

1 **Aging Effects on Chemical Transformation and Metal(loid) Removal by Entrapped**
2 **Nanoscale Zero-Valent Iron for Hydraulic Fracturing Wastewater Treatment**

3 Yuqing Sun^{1,2}, Cheng Lei^{1,3}, Eakalak Khan⁴, Season S. Chen¹, Daniel C.W. Tsang^{1,*}, Yong Sik Ok⁵, Daohui
4 Lin³, Yujie Feng^{2,*}, Xiang-dong Li¹

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6 ¹ Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom,
7 Kowloon, Hong Kong, China.

8 ² State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin
9 150090, China.

10 ³ Department of Environmental Science, Zhejiang University, Hangzhou 310058, China

11 ⁴ Department of Civil and Environmental Engineering, North Dakota State University, Dept 2470, P.O. Box
12 6050, Fargo, ND 58108, USA.

13 ⁵ O-Jeong Eco-Resilience Institute (OJERI) & Division of Environmental Science and Ecological Engineering,
14 Korea University, Seoul 02841, Republic of Korea.

15 **Corresponding author (dan.tsang@polyu.edu.hk).*

16 **Co-corresponding author (yujief@hit.edu.cn).*

17 **Abstract**

18 In this study, alginate and polyvinyl alcohol (PVA)-alginate entrapped nanoscale zero-valent iron (nZVI)
19 was tested for structural evolution, chemical transformation, and metals/metalloids removal (Cu(II), Cr(VI),
20 Zn(II), and As(V)) after 1-2 month passivation in model saline wastewaters from hydraulic fracturing. X-ray
21 diffraction analysis confirmed successful prevention of Fe⁰ corrosion by polymeric entrapment. Increasing
22 ionic strength (*I*) from 0 to 4.10 M (deionized water to Day-90 fracturing wastewater (FWW)) with
23 prolonged aging time induced chemical instability of alginate due to dissociation of carboxyl groups and
24 competition for hydrogen bonding with nZVI, which caused high Na (7.17%) and total organic carbon
25 (24.6%) dissolution from PVA-alginate entrapped nZVI after 2-month immersion in Day-90 FWW.
26 Compared to freshly-made beads, 2-month aging of PVA-alginate entrapped nZVI in Day-90 FWW
27 promoted Cu(II) and Cr(VI) uptake in terms of the highest removal efficiency (84.2% and 70.8%),
28 pseudo-second-order surface area-normalized rate coefficient k_{sa} ($2.09 \times 10^{-1} \text{ L m}^{-2} \text{ h}^{-1}$ and $1.84 \times 10^{-1} \text{ L m}^{-2}$
29 h^{-1}), and Fe dissolution after 8-h reaction (13.9% and 8.45%). However, the same conditions inhibited Zn(II)
30 and As(V) sequestration in terms of the lowest removal efficiency (31.2% and 39.8%) by PVA-alginate
31 nZVI and k_{sa} ($4.74 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$ and $6.15 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$) by alginate nZVI. The X-ray spectroscopic
32 analysis and chemical speciation modelling demonstrated that the difference in metals/metalloids removal
33 by entrapped nZVI after aging was attributed to distinctive removal mechanisms: (i) enhanced Cu(II) and
34 Cr(VI) removal by nZVI reduction with accelerated electron transfer after pronounced dissolution of
35 non-conductive polymeric immobilization matrix; (ii) suppressed Zn(II) and As(V) removal by nZVI
36 adsorption due to restrained mass transfer after blockage of surface-active micropores. Entrapped nZVI was
37 chemically fragile and should be properly stored and regularly replaced for good performance.

38 **Keywords:** Nanoscale zero-valent iron; Alginate entrapment; Hydraulic fracturing; Aging effect; Chemical
39 speciation; Metal/metalloid removal.

40

41 **1. Introduction**

42 Shale gas substitutes for natural gas as one of the main fossil fuels in the global energy supply, and it has
43 attracted tremendous attention in 41 countries such as USA, Canada, and China (Melikoglu, 2014).
44 Hydraulic fracturing, a common process for shale gas extraction, injects substantial amounts of “fracking
45 fluid” (nearly 2-5 million gallons per well) at high flow rate and pressure into the well (Clark et al., 2013),
46 with commensurate generation of over 1.4 billion gallons of highly-contaminated wastewater (combination
47 of flowback and produced waters) in Marcellus Shale, the largest shale region in USA, each year (Goss et al.,
48 2015). This wastewater stream contains high concentrations of salts (up to 350,000 mg L⁻¹),
49 metals/metalloids (up to 116 mg L⁻¹ Cu, 247 mg L⁻¹ Zn, 2.2 mg L⁻¹ Cr, 1.1 mg L⁻¹ As), and organic
50 compounds (such as hydrocarbons, benzenes, hetero-chlorides, surfactants, oil and grease) (Abualfaraj et al.,
51 2014; Shih et al., 2015; Oetjen et al., 2017).

52

53 Fracturing wastewater (FWW) treatment has become an emerging and important topic for many researchers
54 (Camarillo et al., 2016; Sun et al., 2017a; Sun et al., 2017b). Deep-ground injection and *in-situ* reuse, as the
55 most popular management for this wastewater, are becoming less viable due to high environmental risks
56 (Lutz et al., 2013) and reduced gas production after long-term barite scaling (Paukert Vankeuren et al., 2017).
57 Membrane filtration (He et al., 2014; Jiang et al., 2013), electrocoagulation (Kaulsey et al., 2017; Lobo et al.,
58 2016), and advanced oxidation (Abass et al., 2017; Turan et al., 2017) are efficient treatment technologies of
59 FWW, but continue to be impeded by high operational costs and energy consumption. Our previous
60 research demonstrated that granular/nanoscale zero-valent iron (ZVI) could remove metals/metalloids from
61 FWW (Sun et al., 2017a; Sun et al., 2017b). Meanwhile, alginate and polyvinyl alcohol (PVA) entrapped
62 nZVI was more stable, environmentally benign, and cost-effective than bare nZVI, which could be used to

63 remove metals/metalloids from FWW above ground under aerobic conditions before subsequent biological
64 treatment for reuse/disposal (Butkovskiy et al., 2017; Camarillo et al., 2016; Kekas et al., 2015). However,
65 to assess the applicability of entrapped nZVI for FWW treatment, it is essential to investigate the chemical
66 transformation, structural evolution, and removal performance of entrapped nZVI after long-term exposure
67 in high-salinity FWW.

