H31J-06

On the Sensitivity of SIP to the Presence and Transport of Nanoparticles in Saturated Porous Media

Gamal Z Abdel Aal[1], Estella E Atekwana[1] and Dale Werkema Jr.[2]

[1]Oklahoma State University

[2]U.S. Environmental Protection Agency

AGU FALL MEETING
San Francisco | 9–13 December 2013

Introduction

- Nanoparticles use has rapidly increased.
- The potential risk and hazard to the environment and human health as also increased.
- Nanoparticles fate and transport in porous media are largely unknown.
- To assess such threats to the environment, techniques are needed that are sensitive to nanoparticles in the subsurface.
- Spectral induced polarization (SIP) is sensitive to the presence of nano-materails in porous media.

Objectives

- Investigate the sensitivity of (SIP) measurements to different concentrations of Ag and ZVI nanoparticles in saturated porous media

- Assess the potential use of SIP to monitor the transport of Ag and ZVI nanoparticles in the subsurface.

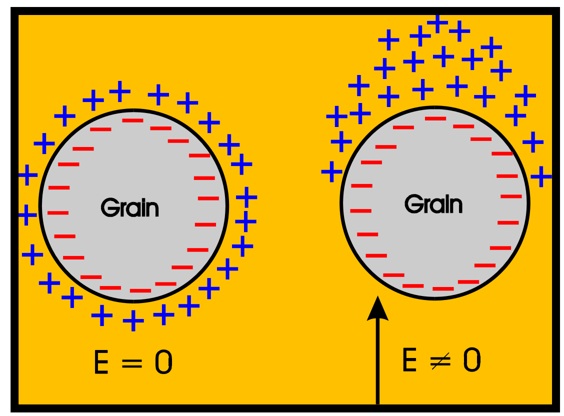
Method

Spectral Induced Polarization (SIP) or Complex Conductivity

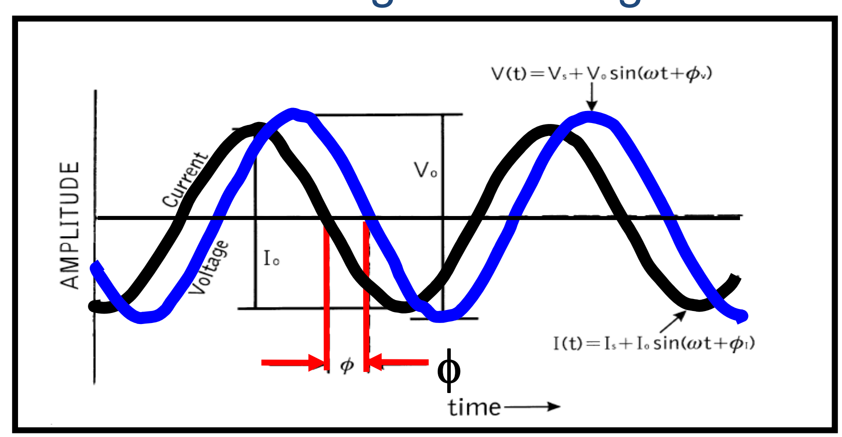
Induced polarization phenomenon

- Polarization:
  [1] redistribution of ions within electrical double layer of interconnected pore surface following application of electric current
  [2] relaxation of ions upon current termination:
  measured with time-domain IP equipment

  in frequency domain phase shift (*f*) between voltage & current waveforms



Simple schematic for polarization of electrical double layer of interconnected pore surface around a single mineral grain



Method

Measured quantities of SIP

- **Impedance conductivity** $|\sigma|$
- **Phase** φ

$$\phi = \tan^{-1}\left(\frac{\sigma''}{\sigma'}\right) \cong \frac{\sigma''}{\sigma'}$$

$$\sigma' = |\sigma|\cos\phi$$

$$\sigma'' = |\sigma|\sin\phi$$

Real conductivity

Sensitive to fluid chemistry and contains an electrolytic and interfacial component

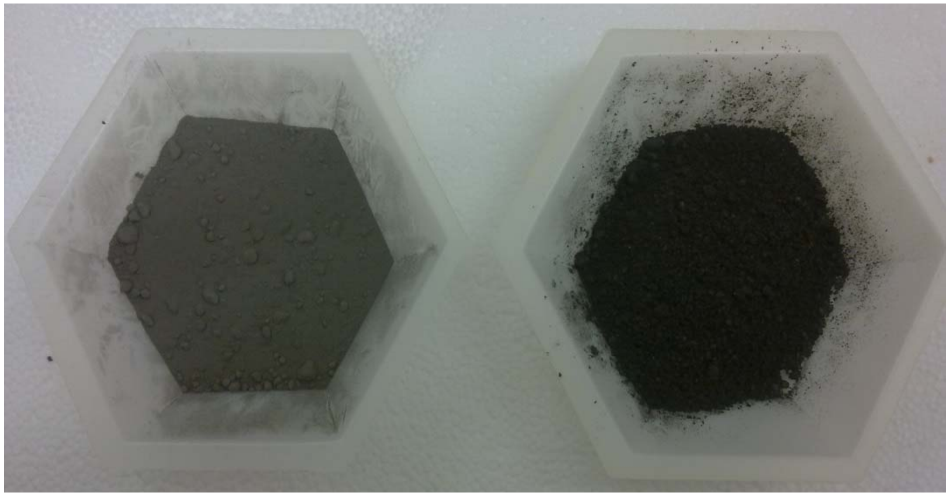
Imaginary conductivity

Sensitive to physicochemical properties at fluid-grain interface (e.g., ***surface area ,***surface charge density, ionic mobility,, and tortuosity)

Materials

Two of the most commonly used nanoparticles

AgNPs **ZVINPs**



Nanostructured & Amorphous Materials, Inc.

