

1 **Application of Nanotechnology in Removal of NAPLs from Contaminated**
2 **Aquifers – A Source Clean-up Experimental Study**

3 Tannaz Pak^{1*}, Nathaly Lopes Archilha², Raaid Al-Imari¹

4 ¹Teesside University, ² Brazilian Synchrotron Light Laboratory (LNLS)

5 Email: t.pak@tees.ac.uk, T: +44 (0)1642 342466

6 ORCID: Tannaz Pak (0000-0001-7635-9333), Nathaly Lopes Archilha (0000-
7 0003-0324-3748)

8 **Keywords:** Nanotechnology, Porous media, Removal of organic contaminants,
9 Nonaqueous phase liquids (NAPLs)

10

11 **Abstract**

12 This work investigates the removal of non-aqueous phase liquids (NAPLs) from
13 groundwater resources using nanotechnology. We present results of a series of
14 multiphase fluid displacement experiments conducted in a naturally occurring
15 sandstone rock. These experiments involve injection of an aqueous suspension of
16 silica nanoparticles to remove a trapped NAPL phase. Specifically, the effect of
17 nanoparticle concentration on the efficiency of the NAPL removal is studied. Our
18 results show that silica nanoparticles successfully remobilised the trapped NAPL
19 phase and resulted in 13% increase in its removal efficiency. The optimal
20 concentration for NAPL removal efficiency is found to be 0.3 wt%.

21 **1. Introduction**

22 Cleaning the subsurface groundwater resources contaminated with nonaqueous
23 phase liquids (NAPLs) have been the subject of extensive research in the recent
24 decades (Soga, Pagea and Illangasekare, 2004; Trellu *et al.*, 2016). New
25 technologies which offer effective contaminant removal efficiencies at lower costs
26 are always in demand. When dealing with removal of NALP form contamination
27 source (i.e. source remediation) the main mechanism to overcome is capillary
28 trapping (Wilson, 1990). It is well-established that removal of a non-wetting fluid
29 from porous media by injection of the wetting phase is always less than 100%
30 efficient (Wilson, 1990). The wetting phase is a fluid that has a higher tendency to
31 spread on a solid surface in presence of another non-wetting fluid (Craig, 1971).
32 As a result, a portion of a non-wetting phase will remain trapped in the porous
33 media. Capillary trapping has previously been directly observed in micro-model
34 studies (Jeong, Corapcioglu and Roosevelt, 2000). More recently, non-destructive
35 3D imaging techniques, such as X-ray computed micro-tomography, have enabled
36 direct observation of capillary trapping of non-wetting fluids in naturally occurring
37 porous media (Iglauer *et al.*, 2011; Berg *et al.*, 2013; Pak *et al.*, 2015). Capillary
38 trapping is governed by the competition between the capillary, viscous, and
39 gravitational forces. Specifically, the relative importance of the viscous to capillary

40 forces is measured using capillary number ($N_c = \mu V / \sigma$) where μ is viscosity (Pa.s),
41 V is velocity (m/s) and σ is the interfacial tension (IFT) in N/m.

42 Bioremediation is one of the widely practiced and cost-effective technologies that
43 uses microbes to degrade the contaminant in-situ (Aulenta, Majone and Tandoi,
44 2006; Daghighi *et al.*, 2017). Another successful NAPL removal method involves
45 injection of surfactants to reduce the IFT between the aqueous and the oil phases
46 (Mulligan, Yong and Gibbs, 2001; Paria, 2008; Cheraghian and Hendraningrat,
47 2016). This reduces the capillary forces and hence eases the remobilisation and
48 removal of the trapped NAPL phase. Within this context, among the more recent
49 technologies is the use of nanofluids (nanoparticle suspensions) to improve the
50 efficiency of NAPL removal at microscopic level. More specifically, reactive
51 nanoparticles (NPs) such as zero-valent iron (Fe^0) NPs are successful in in-situ
52 degradation of some contaminants (specifically chlorinated ones) into less harmful
53 ones (Tosco *et al.*, 2014). Further, recent developments in industrial scale
54 manufacturing of engineered NPs at low cost makes NP-based NAPL removal an
55 attractive option. However, although promising, the health implications of long-
56 term exposure to reactive particles such as Fe^0 are not yet fully understood, i.e.
57 the environmental aspects of this technology requires further research (Bardos *et al.*,
58 2011). In this sense, NPs with better biocompatibility are more favourable.
59 Specifically, silica NPs have been safely used in diagnosis and target drug delivery
60 in the bio-medical field, widely (Santra *et al.*, 2004; Jin *et al.*, 2007; Bharti *et al.*,
61 2015). Silica-based NAPL removal method is hence a more environmentally
62 friendly candidate. Literature studies have shown that silica, alumina, and titanium
63 oxide nanoparticles are suitable candidates for designing nanotechnology-based
64 enhanced oil recovery processes (Ogolo, Olafuyi and Onyekonwu, 2012; Ahmadi
65 *et al.*, 2013; Hendraningrat, Li and Torsæter, 2013; Roustaei, Saffarzadeh and
66 Mohammadi, 2013; Bennetzen and Mogensen, 2014; Zhang *et al.*, 2014;
67 Hendraningrat and Torsæter, 2015; Negin, Ali and Xie, 2016).

68 This work investigates the effect of nanofluid concentration on the recovery
69 efficiency of NAPLs from a naturally occurring sandstone. In our experiments, we

70 used hydrophilic 30-nm silica NPs, in three different concentrations of 0.1, 0.3 and
71 0.5 wt%. We monitored the fluid pressure drop as well as the concentrations of
72 NPs in the effluent. This allowed determining the NP retention in the rock. In
73 addition to the removal of NAPL contaminants from water resources. Results of
74 this study has implications for a broad range of applications, including enhanced
75 hydrocarbon recovery from geological formations and secure CO₂ storage in the
76 carbon capture and storage (CCS) process.

