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Volume 2:

# MINERAL PROCESSING

Edited by:

Instituto de Ingenieros de Minas de Chile (IIMCh)



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## ReAK – Reduction of arsenic in copper concentrates WP 3.3.3: Electrochemical oxidation

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### Abstract

*ReAK (Reduction of arsenic in copper concentrates) is a project build of German and Chilean partners. The aim of the project is the optimization and further development of process steps in copper production, which deals with the treatment of ore fractions that are particularly rich in arsenic.*

*The project focuses on different process steps and tries to find the most cost-efficient and environmentally friendly way for arsenic separation and disposal. One of many tasks is to oxidize the arsenite from the arsenic-rich wastewater of the gas scrubbers to arsenate in order to precipitate it subsequently as scorrodite. This iron arsenate compound is more stable and can therefore be landfilled in a more environmentally friendly manner.*

*In work package 3.3.3 an electrochemical oxidation method is investigated which uses a special diamond electrode. So far, the principal capability has already been demonstrated within the project. Also, high concentrations of arsenite could already be oxidized to arsenate in a relatively short time.*

## 1. Introduction

Arsenic oxide is one of the most famous poisons of the Middle Ages and the Renaissance. Napoleon, for example, was poisoned with arsenic, which could only be proven by modern analysis using a hair analysis. (Süss-Fink, 2012)

Due to its extremely toxic properties, arsenic is nowadays becoming more and more of a problem for the copper industry (Gilsbach & Dorner, 2020). Copper has always been an essential part of almost all technological progress and is therefore an indispensable part of the industrial and everyday surroundings.

The arsenic already enters the copper extraction process with the ore. In many mines, including those in Chile, the mining process leads to deeper ore layers, which contain more sulphide minerals than nearer-surface layers of ore. These sulfidic ores are rich in Copper but also have high contents of arsenic, which then has to be separated in the course of the process chain and subsequently deposited. (Gilsbach & Dorner, 2020)

The ReAK project deals in its entirety with different process steps in copper production and focuses on the most environmentally friendly ways of separating and depositing the arsenic residues. In the course of arsenic separation from the copper concentrate, the arsenic enters a sulphuric acid solution as arsenite via the gas phase. The state of the art is now to oxidise the trivalent arsenic to arsenate (pentavalent) by means of hydrogen peroxide and to precipitate it as a calcium compound. Alternatively, due to the high cost of hydrogen peroxide, the arsenite is precipitated as calcium arsenite without an oxidation step. The latter form in particular is comparatively soluble in water, which is why the arsenic can be flushed out of the landfills and thus enter the environment. (Nazari, Radzinski, & Ghahreman, 2016)

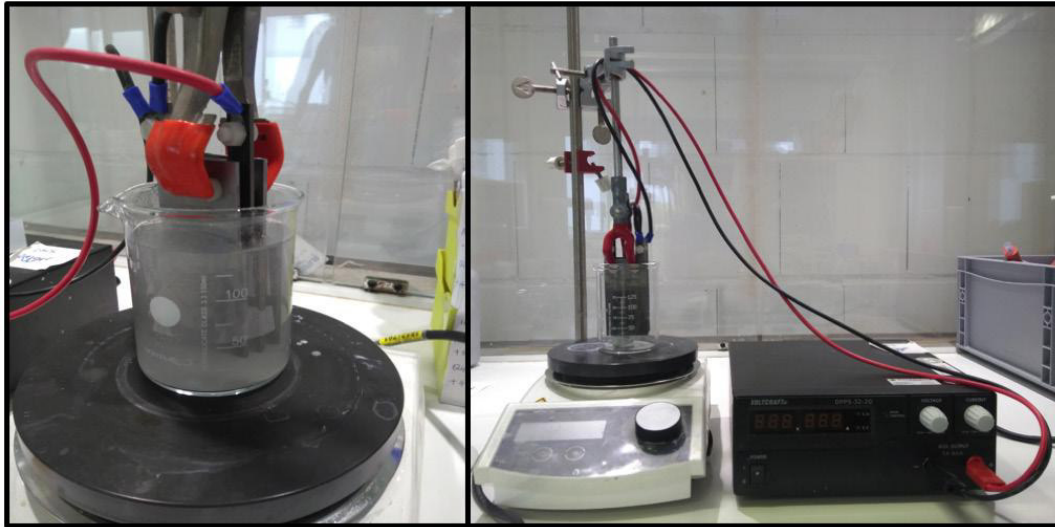
In work package 3.3.3 of the ReAK project, electrochemical oxidation is being investigated as an alternative oxidation method instead of hydrogen peroxide. The aim is also the conversion of As(III) to As(V), which should finally be precipitated as scorodite, an iron arsenate compound. The question of whether electrochemistry provides a practicable and cheaper way of oxidation than, comparatively the peroxide, is to be answered at the end.