68

69 The structural characteristics and evolution process of bare nZVI during long-term aging in water has been
70 widely reported (Stefaniuk et al., 2016). The core-shell structure gradually transforms into a hollow
71 spherical shape with Fe^0 core diffusing outwardly and the iron oxide shell collapsing flakily (Liu et al.,
72 2015). The corrosion products of nZVI progressively change from rapid formation of ferrihydrite and
73 magnetite (< 1 d) to slow transformation of lepidocrocite (< 4 weeks), and finally to stabilization of goethite
74 (> 4 weeks) (Pullin et al., 2017). The performance of aged nZVI depends on the removal mechanisms of the
75 contaminants and solution chemistry. Passivated nZVI commonly shows a remarkable decrease in
76 contaminant removal efficiency based on reduction mechanism, which is attributed to hindrance in electron
77 transfer due to the loss of Fe^0 and increase of surface oxide layer (Calderon and Fullana, 2015; Xie and
78 Cwiertny, 2012). Meanwhile, goethite (FeOOH) as the dominant iron corrosion product on nZVI surface in
79 the long term was reported to possess higher adsorption affinity and capacity for metals/metalloids (Yan et
80 al., 2010). High-level dissolved solutes, such as chloride, bromide, and nitrate salts were found to destroy the
81 passive oxide coatings, which helped to maintain the degradation efficiency of Fe^0 within 0-7 days of water
82 exposure, whereas divalent cations (Ca^{2+} , Mg^{2+}) and alkalinity ions (HCO_3^- , OH^-) were involved in nZVI
83 surface passivation and gradually dampened nZVI reactivity (Xin et al., 2016).

84

85 In view of the above, it is hypothesised that complicated solution chemistry of high-salinity (Cl^- , NO_3^- , Ca^{2+} ,

86 Mg²⁺, etc.) and coexistence of multi-metals/metalloids (Cu(II), Cr(VI), Zn(II), and As(V)) involving various
87 removal mechanisms in FWW would cause uncertainties in structural evolution, thereby affecting the
88 removal performance of entrapped nZVI upon aging. Dong et al. (2016) observed that coating of polymeric
89 materials, carboxymethyl cellulose (CMC), on bare nZVI surface could slow down the aging rate of nZVI
90 and result in more crystalline lepidocrocite (γ -FeOOH) of the corrosion products after 90 days of aging in
91 static water. Huang et al. (2016) also suggested that alginate modification prevented nZVI particles from air
92 oxidation and increased Cd removal in polluted sediments. However, the long-term chemical stability of
93 alginate and PVA in high-salinity FWW remains questionable, as higher level of total organic carbon (TOC)
94 in the effluent was documented after reaction with PVA/alginate entrapped Fe⁰-Fe₃O₄ (Lv et al., 2013) or
95 nZVI particles (Sun et al., 2017b). The dissolution of TOC from entrapped beads, which was probably
96 caused by water swelling and ion exchange of alginate (Hua et al., 2010; Huang et al., 2017), could in turn
97 expose nZVI to FWW with uncontrolled structural evolution, inhibited reactivity, and uncertain release of
98 adsorbed contaminants upon aging.

99

100 In this study, both alginate and PVA-alginate entrapped nZVI were tested for chemical transformation,
101 structural evolution, and metals/metalloids removal after 1 or 2 months of exposure to model FWW. The
102 target metals/metalloids were Cu(II) (116 mg L⁻¹), Zn(II) (247 mg L⁻¹), Cr(VI) (2.2 mg L⁻¹), and As(V) (1.1
103 mg L⁻¹), which represented the maximum concentrations reported in Marcellus fracturing wastewater
104 (Abualfaraj et al., 2014; Shih et al., 2015). The objectives of this research were to: (i) evaluate the structural
105 and chemical changes of entrapped nZVI as it corrodes in FWW with increasing salinity; (ii) investigate
106 how corrosion of entrapped nZVI affects the removal of target metals/metalloids and the associated Fe and
107 TOC dissolution; (iii) reveal how different removal mechanisms correlate to the performance of entrapped
108 nZVI after aging via X-ray spectroscopic analysis and speciation modelling. These findings would advance

109 our understanding of the long-term fate of entrapped nZVI in aqueous environment and FWW treatment.

110

111 **2. Experimental methods**

112 *2.1 nZVI and FWW*

113 The dry powder of nZVI (NANO FER STAR) used in this study was purchased from NANO IRON
114 (Czech Republic), which had average size of 50 nm, specific surface area of $19.4 \text{ m}^2 \text{ g}^{-1}$, and Fe^0 content of
115 65-80%. The chemicals used in this research were reagent grade from Sigma Aldrich (viz. NaOH, HCl,
116 KCl, NaBr, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl, H_3BO_3 ,
117 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CrO_3 , $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, polyacrylamide, ethylene glycol,
118 glutaraldehyde, Na-alginate, PVA, Na-citrate, citrate acid, Na_2HPO_4 , NaH_2PO_4). Model FWW
119 (representing the fluids returning to the ground surface in 1 and 90 days after well creation, referred to as
120 Day-1 and Day-90 FWW, respectively) (Table 1) were synthesized according to a comprehensive report of
121 “Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas”
122 (Hayes, 2009), which was consistent with our previous studies (Chen et al., 2016; Chen et al., 2017; Sun et
123 al., 2017a; Sun et al., 2017b). The speciation of Cu(II), Zn(II), Cr(VI), and As(V) in Day-90 model FWW
124 was calculated using Visual MINTEQ ver. 3.0 (Table S1).

