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The recovery of precious metals (Ag and Au) by electrodeposition-redox replacement (EDRR) method was studied in three different solutions: sulfate based Zn-Fe-Ag solution, chloride based Cu-Fe-Au solution and industrial multimetal chloride solution. The common factor to these solutions is that the base metal is present in g/L scale while the precious metal is present in ppm or lower level. The results showed that the presence of Fe (in g/L scale) decreases the recovery efficiency of precious metals but at the same time, it may lead to selective dissolution of the base metal (Zn or Cu) resulting in the higher purity of the precious metal deposit. Moreover, a successful deposition of Au on carbon nanotube (CNT) films from industrial multi-metal solution was demonstrated.

Introduction

It has become obvious that in order to fulfill the global demand of precious metals, secondary raw material sources need to be identified and utilized more effectively (1,2). As a result, also minor metals present in industrial solid or liquid wastes could act as a potential raw material source (3). However, the low concentration of these minor metals *cf.* the base metal poses a challenge as how to recover metals from liquid side-streams energy and cost efficiently; often the precious metals are present in ppm (or even ppb) level while the base metal can be present in tens of g/L in hydrometallurgical solutions.

In addition to scarce precious metal resources, these solutions may also possess environmental risks, often due to inherent nature of the base metal or impurities (Pb, As, Ni, Co, etc.). Therefore, the circular economy principles – reduce, reuse, recycle, recover – are becoming ever more important in the global metal manufacturing (4).

Typically, the recovery of metals from industrial streams is performed by solvent extraction, cementation or precipitation, chemical reduction, or electrowinning. However, such methods are not always applicable when it comes to the solutions containing only trace amounts of valuable metals.

Recently, we utilized electrodeposition-redox replacement (EDRR) method to extract Ag from Zn process streams (5). In EDRR method, the base metal (such as Zn) is first deposited during the electrodeposition step, followed by a redox replacement step in the absence of applied potential or current. During this latter step, the deposited less noble metal is spontaneously replaced by a more noble metal (such as Ag) still present in the solution. As a result, Ag is enriched on the electrode. The EDRR proved to be extremely successful for synthetic solutions mimicking the Zn/Ag ratio typical in hydrometallurgical processes and actually, Ag was recovered even from as low as ppb concentrations of the solutions while Zn concentration was 60 g/L (5).

Principles of redox replacement has earlier been used in the preparation of defect free monolayers for example by surface-limited redox replacement (SLRR), pioneered by Brankovic *et al.* (6) or electrochemical atomic layer deposition, pioneered by Gregory and Stickney (7). In these methods, underpotential deposition of the sacrificial metal is considered critical, and as only the upmost layer experiences such a redox

replacement (8), SLRR and e-ALD results in smooths monolayers which may be expanded to multilayers by repetitive cycling of SLRR or e-ALD steps. However, instead of underpotential deposition which is used in SLRR and e-ALD, electrodeposition often results in the deposits with porous nature, and thus the redox replacement can take place also "deeper" in the deposit of the sacrificial base metal in EDRR. Therefore, the high concentration of base metal – which often causes problems in the traditional recovery methods – is actually beneficial for the precious metal enrichment.

Our previous study was performed only in two-component synthetic solution while the real industrial solutions typically have a complex multi-metal solution matrix, Fe being the most typical impurity present in the hydrometallurgical processes. Therefore, in this paper, the effect of impurities on the EDRR operation is studies in three different cases; Fe in Zn-Ag system, Fe in Cu-Au system and multimetal impurities in Cu-Au system.

Experimental

<u>Chemicals and Solutions</u>

The solution compositions reflect the typical Zn and Cu process solution. The composition of solutions with Zn as a base metal was 60 g/L Zn (from $ZnSO_4 \cdot 7H_2O$, ≥99%,VWR, Belgium), 10 g/L H_2SO_4 (H_2SO_4, 95-97% for analysis，EMD Millipore, Gemany), 100 ppm Ag (ReagentPlus® $AgNO_3$, ≥99.0%, Sigma-Aldrich, USA) and 1-10 g/L Fe (with Fe^{2+}/Fe^{3+} ratio of 1/0.08 ($FeSO_4 \cdot 7H_2O$, ≥ 99%, ACS grade, Alfa Aesar, $Fe_2(SO_4)_3 \cdot x H_2O$, Fe^{3+} ≥22%, VWR, EC).

