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Total Reducing Capacity in Aquifer Minerals and Sediments: Quantifying the Potential to Attenuate Cr(VI) in Groundwater

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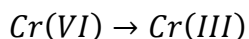
ABSTRACT

Hexavalent chromium, Cr(VI), is present in the environment as a byproduct of industrial processes. Due to its mobility and toxicity, it is crucial to attenuate or remove Cr(VI) from the environment. The objective of this investigation was to quantify potential natural attenuation, or reduction capacity, of reactive minerals and aquifer sediments. Samples of reduced-iron containing minerals such as ilmenite, as well as Puye Formation sediments representing a contaminated aquifer in New Mexico were reacted with chromate. The change in Cr(VI) during the reaction was used to calculate reduction capacity. This study found that minerals that contain reduced iron, such as ilmenite, have high reducing capacities. The data indicated that sample history may impact reduction capacity tests due to surface passivation. Further, this investigation identified areas for future research including: a) refining the relationships between iron content, magnetic susceptibility and reduction capacity, and b) long term kinetic testing using fresh aquifer sediments.

I. INTRODUCTION

Hexavalent chromium Cr(VI) is acutely toxic, mutagenic, and carcinogenic. Traditional ex-situ chromium contaminated soil and groundwater treatment methods such as pump and treat require extraction of the Cr(VI) from the subsurface. These extraction methods can be expensive both in the long and short-term and may not be effective at remediating source-zone Cr(VI). In-situ treatments, including geochemical fixation, permeable reactive barriers, phytoremediation, and monitored natural attenuation (MNA) however, have the ability to immobilize Cr(VI) underground by converting it into Cr(III) thus decreasing the toxicity, mobility, and solubility. In situ treatments and MNA have the potential to lower water phase concentration of Cr(VI) and to decrease costs and increase safety.

Monitored natural attenuation (MNA) according to the EPA, includes “a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater”.¹To attenuate something is to weaken or reduce the intensity of and natural attenuation processes are typically occurring at all sites but to varying degrees.² In aerobic settings, chromate remediating minerals are those that contain reduced iron. Those reactive minerals have three electrons available for the reaction of Cr(VI) to Cr(III).