125

126 *2.2 Entrapment of nZVI in alginate and PVA-alginate*

127 To immobilize nZVI without lowering its reactivity, entrapment was carried out (Fig. S1) according to the
128 procedures reported by previous research (Babuponnusami and Muthukumar, 2013; Bezbaruah et al., 2014).
129 For alginate entrapped nZVI, 2% (w/v) Na-alginate solution (i.e., *solution 1*) was prepared by dissolving 2 g
130 Na-alginate in 100 mL deionized water (DIW) at room temperature, and stirring with a magnetic stirrer for
131 3-5 h until the solution appeared uniform, followed by 30-min rest to allow air bubbles to escape and ensure

132 no alginate floats in the solution. Then, 3.5% (v/v) CaCl₂ solution (i.e., *solution 2*) was prepared by adding
133 23.2 g CaCl₂ into 500 mL DIW at room temperature. Next, 1 g nZVI powder was added into *solution 1* (i.e.,
134 *solution 3*). Using a peristaltic pump (BT100-2J Peristaltic Pump, Baoding Longer Precision Pump Co.,
135 Ltd.), *solution 3* was drop-wisely transferred into *solution 2* from 12 cm vertically above the water surface,
136 with a 0.5 mm ID tubing at 2.5 mL min⁻¹ of flow rate to form alginate-nZVI beads. *Solutions 2* and *3* were
137 constantly stirred with glass rods while pumping to ensure almost all nZVI was transferred into the beads
138 and no alginate-nZVI beads clustered together. Beads were hardened by immersion in *solution 2* for 6-9 h
139 so that adequate hardness and porosity were obtained. Beads were rinsed and stored in DIW before use.

140
141 For PVA-alginate entrapped beads, 7.5% (w/v) PVA solution (i.e., *solution a*) was prepared by dissolving 3
142 g PVA in 40 mL DIW at room temperature, and heating to 80°C for 1 h while stirring with a magnetic
143 stirrer until complete dissolution. Then, 10% (w/v) Na-alginate solution (i.e., *solution b*) was prepared by
144 dissolving 5 g Na-alginate in 50 mL DIW. Next, 10 mL *solution b* was added to *solution a*, and gently
145 stirred for 45 min. After cooling down to 35°C, 1 g nZVI was added (i.e., *solution c*), and gently stirred for
146 complete dispersion. The rest of the procedure to produce PVA-alginate entrapped nZVI beads was the
147 same as the procedure for alginate entrapped nZVI beads as described above.

148
149 *2.3 Aging of entrapped nZVI in DIW, Day-1, and Day-90 FWW*

150 To investigate how salinity in FWW would affect the chemical transformation and structural evolution of
151 entrapped nZVI during aging, freshly-made alginate and PVA-alginate entrapped nZVI beads were
152 transferred into 500-mL centrifuge bottles containing 300-mL DIW, Day-1, and Day-90 FWW,
153 respectively. The aging process was carried out in aerobic condition and room temperature for 1 or 2
154 months with 5-min shaking every day. After aging, the entrapped nZVI beads were separated from the

155 solution and washed 3 times with DIW before use. The supernatants were filtered through a 0.45- μ m
156 pore-size mixed cellulose esters membrane filter (Millipore) and analyzed for Na, Fe, and TOC as described
157 in *Section 2.4*.

158

159 *2.4 Metal/metalloid removal from Day-90 FWW by entrapped nZVI after aging*

160 To investigate the kinetics of Cu(II), Zn(II), Cr(VI), and As(V) removal from FWW by entrapped nZVI
161 after aging, 2 g L⁻¹ nZVI (i.e., 94 alginate entrapped nZVI beads or 44 PVA-alginate entrapped nZVI beads)
162 was reacted with 116 mg L⁻¹ Cu(II) or 247 mg L⁻¹ Zn(II), and 1 g L⁻¹ nZVI (i.e., 47 alginate entrapped nZVI
163 beads or 22 PVA-alginate entrapped nZVI beads) was reacted with 2.2 mg L⁻¹ Cr(VI) or 1.1 mg L⁻¹ As(V)
164 in 50-mL polypropylene copolymer centrifuge tubes containing 25-mL Day-90 FWW. Freshly-made
165 alginate and PVA-alginate entrapped nZVI was used as control. The nZVI dosages were selected to achieve
166 the highest removal efficiency as well as removal rate, while Day-90 FWW was selected to represent the
167 worst-case scenario of metals/metalloids removal by entrapped nZVI (i.e., the lowest rate coefficient and the
168 highest Fe dissolution) according to our previous work (Sun et al., 2017b). All experiments were performed
169 in aerobic conditions with dissolved oxygen concentration of 5.39 \pm 0.34 mg L⁻¹ in Day-90 FWW during
170 metals/metalloids removal.

171

172 Stock solutions of Cu(II), Zn(II), Cr(VI), and As(V) were prepared by dissolving Cu(NO₃)₂·3H₂O,
173 Zn(NO₃)₂·6H₂O, CrO₃, and Na₂HAsO₄·7H₂O in DIW, respectively, which were added to model FWW.
174 The initial pH value of model FWW was adjusted to 5.9-7.2 using 0.1 M NaOH or HCl. The samples were
175 shaken on a rotary shaker (30 rpm) at room temperature for 5-480 min, and then separated by centrifugation
176 at 4,000 rpm for 5 min. The supernatants were filtered through a 0.45- μ m pore-size mixed cellulose esters
177 membrane filter (Millipore) and analyzed for As by atomic absorption spectrometry (AAS) with vapour

178 generation accessory (VGA-AAS, Agilent VGA77, limit of detection of $1 \mu\text{g L}^{-1}$) and AAS for Zn, Fe, and
179 Na (limit of detection of 0.1 mg L^{-1}). The selective-reduction-VGA-AAS technique was employed for
180 measuring the concentration of As(V) based on Shraim et al. (1999). The Cr(VI) and Cu(II) concentrations
181 were determined by UV-Vis spectrophotometer (US EPA Clean Water Act Analytical Methods,
182 3500-B-2009). Pseudo-second-order kinetics of metals/metalloids removal was reported in Tables S2-S5.