The composition of solutions with Cu as a base metal was 2.7 g/L Cu (from $CuCl_2 \cdot 2H_2O$, ≥99%, analytical grade, ACROS Organics, US), 2 M NaCl (technical grade), 8 ppm Au (PrimAg® Au reference solution, 1000 mg/L Au in 5 M HCl matrix, ROMIL Ltd., UK) and 0.32 g/L Fe ($FeCl_3 \cdot 6 H_2O$, ACS grade, Merck Millipore, Germany).

Table I shows the main elemental composition of the industrial chloride based process solution, originating from HydroCopper demonstration plant (9).

TABLE I. ICP-MS and ICP-OES analysis of the utilized industrial process solution.

Element	mg/l
Cu	39000
Fe	3.54
Te	0.013
Se	7450
Ni	49.1
Si	14.1
Au	0.0313
Ag	2.31

<u>Electrodeposition – Redox Replacement (EDRR)</u>

The Electrodeposition – Redox Replacement (EDRR) was performed in a typical three-electrode cell: Pt sheets (Kultakeskus, Finland) were used as a working and counter electrodes. The reference electrode was either saturated mercury/mercurous sulfate electrode MSE (Zn-Fe-Ag solutions) or standard calomel electrode SCE (Cu-Fe-Au solutions). For clarity and to ease the comparison, all potentials are referred towards SCE.

Prior the EDRR, cyclic voltammograms were measured in the solutions of question, in order to find relevant EDRR parameters. The electrodeposition step was controlled by the deposition potential, time and redox replacement step was controlled either by so called cut-off potential – i.e. the open circuit potential which the system was allowed to reach before next electrodeposition step took place - or cut-off time.

For Zn-Fe-Ag solutions, the deposition took place at -1.1 V vs. SCE for 5 s and the cut-off potential was + 0.3 V vs. SCE or alternatively, cut-off time (1000 s) was used. For Cu-Fe-Au solutions, the deposition took place at -0.3 V vs. SCE for 5 s and the cut-off time was 120 s. For Au particle formation directly on the free-standing carbon nanotube (CNT) films, the EDRR was performed for 24 h so that the deposition potential was -0.3 V vs. SCE, deposition time 10 s and the cut-off time 600 s.

Analysis of the deposits: Stripping of precious metals and SEM-EDS
After EDRR, the samples were rinsed with distilled water and the deposits were analyzed either by detecting the stripping peak of the cyclic voltammograms or SEM-EDS (Scanning Electron Microscope – Energy Dispersive Spectroscopy, Tescan Mira[3] GM, Czech Republic). Stripping peaks were detected in 10 g/L H_2SO_4 solution (Zn-Fe-Ag) or 2 M NaCl solution (Cu-Fe-Au), i.e. in the pure solution media without any metals. In prior to SEM-EDS analyses, the samples were rinsed with distilled water and dried in air at room temperature. The applied acceleration voltage was 15 kV and 10-15 spectra were taken from each sample.