Particle name	Surface area (m2/g)	Density (g/cm3)	Bulk density (g/cm3)	Particle size (nm)	Particle shape
Silver (Ag)	2.4 - 4.42	10.5	0.5 – 1.3	90 - 210	spherical
Zero Valent Iron (ZVI)	3 - 7	7.87	3.677	100 - 250	spherical

Materials

0.2 % Agar solution
EC= 554 μS/cm, pH = 6.84

Sonication bath
30 minutes

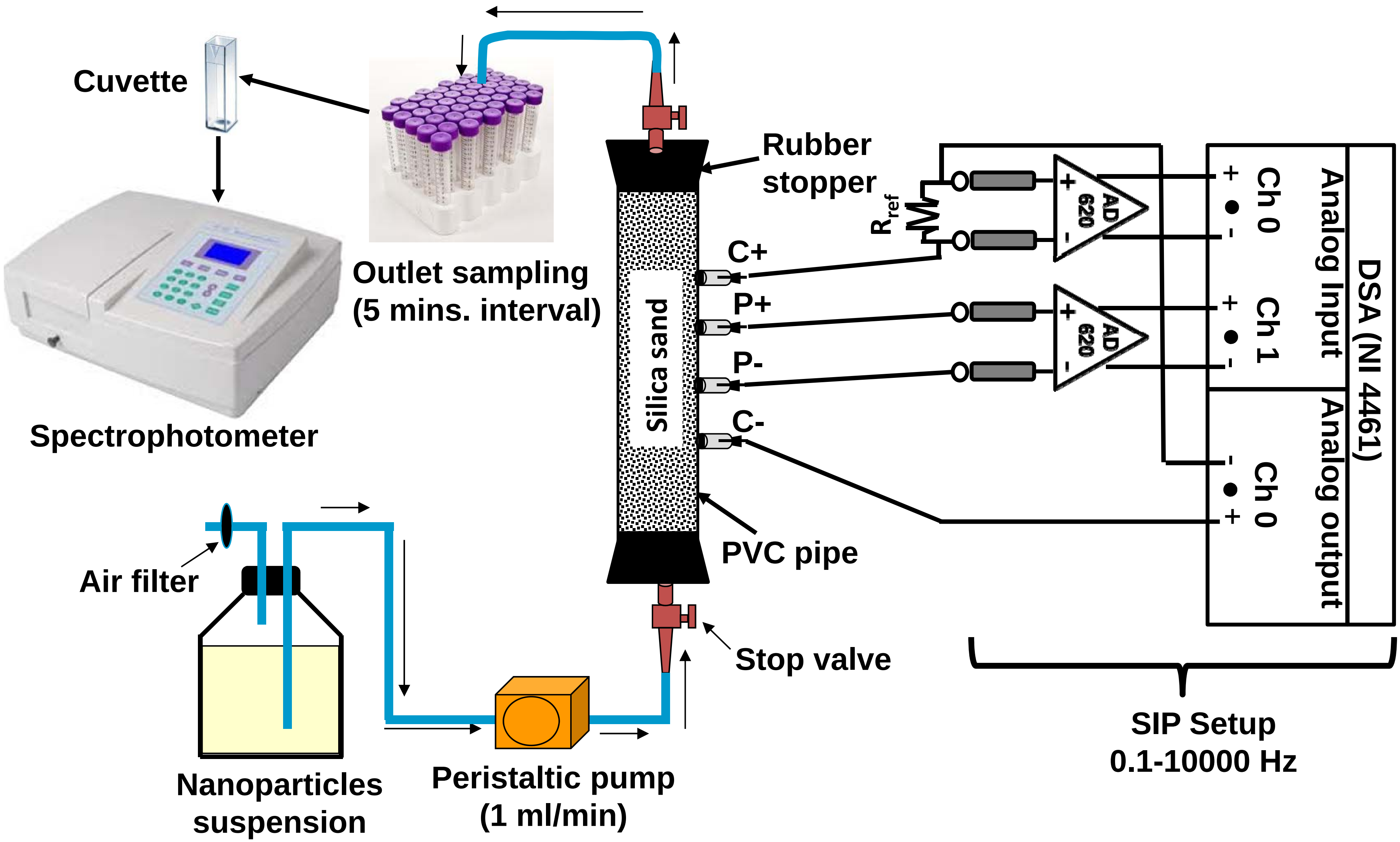
Cuvettes for optical density measurements

Silica sand (Ottawa)
Grain diameter = 500 -700 μm
Porosity = 0.45

Sample holder (PVC)
L = 10 cm
ID = 3.81 cm

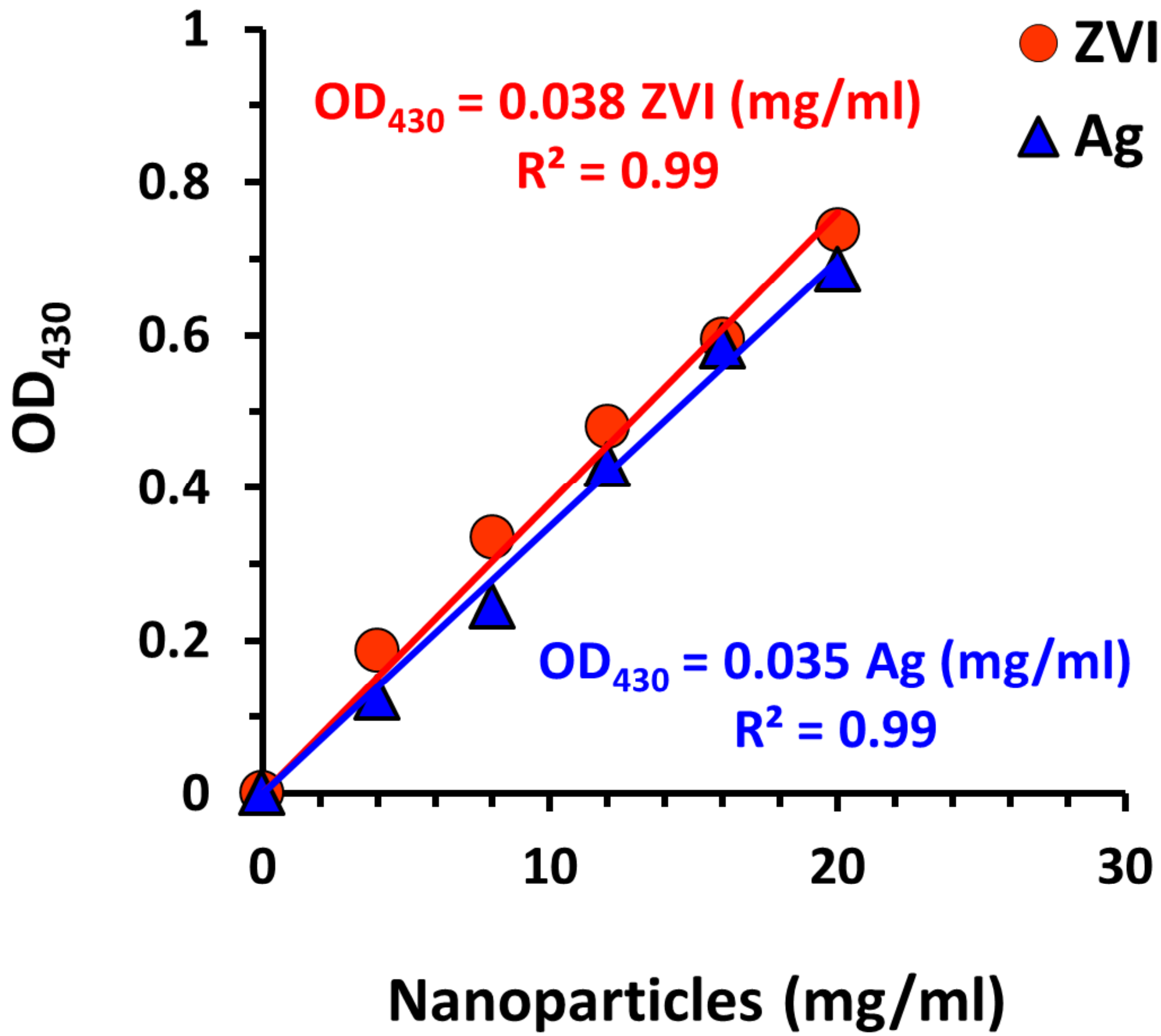
Spectrophotometer
OD at 430 (nm)

