

# Electrochemical Cover for the Prevention of Acid Mine Drainage- A Laboratory Test

<sup>1</sup>Mei Lin Shelp, <sup>2</sup>Gordon L. Hayward, <sup>3</sup>Leonard P. Seed and <sup>3</sup>Gene S. Shelp

<sup>1</sup>Golder Associates Ltd. Mississauga, Ontario. <sup>2</sup>School of Engineering, The University of Guelph, Guelph, Ontario.  
<sup>3</sup>Enpar Technologies Inc. Guelph, Ontario.

## **Abstract**

Acid mine drainage resulting from sulphide mineral oxidation is the greatest environmental problem facing the mining industry. An electrochemical cover system has been developed for the prevention of acid mine drainage by reducing the partial pressure of oxygen ( $PO_2$ ) or dissolved oxygen (DO) available to sulphide containing mine waste. A laboratory scale combined soil-electrochemical cover was built to determine the current requirement and reduction in  $PO_2$  beneath the electrochemical cover. Results showed that with an input of 45 Amp per ha (equivalent to approximately an annual magnesium anode consumption cost of \$1400 CND), the electrochemical cover was capable of reducing the  $PO_2$  by 50 times based on the cover design used in the laboratory.

## **Background**

The problem of acid mine drainage (AMD) is often associated with improper disposal of acid generating mine wastes, resulting from the oxidation of sulphide minerals. A key strategy of most mine waste disposal methods, such as sub-aqueous disposal and surface disposal of tailings and tailings paste, and soil and/or synthetic liner covers, is to reduce the exposure of acid generating mine waste to gaseous or dissolved  $O_2$  (Grabinsky et al, 2002; Verburg, 2002). In general,  $O_2$  is transported mainly through gaseous diffusion in tailings and through air advection in waste rock piles (E.K. Yanful, 1992).

Among the available waste disposal methods, soil/synthetic liner covers and the application of thickened tailings (paste) technology (Grabinsky, 2002; Verburg, 2002) do not involve the construction and maintenance of a large water body. Consequently, these methods reduce the risk of dam failure. However, the application of the above methods are hindered by uncertainty related to their long-term performance. For example, the integrity of soil and synthetic liner covers, can be adversely affected by several environmental factors, including freeze-thawing (Lin Shelp and Yanful, 1999, unpublished data), desiccation, and ageing of the synthetic liners (Rowe, 1998). Similarly, the long-term benefit of paste technology in the reduction of acid generation has not yet been reported. Bench-scale tests indicated that surface

deposited paste may only delay the onset of acid production (Verburg, 2002).

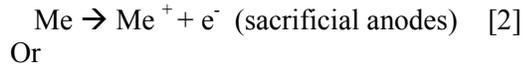
The electrochemical cover for the prevention of AMD is a patented innovative technology that can be used as a system enhancement to a soil/synthetic liner cover and surface tailings or paste paste disposal (ENPAR Technologies Inc. 2000). A successful pilot scale study conducted at Hardy tailings disposal area, near Sudbury and related studies have been reported (Lin Shelp et, 1999). The latest design of the electrochemical cover consists of a steel mesh cathode that covers the entire mine waste disposal area combined with a series of either galvanic or inert anodes that are spaced according to the required electrical current distribution. The electrochemical cover can be installed within a soil oxygen barrier (Figure 1a) or the top layer of thickened tailings (Figure 1b). The system can operate as galvanic cells (driven by internal electrical potential when sacrificial anodes are used), or electrolytic cells (powered by an external power source when inert anodes are used).

The anticipated major electrochemical reactions at the surface of the electrodes are listed below.

Cathodic Reaction:



Anodic Reaction:



The major mechanisms of the electrochemical cover are to :1) consume  $\text{O}_2$  at the surface of the mesh cathode, 2) lower the oxygen flux into deeper layers by reducing the  $\text{O}_2$  gradient (Figure 2), and (3) maintain tailings/paste saturation near the mesh cathode due to electroosmosis, forming an oxygen barrier. Theoretically, the higher the current density of the electrochemical cover, the greater the power of the oxygen sink and the migration of water towards the cathode.

The application of the electrochemical cover technology can be carried out by using a modified testing, design and operation methods and equipment widely used in the corrosion protection industry.

