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Environmental Aspects of the Electrochemical Recovery of Tellurium by Electrochemical Deposition-Redox Replacement (EDRR)

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Abstract

The current study investigates the energy consumption and the corresponding global warming potential (GWP) of tellurium recovery from multimetal solution by the use of a tailored electrochemical recovery approach based on electrodeposition-redox replacement (EDRR). A three electrode cell was used to recover Te from synthetically prepared pregnant leach solution similar to the PLS of leached Doré slag (30% aqua regia, $[Cu] = 3.9$ g/L, $[Bi] = 4.6$ g/L, $[Fe] = 1.4$ g/L, and $[Te] = 100-500$ ppm). Enrichment of Te on the electrode (with 100 EDRR cycles) had a calculated global warming potential of 3.7 CO₂-eqv from a solution with 500 ppm Te based on a Finnish energy mix. In comparison, a decrease of Te concentration to 100 ppm increased the corresponding environmental impact to 16.9 CO₂-eqv. Overall, GWP was shown to be highly dependent on the geographical area *i.e.* the dominating energy production methods.

Keywords: Tellurium, Metals Circular Economy, Energy Efficiency, Life Cycle Assessment (LCA)

Introduction

Tellurium is a rare metalloid element, which has an abundance in the Earth's crust of approximately 1 ppb [1] *cf.* gold is ~5 ppb [2]. Although the application of tellurium is at present rather limited - semiconductors [3]

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thermoelectrics [4] and CdTe solar panels [5], which have potentially higher efficiency compared to the traditional solar panels [6] – the heightened demand for renewable energy systems [7] will require access to increased levels of tellurium. However, as the content of tellurium in Earth's crust is relatively low, the production of applications employing tellurium is also relatively low but the demand is increasing. Currently, the primary source of tellurium comes from the treatment of copper anode slime via a variety of different pyro- and hydrometallurgical unit processes [8], [9]. Nevertheless, in order to promote a more ambitious circular economy of metals, different methods for the recovery of minor/trace concentrations of tellurium (and other rare metals) which are currently lost are essential.

The electrodeposition redox-replacement (EDRR) technique has recently been investigated as an alternative route for the recovery of metals like gold, silver, platinum and tellurium in the field of hydrometallurgy [10] – [14]. The method is based on a multistep approach that involves the electrodeposition of a less noble - typically base metal - material on an electrode surface with short pulses (typically a few μs to few s) followed by a pre-defined time under open circuit conditions (OCP) to allow the spontaneous redox replacement of the electrodeposited layers by the nobler target element. The parameters applied during EDRR include deposition potential (E_1), cut-off potential (E_2) or deposition current (i), deposition time (t_1), cut-off time (t_2) and number of EDRR cycles (n). More details about the overall procedure can be found elsewhere [10] – [14]. This tailored electrochemical method for the recovery of minor metals or trace amounts of metals from complex multimetal solutions offers a way to increase the sustainability of metals processing.

Life cycle assessment (LCA) is a standardized, systematic method (ISO 14040) to evaluate the environmental impacts of a product or a process through the calculation of a number of impact category indicators. One of the main indicators used is global warming potential (GWP), which relates to atmospheric heat captured due to the associated greenhouse gases emitted and allows different processes or methods to be compared based on their ecological effects. This study demonstrates the environmental impact, specifically GWP, related to energy consumption by a novel direct Te recovery method, EDRR.

Experimental

The base solution utilized consisted of 30% aqua regia [10] (1:3 molar ratio of nitric and hydrochloric acids, VWR Chemicals, Belgium) diluted with Milli-Q ion exchanged water (Merck Millipore, USA). Due to the aqua regia medium, the high concentration metals - Bi, Cu and Fe - were sourced from nitrite and chloride salts (bismuth(III)nitrate pentahydrate, Alfa Aesar, Germany, copper(II)chloride dehydrate, VWR Chemicals, Belgium and iron(III)nitrate nonhydrate, Alfa Aesar, Germany) in order to avoid any potential sulfate contamination. Tellurium content of the solution was varied between 100-500 ppm through use of a Te AAS standard (Sigma Aldrich, USA) and all chemicals were of technical grade. The electrochemical setup was a typical three-electrode cell with saturated calomel electrode (SCE, B521, SI Analytics, Germany) as a reference electrode (RE), 0.1 mm thick ($A = 24 \text{ cm}^2$) platinum plate as counter electrode (CE) and 0.1 mm thick ($A = 0.4 \text{ cm}^2$) platinum plate as a working electrode (WE). Both Pt plates were from Kultakeskus (Finland) with the purity of 99.5%. A potentiostat (Ivium-Stat 24-bit CompactStat, Ivium Technologies, the Netherlands) was employed for the electrochemical measurements. In order to determine the mass of the deposit, the working electrode was weighed before and after the electrochemical experiments by Mettler-Toledo (XSE205, DualRange, USA), weightings done in triplets. SEM-EDS (scanning electron microscope, Mira³ Tescan GM, Czech Republic, energy dispersion spectroscopy, Thermo Scientific 50 mm² UltraDry, USA) was used to estimate the purity of the deposit with ten spot analyses performed for each sample and the average values are reported.

