

## ALTERNATIVE METHOD FOR THE PRODUCTION OF COPPER BARRIERS

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*The research in this paper explores optimization of a copper electroplating process as an alternative method for the production of corrosion barriers for spent nuclear fuel and high-level waste (HLW), supporting the implementation of deep geological disposal repository concepts. The production method of these canisters has to be selected carefully to ensure the material obtained meets the required properties. Compositional analysis, microstructure screening and mechanical tests have been performed on electroplated copper to understand the implications of operating parameters on chemical and mechanical properties. Possible means of monitoring and controlling the electroplating process over an extended period of time for producing free-standing copper shells is also addressed. Although further adjustments are required to comply with KBS-3 specifications, preliminary characterization showed that the electroplated copper can be tailored to specific needs.*

### I. INTRODUCTION

Many disposal concepts for nuclear waste include copper and/or steel canisters as corrosion barrier for housing spent nuclear fuel. The KBS-3 design, proposed by the Swedish Nuclear Fuel and Waste Management Company (SKB), specifies an outer high-purity (oxygen-free) 50 mm thick copper canister for corrosion resistance, supported by a cast iron inset providing rigidity and mechanical strength<sup>1</sup>. The Mark II design, proposed by the Canadian Nuclear Waste Management Organization (NWMO), specifies a 3 mm gap-free copper coating onto a steel vessel with hemi-spherical heads<sup>2</sup>.

Mechanical drawing and forming processes (extrusion, pierce and draw, forging and roll forming) are currently employed for the experimental production of the 50 mm thick KBS-3 copper shells<sup>3,4,5</sup>, whereas the Canadian concept is focusing on copper electro-deposition processes to coat its steel vessels<sup>6,7</sup>. Compared with pierce and draw forming methods, electroplating is more efficient and environmentally friendly, allows better

surface finishes, removes the need for machining the inside of the free-standing copper shells, and enables the production of thinner copper layers (or shells) than is possible via a mechanical forming processes.

Knowledge and capability for the production of large cylindrical process rolls via electroforming already exists, with typical application in the packaging and laminating industries. The manufacturing process of some of these rolls involves the production of free-standing copper shells of up to 16 mm thick wall (BEP Surface Technologies Ltd. - <http://www.bep-st.com>). Nonetheless, electro-deposition of copper deposits of 50 mm thickness is challenging, and can only be achieved by understanding and controlling underlying electroplating process parameters. Control of the electroplating process is even more challenging, when thick copper deposits with controlled chemical composition need to be manufactured to comply, for example, to KBS-3 chemical composition requirement.



Fig. 1. Free-standing copper shell produced by electroforming at BEP Surface Technologies Ltd. Dimensions: 1 m diameter, 2.5 m long and 16 mm wall thickness.

Research conducted over several years showed the negative effects of low ppm levels of impurities, like hydrogen, oxygen and sulphur, in the corrosion and mechanical properties of the copper. Chemical specifications for these impurities for the KBS-3 copper canisters are 0.6 ppm for hydrogen, 12 ppm for sulphur, 30-100 ppm for phosphorus and “some tens of ppm” for oxygen<sup>8</sup>. In particular, the rationale behind the oxygen content restriction is associated with the fact that oxygen can concentrate at the grain boundaries and reduce the corrosion resistance and the weldability; furthermore sulphur directly affects the ductility of copper reducing the tensile strength whilst hydrogen increases the risk of embrittlement reducing the ductility<sup>9,10</sup>. Conversely, the presence of 30-100 ppm of phosphorus in copper has the objective of increasing the creep ductility<sup>11</sup> by competing with sulphur atoms for their positions in grain boundaries<sup>12</sup>. There are also requirements in terms of grain size which cannot exceed 360 micrometres<sup>13</sup> since too large grains and non-uniform grain size distributions can lead to low detectability of defects during ultrasonic testing<sup>8,14</sup>. Finally, it is expected that the canister will be deformed 4 % whilst in service due to handling and operation. In this respect, the minimum ductility and creep ductility of the copper have been set to 40 % (room temp.) and 10 % elongation (100 °C)<sup>13</sup>.

NWMO has not yet issued the chemical specification for the 3 mm copper coating. However, as the copper will be a gap-free coating, and not a free standing shell as the KBS-3 model is, it is expected that no phosphorus will be needed to increase the creep ductility, and the specifications for the other impurities will also be more relaxed, compared to the KBS-3 specifications.