Experimental Setup



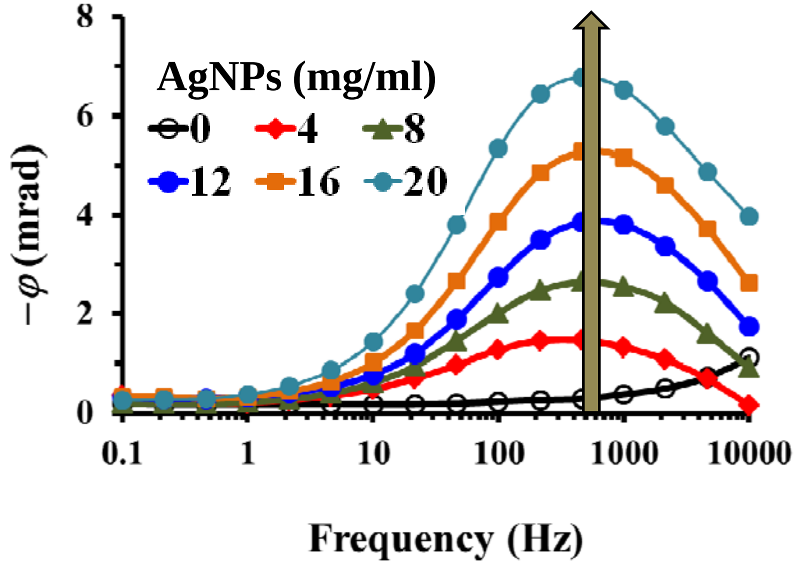
Results

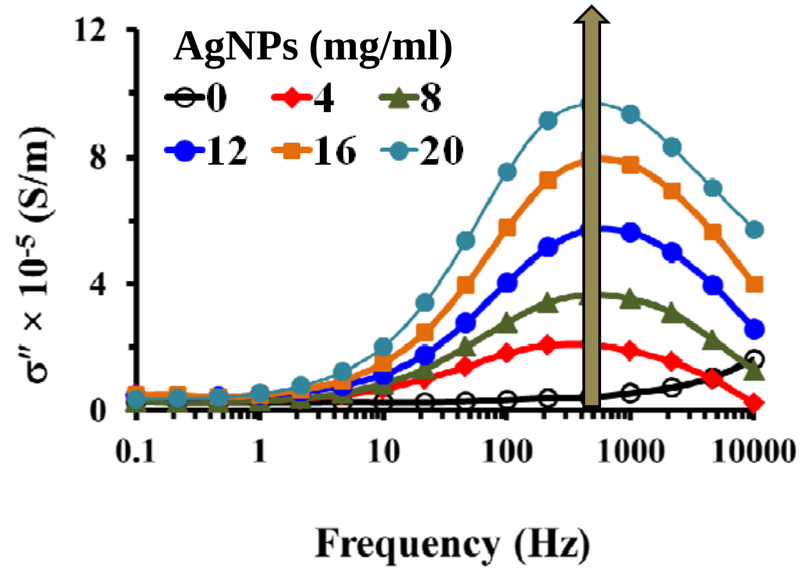
Optical density at 430 (nm) of different conc. Of NPs (Ag & ZVI) in suspensions

