



# ENHANCED REDUCTIVE DECHLORINATION OF TRICHLOROETHYLENE BY SULFIDATED NANOSCALE ZERO VALENT IRON

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## Summary

Direct injection of nanoscale zero valent iron (NZVI) particles into the subsurface has been proposed for the remediation of aquifers contaminated with chlorinated solvents such as trichloroethylene (TCE). The transport and reactivity of NZVI under representative aquifer conditions need to be determined to better optimize remediation operations.

In this study we assess the effects of sulfide ions, which are ubiquitous in groundwater environments, on the reactivity of NZVI. NZVI particles (~180 nm diameter) were combined with varying concentrations sulfide ions and reacted with TCE. In the presence of sulfide the surface-area normalized ( $k_{sa}$ ) first order TCE degradation constant increased by up to 40 times depending on the Fe:S ratio, likely due to the formation of FeS (mackinawite) on the NZVI surface.

## Introduction

Chlorinated solvents such as TCE are widely used in industry, especially for metal degreasing in manufacturing plants.

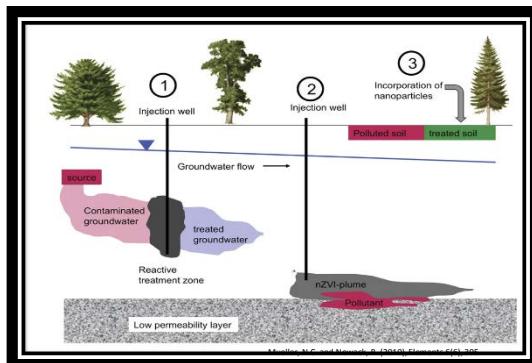


Figure 1: In situ remediation using zero valent iron

Several studies have shown both enhancements as well as decreases in TCE degradation rates by NZVI in the presence of certain dissolved groundwater ions such as nitrate, phosphate, chloride, sodium, magnesium and bicarbonate. The changes in reactivity are caused by increased iron corrosion or the deposition of insoluble precipitates on the NZVI. Little is known about the effects of sulfide or sulfate ions on NZVI reactivity.

## Objectives

The overall objective was to assess the effect of dissolved sulfide on the reactivity of NZVI.

The specific objectives were to characterize the:

- Effects of sulfide concentration on the reactivity of NZVI;
- Changes in NZVI surface chemistry, size and morphology due to addition of sulfide ions;
- Effects of groundwater composition on NZVI reactivity in the presence of sulfide.

## Acknowledgements

The work was done under the supervision and advise of Prof. Subhasis Ghoshal, McGill Univ. Funding from NSERC, CFI, FQRNT and Golder Associates are gratefully acknowledged.



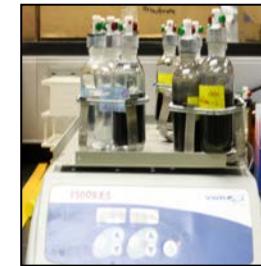
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## Methods

**Nanoparticles:** NZVI particles were synthesized under strict anaerobic conditions by reduction of  $\text{FeSO}_4$  by drop-wise addition of  $\text{NaBH}_4$ .

**Characterization:** Size and surface chemistry was measured using Transmission Electron Microscopy (TEM), Nanoparticle Tracking Analysis (NTA) and X-ray Photoelectron Spectroscopy (XPS).

**TCE degradation experiments:** TCE degradation experiments were conducted in completely mixed, sealed vials with 23mL headspace. Sulfide was added as  $\text{Na}_2\text{S}$  to provide desired concentrations ranging from 0.17mM to 17.32mM. The reactions were carried out under strict anaerobic conditions, in triplicates. TCE and degradation products in the headspace were analyzed using a GC-FID.



## Results and Discussions

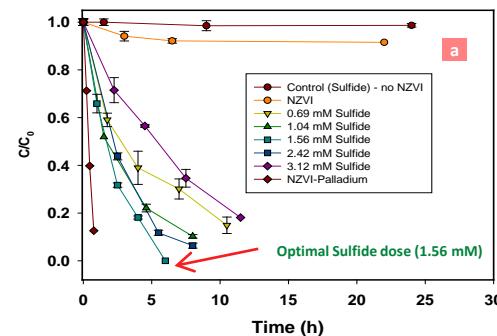


Figure 2a: Effect of sulfide concentration on TCE degradation in systems containing 2.0 g/L NZVI. Initial TCE conc. was 0.11 mM.

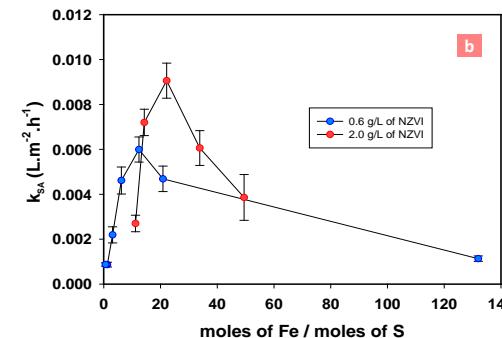


Figure 2b: Surface area normalized first order TCE degradation rate constants in systems with different Fe to S mole ratios.

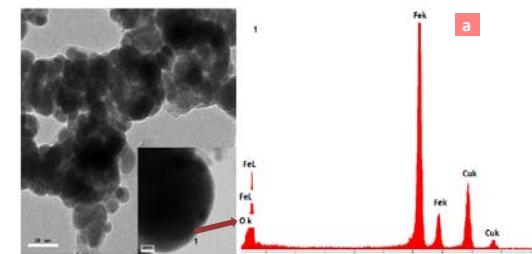


Figure 3a: TEM-EDX of unamended NZVI Low and high-magnification (inset) images and EDX spectra.

