

## Technical Article

### Electrochemical Treatment of Pyrrhotite-rich Tailings--a Laboratory Study

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**Abstract.** Many sulphide minerals are semiconductors and are therefore amenable to electrochemical manipulation. Large scale massive sulphide bodies can act as solitary electrodes in electrochemical cells. In mill tailings, however, sulphide minerals occur as silt- to sand-sized particles. The present study was conducted to determine if the same *in-situ* electrochemical treatment system used for sulphide bodies might work on a tailings deposit that is greater than 75% pyrrhotite. The objective was achieved by determining two key factors: (1) the mechanism of charge transfer within tailings: electronic vs electrolytic and (2) where cathodic reduction reactions occur, i.e., on the surface or within the tailings body. Results showed that electronic conduction predominated over electrolytic conduction in the tailings sample. Most of the reduction reactions took place at the outer surface of the tailings mass rather than within the tailings matrix. This study confirmed that the identified tailings deposit behaves as a single conductive body and is therefore a potential site for installation of an *in-situ* electrochemical treatment system.

**Key words:** Acid rock drainage, Electrochemical treatment, Electrolyte, Pyrrhotite, Redox potential, Semiconductor, Sulphide tailings.

#### Introduction

Many sulphide minerals, such as chalcopyrite ( $\text{CuFeS}_2$ ), pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), and pyrite ( $\text{FeS}_2$ ), are

classified as semiconductors (Koch 1954; Shuey 1975). Resistivity measurements of a single crystal have revealed that pyrrhotite is a good semiconductor with resistivity ranging between  $10^{-4}$  and  $10^{-6} \Omega\text{-m}$  (Harvey 1928; Parasnis 1956; Theodossiou 1965), followed by chalcopyrite with a resistivity between  $10^{-3}$  and  $10^{-4} \Omega\text{-m}$  (Shuey 1975), pyrite, at a range of  $10^{-2}$  and  $10^{-3} \Omega\text{-m}$  (Shuey 1975) and sphalerite, between  $10^5$  and  $10^{12} \Omega\text{-m}$  (Keys et al. 1968; Korsun et al. 1970). The electrical resistivity of sulphide bodies is a function of the type, trace element chemistry and morphology of component sulphide minerals, content of sulphide minerals, and environmental factors, such as temperature.

Sulphide bedrock deposits consist of sulphide minerals and are thus amenable to electrochemical manipulation. Shelp et al. (1995) showed in a unique field study that sulphide bedrock can exhibit electrical continuity and, can therefore act as a solitary electrode of an electrochemical cell. The objective of their study was to determine if an *in situ* electrochemical treatment system can prevent acid rock drainage (ARD), namely the production of acidic leachate contaminated with metals that results from oxidation of sulphide-rich bedrock and waste materials. The sulphide bedrock, in this case, was made to be the cathode of the cell upon which reduction reactions occurred. A scrap iron block was used as the anode where oxidation reactions occurred, and the leachate, characterized with high metal content and low pH (between 2 and 3), served