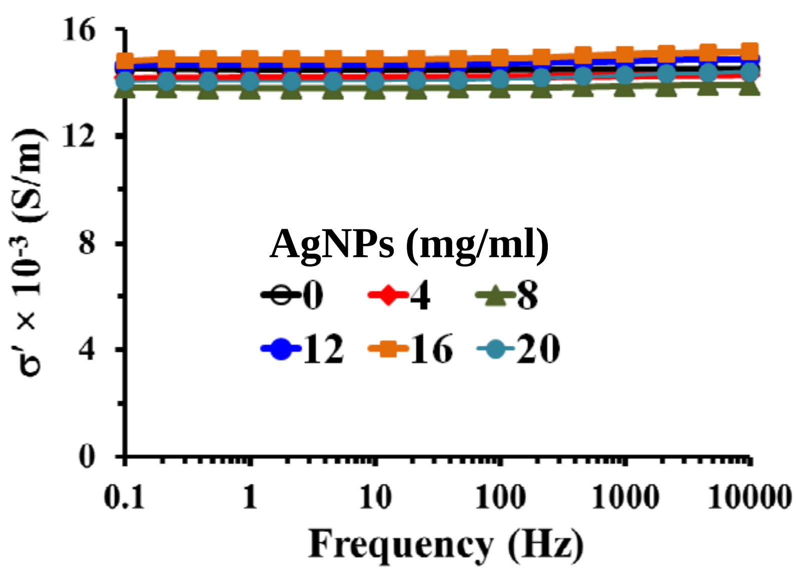


Results

SIP response of different AgNPs concentrations





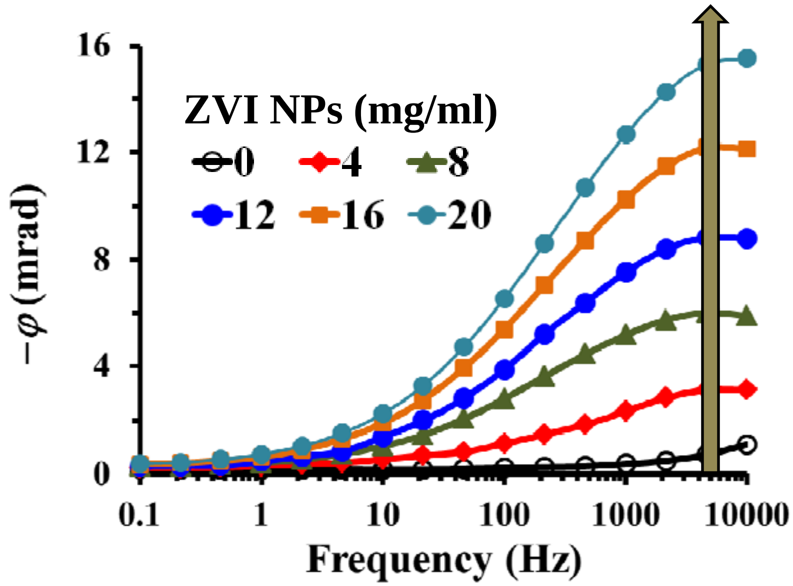


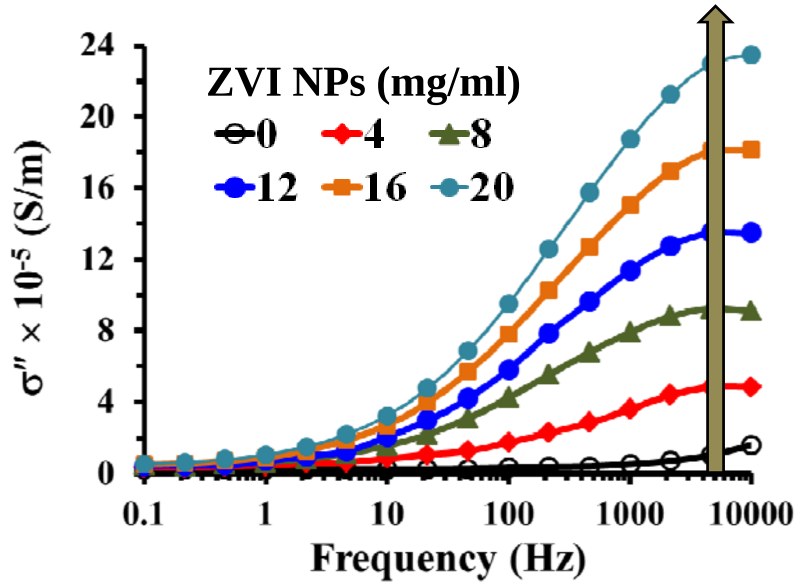
- **The φ and σ″ parameters increased with increasing concentrations of Ag NPs with a well defined relaxation peak at 500 Hz**

