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Corrosion properties of copper materials

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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Summary

A method to measure the relative nobility of copper materials has been applied to three different phosphorous doped copper materials relative to a high purity copper. The method, consisting of measuring the electrode potentials under conditions where Nernst's law is applicable, gives consistent and meaningful results.

The materials studied are here referred to as High purity copper, Reference copper, Low-P copper and High-P copper.

The apparent nobility of the Reference copper and the Low-P copper is estimated to about 2.5 mV more positive than High purity copper. The apparent nobility of the High-P copper is estimated to about 4.5 mV more positive than High purity copper. Freshly polished surfaces may behave as less noble than aged surfaces.

When forced to corrode the phosphorous doped materials produce surfaces of widely differing roughness. The corrosion seems to follow crystallographic planes in the grains. For an average depth of attack of 0.1 mm, the Reference copper has maximum depth of attack not exceeding 0.12 mm. The Low-P copper has a maximum depth of attack of about 0.24 mm. The High-P copper has an intermediate value of 0.14 mm as maximum depth of attack.

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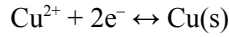
1 Background

Svensk Kärnbränslehantering AB (SKB) intend to use a phosphorous doped copper material in canisters for final deposition of spent nuclear fuel. The composition of the copper material is specified in SKB (2010), and is a highly pure copper (>99.99%) with a phosphorous addition of 30–100 ppm. In this investigation the electrochemical and corrosion behavior of different phosphorous doped copper materials is studied relative to a very pure copper material. The variations in composition reflect also the differences that may arise at large scale production of copper canisters. The electrochemical properties studied are the equilibrium potential in copper containing solution and the surface morphology that arises when the material is forced to corrode electrochemically.

2 Theory

In this study we investigate the apparent nobility of various copper materials relative to very pure copper.

The equilibrium reaction between copper metal and copper ions in the solution can be written:



Applying the general expression for Nernst's law for a general redox reaction (Hägg 1973) to copper metal in a solution containing Cu^{2+} ions gives the following expression:

$$E = E^0 + \frac{RT}{2F} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu(s)}}} \quad (2-1)$$

E is the equilibrium potential that can be measured relative to a reference electrode. E^0 is the normal potential for the redox couple Cu/Cu^{2+} , R is the molar gas constant, T is the absolute temperature, F is Faraday's constant and n is the number of electrons transferred, $n=2$.

$a_{\text{Cu}^{2+}}$ in Equation 2-1 is the activity of Cu^{2+} in the solution. In a solution that contains a much higher concentration of inert ions, the activity of Cu^{2+} is proportional to the concentration.

$$a_{\text{Cu}^{2+}} = \gamma_{\text{Cu}^{2+}} [\text{Cu}^{2+}] \quad (2-2)$$

$\gamma_{\text{Cu}^{2+}}$ is the activity coefficient for Cu^{2+} . At infinite dilution the activity coefficient approaches one because that is the standard state used for dissolved species (Hägg 1973).

$a_{\text{Cu(s)}}$ is normally set to one because that is the standard state for a pure solid (Hägg 1973).

For a certain copper electrode in a medium of high and constant ionic strength, the constant activity coefficient of Cu^{2+} ions and the activity of copper metal deviating from its standard state ($a_{\text{Cu(s)}} \neq 1$), can be collected in one term and included in a conditional 'normal' potential $E^{0'}$:

$$E = E^0 + \frac{RT}{2F} \ln \frac{\gamma_{\text{Cu}^{2+}} [\text{Cu}^{2+}]}{a_{\text{Cu(s)}}} = E^{0'} + \frac{RT}{2F} \ln [\text{Cu}^{2+}] \quad (2-3)$$

Comparing experimentally determined values of $E^{0'}$ for different copper materials should thus reveal differences in the activity of copper in these materials.

2.1 Copper-saturated copper sulfate electrode

Copper in a saturated solution of copper sulphate is a commonly used reference electrode (Stern et al. 2011). Jones (1996) gives the following expression for the electrode potential in solutions of varying copper concentration.

$$E = E^{0'} + 0.0295 \cdot \log [\text{Cu}^{2+}] \quad (2-4)$$

The value of $E^{0'}$ is 0.342 (Jones 1996). The factor of 0.0295 is approximate value at 25°C for the expression:

$$\ln(10) \cdot RT / (nF) \approx 0.0296 \quad (2-5)$$

using the values of the constants provided by Hägg (1973): $R= 8.3143 \text{ J/K, mol}$, $F=96487 \text{ As/mol}$, $T=298.15$, $n=2$.

2.2 Electrochemical experiments

Khairy and Darwish (1973) measured the potential of a copper/copper sulphide electrode in solutions of varying concentrations of Cu^{2+} . They found that Nernst's law was applicable to the system. They found a slope of 0.028 V/decade and an extrapolated value of $E^{0'}$ of 0.340 V vs NHE. They used a background electrolyte of 0.5 M KNO_3 and made additions of CuSO_4 .

Hurlén et al. (1978) studied the kinetics of copper dissolution and deposition in aqueous sulphate solution. They used a background electrolyte of 0.5 M MgSO_4 at pH 2.5.

For the present study we select the same background electrolyte as Hurlén et al. Maintaining a constant sulfate concentration seems desirable because then a constant fraction of the Cu^{2+} will be complex bound to SO_4^{2-} . When as in the experiments of Khairy et al. the sulfate concentration changes with the copper ion concentration, the fraction of the copper bound to sulfate will vary slightly and possibly cause non-linearity or a slope deviating from the theoretical.

In the rest of this report we will use E_0 to denote the 'conditional normal' potential of a copper material in solution containing Cu^{2+} .

3 Experimental

3.1 Material

Table 3-1 shows the composition of the different copper materials in the present study. The high purity copper was supplied by Espi Metals. The three phosphorous doped copper materials were supplied by SKB. The 2 materials with ID:111025101 and ID:111032101 were specially made with low and high content of phosphorus, slightly outside the specification of 30–100 ppm. The content of sulphur and oxygen are deliberately slightly above specification for ingots (S<12 ppm, O<5 ppm). The material ID:11102710 is produced with the same production method (not the same as for large ingots for production of copper tubes), but has a chemical content within specification. The shorter names Ref, Low-P and High-P are introduced in Table 3-1.

Table 3-2 shows available data on grain size for the three phosphorous doped copper materials. The High- and Low-P materials were deliberately produced to get a larger grain size, in order to deviate from the specification for the canister material (<360 μm).

