Spectral Induced Polarization (SIP) Measurements of Nanoparticles in Laboratory Column Experiments

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Why do we care about nanoparticles?

Engineered nanoparticles (ENPs) are prevalent as:

- **Consumer products:**
  - Skin care, oral hygiene, hair care, cleaning, baby care,
  - Textiles, clothing, shoes, toys, flooring,
  - Electronics: appliances, computer hardware, mobile devices,

- **Manufacturing product and processes,**
- **Industrial processes**
  - Filtration, cleaning, coatings...
- **Remediation technologies, e.g., nZVI**
  (nano Zero Valent Iron)

Prolific Growth of Nanotechnology

![Graph showing the growth of total products listed from 2005 to 2011.](source: Project on Emerging Nanotechnologies)
Are nanoparticles harmful?

- Of ~1,000 consumer nano-products more than 25% contain silver nanoparticles (Ag NPs) the most of all metal based ENP.

Zebra fish mortality rate

Concentration dependent increase in mortality and hatching delay was observed in AgNPs treated embryos of Zebra fish.

Adapted from: Asharani et. al. Nanotechnology, 19 (2008) 255102

- ZVI NPs are used for remediation, so Iron is also of interest.

The intentional and accidental introduction of NPs into the subsurface pose a potential risk to the environment and public health.
The Broad Research Questions?

➢ What physical and chemical properties and processes determine the environmental release, fate, and transport of ENMs?

➢ Are they detectable in the environment?

Research Objectives

Experiment #1 ➡ SIP detection and transport sensitivity to Ag NP and ZVI NP in saturated quartz sand packed columns.

Experiment #2 ➡ SIP response of Ag NP in partially saturated columns.

<table>
<thead>
<tr>
<th>Particle name</th>
<th>Surface area (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Bulk density (g/cm³)</th>
<th>Particle size (nm)</th>
<th>Particle shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver (Ag)</td>
<td>2.4 - 4.42</td>
<td>10.5</td>
<td>0.5 – 1.3</td>
<td>90 - 210</td>
<td>spherical</td>
</tr>
<tr>
<td>Zero Valent Iron (ZVI)</td>
<td>3 - 7</td>
<td>7.87</td>
<td>3.677</td>
<td>100 - 250</td>
<td>spherical</td>
</tr>
</tbody>
</table>
Spectral Induced Polarization

Measured in frequency domain (SIP):
1. Impedance (amplitude) conductivity, \( |\sigma| \)
2. Phase (Rx:Tx phase shift), \( \phi \)

Calculate:

Real conductivity

\[
\sigma' = |\sigma| \cos \phi
\]

Imaginary conductivity

\[
\sigma'' = |\sigma| \sin \phi
\]

Response due to:
- fluid chemistry
- Electrolyte
- Grain interface

Response due to:
- physicochemical properties at fluid-grain interface
  - surface area
  - surface charge density,
  - ionic mobility
  - tortuosity

Metallic polarization enhances IP effects

\[
\sigma' = f(\sigma_{el}, \sigma_{elc}, \sigma_{int}^{\prime})
\]

\[
\sigma'' = \sigma_{int}^{\prime}\]

\( \sigma_{el} \) = conductivity of interconnected, fluid-filled pore space

\( \sigma_{elc} \) = electronic conduction through metal minerals (e.g. ZVI)

\( \sigma_{int}^{*} \) = conduction/polarization at iron mineral/electrolyte interfaces
Why use SIP for nanoparticle detection?

1. Preliminary experiments show a SIP response to nano-materials in porous media.

2. SIP is sensitive to specific surface area (Spor).

3. SIP was originally developed and used to locate disseminated metallic mineral deposits.
#1. SIP detection & transport sensitivity to Ag & ZVI

Spectrophotometer
Optical density at \(\lambda = 430\) nm
Converted to NP conc. per linear correlation

Ag-AgCl electrodes, agar gel with 3M conc of KCL; ‘a’ = 2 cm

Ottawa sand: \(d_{50} = 200 \pm 10\) µm and a porosity of 0.45 ± 0.02
SIP detection sensitivity Results

