**Title: 4D Investigation of groundwater remediation using nanotechnology- a synchrotron-based X-ray micro-tomography study**

Authors: Tannaz Pak[1], Luiz Fernando de Lima Luz Jr[2], Tiziana Tosco[3], Paola Rosa[4], Gabriel Schubert[4], Nathaly Lopes Archilha[4]

[1]Teesside University, [2]Federal University of Parana, [3]Polytechnic University of Turin, [4]Brazilian Synchrotron Light Laboratory (LNLS) - Brazilian Centre for Research in Energy and Materials (CNPEM)

- Presenting author: Tannaz Pak
- Keywords: nanoparticles, zero-valent iron, groundwater remediation, DNAPL, In-situ, X-ray computed micro-tomography, synchrotron, reactive transport

Reactive transport in porous media is a dynamic field of research with open questions particularly at pore-scale. Despite our detailed understanding of non-reactive multiphase flow in porous media, across scales, little is known about the pore-scale dynamics of processes involving chemical reactions alongside fluid flow in porous media. Reactive flow plays a key role in a rage of application including groundwater remediation, $CO_2$ sequestration, metal recovery, and heavy oil recovery. In these processes a chemical reaction is engineered to impact the structure/properties of the host porous medium or the arrangement of fluids it confines. In this contribution we study the classic problem of groundwater contamination with chlorinated solvents but from a pore-scale perspective. Chlorinated solvents are known as a persistent family of aquifer contaminants which, over the past decades, have caused serious health problems (e.g. kidney and liver damage) and some are considered as carcinogenic. Being denser than water, when a leakage occurs at the surface these contaminates sink into the groundwater system and create a source of contamination in form of trapped DNAPLs (i.e. dense non-aqueous phase liquids). The scale of the problem posed by these contaminants is globally significant due to their wide industrial use since the beginning of 20$^{th}$ century e.g. in metal processing plants and dry cleaning.

In this work we performed a synchrotron-based micro-tomography imaging experiment to study the dynamics of the reactive transport process during application of nanoremediation[1]. Nanoremediation is a new technology that injects aqueous suspensions of zero valent iron nanoparticles (nZVI) into contaminant bearing subsurface sediments. These nanoparticles are highly reactive and excellent

electron donors ($Fe^0 \rightarrow Fe^{2+} + 2e^-$). Chlorinated solvents accept those electrons and release their chlorine atoms in form of ions. Example reaction: ($C_2H_2Cl_2 + Fe^0 + 2H^+ \rightarrow C_2H_4 + 2Cl^- + Fe^{2+}$). While nanoremediation concept is proven to be successful at laboratory, pilot, and field scales, the existing practice is far from optimised. A contributing factor to this is the lack of understanding around pore-scale mechanisms that control the nanoremediation process.

Our 4D (time-resolved, 3D) experiment comprised of fluid injections in a column (packed with glass beads) and simultaneous 3D imaging using X-ray micro-CT technique. The study was conducted at the Brazilian synchrotron. For the first time, we captured the evolution of the DNAPL phase structure/distribution, in 3D, during the nanoremediation process. Our data show that a gas phase is released during nanoremediation which remobilises the trapped DNAPL phase, facilitating its complete removal in subsequent soil flushing processes. Our findings also show the evolved gas reduces the relative permeability of the contaminated water phase from 60% to less than 1%. This suggests that the gas evolution provides a temporary control on the contamination plume propagation. This favourable outcome is caused by pore-scale blockage of water flow-pathways by the released gas. In field applications of nanoremediation (or similar in-situ remediation technologies) gas formation is considered as a sign of effectiveness of the process. This study provides a quantitative evidence on how this gas release can impact the contamination removal and limit its propagation.

Reference:

1. Pak, T. *et al.* Pore-scale investigation of the use of reactive nanoparticles for in situ remediation of contaminated groundwater source. *Proc. Natl. Acad. Sci.* **117**, 201918683 (2020).