The research in this paper explores optimization of a copper electroplating process as an alternative method for the production of corrosion barriers for spent nuclear fuel and high-level waste (HLW), supporting the implementation of deep geological disposal repository concepts. For that end, the investigation is focused on understanding the effect of operating parameters on microstructure, mechanical properties and chemical composition of the electroplated copper.

Results obtained in earlier stages of the research reported that the oxygen concentration on electroplated copper is strongly dependent on the additive employed in the plating process<sup>15</sup>. With the exception of one of the additives tested, the oxygen concentration in the electroplated copper from all the additive-based electrolytes was within KBS-3 specifications. Furthermore, all copper samples electroplated from additive-based electrolytes which met the specifications showed much lower oxygen content (as low as 7 ppm<sup>15</sup>) than that obtained from additive-free electrolytes.

Providing the appropriate selection of additive, electroplated copper produced can comply with KBS-3 specifications for oxygen concentration; therefore, the

next stages of the research has been focused on the study of the effect of the operating parameters on the concentration of other impurities, such as hydrogen, sulphur and phosphorus.

## II. EXPERIMENTAL

Experiments to better control and underpin the copper electro-deposition process were carried out on laboratory scale using a 1 litre electroplating cell and on pilot plant scale in a 100 litre electroplating tank. The idea behind this approach is to explore the production of controlled copper layers on lab-scale, followed by subsequent up-scaling of process parameters to a small scale production plant, before a full-scale experiment (tanks with 1000's litre of electrolyte) is carried out.

All small scale electroplating experiments for chemical analysis and microstructure screening were performed by using steel sheets as cathode material, allowing the production of small rectangular flat samples (Fig. 2) with typical dimensions of 40 mm x 30 mm x 0.5 mm (l x w x d) which could easily be detached from the substrate.

Acid copper plating electrolytes were employed, preparing a fresh solution for each experiment using copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and sodium chloride ( $\text{NaCl}$ ). As anode materials, phosphorized deoxidized (PDO) copper was used, with electrolyte additives used in this study obtained from commercial suppliers (Atotech® & MacDermid®). The glassware employed for preparing the acid copper electrolyte was cleaned with potassium permanganate ( $\text{KMnO}_4$ ) solution to remove any organic contaminant. The glassware was then rinsed with water, and any remaining  $\text{KMnO}_4$  was neutralized by means of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) rinsing.

For pilot-plant experiments, a 100 L electroplating tank was employed, with a cylindrical steel mandrel as cathode material. This allows production of small-scale cylindrical free-standing copper shell with dimensions of 10 cm inner diameter, 20 cm length and several mm in thickness (Fig. 2). Constant rotation speed was provided to the cathode via a driving belt connected to a motor and the mandrel. The electroplating electrolyte was recirculated through a 25 micron filter, with the purpose of removing dust and small particles from the electrolyte.

In all experiments the temperature of the electrolyte was controlled within +/- 0.1 °C by means of an immersion heater and a K-type thermocouple connected to a temperature controller. The electroplating processes were carried out in the galvano-static mode in order to keep a constant current density throughout the electroplating process under the assumption that the area did not increase due to roughness. The copper deposits were removed from the steel sheet and from the mandrel, rinsed with deionized water, dried in hot air and then

stored in sealed polypropylene bags prior to microstructure, mechanical and compositional analysis.

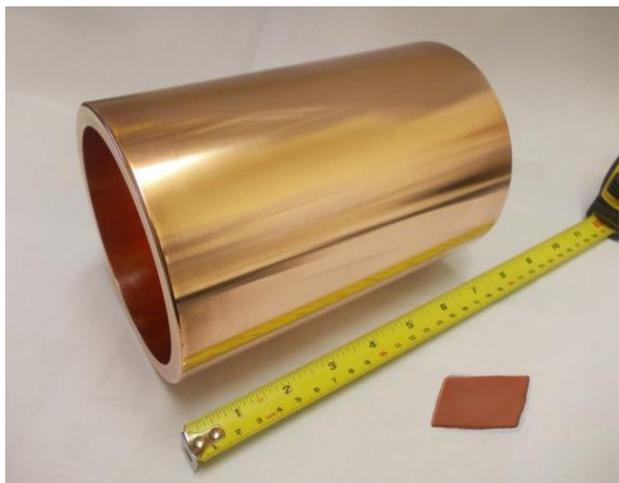


Fig. 2. Small cylindrical free-standing copper shell electroplated from the 100 L plating tank (left); and small flat sample electroplated from the 1 litre lab set-up (right).