Table 3-1. Composition of the different copper materials in the present study. The copper contents are given in percent. All other elements are given as parts per million (ppm). Both units by weight.

	High purity copper (6N)	Material ID:11102710 Ref	Material ID:111025101 Low-P	Material ID:111032101 High-P
Cu	99.9999	99.991	99.994	99.985
P		66	32	112
Ag	0.2	7.7	7.6	8.6
Al		0.08	0.08	0.08
As		0.3	0.3	0.6
Bi		0.3	0.3	0.7
Cd		0.4	0.4	0.4
Co		0.1	0.2	0.4
Cr		0.05	0.05	0.14
Fe	0.1	0.7	1.4	2.3
H		0.53	0.48	0.45
Mn	0.1	0.1	0.2	0.2
Ni		1.3	1.6	1.9
O		3.1	7.1	7.6
Pb		0.7	0.7	0.7
S		3	11.7	11.9
Sb		1	1	1
Se		0.7	0.7	0.7
Si	0.2	0.2	0.2	0.2
Sn		0.7	1.1	0.9
Te		2	2	2
Zn		0.1	0.2	0.2
Zr		0.1	0.1	0.2
Ca	0.3			

Table 3-2. Grain sizes of the different phosphorous doped copper materials in the present study.

Material# (cast#)	Grain size [mm]
Ref (cast # 111027101)	0.15
Low-P (cast # 111025101)	0.42
High-P (cast # 111032101)	0.60

3.2 Performance

The experiments were performed in a glass cell with a volume of about 1 liter. A supporting electrolyte consisting of 0.5 M MgSO_4 at pH 2.5 was selected. This solution was selected to allow minor differences in the corrosion properties of the metal itself to manifest and not be clouded by solid corrosion products forming at the surface. Nitrogen gas was continuously bubbled through the test solution. The nitrogen gas came from the building's central gas system which is fed by nitrogen gas of quality Instrument 5.0, AGA. All additions during the course of the experiments were, however, made using solutions not previously de-aerated.

3.3 Electrodes

Electrodes of the three phosphorous doped copper materials were made by casting half cylinders of copper, with electrical contact to a wire, in a two component epoxy resin (Epofix, Struers) used for this purpose (Struers 2014). The electrodes of phosphorous doped copper consisted of two half cylinders, electrically insulated, and with separate electrical conductors. Each cylinder half having an area of about 3.5 cm^2 exposed.

The electrode of high purity copper consisted of two oblong balls or 'shots'. The electrical connection was made by gluing a wire to the copper balls and a piece of copper sheet, using electrically conducting glue (Conductive Epoxy CW2400, Chemtronics). This arrangement was then cast in a resin (Epofix, Struers) so that only the high purity copper was exposed. Because of the small size of the copper balls, the exposed area was only about 5 mm^2 . All copper electrodes were polished to 600 grit on SiC-paper.

3.4 Equilibrium potentials for the copper materials

In order to measure how noble or un-noble the different copper materials behave, the electrodes' potential in solution were measured relative to a reference electrode of saturated calomel (SCE). All potentials are given relative to the potential of the SCE.

The copper content of the test solution was increased stepwise in order to verify that Nernst's law is applicable. Under conditions where Nernst's law is applicable the measurement of the electrode potentials gives a measure of the normal potential for the different copper materials.

The values of the normal potential, thus determined, are measurements of how noble the different copper materials behave relative to high purity copper. All potentials were measured using a potentiostat: Solartron Electrochemical Interface 1286. Before and after each experiment, the potential of the reference electrode was measured relative to a similar electrode that is always kept in saturated KCl. The difference was always less than 1 mV.

The copper content in the solution was increased by successive additions of a stock solution of 0.5 M CuSO_4 to the supporting electrolyte.

3.4.1 Run 1

The test electrodes were carefully polished by hand on 600 grit SiC just before they were immersed into the solution. This was made in order to obtain a reproducible surface. The high purity electrodes were however not polished after the manufacturing polish. The electrodes were then rinsed in ethanol and de-ionized water. The experiment was made using nitrogen bubbling as the only stirring. Electrode potentials were monitored by logging at a rate 2 points per minute. In order to measure all eight electrodes, the connection was moved manually from one electrode to another. The intention was to monitor one electrode through most of the experiment and measure the other electrodes only periodically. Careful notes were kept to ensure that each measured value would be attributed to the correct electrode. Because of a computer error, all logged electrode potentials were lost from this run and the results presented come exclusively from the notes kept.

3.4.2 Run 2

The same stock solutions and the same electrodes were used as in run 1. The electrode surfaces were not repolished before this run. The electrode surfaces may thus have traces from run 1 as well as from a subsequent time in air. The electrodes were only rinsed with ethanol and then with de-ionized water. The experiment was started with 600 ml 0.5 M MgSO_4 with addition of 10 ml 0.5 M CuSO_4 and 10 ml 0.5 M MgSO_4 . The latter addition was made to rinse the feed channel from remaining droplets of CuSO_4 . The electrode potentials were monitored, one at the time during 190 hours. An addition of 50 ml 0.5 M CuSO_4 and 10 ml 0.5 M MgSO_4 was made. The electrode potentials were monitored for 90 hours and then a new addition of 50 ml 0.5 M CuSO_4 and 10 ml 0.5 M MgSO_4 was made. The additions of copper ions to the solution led to observable increases in electrode potential. However, the potential was observed to increase slightly also between changes in solution composition. Thus it could not be excluded that part of the observed increase in the potential was caused by the time in the solution.

In order to distinguish effects of time in solution from effects of copper ion concentration, a sequence of additions of EDTA to the solution were made. EDTA binds to copper ions in a form that is 'invisible' for the electrode. The electrode potential responds to the free copper ion concentration. An addition of EDTA is thus, in this respect, equivalent to a removal of some copper ions from the solution.

It was concluded that the high purity copper follows Nernst's law within experimental error. It was judged sufficient to measure the difference in potential between the phosphorous containing copper materials and the high purity copper at decreasing concentrations of free copper ions. A constant difference in potential would show that also the phosphorous containing copper materials follow Nernst's law. Knowledge of the exact concentrations of EDTA or the complex strength between EDTA and Cu^{2+} at the resulting pH not necessary.