183
184 The total organic carbon was measured by a TOC analyzer (SSM-5000A). Gas chromatography/mass
185 spectrometry (GC-MS) (Agilent 7890B GC analyzer, 5977 Mass Selective Detector) was used to identify
186 the content of dissolved organics subsequent to a liquid-liquid extraction by hexane. A DB-5 MS column
187 (30-m long and $0.25\text{-}\mu\text{m}$ thick film with 0.25 mm internal diameter, Agilent Technologies) was used, and
188 helium was the carrier gas. Oven temperature was maintained at 35°C for 4 min, increased at $10^\circ\text{C min}^{-1}$
189 until reaching 100°C , then increased at $30^\circ\text{C min}^{-1}$ until reaching 190°C . Samples were injected with a rate
190 of 1 mL min^{-1} at 230°C and detected at 280°C . Selected ion monitoring was chosen for result acquisition.
191 Dissolution of Fe (Table S6) and TOC (Table S7) was reported after 8-h reaction.

192

193 *2.5 Solid-phase characterization of entrapped nZVI*

194 The crystalline structure of the alginate and PVA-alginate entrapped nZVI after aging in FWW was
195 determined by using a high-resolution X-ray diffraction (XRD) (Rigaku SmartLab). The scanning degrees
196 were from 5° to 70° 2θ with 5° min^{-1} speed duration at 45 kV and 200 mA. After reaction with
197 Cu(II)/Zn(II)/Cr(VI)/As(V) in Day-90 FWW, PVA-alginate entrapped beads were separated by
198 centrifugation and gently washed with DIW three times to remove entrapped and loosely attached metals
199 and salts. For X-ray photoelectron spectroscopy (XPS) analysis, the entrapped nZVI was released by
200 dissolving the beads in 0.3 M sodium citrate solution and 20 mM phosphate buffer solution according to a

201 previous study (Pramanik et al., 2011) (otherwise dense polymeric matrix enclosing nZVI interfered with
202 the surface analysis). The solid samples were freeze-dried and kept in a desiccator before analysis. The
203 oxidation states of target metals/metalloids on the nZVI surface were determined using XPS (VG Multilab
204 2000) with Al K-alpha radiation. A broad scan was obtained using 100 eV pass energy, while narrow
205 high-resolution scans of Cu_{2p}, Zn_{2p}, Cr_{2p}, and As_{3d} were obtained using 25 eV pass energy with step size of
206 0.05 eV. The charge effect was corrected using the C 1s line at 284.6 eV. The obtained spectra were fitted
207 using a curve-fitting program (Advantage) and a least-squares procedure with peaks of 30% of the
208 Lorentzian-Gaussian peak shape after subtraction of a Shirley baseline. The component peaks were
209 identified by comparing their binding energies (BE_s) with the values reported in the literature, which was
210 summarized in Tables S8-S11.

211

212 2.6 Statistical analysis

213 All experiments were performed in duplicate. Experimental data were statistically analysed using two-way
214 ANOVA followed by Turkey's multiple comparisons with SPSS 22.0 for Windows (SPSS, USA).
215 Lower-case letters in Figs. 1-4 and Table S6 indicate the significance level ($p < 0.05$) in the results.

216

217 3. Results and discussion

218 3.1 Chemical transformation and structural evolution of entrapped nZVI after aging in FWW

219 During the aging process of entrapped nZVI exposed to FWW, the diameters of entrapped beads changed
220 with increasing time and salinity. As shown in Fig. S2, the diameter of alginate entrapped beads increased
221 from 1.5 cm (freshly-made) to 1.7 cm after aging in DIW (2 months), Day-1, and Day-90 FWW (1 or 2
222 months). In contrast, high salinity of FWW caused a little shrinkage of PVA-alginate entrapped beads
223 reducing the diameter from 2.0 cm (freshly-made) to 1.9 cm in DIW or 1.7 cm in high-salinity FWW after 1

224 or 2-month exposure.

225

226 Along with the obvious change of size, the major components dissolved from alginate and PVA-alginate
227 entrapped beads after aging. Prolonged exposure in FWW with increasing salinity resulted in higher
228 dissolution of Fe, Na, and TOC, although the loss of Fe was relatively minor (Table 2). The highest Fe
229 dissolution from alginate (0.213%) and PVA-alginate (0.242%) entrapped beads was found after 2-month
230 aging in Day-90 FWW, while it was less than 0.03% under other conditions. The XRD analysis confirmed
231 the stabilization of nZVI by polymeric entrapment during long-term aging in high-salinity FWW, where
232 two distinctive peaks representing crystalline Fe⁰ at 2θ of 45° and 65° were identified in freshly-made and
233 aged nZVI beads after 2-month exposure in DIW, Day-1 and Day-90 FWW (Fig. S3). Although Dong et al.
234 (2016) reported that CMC modification could slow down the aging rate of bare nZVI, the XRD analysis
235 clearly showed the presence of crystalline lepidocrocite and magnetite/maghemite on CMC-nZVI after
236 60-day exposure in static water under aerobic conditions. In comparison, the alginate and PVA-alginate
237 entrapped nZVI in this study successfully prevented nZVI passivation throughout 2-month exposure in
238 high-salinity FWW.