During the EDRR experiments, a previously determined deposition potential (E_1) of -500 mV vs. SCE and cut-off potential (E_2) of +150 mV vs. SCE was used [10]. Deposition time (t_1) was 2s, the cut-off time (t_2) 1000s and the total number of applied EDRR cycles (n) was 100. The specific energy (E_s) consumption [kWh/kg] of the EDRR method for recovering tellurium was calculated by using equation (1) [13]:

$$E_s = \frac{E_{cell} \cdot \int_0^{t_1} i(t) dt}{m_{Te}} \quad (1),$$

where E_{cell} is the cell voltage [V], $i(t)$ is the function of current with time *i.e.* electrical current is integrated over the time spent for the ED step, resulting in consumed electrical charge [As], t_1 is the time spent for the ED step [s], and m_{Te} is the mass of recovered tellurium [g].

Results and Discussion

The measured tellurium content in the deposits on the electrode surface is presented in Table 1. The enrichment Te on the electrode surface was almost the same (~76-80 wt-% by SEM-EDS), regardless of the tellurium content on the original solution. Other metals that were found to predominate in the surface metal deposit analysis included Cu (from 2.4 to 7.8 wt-%) and Bi (from 13.0 to 16.3 wt-%). Tellurium within the deposits is suggested to be either in the pure metallic form or as an alloy with Cu and Bi (e.g. CuTe and Bi₂Te₃). The purity of the recovered tellurium was also found to be in good agreement with previously published results [10]. Moreover, in solutions with 500, 250, 125 and 100 ppm tellurium, the corresponding tellurium recoveries on the electrode with 100 cycles were 0.34%, 0.43%, 0.35% and 0.36%, respectively. Although the recovery of tellurium is rather low, it is worth noting that the total processing time was also short. For example, when $n = 100$, the total EDRR time spent with a 500 ppm tellurium solution was only ~1 h. Furthermore, it is assumed that an increase in the number cycles (n) will lead to enhanced levels of tellurium recovery.

Table 1. Purity of Te in the metal deposits (analysed by SEM-EDS) on the electrode surface after conducting the EDRR experiments with $E_1 = -500$ mV and $E_2 = +150$ mV vs. SCE, $t_1 = 2$ s, $t_2 = 1000$ s and $n = 100$.

Te content in the solution [ppm]	Purity of Te on the electrode [wt-%]
500	76
250	79
125	80
100	80

The calculated specific energy consumption for tellurium recovery - defined by the deposit mass multiplied by the Te content (SEM-EDS) - varied from ~14 to ~63 kWh/kg with tellurium content of 500 ppm originally in solution to 100 ppm in solution, Figure 1. Moreover, one of the limiting

factor for EDRR is mass and/or charge transfer [10] – [14] and the ion movement from further away from the electrode surface requires in order of an magnitude more time *cf.* the ions that are closer to the electrode surface. Therefore, also the energy consumptions are increased when decreasing the tellurium content due to lower amount of ions in the solution, leading to a situation, where there is lower amount of ions closer to the electrode surface. However, the lower content of tellurium has not a direct effect to the recovered purity (Table 1) or to the recovery rates, but more energy is consumed during the process. The specific energy consumption for tellurium recovery was found to be approximately the same with the two highest concentrations employed (250 and 500 ppm), however it was found to drastically increase as the level of Te in the solution decreased, Figure 1.

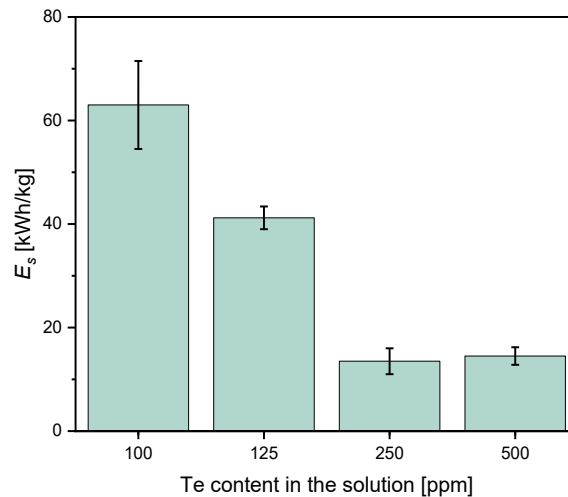


Figure 1. Calculated specific energy consumptions of the EDRR method as a function of tellurium in the solution.

