# Electrobiological reduction for low level selenium removal from mine water and reverse osmosis brine

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## Abstract

Laboratory-scale assessment of an electro-biochemical reactor (EBR) system was performed to determine its potential ability to meet a 1 µg/L mine effluent threshold for selenium (Se) at the Boinás gold mine in Asturias, Spain. The EBR process is differentiated from conventional biologically-mediated reduction through the administration of a constant low µAmp-level current to overcome rate-limitations associated with electron demand. Trials performed using Boinás mine water and RO brine containing Se at 40 µg/L and >200 µg/L respectively yielded post-treatment concentrations of between 0.1 and 0.05 µg/L in mine water and <2 µg/L in RO brine. Based on these results, EBR may offer both improved performance and significant Opex savings relative to the existing reverse osmosis treatment system deployed at Boinás mine.

**Keywords:** Selenium, water treatment, Electro Biological Reactor (EBR), Spain.

## Introduction

Las Boinás mine is located approximately 36 km west of Oviedo in Asturias, northern Spain. The mine lies in the Rio Narcea Gold Belt, in which several historical centres of gold production exist. Mineralization at Boinás is associated with acid-intermediate intrusions which were emplaced into a regional dolomite sedimentary sequence of Palaeozoic age between around 300 and 250 Ma. Two phases of mineralization are evident, the first associated with metasomatism and skarn formation along intrusive–dolomite contacts and the second with epithermal overprinting. As observed widely in the Rio Narcea Gold Belt, gold is accompanied by the metalloid elements arsenic (As) and selenium (Se), which occur both as discrete sulphides and as lattice substitutes in pyrite and copper sulphides.

The Las Boinás mine was initially developed in 1997 by Río Narcea Gold Mines (RNGM). The property was later acquired by Orovalle Minerals, who commenced production in 2011. Mining is undertaken exclusively by underground methods. Due to the juxtaposition of the ore-zones against a high-yield dolomite aquifer, continuous dewatering of the mine is required at rates which typically exceed 100 L/s. This is achieved by a combination of dewatering wells completed in the dolomite and sumps within the underground workings.

Boinás mine water is of near-neutral pH and low (<1000 mg/L) total dissolved solids (TDS). However, levels of Se and As in water discharged from sumps in the 'Boinás Este' sector of the mine are commonly in the ranges 40 – 160 µg/L and 0.15 to 0.4 mg/L respectively. This precludes direct environmental without treatment as Orovalle is required to comply with criteria of 1 µg/L and 0.1 mg/L for Se and As respectively. While concerted effort is made by Orovalle to consume non-compliant mine water as process plant make-up, an excess of the order of 30 L/s must typically be treated and discharged to neutralize the overall mine water balance.

Orovalle currently operates a two-stage system for treatment water from the Boinas Este sector of the mine, plus contact water from two waste rock storage areas. The first stage consists of an ACTIFLO unit for sediment removal and clarification, with the second deploying reverse osmosis (RO). Two limitations are associated with the current treatment system. Firstly, its design capacity of 60 $m^3/h$ is insufficient to treat the flows discharged from the underground mine and waste rock facility source-terms. Secondly, RO brine is generated at an average volume equating to 21% of the RO feed. The discharge of brine to the Boinás tailings storage facility (TSF) produces a positive water balance and attendant build-up of solution inventory in the TSF.

In 2016, Orovalle initiated screening of technology alternatives which may be of utility to meet one or more of the following objectives: (i) supplementation of existing RO capacity, (ii) replacement of RO to avert the impact of RO brine disposal on the TSF water balance, and (iii) treatment of RO brine to a quality which would permit discharge in conjunction with RO permeate. An electro-biochemical reactor (EBR) system was identified as potentially applicable to the flow rate, feed chemistry and broader site characteristics of the Boinás setting. This paper describes the design, results and practical implications of bench-scale testing of EBR for the treatment of Boinás mine water and RO brine performed in 2017.