After a total of 335 hours an addition of 10 ml of a saturated EDTA solution (Titrisol) was made. This addition was found to have very small effects on the measured potentials. A new addition of 50 ml EDTA solution was made after 336 hours. Further additions of 50 ml EDTA solution were made after 354 hours and 380 hours. After these additions of EDTA the potential showed values corresponding to low concentrations of free copper ions.

3.5 Surface morphology after forced corrosion

One of the duplicate electrodes of the phosphorous containing copper materials was forced to corrode by application of a constant anodic current of 2 mA. With the electrode area of about 3.5 cm^2 , the average current density was about 0.57 mA/cm^2 . The time of the galvanostatic polarization was set to 133 hours so that the average corrosion depth would be 0.1 mm.

The three phosphorous containing copper materials were thus corroded separately one after the other, each time starting with fresh solution of 0.5 M MgSO_4 at pH 2.5.

4 Results

4.1 Equilibrium potentials for the copper materials

4.1.1 Run 1

Table 4-1 shows the composition of the test solution during run 1.

Measured potentials during run 1

Figure 4-1 shows the open circuit potential for the different copper materials as function of experiment duration for run 1.

Table 4-1. Data from run 1. Concentrations.

Logg time (s)	Addition (ml)	Addition (mol Cu)	Total Volume (ml)	Total Amount (mol Cu)	[Cu] (M)
	570	0.0005	570	0.0005	0.00088
3,300	20	0.0005	590	0.0010	0.00169
100,981	20	0.0005	610	0.0015	0.00246
179,103	60	0.0025	670	0.0040	0.00597
358,266	60	0.0025	730	0.0065	0.00890
602,380	60	0.025	790	0.0315	0.03987
865,394	60	0.025	850	0.0565	0.06647

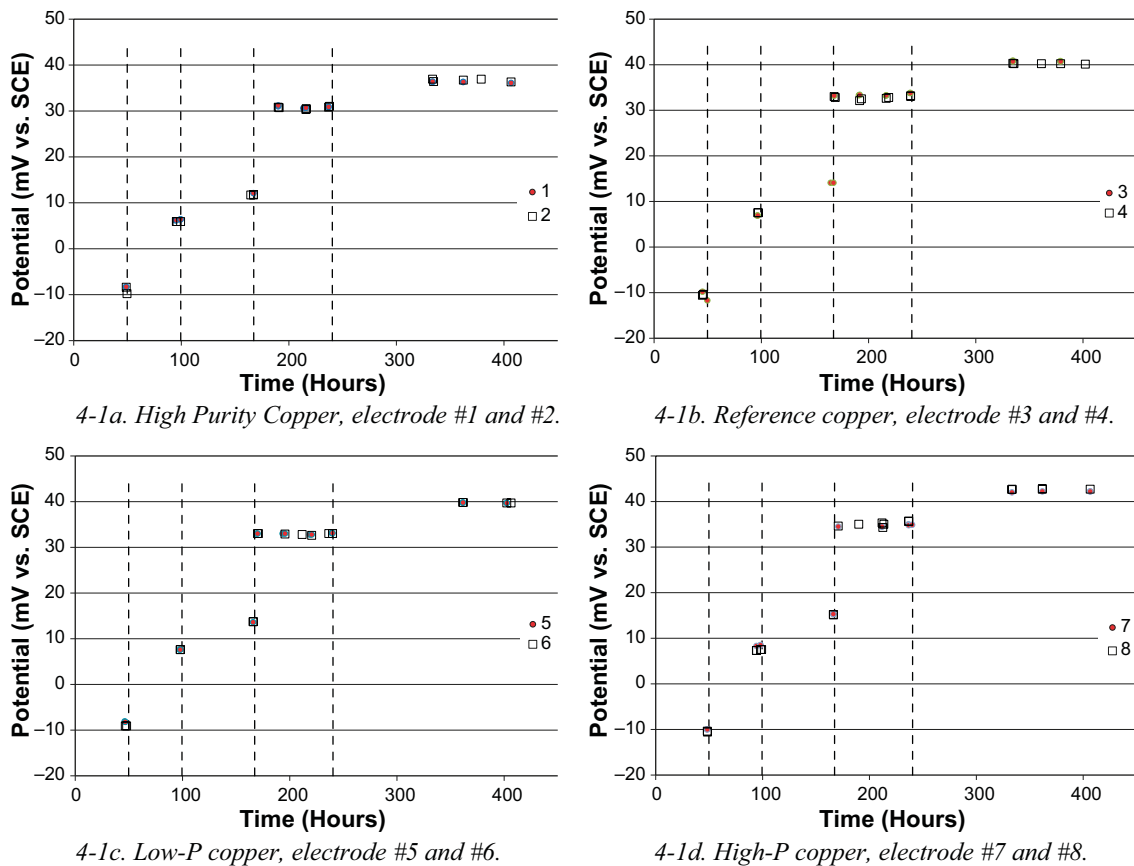
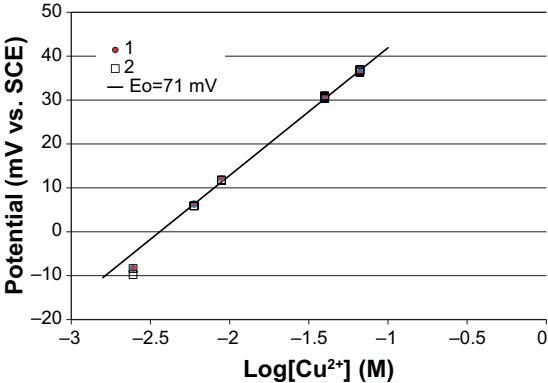


Figure 4-1. Open circuit potentials for the different copper electrodes as function of experiment duration. The vertical dashed lines indicate times when the copper content in the solution was increased by the addition of a copper rich stock solution.

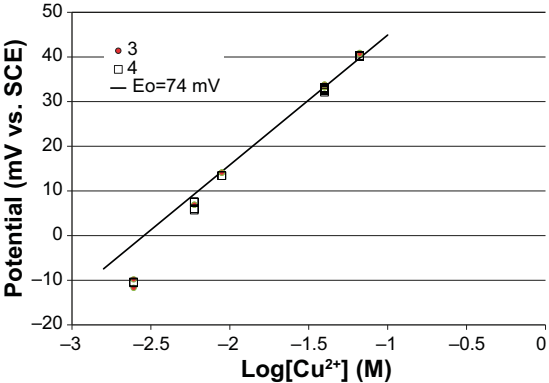
Figure 4-2 shows the measured potentials as function of the logarithm of the copper ion concentration. Ideally, the points should form a straight line with a slope of about 30 mV per logarithmic unit. A more exact value for 20°C is 29.1 mV. This value is found from $RT \cdot \ln(10)/(2F)$, where R , T and F are defined in Section 2 and T is set to 293 K. The straight lines in Figure 4-2 have this slope of 29.1 mV and are drawn through the point representing the highest concentration used in the experiment. The legend for each diagram shows the value of this line for $\log[\text{Cu}^{2+}]=0$.