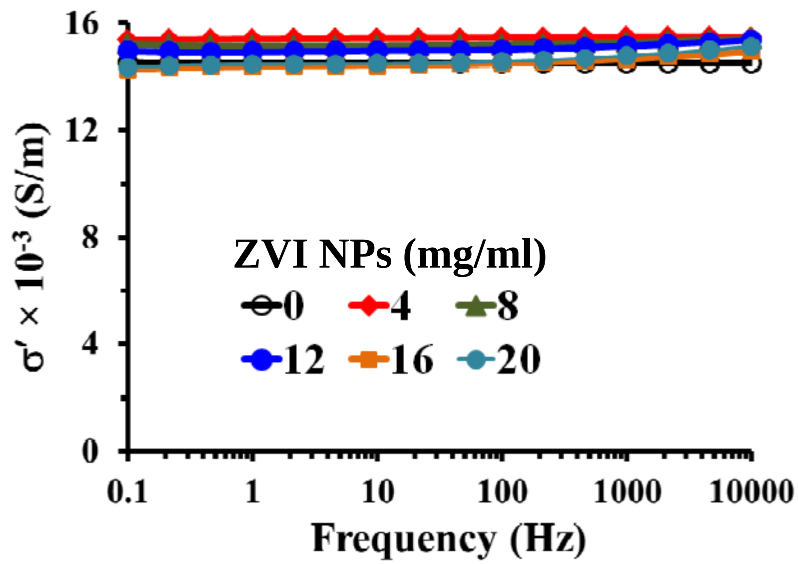
- **Insignificant changes for the σ′**

Results

SIP response of different ZVI concentrations



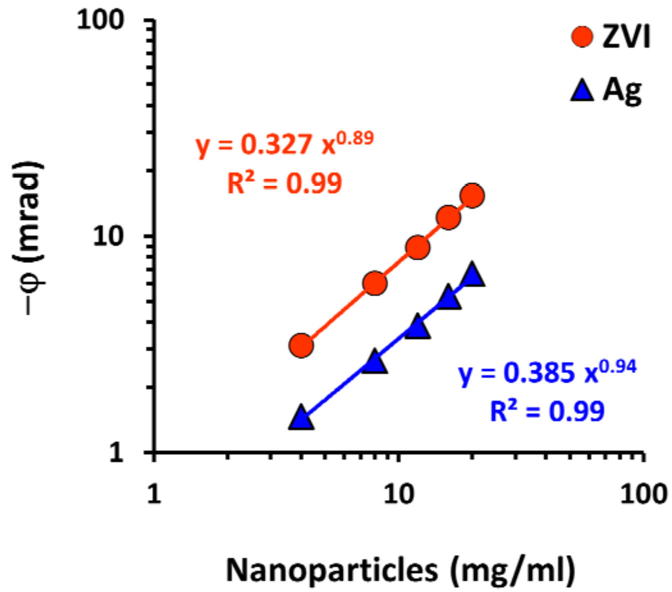


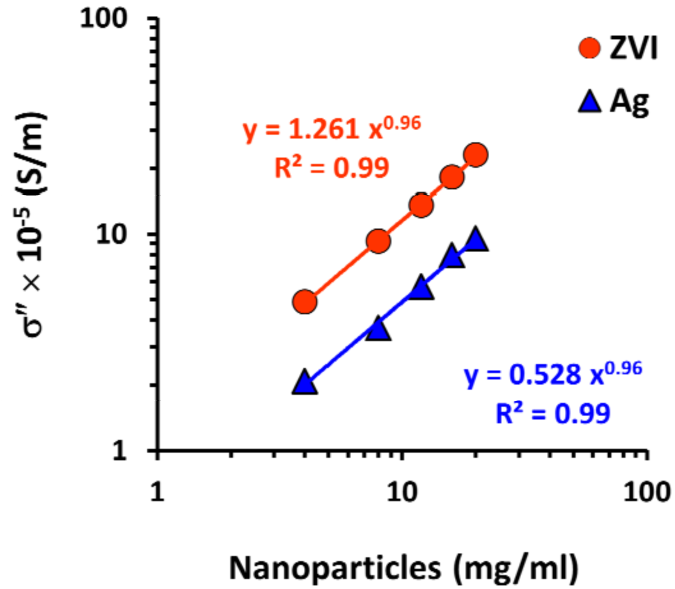


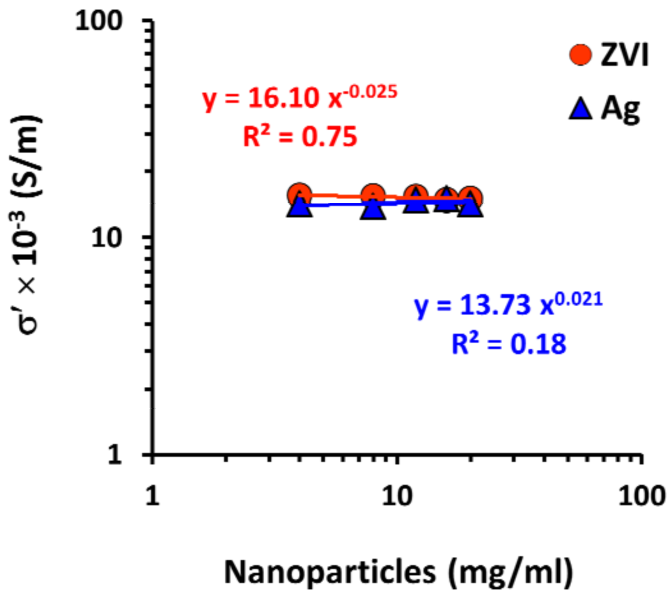
- ❑ The φ and σ″ parameters increased With increasing concentrations of ZVI NPs with a incomplete relaxation peak at 5000 Hz
- ❑ Insignificant changes for the σ′

Results

SIP parameters vs. NPs conc. at relaxation frequency



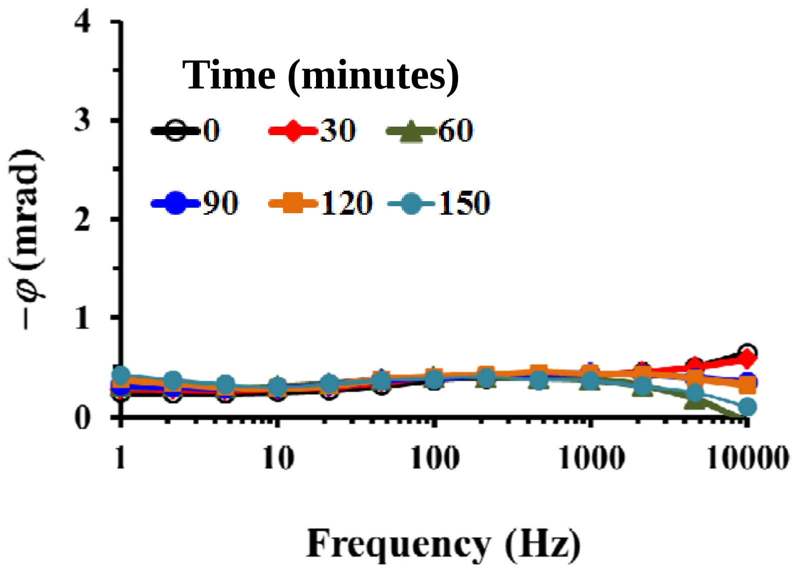


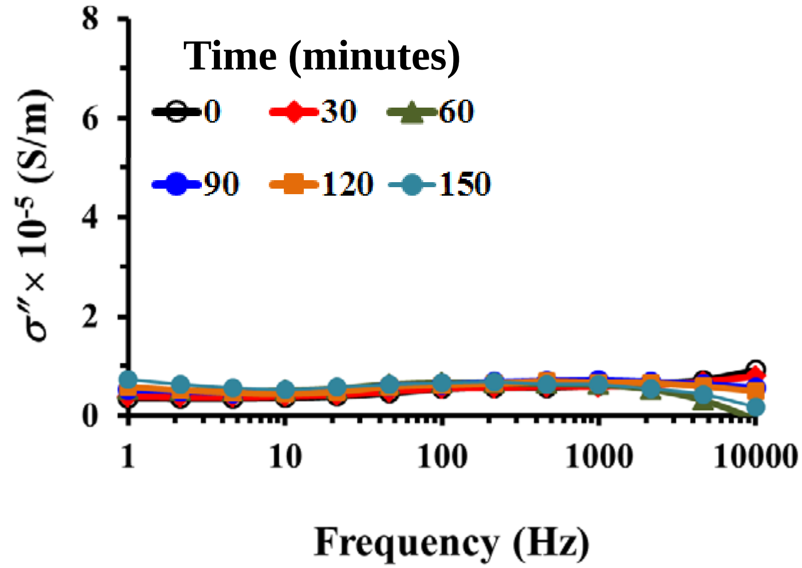


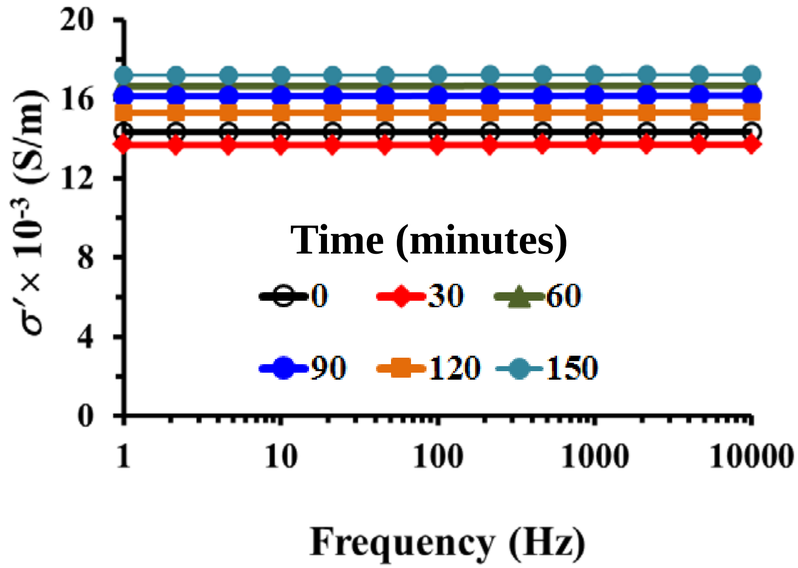
- ❑ **The ZVI NPs show higher φ and σ″ magnitude compared to AgNPs as a function of concentrations**
- ❑ **Insignificant changes for the σ′**