The objectives of the study were (1) to determine the relationship between electrical current density and the oxygen level ( $\text{PO}_2$  or DO) beneath the cathode of the electrochemical cover, and (2) to confirm the electrochemical cover acts as an oxygen sink. Tests in this study were conducted using the soil-electrochemical cover scenario.

## **Materials and Method**

### ***Laboratory Soil-Electrochemical Cover***

A flow-through chamber system was used to simulate a combined soil-electrochemical cover for the prevention of AMD (Figure 3). The chamber is a 1.0-m high drum with a diameter of 0.58 m.

The simulated soil-electrochemical cover consisted of three layers of earthy materials and two electrochemical cells. The bottom earthy layer consisted of a 10-cm sand layer overlain by a 5-cm mixture of sand and gravel layer. This layer was used to simulate the capillary break layer in a typical engineered soil cover. A 55-cm soil  $\text{O}_2$  barrier was compacted on the top of the capillary break layer. The soil used in this laboratory test was Guelph loam with an

electrical resistivity of 3000  $\Omega\text{-cm}$  and a pH of 7.9. The soil was air dried and passed through an ASTM standard No. 4 sieve. A standard ASTM compaction test (ASTM D698-91) was performed to determine the optimum moisture content by weight, 16%, and the maximum bulk density, 1.8  $\text{g cm}^{-3}$ .

The air-dried soil was wetted to the optimum moisture content and compacted to 3-cm thickness per layer using the same effort as in the compaction test. A 3-cm clean sand and an 8-cm layer of Styrofoam chips were placed on top of the soil to reduce evaporation.

Two electrochemical cells were positioned in the chamber: the uppermost cell was used to simulate an electrochemical cover; a second electrochemical cell was installed in the base of the chamber to simulate an oxygen sink (representing sulphide oxidation). The electrochemical cover consisted of a steel mesh cathode (plain steel window screen mesh size 18 x 14 mesh, 0.011" wire, 0.045" width of opening) and Magnesium (Mg) rod anodes. The  $\text{O}_2$  sink (lowermost cell) was installed in a 10-cm sand layer (Figure 3). The anodes were located at the bottom of the sand layer; the corresponding steel mesh cathode was positioned at the top of the sand layer.

### ***Oxygen Measurement***

A new method of measuring DO/ $\text{PO}_2$  was used in the laboratory study. (Assuming equilibrium between the air and the liquid phase,  $\text{PO}_2$  can be expressed in equivalent DO values, using Henry's law constant.) The method is designed for conducting continuous *in-situ* measurements of  $\text{PO}_2$  or DO by means of half-cell potential (Eh) probe and a bench-top Eh-DO apparatus (ENPAR Technologies Inc. 2001). Half-cell potentials are measured as the overall electromotive force (potential) of an electrochemical cell consisting of a target half-cell reaction and a standard hydrogen electrode (SHE) of which the Eh is arbitrarily assigned as 0 mV. A unique relationship between Eh-DO and Eh for each soil or tailings medium can be established using the bench top Eh-DO apparatus.

Platinum (Pt) probes (not shown in Figure 3) and a Cu-CuSO<sub>4</sub> reference electrode (MCN McMiller Co. Model 375) were used for the Eh

measurements. All Pt probes were calibrated using the standard Zobell solution (YSI 3682). The Cu-CuSO<sub>4</sub> reference electrode was located at the top of the soil layer. One Pt probe was positioned in every 10 cm of the soil layer. Three Pt probes were installed within the sand and gravel layer below the active electrochemical cover. The half-cell (Eh) potentials were measured using a Corning mV monitor. The electrochemical cell was turned off during Eh measurement.

As Eh levels under the mesh cathode are considered critical to predict the overall performance of the cover, two air purging tests were done to verify that the mesh cathode is an O<sub>2</sub> sink. Two pieces of 3/8" diameter tubing, each connected to a two-way valve, were also installed for the purpose of conducting purging tests described in the next section.

Three parameters: 1) oxygen fluxes into the top soil, 2) half-cell potentials within the soil cover and under the electrochemical cell, 3) and the current density of the electrochemical cell were measured. The measurement of O<sub>2</sub> fluxes was based on the principle of mass balance. Oxygen consumed within the chamber was equal to the total oxygen input minus the total oxygen output. Both the air inlet and outlet ports were located in the headspace at the top of the chamber. A YSI Dissolved Oxygen Sensor (Model 58) was used to measure the DO.

