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Electrochemical Characterization of Grouted Radioactive Waste

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Westinghouse
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Electrochemical Characterization of Grouted Radioactive Waste.

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ABSTRACT

We are investigating the possibility of monitoring the degree of immobilization of the low level radioactive waste by embedding an array of long lasting electrodes in grout. This work describes our ongoing attempts to understand the physics and chemistry of charge carriers in the grout under various load conditions.

INTRODUCTION

Any long-term disposal system of radioactive waste will require monitoring to warn against structural deterioration and leach of the radioactive or hazardous components into the environment. Although, the existing methods, based on physical sampling and testing, provide a higher level of confidence in the data, it also results in generation of secondary waste streams and increased exposure to radiation for workers. Therefore, it is highly desirable that a method be developed for remotely sensing the grout.

Our efforts[1,2] are focused on the application of an array of long lasting electrodes that will sense the dynamic properties of ions in the grout. The basic unit structure consists of four electrodes through which we perform a variety of measurement such as impedance, single frequency conductivity, electrochemical potential, cyclic voltametry, etc.

Grout and other cementitious materials are described within the general context of composite media in which morphology, chemistry and conductivity are interdependent. We describe experimental results that include time evolution over many months of the impedance and electrochemical potential of hydrating(and drying) cement composite and our attempts at interpreting these data in terms of conductivity and dielectric constant of the matrix

Along with the time evolution tests; we have performed the resistivity measurement during simulated deionized water flooding into the dry grout. The leach test experiment is designed to establish possible correlation with present quality verification methods and standard leach test such as the ANS 16.1[3] or other such accepted tests.

EXPERIMENTAL

Sample preparation

We report here results on the cementitious blend that was proposed to be used at the Hanford site with the following composition; Portland Cement Type I/II 20.7 wt%, Fly Ash Class F 68.3 wt%, and Attapulgite Clay 11 wt%. The three powders in the composite were mixed for 48 hrs in a V-shape blender, then mixed with appropriate electrolytes(w/c =1:1) in a mixture for 15 minutes to form a consistent paste. Stainless steel wires of 0.024" diameter were used as

electrodes. Rectangular shape (4.5cm x 5cm x 13.5cm) Lucite™ box mold is used for setting the samples for testing the time evolution during the hydration and drying processes of the grout. Typical setting condition includes covering the cement paste with the electrolyte in a sealed container for 24 hr at room temperature.

Samples for deionized water flooding experiment were set in cylindrical (3cm diameter and 15cm high) Lucite™ mold and cured at normal room temperature conditions for 28 days. Dry grout samples were carefully cut either into four or two electrode configurations and then fitted into the specially design electrochemical cell (figure 1) with an epoxy coat.

Figure 1: Electrochemical cell for concurrent measurement of resistivity and ANS 16.1 leach test.

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Impedance

Our experimental setup for impedance measurement was described before[4]. It is based on the Solatron 1256 and Hewlett-Packard (HP) network analyzers.

It has been shown [1,2] that impedance measurement at the range of frequencies from 10^{-2} - 10^{-7} Hz do not contain more information than a single frequency measurement. Therefore we have elected to perform a single frequency conductivity measurement for water flooding experiment. An applied AC voltage (30mV at 500Hz) of the generator was imposed between the outer electrodes, and the voltage drop between the inner electrodes was measured. The current flowing through sample was measured through the voltage drop across a series resistor with a known resistance.

TIME EVOLUTION OF IMPEDANCE DURING HYDRATION

We have evaluated the time evolution of the composite grout with different NaNO_3 concentrations. The procedure was that in all cases the setting has started with a blanket of the

Figure 2: Evolution of Resistance and Capacitance as a function of time and electrolyte concentration for three grout samples prepared with NaNO_3 and the reference dry blend ($w/c=1:1$).

electrolyte on the top of sample. We have used three electrolyte concentrations 1M, 0.2M and 0.04M and prepared five identical samples with each electrolyte. Some of the samples were covered with an electrolyte for one week and then were let dry; other samples were covered for two weeks and then were allow to dry. This procedure has shown to be effective in minimizing the development of cracks[2] in the samples. Figure 2 shows the time evolution of the resistance and capacitance of the three samples. As expected, the resistance increases with the setting time. However, the resistance, after reaching a maximum at about 200 days in all samples, show steady decrease. We are currently investigating the underlying mechanism; the data presented here show a possible correlation between the peak position and the NaNO_3 concentration of the solutions used in the grout mixture.

DEIONIZED WATER FLOODING AND SATURATION

We have observed three distinctive regions for the time evolution of the resistance. Initial flooding stage with decreasing resistance as the deionized water enters into the sample and the intermediate saturation stage where the resistance tends to reach a constant value as the dissolution-precipitation process brings the system into equilibrium. Figure 3a shows a typical variation of the resistance, as the system goes through initial flooding to intermediate saturation stage. This can reasonably be described by assuming non-Gaussian type diffusion.

For such a case, the concentration $C(x,t)$ at a point x , at time t , with dimensionaless variable; $x^* = x/l$, $\tau = D_{\text{eff}}t/l$ and $C^* = C(x,t)/C_0$ can be written as follows;

$$C^* = 1 - \text{erf}\left(\frac{x^*}{2\tau^n}\right)$$

where l and D_{eff} are a characteristic length and the effective diffusion coefficient of the system. The value of n reflects the deviation from normal Gaussian type (i.e. when $n=0.5$) diffusion.

By assuming a simple relation; $C \sim 1/R$ holds between the concentration and the resistance of the sample, we can obtained the D_{eff} and n for a given system (Figure 3b).

These two stages of electrolyte dynamics occur in relatively shorter time scale compared to the third and final stage of the process, where we see the increase in resistance due to leaching of ions into the outer environment. Resistance data (hence the concentration) of this stage and the concentration of the leachate through chemical analysis, such as flame photometry and/or atomic absorption, will be used to obtained the Leach coefficient(D_{eff})[3] of the grouts. These and other results will be published in a separate communication.

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Figure 3: (a) Time variation of the resistance during initial flooding and saturation stages.
(b) Typical data fit for non-Gaussian type diffusion process

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