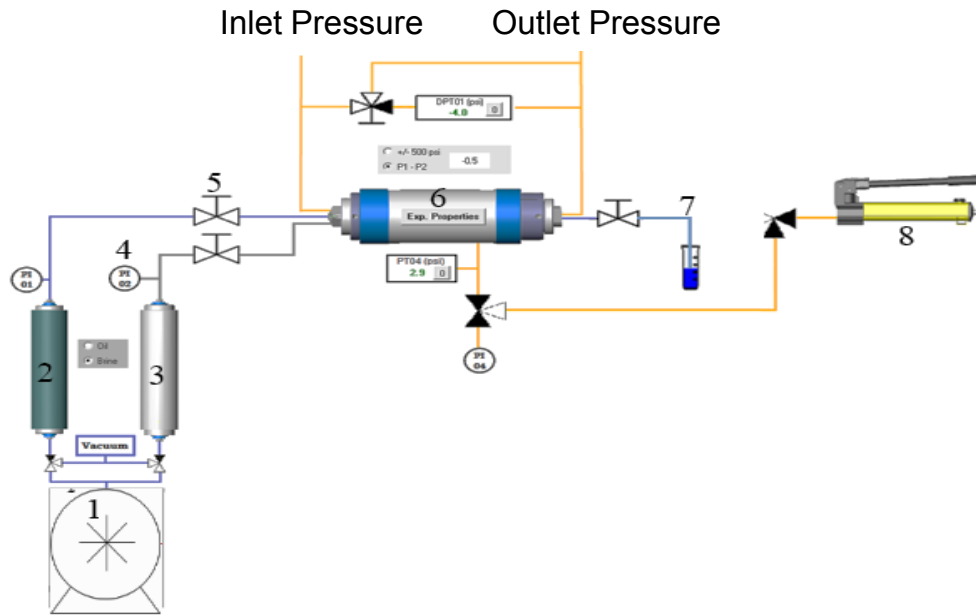
77 **2. Materials and Methods**

78 **Materials:** At nanoscale matters display high surface area per unit volume when
79 compared to larger scales. Therefore, nanomaterial are known to show properties
80 closer to the behaviour of individual molecules (Khler and Fritzsche, 2004). For
81 instance, a substance may not dissolve in water at macro scale while it may be
82 easily soluble in water at nanoscale. Nanofluids are referred to fluids that consist
83 of a base fluid (aqueous or organic) with nano-sized particles (< 100 nm) dispersed
84 in them. A key property of nanofluids that rules the effectiveness of their application
85 is their stability which needs to be closely monitored when designing a NP-based
86 NAPL removal process (Metin *et al.*, 2011; Yu and Xie, 2012).

87 We performed fluid displacement experiments in a cylindrical core plug (D=2.53
88 cm, L=6.23 cm) from a water-wet Scottish sandstone outcrop (Locharbriggs).
89 Laboratory measurements showed effective porosity of 23.3% and the
90 permeability of 284.9 mD for this core sample. Scanning electron microscopy
91 images (See Figure S1 in the supporting information) show the pore-sizes in this
92 sandstone are in the range of tens of μm . Analysis of oil/water displacement
93 experiments (see Figure S2 in the supporting information) show that the pore-
94 throat sizes are in the range of a few μm . This makes the pore structure of this
95 sandstone sufficiently open to allow transport of stable suspensions of
96 nanoparticles. It should be noted that the pore-throat size distribution of a porous
97 material is accurately determined using the mercury intrusion porosimetry

98 technique. Nevertheless, an approximate estimate of the size range of pore-throats
99 could be obtained by employing the pressure drop signal of oil/water drainage step.
100 The nanofluids were prepared by diluting a highly concentrated (25%) suspension
101 of hydrophilic silica NPs (APS = 30 nm) to achieve 0.1, 0.3, and 0.5 wt%. We used
102 both deionized water and brine (3 wt% NaCl) for this dilution. To maximize colloidal
103 suspension the diluted nanofluids were placed in an ultrasonic bath for 30 minutes.
104 Viscosity of the nanofluids shows changes insignificant to the flow processes
105 studied here, i.e. only ~1%, hence viscosity is assumed to be equal to that of water.
106 A mineral oil (n-decane) was used as the NAPL phase.

107 **Experimental Set-up and Fluid Displacement Test Procedure:** Figure 1 shows
108 a schematic of the experimental setup used in this study. The tests comprised of
109 fluid injections (oil/water/nanofluid) while monitoring the effluent fluid as well as
110 recording the pressure drop across the core plug. The outlet stream was open to
111 atmospheric pressure and the experiment was conducted under ambient
112 temperature. Initially, the core plug was vacuum saturated with the aqueous
113 solution. After loading the core in this set-up the confining pressure of 1000 psi
114 was applied to ensure the fluid flow is one-dimensional, i.e. from the core inlet to
115 its outlet. During the flow process the differential pressure (ΔP) across the core
116 was recorded every 30 seconds. Subsequently, the oil was injected at three
117 different flowrates (1 mL/min, 3 mL/min and 4 mL/min) until no more brine was
118 produced. This was to ensure the core contains a substantial amount of oil before
119 the subsequent displacements were performed. At this point, 22 pore volumes of
120 oil were injected in the core.