### ***Experimental Tests***

To assess the effectiveness of the electrochemical cover to reduce PO<sub>2</sub>, the current density of the electrochemical cell, Eh in the soil cover layer and beneath the electrochemical cover were measured daily. The test cell was initially allowed to equilibrate for 20 days with the electrochemical cover inactive, in order to establish background readings for the soil Eh profile. After a stable Eh profile had been established, the electrochemical cover was activated and then operated continuously for 16 days. The effect of the electrochemical cell was demonstrated by the difference between the new and the background Eh profile within the test soil/electrochemical cover.

To verify the performance of the electrochemical cover, an air-purging test was

carried out. This later test was designed to show that the electrochemical cell could consume the O<sub>2</sub> after O<sub>2</sub> rich air was forced into the layer beneath the cathode of the electrochemical cover for 18 minutes. Half cell potentials before and after the air purging were measured.

## **Results and Discussion**

### ***Downward oxygen flux***

To determine the magnitude of soil O<sub>2</sub> consumption rate in the laboratory soil cover, the O<sub>2</sub> flux into the soil was estimated by measuring the differences in DO values between the inlet and the outlet of the air stream in the chamber head-space. Results of O<sub>2</sub> flux measurements (Table 1) showed that downward oxygen fluxes were between 10 and 25 g/m<sup>2</sup>/day. In general, the oxygen flux increased for soils with high soil microbial activity and high oxygen diffusion coefficients, and decreased with increases in degree of saturation of the soil.

Table 1. Measured O<sub>2</sub> fluxes into the laboratory soil cover system without the electrochemical component.

Flow in the headspace mL/min	Temperature °C	Flux g/m <sup>2</sup> /day
50	26.6	10.1
50	25	25.2
50	22	22.8

### ***Cell current and oxygen level***

A laboratory scale soil-electrochemical cover was operated for total of eight weeks. Prior to establishing the electrochemical cover component, the baseline Eh/PO<sub>2</sub> profile within the soil cover was measured daily. Twenty days after the soil cover was packed into the drum, the Eh value at each of the 10-cm layers stabilized (Figure 4). Since the design of the soil-electrochemical cover was such that the only source of O<sub>2</sub> was the constant air supply at the top of the chamber; the sinks were the soil layer, the electrochemical cover, and the

artificial electrochemical sink at the lower part of the chamber. Ideally, oxygen diffuses from the top of the soil layer (with a higher  $PO_2$ ), to the bottom of chamber (with a lower  $PO_2$ ). On average, Eh/  $PO_2$  readings in this study reflected this pattern with the highest  $PO_2$  of 0.2 (Eh = 450 mV) at the top of the soil layer. However, some of the Eh readings in the lower depths did not exhibit the expected trend with  $PO_2$  values decreasing with soil depth (Figure 4). Since high spatial variations in soil  $PO_2$  due to microbial activities are not uncommon, an average Eh measurement in the soil was more appropriate to represent the soil oxygen level. The 7-day average stable Eh value between the 20 and 50 cm layers was -100 mV (SHE), equivalent to a  $PO_2$  of  $3 \times 10^{-5}$  (0.001 mg/L DO at 25°C).

The Eh readings measured in the sand and gravel layer had similar values as those measured in the nearest soil layer. The electrochemical cell was then activated at a current level of 1.2 mA (equivalent to 46 Amp per ha). Within 24 hours, the Eh readings under the mesh electrode decreased by 200 mV and the variability among the three Pt electrode readings became less than 10 mV. In Figure 4, the three half-cell readings below the mesh electrode were identical. The corresponding  $PO_2$  level decreased from  $3 \times 10^{-5}$  to  $5 \times 10^{-7}$  (equivalents to  $6.5 \times 10^{-7}$  mg/L DO at 25°C) which was about 40 to 50 times less than the initial  $PO_2$  level. The measurement continued for 16 days (Figure 5). Based on the equivalent current density of 46 Amp per ha, the estimated power and the Mg anode consumption cost is about \$1400 (CDN) per year. An essential question need to be addressed in all ARD prevention approach is what is the  $O_2$  level at which, for all intents and purpose, the oxidation of sulphide minerals are insignificant. This issue needs to be dealt with in a separate study.