239

240 Nevertheless, the long-term chemical stability of alginate and PVA was not satisfactory in FWW due to
241 pronounced dissolution of Na and TOC (Table 2). After aging of alginate entrapped beads in DIW for 1 or 2
242 months, only 0.09% and 0.36% Na leached, while exposure to Day-1 FWW (*I* = 0.35 M) dissolved more
243 Na (0.75% and 0.84%) and Day-90 FWW (*I* = 4.10 M) resulted in high Na dissolution (3.18% and 3.97%)
244 for the same period of time. The PVA-alginate entrapped beads showed more severe Na dissolution, which
245 reached 0.84%, 2.89%, and 7.07% after 1-month exposure in DIW, Day-1, and Day-90 FWW, respectively.
246 Extended aging for 2 months elevated Na dissolution from PVA-alginate entrapped beads to 1.16% (DIW),

247 3.71% (Day-1 FWW), and 7.17% (Day-90 FWW), respectively. At the same time, there was significant
248 TOC dissolution from entrapped beads after aging in FWW, especially for PVA-alginate entrapped beads
249 (Table 2). When soaked into Day-1 and Day-90 FWW for 2 months, 18.0% and 20.9% of TOC dissolution
250 from alginate-entrapped beads was observed while it was non-detectable under other conditions. In
251 comparison, 2.09%-9.0%, 10.1%-19.2%, and 17.5%-24.6% TOC leached from PVA-alginate entrapped
252 beads after 1-month or 2-month exposure in DIW, Day-1, and Day-90 FWW, respectively. Subsequent
253 GC-MS analysis identified the majority of organic compounds with C=O bond in the aging solutions, which
254 was similar to alginate monomer. Thus, high concentrations of Na and TOC were probably due to the
255 dissolution of alginate in high-salinity FWW.

256
257 Alginate is a polyanionic linear copolymer of 1,4-linked- α -L-galuronic acid and β -D-mannuronic acid
258 residues found in brown seaweeds with abundant of carboxyl group (-COOH) and hydroxyl group (-OH)
259 (Hua et al., 2010). Alginic acid can form ionic crosslinks with metal ions through ionotropic gelation, with
260 the affinity for metal ions following the order of $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$ (Lim et al., 2008).
261 According to previous FTIR analysis (Lim et al., 2008), the C-O bond in carboxyl group shifts to the lower
262 frequency and the C=O bond shifts to the higher frequency due to the change of electron density induced by
263 the adsorption of metal ions. As shown in Table 1, Day-1 and Day-90 FWW contains high concentrations
264 of divalent metal cations (Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , etc.), which resulted in substantial ion exchange with Na in
265 polymeric matrix and in turn caused polymer swelling (Fig. S2) and Na and TOC dissolution (Table 2) from
266 alginate entrapped beads as observed in this study.

267
268 As PVA is a water-soluble non-ionic polyhydroxy polymer with higher density of -OH group than alginate,
269 nZVI, alginate, and PVA are incorporated in the PVA-alginate entrapped beads by intermolecular and

270 intramolecular hydrogen bond between -OH groups (Zain et al., 2011). According to previous FTIR
271 analysis (Bai et al., 2009), all major bands of PVA immobilized nZVI were shifted to the lower frequency
272 with stable complex of PVA-Fe²⁺ on the nZVI surface. Compared to -COOH group in alginate, PVA
273 possibly outcompeted alginate for hydrogen bonding with nZVI and therefore accelerated alginate
274 dissolution from PVA-alginate entrapped beads upon aging. To overcome the instability of alginate and
275 PVA-alginate entrapped nZVI, chemical cross-linking with boric acid (Zain et al., 2011), phosphate (Huang
276 et al., 2017), and sulphate (Wang and Wang, 2016) may be applied to enhance the bonding between nZVI
277 and the strength of physical matrix in high-salinity FWW, which requires future investigation.

278

279 *3.2 Aging of entrapped nZVI in FWW promoted Cu(II) and Cr(VI) removal*

280 It was observed that long-time passivation with increasing salinity in DIW, Day-1, and Day-90 FWW
281 promoted Cu(II) and Cr(VI) removal by entrapped nZVI. As shown in Fig. 1a, the performance of
282 entrapped nZVI for Cu(II) removal in Day-90 FWW was not affected after aging in DIW for 1 month
283 (alginate nZVI: 18.2±0.4%, PVA-alginate nZVI: 17.0±1.4%) compared to freshly-made entrapped beads
284 (21.5±0.2% and 21.0±0.6%), while there was a pronounced increase in removal ($p < 0.05$) following
285 2-month soaking in DIW (77.9±0.1% and 74.0±4.2%). Due to the variation of ionic strength in the aging
286 solutions (Fig. 1a), the removal efficiency of Cu(II) after 8-h reaction with PVA-alginate entrapped nZVI
287 were 65.7±1.9% and 75.9±1.5% after passivation in Day-1 ($I = 0.35$ M) and Day-90 ($I = 4.10$ M) FWW for
288 1 month. After extended soaking in Day-1 and Day-90 FWW for 2 months, Cu(II) removal further
289 increased to 78.7±1.6% and 84.2±1.2%. For alginate-entrapped nZVI, Cu(II) removal was also enhanced
290 after 2-month immersion in Day-1 FWW (82.9±0.8%) and Day-90 FWW (82.3±0.6%).

291

292 As shown in Fig. 2a, passivation in DIW for 1 or 2 months did not affect Cr(VI) removal by alginate

293 entrapped nZVI ($53.2\pm 2.4\%$ and $51.2\pm 3.8\%$) and PVA-alginate entrapped nZVI ($43.4\pm 1.2\%$ and
294 $43.8\pm 2.2\%$), compared to freshly-made entrapped beads (alginate: $52.6\pm 2.9\%$, PVA-alginate: $43.3\pm 2.9\%$).
295 However, passivation in high-salinity FWW slightly improved Cr(VI) removal by alginate-entrapped nZVI
296 after 1-month soaking in Day-1 FWW ($58.5\pm 2.4\%$) and Day-90 FWW ($56.9\pm 2.1\%$). Prolonged passivation
297 in Day-90 FWW for 2 months further promoted Cr(VI) removal ($p < 0.05$) to $64.8\pm 2.5\%$, while extended
298 aging in Day-1 FWW made no obvious difference ($58.2\pm 1.8\%$). For PVA-alginate entrapped nZVI, Cr(VI)
299 removal from Day-1 FWW reached to $49.0\pm 1.4\%$ (1 month) and $62.5\pm 1.7\%$ (2 months), while Cr(VI)
300 removal from Day-90 FWW reached $61.1\pm 3.2\%$ (1 month) and 70.8% (2 months), which clearly increased
301 with increasing salinity.

