

Final Technical Report

Optimizing Metalloporphyrin-Catalyzed Reduction Reactions for In Situ Remediation of DOE Contaminants

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Executive Summary

Past activities have resulted in a legacy of contaminated soil and groundwater at Department of Energy facilities nationwide. Uranium and hexavalent chromium are among the most frequently encountered and highest-priority metal and radionuclide contaminants at DOE installations. Reduction of hexavalent uranium to tetravalent uranium (i.e., U(VI) to U(IV)) and hexavalent chromium to trivalent chromium (i.e., Cr(VI) to Cr(III)) at contaminated DOE sites can be beneficial because the reduced metal species are less soluble in water, less mobile in the environment, and also less toxic to humans and ecosystems. Although direct biological reduction has been reported for U(VI) and Cr(VI) in laboratory studies and at some field sites, the reactions can sometimes be slow or even inhibited due to unfavorable environmental conditions. One promising approach for the *in-situ* remediation of DOE contaminants is to develop biomimetic redox catalysts that can be delivered precisely to the specific subsurface locations where the contaminants reside.

Previous research studies have demonstrated that chemical and/or biological reduction of oxidized organic and inorganic contaminants often can be catalyzed by electron shuttle systems. Metalloporphyrins and their derivatives are well known electron shuttles for many biogeochemical systems, and thus were selected to study their catalytic capabilities for the reduction of hexavalent chromium and hexavalent uranium in the presence of reducing agents. Zero valent iron (ZVI) was chosen as the primary electron donor in most experimental systems, although other electron donors were also investigated.

The experimental research was conducted in three principal phases, with the knowledge gained from the earlier phases guiding the subsequent studies. Key activities, findings, and lessons learned during each phase were:

Phase I

- This exploratory phase utilized reduction reactions of Cr(VI) because of their relatively rapid rates and ease of analysis.
- Reductants (i.e., electron donors) examined included micro-sized ZVI, which is available commercially, and nano-sized ZVI which was synthesized as part of this study. Because the nano-sized ZVI is prone to processes that limit its effectiveness with time (e.g., agglomeration), novel methods to immobilize/support the material were investigated.
- Catalysts (i.e., electron shuttles) that were tested included cobalt- and iron-containing complexes of uroporphyrin and protoporphyrin, two naturally occurring porphyrins that are produced in organisms during heme biosynthesis, and Vitamin B12 which is a cobalt-containing complex related to metalloporphyrins. Because recycling and reuse of the catalysts would be desirable and because the catalysts themselves are soluble in water, methods to immobilize/support the catalysts were investigated.
- Silica-based sol-gels and calcium-alginate gel beads were the two different immobilization approaches that were examined in this phase.

- Preliminary attempts to immobilize nano-sized ZVI within sol-gel matrices were not successful. While the sol-gels were forming and hardening, their small pore spaces tended to exclude the nano-sized ZVI from the matrix. Gravity and the high density of the small iron particles also exacerbated the situation. The result of these effects were sol-gels that contained very little of the originally added reductant iron particles.
- In contrast with the nano-sized ZVI, we were able to successfully incorporate the water-soluble catalysts within sol-gel matrices. Long-term studies demonstrated that the catalysts did not leach out of the matrices.
- Because of the complications in trying to incorporate nano-sized ZVI within sol-gels, we examined their incorporation within calcium alginate beads which have larger pores and can be formed more rapidly such that exclusion does not occur. While these efforts to immobilize the iron particles were successful, we discovered that the pore sizes of the calcium alginate gel beads were too large and thus enabled the water-soluble catalysts to leach out of the matrix with time.
- The addition of the catalytic electron shuttles will be most useful when the micro-sized or nano-sized ZVI becomes less reactive due to aging or other effects.
- In general, immobilization of the nano-sized ZVI in gel beads and of the catalysts in sol-gels tended to result in slower rates of Cr(VI) reduction, but these effects will likely be overcome by the benefits that can be obtained when recycling and reusing the materials due to their incorporation within these matrices.

Phase II

- Reductants tested in this phase included sodium dithionite, L-ascorbic acid, and nano-sized ZVI.
- Continued work in the area of nano-sized ZVI immobilization led to procedures that were successful in incorporating the iron particles in sol-gel matrices.
- Use of the water soluble reductants dithionite and ascorbic acid tended to lead to formation of complexes with the uranyl cation, which limited their effectiveness.
- Although the sol-gel supported nano-sized ZVI showed some promise at reducing uranium, the fluoride used in the sol-gel synthesis protocol appeared to lead to formation of uranyl-fluoride complexes that were less reactive. A substitute for fluoride in the sol-gel synthesis is a future need.
- Because hexavalent chromium is an anion and does not form complexes with fluoride, it was used to demonstrate the intrinsic reactivity of the sol-gel immobilized nano-sized ZVI. Consistent with our observations in Phase I, the sol-gel matrix once again slowed down the reduction reaction but the expected benefits should outweigh this adverse effect.

