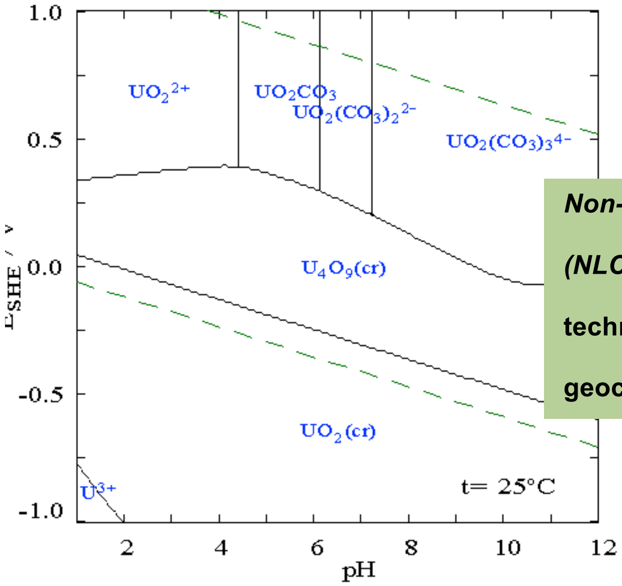
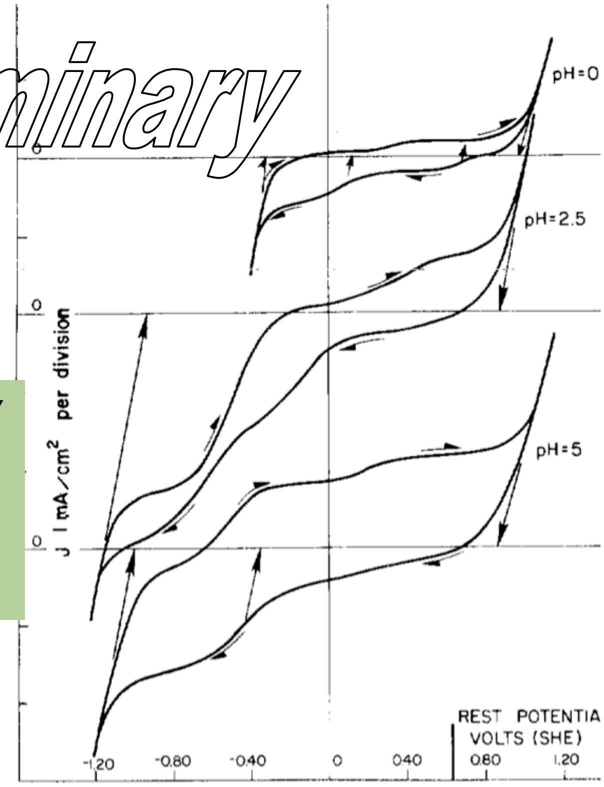
Earth Science Systems

ESSential Underground Information

Preliminary



***Non-linear complex resistivity (NLCR)* is a geophysical technique for assessing geochemical systems.**



Introduction

Non-linear complex resistivity (NLCR) is an emerging geophysical method for assessing the state of geochemical systems. The method is closely related to complex resistivity (CR) and induced polarization (IP), but adds the effects of non-linearity due to electrochemical reactions. These methods are routinely used in laboratory settings for a wide variety of investigations. For example, the paint industry uses CR as a sensitive corrosion monitoring technique for testing the effectiveness of coatings. Electrochemical analysis techniques such as (non-linear) voltammetry are commonly used for chemical species identification and concentration measurements. In the field, IP and CR have ben very successful techniques for locating and characterizing mineralized zones.

Applications

NLCR can be used to determine the concentration of chemical species when it carefully applied in a controlled environment. The following examples illustrate some applications for this technology. In base-metal resource development, identifying the oxidation state and mineralogy of metals is useful for the exploration, production, and environmental management stages. For solution mining applications, it may be possible to determine if a mineral assemblage is suitable for solution mining and to monitoring this process *in-situ*. Previously, a group at the University of Utah (Klein, 1980) built an electrochemical borehole logging tool for conducting copper assay in sulfide minerals. They successfully discriminated between copper sulfides and iron sulfides. Contamination sites may benefit by making *in-situ* NLCR measurements to insure that contaminant speciation is properly maintained to keep contaminants immobile.