## Principles of electro-biochemical reactor system

Biologically-mediated reduction and attendant immobilization of several metals and metalloids may occur in virtually any aqueous environment in which anaerobic conditions are established and residual organic carbon is available. In the decomposition of organic matter, consumption of $O_2$ is succeeded by reduction of $NO_3$, $SO_4$ and metals/metalloids, including Se, which provide electron acceptors. In the case of Se, the reaction can be expressed as:

$$SeO_4^{-2} + 6\,e + 8\,H_2O \rightarrow Se(s) + 4\,H_2O$$

In the above reaction, six electrons are required to reduce one mole selenite to elemental Se. In conventional anaerobic treatment systems, the supply of electrons exerts the critical rate-control. EBR overcomes this through the application of a low voltage (1 to 3V), micro-amp level current through the reactor cell. In addition to reducing the sensitivity of the system to its nutrient (principally glucose) balance, the application of a direct electron stream inhibits efficiency fluctuations associated with temperature and pH/Eh regime.

The mechanisms of removal of contaminants from solution in the EBR process are essentially the same as those operative in any anaerobic cell and involve the biochemical reduction of $SO_4^{2-}$, metals and metalloids to low mobility metal sulphides, or to an insoluble elemental-state. The efficiency of reduction of any specific target element is, however, highly dependent on the redox potential at which the reactor cell is operated, the make-up of the microbial population present and the range of competing 'reducible solutes' in the influent water. This necessitates that any EBR system is judiciously optimized to meet the requirements of water to be treated on a site-specific basis.

## Methods

### *Structure of laboratory investigation*

Laboratory scale testing of the viability of EBR treatment for Boinás Mine water and RO brine was undertaken over the period May to November 2017 at the INOTEC laboratory in Utah, USA. The test program comprised two principal phases of investigation:

1. Assessment of the suitability of the mine water and brine solutions for treatment in an EBR cell, as dictated by multi-element chemistry, the presence of potential microbial toxins and competing ions.
2. Assessment of performance efficiency under variable conditions of EBR cell operation with respect to hydraulic residence time (HRT), temperature and nutrient dosing regimen.

### *Sample sources*

For each of the two phases of laboratory assessment, stock solutions were collected from (a) the outflow from the ACTIFLO system at the Boinás water treatment plant, and (b) the reject stream of the second of the two-stage RO configuration operated at Boinás. Transport of samples to INOTEC was undertaken prior to each of the two phases of investigation to avert any requirement for prolonged storage and associated risk of chemical or microbiological alteration. Sub-samples were subject to chemical analysis prior to shipment and on receipt by by INOTEC. Variability between the Phase 1 and 2 sample consignments, and also between pre- and post-shipment analytical data, was found to be minimal (<5%) for all parameters with the exception of dissolved oxygen and ORP. Table 1 provides a summary of the composition of the Phase 1 stock solutions, as reported following analysis by INOTEC.

The mine water and brine Se concentrations shown in Table 1 are typical of those reporting to the RO stage of treatment and discharged in the reject stream in the existing Boinás plant. Concentrations of As shown for the mine water in Table 1 are, however, significantly lower than those in the mine dewatering stream. This reflects the collection of the mine water stock solution from the point of discharge of the ACTIFLO plant which feeds the Boinás RO system. In conjunction with sediment removal, the addition of flocculant in the ACTIFLO circuit typically removes up to 90% of the As load from the influent water.

### *Treatability assessment and microbial screening*

Water quality data shown in Table 1 were screened to assess the presence of solutes which may inhibit the establishment of a suitable microbial population in an EBR cell, or which may adversely impact the immobilization of Se through competitive consumption of nutrients and electrons. Typical microbial toxins in mine waters with respect to anaerobic treatment systems include cyanide species and chloride. These were confirmed to occur at concentrations of no practical significance.