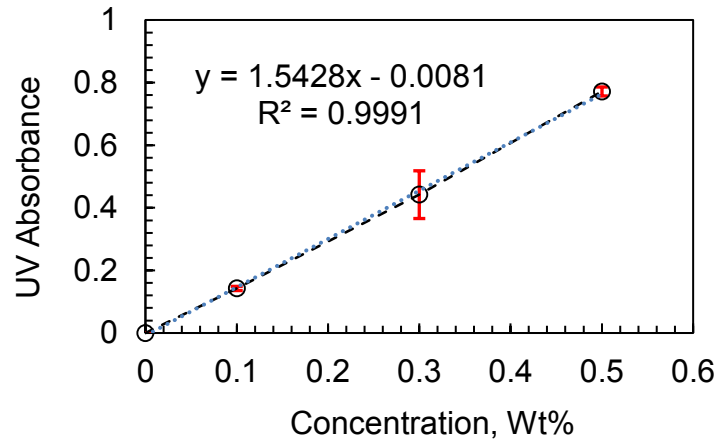
121

122 Figure 1: *Experimental setup*, (1) pump, (2) oil reservoir, (3) water reservoir, (4)
 123 pressure gauges, (5) valves, (6) flow cell (Hassler type), (7) effluent into test
 124 tubes, (8) confining pressure pump.

125 After the initial oil saturation, the fluids were injected at a constant rate of 0.25
 126 mL/min, equivalent to 3.4% pore-volume/min. This is equivalent to capillary
 127 numbers (N_c) in the order of 10^{-7} , which ensures that the fluid displacements are
 128 representative of flow at aquifer scale. The next stage was water injection until no
 129 more oil was produced, which established the residual oil saturation (S_{or}). The
 130 experiment continued by injecting nanofluids at three different concentrations of
 131 0.1, 0.3, and 0.5 wt%. Any additional oil produced at these stages indicates the
 132 effectiveness of nanofluid injections in remobilisation of the trapped oil. At all
 133 injection steps, samples of the effluent fluids were collected at the core outlet. This
 134 allowed measuring the amount of oil and nanofluid remained in the core using the
 135 principle of material balance. These values were used for calculation of fluid
 136 saturations and the NAPL removal efficiency. The NP retention curve was also
 137 plotted by analysing these samples.

138 **Analysis of the Effluent Samples and IFT Measurement:** The ultraviolet–visible
 139 (UV) spectrometry was used to measure the concentration of NPs in the effluent

140 fluid. Figure 2 shows the UV absorbance response for deionised water and the
141 nanofluids at the three concentrations used in this study. This is a calibration curve
142 that was used to find the concentration of NPs in the effluent samples based on
143 their UV absorbance.



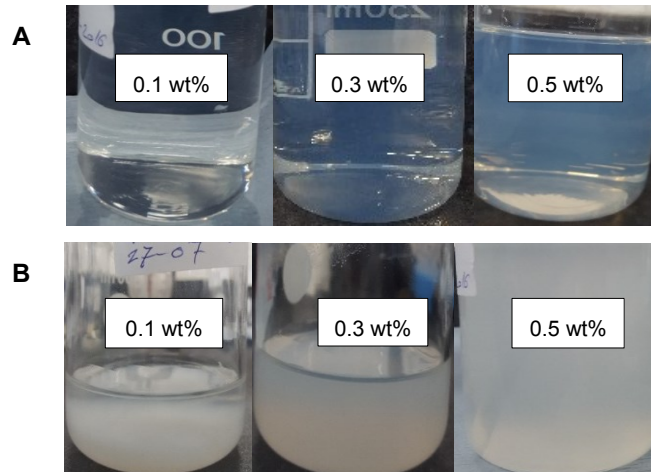
144

145 Figure 2: Calibration curve used to find nanofluid concentration based on its UV
146 absorbance.

147 IFT was measured using the Du Nouy ring method (Macy, 1935), which works with
148 raising a ring initially immersed in a liquid into a second liquid sitting on the top.

149 3. Results and Discussion

150 **Nanofluid Stability:** The brine-based nanofluids (3 wt%, NaCl) showed significant
151 instability which resulted in agglomerations of NPs. Figure 3 shows the brine-
152 based nanofluids at various concentrations on the day of preparation (A) and after
153 two days (B). The nanofluid became cloudy resulting in NP aggregation and
154 sedimentation.

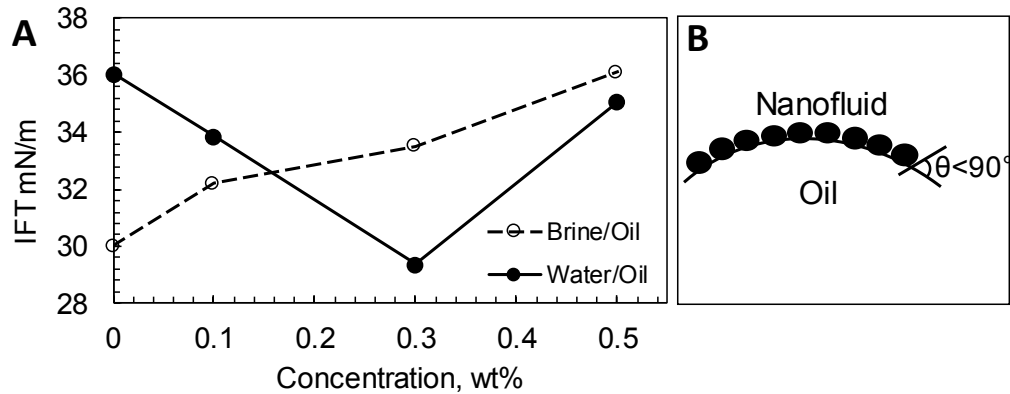


155

156 Figure 3: Brine-based (3 wt%, NaCl) nanofluids at three concentrations of 0.1,
 157 0.3, and 0.5 wt%), (A) on the day of preparation, and (B) after two days.