## 2. Experimental section

The heart of the experimental setup is a boron doped diamond electrode (BDD) from the company DiaCCon. For this type of electrode, a carrier material, in our case niobium, is coated with a diamond layer. The diamond layer is  $\geq 12 \mu\text{m}$  thick and doped with boron to achieve conductivity. Stainless steel was basically used as the cathode material. (Diacon GmbH, 2022)

For the investigations,  $\text{As}_2\text{O}_3$  was dissolved in a 7.5 % sodium hydroxide solution at 40 °C and the solution was then diluted again 1:1 with water, so the final concentration was 3.75 % NaOH. This procedure worked without problems up to 20 g/L.

To perform the experiment, usually 40 cm<sup>2</sup> of the diamond electrode were positioned in the solution. The solution was kept in motion via a magnetic stirrer. The distance between anode and cathode was 5mm. The standard current was 2 A. The electrochemical oxidation always started at room temperature. Figure 1 shows the experimental setup.



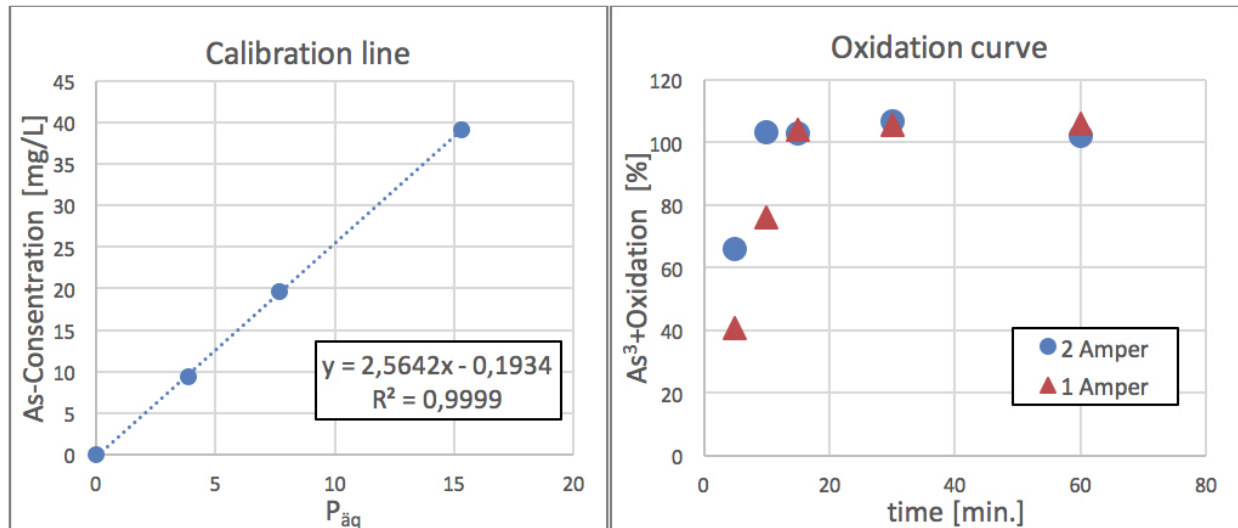
**Figure 1: Experimental setup of electrochemical oxidation on a laboratory scale.**

The analytical differentiation of arsenic(III) and arsenic(V) was carried out directly after the end of the experiment by means of photometric determination via the formation of molybdenum blue. This is a ready-made rapid test determination for phosphate in water samples, which is provided by the company Hach Lange GmbH and which has been transferred to the purpose of arsenic differentiation (Hach Lange GmbH, 2022). The total arsenic content was determined by optical emission spectrometry with inductively coupled plasma (ICP-OES).