Results

SIP response of agar solution transport in sand column



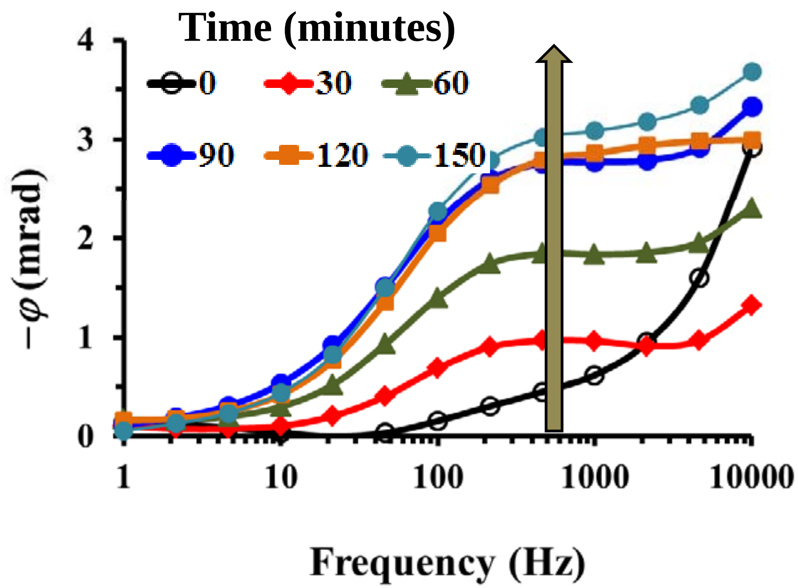


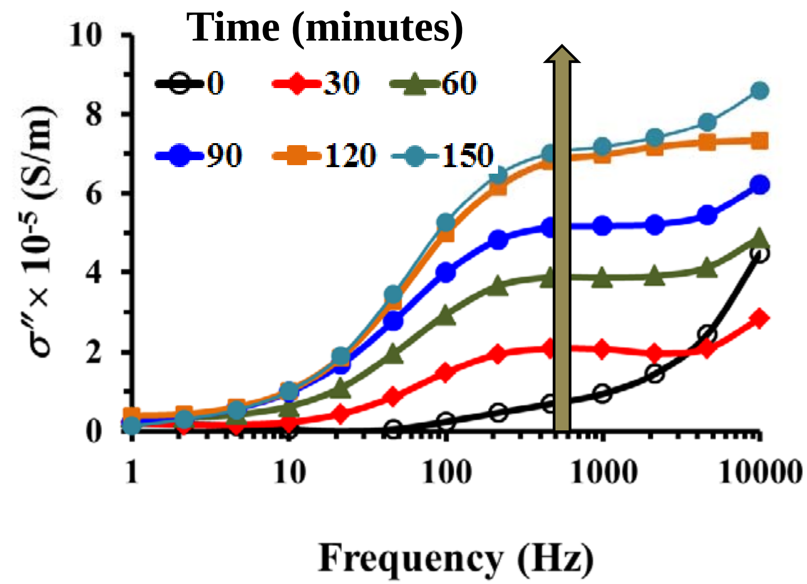


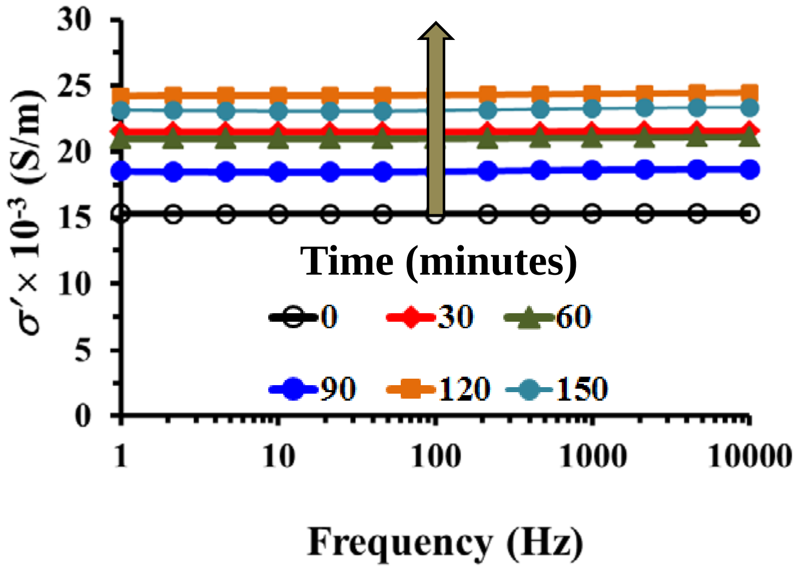
- **Insignificant changes are observed in the SIP parameters due to transport of agar solution in sand column.**