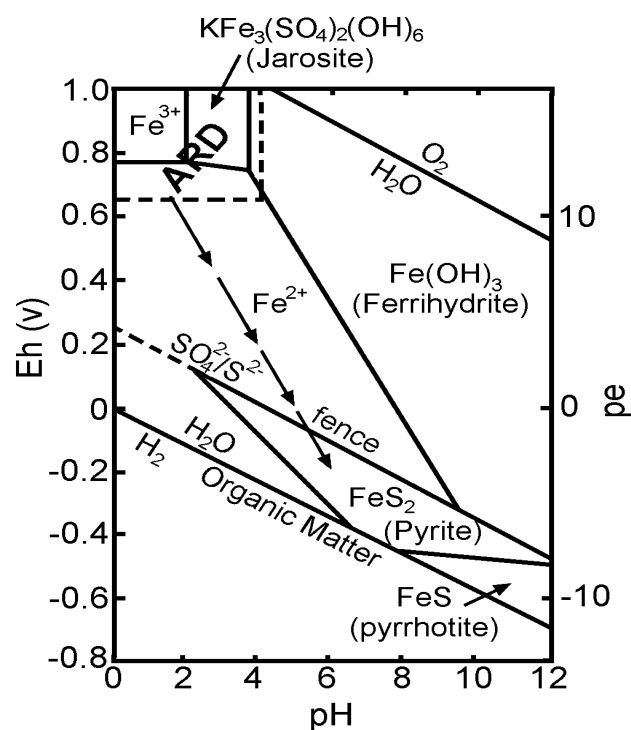
as the electrolyte. The half-cell potential of a cathode consisting of a sulphide mineral or a body of massive sulphide mineralization can be reduced as electrons flow from the anode to the cathode via an external circuit. As the half-cell potential of the cathode decreases to that of the field of a specific sulphide mineral or mixture of sulphide minerals, oxygen is reduced to produce  $\text{OH}^-$  ions. Figure 1 shows the ARD and pyrite fields. The net result is that oxidation of sulphide minerals is prevented. The *in situ* application of this principle has shown promise as an alternative method of preventing ARD. Compared to conventional ARD treatment approaches (e.g., liming, soil covers, and water covers), electrochemical protection of sulphide containing materials potentially represents a modular, cost-effective alternative with minimal maintenance requirements.

The application of electrochemical treatment to sulphide-rich tailings, however, requires additional consideration of electrical continuity and charge transfer, as tailings are granular rather than solid in form. In addition to those factors related to a solid mass of sulphide mineralization, the electrical properties of tailings are affected by contact resistance between sulphide particles and the electrochemical properties of the pore water (electrolyte). Lázaro et al. (1995), Cruz et al. (1997) and Cruz et al. (2000) used carbon paste electrodes of sulphide minerals, such as pyrite and pyrrhotite granular samples, as working electrodes to test the electrochemical reactivity of sulfide minerals under different conditions. The mixture of sulphide samples and graphite paste, indeed, behaved as a single electrode in these laboratory studies. With the exception of geophysical surveys designed to identify acid versus non-acid generating tailings, little is available in the literature on the characterization of the electrical properties of sulphide tailings.

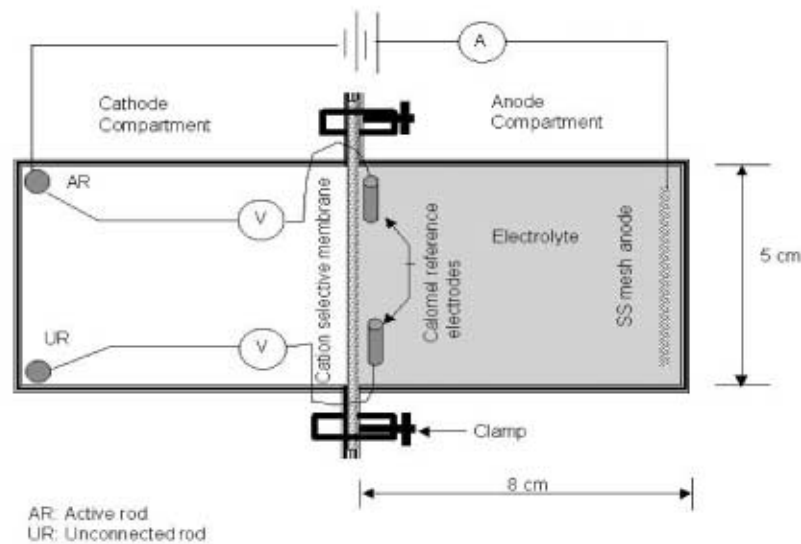
The mechanism of electron or charge transfer can be either electronic, via the sulphide particles, or electrolytic, via the electrolyte, or both. In situations where electronic conduction predominates, the tailings mass should behave as a single conductive body.