Oxygen and hydrogen concentrations in copper were determined by means of solid state infrared absorption and thermal conductivity, respectively, using an Oxygen / Hydrogen Analyzer OH-900 (Eltra®). Samples were prepared prior analysis, including superficial oxygen removal, and analysed as per ASTM E 2575-08 (Standard Test Method for Determination of Oxygen in Copper and Copper Alloys).

In order to determine the phosphorus concentration in copper, a known weight of copper sample was digested in nitric acid, and then diluted with demineralized water up to a known total volume. The solution was then analysed for phosphorus by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) employing a Perkin-Elmer® Optima 5300 dual view. Nitric acid for metal trace analysis and high purity water (0.05  $\mu\text{S}/\text{cm}$ ) were employed for preparing the solution in order to ensure no phosphorus was coming from these.

Cyclic voltammetry studies of the copper plating electrolyte were conducted to check the effect of the additives on the correlation between the copper sulphates concentration and the current maximum of the voltammogram, obtained from the Randles-Sevcik equation<sup>16</sup>. The voltammograms were performed using a CompactStat device (Ivium Technologies®) connected to a PC for data acquisition. Glassy carbon and platinum were employed as working electrode and counter-electrode, respectively. A Standard Calomel Electrode (SCE) was used as reference electrode. The glassy carbon electrode was polished to mirror finish with alumina powder and rinsed with demineralized water before each experiment. The electrolyte was deaerated by bubbling argon through the solution prior to all electrochemical

experiments, and was kept at constant temperature during the experiments by using a thermostatic bath.

### III. RESULTS AND DISCUSSION

#### III.A. Process Optimization – Elemental Composition & Mechanical properties

Optimization of the electroplating process is carried out in order to comply with the chemical specifications and microstructure requirements of KBS-3 copper canisters.

The elemental concentration of oxygen, hydrogen and sulphur in the electroplated copper are reported in Table 1 as a function of different conditions. The hydrogen concentration obtained from the additive-free electrolyte was more than 8 times higher than the limit specified for the KBS-3 copper canister. By modifying the electroplating parameters, such as current density and temperature it was possible to achieve lower hydrogen concentration in the electroplated copper, which however was still out of KBS-3 specifications. Similar to that found for the oxygen content<sup>15</sup>, the presence of some additives appeared to considerably reduce the hydrogen concentration in the electroplated copper. In this respect, two of the additives employed reduced the hydrogen concentration with respect to that obtained in the electroplated copper from additive-free electrolyte. Additive B reduced the concentration by half, from 4.2 ppm to 2.1 ppm; whereas Additive A reduce the concentration around 85 %, from 4.2 ppm to 0.7 ppm, a value very close to the maximum hydrogen concentration specified by SKB. On the other hand, however, the presence of Additive C in the process had a minor effect, increasing the hydrogen content only 0.2 ppm, from 4.2 ppm to 4.4 ppm.

Table I. Hydrogen, sulphur & oxygen concentration of electroplated copper at different conditions. Base parameters: 200 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  + 60 g/L  $\text{H}_2\text{SO}_4$  + 100 ppm NaCl, 30 °C, 6 A/dm<sup>2</sup>. (N/T = not tested).

Condition	ppm H	ppm S	ppm O
Additive-free	4.2	N/T	N/T
Additive-free, 3 A/dm <sup>2</sup>	3.8	N/T	N/T
Additive-free, 40 °C	2.7	N/T	N/T
Additive A	0.7	< 1	9
Additive B	2.1	10	7
Additive C	4.4	< 1	25

Results about sulphur and oxygen concentration on electroplated copper from additive-based electrolytes employing Additives A, B & C (Table 1) shows again

how the concentration of this impurities in the electroplated copper depends on the specific additive employed. These results emphasise the importance of the correct selection of a proper additive in order to comply with KBS-3 chemical specifications. In this respect, Additive A appeared to be a good a starting point for tailoring the process since the hydrogen concentration was already close to KBS-3 specifications.

