Electrochemical modelling of the SIP response to oxidation of disseminated metallic particles

E. Placencia-Gómez(1) and L. Slater(2)

(1) *Aalto University, Finland School of Engineering, Department of Civil and Environmental Engineering, FI-00076 Aalto, Finland*
(2) *Rutgers University, Department of Earth & Environmental Sciences, Newark, New Jersey. U.S*

We investigated the SIP response of, and performed electrochemical modelling on, disseminated pyrite and pyrrhotite particles in sand, and mine waste material (tailings), in contact with electrolytic solutions composed of both inactive (non-oxidizing) and active (oxidizing) ions. The electrochemical model describes reasonably well the SIP response, and suggests that the activation of charge transfer reactions described by the corresponding model parameters can be used to evaluate the oxidation-diagnostic potential of the method.

Environmental relevance

The presence of metallic particles like sulphides, e.g., pyrite [Fe_2S] and pyrrhotite [$Fe_{1-x}S$], in granular media, constitutes a source of contamination to the soils, surface and ground waters which can affects some human activities and drinking water supplies. When these metallic particles enter in contact with oxidizing agents in conjunction with water, i.e., atmospheric oxygen (O_2) or dissolved in the pore water (DO), or with ferric iron (Fe^{3+}) ions in solution, they tend to be dissolved by means of oxidative-weathering mechanisms driven by electrochemical cathodic (reduction) and anodic (oxidation) reactions. This results in the release of ferrous iron (Fe^{2+}), sulphate (SO_4^{2}) and hydrogen (H^+) ions to the pore-water. This acid metal-sulphate rich pore water forms a leachate which is transported down hydraulic gradient to impact water sources. The generation of such acid metal-rich contaminated plumes is documented to occur in mine waste dumps such as tailings impoundments and rock mine piles over the time of mining activities and is commonly termed acid mine drainage (AMD).

Materials and methods

Our study focused on investigating the SIP response and performing electrochemical modelling using the Wong (1979) model for (1) artificial sulphide-sand mixtures composed of disseminated pyrite and pyrrhotite particles, respectively, and (2) mine waste material (tailings) rich in pyrrhotite and pyrite collected from the Haveri Au-Cu mine tailings impoundment in Finland, exposed to oxidative-weathering conditions in laboratory columns. In the first case, using artificial sulphide-sand mixtures, the metal sulphides were subjected to oxidation promoted by O_2, both DO and atmospheric, and continuously monitored with SIP measurements. In the second case, tailings were subjected to alternating non-oxidizing (inactive) and oxidizing (active) ions in solution by saturating the pore space with $CaCl_2$ (inactive ions), $FeSO_2$ (active-inactive ions) and $FeCl_3$ (active-inactive ions) solutions.

The oxidation extent of metallic sulphides is deduced from the model parameters which contain information related to the charge transfer mechanisms, i.e., the oxidation-reduction reactions on the metal-electrolyte interface. The associated SIP signal due to the EDL polarization resulting from the type of ions in the electrolyte is analyzed here.

Results

The electrochemical model describes reasonably well the SIP response in both artificial and tailings material samples, and suggests that the activation of charge transfer reactions inferred by the model parameters can be used diagnose the oxidation state of the system. Chemical analysis results on pore-water samples from artificial sulphide-sand mixtures showed that the greatest release of total iron ($Fe^{2+} + Fe^{3+}$) associated with the oxidation extent of metallic particles occurred during atmospheric O_2 conditions. The SIP response to the atmospheric oxidation conditions resulted in depletion decrease of the phase angle (φ) (≈20 mrad) and imaginary conductivity (σ''), along with a broader relaxation spectrum similar to a Warburg mechanism as suggested by Wong (1979); the latter is more evident in the case of pyrrhotite than pyrite minerals (Fig. 1). The sensitivity of the model parameters to the charge-transfer associated with the oxidation-reduction chemical reactions at the metal-electrolyte interface, such as the equilibrium exchange current density (i_0) and current reaction parameters (α) and (β), is consistent with the associated oxidation conditions promoted governing the changes in the modelled SIP spectra. The model suggests an increase of α, β and i_0 with an increase in the total iron released, defining SIP spectra consistent with the measured data following an increase in the oxidative-weathering (dissolution) on the metallic sulphides.

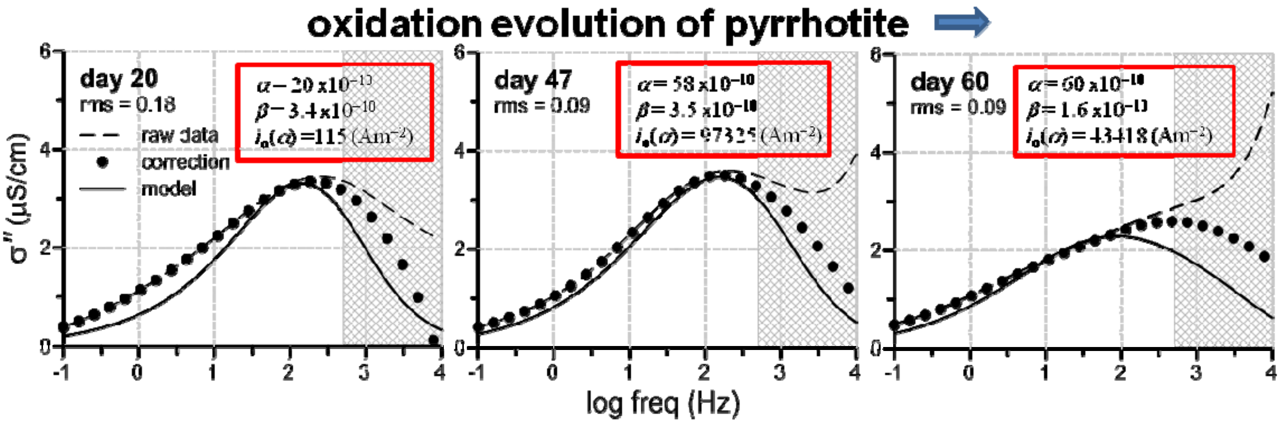

Fig. 1. Imaginary conductivity (σ'') spectra associated with the oxidation evolution of pyrrhotite on day 20 during DO oxidations conditions, and day 47 and day 60 during atmospheric oxidations conditions.

The SIP response of tailings due to inactive and active (ions) electrolytes filling the pore space is a reduction of φ with an increase in the total Fe released as an oxidation by-product. Both σ'' and σ' increases with the total Fe released. However, the shape and magnitude of the measured φ and σ'' spectra appear to be determined by the *in-situ* oxidation conditions. In summary, the electrochemical modelling seems be consistent with the *in-situ* oxidation of tailings in most of cases.

Reference

Wong, J., 1979. An electrochemical model of the induced-polarization phenomenon in disseminated sulfide ores. *Geophysics*, 44, 1245-1265.