Unlike a solitary conductor/semiconductor electrode, the tailings mass is porous; thus, the tailings/electrolyte interface exists throughout the matrix of moist tailings. When the tailings mass acts as a solitary cathode, the location of cathodic reactions has a profound effect on the design of *in-situ* treatment systems. If the reactions occur on the outside surface of the tailings body, oxidation of a body of tailings can be prevented by electrochemical manipulation similar to that employed in the cathodic protection of bedrock and metal conductors (e.g., a pipeline or fuel tank). However, as electrolytic conduction increases in importance and cathodic reactions take place on the surface of individual sulphide particles, the configuration of the electrochemical treatment system needs to be modified accordingly.

The objective of this laboratory study was to determine



**Figure 1** Predominance field in the system Fe-S-K-O-H for  $a_{\text{Fe}} = 10^{-6}$ ,  $a_{\text{S}} = 10^{-3}$ ,  $a_{\text{K}} = 10^{-4}$ . The characteristic field of ARD is shown. The arrows indicate amelioration of ARD by electrochemical means. Modified from Shelp et al. 1995).



**Figure 2.** Schematic of the depolarization cell (overview).

if the same *in-situ* electrochemical treatment system used for sulphide bedrock can be used for a high sulphide tailings deposit. Two key factors were determined: the mechanism of charge transfer in the identified tailings deposit (i.e., electronic or electrolytic) and the location of the cathodic reduction reactions (i.e., surface of the tailings body or the surface of individual particles, under conditions of electronic conduction).

## Materials and Methods

Tailings samples known to contain approximately 75% pyrrhotite (Data provided by Falconbridge Ltd.) were collected in the Falconbridge Hardy Mine Tailings Management Facility, located in Ontario, Canada. Unoxidized tailings samples were collected 5 m below the surface, well below the bottom of the oxidized layer located at about 2 m in depth. The unoxidized tailings were dark blue-black in colour. Samples were sealed in air tight plastic bags and containers to prevent oxidation during transportation and storage. In the laboratory, some samples were allowed to oxidize for use later in one of the experiments described below.

Five experiments were conducted in this study. Experiments 1, 2 and 3 were designed to identify the dominant mechanism of charge transfer in sulphide rich tailings. Experiments 4 and 5 were designed to determine the location of cathodic reactions.

### Electronic vs. Electrolytic Conduction

A divided plexiglass electrochemical cell with anode and cathode compartments separated by a cation selective membrane was used in Experiments 1-3 (Figure 2). The anode compartment contained a saturated NaCl solution and a stainless steel screen anode. In Experiment 1, both compartments were filled with the NaCl solution. In the cathode compartment, two stainless steel rods were installed in the opposite corners located furthest from the membrane. One rod, referred to as the active rod (AR), was connected to the negative output of a constant current (DC) power supply and acted as the contact rod while the second rod, referred to as the unconnected rod (UR), remained outside the circuit. In Experiments 2 and 3, sulphide tailings were packed into the cathode compartment to a depth of 12 cm. Media utilized in the

cathode compartment are listed in Table 1.

Two saturated calomel reference electrodes (SCE) were positioned in the anode compartment adjacent to the membrane and connected to two Fluke multimeters, which were connected to the AR and UR. This multimeter has a resolution of 0.001 V and an accuracy of  $\pm 0.1\%$ . With this setup, half-cell potentials of these rods were monitored simultaneously. AR was polarized at 30 mA for 10 minutes, at which time the power was interrupted and the changes in potentials, or depolarization curves, for both AR and UR were recorded. Each experiment was repeated at least once.

These experiments represent standard testing procedures of the cathode protection industry. A synchronized depolarization behaviour between active and unconnected electrodes indicates the existence of electronic continuity.

**Table 1.** Medium and electrode material utilized in a cathodic compartment in the five experiments.

#	Media
1	Saturated salt solution (NaCl) using distilled water
2	Unoxidized tailings
3	Oxidized tailings with or without saturated salt solution
4	Unoxidized tailings with/without a 1 cm layer of oxidized tailings
5	Fresh tailings

#### Outer Surface vs Inner Surface Reactions

The apparatus used in Experiments 4 and 5 was identical to that used in Experiments 1-3 except that in Experiment 4, the cathodic compartment was filled with fresh tailings with and without a 1-cm layer of oxidized tailings adjacent to the cation selective membrane (Figure 2). In contrast to previous

experiments in which tailings was made the cathode or more cathodic, the cell setup in Experiment 5 was designed such that anodic oxidation of the unoxidized tailings was encouraged by reversing the polarity of the electrochemical cell. The stainless steel screen anode became the cathode; the AR in tailings became an anodic contact.