Results and Discussion

Recovery of Ag from Zn Process Solutions
Figure 1 shows the cyclic voltammograms of solutions containing Zn+Ag and Zn+Fe+Ag. The peaks for reversible oxidation and reduction of Fe^{2+}/Fe^{3+} pair is observed around 0.4 V vs. SCE and it overlaps with Ag stripping. The cathodic peak which starts from -0.4 V vs. SCE indicates the H_2 evolution. When the cathodic polarization increases to -1.5 V vs. SCE, high efficient Zn deposition occurs and no visible H_2 bubbles were observed on the electrode surface during Zn electrodeposition. This behavior is similar as observed by Salles *et al*. (10). therefore, the EDRR parameters of Zn-Fe-Ag solutions, the deposition was conducted at -1.1 V vs. SCE and the redox replacement step was allowed to take place either when a pre-determined open circuit potential (+0.3 V vs. SCE) or time (1000 s) solutions was reached. Figure 2 shows the typical EDRR profiles in Zn-Ag and Zn-Fe-Ag solutions and Figure 3 shows the comparison of Ag stripping peaks, performed in 10 g/L H_2SO_4 after EDRR. As Figure 2 shows, typically only the first cycle reached the cut-off time before cut-off potential was achieved while in the following steps, the cut-off potential was reached relatively fast (in 100-200 s.)
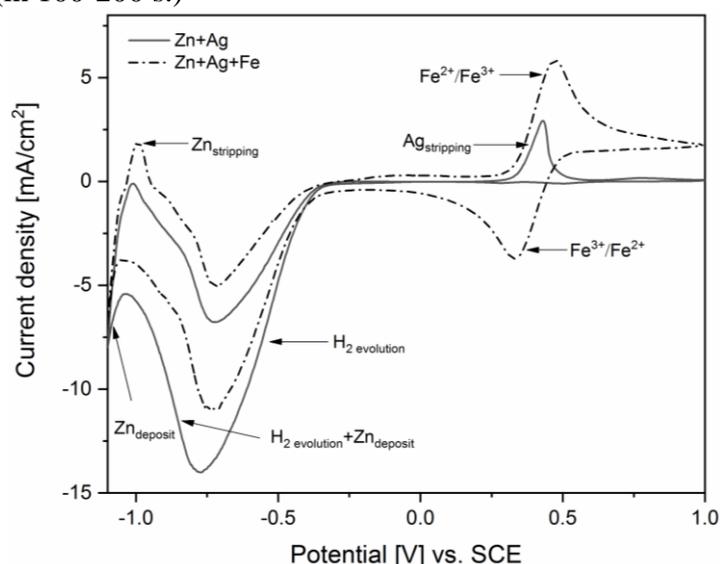

