

## NANOSCALE ZERO-VALENT IRON FOR METAL SEQUESTRATION FROM FRACTURING FLOWBACK WATER AND WASTEWATER

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### Introduction

Hydraulic fracturing process is a common method for extracting oil and natural gas from underground shale formations by injecting large volume of high-pressurized fracturing fluid. High-salinity fracturing flowback water (FBW) and wastewater (WW) containing hazardous heavy metals could raise serious environmental pollution. Nanoscale zero-valent iron (nZVI) has been used as to treat metal-contaminated groundwater for years, and its application for fracturing is worth investigation. In this study, nZVI and Ca-alginate entrapped nZVI were used for Zn(II), Cu(II), Cr(VI), As(V) sequestration from synthetic fracturing FBW and WW. The objectives were to (i) unravel the effect of ionic strength in fracturing FBW and WW on nZVI performance for metal sequestration, (ii) compare the performance of bare nZVI and Ca-alginate entrapped nZVI, (iii) investigate iron dissolution from nZVI for determining feasibility of in-situ application.

### Methods

NANOFER STAR (Nanoiron, Czech Republic) dry nZVI powder was used, with 50 $\mu$ m average size, 20-25 m<sup>2</sup> g<sup>-1</sup> specific surface area and 65-80% ZVI content. Chemical composition of synthetic fracturing FBW, WW and target metal concentrations were chosen based on literature review (Hayes, 2010; Abualfaraj et al., 2014; Shih et al., 2015). Method for entrapping bare nZVI with Ca-alginate was adopted from literature (Bezbaruah et al., 2009). Batch experiments were carried out in 50ml centrifuge tubes by end-over-end shaking (30 rpm) at room temperature. Cu (116 mg L<sup>-1</sup>) or Zn (247 mg L<sup>-1</sup>) was reacted with 2 g L<sup>-1</sup> nZVI in DIW and FBW. Cr (2200  $\mu$ g L<sup>-1</sup>) or As (1100  $\mu$ g L<sup>-1</sup>) was reacted with 1 g L<sup>-1</sup> nZVI in DIW and WW. Metal concentrations (Zn, Cu, Cr, As, Fe) were tested after different reaction time (5-480 min) using Vapor Generation Accessory (Agilent VGA77)-Atomic Absorption Spectrometry (AAS).

### Results and Discussion

Pseudo-second-order kinetics was used to describe metal sequestration by nZVI in fracturing (Table 1). It has been demonstrated that increasing ionic strength from 0 M (DIW) to 4.10 M (Day 90 FBW) promoted Cu removal (DIW: 14.7 g kg<sup>-1</sup>, Day 90 FBW: 53.2 g kg<sup>-1</sup>) but inhibited Zn removal (DIW: 80.0 g kg<sup>-1</sup>, Day 90 FBW: 54.6 g kg<sup>-1</sup>). The Cr removal (DIW: 1.33 g kg<sup>-1</sup>, P90 WW: 1.01 g kg<sup>-1</sup>) and As removal (DIW: 0.864 g kg<sup>-1</sup>, P90 WW: 0.851 g kg<sup>-1</sup>) was nearly unaffected with increasing ionic strength from 0 M (DIW) to 3.81 M (P90 WW).

The Ca-alginate entrapped nZVI achieved higher removal for Zn (Day 90 FBW: 66.2 g kg<sup>-1</sup>) and Cr (P90 WW: 1.21 g kg<sup>-1</sup>), while Cu removal (Day 90 FBW: 12.8 g kg<sup>-1</sup>) was lower compared to that of bare nZVI. The removal of As by entrapped nZVI (P90 WW: 0.850 g kg<sup>-1</sup>) was similar, but with higher rate coefficient (bare nZVI: 2.52 $\times$ 10<sup>-2</sup> min<sup>-1</sup>, entrapped nZVI: 3.09 $\times$ 10<sup>-2</sup> min<sup>-1</sup>). Increasing ionic strength also induced higher Fe dissolution (Table 1), which could be mitigated by Ca-alginate entrapment.