Phase III

- The major emphasis in this last phase of the study was to simultaneously incorporate nano-sized ZVI and water-soluble catalysts in the same sol-gel matrix.

- The catalysts tested in this phase were cobalt complexes of uroporphyrin and protoporphyrin.
- As in Phase I, Cr(VI) reduction was used to test the efficacy of the combined “catalyst + reductant” sol-gel matrix.
- When enough catalyst was added to the sol-gels, enhancement of the Cr(VI) reduction reaction was observed. At the lowest levels of catalyst addition, however, the rates of Cr(VI) reduction were similar to those systems which only used sol-gel immobilized nano-sized ZVI without any catalyst present.
- These findings suggest future areas of research that should be pursued to further optimize abiotic reduction reactions of metals with combined “catalyst + reductant” matrices.

Original Project Hypotheses, Objectives and Relevance

Hypotheses

Metalloporphyrins and related derivatives are well known for their electron transfer roles in many natural systems. In addition, several metalloporphyrins have been shown to be efficient catalysts for the reductive transformation of certain organic contaminants. However, despite their great promise as environmental redox catalysts, several key issues will ultimately need to be resolved to determine the suitability of using metalloporphyrins for remediation of contaminants of concern at DOE facilities. The hypotheses guiding the proposed research are: (1) The presence of surfactants or other solubilizing agents will enhance metalloporphyrin catalytic reactivities, (2) Solubilized or encapsulated metalloporphyrins retaining their catalytic reactivity can be designed and delivered to subsurface environments utilizing and/or modifying common subsurface remediation techniques, and (3) Sol-gel matrices containing both zero valent iron and active metalloporphyrin catalysts can be prepared, delivered, and utilized as effective in situ remediation systems in subsurface environments.

Objectives

The objectives of the proposed research project are to (1) elucidate the effects of solubilizing agents on metalloporphyrin-catalyzed reduction of U(VI) and Cr(VI), (2) elucidate the effects of encapsulating agents on metalloporphyrin-catalyzed reduction of U(VI) and Cr(VI), and (3) investigate the feasibility of encapsulating nanosized zero-valent iron directly in sol-gel matrices with metalloporphyrins to form novel and complete reaction arrays containing both catalysts and reducing agent. Of particular interest to us is understanding the role of complexing agents on metal reactivity, solubilizing/encapsulating agents on metalloporphyrin reactivity, and development of the knowledge base necessary to understand the processes and conditions under which metalloporphyrins can be immobilized by novel sol-gel technologies to enable their efficient heterogeneous catalysis.

Relevance to DOE

Legacy contamination problems at DOE facilities require more effective *in situ* remediation technologies. Solubilized and/or encapsulated metalloporphyrins are a relatively new and promising technology for developing heterogeneous catalysts to rapidly degrade pollutants under anaerobic conditions. To date, however, they have not been utilized to treat contaminants of concern to DOE. The relevance to DOE of the proposed studies include an enhanced understanding of (1) the effectiveness of metal reduction and immobilization (e.g., precipitation) using metalloporphyrin catalysts, (2) the roles of solubilizing, encapsulating, and complexing agents in enhancing, limiting, or controlling the reaction rates in the catalyzed reaction systems, (3) the roles of solubilizing, encapsulating, and complexing agents in the

delivery of metalloporphyrin catalysts in subsurface environments, and (4) the use of nanotechnology for environmental applications through implementation of nano- and molecular-scale materials incorporated within a support containing nanoscale porosity.

Detailed Project Results

Phase I. Exploratory Studies – Hexavalent Chromium Reduction by Zero Valent Iron (ZVI)

Preliminary studies with Cr(VI) utilized protoporphyrin IX and uroporphyrin I which are naturally occurring porphyrins produced during heme biosynthesis. Different metalloporphyrins were prepared from these two porphyrins by inserting Co(II) or Fe(II) into the parent porphyrin molecules. These four synthesized metalloporphyrins, along with the widely-used electron shuttle Vitamin B12, were tested in Cr(VI) reduction reactions using the following electron donors: micro-sized ZVI, nano-sized ZVI, and nano-sized ZVI immobilized in calcium-alginate gel beads. The reduction of Cr(VI) as a function of time was analyzed using pseudo-first order kinetic models, and the catalytic capability of each electron shuttle was evaluated by comparison of reactions without the catalyst present versus the presence of the catalyst at various concentrations.