The electrical current supply for this test had a range between 1.2 and 4 mA. Theoretically, if all the current is used to consume  $O_2$ , increases in the current density would further lower the  $PO_2$  level to the same proportion since more  $O_2$  can be consumed. The tests showed that Eh readings below the electrochemical mesh cover decreased further by only about 60 mV (15% of

the Eh reading) when the current was increased by 100% to 2.4 mA. The results suggested that the efficiency of oxygen consumption could decrease at a higher current density. Firstly, with a higher current density, other electron acceptors, such as soil nitrate ( $NO_3^-$ ) or manganese oxides ( $MnO_2$ ), may consume portions of  $O_2$ , since the rate of reaction involving  $O_2$  at the cathode surface may be limited by activation energy or diffusion rate. Secondly, as the electrochemical cover became a greater sink for  $O_2$ , the downward  $O_2$  gradient would be greater; consequently, more  $O_2$  can reach the cover through diffusion. Evidently, an optimum current density should be determined for each site to achieve the highest current efficiency and the lowest amount of mesh cathode material usage.

#### *Air purging test*

To demonstrate that an electrochemical cover is an oxygen sink, two air purging tests were carried out. Results of the two tests were similar to each other, so that only the first test is presented in Figure 6.

An air stream was forced to flow through the sand and gravel layer beneath the electrochemical cell for 18 minutes. The Eh values in this layer increased by 300 mV. The electrochemical cell was then activated. The Eh readings under the electrochemical cells decreased sharply within the first 2 hours. Over the time period from 2 to 50 hours after the start of purging, the Eh values slowly decreased to the initial level (between -300 to -400 mV). During this period, the Eh values measured in all the above soil layers remained stable. This confirmed that the consumption of  $O_2$  in the sand/gravel layer was not due to soil microbial activity, but controlled by the rate of cathodic reaction in the electrochemical cell.

#### Conclusion

The laboratory experiment showed that the electrochemical cover can remove the residual  $O_2$  that would normally pass through a compacted soil cover. Furthermore, the electrochemical cover can decrease  $PO_2$  levels in the cover using a relatively small current input. A US EPA funded field scale tests is under way currently at a mining site in Montana.

Future technology development will include determining the critical  $PO_2$  level at which ARD becomes insignificant, and testing of various combinations of electrochemical covers with surface deposited thickened tailings and paste systems.

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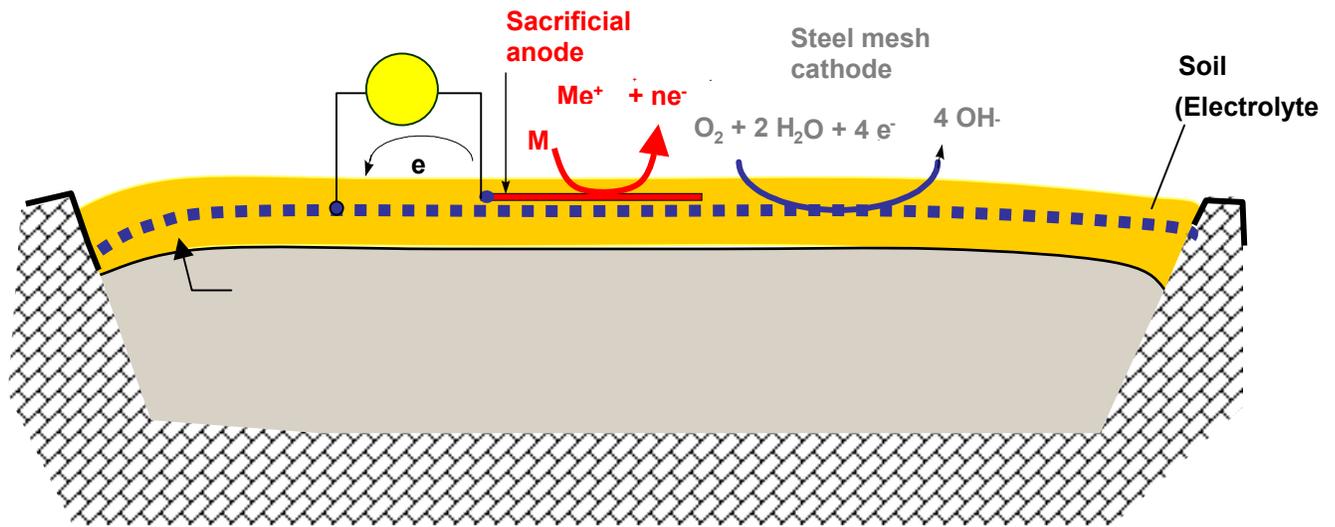