Figure 1. Cyclic voltammetry measurements from 0 V $\rightarrow$ +1.0 V$\rightarrow$ -1.1 V $\rightarrow$0 V vs. SCE (20 mV/s) in a solution containing 60 g/L Zn, 100 ppm Ag, and 10 g/L H_2SO_4 and solution containing 60 g/L Zn, 2g/L Fe, 100 ppm Ag, and 10 g/L H_2SO_4.
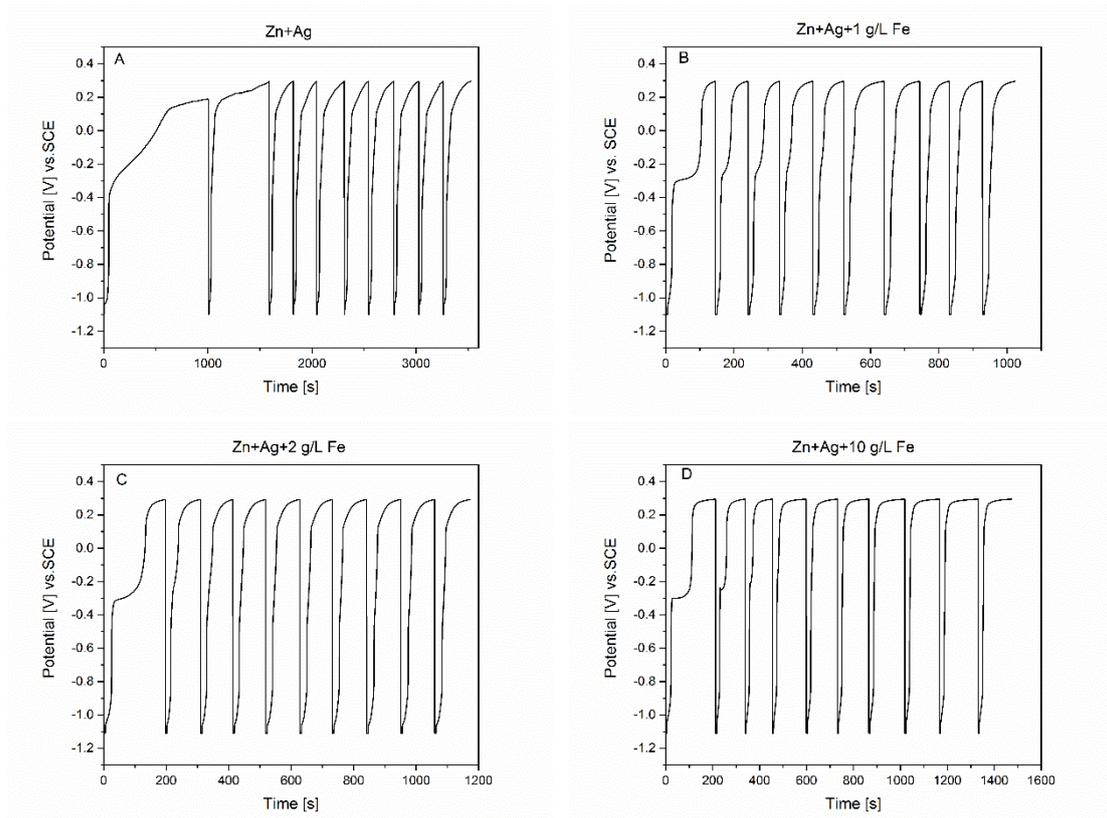
Figure 2. Potential profile during EDRR measurements in 60 g/L Zn, 100 ppm Ag, and 10 g/L H_2SO_4 solution containing (A) 0 g/L Fe (B)1 g/L Fe (C) 2 g/L Fe (D) 10 g/L Fe. EDRR parameters used were $E_1 = -1.1$ V and $E_2 = +0.3$ V vs SCE, $t_1 = 5$ s, and n = 10.
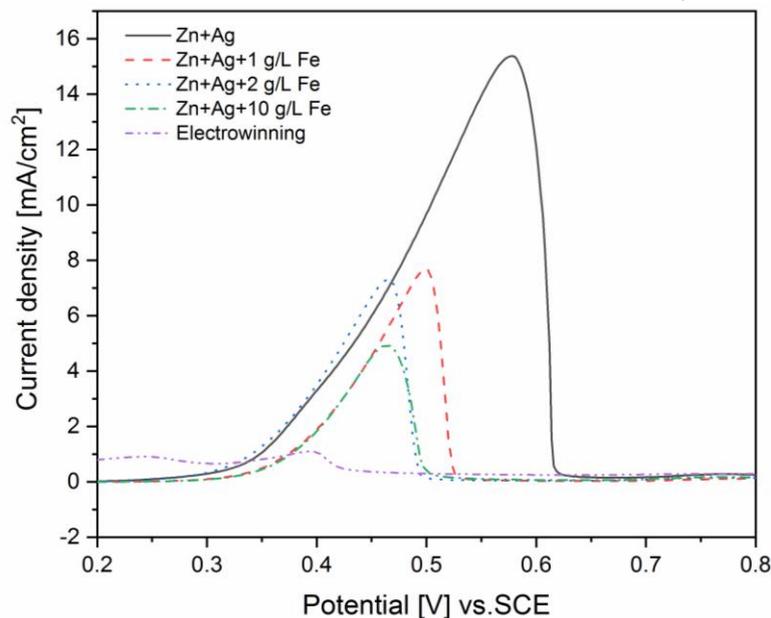

Figure 3. Silver stripping peaks after electrowinning (E= -1.1 V vs. SCE, t= 50s) in solution (60 g/L Zn, 100 ppm Ag and 10 g/L H_2SO_4) and after the EDRR experiments in solutions (60 g/L Zn, 100 ppm Ag and 10 g/L H_2SO_4) with varying Fe content (0-10 g/L), $E_1 = -1.1$ V and $E_2 = +0.3$ V vs SCE, $t_1 = 5$ s, and n = 10.