According to Equation 4-1, this is the value of E_0 for this copper material.

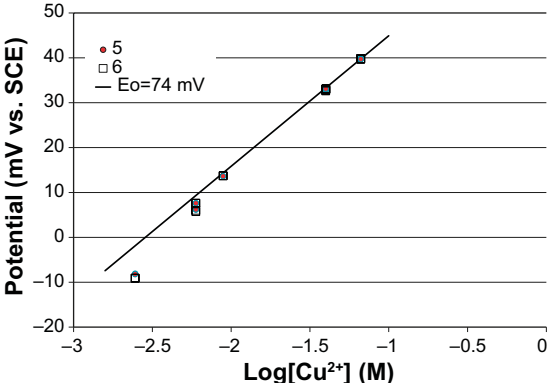
$$E = E_0 + 29.1 \cdot \log[\text{Cu}^{2+}] \quad (\text{mV}) \tag{4-1}$$



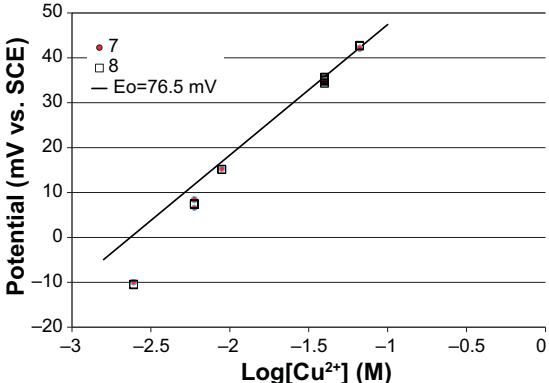
4-2a. High Purity Copper, electrode #1 and #2.



4-2b. Reference copper, electrode #3 and #4.



4-2c. Low-P copper, electrode #5 and #6.



4-2d. High-P copper, electrode #7 and #8.

Figure 4-2. Equilibrium potentials for the different copper materials as function of the logarithm of the copper ion concentration during run 1. The solid lines have the theoretical slope of 29.1 mV per decade. The legend in each graph shows the value of the estimated E_0 .

4.1.2 Run 2

This experiment was made in order to answer the question whether the difference in apparent nobility of the different copper materials depended on the potential range or of the time in solution.

Measured potentials during run 2

Figure 4-3 shows the open circuit potential for the different copper materials as function of experiment duration for run 2. When potentials appeared to have stabilized, various additions to the solution were made in order to change the redox potential of the system. The potentials just prior to a change in the composition of the solution are here interpreted as the equilibrium potential of the electrode.

These equilibrium potentials as function of the logarithm of the copper ion concentration are shown in Figure 4-4.

Table 4-2 shows a compilation of equilibrium potentials for the different electrodes at various solution compositions. The concentration of the EDTA solution that was added after 355 hours was not exactly known and no calculation of the influence on the free copper ion concentration has been made.

Figures 4-3 and 4-4 show that the High purity copper (electrode #1 and #2) behave as the least noble and the High-P copper behaves as the most noble.

The values of E_0 shown in Figure 4-4, for run 2, agree well with the values shown in Figure 4-2, for run 1. In run 1 there was a trend that the phosphorous doped materials behaved successively more noble at higher copper ion concentrations. Because the copper ion concentration was increased monotonously in that experiment it is not possible to decide whether the observed trend depends on the copper ion concentration and potential or on the time in solution.

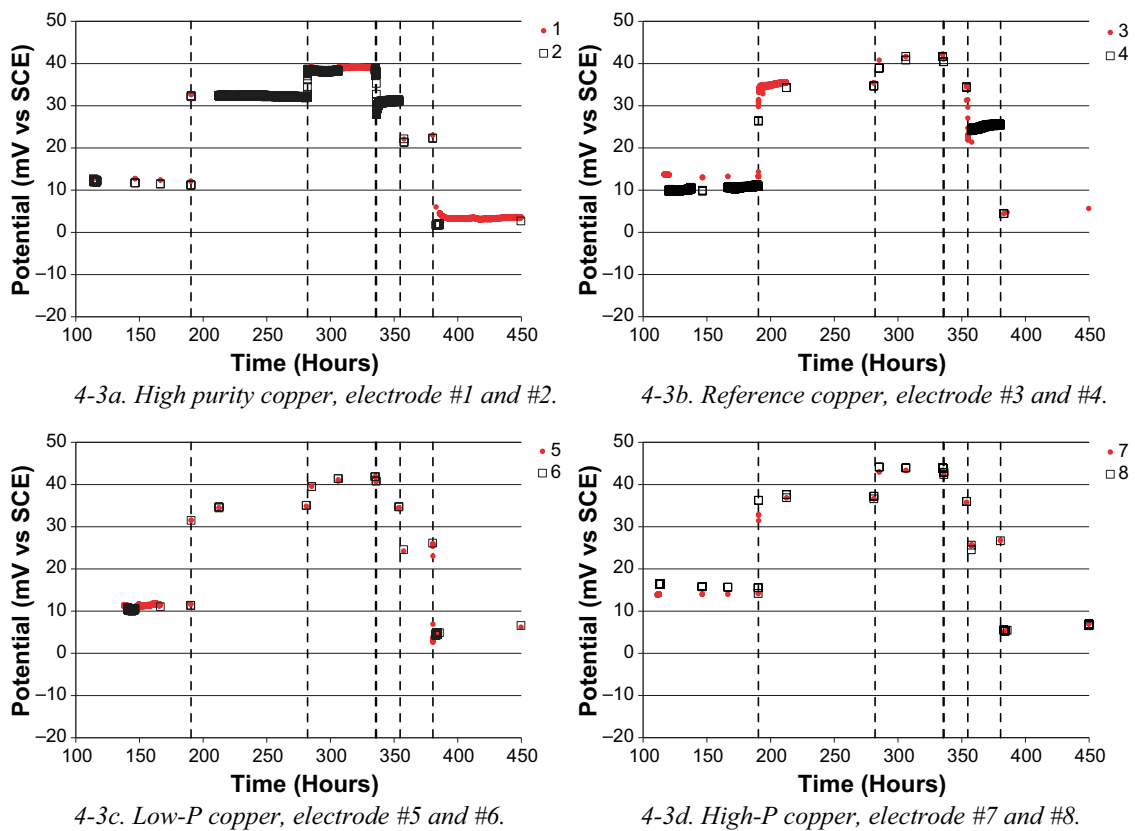
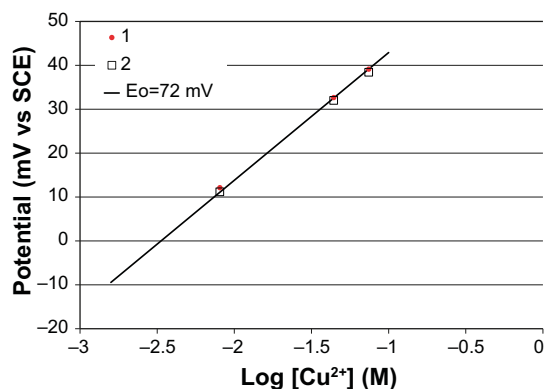