### 3. Results

#### Proof of concept:

To prove the general possibility of oxidising arsenic by electrochemical oxidation with a BDD electrode, 200 ml of an arsenic solution containing 760 mg/L As(III) was prepared and treated electrochemically. The electrode area used was 40 cm<sup>2</sup> and the current was varied between 1 and 2 amperes. In parallel, the linearity of the photometric analysis was demonstrated.



**Figure 2: left: Calibration line concentration of As(V) in solution; right: Oxidation curve of As(III) to As(V) with an applied current of 1A and 2A, respectively.**

For the calibration curve (Figure 2 left), the test solution was diluted down from 760 mg/L to 40, 20 and 10 mg/L, as the colour reaction loses its linearity at higher concentrations. In the next step, the As(III) contained was oxidised to As(V) using the rapid test's own oxidation method. The test itself only detects the As(V). The exact As concentration was determined by ICP-OES. It can be seen very clearly in the graph that the value " $P_{\ddot{a}q}$ " delivered by the photometer for the rapid test is linear to the arsenic concentration.

For the detection of the oxidation progress in Figure 2 on the right, the sample taken was not oxidised again via the rapid test oxidation method, but the sample was analysed directly via the colour reaction. Only the contained As(V) was detected, which must have been oxidised via the electrochemical reaction. It can be seen that the oxidation reaction took place very quickly at both 1 ampere and 2 amperes. After only 15 min (1A) or 10 min (2A), the entire arsenic(III) content had been oxidised to arsenic(V).

### Effect of the arsenic concentration

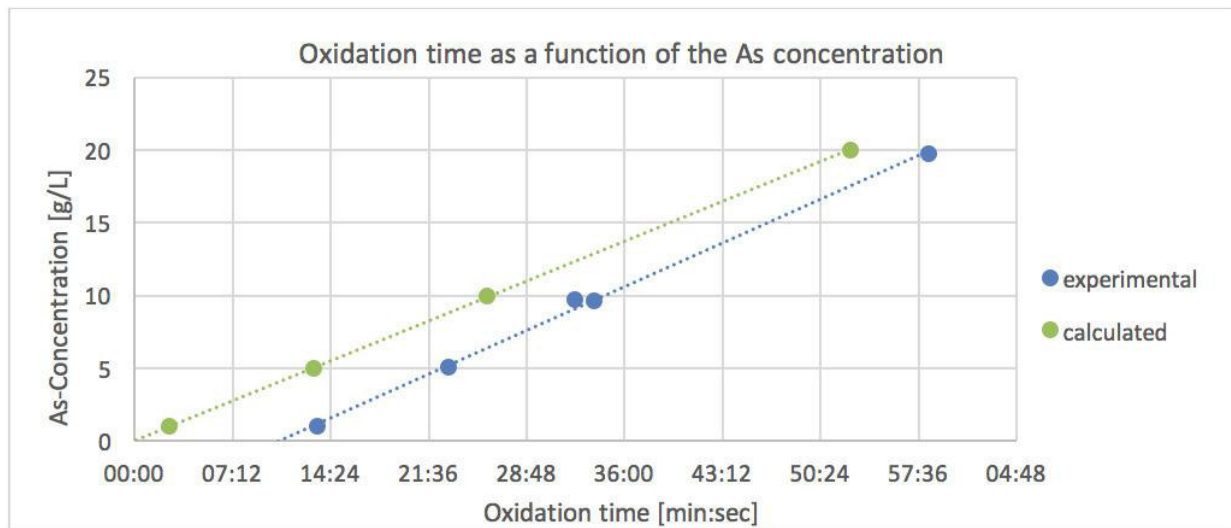
In theory, it should be possible to calculate the oxidation time according to Faraday's law (Walsh, 1991):

$$n = \frac{m}{M} = \frac{I * t}{z * F}$$

$n$  = amount of substance [mol]  
 $m$  = Mass [g]  
 $M$  = molar mass [g/mol]  
 $I$  = Current [A]  
 $t$  = Time [s]  
 $z$  = chemical charge number  
 $F$  = Faraday constant [C/mol = A\*s/mol]

However, some disturbing effects are not taken into account here. For example, side reactions are not taken into consideration. If chloride is present in the solution, it is oxidised to chlorine gas, for example. Diffusion problems also occur in the solution, especially at lower concentrations. In addition, processes could occur that lead to a passivating layer on the electrode. For these reasons, longer reaction times are to be expected compared to Faraday's law.