302
303 The time-dependent removal of Cu(II), Cr(VI), Zn(II), and As(V) by entrapped nZVI (Figs. S4-S7) in
304 Day-90 FWW after 1- or 2-month aging in DIW, Day-1, and Day-90 FWW conformed to
305 pseudo-second-order kinetics model (Tables S2-S5). As illustrated in Fig. 1b, long-time passivation with
306 increasing salinity raised the surface area normalized rate coefficient (k_{sa} , $L m^{-2} h^{-1}$) for Cu(II) by alginate (or
307 PVA-alginate) entrapped nZVI, from $2.63\times 10^{-2} L m^{-2} h^{-1}$ (or $6.79\times 10^{-2} L m^{-2} h^{-1}$) after 1-month aging in
308 DIW to $4.73\times 10^{-2} L m^{-2} h^{-1}$ (or $9.09\times 10^{-2} L m^{-2} h^{-1}$) in Day-90 FWW, while from $3.56\times 10^{-2} L m^{-2} h^{-1}$ (or
309 $8.77\times 10^{-2} L m^{-2} h^{-1}$) in DIW to $5.89\times 10^{-2} L m^{-2} h^{-1}$ (or $2.09\times 10^{-1} L m^{-2} h^{-1}$) in Day-90 FWW following
310 2-month aging. Similarly, for Cr(VI), an obvious trend of increasing k_{sa} with prolonged passivation in
311 high-salinity FWW (Fig. 2b) was obtained by alginate entrapped nZVI from $8.10\times 10^{-2} L m^{-2} h^{-1}$ (1 month)
312 and $1.14\times 10^{-1} L m^{-2} h^{-1}$ (2 months) in DIW to $8.81\times 10^{-2} L m^{-2} h^{-1}$ (1 month) and $1.33\times 10^{-1} L m^{-2} h^{-1}$ (2
313 months) in Day-90 FWW, while from $1.34\times 10^{-1} L m^{-2} h^{-1}$ (1 month) and $1.46\times 10^{-1} L m^{-2} h^{-1}$ (2 months) in
314 DIW to $1.45\times 10^{-1} L m^{-2} h^{-1}$ (1 month) and $1.84\times 10^{-1} L m^{-2} h^{-1}$ (2 months) in Day-90 FWW by
315 PVA-alginate entrapped nZVI.

316
317 Continuous Fe and TOC dissolution of entrapped nZVI was observed during metals/metalloids removal
318 from FWW after aging in DIW, Day-1, and Day-90 FWW for 1 or 2 months. Interestingly, Fe dissolution
319 was accelerated with long-term aging in high-salinity FWW (Tables S6). Following 1-month passivation,
320 Fe dissolution from alginate-entrapped nZVI remained in the range of $6.99\pm 0.04\%$ (Day-90 FWW) to
321 $8.07\pm 0.24\%$ (DIW), while 2-month aging promoted Fe dissolution ($p < 0.05$) to $10.2\pm 0.04\%$ (DIW) and
322 $12.3\pm 0.02\%$ (Day-90 FWW) after 8-h reaction with Cu(II) in Day-90 FWW. As for PVA-alginate
323 entrapped nZVI, prolonged soaking in FWW with increasing salinity enhanced Fe dissolution ($p < 0.05$)
324 during reaction with Cu(II) after 1- or 2-month aging in DIW ($6.03\pm 0.08\%$ or $9.41\pm 0.05\%$), Day-1
325 ($9.33\pm 0.19\%$ or $10.09\pm 0.21\%$), and Day-90 FWW ($11.2\pm 0.1\%$ or $13.9\pm 0.5\%$). Similar trends were
326 observed during reaction with Cr(VI). Meanwhile, TOC dissolution (Table S7) from alginate-entrapped
327 nZVI was undetectable, whereas it was minor ($0.17\pm 0.03\%$ to $2.39\pm 0.06\%$) for PVA-alginate entrapped
328 nZVI after aging.

329
330 After reaction with Cu(II) or Cr(VI), the XPS analysis showed both the reduced states and the initial ionic
331 metals/metalloids on the surface of entrapped nZVI. The Cu_{2p} spectra of the entrapped nZVI after 1-month
332 aging in DIW (Fig. 3a) exhibited two peaks at 932.0 eV (36.1%) and 933.0 eV (63.9%), respectively. The
333 peak positions were in close agreements with the Cu(0) and Cu(II) (as $=\text{FeOCu}^+$) 2p BEs, respectively. It is
334 evident that Cu(II) was removed by co-precipitation and adsorption on entrapped nZVI, and then reduced to
335 Cu(0) on the surface, corroborating previous findings for bare nZVI (Karabelli et al., 2008) and entrapped
336 nZVI (Sun et al., 2017b). As illustrated in Fig. 3a, passivation of entrapped nZVI with increasing salinity
337 promoted Cu(0) formation to 53.1% (932.0 eV) and 63.4% (932.0 eV) after 1-month aging in Day-1 ($I =$
338 0.35 M) and Day-90 FWW ($I = 4.10$ M). Extended immersion for 2 months in DIW, Day-1, and Day-90

339 FWW further increased the proportion of Cu(0) on nZVI surface to 62.2% (932.0 eV), 68.2% (931.2 eV),
340 and 89.0% (931.9 eV), respectively (Fig. 3b).