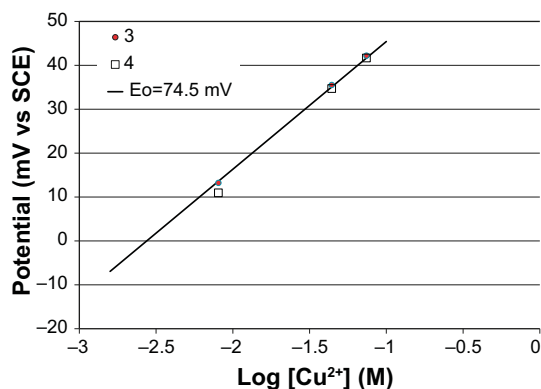
Figure 4-3. Open circuit potentials for the different copper electrodes as function of experiment duration. The vertical dashed lines indicate times when the copper content in the solution was increased by the addition of a copper rich stock solution.

Table 4-2. Electrode potentials interpreted as equilibrium potentials for the different electrodes.

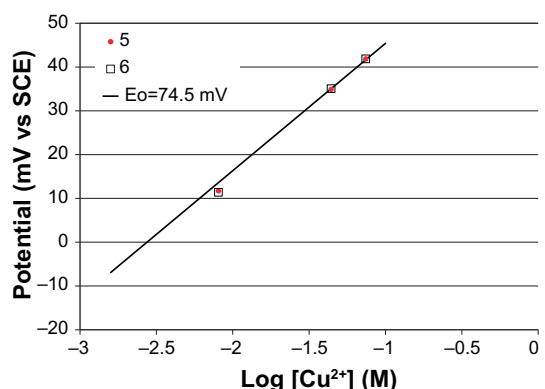
Time (Hours)	[Cu ²⁺] (M)	Electrode Potential (mV vs SCE)							
		1	2	3	4	5	6	7	8
190	0.008	12.1	12.1	11.2	13.2	11.0	11.7	11.4	14.2
281	0.044	32.7	32.7	32.0	35.5	34.7	34.9	35.0	36.6
335	0.074	39.1	39.1	38.4	42.2	41.7	41.8	41.9	43.4
380	–	23.0	23.0	22.4	25.7	25.5	25.6	26.1	26.7
451	–	3.5	3.5	2.7	5.4	5.4	6.1	6.3	6.9



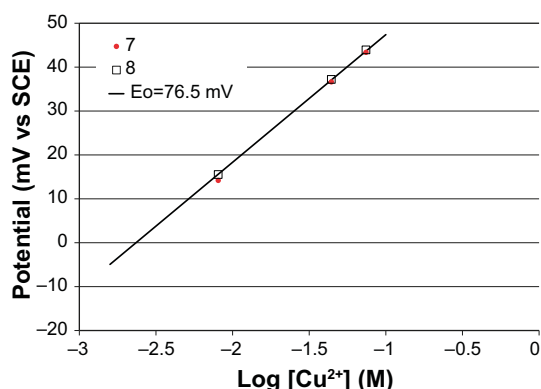
4-4a. High purity copper, electrode #1 and #2.



4-4b. Reference copper, electrode #3 and #4.



4-4c. Low-P copper, electrode #5 and #6.



4-4d. High-P copper, electrode #7 and #8.

Figure 4-4. Equilibrium potentials for the different copper materials as function of the logarithm of the copper ion concentration during run 2. The solid lines have the theoretical slope of 29.1 mV per decade. The legend in each graph shows the value of the estimated E_0 .

In order to determine whether the materials behave in the same way, with regard to relative nobility at decreasing potentials, a diagram was constructed where the potentials of the electrodes 1 through 8 were plotted as function of the potential of electrode number 1. This diagram is shown in Figure 4-5.

The potential increases successively from point 1 where the experiments starts via point 2 to point 3 where additions of EDTA are made so that the potential decreases via point 4 to point 5.

The diagram shows that the same trend in relative nobility prevails at high potentials as at low potentials. Thus, all three phosphorous doped copper materials behave as more noble than High purity copper. Initially, phosphorous doped copper materials may behave as less noble but after some time in the solution, which no doubt contains traces of oxygen, the more noble behavior is attained. The nobility of the Reference copper and the Low-P copper is estimated to about 2.5 mV more positive than High purity copper. The nobility of the High-P copper is estimated to about 4.5 mV more positive than High purity copper.