158 The salinity of these brine-based nanofluids, i.e. 3 wt%, is higher than the NaCl's
 159 critical salt concentration (CSC). CSC is the maximum salt concentration at which
 160 the stability can be achieved. To achieve better stability, one should use smaller
 161 NPs or reduce the salt concentrations. Here, the 3 wt% concentration was used to
 162 represent aquifers with average salinity. Temperature is another parameter that
 163 affects colloidal stability. At higher temperatures the CSC decreases making the
 164 application of brine-based nanofluids more challenging for injection in geological
 165 formations with high temperatures. Water-based nanofluids were stable.

166 **Interfacial Tension:** For the water-based nanofluids, the IFT decreases as the
 167 nanofluids concentration increases (Figure 4). The 0.3 wt% water-based nanofluid
 168 showed the minimum IFT, i.e. 29.6 mN/m, this represents a reduction of 18%
 169 compared to the oil/water system. At of 0.5 wt% concentration the nanofluid
 170 instability causes the IFT to measure at 35.06mN/m, a value very close to the
 171 original oil/water system (36.06 mN/m).



172

173 Figure 4: (A) IFT as a function of nanofluid concentration, (B) NPs position
 174 themselves at the oil/water interface, acting as surfactant molecules (Binks,
 175 2002)

176 The reduction in IFT is due to adsorption of NPs to the fluid/fluid interface (Figure
 177 4B). Silica is hydrophilic, therefore, the bulk of the particles preferably remains
 178 within the aqueous phase. The fluid/solid contact surfaces have lower energy
 179 levels compared to fluid/fluid interfaces. As a result, the system will have a lower
 180 total interfacial energy with the particles adsorbed the fluid/fluid interface (Binks,
 181 2002).

182 The brine-based nanofluids showed an increasing trend with the NP concentration.
 183 This also confirms the brine-based nanofluids were unstable suspensions.
 184 Therefore, for the subsequent fluid displacement experiments we only used the
 185 water-based nanofluids.

186 **NAPL Removal Efficiency:** Figure 5 shows the remaining NAPL saturation after
 187 the four oil displacement steps (i.e. water and nanofluid injections). Initially, 72.6%
 188 of the pore space was occupied with the NAPL phase, making the water saturation
 189 27.4%. The water injection resulted in production of 64% of this NAPL phase,
 190 reducing the remaining NAPL saturation to 26.13%.

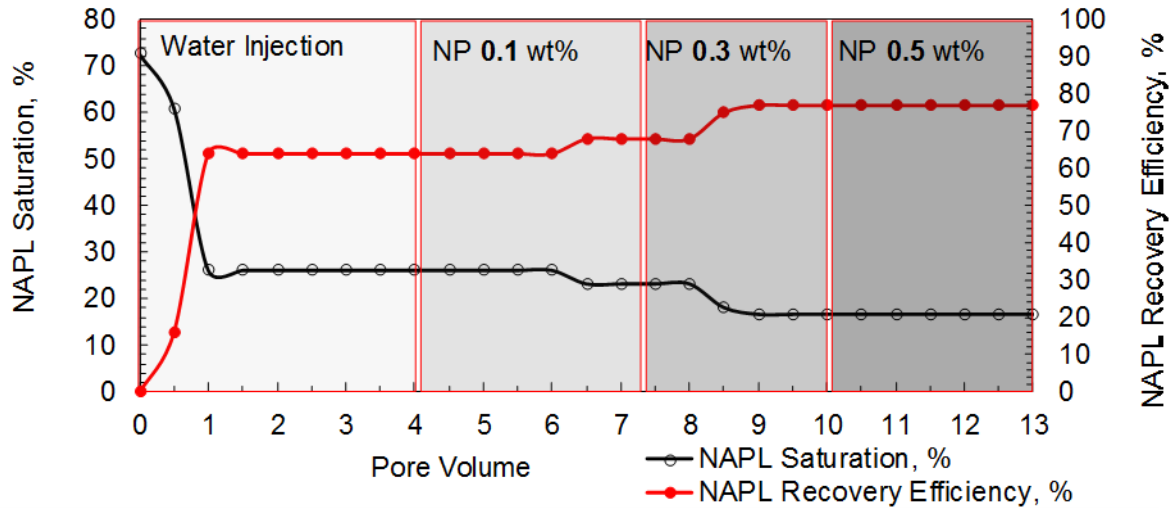


Figure 5: NAPL saturation during the fluid displacement steps.

191

192

193 As shown the NAPL production has occurred during the first PV of water injection.

194 This behaviour is an indication of a water-wet system where the non-wetting fluid

195 becomes trapped in a single pore or within multiple connecting pores, surrounded

196 by the wetting corner films (Berg *et al.*, 2013; Pak, 2015). It is, therefore, impossible

197 to produce this remaining oil unless one or more of the key parameters controlling

198 the capillary trapping are changed. These include the flow regime, rock wettability,

199 and fluid/fluid IFT. Here, the introduction of the nanofluids targets the IFT

200 alteration. It should be noted that in cases where the rock is preferentially oil wet

201 the effect of nanofluids can be two-folds impacting both the wettability and IFT (Li

202 and Torsæter, 2015).