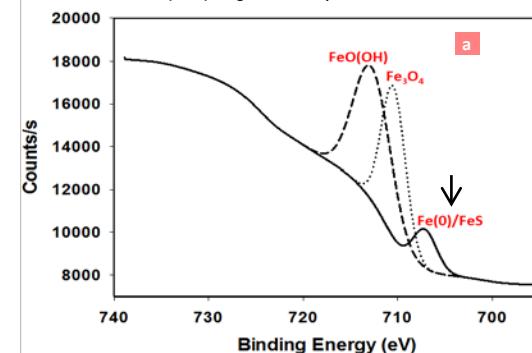


Figure 4a: Narrow scans of Fe 2p spectra of NZVI reacted with 0.86 mM of sulfide.

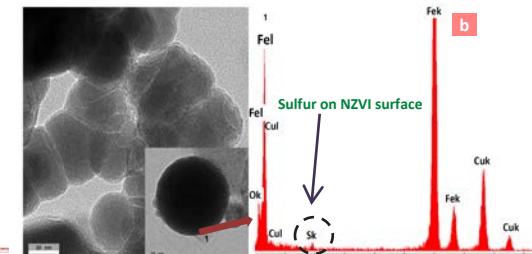


Figure 3b: TEM-EDX of NZVI reacted with 0.86 mM of sulfide Low and high-magnification (inset) images and EDX spectra

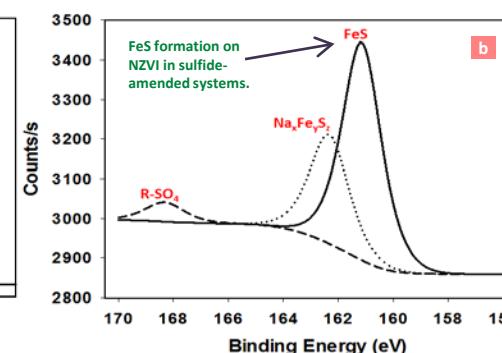


Figure 4b: Narrow scans S 2p XPS spectra of NZVI reacted with 0.86 mM of sulfide

System	Hydrodynamic diameter, NTA (nm)	BET Surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )
NZVI (no amendment)	157.67 $\pm$ 9.8	26.1
NZVI with 0.86 mM sulfide	191.00 $\pm$ 8.5	23.8
NZVI with 1.56 mM sulfide	195.33 $\pm$ 6.6	21.7
NZVI with 1.73 mM sulfide	181.00 $\pm$ 3.2	26.5

Table 1: Size and surface area measurements for different NZVI systems

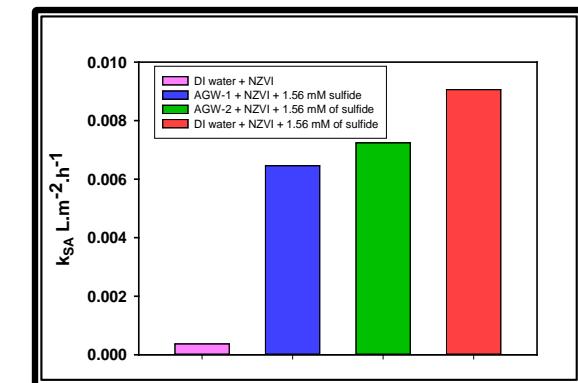


Figure 5: Effect of water composition on TCE degradation rate constants by NZVI. AGW-1 and AGW-2 are two different artificial groundwaters comprised of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$

## Conclusions

- The addition of sulfide increased the reactivity of the NZVI ~ 40 fold.
- Addition of sulfate did not have any significant influence on reactivity.
- Sulfide dosage (Fe/S) is a critical factor for NZVI reactivity to TCE.
- TCE is primarily degraded to ethene and acetylene.
- There was no significant change in nanoparticle size with sulfide addition.
- The increased reactivity of NZVI in the presence of sulfide can be used to improve remediation performance.
- Overall sulfidation is an inexpensive alternative to palladium and can sustain a more longer and effective remediation.

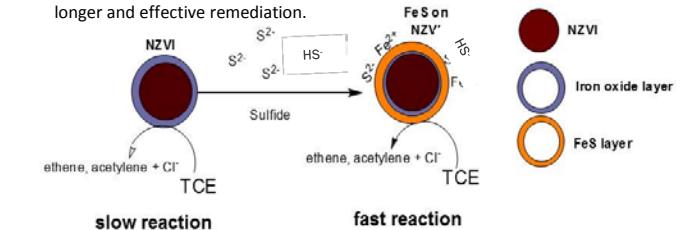


Figure 6: Schematic of TCE dechlorination with sulfide-amended NZVI.

## References

- Butler, E. C.; Hayes, K. F., Environmental Science & Technology, 2001, 35, (19), 3884-3891.
- Hansson, E.B., Odziemkowski, M.S. and Gillham, R.W. (2008), Journal of Contaminant Hydrology, 98(3-4), 128-134.
- Kim, E.-J., Kim, J.-H., Azad, A.-M. and Chang, Y.-S. (2011), ACS Applied Materials & Interfaces, 3(5), 1457-1462.
- Liu, Y., Majetich, S.A., Tilton, R.D., Sholl, D.S. and Lowry, G.V. (2005), Environmental Science & Technology, 39(5), 1338-1345.