

## **Spectral Induced Polarization Measurements of Nanoparticles in Laboratory Column Experiments**

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Nano sized materials are prevalent in consumer goods, manufacturing, industrial processes, and remediation technologies. The intentional and accidental introduction of nanoparticles (NP) into the subsurface pose a potential risk to the environment and public health. This research begins to address the need for the development of techniques to detect their presence and transport in the subsurface. Two sets of laboratory column experiments will be presented to achieve this objective.

The sample columns for both experiments were constructed from polyvinyl chloride (PVC) pipe with an inner diameter of 3.4 cm and a length of 12 cm. Four non-polarizing Ag-AgCl electrodes housed in electrolyte (agar gel mixed in 3M concentration of KCl) filled chambers were placed 2 cm apart along the length of the column and located just outside the current flow path. Ottawa sand was used to fill the column with a median grain diameter distribution of  $d_{50} = 200 \pm 10 \mu\text{m}$  and a porosity of  $0.45 \pm 0.02$  (calculated from the total volume of the column minus the volume of the sand). SIP measurements for both experiments used the dynamic signal analyzer (DSA) National Instruments (NI) – 4461. The impedance magnitude  $|\sigma|$  and the phase shift  $\phi$  of the sample were measured relative to a high-quality resistor. The real ( $\sigma'$ ) and imaginary ( $\sigma''$ ) parts of the sample complex conductivity were calculated. Experiment 1 obtained data between 0.1 to 10000 Hz at 16 equal logarithmic intervals and Experiment 2 between 0.1 and 1000 Hz at 13 equal logarithmic intervals.

Experiment 1 was conducted to investigate the sensitivity of the spectral induced polarization (SIP) method to the presence and transport of silver nanoparticles (Ag NP) and zero valent iron nanoparticles (ZVI NP) in saturated quartz sand packed columns. In addition the SIP sensitivity test, a SIP column transport detection experiment was conducted using a 12 mg/mL concentration NP suspension. A peristaltic pump with flow at 1 mL/minute was used to introduce the suspension into the sand columns. Effluent samples of the suspensions from the sand columns and complex conductivity measurements were collected every five minutes for 180 minutes. The optical density of the nanoparticles in the effluent samples were determined at 430 nm wavelength using a spectrophotometer and then converted into concentrations using relationships determined from the linear correlation between concentrations of nanoparticle suspensions and their measured optical densities. A breakthrough curve (BTC) was obtained by plotting the normalized outlet NP concentration as a function of time.

Experiment 2 was performed to determine the SIP response of Ag NP within partially saturated conditions. SIP measurements were made as described above but under different Ag NP concentrations (0, 2, 4, 6, 8 and 10 mg/g) and moisture contents (5%, 10%, 15%, 20% and 30%).

Results from Experiment 1 show that at frequencies above 1 Hz, the magnitudes of the phase and imaginary conductivity increased with increasing concentration of the NP concentration with well-defined relaxation peaks centered at 500 Hz for Ag NP and 5000 Hz for ZVI NP. At the relaxation frequencies, the magnitudes of the phase and imaginary conductivity of the ZVI NP were twice the magnitude of the Ag NP. The BTC of normalized outlet Ag NP was higher in magnitude compared to the BTC of the normalized ZVI NP, suggesting the retention of ZVI NP in the sand column was higher than Ag NP. Higher retention of ZVI NP was reflected in higher magnitudes for the normalized phase and the imaginary conductivity component. Interestingly, the trends of the BTC of the normalized phase and imaginary conductivity components were similar to the BTC trends of normalized outlet NP concentration.

For Experiment 2, the SIP response was analyzed for Ag NP at 15% water content and at different Ag NP concentrations (0, 2, 4, 6, 8, and 10 mg/g) within similar sand columns and procedures as described above. The results show the magnitude of the imaginary conductivity component generally increases with increasing Ag NP concentrations from 0 to 10 mg/g and by almost one order of magnitude at frequencies greater than 10 Hz. However, the increase in Ag NP concentration showed relatively small change in the real conductivity response compared to the imaginary conductivity. Plotting the 10 Hz results of imaginary and real conductivity components obtained similar results as a function of different water saturation and Ag NP concentrations. These plots were fit with power law relationships. The results show that at different Ag NP concentrations, the magnitude of both the imaginary and real conductivity components increases by increasing the water saturation. However, the rate of change in the magnitude of the imaginary conductivity is greater than the real conductivity component. That is, for the imaginary conductivity component, the power law exponents from the fitted trend lines are increasing from 0.35 to 1.35 with increasing Ag NP concentrations from water saturation of 0.05 to 0.30 and with correlation coefficients greater than 0.88. The power law relationships for the real conductivity components were very poor with correlation coefficients less than 0.55.

Overall, these results demonstrate the sensitivity of the SIP technique to both silver and zero valent iron nanoparticles and their transport in saturated porous media and in partially saturated conditions. Our results demonstrate that SIP measurements show potential for this technique in guiding the detection and remediation processes of such contaminants within the vadose zone or their detection as part of remediation schemes. Future research will consider agglomeration and longer term experimentation investigating the biogeophysical response.