203 The subsequent injections of the nanofluids further reduced the NAPL saturation

204 to 23.23% and 16.69%, respectively for the 0.1 and 0.3 wt% concentrations. This

205 corresponds to increase of the recovery efficiency to 68% and 78%, respectively.

206 No more additional oil was produced by injecting nanofluid at 0.5 wt%

207 concentration. This can be explained by the IFT vs NP concentration trend, shown

208 in Figure 4A. At 0.5 wt% the water-based nanoparticle solution becomes unstable

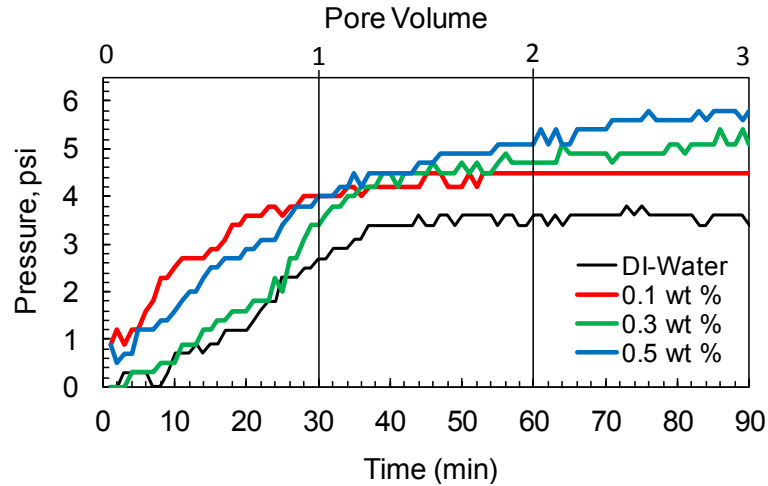
209 showing an IFT close to that of the water/oil IFT with no NPs in. Therefore, our

210 results suggest that unstable suspensions have little effect on IFT and hence NAPL

211 removal.

212 **Nanoparticle Retention:** The studied particle-rock pair was selected such that the
213 particle attraction to the rock surface and hence the particle retention in the core
214 is minimised. The particle adsorption onto the rock surface is controlled by the
215 balance of the attractive/repulsive forces between the particles and the rock
216 surface. Zeta potential measurement reflects this resultant force (Hunter, 1981).
217 This sandstone is mainly composed of quartz (i.e. SiO₂) mineral. Zeta potential
218 analysis on powdered samples of this rock measured values of -19.5 mV at pH~7.
219 From the literature the zeta potential for silica nanoparticles is measured to be
220 close to -30 mV at pH~7 (Kumar *et al.*, 2004). Therefore, no particle-particle and
221 particle-rock attraction is expected. Hence, particle retention on this sandstone
222 should be negligible.

223 An insignificant increase in the differential pressure across the core plug was
224 observed during the nanofluid injection steps compared to water injection step. As
225 shown in Figure 6, the pressure drop increases with increase in particle
226 concentrations. The injection flow rate was kept constant, hence the increased
227 differential pressure reflects some progressive pore-structure clogging caused by
228 particle entrapment within the rock. It is well-established that when transported in
229 porous media, nanofluids lose a portion of their particles through adsorption to the
230 solid surface (Bradford and Torkzaban, 2008). The amount and pattern of this
231 retention has implications for transport properties of the porous media (e.g.
232 permeability), therefore, measuring NP retention is critical in designing a
233 successful nanofluid-based NAPL removal process. Here the permeability is
234 measured to decrease from 284.904 mD to 227.92 mD, 183.15 mD, and 170.94
235 mD for the nanofluid injection steps at 0.1 wt%, 0.3 wt% and 0.5 wt%
236 concentrations, respectively. It should be noted that these measurements are end
237 point relative permeability values calculated based on the pressure drop recorded
238 at the end of each fluid injection step (Figure 6). These measurements suggest
239 that although the relative permeability has decreased, it has remained within the
240 same order of magnitude as the absolute permeability, making nanofluid injection
241 a feasible option for NAPL removal from this rock.