Figure 3 clearly demonstrates the effect of impurity Fe to the silver recovery by EDRR: the stripping peaks decrease with increasing Fe content in the solution, i.e. impurity Fe decreases the recovery. This is believed to be due to competing Fe^{3+}/Fe^{2+} reduction during the redox replacement step. Without Fe in the solution, deposited Zn is oxidized

back to the solution (as Zn^{2+}) and Ag^+ is reduced to Ag^0 and deposited on the surface, resulting in high recovery of Ag. However, when Fe is present in solution, part of deposited Zn is also oxidized with Fe^{3+}, resulting in reduction of Fe^{3+} to Fe^{2+} and dissolution of Zn (as Zn^{2+}) into the solution. Nevertheless, it is important to note that the EDRR method is clearly more effective in Ag recovery even at 10 g/L impurity Fe concentration than electrowinning, performed in pure Zn-Ag solutions, showing that EDRR is indeed a powerful method in Ag recovery sulfate based Zn process solutions even in the presence of impurity metals.

Table II further demonstrates the effectiveness EDRR when compared to electrowinning: in the latter method, the deposit contains mostly Zn while in EDRR the enrichment takes place (due to RR step) and despite of high impurity Fe concentrations in the solution, Ag is clearly the dominant element in the deposit while Zn and Fe vary 1-3 % and 0.1-0.2 %, respectively. Moreover, the purity of the deposit (Ag/(Fe+Zn) ratio) is actually higher when Fe is added to the solution with 1 and 2 g/L Fe impurity. This too is believed to be due to competing oxidation of Zn by Fe^{3+} as discussed earlier in the Ag stripping results, resulting in higher Ag purity. Thus, despite of the fact that Fe decreases the recovery, it may have a positive effect on the purity of the deposit.

Table II: Weight Percentages of Zn, Ag and Fe Present on Electrode Surface Based on SEM-EDS Analysis (average of 10-15 point analysis).

Method	Solution composition	Zn(wt %)	Ag(wt %)	Fe(wt %)	Ag/(Fe+Zn)
EDRR	Zn+Ag	3.8	30.9	-	8.1
	Zn+Ag+Fe(1g/L)	1.7	17.1	0.1	9.2
	Zn+Ag+Fe(2g/L)	0.8	11.2	0.1	11.9
	Zn+Ag+Fe(10g/L)	0.9	8.2	0.2	7.5
Electrowinning	Zn+Ag	37.5	1.7	-	0.05

Recovery of Au from Chloride Process Solutions

In order to understand the impact of impurity Fe more, also the chloride based Cu-Fe-Au process was studied. Figure 5 shows a typical current density profile for EDRR in Au containing solutions and Figure 6 shows the stripping peaks of Au for different solution compositions.

Average current density at Cu deposition step is similar in both cases meaning that amount of copper deposited on cathode surface shall be virtually the same. However, the Au stripping peak after EDRR in absence of Fe in the solution is nine times higher when compared to Fe containing solution. The results show clearly a similar behavior as in the case of Zn-Fe-Ag solutions is, i.e. the competing Fe^{3+}/Fe^{2+} reduction decreases the overall recovery of Au.
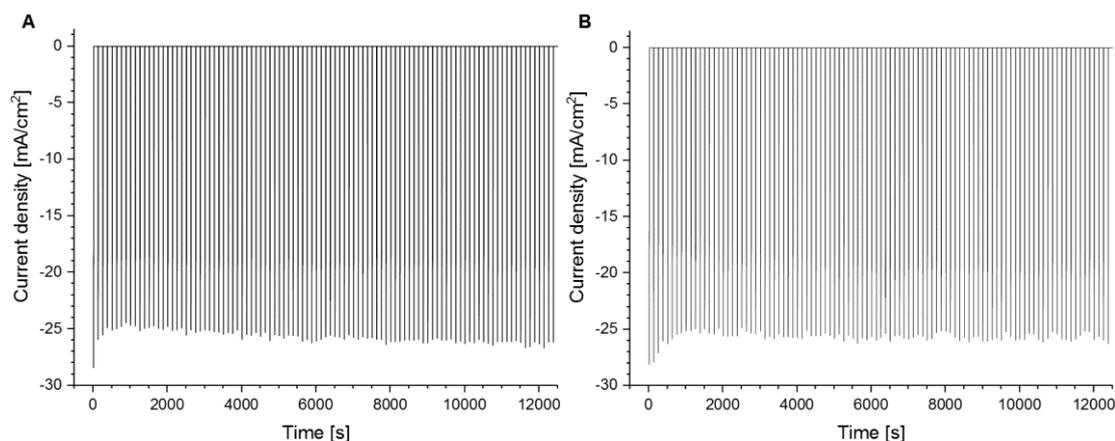