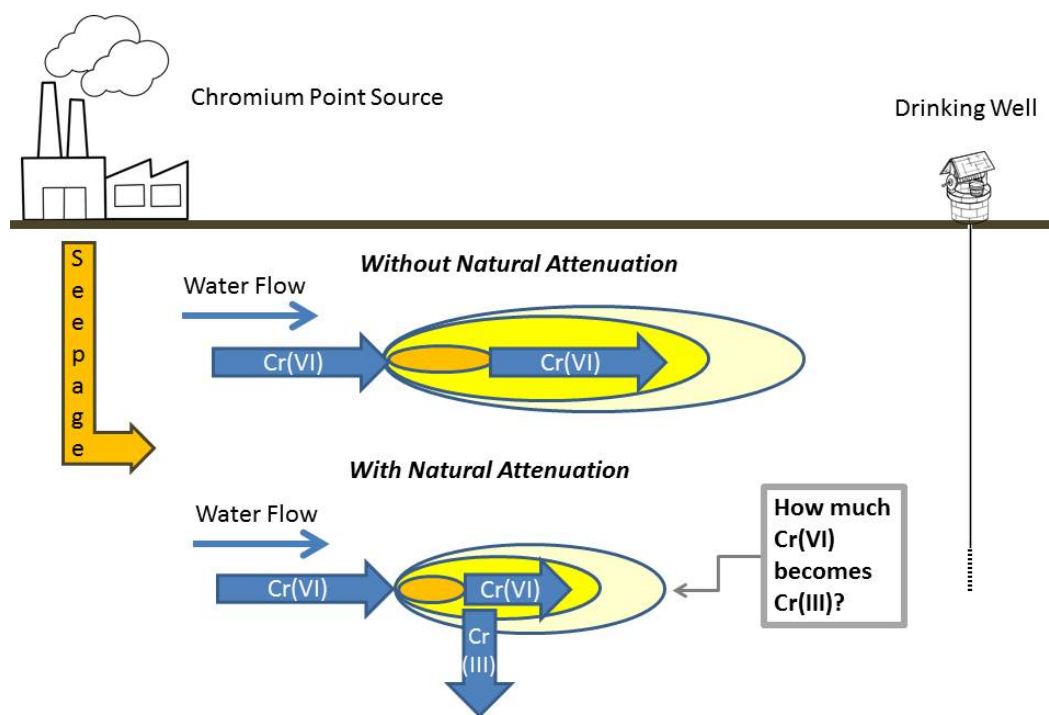
↑

3e⁻ from reduced iron – containing minerals

It is important to understand the geochemical environment of a Cr(VI) contaminated site due to the cyclic and interactive nature of chromium phases. Chromium when in natural water systems occurs as either Cr(III) or Cr(VI). Cr(VI) is the most oxidized and mobile chromium

state and in soils, the reduction of Cr(VI) to Cr(III) can occur as a result of reduced-iron containing compounds in certain minerals.³ Anderson et al (1994) conducted experiments reacting sand collected from an aquifer with hexavalent chromium and observed that Cr(VI) reduction occurred primarily on Fe(II)-bearing minerals.⁴ Further, Palmer (1996) justified that in order to determine the potential for Cr(VI) natural attenuation, not only must there be a reducing agent, such as iron in the aquifer, but the reduction product, Cr(III), must remain immobile (i.e. there must be no net oxidation of Cr(III) to Cr(VI) and the amount of Cr(VI) must not exceed the reduction capacity of the aquifer).⁵ Thus, there is a need for further research in order to test and quantify the reducing capacity of an aquifer and the several interacting parameters that influence reducing capacity (Figure 1).

Figure 1. Schematic of Cr(VI) transformation in an aquifer demonstrating that with natural attenuation, Cr(VI) can become Cr(III) thus decreasing the size and impact of Cr(VI) contamination on a well down-gradient.



The objective of my 10-week Science Undergraduate Laboratory Internship (SULI) experience was to quantify the total reduction capacity (TRC) of reduced iron-bearing minerals for an abiotic, homogenous aquifer. In this paper, I describe how the experiments were setup, how the reduction capacity was calculated and analyzed, and finally discuss the significance and future work regarding estimating the reduction potential of an Cr(VI) contaminated aquifer.

II. METHODS

A. Reduction Capacity Experiments

The mineral samples used to test reduction capacity were: ilmenite, magnetite, staurolite, zircon, and magnetic leucoxene provided by ILUKA Resources located in Stony Point, Virginia, USA as well as “white” silica sand (as the control). Scoping tests were also performed on Puye sediments taken from Los Alamos, New Mexico, USA. The Puye formation sediment outcrop samples were air-dried and the fraction sieved was larger than 60 mesh and smaller than 10 mesh. CHEMetric brand chromate Vacu-vial kits were used to quantify the chromate concentration after the reaction time. A V-2000 CHEMetric photometer was pre-programmed to measure the chromate. Bulk Puye sediments were tested along with magnetic splits of the sieved material that were separated using a Frantz LB1 magnetic separator set at 0.5, 1, and 1.8 amperes; the magnetic field was applied to vertical falling grains.

Minerals were tested for their reducing capacity by comparing chromate equivalents at 24, 48, 72 hours after the initial reaction time and the Puye sediments were reacted for up to 168 hours. Approximately 1 gram of the sediment (either mineral or Puye) sample was placed into a 50 mL centrifuge tube. The sediment was then combined with either 0.01N H₃PO₄ or 1N H₂SO₄ and K₂Cr₂O₇ and gently swirled. The quantity of K₂Cr₂O₇ was adjusted for each sample so that

approximately 5 to 50% of the initial spike was reduced. The centrifuge tubes were then set aside in a shaker and allowed to react for 24-168 hours. The subsequent tubes were then centrifuged and an aliquot of the supernatant sample removed. The supernate was diluted according to the photometer range-reading values. The diluted samples were then analyzed using a Chemetrics Cr(VI) test kit. The spectrophotometer value was converted to available reducing capacity by a series of calculations. These series were repeated using different volumes of $K_2Cr_2O_7$ and different reduced-iron minerals.