In our series of experiments, an area of 40 cm<sup>2</sup> BDD electrode was used for all experiments. The current was 2 amperes and the volume of the solution that was oxidised was 130 ml. A pure arsenic solution was used, so that side reactions can be practically ruled out. Also, no layer on the electrodes was observed during the experiments that could have a passivating effect. Nevertheless, the reaction times of the experiments are slightly longer than the values calculated according to Faraday's law, especially at lower concentrations, see Figure 3.



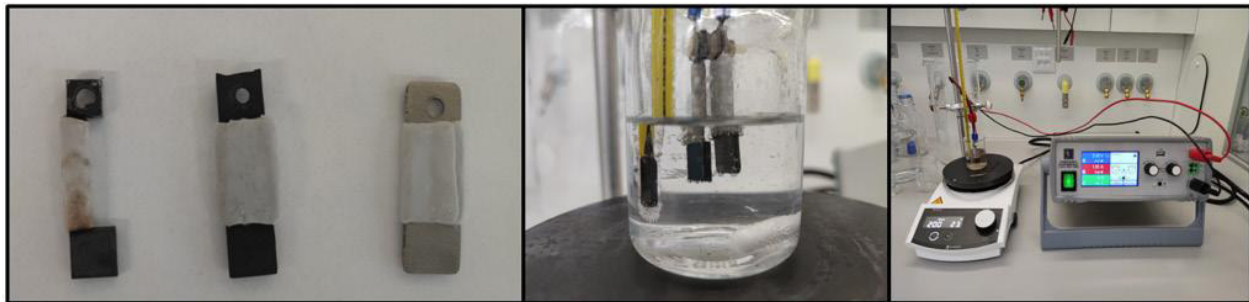
**Figure 3: The oxidation time as a function of arsenic concentration, compared with the calculated optimum using Faraday's law.**

Figure 3 shows a clearly linear dependence between As concentration and oxidation time, even though this can no longer be true for concentrations <1 g/L, since the curve must automatically have an oxidation time curve towards zero for very small concentrations. In general, more time is needed for oxidation than the calculated optimum, and this is true already for a pure arsenic solution without accompanying ions. This effect is even more prominent for low As concentrations. Thus, the oxidation of 1g/L takes five times longer than theoretically expected, whereas the oxidation of 20g/L takes only approximately 10% longer than calculated. Most likely, diffusion effects are the cause of this difference between low and high concentrations, as other effects can be largely excluded due to the same pure solution.