- $\sigma''$ increased with increasing concentrations of Ag NPs and ZVI NPs.
- Relaxation peak at 500 Hz for Ag NPs and 5000 Hz for ZVI NPs.
- $\sigma''$ magnitude of ZVI NPs $\sim 2x$ Ag NPs.
- Insignificant changes for the $\sigma'$.
SIP transport sensitivity

- SIP parameters increased over time due to the retention of AgNPs and ZVI NPs during transport in sand column
- $\sigma''$ show well defined relaxation peak at 500 Hz for AgNPs and 5000 Hz for ZVI NPs
Comparison of Break Through Curves (BTC’s), normalized NPs Concentration and $\sigma''$

BTC’s of the normalized imaginary conductivity component ($\sigma''/\sigma''_o$) mimic the BTC’s of normalized NPs concentrations ($C/C_o$) and the control agar solution.
Experiment #1 Summary

SIP Detection Sensitivity

- $\sigma''$ increased with increasing concentration of Ag and ZVI
- At $\sigma''$ relaxation peak frequencies, magnitude of ZVI = 2 x Ag magnitude due to the higher surface area of ZVI and its magnetic properties.
- Insignificant $\sigma'$ response, suggesting SIP response due to grain-fluid interface changes, i.e., surface area & metallic properties.

SIP Transport Detection Sensitivity

- ZVI higher retention vs. Ag reflected in higher normalized ZVI $\sigma''$ magnitude.
- BTC’s of normalized imaginary conductivity ($\sigma''/\sigma''_o$) mimic the BTC’s of normalized NPs concentrations ($C/C_o$) and the control agar solution.

Overall

- Results demonstrate SIP sensitivity to the presence and transport of nanoparticles within saturated porous media.
#2. SIP response of Ag in partially saturated columns

WHY PARTIAL SATURATION?
• Likely pathway for NP subsurface contamination is through the unsaturated zone due to a surface spill or leak.
• SIP response of NPs in the vadose zone should be understood

EFFECT OF SATURATION & AgNPs CONC.
• Fine sand + Artificial Ground Water (AGW) (0.0275 S/m)
• different concentration of AgNPs (90-210 nm) (0, 2, 4, 6, 8, 10 mg/g)
• different water saturation (0.05, 0.10, 0.15, 0.20, and 0.30)

EFFECT OF AgNPs GRAIN DIAMETERS
• Fine sand + AGW (0.0275 S/m) at 0.15 saturation
• AgNPs (35 nm, 90-210 nm and 1250-2500 nm)
SIP response at 10 Hz of different AgNPs concentrations at different water saturation

- $\sigma''$ increased with increasing concentrations of Ag NPs and increasing water saturation
- $\sigma'$ response increase with water saturation, but shows insignificant response to AgNPs concentration
Grain Size variability of AgNPs (6 mg/g) in 15% partially saturated sand

- Smaller the AgNP grain size the larger the SIP response for both $\sigma'$ and $\sigma''$
- Results have implications to nanoparticle agglomeration
Experiment #2: Summary

- $\sigma''$ increase by about one order of magnitude with increasing concentrations of AgNPs and increasing water saturation.

- $\sigma'$ response increased with water saturation; but showed insignificant response to increasing AgNPs concentration.

- The magnitude of both $\sigma'$ and $\sigma''$ increased with decreasing grain size diameters of AgNPs due to the increase in surface area.

Overall

- Our results demonstrate that SIP measurements are sensitive to the presence of AgNPs in partially saturated porous media.
Conclusions

• SIP detection of nAg and nZVI as low as 4 ppt in saturated sand and 2 ppt in partially saturated sand.

Are These Concentrations Environmentally Relevant?

➤ Tang and Lo (2013) report the use of 5 ppt for nZVI remediation in water systems.

➤ Transformation and agglomeration of ENPs depend on the characteristic properties of the ENPs and the interactions within the environment at the physicochemical, macromolecular, and biological levels.

➤ Each NPs property and its environmental interactions need to be evaluated to understand the geophysical response.

➤ The geophysical response is likely a function of these interactions and the resulting physicochemical alterations.

➤ Many questions remain on the ENPs transformation in natural environments and the resulting SIP response.
QUESTIONS ?