In order to get more understanding about the environmental impact of the selected tellurium recovery method, the GWP (global warming potential) of EDRR was calculated by using GaBi software [15] (ecoinvent 3.5, [16]). GWP indicates the measured heat trapped in the atmosphere by various greenhouse gases when compared to CO₂ over a 100 year time window. The GWP is scaled for one unit (kg) of CO₂, therefore, *e.g.* methane has 21 CO₂-eqv and N₂O 310 CO₂-eqv. The selected countries for GWP determi-

nation were the top four tellurium producing countries (China, Japan, Sweden, and Russia [17]), along with Finland and the European average without Switzerland. The database values for the electricity production mixes were from the year 2018/2019 and the GWP values were calculated for the electricity consumption of tellurium recovery from 100 (~63 kWh/kg) and 500 ppm (~14 kWh/kg) solutions.

The results suggests that the GWP values for the recovery of tellurium from 100 ppm solutions was considerably larger than from 500 ppm solutions, Figure 2. The average energy production mix (ecoinvent 3.5, [16]) suggests that the impacts of producing tellurium are expected to be larger in China, Japan and Russia compared to Europe. The main factor for the increased GWP values results from the database that includes high level GWP fossil fuel-driven energy sources, whereas nuclear power is listed as GWP energy sources that produce no direct emissions. Nevertheless the database *does not* take into account the other aspects related to power sources, for example, the radioactive waste produced by nuclear power or the huge demand of critical metals needed required for renewable energy applications like solar panels [18], [19].

In Russia the share of nuclear power utilized is relatively large, whereas the Fukushima incident in 2011, has largely decreased nuclear power use in Japan [20] and consequently, increased the share of imported fossil fuels in Japan. Although Finland's electricity sector is far less CO₂-intensive than the European average, Finland (16.9 and 3.7 kg CO₂-eqv/kg) was still reliant on fossil fuels *cf.* to Sweden (1.8 and 0.4 kg CO₂-eqv/kg), Figure 2. Although both Nordic countries primarily utilize nuclear and hydropower as their sources of low-emission electricity, the extent is much larger in Sweden, which explains the discrepancy [21].

This study suggests that the concentration of tellurium in solution has a marked effect on the energy consumption required for Te recovery. Nevertheless, the GWP value related to tellurium recovery, is not necessarily dependent on the process, process optimization and process conditions, but rather that the origin of energy *i.e.* the energy production method used is also a key factor. For example, despite the higher energy consumption required for EDRR with a 100 ppm tellurium solution, the related GWP

value for tellurium recovery is calculated to be lower in Sweden when compared to tellurium recovery from a 500 ppm solution in Finland. Therefore, the local electricity production methods used for tellurium recovery by EDRR will have significant impact on the environment and overall global warming potential. Therefore, the individual energy mix, which is averaged across a whole country, is not always accurate as there are often local variations. Nevertheless the results presented in Figure 2, highlights both the opportunities and challenges related to energy production methods, as usage of fossil fuels and their direct greenhouse gas emissions ultimately have a dominating impact on the sustainability of the industrial scale application of “electricity based technologies” like EDRR for tellurium recovery.

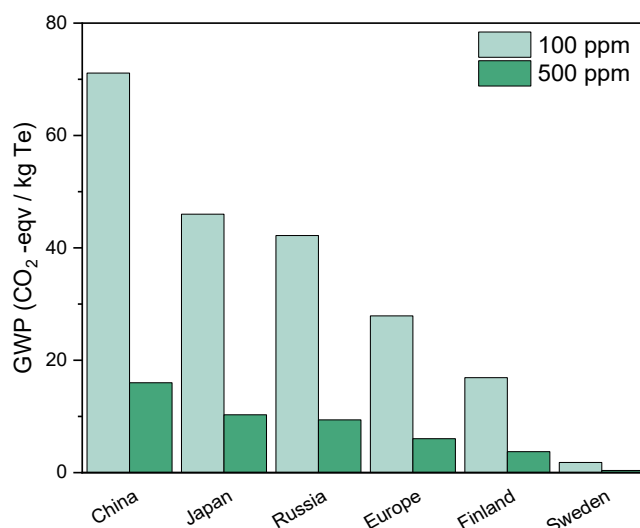


Figure 2. GWP values for tellurium recovery by EDRR from 100 and 500 ppm solutions in the largest tellurium producing countries, Europe and Finland based on the specific energy consumption based on the ecoinvent 3.5 database.

Conclusions

The specific energy consumption of the EDRR process in terms of recovering tellurium was determined to increase with decreasing Te solution content. Correspondingly, the global warming potentials (GWP) of the EDRR method were also found to be increased with reduced tellurium concentrations. With 250 to 500 ppm tellurium in solution, the emissions were

only ~16% of those calculated for the 100 ppm solution of tellurium. Moreover, the geographical location and especially, the national or local energy production mix was found to have a major impact effect on the level of GWP expected.

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