Fig.1 a Schematic of an electrochemical protective layer for a soil cover

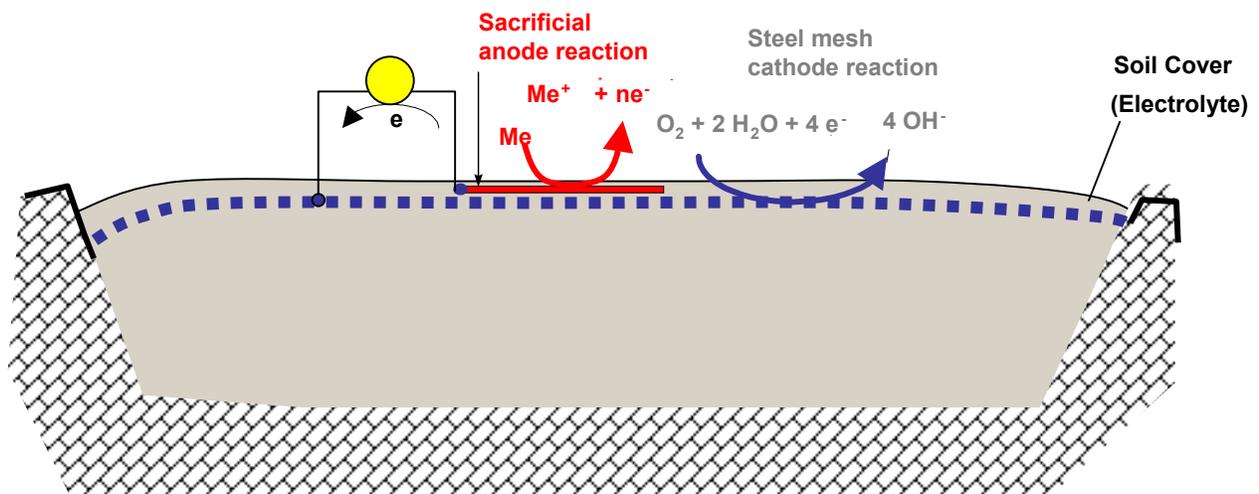
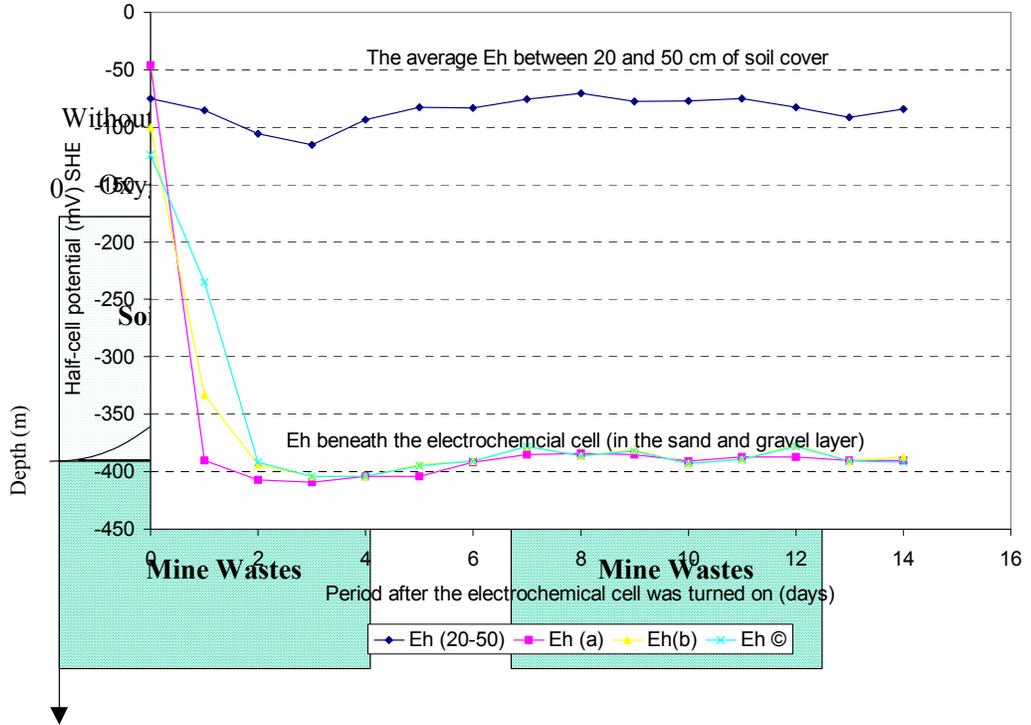
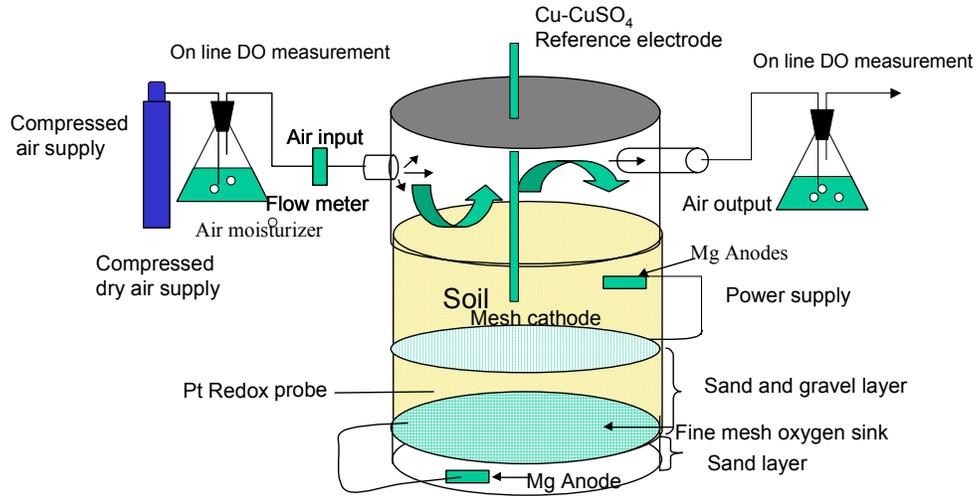