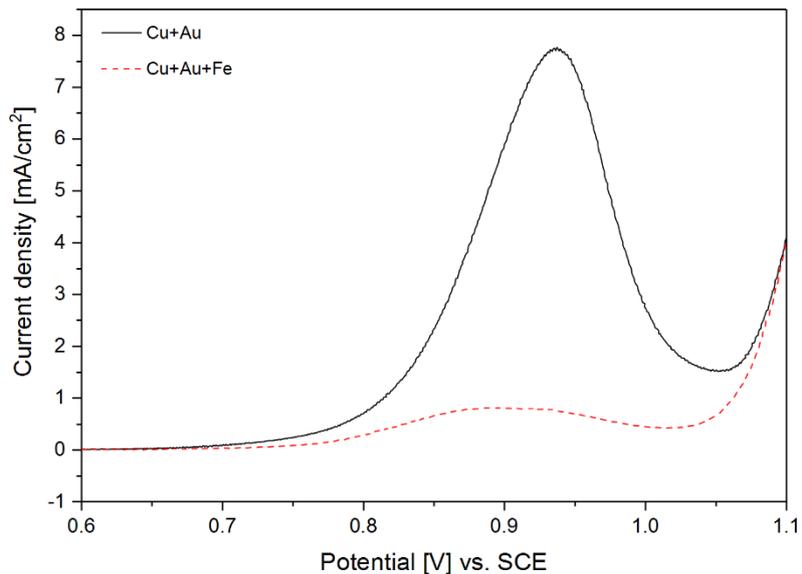Figure 5. Typical current profile without Fe (A) and with Fe (B) in Au/Cu solution.

Figure 6. Au stripping peaks (scan rate 50 mV/s) after 100 EDRR cycles in solutions without and with Fe.

The results of SEM-EDS analysis of the cathode surface after EDRR shown in Table III support the hypothesis that Fe may increase the product purity. For instance, the Au/Cu ratio on the surface is 2.9 without Fe in solution and 3.7 in presence of Fe. The morphology of the deposit obtained from both solutions is illustrated with secondary electron image on Figure 7. When Fe is absent in the solution, formed deposit has porous structure but more uniformly distributed over the surface of electrode. On the other hand, when Fe was present in the solution, EDRR resulted in formation of Au particles of high purity sparsely dispersed at the surface.

TABLE III. SEM-EDS analysis of the cathode surface after 100 EDRR cycles in Cu/Au solutions (average of 10-15 points).

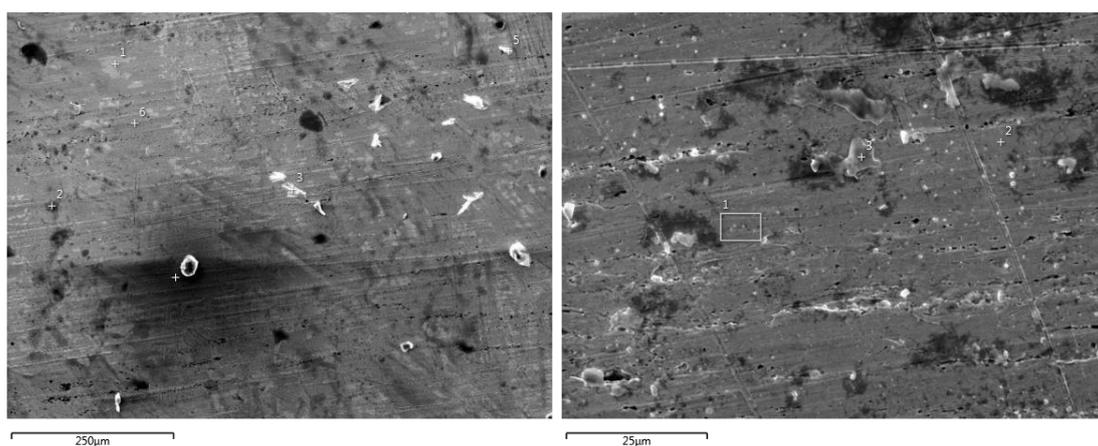| Sample ID	Pt, wt. %	Au, wt. %	Cu, wt. %	Au/Cu ratio
Without Fe	93.6	4.7	1.7	2.9
With Fe	93.5	5.1	1.4	3.7