Further research into the chemical composition of the electroplated copper has been focused on the co-deposition of phosphorus, required to get a phosphorus concentration between 30-100 ppm, as specified by SKB<sup>8</sup>. Research carried out by other workers in this matter indicates that red phosphorus can be employed for this purpose<sup>17,18</sup>. In our research, finely divided red phosphorus powder was added as a suspension to the plating solution in a concentration of 0.5 g/L. The electroplating process was carried out as per normal, using air agitation directed to the bottom of the plating cell to keep the red phosphorus particles in suspension and prevent settling. Red phosphorus concentration in the electroplated copper was 133 ppm, which agrees with the results obtained by Graydon et al.<sup>18</sup>. In order to obtain electroplated copper within the KBS-3 specifications (30-100 ppm), it is postulated that by reducing the concentration of the red phosphorus suspension in solution it is possible reduce the phosphorus concentration in the electroplated copper. However, it is important to bear in mind that the only reason for using phosphorus for the production of the KBS-3 copper canisters seems to be to reduce the embrittlement caused by the high levels of sulphur concentrated in the grain boundaries<sup>11</sup>. Therefore, if the right plating additive is employed, it is possible to obtain an electroplated copper that is sulphur-free (Table 1) and therefore the necessity to incorporate phosphorus additions needs to be revisited.

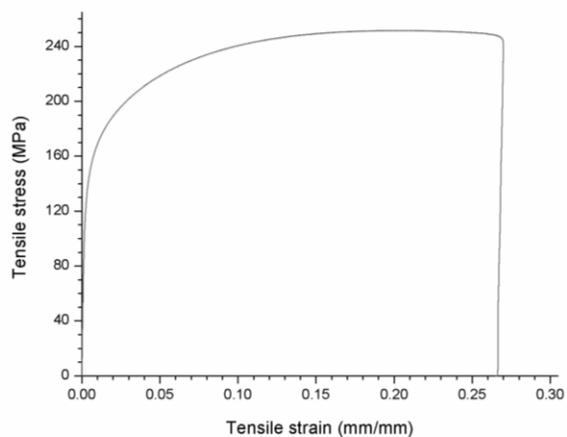


Fig. 3. Stress-strain curve generated at 2 mm/min at room temperature. Electroplated copper: 200 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  + 60 g/L  $\text{H}_2\text{SO}_4$  + 100 ppm NaCl, 30 °C, 6 A/dm<sup>2</sup>.

An example of the stress/strain curve for the electroplated copper from additives free-solution is shown in Fig. 3. Elongation of the electroplated copper was 27 %. Results obtained by other workers claim that elongation can be increased by using specific additives during electroplating<sup>19,20</sup> and will be the subject of future work. Even so, the elongation results obtained in this test are considerably higher than those obtained by other authors (12.5 % - 20.1 %)<sup>20,21,22</sup>.

Fig. 4 shows a homogeneous microstructure and fine grains of the electroplated copper. From Fig. 4 the grain size is estimated to be approximately 10-20 microns, which is more than x10 times lower than the maximum grain size specified by SKB<sup>13</sup>. In addition, this should overcome the low detectability limitations of the ultrasonic testing due to the large grain size and non-uniform grain size distribution<sup>8,14</sup>.

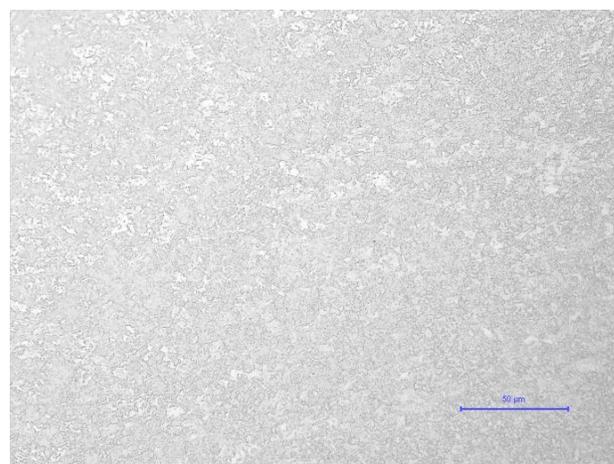


Fig. 4. Microstructure of electroplated copper. Sample was ground and polished to 0.25  $\mu\text{m}$  before etched in 40g  $\text{CrO}_3$ , 7.5 g  $\text{HN}_4\text{Cl}$ , 50 mL  $\text{H}_2\text{SO}_4$ , 50 mL  $\text{HNO}_3$  and 1900 mL  $\text{H}_2\text{O}$ .