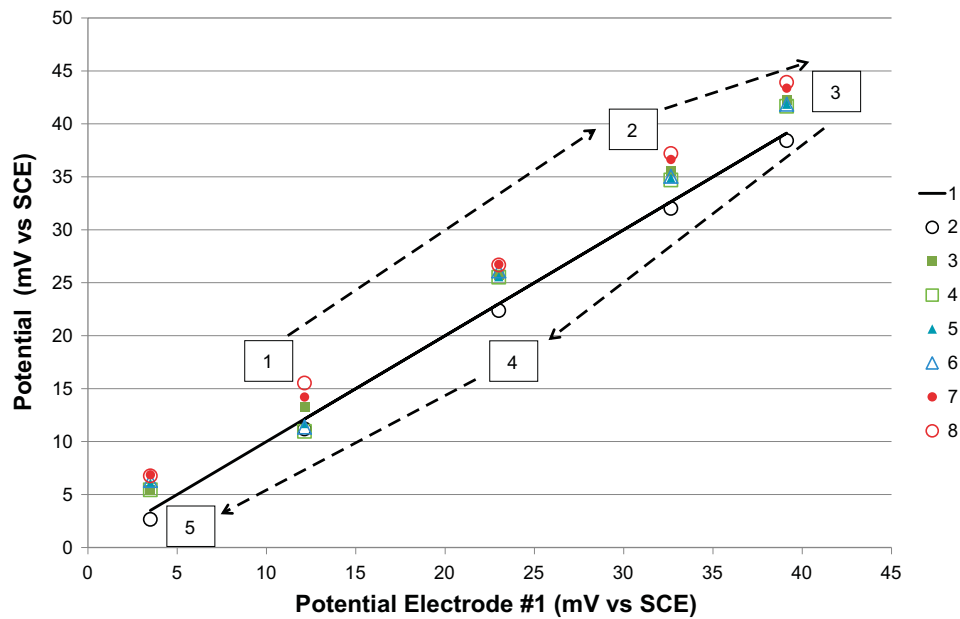


Figure 4-5. The potential of the electrodes as function of the potential of electrode #1. The experiment starts at point 1. The potentials increase first as a result of increased copper ion concentration via point 2 up to point 3 and decrease then as a result of additions of EDTA via point 4 to point 5.

4.2 Surface morphology after forced corrosion

After forced corrosion for 133 hours to a calculated average depth of attack of 0.1 mm, the electrodes were photographed and studied by confocal microscopy. Figures 4-6, 4-7 and 4-8 show photographs of the electrodes. One of two twin electrodes was corroded for each material. The corroded surfaces have an etched appearance and the bright reflections in Figures 4-6 through 4-8 indicate that the corrosion followed the crystallographic orientation of individual grains.

Figure 4-9 shows a microscope image and depth profile for the Reference copper. Figures 4-10 and 4-11 show the corresponding results for the Low-P copper and the High-P copper, respectively.

Figures 4-9a, 4-10a and 4-11a show optical images of a small part of the electrode surface (2.6×2.6 mm). Figure 4-9b, 4-10b and 4-11b show depth profiles of the areas. The images are color coded after the depth. The closest objects (peaks) are coded red and the most distant objects are coded blue.

The images are composed of square arrays of data 1,024×1,024.

Figures 4-9c, 4-10c and 4-11c show depth profiles along one direction. Rows 200, 500 and 800, counting from the top, were selected. The actual depth was calculated from the known average corrosion and applying this value as a row average.

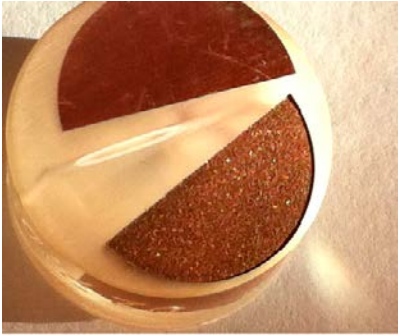


Figure 4-6. Reference copper.



Figure 4-7. Low-P copper.



Figure 4-8. High-P copper.

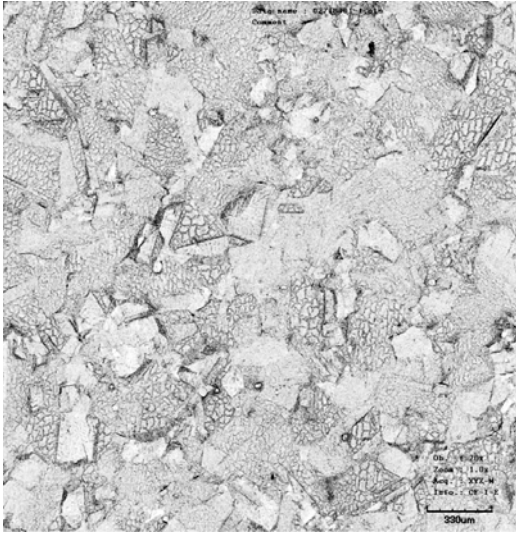


Figure 4-9a. Gray scale photograph of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. Reference copper.

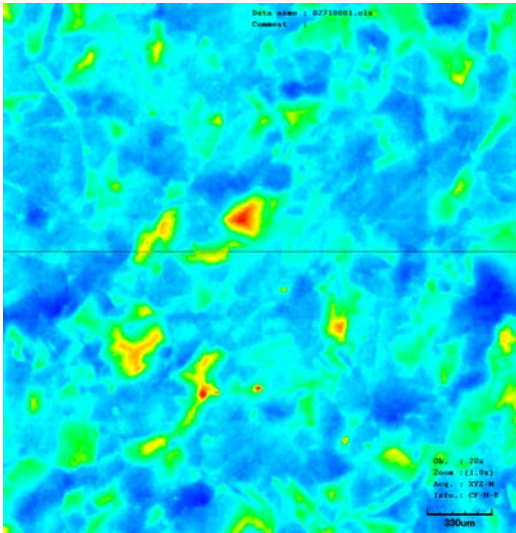


Figure 4-9b. Depth profile of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. Reference copper.

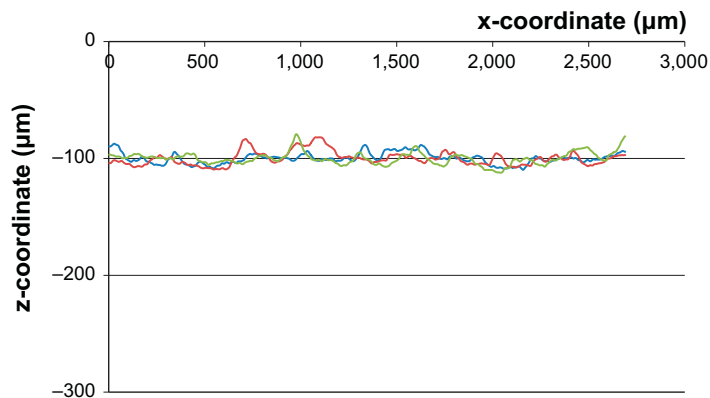


Figure 4-9c. Depth profile from the original surface of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. The different lines represent different parallel lines across the surface in Figure 4-9b. Reference copper.

