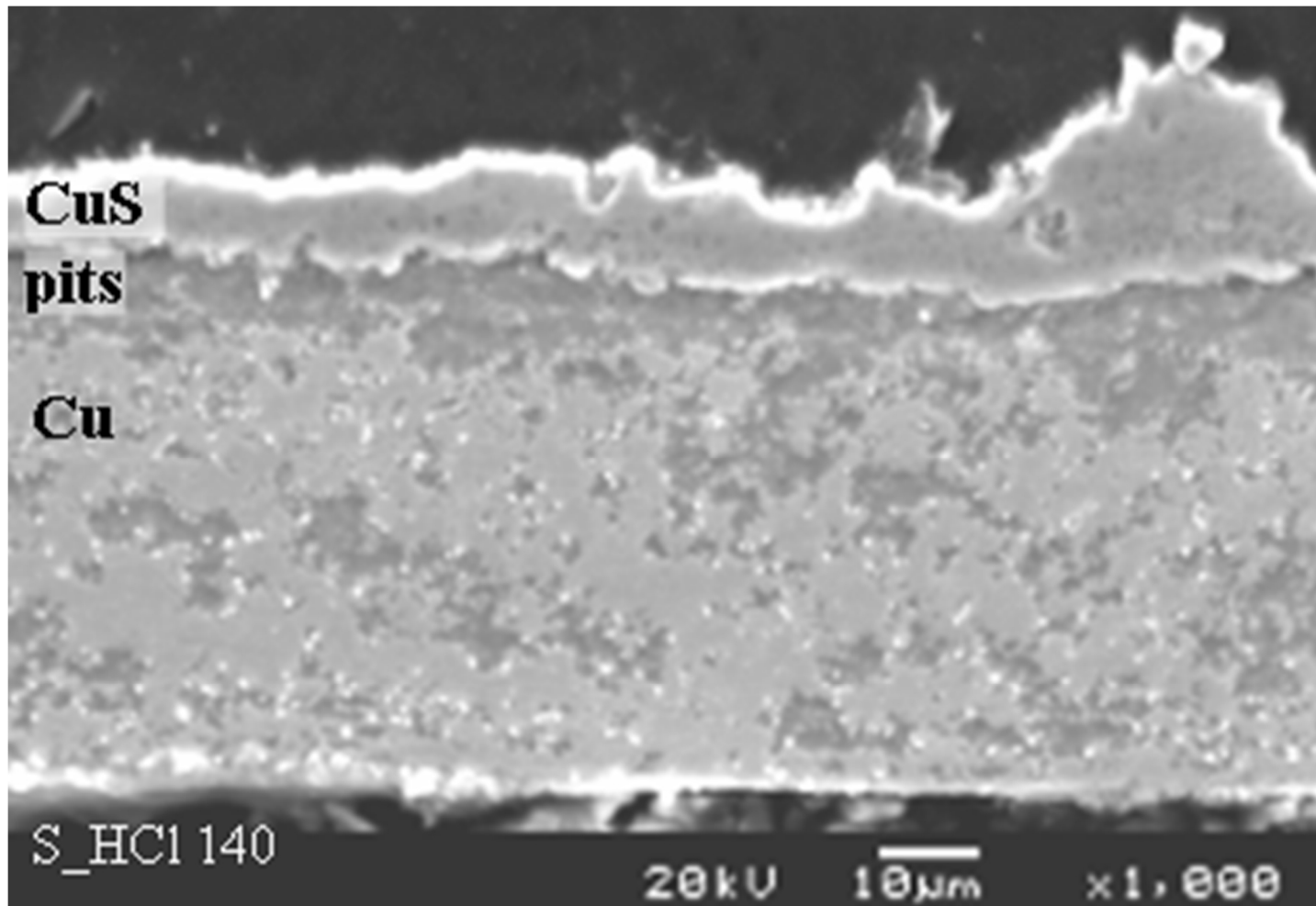


Figure 8: BSE image of the corrosion product which formed when copper was reacted from 80 °C to 140 °C in a sulphur vapour and water vapour atmosphere.