## Results and Discussions

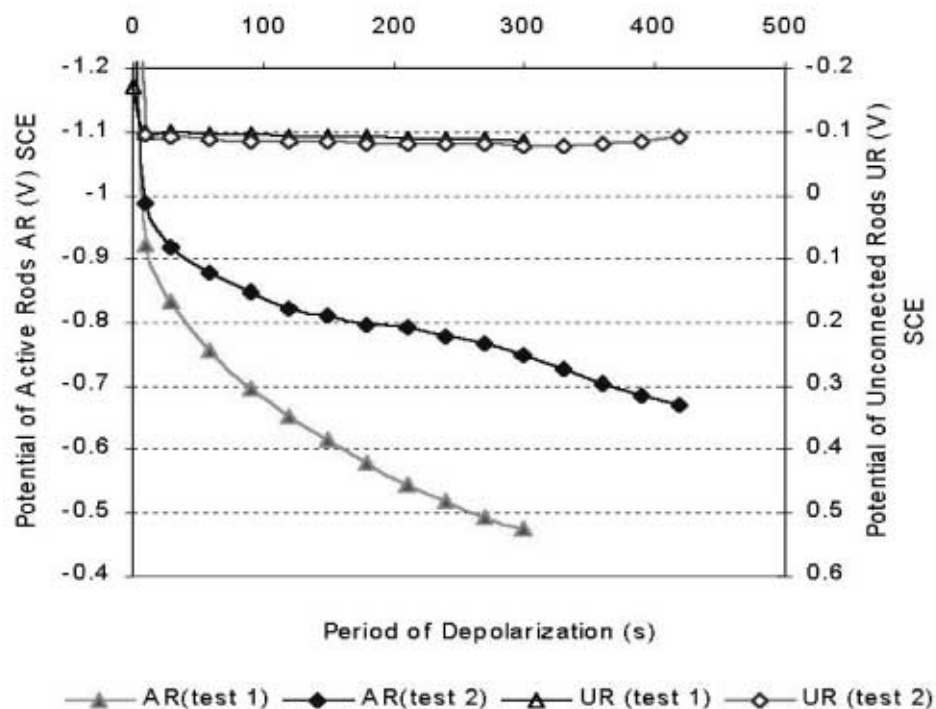
### Electronic vs Electrolytic Conduction

In Experiment 1, the slopes of the depolarization curves of AR placed in a salt solution were steeper than those of the UR (Figure 3) as the latter did not exhibit any obvious depolarization behaviour. All half-cell potential readings in this study were against SCE. This experiment showed that a medium with a strong electrolytic conduction does not provide an electronic contact between the two rods indicated by the lack of synchronized depolarization behaviour. The result demonstrated that: (1) with only electrolytic conduction between two rods, the UR did not behave as the AR did during the depolarization test, and (2) synchronized depolarization would only occur between the two rods if the tailings, not the pore water within, provided electronic contact.