341
342 As shown in Fig. 4a, the Cr_{2p} survey on entrapped nZVI surface after 1-month aging in DIW revealed two
343 peaks at 582.0 eV (48.0%) and 589.3 eV (52.0%), suggesting the presence of both Cr(VI) as CrO₄²⁻ and
344 Cr(III) as Cr(OH)₃. Thus, Cr(VI) was first adsorbed on nZVI surface and gradually reduced to Cr(III),
345 which could precipitate as Cr(OH)₃ and co-precipitate with dissolved Fe as Fe/Cr (oxy)hydroxides that
346 remain stable at high pH (Cornell and Schwertmann, 2003; Liu et al., 2008; Sun et al., 2017b). Figure 4a
347 further revealed that more Cr(VI) was reduced to Cr(III) by nZVI following 1-month aging in Day-1
348 (57.3%, 584.0 eV) and Day-90 FWW (63.1%, 586.3 eV) with elevated salinity. Prolonged aging for 2
349 months (Fig. 4b) similarly promoted Cr(III) formation of 57.6% at 584.0 eV (Day-1 FWW) and 78.8% at
350 583.0 eV (Day-90 FWW).

351
352 It could be concluded that long-time passivation of entrapped nZVI in FWW with increasing salinity
353 enhanced Cu(II) and Cr(VI) removal by reduction on nZVI, which was evidenced by elevated metal
354 removal efficiency (Figs. 1a and 2a), accelerated reaction rate (Figs. 1b and 2b), and increased Fe
355 dissolution (Table S6) as discussed above. Previous research demonstrated that metal/metalloid reduction by
356 ZVI media was less affected by intraparticle- or film-diffusion mass transfer, but it was limited by the ability
357 of Fe⁰ to release and transfer electrons at anodic sites (Melitas et al., 2001). Tafel scans showed a nearly
358 linear potential drop during Cr(VI) reduction by ZVI within 47-day passivation, suggesting that electron
359 transfer was inhibited by increasing amount of non-conductive iron oxides (Melitas et al., 2001). Our
360 research revealed that after aging in high-salinity FWW, alginate significantly dissolved from PVA-alginate
361 entrapped nZVI (Table 2) due to dissociation of carboxyl bond caused by ion exchange and competition for

362 hydrogen bonding on nZVI surface between PVA and alginate. Obvious shrinkage of PVA-alginate
363 entrapped beads (Fig. S2) indicated the loss of non-conductive polymeric matrix outside nZVI surface
364 (Table S7), which accelerated electron transfer from Fe^0 core and improved reduction by entrapped nZVI.
365 Metals with standard redox potential greater than Fe^0 (-0.44 V), such as Cu(II) (+0.34 V) and Cr(VI) (+1.51
366 V) could be further reduced to Cu(0) and Cr(III) after adsorption onto the surface of entrapped nZVI (Li and
367 Zhang, 2007), along with induced Fe dissolution due to Fe^0 oxidation ($\text{Fe}^0 + \text{M}^{n+} \rightarrow \text{Fe}^{m+} + \text{M}^{(n-m)}$, $m = 1-3$)
368 (Table S6).

369

370 *3.3 Aging of entrapped nZVI in FWW inhibited Zn(II) and As(V) adsorption*

371 In contrast, long-time passivation with increasing salinity in DIW, Day-1 and Day-90 FWW inhibited Zn(II)
372 and As(V) removal by entrapped nZVI. Figure 5a showed that Zn(II) removal by alginate entrapped nZVI
373 slightly decreased from $51.6 \pm 0.1\%$ to $49.1 \pm 0.3\%$, $47.5 \pm 0.4\%$, and $47.5 \pm 2.0\%$ after 1-month aging in DIW,
374 Day-1 and Day-90 FWW, respectively. Extended immersion for 2 months further reduced Zn(II) removal
375 ($p < 0.05$) to $46.2 \pm 1.0\%$ (DIW), $43.7 \pm 1.0\%$ (Day-1 FWW), and $43.9 \pm 1.1\%$ (Day-90 FWW), respectively.
376 For PVA-alginate entrapped nZVI, the deficiency in Zn(II) removal was more obvious ($p < 0.05$),
377 decreasing from $41.7 \pm 2.9\%$ to $38.6 \pm 0.2\%$ (DIW), $35.2 \pm 4.7\%$ (Day-1 FWW), and $29.3 \pm 3.2\%$ (Day-90
378 FWW) after 1 month, and to $33.8 \pm 1.0\%$ (DIW), $33.2 \pm 1.1\%$ (Day-1 FWW), and $31.2 \pm 2.0\%$ (Day-90 FWW)
379 following 2-month passivation, respectively.

380

381 As shown in Fig. 6a, compared to $73.8 \pm 1.4\%$ removal of As(V) by freshly-made alginate entrapped nZVI,
382 the removal slightly decreased after 1-month aging in Day-1 ($71.1 \pm 0.6\%$) and Day-90 ($68.7 \pm 0.9\%$) FWW,
383 while 1-month soaking in DIW did not affect As(V) removal ($73.8 \pm 2.7\%$). In comparison, there was a
384 notable decrease ($p < 0.05$) after 2-month aging in DIW ($53.4 \pm 0.6\%$), Day-1 FWW (53.1%), and Day-90

385 FWW ($53.4\pm 1.4\%$), respectively. A decreasing trend was similarly observed for As(V) removal by
386 PVA-alginate entrapped nZVI ($p < 0.05$) from $71.5\pm 4.0\%$ to $67.7\pm 1.1\%$ (DIW), $67.5\pm 0.4\%$ (Day-1 FWW),
387 and $65.4\pm 0.6\%$ (Day-90 FWW) after 1 month, and to $46.4\pm 1.2\%$ (DIW), $44.8\pm 1.7\%$ (Day-1 FWW), and
388 $39.8\pm 3.0\%$ (Day-90 FWW) after 2 months, respectively.