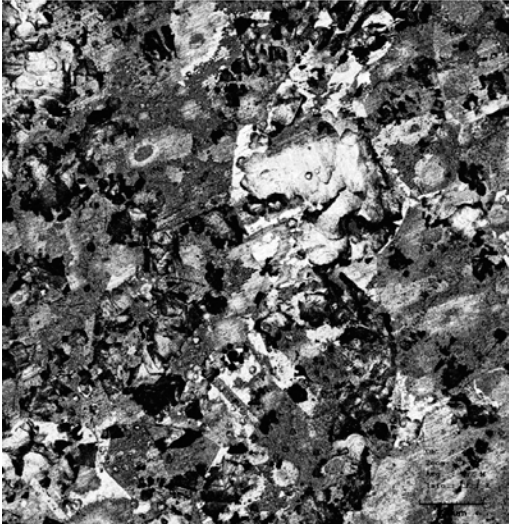


Figure 4-10a. Gray scale photograph of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. Low-P copper.

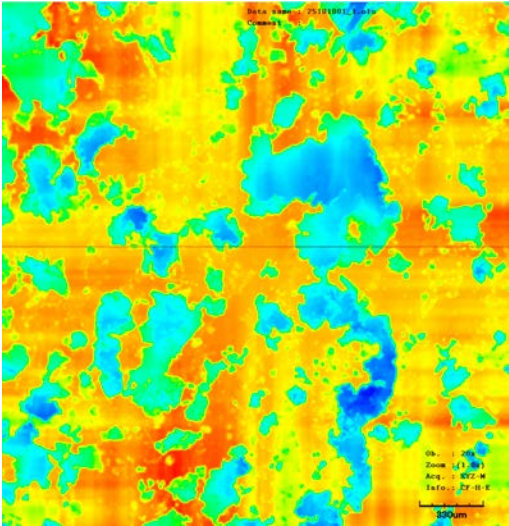


Figure 4-10b. Depth profile of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. Low-P copper.

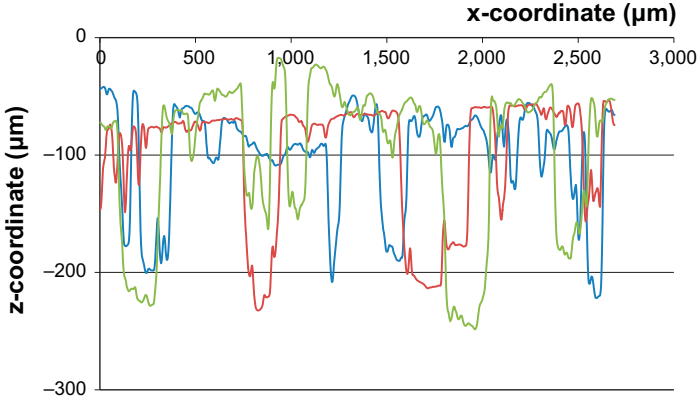


Figure 4-10c. Depth profile from the original surface of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. The different lines represent different parallel lines across the surface in Figure 4-10b. Low-P copper.

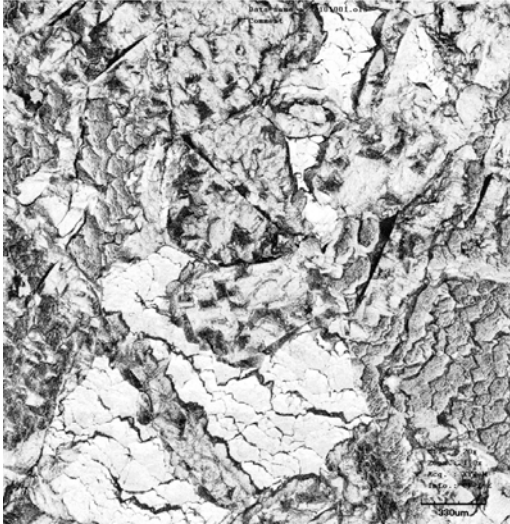


Figure 4-11a. Gray scale photograph of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. High-P copper.

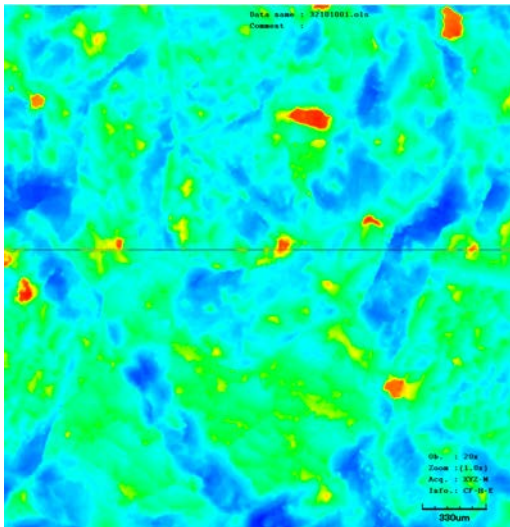


Figure 4-11b. Depth profile of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. High-P copper.

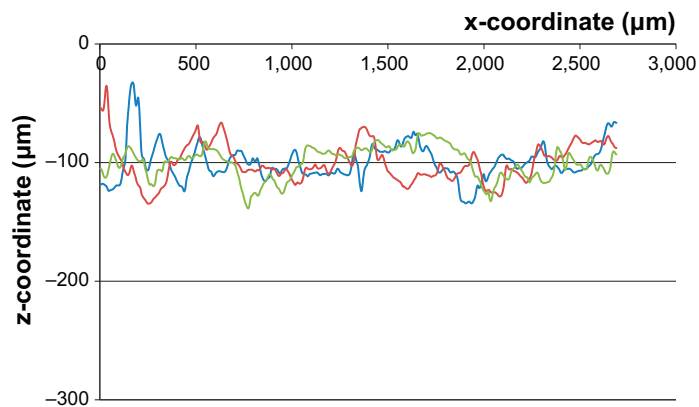


Figure 4-11c. Depth profile from the original surface of a part of the copper surface after forced corrosion to an average depth of 0.1 mm. The different lines represent different parallel lines across the surface in Figure 4-11b. High-P copper.

5 Discussion

5.1 Potentials

The results in this investigation show that the electrodes made by the copper material with the highest content of phosphorous, the High-P copper, behave as the most noble. The High purity copper behaves as the least noble. A trend is observed where newly polished surfaces behave as less noble than surface that have not recently been polished. Thus, Figure 4-2 from run 1 with freshly polished surfaces, shows that the potentials at the lower concentrations generally fall below the line with the theoretical slope. In Figure 4-4, from run 2 without repolishing the surfaces, this trend is absent or at least much less pronounced.