Figure 7. Micrographs of Au/Cu deposit obtained in the EDRR experiments

Effect of Industrial Multi-metal Solutions on Au Purity
Also, real industrial solution (Table I) was investigated as a potential raw material for Au recovery. Moreover, the base material used as electrode was a free-standing carbon nanotube (CNT) film (11), in order to test applicability for direct "manufacturing" of high-added value gold based product from industrial multi-metal solution.

Figure 8 shows successful formation of appr. 2 µm particles with 35 wt-% of Au: this is an encouraging result, as the industrial solution used contained only 0.03 ppm of Au. In addition, impurities such as Se, Te, Ag, Cu and smaller amounts of Si and Cl accumulated on the surface. This clearly demonstrates that despite of large scale and concentration of other metals present in the solution, gold can be recovered with relatively high purity. It is worth noting that tailoring of the EDRR process parameters as well as solution composition can even further improve the product quality.
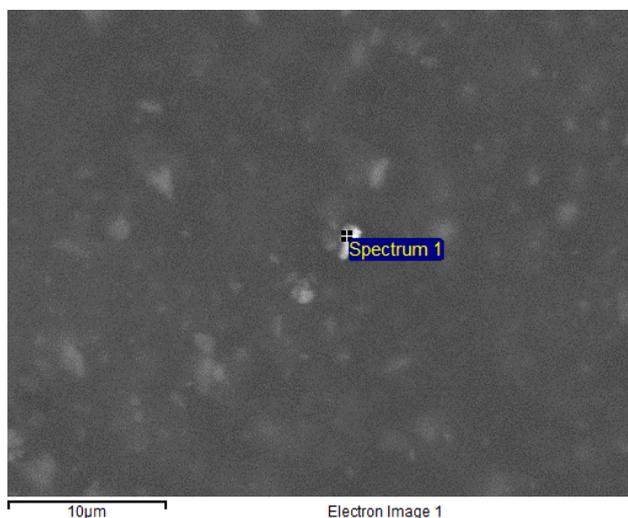

Figure 8. Au nanoparticle on carbon nanotube film from industrial process solution.

Conclusions

The effect of impurities, especially Fe, on the precious metal recovery by electrodeposition-redox replacement (EDRR) was studied in three different cases; Fe in Zn-Ag system, Fe in Cu-Au system and multimetal impurities in Cu-Au system. The EDRR parameters were tailored for each solution and after a number of EDRR cycles, the deposits were analyzed for Ag and Au.

These results clearly demonstrate that the presence of Fe decreases the recovered amount of valuable metal. This is suggested to be due to competition of precious metal (Au or Ag) reduction and Fe^{3+} reduction at the cathode. However, this phenomenon might also benefit the purity of the precious metal deposit, as the base metal (Zn/Cu) can also be selectively oxidized by Fe^{3+}, thus enriching the surface with Au or Ag. The results also show that EDRR gives high enrichment of Au on carbon nanotube (CNT) surface, even from the industrial multimetal solution.

Therefore, it can be concluded that EDRR is an effective enrichment method when it comes to the high-quality recovery of precious metals from industrial streams where the concentration of precious metals is low (ppm scale) and of other metals is high (g/L) scale. Furthermore, it can provide a direct route for high-added value product preparation, such as Au particles on CNT.

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