Different concentrations of metalloporphyrins or Vitamin B12 were added to catalyze Cr(VI) reduction at pH 7 by 1.7 g/L micro-sized ZVI or 0.1 g/L nano-sized ZVI (both with and without immobilization). No significant catalytic effects were found for Cr(VI) reduction by micro-sized ZVI in the presence of 20 μ M Co-protoporphyrin or Fe-protoporphyrin. Conversely, at the same catalyst concentration of 20 μ M, Co-uroporphyrin and Fe-uroporphyrin accelerated the reaction slightly (approximately 7% and 4%, respectively). At a concentration of 20 μ M, Vitamin B12 dramatically increased Cr(VI) reduction by the micro-sized ZVI, approximately 20% in 200 minutes.

In catalyst reuse tests with a more reactive form of micro-sized ZVI, Cr(VI) reduction in the presence of Vitamin B12 was not significantly enhanced in the first and second runs. However, by the third reuse cycle when the micro-sized ZVI had become less reactive, the Vitamin B12 significantly catalyzed Cr(VI) reduction. This finding suggests that catalysts such as Vitamin B12 are likely to be more important for long-term remediation applications when a solid-phase electron donor such as ZVI has aged and is no longer as highly reactive as when fresh.

Small amounts of Vitamin B12 (0.1 μ M) made Cr(VI) reduction by nano-sized ZVI reach completion approximately three times faster than when no catalyst was present. Encapsulation of the nano-sized ZVI in Ca-alginate gel beads hindered Cr(VI) reduction by a factor of 8 at pH 6 and a factor of 3 at pH 7 versus the original nano-sized ZVI. Upon adding 5 μ M Vitamin B12 to catalyze the reaction at pH 7, however, the reaction rate was significantly enhanced. For this particular test, 100 μ M of Cr(VI) was completely reduced in 20 minutes by the immobilized nano-sized ZVI, which was faster than without the Vitamin B12 catalyst (150 min) but also faster than the original (non-immobilized) nano-sized ZVI without catalyst (50 min).

Reuse of the nano-sized ZVI gel beads were tested multiple times at pH 6. After four reuse cycles, the beads were nearly completely broken apart but they clearly had collected most of the precipitated products. Therefore, using this kind of material for *in-situ* remediation of

oxidized metals may be beneficial from an aesthetic standpoint. In a related, unanticipated finding, we observed that the immobilized nano-sized ZVI gel beads became more reactive after being stored in an anaerobic chamber three months, during which time there may have been an enlargement in the overall gel pore size, microcracks on the gel bead surfaces, or perhaps ferrous iron production by hydrolysis of the nano-sized ZVI. Further research into the use of nano-sized ZVI that is immobilized in gel beads may be a promising topic to pursue.

In a final series of preliminary experiments, the catalyst Vitamin B12 was immobilized directly in sol-gel matrices to enhance its reclamation and reuse. The sol-gel matrix decreased the catalytic effectiveness of the Vitamin B12 versus its free, dissolved, state, but the immobilized catalyst was still able to greatly enhance the reduction of Cr(VI) by micro-sized ZVI and nano-sized ZVI.

The collective results of the preliminary experiments in Phase I indicated that certain metalloporphyrins and related electron shuttles can facilitate electron transfer and enhance the reduction of Cr(VI) by various types of ZVI under the right conditions. Vitamin B12 proved to be the most promising catalyst, followed by Co-uroporphyrin and Fe-uroporphyrin. Immobilizing Vitamin B12 in a sol-gel matrix only slightly inhibited its overall catalytic capability in Cr(VI) reduction tests, suggesting that this procedure has promise as a means to recapture and reuse the soluble electron shuttles.

Phase II. Hexavalent Uranium and Chromium Reduction by Various Electron Donors

Based on the findings obtained in Phase I, we commenced to examine several electron donors for remediation of low pH aqueous uranium contamination by reductive precipitation. The electron donors examined in this phase included sodium dithionite, L-ascorbic acid, and nano-sized ZVI. Additionally, the reductive capacity of nano-sized ZVI that was successfully entrapped within a silicate matrix (sol-gel) was also examined. This sol-gel-supported nano-sized ZVI was expected to increase the stability of the nano-sized ZVI in subsurface environments, as well as to provide a convenient *in-situ* delivery mechanism for other remediation systems which may combine entrapped reductant and catalyst.

Fluorescence and absorbance spectroscopies were used to investigate the interaction between hexavalent uranium (U(VI), uranyl) and both sodium dithionite and L-ascorbic acid at pH 2. The experimental results suggested complex formation between U(VI) and dithionite decomposition products, and also between U(VI) and L-ascorbic acid. Some evidence of U(VI) reduction by both sodium dithionite and L-ascorbic acid was observed; however, neither electron donors are promising for *in-situ* remediation due to complex formation with U(VI). In addition, for sodium dithionite, the aqueous instability of the dithionite ion at low pH limits its usefulness.