Targeting of Se in anaerobic treatment systems, and in particular avoidance of competitive effects arising from $SO_4^{2-}$ reduction, can be achieved through establishing a redox condition adequate to induce Se reduction without further progression through the sequence of electron acceptors which assume

***Table 1*** *Chemical composition of Boinas mine water and RO brine used for EBR performance trials*

| Parameter | Mine water | RO brine |
|---|---|---|
| Dissolved oxygen (mg/L) | 4.30 | 3.91 |
| Electrical cond. (µS/cm) | 851 | 6370 |
| pH | 8.02 | 7.74 |
| CN total (mg/L) | <0.001 | <0.001 |
| Salinity (% () | 0.43 | 3.18 |
| $NO_{3-}N$ (mg/L) | 1.13 | 11.31 |
| $NO_{2-}N$ (mg/L) | <0.003 | <1.5 |
| Alkalinity (mg/L $CaCO_3$) | >300 | >300 |
| $Cl^-$ (mg/L) | 17.9 | 290 |
| $SO_4^{2-}$ (mg/L) | 271 | 2680 |
| Al (mg/L) | <0.005 | <0.005 |
| As (mg/L) | 0.024 | 0.197 |
| Ba (mg/L) | 0.076 | 0.643 |
| Cd (mg/L) | 0.001 | 0.002 |
| Ca (mg/L) | 98 | 1061 |
| Cu (mg/L) | 0.008 | 0.10 |
| Fe (mg/L) | <0.02 | 0.152 |
| Mg (mg/L) | 55.2 | 547 |
| Mn (mg/L) | 0.026 | 0.25 |
| Ni (mg/L) | 0.003 | 0.034 |
| Pb (mg/L) | <0.005 | 0.007 |
| Se (µg/L) | 46 | 625 |
| Na (mg/L) | 9.3 | 48.6 |
| Zn (mg/L) | 0.026 | 0.49 |

dominance at lower Eh. This is not, however, possible with respect to $NO_{3-}$, which constitutes the primary competing solute in most mine waters. The concentrations of $NO_{3-}$ recorded in Boinás mine water (1.13 mg/L) and RO brine (11.3 mg/L) are, however, well within the range demonstrated through independent EBR trials to permit uninhibited Se removal.

Microbial screening of the Boinas mine water and RO brine, performed to discriminate the production of elemental Se, indicated that the autochthonous microbial population in the waters possesses substantial capacity to mediate Se reduction. Selected microbes from both solutions were nonetheless used to cultivate biofilms for prospective EBR system inoculation if necessary.

### *Steady and transient-state treatment trials*

Steady- and transient-state testing of the EBR process for removal of Se from Las Boinás mine water and RO brine was performed at INOTEC using identical sets of two in-sequence EBR cells. Each pair of cells was continuously supplied with mine water or RO brine using a peristaltic pump over a total test period of 115 days. A continuous current of approximately 3V was applied to each cell for the duration of the test period.

The overall period of testing was subdivided into three principal phases, as summarized in Table 2. The first, referred to as the 'validation period', was intended to define the level of Se removal efficiency achievable under near-optimum conditions of nutrient dosing. Flow rates into the EBR cells were maintained throughout the validation period such that a total of 8 hours HRT could be accommodated in each of the two cells. Subsequent phases of the testing were dedicated to assessing EBR system performance sensitivity to transient conditions of nutrient dosing and HRT.

Throughout the test period, analysis of influent feed solution was performed at approximately weekly intervals to confirm consistency. Effluent analysis for each cell was performed at 2 to 3 day intervals for Se and at weekly to bi-weekly intervals for $SO_4^{2-}$ plus a full suite of metals (by ICP-MS). Physicochemical parameters (pH, temperature, ORP and EC) were recorded continuously.