Results

SIP response of AgNPs transport in sand column





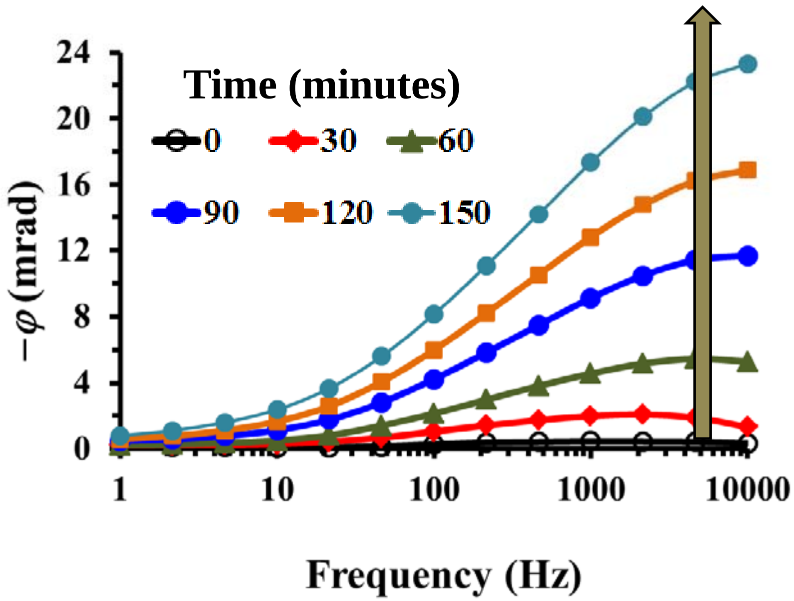


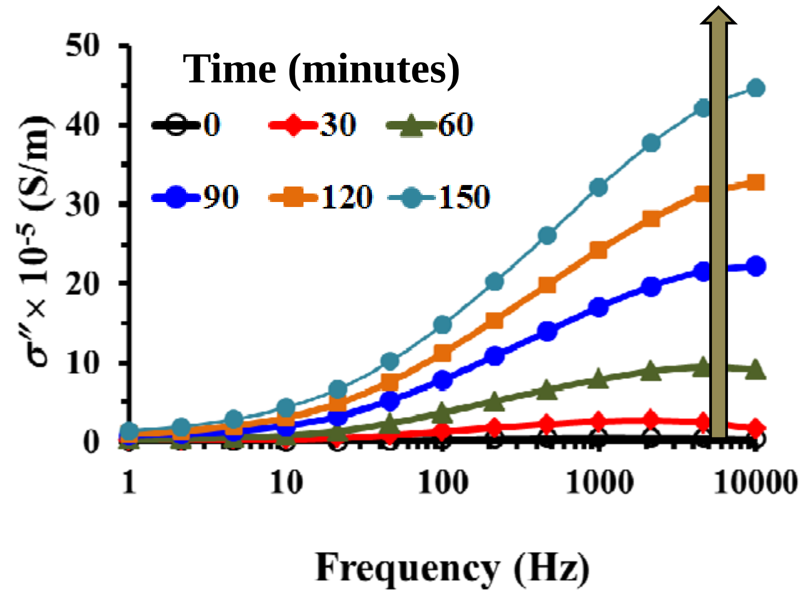
- **SIP parameters increased over time due to the retention of AgNPs during transport in sand column**

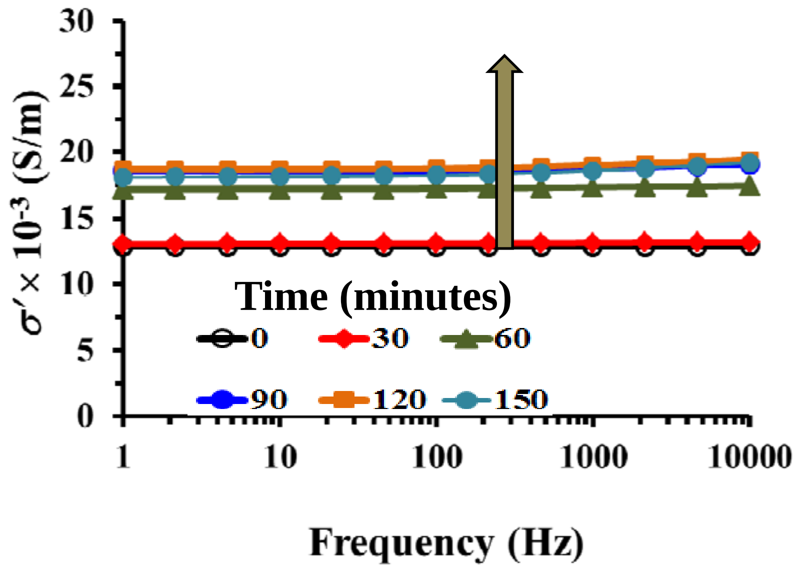
- **φ and σ″ show well defined relaxation peak at 500 Hz.**