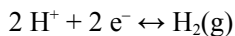
5.2 Surface morphology

Rather large differences in surface morphology emerge. After forced corrosion to an average depth of 0.1 mm the Reference copper is very evenly corroded and has maximum depth of attack not exceeding 0.12 mm. The Low-P copper on the other hand is very rough and has a maximum depth of attack of about 0.24 mm. The High-P copper has an intermediate value of 0.14 as a maximum depth of attack.

5.3 Possible corrosion consequences of differences in apparent nobility

The worst case, from a corrosion perspective, seems to be when the copper metal is heterogeneous with some parts behaving as less noble than other parts. A whole canister where the apparent nobility is uniform but deviates from that of pure copper seems to be a less severe case. The reason for this relative insensitivity to apparent nobility of the copper metal in the canister is that molecular oxygen and sulphide are expected to corrode the copper irrespective of minor variations in the apparent nobility. The partial pressure of hydrogen gas that can be evolved from corrosion to Cu_2O and to aqueous copper species will vary slightly with the apparent nobility of the copper.

The Nernst's equation for hydrogen evolution can be written:



$$E = E_0 + \frac{RT}{2F} \ln \frac{(a_{\text{H}^+})^2}{p_{\text{H}_2}} \quad (5-1)$$

a_{H^+} is the activity of the hydrogen ion and p_{H_2} is the partial pressure of hydrogen gas, E_0 in Equation 5-1 is the normal potential for the hydrogen gas evolution, R , T and F are defined in Section 2. The maximum variations in apparent nobility found in this study are in the order of 5 mV.

A change in E in Equation 2-1 by 5 mV results in a change in p_{H_2} by about 20%.

$$\frac{\Delta p_{\text{H}_2}}{p_{\text{H}_2}} \approx \frac{2F}{RT} \Delta E \quad (5-2)$$

Equation 5-2 was obtained by differentiating Equation 2-1 and applying a linear approximation.

Entering $F=96,487 \text{ As/mol}$, $R=8.314 \text{ J/K}$, $T=298 \text{ K}$ and $\Delta E=0.005 \text{ V}$ gives a relative change in the partial pressure of about 0.195.

Thus a copper material that behaves as 5 mV more noble than high purity copper would produce an equilibrium partial pressure of hydrogen that is about 20% lower than high purity copper if all other parameters are kept constant. (A copper material that is 5 mV less noble would then produce a partial pressure of hydrogen that is about 20% higher.)

When local variations in apparent nobility within one canister are considered, several different cases should be treated separately.

5.3.1 Corrosion under activation control

When the corrosion is said to be under activation control, the rate varies exponentially with the electrochemical potential. The Tafel slope is the change in potential required to change the reaction rate by a factor of ten. Table 5-1 shows the relative changes in corrosion rate for various Tafel slopes of the anodic corrosion reaction.

The effect of a change in the apparent nobility of the copper material is much larger for a corrosion process that has a strong dependence of the electrochemical potential. A Tafel slope of 30 mV give a local increase in the corrosion rate by about 38% at a site where the copper material behaves as 5 mV less noble.

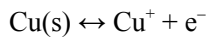
5.3.2 Passive behavior or mass transport limited corrosion

Under conditions where the corrosion rate is limited by protective layers of corrosion products; passive behavior, and when the corrosion rate is limited by the supply of a reactant to the surface, the apparent nobility has no or negligible effect on the corrosion rate.

5.3.3 Local equilibrium limits the rate of corrosion

When the main corrosion product is dissolved copper, the rate of production cannot be higher than the rate of consumption or diffusion from a maximum concentration that is given by electrochemical equilibrium at the prevailing potential. Nernst's law is applicable to this maximum concentration at the surface which in turn determines the rate of diffusion.

This situation is most likely to occur for Cu(I) because the rate of the oxidation to monovalent copper is very fast. The production of Cu(II) is likely to be, at least partly, under activation control. The corrosion to Cu(I) can be written:



Various complexing agents, mainly chloride, can convert the Cu^+ ions to other dissolved forms. The concentration of these complex forms of Cu(I) is, however, proportional to the concentration of the free Cu^+ ion so the arguments applied here will be valid also for complexes.

Nernst's law for the reaction can be written:

$$E = E_0 + \frac{RT}{F} \ln(a_{\text{Cu}^+}) \quad (5-3)$$

E_0 in Equation 5-3 is the normal potential of the copper material in question. a_{Cu^+} is the activity of Cu^+ and is proportional to the concentration. For the case where there are variations in the apparent nobility in a canister, there may be several local values of E_0 and still only one value of the electrochemical potential, E . This will result in a variation in the equilibrium concentration of Cu^+ along the canister surface. The mass transport and the corrosion rate will thereby also vary. A 5 mV less noble copper material will result in a Cu(I) concentration that is about 20% higher. Mass transport will then allow a 20% higher corrosion rate at the sites where this less noble behavior prevails. However, there will also be a tendency for the dissolved Cu(I) to redeposit at the copper surface to a state which is more stable than the original. A less noble behavior can be associated with a higher activity of the copper metal. Thus there is a driving force to attain a more stable arrangement and the corrosion to Cu(I) and redeposition to Cu(s) is one path that allows the more stable arrangement to be attained.

Table 5-1. The relative change in corrosion rate caused by a change in the apparent nobility by 5 mV. Various alternative values of the Tafel slope are considered.

Tafel Slope (mV)	Relative change in corrosion rate
30	0.38
40	0.29
60	0.19
120	0.10

6 Conclusions

- A method to measure the relative nobility of copper materials has been applied to three different phosphorous doped copper materials relative to a high purity copper.
- The method, consisting of measuring the electrode potentials under conditions where Nernst's law is applicable, gives consistent and meaningful results.
- The apparent nobility of the Reference copper and the Low-P copper is estimated to about 2.5 mV more positive than high purity copper. The apparent nobility of the High-P copper is estimated to about 4.5 mV more positive than high purity copper.
- Freshly polished surfaces may behave as less noble than aged surfaces.
- When forced to corrode the phosphorous doped materials produce surfaces of widely differing roughness. The corrosion seems to follow crystallographic planes in the grains.
- For an average depth of attack of 0.1 mm, the Reference copper has a maximum depth of attack not exceeding 0.12 mm. The Low-P copper has a maximum depth of attack of about 0.24 mm and the High-P copper has an intermediate value of 0.14 mm as maximum depth of attack.

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