## Results

### *Selenium removal from mine water*

Influent and effluent Se concentrations in the EBR cell pair deployed for treatment of Boinás mine water during the first 40 days of the test program are shown in Figure 2. Data for the first 7 days of the test were not compiled as the system is initially inherently unstable with respect redox condition and microbial productivity. By day 11, concentrations of Se in effluent were reduced from by more than a factor of 100 relative to the feed, with residual Se levels of around 0.3 µg/L. Such levels were sustained in effluent from cell throughout the

***Table 2** Summary of EBR test protocol and operating variables during test duration*

| Test week | Test phase | Description | Conditions | Variable adjustment |
|---|---|---|---|---|
| **1 to 4** | Validation | Assessment of EBR removal efficiency for Se and other solutes under stable conditions | Iterative adjustment to produce optimum operating environment | No adjustment following initial optimization |
| **5 to 9** | Nutrient stress testing | Assessment of EBR performance sensitivity to changes of nutrient dosing regime. | Progressive reduction of nutrient dose rate until point of significant performance degradation reached | Nutrient concentration |
| **10 – 16** | HRT optimization | Assessment of sensitivity of treatment efficiency to hydraulic residence time | Progressive increase of treatment flow rate until significant degradation of performance efficiency observed. | Flow rate |

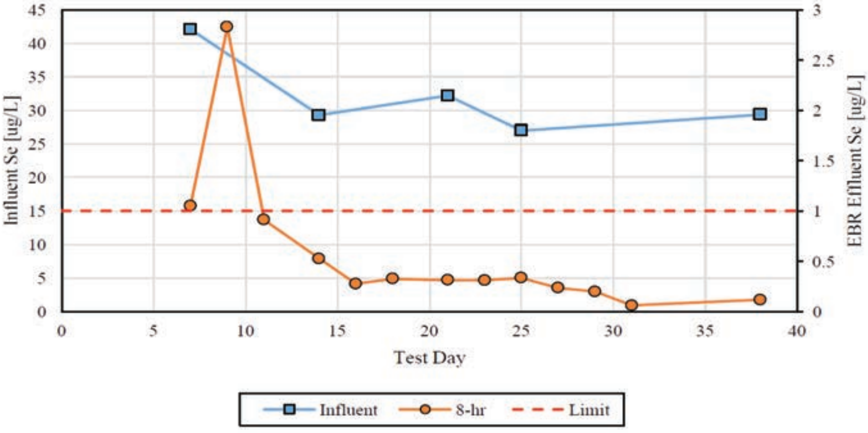


*Figure 2 Inflow and effluent Se concentrations during the validation phase of EBR testing of treatment of Boinás mine water*

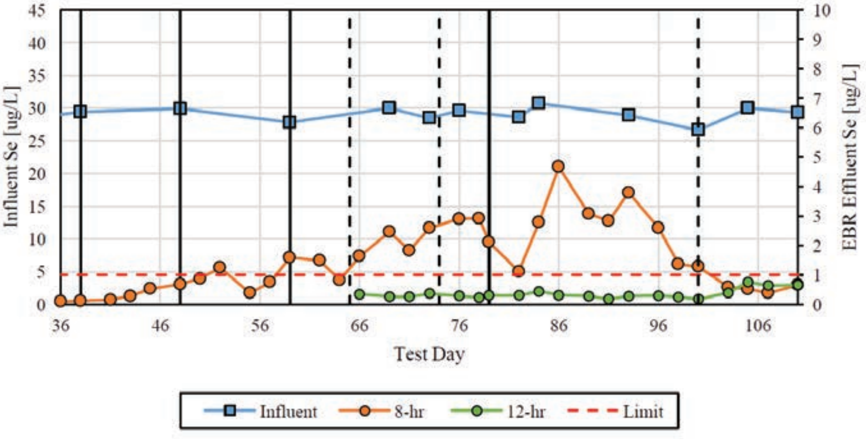


*Figure 3 Inflow and effluent Se concentrations during the stress testing phase of EBR assessment for Boinás mine water. Solid vertical lines indicate points of step-wise reduction of nutrient dosing rates. Dashed vertical lines indicate points of step-wise reduction of HRT.*

remainder of the validation period. The flow rate throughout this period was set such that cell 1 HRT was consistently 8 hours.