389
390 The rate coefficients k_{sa} for Zn(II) removal by alginate and PVA-alginate (Fig. 5b) after 1-month aging in
391 Day-90 FWW (5.90×10^{-2} L m⁻² h⁻¹ or 8.43×10^{-2} L m⁻² h⁻¹) were smaller than those in DIW (7.52×10^{-2} L m⁻²
392 h⁻¹ or 1.07×10^{-1} L m⁻² h⁻¹). They were further reduced to 4.74×10^{-2} L m⁻² h⁻¹ or 7.69×10^{-2} L m⁻² h⁻¹ following
393 2-month aging in Day-90 FWW. Similarly, the k_{sa} values of As(V) by alginate and PVA-alginate entrapped
394 nZVI (Fig. 6b) after 1-month aging in Day-90 FWW (1.46×10^{-1} L m⁻² h⁻¹ or 1.72×10^{-1} L m⁻² h⁻¹) were
395 smaller than those in DIW (2.67×10^{-1} L m⁻² h⁻¹ or 1.98×10^{-1} L m⁻² h⁻¹). After 2-month gaining in Day-90
396 FWW, the removal of As(V) further slowed down to 6.15×10^{-2} L m⁻² h⁻¹ or 1.28×10^{-1} L m⁻² h⁻¹. In the
397 meantime, Table S6 showed that increasing salinity enhanced Fe dissolution ($p < 0.05$). For instance, Fe
398 dissolution of alginate-entrapped nZVI during Zn(II) removal slightly increased from $3.03\pm 0.23\%$ (DIW) to
399 3.48 ± 0.02 (Day-90 FWW) after 1-month aging and from $3.09\pm 0.10\%$ (DIW) to $3.57\pm 0.02\%$ (Day-90
400 FWW) after 2-month aging, respectively. The lowest Fe dissolution ($3.03\pm 0.23\%$ to $4.84\pm 0.14\%$) was
401 detected during Zn(II) removal compared to those for Cu(II) ($6.99\pm 0.04\%$ to $13.9\pm 0.51\%$), Cr(VI)
402 ($6.18\pm 0.17\%$ to $8.45\pm 0.17\%$), and As(V) ($6.06\pm 0.08\%$ to $8.68\pm 0.45\%$).

403
404 It should be noted that the valence state of Zn(II) and As(V) on the surface of entrapped nZVI remained the
405 same as the dissolved ions in FWW. The Zn_{2p} survey of freshly-made entrapped nZVI (Fig. 7a) showed two
406 peaks at 1017.5 eV (54.8%) and 1018.9 eV (45.2%), corresponding to Zn(II) species and ZnFe₂O₄.
407 Similarly, the As_{3d} survey of freshly-made entrapped nZVI (Fig. 7b) presented three photoelectron peaks at

408 44.0 eV (76.9%), 44.5 eV (19.2%), and 45.8 eV (3.9%), representing As(V) in the forms of AsO_4^{3-} ,
409 HAsO_4^{2-} , and H_2AsO_4^- . Both Zn(II) and As(V) were bound to the surface of entrapped nZVI, possibly by
410 electrostatic interaction and specific bonding (Li and Zhang, 2007). Adsorbed Zn(II) on the surface of
411 entrapped nZVI could gradually co-precipitate as ZnFe_2O_4 with dissolved Fe, which was in accordance with
412 the lowest Fe concentration during Zn(II) removal (Table S6). Figure 7a demonstrated that the inhibition of
413 Zn(II) removal by entrapped nZVI after aging in FWW was a result of reduced proportion of ZnFe_2O_4 in
414 Day-1 (25.8%, 1021.5 eV) and Day-90 FWW (14.7%, 1023.0 eV) with increasing salinity. On the other
415 hand, the predominant form of As(V) as H_2AsO_4^- in Day-90 FWW (96.6%, Table S1) was transformed to
416 HAsO_4^{2-} (19.2%) and AsO_4^{3-} (76.9%) upon adsorption on the surface of entrapped nZVI (Fig. 7b),
417 suggesting that the majority of As(V) was coordinated as bidentate inner-sphere surface complex by edge-
418 and double-corner sharing (Peng et al., 2017; Sun et al., 2017b). Nevertheless, the formation of AsO_4^{3-} on
419 entrapped nZVI surface was reduced to 65.7% at 44.3 eV (DIW), 63.1% at 43.9 eV (Day-1 FWW), and
420 62.5% at 44.3 eV (Day-90 FWW) after 2-month aging.

421
422 Thus, long-time passivation in FWW with increasing salinity inhibited Zn(II) and As(V) removal by
423 entrapped nZVI due to the restrained surface adsorption of ZnFe_2O_4 and AsO_4^{3-} , corroborating the observed
424 decrease of removal efficiency (Figs. 5a and 6a) and reaction rate (Figs. 5b and 6b). The intraparticle and
425 film diffusion was found to be the rate-limiting step for metals/metalloids adsorption by
426 chitosan-carboxymethyl- β -cyclodextrin entrapped nZVI (Sikder et al., 2014). Escudero et al. (2009) reported
427 much lower rate constants of As(V) removal by Ca-alginate entrapped metal hydroxide than pure hydroxide
428 due to inhibited mass transfer into alginate matrix. As high concentration of NaCl ($> 3 \text{ g L}^{-1}$) could be
429 substantially adsorbed onto nZVI surface ($\sim 26.5\%$) as revealed by Hwang et al. (2015), the micropores of
430 entrapped nZVI were probably blocked by salt deposition after 1- or 2-month passivation in high-salinity

431 FWW, which in turn inhibited the mass transfer and adsorption of Zn(II) and As(V).

432

433 **4. Conclusions**

434 This study demonstrated that nZVI entrapment by alginate and PVA successfully mitigated Fe⁰ passivation
435 up to 2-month immersion in high-salinity fracturing wastewaters. However, alginate entrapped nZVI was
436 chemically fragile and associated with Na and TOC dissolution due to ion exchange of alginate in fracturing
437 wastewaters, whereas PVA-alginate entrapped nZVI accelerated TOC dissolution due to preferential
438 competition for hydrogen bonding on nZVI surface. Prolonged aging in fracturing wastewaters with
439 increasing salinity promoted Cu(II) and Cr(VI) removal via enhanced reduction by nZVI, but it inhibited
440 Zn(II) and As(V) removal due to restrained surface adsorption. These results provided useful guidance for
441 proper storage and routine replacement of entrapped nZVI for achieving satisfactory removal of
442 contaminants via different mechanisms during fracturing wastewater treatment.

443

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449

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