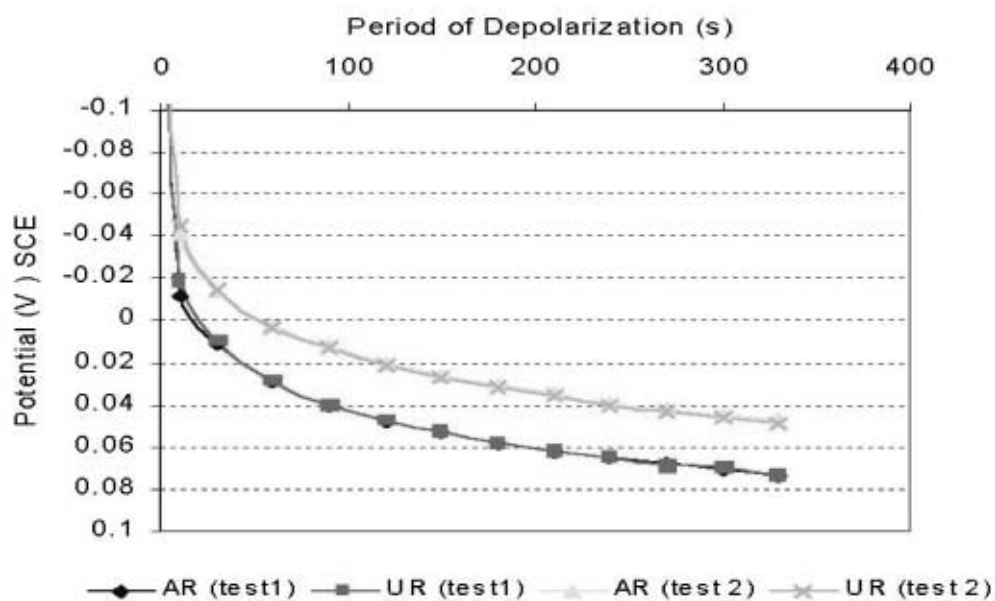
The small half-cell potential drift measured at UR was likely associated with the redox potential of the salt solution and the effect of the electrical field during the depolarization of AR. As the same AR was used in the two sequential tests, the accumulated polarization effect resulted in the lower resting potential after the 5 min depolarization in Test 2 than in Test 1 (Figure 3).

Both AR and UR exhibited synchronized depolarization behaviour (Figure 4) in Experiment 2, where unoxidized or fresh tailings in the cathode compartment replaced the salt solution used in Experiment 1.

Accordingly, the tailings mass must provide electrical contact between the two rods. Given the fact that there



**Figure 3.** Comparison of depolarization curves of active (AR) and unconnected rods (UR) in a salt solution (Experiment 1).



**Figure 4.** Comparison of depolarization curves of active (AR) and unconnected rods (UR) in unoxidized tailings (Experiment 2).

was electrical contact, the tailings must also be polarized and depolarized as AR and UR during the test. Indeed, they behaved as a single electrode. This concept is verified by the fact that the resting potentials of AR and UR in unoxidized tailings in Experiment 2 (between 0.4 and 0.6 V, Figure 4) were more positive than that of AR in the salt solution in Experiment 1 (between -0.5 and -0.7 V, Figure 3). Since the same AR and UR were used in both of the experiments, the significant difference in the potentials confirmed that the tailings, AR, and UR acted as a single cathode. The outer surface of the *new* cathode is the tailings/electrolyte interface near the cation-selective membrane (Figure 2). Thus, the potentials measured with AR/UR in tailings in Experiment 2 represented the potentials at the interface of the tailings/electrolyte in the anodic compartment, not the interface of AR/tailings pore water. Since this is a critical element in the application of electrochemical technologies to prevent ARD, further tests of this concept were conducted in Experiments 4 and 5.