### III.B. Process Optimization – Copper Electrolyte Monitoring & Control

With the objective of monitoring and controlling the electroplating process over extended periods of days/weeks, the feasibility of using cyclic voltammetry to monitor electrochemically active species was carried out. In previous papers we reported that the copper concentration tends to increase during the electroplating process and how cyclic voltammetry can be used to determine the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration from the current maximum of the deposition peak<sup>15</sup>. Two different correlations were obtained: one subtracting the background current (Eq. (1)) and the other without background subtraction (Eq. (2)).

$$\text{g/L CuSO}_4 \cdot 5\text{H}_2\text{O} = -206.50 + 263.04 \cdot I_{pc} \quad (1)$$

$$\text{g/L CuSO}_4 \cdot 5\text{H}_2\text{O} = -34.02 + 16.37 \cdot I_{pc} \quad (2)$$

Further research on this matter was focused on investigating the effect of the  $\text{H}_2\text{SO}_4$  and  $\text{Cl}^-$  concentration on the current peaks obtained by cyclic voltammetry. Fig. 5 shows the cyclic voltammograms obtained from acid copper plating solutions with different  $\text{H}_2\text{SO}_4$  concentration. Table 2 shows the current maxima ( $I_{pc}$ ) obtained from these cyclic voltammograms, together with the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  calculated from the Eq. (1) and Eq. (2) and the relative error ( $\delta$ ) of each calculation. The relative error ( $\delta$ ) has been calculated as the difference between the real  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration and the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration calculated from Eq. (1) and (2), normalized by the real  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration. By comparing the relative errors of the calculations employing Eq. (1) and Eq. (2), it can be concluded that the relationship obtained subtracting the background current (Eq. (1)) is strongly dependent on the sulphuric acid concentration. Different sulphuric acid concentrations affect the results obtained for copper sulphates concentration from the cathodic current maximum. On the other hand, the relative errors obtained from the use of the relationship obtained without subtracting the backgrounds current (Eq. (2)) appears to be acceptable for copper sulphate concentration monitoring purposes.

Fig. 6 shows the cyclic voltammograms obtained from acid copper plating electrolytes with different chlorides concentrations. As it can be deduced from the overlapping of the cathodic side of voltammograms performed at the three chlorides concentrations, the chlorides do not appear to affect the current maximums and hence they do not introduce any error in the relationship obtained.

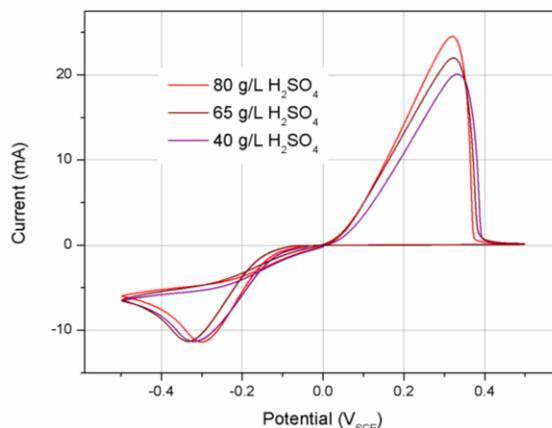


Fig. 5. Cyclic voltammogram of an acid copper plating process with different sulphuric acid concentrations. 150 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 100 ppm NaCl. 30 °C. 50 mV/s.  $\text{H}_2\text{SO}_4$  concentrations: 40 g/L (violet), 65 g/L (brown), 80 g/L (red).

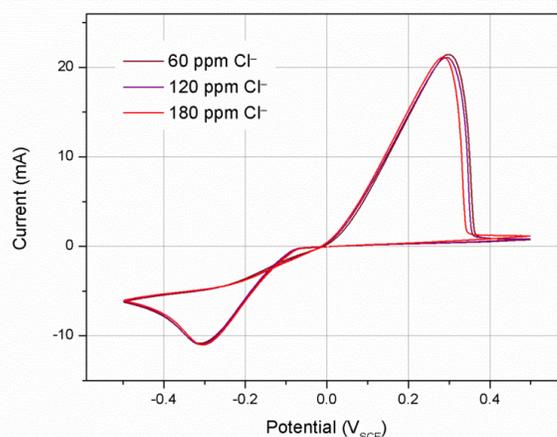


Fig. 6. Cyclic voltammogram of an acid copper plating process with different chlorides concentrations. 150 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 65 g/L  $\text{H}_2\text{SO}_4$ . 30 °C. 50 mV/s.  $\text{Cl}^-$  concentrations (as  $\text{Cl}^-$ ): 60 g/L (brown), 120 g/L (violet), 180 g/L (red).