Chemical Equilibrium and NLCR

The equilibrium concentrations of the species in an electrochemical system are a function of temperature, pH, and oxidation potential (Eh) of the system. A Pourbaix diagram is shown in the top-left of this page, which indicates the stable regions in Eh-pH space for a given electrochemical system (i.e. a certain collection of chemical species). The NLCR method modulates the oxidation potential, which enables or accelerates some reactions, and retards or stops other reactions as the system moves from a stable region for one species to that of another. As this occurs, the electrical impedance changes in a non-linear fashion as shown in the top-right voltammetry diagram. Changes in impedance (slope of line on the voltammetry plot) occur when the electrochemical system passes from one stability region to another.

NLCR Experiments

Non-linear effects are not usually seen in conventional CR and IP measurements because the potential developed across the electrolyte-mineral boundaries is insufficient to change the equilibrium conditions. Nevertheless, standard laboratory CR and IP equipment can be used for NLCR measurements if the excitation is sufficient for the electrode geometry being used for the measurements. In the field, NLRC surveys using

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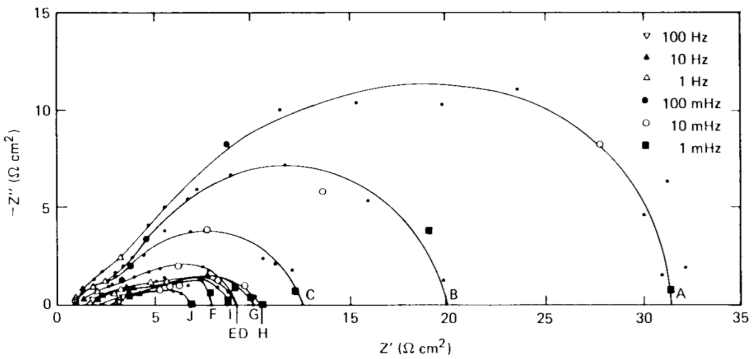

Argand **diagram showing the changing complex impedance due to rust progression in painted carbon steel.**

surface electrodes are only feasible with compact electrode arrays. Electrode arrays must be kept small so that potentials across individual electrolyte-mineral grains are able to move the system from equilibrium conditions. Custom borehole equipment can be produced for NLCR surveys because the electrode geometries can be kept reasonably small.

Analysis

The analysis of NLCR is a complex procedure that is still evolving. First, it is necessary to know which chemical species are present in the system. This allows geochemical modeling programs such as PHREEQC to calculate Pourbaix diagrams, equilibrium responses, and the kinetic response when moving from one stability region to another. Samples will need to be collected from the region of interest for laboratory assays so that a reference assemblage of chemical species can be established. Next, the reference assemblage of chemical species is used to model the geochemical system's kinetic response and model the NLCR data. With this geochemical model, the NLCR data are inverted using and obtain concentrations of each species.

Research and Development

Initial results from NLCR as well as the success of closely relate methods (CR, IP, voltammetry) indicate the potential of the method. More pilot studies are needed that investigate the electrochemical system response for specific mineral assemblages. Like all geophysical methods, NLCR will not work for all problems or sites. However, when the initial electrochemical analysis shows that the technique has a quantifiable response to a species of interest, it will likely provide valuable and cost-effective information.

Selected References

Barsoukov, E., and Macdonald, J., 2005, Impedance Spectroscopy Theory, Experiment, and Applications, Wiley and Sons, New York, 595 p.

Klein, J., 1980, Specific Mineral Identification in Electrochemical Logging of Drill Holes, PhD Thesis, U. Utah.

Parkhurst, D., and Appelo, C., 1999, User's guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch Reduction, One-Dimensional Transport, and Inverse Geochemical Calculations, U.S. Geological Survey, Water-Resources Investigations Report 99-4259, Denver, CO.

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