Fig.1 b Schematic of an electrochemical protective layer for surface tailings and paste tailings disposal.



**Fig.2 An illustration of the effect of an electrochemical cover on oxygen profile within soil covers.**



**Fig. 4 schematic of a flow-through chamber for the evaluation an electrochemical cover.**

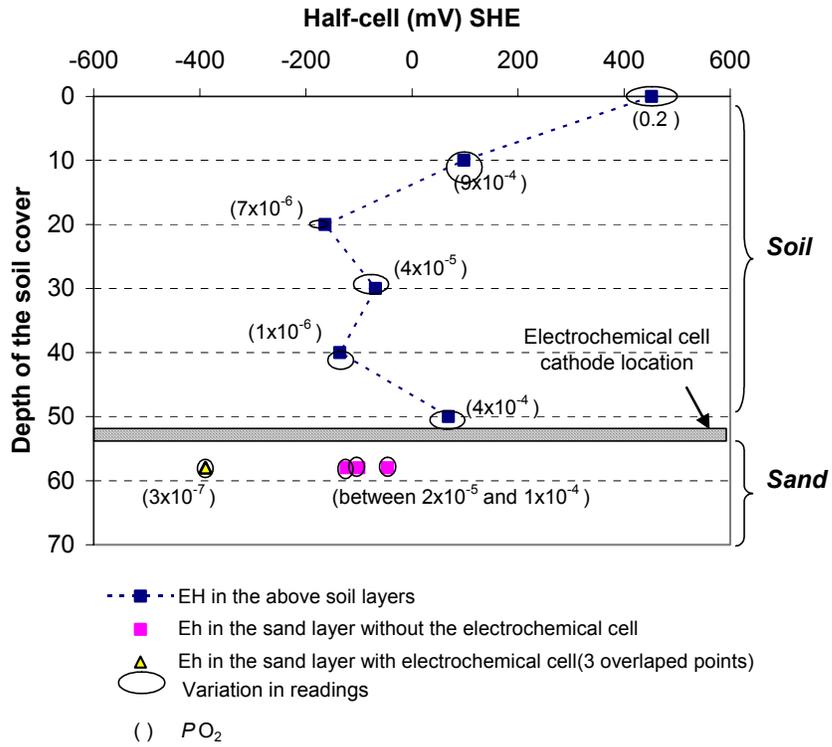


Fig. 4. Half-cell potentials before and after electrochemical cell was turned on.