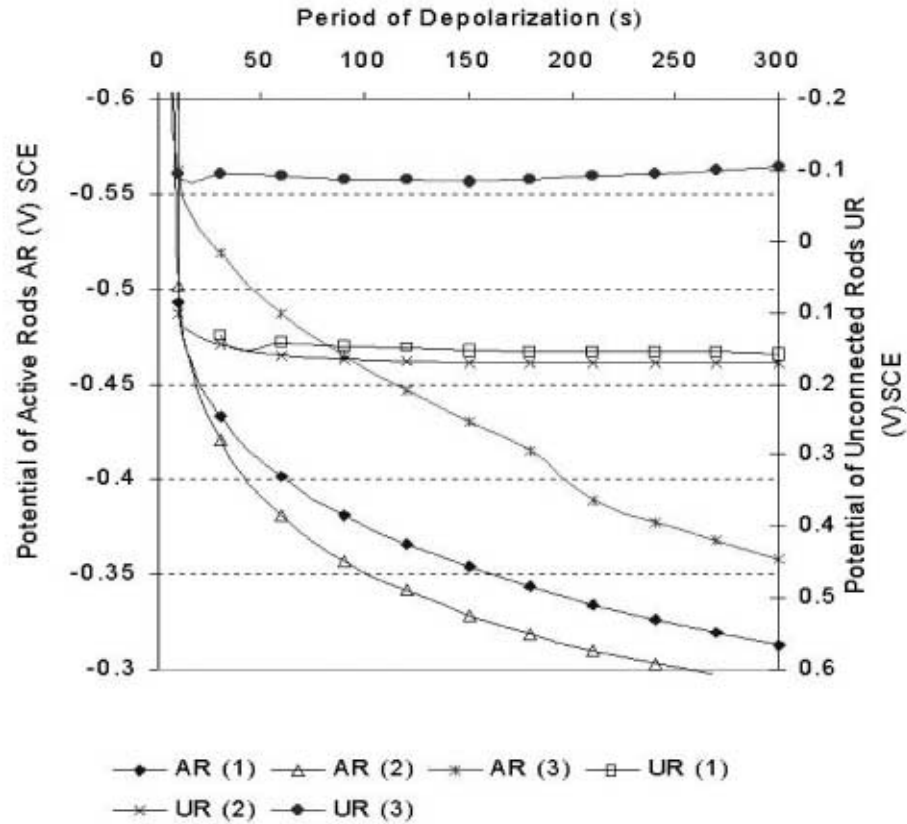
The electrical conductivity of the unoxidized tailings is controlled by the content and type of sulphide minerals present. Oxidized or partially oxidized tailings, however, are generally characterized by poor electrical conductivity due to their reduced content of sulphide minerals and the presence of coatings of secondary iron solid phases. This was shown in Experiment 3 where virtually oxidized tailings replaced unoxidized tailings in the cathode compartment. UR failed to polarize/depolarize whether or not the salt solution was added to the tailings medium (Figure 5). The mechanism of electron or charge transfer is likely electrolytic in nature; therefore, the oxidized tailings mass is not an electronic conductor. The instant off half-cell potential measured represented the AR contact with the tailings, not the bulk tailings body. Another significant difference between the oxidized and the unoxidized tailings used in this study was the resting potential after depolarization measured using UR in Experiments 2 and 3. The range of resting potential was between 0.06 and 0.08 V for unoxidized tailings (Figure 4), and between 0.15 and 0.17 V for oxidized

tailings (Figure 5). Assuming good contacts between UR and tailings were maintained during measurements, the higher resting potential of oxidized tailings indicated higher oxidation states compared with unoxidized tailings. Because of short polarization or reaction time (10 minutes) in this study, changes in chemical composition and electrochemical characteristic of the electrolyte were thought to be insignificant.

Experiments 1-3 show that electronic conduction is the dominant charge transfer mechanism (electrons are transferred within the solid phase) for the Hardy tailings samples. This information is an essential parameter for designing an *in situ* electrochemical protection system.

### Outer Surface vs Inner Surface Reactions

Experiments 4 and 5 were designed to confirm the location of the cathodic reactions (i.e., within the tailings mass at the interface of sulphide particles/electrolyte or at the interface of the outer surface of the body of the tailings/electrolyte). In Experiment 4, the cathode compartment was filled with unoxidized tailings with and without a 1-cm layer of oxidized tailings placed between the tailings and the cation-selective membrane. After 5 min of depolarization, the average half-cell potential of unoxidized tailings was 0.04V compared to 0.15V for unoxidized tailings with an oxidized layer (Figure 6). Based on the fact that UR in both setups responded to polarization and depolarization test cycles, good electrical contact between AR, UR, and tailings must have been maintained. Therefore, when the same current was applied in both designs during polarization, and under zero current conditions, the difference in the resting potentials represents the half-cell potential when depolarization potentials were measured at the electrolyte interface with either the outer surface of the tailings mass or the surfaces of individual particles. If the cathodic reactions occurred at the surfaces of