Analytical difficulties prevented an accurate study of the U(VI) interaction with nano-sized ZVI and sol-gel supported nano-sized ZVI. However, preliminary experimental data indicated some U(VI) removal by the supported nano-sized ZVI at pH 2. Because U(VI) has a low adsorption

affinity for silica at this low pH, the uranyl removal was thus attributed to its reduction. The presence of fluoride in the experimental system, which resulted from the sol-gel synthesis reaction, also may have negatively impacted uranyl reduction by the supported nano-sized ZVI due to the formation of stable aqueous U(VI)-fluoride complexes.

Because its chemical analysis was easier and its reactions faster than U(VI), the reduction of Cr(VI) by nano-sized ZVI and sol-gel supported nano-sized ZVI was also examined in Phase II. In these tests, reaction with both nano-sized ZVI and supported nano-sized ZVI resulted in Cr(VI) reduction at pH 2 and 4. Calculated rate constants were 0.055 and 0.22 hr⁻¹ for supported nano-sized ZVI at pH 4 and 2, respectively, and 7.86 hr⁻¹ for free nano-sized ZVI at pH 4. Although too rapid to accurately calculate, the rate constant for the reaction of nano-sized ZVI with Cr(VI) at pH 2 was greater than 50 hr⁻¹.

Despite some experimental and analytical difficulties, the collective results of the experiments conducted in Phase II led to some promising observations. For example, to our knowledge this is the first report of successful Cr(VI) reduction by nano-sized ZVI entrapped within a sol-gel. Our Phase II results also appear to be the first known report of U(VI) reduction by dithionite. Additionally, the work conducted in this phase provided the initial framework needed for further studies that aim to demonstrate the full potential of supported nano-sized ZVI for in situ subsurface remediation of metal (and other) contaminants.

Phase III. Chromium Reduction by Sol-Gel Supported Nano-sized ZVI and Metalloporphyrins

Based on the findings from Phases I and II, we commenced in this final phase to test the reduction of Cr(VI) by nano-sized ZVI contained in a supported silica sol-gel matrix by itself and with additions of two metalloporphyrin catalysts: Co-protoporphyrin and Co-uroporphyrin.

Experimental results demonstrated that Co-uroporphyrin and Co-protoporphyrin additions to the sol-gel supported nano-sized ZVI system each increased the rate constants compared to the supported nano-sized ZVI alone. Concentration data for the reaction kinetics were fitted as two pseudo-first order reactions, a k_{fast} for the initial decline and a k_{slow} once the initial steep decline was complete. The Co-protoporphyrin increased the slow reaction rate constant from 0.0080 to 0.0192 min⁻¹ (increase of ca. 2.5 ×) when added to the sol-gel supported nano-sized ZVI at a reductant:catalyst molar ratio of 100:1. Under comparable conditions, the Co-uroporphyrin also increased the slow reaction rate constant by a factor of ca. 2 (increase in k_{slow} to 0.0161 min⁻¹). Co-uroporphyrin and Co-protoporphyrin additions were also studied at other reductant:catalyst molar ratios in the sol-gel supported nano-sized ZVI systems: 1500:1, 750:1, 500:1, and 100:1. The reductant:catalyst molar ratios of 1500:1 and 750:1 had negligible effects on the reaction rate constants of the reduction system, but the reductant:catalyst molar ratios of 400:1 and 100:1 demonstrated clear beneficial effects in enhancing the rates of Cr(VI) reduction. Findings from Phase III showed that the catalytic effect of Co-uroporphyrin was somewhat higher than that of Co-protoporphyrin at lower molar ratios such as 1500:1 and 750:1, but that at the higher ratios such as 100:1 the Co-protoporphyrin acted as a more effective catalyst.

Products Delivered

Mark A. Schlautman, Elizabeth R. Carraway, Shanna L. Estes and Rong Zhang. Optimizing Metalloporphyrin-Catalyzed Reduction Reactions for In Situ Remediation of DOE Contaminants, Presented at the Department of Energy Environmental Remediation Science Program 3rd Annual Principal Investigator Meeting, National Conference Center, Lansdowne, VA, April 2008.

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Shanna Lynn Estes. Uranyl Reactions with Dithionite, L-Ascorbic Acid, and Supported Nanosized Zero-Valent Iron, M.S. Thesis, Clemson University, May 2011.

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Jonathon Hugh Ball. Hexavalent Chromium Reduction Using Supported Nanosized Zero-Valent Iron and Metalloporphyrin Matrices, M.S. Thesis, Clemson University, May 2013.

(full thesis text was not yet available electronically from the Clemson University Library at the time of this report, but it will become available at a time TBD; see www.clemson.edu/library/ for more information)