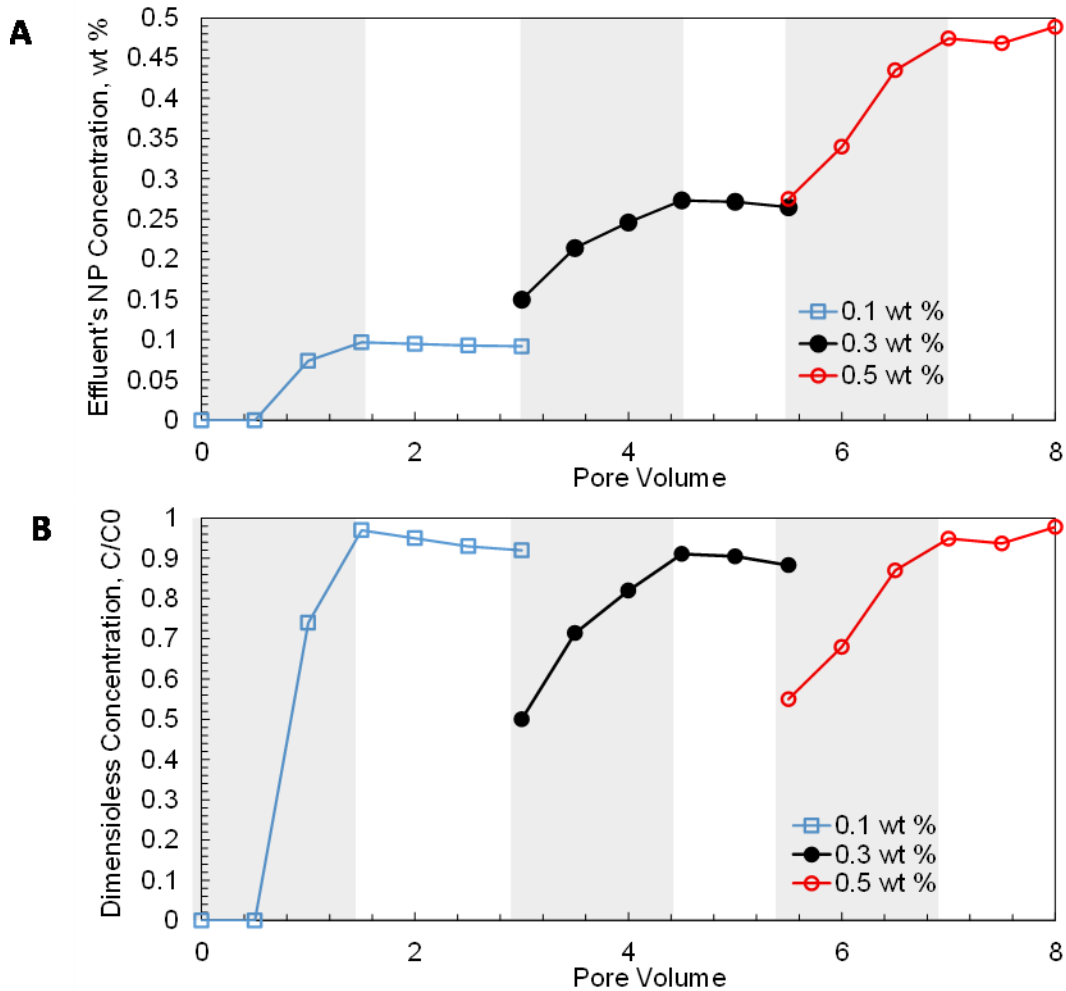


242

243 Figure 6: Pressure drop across the core, recorded during the injection steps.

244 Figure 2 shows the optical absorbance of nanofluids at 228 nm wavelength. For
 245 nanoparticle concentration of 0.1 wt%, 0.3 wt% and 0.5 wt% there is a linear
 246 relationship between the concentration and the optical absorbance. This
 247 calibration curve was used to determine the nanoparticle concentration of effluent
 248 fluids. The adsorption-desorption of NPs on the pore walls should eventually reach
 249 an equilibrium with continuous injection. As a result, the NP concentration of the
 250 effluent fluid will increase over time. For our experiment, the maximum adsorption
 251 capacity of the rock is reached after the 1.5 PVs of fluid injection (Figure 7). Beyond
 252 this point, the pressure drop and the effluent's NP concentrations have converged
 253 to constant values. This convergence point depends on the NP/rock interaction,
 254 available rock surface area, and the heterogeneity of the pore-structure.

255 Figure 7 shows the retention (breakthrough) curves (Ben-Moshe, Dror and
 256 Berkowitz, 2010; Wang *et al.*, 2012) for the injections performed in this study. Both
 257 effluent NP concentration and dimensionless concentrations (i.e. the ratio of NPs
 258 concentration in the effluent to that of the injected fluid) are shown on this plot.
 259 After injection of 1.5 PVs 91% to 97 % of the injected NPs reach the core outlet.
 260 Due to the stability of the nanofluids as well as the significant difference between
 261 the NPs size and that of rock pore-throats (order of micro-meters) for this highly
 262 permeable sandstone shows no significant pore-space clogging.



263

264 Figure 7: Nanoparticles breakthrough curves, (A) Nanoparticle concentration, (B)
 265 Dimensionless concentration normalised by the injection concentration

266 Pore

267 **4. Conclusions**

268 This paper presents the results of a series of multiphase fluid flow injections in
 269 porous media to investigate the effectiveness of silica-nanofluids in removal of
 270 NAPL fluids from contaminated porous media. Specifically, this study investigates
 271 remediation of contamination sources using immiscible displacement processes.
 272 Our experiments show that:

- 273 1. Silica-nanofluid has successfully remobilised the trapped contaminant
274 phase, reducing its saturation by 9.44%. This is equivalent to 13%
275 improvement in the recovery efficiency.
- 276 2. For the fluid pair and the NPs under study the optimum NP concentration in
277 terms of NAPL removal is 0.3 wt%.
- 278 3. The main mechanism which increased the NAPL recovery is the reduction
279 in IFT, with NPs acting as surfactants.
- 280 4. To achieve an effective NAPL removal the primary requirement is to have a
281 stable nanofluid suspension and controlled particle retention.

282 The presented analysis show that only a small fraction of NPs was retained in the
283 sandstone core due to the negative surface charge of the particles and the rock.
284 This particle retention caused only minor increase in the required injection
285 pressure during the nanofluid injection steps. This is mainly due to the rock's high
286 permeability and the significant difference between the NP size (controlled by
287 suspension stability) and the pore-throat sizes. As a result, the studied
288 NPs/fluids/rock combination are suitable for NP-based remediation.

289 **Acknowledgements:**

290 This project was partly supported by the Royal Academy of Engineering under the
291 Newton Research Collaboration Programme (Academy Reference:
292 NRCP1516/1/159). We thank Jeffrey Lawrence, Marwan Rezk, and Richard Medd
293 for their helps in SEM imaging and Zeta potential measurements.