**Table 1.** Pseudo-second-order kinetics parameters and Fe dissolution for metal sequestration by nZVI in fracturing.

Metal	nZVI Type	Solution	Ionic Strength (M)	$q_{e2}$ (g kg <sup>-1</sup> )	$k_2q_{e2}$ (min <sup>-1</sup> )	R <sup>2</sup>	Fe Dissolution (%)
Cu	Bare	DIW	0	14.7	$1.66 \times 10^{-1}$	0.9996	0.73±0.11
		Day 1 FBW	0.35	19.2	$1.02 \times 10^{-1}$	0.9997	1.36±0.01
		Day 14 FBW	2.49	21.0	$6.30 \times 10^{-2}$	0.998	4.44±0.05
		Day 90 FBW	4.10	53.2	$1.15 \times 10^{-2}$	0.99	9.43±0.40
	Entrapped	Day 90 FBW	4.10	12.8	$1.89 \times 10^{-2}$	0.98	6.93±0.50
Zn	Bare	DIW	0	80.0	$1.83 \times 10^{-2}$	0.991	0.77±0.16
		Day 1 FBW	0.35	68.0	$4.91 \times 10^{-2}$	0.999	1.73±0.03
		Day 14 FBW	2.49	64.1	$3.65 \times 10^{-2}$	0.993	4.15±0.42
		Day 90 FBW	4.10	54.6	$5.00 \times 10^{-2}$	0.9994	4.87±0.32
	Entrapped	Day 90 FBW	4.10	66.2	$4.37 \times 10^{-2}$	0.9998	3.20±0.38
Cr	Bare	DIW	0	1.33	$5.78 \times 10^{-2}$	0.9992	0.72±0.03
		P10 WW	0.35	1.44	$8.61 \times 10^{-2}$	0.9994	1.29±0.26
		P50 WW	1.55	1.48	$6.85 \times 10^{-2}$	0.9996	6.79±0.46
		P90 WW	3.81	1.01	$5.85 \times 10^{-2}$	0.9997	13.0±1.0
	Entrapped	P90 WW	3.81	1.21	$3.82 \times 10^{-2}$	0.9996	7.25±0.73
As	Bare	DIW	0	0.864	$5.46 \times 10^{-2}$	0.990	0.37±0.07
		P10 WW	0.35	0.782	$2.06 \times 10^{-2}$	0.993	2.04±0.18
		P50 WW	1.55	0.814	$1.96 \times 10^{-2}$	0.984	5.09±0.57
		P90 WW	3.81	0.851	$2.52 \times 10^{-2}$	0.994	9.40±0.63
	Entrapped	P90 WW	3.81	0.850	$3.09 \times 10^{-2}$	0.997	6.26±0.75

The main mechanism for Cu removal by nZVI in high-salinity fracturing FBW could be (co)-precipitation with Fe and adsorption onto Fe-oxides. While Fe dissolution was elevated with increasing ionic strength, only Cu removal was promoted. Since entrapment could protect nZVI against high electronic compression, less Fe dissolution was found and thus Cu removal was inhibited to some extent. The removal of As & Cr was less susceptible for ionic strength variations, suggesting the possible formation of stable inner-sphere complex with nZVI. In contrast, Zn removal was decreased with higher ionic strength, which was in accordance with weakly bound outer-sphere complex being suppressed by increasing ionic strength. Entrapment made nZVI more suspended with larger active sites for adsorption, so As, Cr, Zn removal were promoted in P90 WW and Day 90 FBW.

## Conclusions

Effect of increasing ionic strength showed different trend in Cu(II) (promoted), Zn(II) (inhibited) and As(V)/Cr(VI) (less susceptible) removal by nZVI in fracturing FBW and WW. Fe dissolution increased with increasing ionic strength. Primary removal mechanism was proposed in each metal including inner-sphere complex in As(V) and Cr(VI), outer-sphere complex in Zn(II) and co-precipitation in Cu(II). Ca-alginate nZVI had better performance than bare nZVI for improved metal removal (except Cu) and less Fe dissolution.

## References

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