Results

SIP response of ZVI NPs transport in sand column



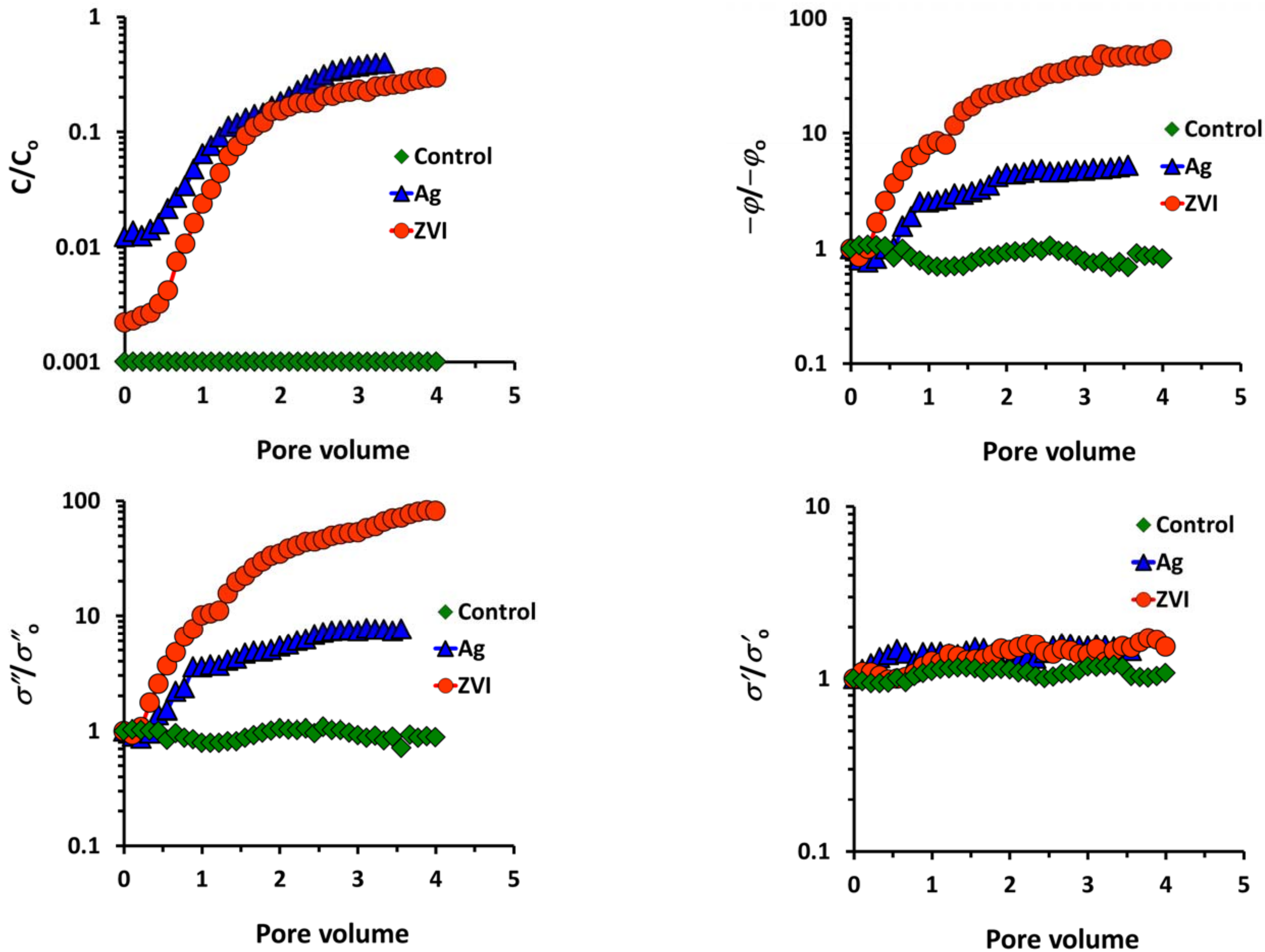




- ❑ **SIP parameters increased over time due to the retention of ZVI NPs during transport in sand column**
- ❑ **φ and σ″ show incomplete relaxation peak at 5000 Hz.**

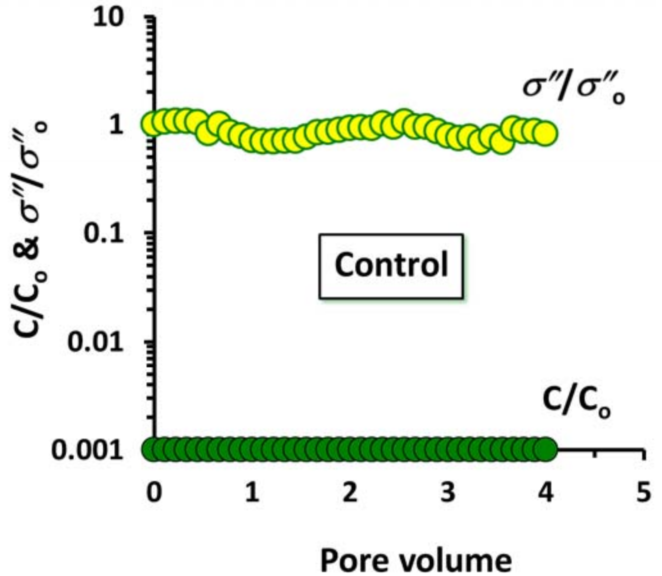
Results

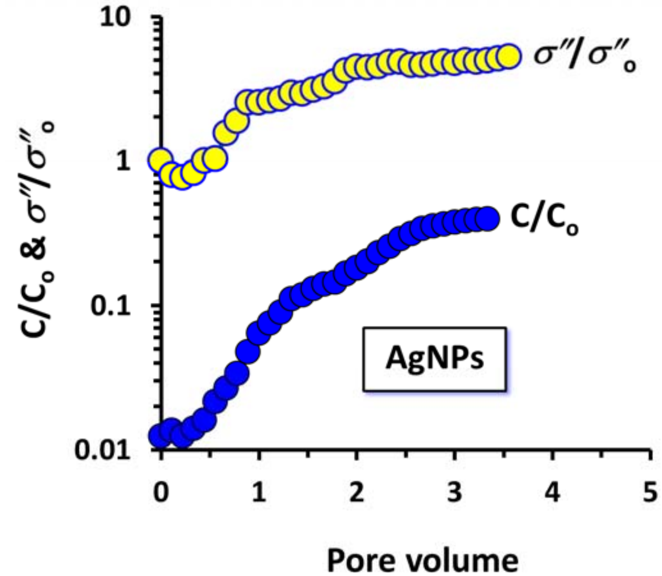
BTC's of normalized NPs C and SIP parameters

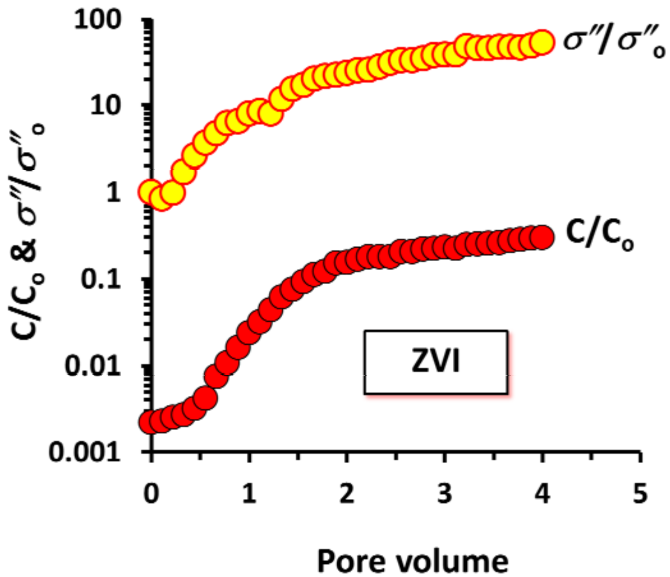


Results

BTC's comparison of normalized NPs C and σ″







- **BTC's of normalized imaginary conductivity component (σ''/σ''_o) mimic the BTC's of normalized NPs concentrations (C/C_o) and the background agar solution.**

Summary & Conclusions

- The magnitude of the φ and σ'' increased with increasing concentration of the nanoparticle concentration with a well-defined relaxation peaks centered at 500 Hz and 5000 Hz for the Ag and ZVI, respectively.

- At the relaxation frequencies, the magnitudes of the φ and σ'' of the ZVI were two times the Ag nanoparticle due to the high surface area of ZVI compared to AgNPs.

- The BTC of normalized outlet Ag was higher in magnitude compared to the BTC of the normalized ZVI which indicates higher retention of ZVI in sand column than AgNPs.

- The higher retention of ZVI reflected in higher magnitudes for the normalized φ and σ''.

Summary & Conclusions

- BTC trends of the normalized phase and imaginary conductivity component were similar to the BTC trends of normalized outlet nanoparticle concentration.

- These results demonstrate the sensitivity of the SIP technique to the presence and transport of nanoparticles within saturated porous media.

- Further studies will investigate the effect of pH, ionic strength, and surface chemistry of nanoparticles and porous media on the subsurface transport of nanoparticles and their associated geophysical signatures.

QUESTIONS

?

AGU FALL MEETING

San Francisco | 9–13 December 2013