294 **References:**

- 295 Ahmadi, M. *et al.* (2013) 'Zeta-potential investigation and experimental study of
296 nanoparticles deposited on rock surface to reduce fines migration', *SPE Journal*,
297 18(3), pp. 534–544. doi: 10.2118/142633-PA.
- 298 Aulenta, F., Majone, M. and Tandoi, V. (2006) 'Enhanced anaerobic
299 bioremediation of chlorinated solvents: environmental factors influencing microbial
300 activity and their relevance under field conditions', *Journal of Chemical Technology*

301 & *Biotechnology*. John Wiley & Sons, Ltd., 81(9), pp. 1463–1474. doi:
302 10.1002/jctb.1567.

303 Bardos, R. *et al.* (2011) ‘A risk/benefit approach to the application of iron
304 nanoparticles for the remediation of contaminated sites in the environment’.
305 Available at: <http://eprints.brighton.ac.uk/14887/1/CB0440FinalReport.pdf>
306 (Accessed: 31 July 2017).

307 Ben-Moshe, T., Dror, I. and Berkowitz, B. (2010) ‘Transport of metal oxide
308 nanoparticles in saturated porous media’, *Chemosphere*, 81(3), pp. 387–393. doi:
309 10.1016/j.chemosphere.2010.07.007.

310 Bennetzen, M. V. and Mogensen, K. (2014) ‘Novel Applications of Nanoparticles
311 for Future Enhanced Oil Recovery’, *International Petroleum Technology*
312 *Conference*, (December), pp. 10–12. doi: 10.2523/17857-MS.

313 Berg, S. *et al.* (2013) ‘Real-time 3D imaging of Haines jumps in porous media
314 flow.’, *Proceedings of the National Academy of Sciences of the United States of*
315 *America*. National Academy of Sciences, 110(10), pp. 3755–9. doi:
316 10.1073/pnas.1221373110.

317 Bharti, C. *et al.* (2015) ‘Mesoporous silica nanoparticles in target drug delivery
318 system: A review.’, *International journal of pharmaceutical investigation*. Medknow
319 Publications, 5(3), pp. 124–33. doi: 10.4103/2230-973X.160844.

320 Binks, B. (2002) ‘Particles as surfactants—similarities and differences’, *Current*
321 *Opinion in Colloid & Interface Science*, 7(1), pp. 21–41. doi: 10.1016/S1359-
322 0294(02)00008-0.

323 Bradford, S. A. and Torkzaban, S. (2008) ‘Colloid Transport and Retention in
324 Unsaturated Porous Media: A Review of Interface-, Collector-, and Pore-Scale
325 Processes and Models’, *Vadose Zone Journal*. Soil Science Society, 7(2), p. 667.
326 doi: 10.2136/vzj2007.0092.

327 Cheraghian, G. and Hendraningrat, L. (2016) ‘A review on applications of
328 nanotechnology in the enhanced oil recovery part A: effects of nanoparticles on
329 interfacial tension’, *International Nano Letters*, 6(2), pp. 129–138. doi:
330 10.1007/s40089-015-0173-4.

331 Craig, F. F. (1971) *The reservoir engineering aspects of waterflooding*. H.L.

332 Doherty Memorial Fund of AIME. Available at: <http://store.spe.org/The-Reservoir-Engineering-Aspects-Of-Waterflooding--P68.aspx> (Accessed: 21 May 2017).

333

334 Daglio, M. *et al.* (2017) 'Electrobioremediation of oil spills', *Water Research*, 114,

335 pp. 351–370. doi: 10.1016/j.watres.2017.02.030.

336 Hendraningrat, L., Li, S. and Torsæter, O. (2013) 'A coreflood investigation of

337 nanofluid enhanced oil recovery', *Journal of Petroleum Science and Engineering*,

338 111, pp. 128–138. doi: 10.1016/j.petrol.2013.07.003.

339 Hendraningrat, L. and Torsæter, O. (2015) 'A Stabilizer that Enhances the Oil

340 Recovery Process Using Silica-Based Nanofluids', *Transport in Porous Media*.

341 Springer Netherlands, 108(3), pp. 679–696. doi: 10.1007/s11242-015-0495-8.

342 Hunter, R. J. (1981) *Zeta Potential in Colloid Science: Principles and Applications*,

343 *Trends in Food Science & Technology*. doi: 10.1016/S0924-2244(97)01001-7.

344 Iglauer, S. *et al.* (2011) 'Residual CO₂ imaged with X-ray micro-tomography',

345 *Geophysical Research Letters*, 38(21), p. n/a-n/a. doi: 10.1029/2011GL049680.

346 Jeong, S.-W., Corapcioglu, M. Y. and Roosevelt, S. E. (2000) 'Micromodel Study

347 of Surfactant Foam Remediation of Residual Trichloroethylene'. American

348 Chemical Society. doi: 10.1021/ES9910558.

349 Jin, Y. *et al.* (2007) 'Toxicity of luminescent silica nanoparticles to living cells',

350 *Chemical Research in Toxicology*, 20(8), pp. 1126–1133. doi: 10.1021/tx7001959.

351 Khler, M. and Fritzsche, W. (2004) *Nanotechnology: an Introduction to*

352 *Nanostructuring Techniques*. Wiley-VCH.

353 Kumar, M. N. R. *et al.* (2004) 'Cationic silica nanoparticles as gene carriers:

354 synthesis, characterization and transfection efficiency in vitro and in vivo.', *J*

355 *Nanosci Nanotechnol*, 4(7), pp. 876–881. doi: 10.1166/jnn.2004.120.