Table 2. Effect of sulphuric acid concentration on the cathodic current maximums (150 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 100 ppm NaCl).

g/L $\text{H}_2\text{SO}_4$	With background current subtraction			Without background current subtraction		
	$I_{pc}$ (mA)	g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ calculated	$\delta$ (%)	$I_{pc}$ (mA)	g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ calculated	$\delta$ (%)
65	1.360	151.2	-0.80	11.32	151.3	-0.87
40	1.205	110.5	26.33	11.34	151.6	-1.07
80	1.526	194.9	-29.93	11.41	152.8	-1.87

Further research regarding monitoring and control of the electroplating process was focused on understanding the effect of the additives on the fundamentals of the electroplating process. Fig. 7 shows the effect of different additives in the voltammograms performed in an acid copper plating solution. The presence of the additives in the electroplating process shifted the cathodic peak potential to more negative values and the anodic peak potential to less positive potentials. Regarding the current maximum, both Additive A and B decrease the cathodic and anodic current maximums. For a reversible electrochemical reaction involving 2 electrons at 30 °C, a separation between anodic and cathodic peak of 30 mV would be expected<sup>23</sup>. The larger separation obtained in the voltammograms could be explained considering the presence of intermediates in the process, involving a chemical reaction in addition to the electrochemical reaction<sup>24</sup>. In this respect, it is widely accepted that the copper electrodeposition reaction takes place through a mechanism of at least two stages, where the cupric ions are reduced to cuprous ions before they reach the metallic state. Different theories contend that the cuprous ions react with chlorides ions<sup>25,26</sup> and additives<sup>27</sup> in solution through mechanism involving adsorption stages, i.e. pure chemical stages, forming intermediates.

The copper sulphate concentrations calculated from Eq. (1) and Eq. (2) are shown in Table 3. Again, if background current is subtracted, the error is larger than the obtained when background current is not subtracted. Even if background current is not subtracted, the magnitude of the error is dependent on the additive employed. Results obtained by other authors in the study of the effect of the interaction of the acid copper additives with the metallic copper and the copper ions in solution show that additives can regulate the presence of cuprous ion/species on the surface, inhibiting the formation of the cuprous ions (levellers/suppressors) or accelerating it (accelerators)<sup>28</sup>. It therefore makes sense that the error implied in the use of the Randles–Sevcik equation relies on the composition of the additive employed, the effect of this on the cuprous ion generation and the presence of purely chemical reactions between copper ions and additives. In this respect, Additive B presents a relative error of -16.3 %, whereas Additive A implies a relative

error of only -6.0 %. Both values are within the acceptable range of error for the monitoring of the  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  concentration.

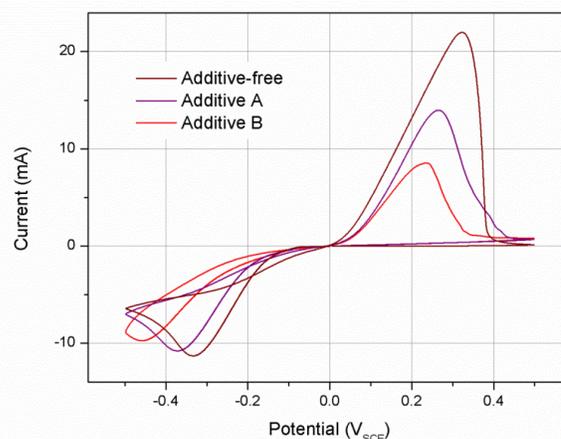


Fig. 7. Cyclic voltammogram of an acid copper plating process with different additives. 150 g/L  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , 65 g/L  $\text{H}_2\text{SO}_4$ , 100 ppm NaCl. 30 °C. 50 mV/s.