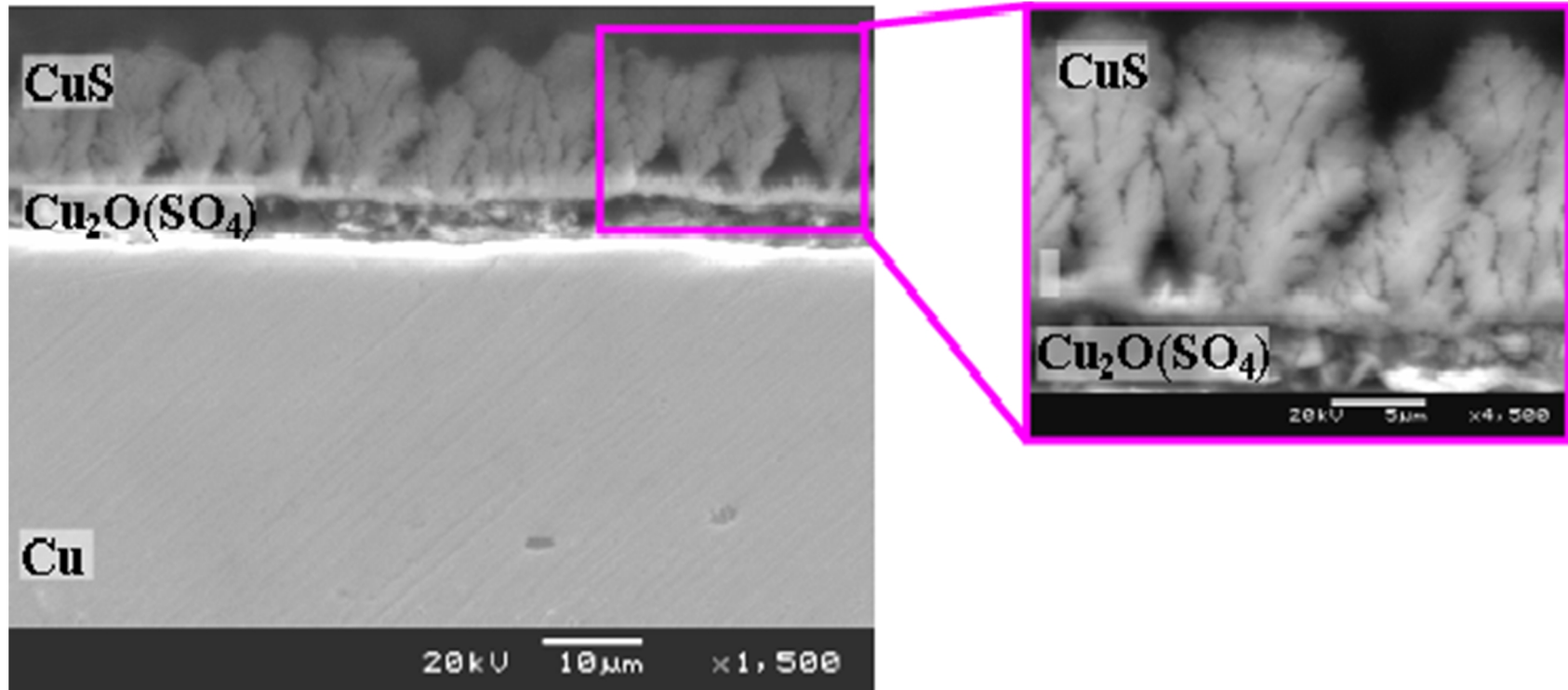


Figure 9: BSE image of a cross-section of the copper foil after exposure to hydrogen sulphide gas at 140 °C.