356 Li, S. and Torsæter, O. (2015) 'The Impact of Nanoparticles Adsorption and

357 Transport on Wettability Alteration of Intermediate Wet Berea Sandstone', in *SPE-*

358 *172943-MS*. SPE. Available at: [https://www.onepetro.org/download/conference-](https://www.onepetro.org/download/conference-paper/SPE-172943-MS?id=conference-paper%2FSPE-172943-MS)

359 [paper/SPE-172943-MS?id=conference-paper%2FSPE-172943-MS](https://www.onepetro.org/download/conference-paper/SPE-172943-MS?id=conference-paper%2FSPE-172943-MS) (Accessed: 4

360 May 2017).

361 Macy, R. (1935) 'Surface tension by the ring method. Applicability of the du Nouy

362 apparatus', *Journal of Chemical Education*. Division of Chemical Education ,

363 12(12), p. 573. doi: 10.1021/ed012p573.

364 Metin, C. O. *et al.* (2011) 'Stability of aqueous silica nanoparticle dispersions',
365 *Journal of Nanoparticle Research*, 13(2), pp. 839–850. doi: 10.1007/s11051-010-
366 0085-1.

367 Mulligan, C. ., Yong, R. . and Gibbs, B. . (2001) 'Surfactant-enhanced remediation
368 of contaminated soil: a review', *Engineering Geology*, 60(1), pp. 371–380. doi:
369 10.1016/S0013-7952(00)00117-4.

370 Negin, C., Ali, S. and Xie, Q. (2016) 'Application of nanotechnology for enhancing
371 oil recovery – A review', *Petroleum*, 2(4), pp. 324–333. doi:
372 10.1016/j.petlm.2016.10.002.

373 Ogolo, N., Olafuyi, O. and Onyekonwu, M. (2012) 'Enhanced Oil Recovery Using
374 Nanoparticles', *Saudi Arabia Section Technical Symposium and Exhibition*, p. 9.
375 doi: 10.2118/160847-MS.

376 Pak, T. *et al.* (2015) 'Droplet fragmentation: 3D imaging of a previously unidentified
377 pore-scale process during multiphase flow in porous media', *Proceedings of the
378 National Academy of Sciences*, 112(7), pp. 1947–1952. Available at:
379 <http://www.pnas.org/content/112/7/1947.abstract>.

380 Pak, T. (2015) *Saturation tracking and identification of residual oil saturation*. The
381 University of Edinburgh. Available at:
382 <https://www.era.lib.ed.ac.uk/handle/1842/17872> (Accessed: 4 May 2017).

383 Paria, S. (2008) 'Surfactant-enhanced remediation of organic contaminated soil
384 and water', *Advances in Colloid and Interface Science*, pp. 24–58. doi:
385 10.1016/j.cis.2007.11.001.

386 Roustaei, A., Saffarzadeh, S. and Mohammadi, M. (2013) 'An evaluation of
387 modified silica nanoparticles' efficiency in enhancing oil recovery of light and
388 intermediate oil reservoirs', *Egyptian Journal of Petroleum*, 22(3), pp. 427–433.
389 doi: 10.1016/j.ejpe.2013.06.010.

390 Santra, S. *et al.* (2004) 'TAT conjugated, FITC doped silica nanoparticles for
391 bioimaging applications.', *Chemical communications (Cambridge, England)*, (24),
392 pp. 2810–2811. doi: 10.1039/b411916a.

393 Soga, K., Pagea, J. W. . and Illangasekare, T. . (2004) 'A review of NAPL source

394 zone remediation efficiency and the mass flux approach', *Journal of Hazardous*
395 *Materials*, 110(1–3), pp. 13–27. doi: 10.1016/j.jhazmat.2004.02.034.

396 Tosco, T. *et al.* (2014) 'Nanoscale zerovalent iron particles for groundwater
397 remediation: a review', *Journal of Cleaner Production*, 77, pp. 10–21. doi:
398 10.1016/j.jclepro.2013.12.026.

399 Trelu, C. *et al.* (2016) 'Removal of hydrophobic organic pollutants from soil
400 washing/flushing solutions: A critical review', *Journal of Hazardous Materials*, 306,
401 pp. 149–174. doi: 10.1016/j.jhazmat.2015.12.008.

402 Wang, C. *et al.* (2012) 'Retention and transport of silica nanoparticles in saturated
403 porous media: effect of concentration and particle size.', *Environmental science &*
404 *technology*, 46(13), pp. 7151–8. doi: 10.1021/es300314n.

405 Wilson, J. (1990) *Laboratory investigation of residual liquid organics from spills,*
406 *leaks, and the disposal of hazardous wastes in groundwater.* Edited by R. Kerr.
407 Environmental Research Laboratory, Office of Research and Development, US
408 Environmental Protection Agency, 1990. Available at:
409 https://books.google.co.uk/books?hl=en&lr=&id=wbVnKvmsOxsC&oi=fnd&pg=PR4&dq=Laboratory+investigation+of+residual+liquid+organics+from+spills,+leaks,+and+the+disposal+of+hazardous+wastes+in+groundwater&ots=vrcIBPD7w_&sig=4-29AfAVIZoFxWR9LcZtv3jF7vc (Accessed: 14 July 2017).

413 Yu, W. and Xie, H. (2012) 'A Review on Nanofluids: Preparation, Stability
414 Mechanisms, and Applications', *Journal of Nanomaterials*. Hindawi Publishing
415 Corp., 2012, pp. 1–17. doi: 10.1155/2012/435873.

416 Zhang, T. *et al.* (2014) 'Investigation of Nanoparticle Adsorption During Transport
417 in Porous Media', *SPE Journal*, preprint(preprint), pp. 1–11. doi: 10.2118/166346-
418 PA.

419