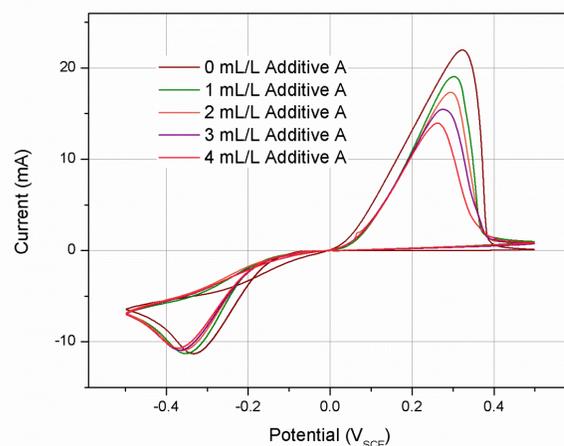


Fig. 8. Cyclic voltammogram of an acid copper plating process with different concentration of Additive A. 150 g/L  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , 65 g/L  $\text{H}_2\text{SO}_4$ , 100 ppm NaCl. 30 °C. 50 mV/s.

Table 3. Effect of different additives on cathodic current maximums (150 g/L  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ , 65 g/L  $\text{H}_2\text{SO}_4$ , 100 ppm NaCl).

Solution	With background current subtraction			Without background current subtraction		
	$I_{pc}$ (mA)	g/L $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ calculated	$\delta$ (%)	$I_{pc}$ (mA)	g/L $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ calculated	$\delta$ (%)
Additive- free	1.360	151.2	0.8	11.32	151.3	0.9
Additive A	1.230	117.0	-22.0	10.69	141.0	-6.0
Additive B	1.152	96.5	-35.7	9.74	125.5	-16.3

Fig. 8 shows the cyclic voltammograms of acid copper plating solutions with different concentration of Additive 2. As it can be seen as the concentration increase it hinders the stripping of the copper during the cathodic scan.

Additives concentration in the electrolyte is one of the most difficult parameters to measure, and consequently, to monitor in the electroplating process. The only widely accepted technique which can universally determine the concentration of organic additives is HPLC (High-performance liquid chromatography)<sup>29</sup>. Commercial additives are made-up from different numbers of chemicals. Then, other techniques, like CVS (Cyclic Voltammetric Stripping)<sup>30,31</sup> are not as widely applicable as HPLC. For the additive considered for this study (Additive A), a characteristic behaviour where current maximums are linearly dependent on the additive concentration is observed (Fig. 8). Fig. 9 shows the plot of the linear trend between these parameters. The coefficients of determination ( $R^2$ ) are 0.9748 and 0.9980 for the cathodic and anodic currents, respectively. These high values indicate that the method is accurate and cyclic voltammetry technique could be employed to determine concentration of Additive A in the electroplating solution.

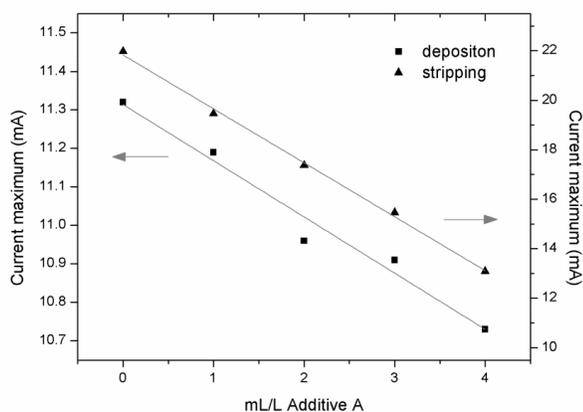


Fig. 9. Linear trend between maximum current and concentration of Additive 1 obtained from cyclic voltammograms (Fig. 8).

In the next stages of this research, with the objective to bring the hydrogen concentration within KBS-3 specifications, the use of Additive A at different operating conditions will be explored. The application of heat treatments will also be assessed as post-plating treatment to release hydrogen from the electroplated copper. In addition, tensile and creep testing will be performed on these samples to reveal if sulphur-free electroplated copper requires the incorporation of phosphorus in the metallic structure to increase the creep ductility.

## IV. CONCLUSIONS

The use of electroplating as manufacturing technology for producing free-standing copper shell for nuclear canisters is currently being studied. The results obtained showed that copper components obtained by means of electroplating are very close to meeting the KBS-3 specifications. For optimizing and controlling the electroplating process to allow the production of thick-walled copper canister, the application of cyclic voltammetry has been considered.

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