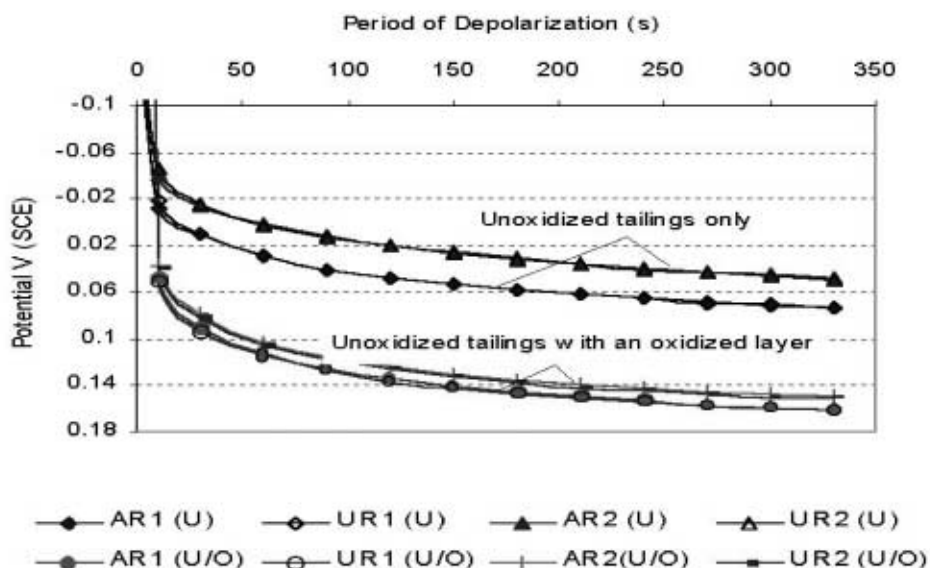


**Figure 5.** Comparison of depolarization curves of active (AR) and unconnected rods (UR) in oxidized tailings AR and UR (1) and (2), and in oxidized tailings with the addition of salt solution AR and UR (3) (Experiment 3).

individual particles within the matrix of the unoxidized tailings and ARs were located at the same position in both designs, the measured resting potentials of the unoxidized tailings should be the same between the two designs. We believe the shift in resting potentials from 0.04 to 0.15V can only be explained by the presence of oxidized tailings that altered the interface of the outer surface of tailings mass and the electrolyte to a more oxidized condition. The resting potentials observed in this experiment are consistent with the resting potentials for unoxidized and oxidized tailings recorded in Experiments 2 and 3. The fact that the resting potentials of the oxidized tailings observed in Experiment 3 (0.15 and 0.17 V) are similar to the resting potential of the unoxidized tailings with an oxidized layer supports the above conclusion.

To present visual evidence to support the finding of the previous experiment, anodic oxidation of tailings was

induced in Experiment 5. Within 3 days, a thick layer of reddish coloured secondary ferric solid phases developed at the interface of the tailings/cation-selective membrane. This phenomenon and the absence of oxidation products within the tailings mass provide strong evidence that the tailings are acting as a single semiconductor. When acting as an electrode in an electrochemical cell, electrochemical reactions will take place at the outer surface of the tailings body. This electrical characteristic of Hardy tailings provides key advantages in the design of an *in-situ* electrochemical treatment system to prevent ARD. Electrodes can be positioned so that current can be directed to the outer surface of the tailings where oxidation generally occurs, and current (power) is required only to treat the outer surface area of the tailings deposit.



**Figure 6.** Comparison of depolarization curves of active (AR) and unconnected rods (UR) in unoxidized tailings with/without a layer of oxidized tailings (Experiment 4). AR1: AR in Test 1, U: Unoxidized tailings, O: oxidized tailings

## Conclusions

This study demonstrated that the mechanism of electron transfer within these specific pyrrhotite-rich tailings is electronic in nature. In this bench-scale study, the tailings mass appears to behave as a single semiconductor with electrochemical reactions occurring at the outer surface of the tailings body rather than on the surface of the separate sulphide particles that constitute the tailings mass. The same *in-situ* electrochemical treatment system used for sulphide bedrock has been successfully established and operated at the Hardy tailings deposit since July 1999. Preliminary analysis of the data appear to confirm the laboratory results reported in this paper. The field study will be reported on in the near future.

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