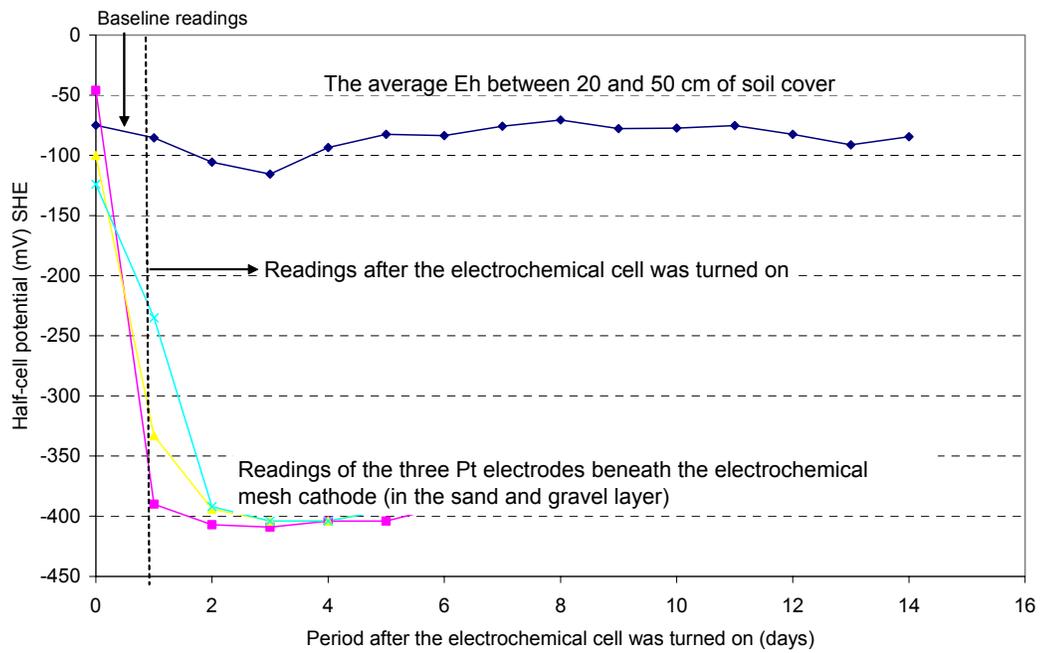


Fig. 5. Half cell potential readings before and after the electrochemical cell was turned on.

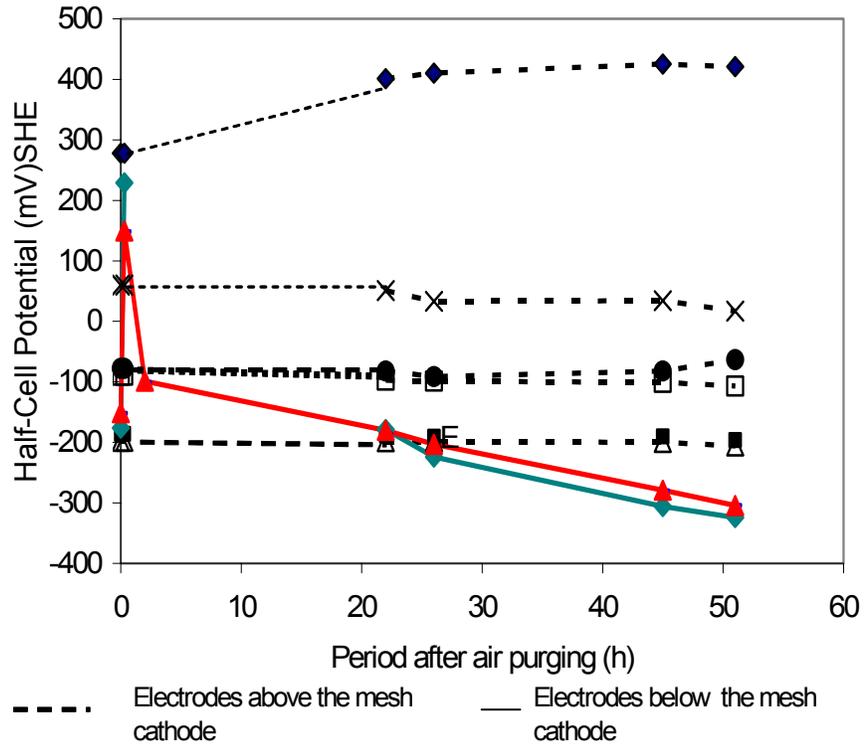


Fig. 6. Air purging test (I) showing decreases in Eh beneath the electrochemical cathode