Results of EBR performance in the treatment of Boinás mine water under transient conditions of nutrient dosing regime and HRT, introduced with effect from day 38 of the test sequence, are shown in Figure 3. Nutrient dose reduction was undertaken in four steps. Following the second of these, involving a 50% reduction from an initial level of around 5 g/L molasses at day 58, effluent Se levels transgressed the 1 µg/L design requirement following 8 hours of EBR cell residence time. At 12 hours HRT, sensitivity to nutrient regimen remained low. Average 12 hour HRT effluent concentrations of Se throughout the stress period were 0.29 µg/L across a molasses dosing range from >5 g/L to as little as 1.8 mg/L.

### *Selenium removal from RO brine*

Results of EBR treatment of RO brine during the first 40 days of the test program are shown in Figure 4. Following initial stabilization, the effluent Se concentration at day 11 was 1 µg/L at 8 hours HRT. Over the remainder of the validation period, effluent Se concentrations remained below 3 µg/L at 8 hours HRT. At 16 hours HRT, concentrations in treated brine effluent remained systematically below 1 µg/L with effect from day 16.

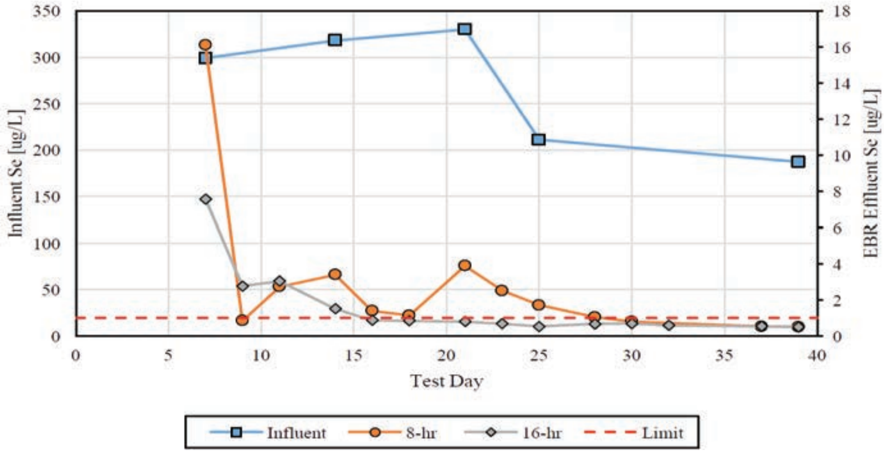


***Figure 4*** *Inflow and effluent Se concentrations during the validation phase of EBR testing of treatment of Boinás RO brine*

During the remainder of the 115 day test period, EBR sensitivity to nutrient dosing and HRT variations appeared closely analogous to that described for the treatment of mine water, with deterioration of performance associated with reduced nutrient supplementation at 8 hours HRT and minimal influence exerted at 15 hours HRT.

### *Removal of other solutes*

Multi-element analysis of feed and effluent chemistry for the mine water and RO brine EBR cells confirmed excellent performance in the removal of a range of other solutes. These included $NO_3$, As Cu, Ni and Zn for which average concentrations reductions of >60%, >90%, >90%, 50% and 75% respectively were observed in both the mine water and RO brine EBR cells at 16 hours HRT.

## Conclusions

Results of laboratory testing of EBR for removal of Se from Boinás mine water confirm its capacity to meet the strict 1 µg/L compliance criterion applicable in discharge from the mine. Treatment of RO brine to a residual Se level apt for blending into treated RO permeate prior to environmental discharge is also indicated to be feasible. Using an 8 hour HRT design criterion, preliminary cost estimates for a full scale plant suggest that Capex would compare favourably with the provision of expanded RO capacity at Boinás, while Opex costs for water treatment using EBR would be around 50% of those associated with RO.

## Acknowledgements

The authors thank Orovalle Minerals for permission to publish this paper.