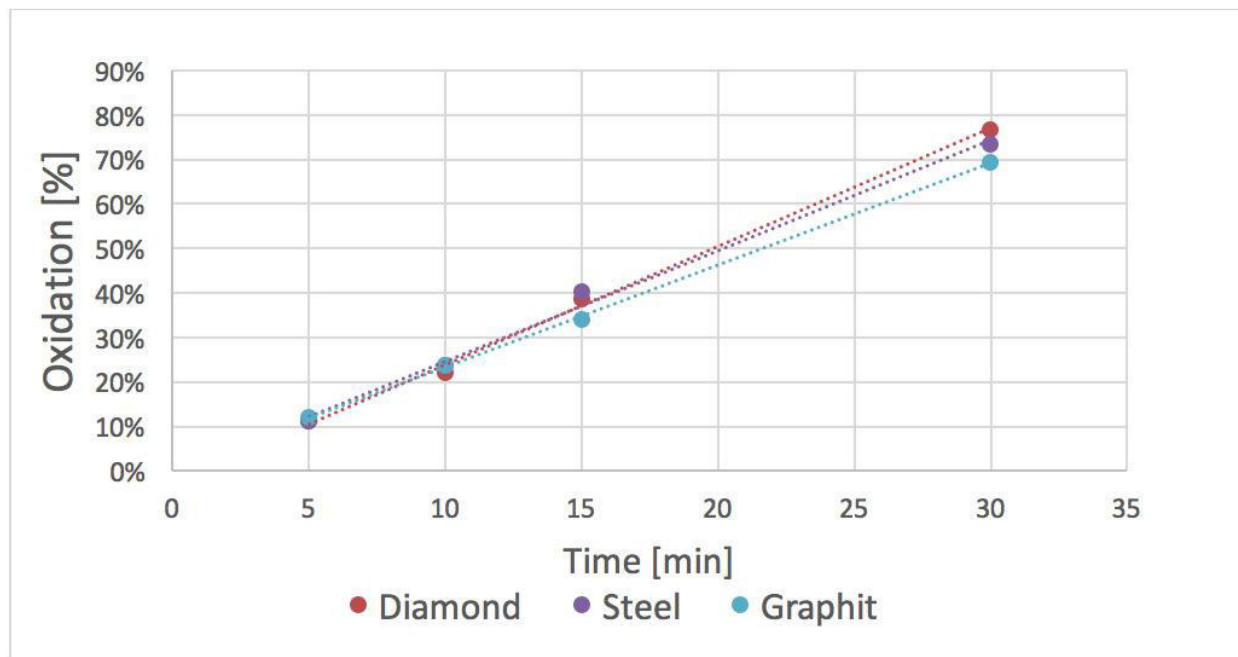


## Choice of cathode

In the majority of the experiments, a steel electrode was used as a counter electrode to the diamond electrode. In a series of experiments with a smaller setup, a diamond cathode and a graphite cathode were used in addition to the steel cathode, see figure 4. The experiments were carried out with an electrode area of 1 cm<sup>2</sup> only. The volume of the solution was 50 ml and the arsenic concentration was 9 g/L. The current was set at 2 A.



**Figure 4:** Left: Diamond electrode, graphite electrode, steel electrode (from left to right); Middle: two diamond electrodes in the arsenic solution; Right: entire experimental set-up.



**Figure 5:** Oxidation curve of the three different cathodes of 50 ml of an arsenic solution with 9 g/L As(III) with a current strength of 2 Amper.

As can be seen in Figure 5, there are no major differences in the oxidation rate. Taking measurement inaccuracies into account, it can be said that all three oxidation experiments proceeded in the same way.

What is noticeable in the experiments with a smaller electrode is the unexpectedly long oxidation time for a comparatively low arsenic concentration and a small volume. For comparison, in the previously shown series of experiments (Figure 3), 130 ml of a 10 g/L concentrated arsenic solution took about 33 minutes to be fully oxidised.

The oxidation time in the case with the smaller electrode with linear progression of the oxidation rate would be 39 minutes for 100% oxidation and this despite the lower concentration and lower volume.

Assuming the linear ratios determined so far, the 130 ml, 10 g/L concentrated arsenic solution would therefore take about 113 minutes to oxidise with an electrode of 1 cm<sup>2</sup>, while only 33 minutes were needed with an electrode area of 40 cm<sup>2</sup>. There seems to be an optimum area for the electrode size, although the electrode area does not play a role in Faraday's equation.

## 4. Conclusions

It can be summarised that the oxidation of arsenic by means of a BDD electrode works reliably and follows a linear law. Even high concentrations of arsenic can be oxidised from arsenic(III) to arsenic(V) within a relatively short time. For example, 200 ml of a solution containing 17.5 g/L arsenic was completely oxidised within about 80 minutes, using a 40 cm<sup>2</sup> electrode and a current of 2 A.

All the work in this paper was done on pure arsenic solutions without interfering other ions. This is not the case in industry. In addition, the solutions used are dissolved in alkali, while the industrial solutions from the gas scrubbers are based on sulphuric acid. More real solutions are still being investigated and the results can be presented at the COPPER conference in 2022.

If we look at the results of these pure solutions and extrapolate via the linear law to a solution to be oxidised of 2000 m<sup>3</sup>/day with a concentration of 18 g/L arsenic, we obtain an electrode area of about 2200 m<sup>2</sup>. With a consistent current density of 2 A/40cm<sup>2</sup>, this results in a total current of 1100 kA. A large electrode area and a high current intensity are therefore necessary to oxidise such a volume flow with such a high arsenic concentration.

According to the current market prices (04.2022) of the manufacturer used, such an electrode area would cost slightly more than 42 million euros (Diaccon GmbH, 2022). However, these projections should be viewed with caution, as the laboratory process still needs to be approximated to a real process in some respects. And the market price can fall due to a correspondingly high demand. Nevertheless, it can be assumed that large electrode areas and current strengths will be required. Taking into account the high resistance and the long lifetime of a BDD electrode, the investment could still pay off by saving on other oxidants, such as hydrogen peroxide.

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