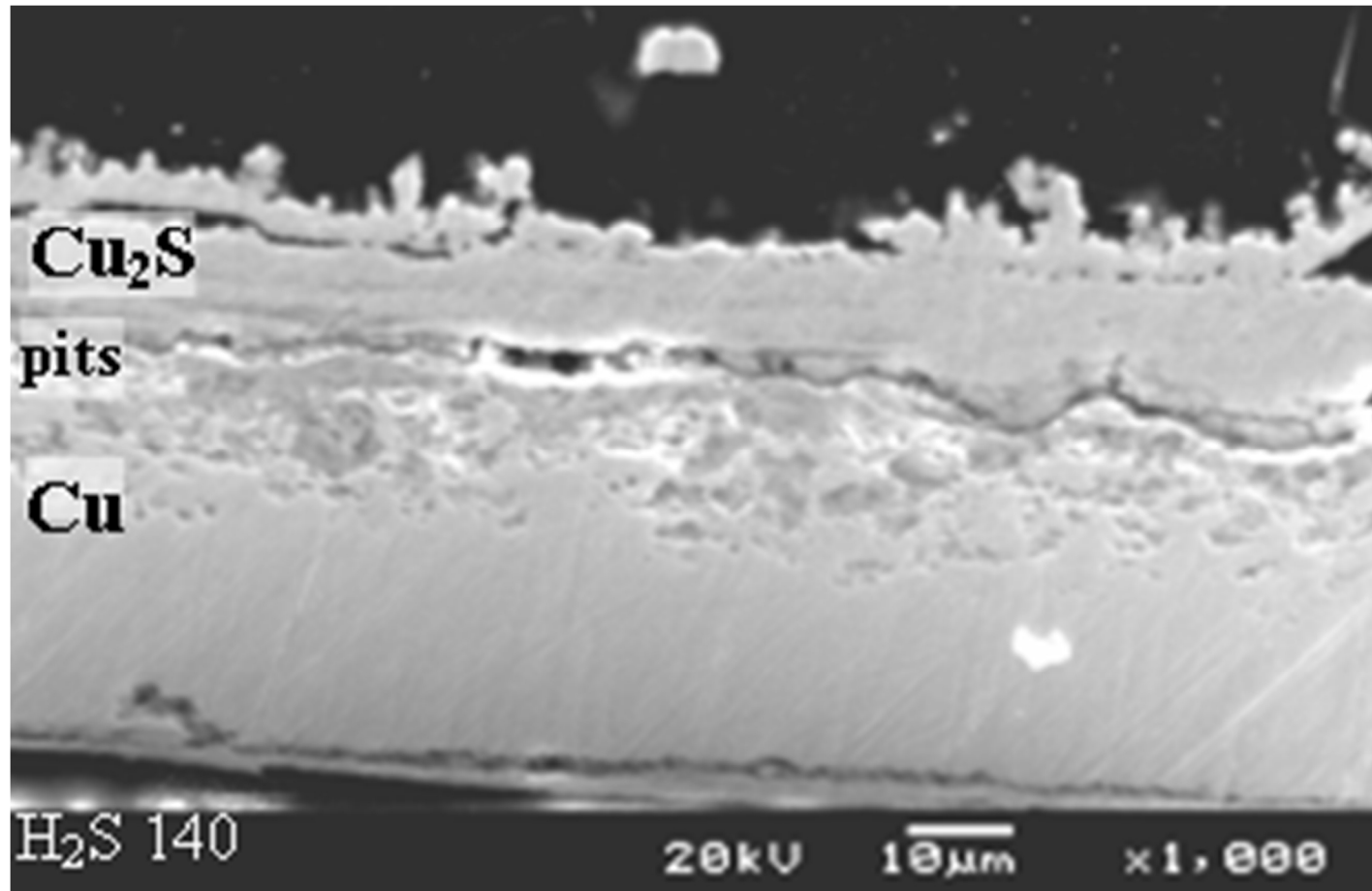


Table 1: Summary of the phases that formed in the corrosion products

Corroding gas	Copper foil temperature	Corrosion product(s)
Sulphur vapour	80 °C	CuS + S (powder)
Sulphur vapour	110 °C	CuS + Cu ₉ S ₅
Sulphur vapour	140 °C	CuS + Cu ₉ S ₈ + S (molten)
Sulphur vapour	80 °C to 140 °C	CuS + S (molten)
Sulphur + HCl	140 °C	CuS + S
Sulphur + HCl	80 °C to 140 °C	CuS + S + CuCl ₂
Sulphur + H ₂ O	140 °C	CuS + S + Cu ₂ O(SO ₄)
H ₂ S	140 °C	Cu ₂ S