B. Calculation of Total Reduction Capacity

Because the initial chromate equivalents are known, a decrease in chromate of the final solution provides the calculation for reduction capacity. The initial equivalents of chromate were calculated by multiplying the normality of the potassium chromate solution by the volume added. Taking into account dilution factors and assuming that 1 mg dichromate = 0.0258 milliequivalents (meq), we were able to convert the photometer reading to meq dichromate in the tube. This value was subtracted from the original spike quantity and converted to reducing capacity (meq/g) by dividing by the mass of soil. We fit the time series results to estimate the total reduction capacity of each mineral or Puye sediment using Equation 1.

$$RC_t = RC_{(t-\Delta t)} + k(TRC_{max} - RC_{(t-\Delta t)})\Delta t \quad (1)$$

Where RC_t is the measured reduction capacity (meq/g) of the mineral at any time t, $RC_{(t-\Delta t)}$ is the reduction capacity of the mineral at the previous time point (meq/g), and k is the kinetic rate of the reaction (1/day), TRC_{max} is the maximum total reduction capacity of the sample as indicated by an asymptote on the graph, and Δt is the time from the previous time point (day).

III. RESULTS

In order to determine the total reduction capacity (TRC) of each mineral or Puye formation sediment, the CHEMetric chromate reading was converted into a meq/g reading and plotted (Figures 1, 2, 3). The asymptote at which the reducing capacities leveled off was qualified as the total reduction capacity of each mineral.

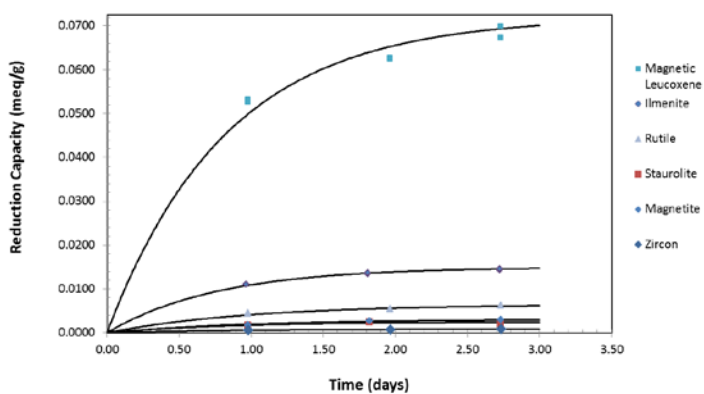


Figure 1. Reduction capacity (Equation1) of ~1g of ilmenite (reacted with 1 mL of chromate), ~1 g of magnetite (reacted with 0.75 mL of chromate), ~1g of staurolite (reacted with 0.5 mL chromate), ~1g of rutile (reacted with 0.5 mL of chromate), ~1g of zircon (reacted with 0.1 mL of chromate), ~1g of magnetic leucoxene (reacted with 2.5 mL of chromate) after 24, 48, and 72 hours in tandem with reduction data. All mineral sands were treated with 2 mL sulfuric acid before addition of the chromate and the concentration of final chromate was measured using photometry following step dilutions.

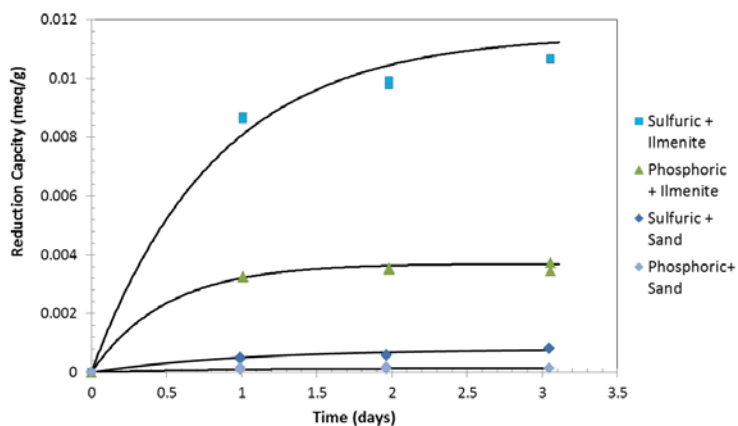


Figure 2. Reduction capacity (Equation) of ~1g of ilmenite (reacted with 0.5 mL of chromate) and ~ 1g of silica sand (reacted with 0.1 mL of chromate) after 24, 48, and 72 hours. Both ilmenite and silica sand were treated with either 2 mL 1N sulfuric acid or 2 mL 0.01N phosphoric acid before addition of the chromate and the concentration of final chromate was measured using photometry following step dilutions.

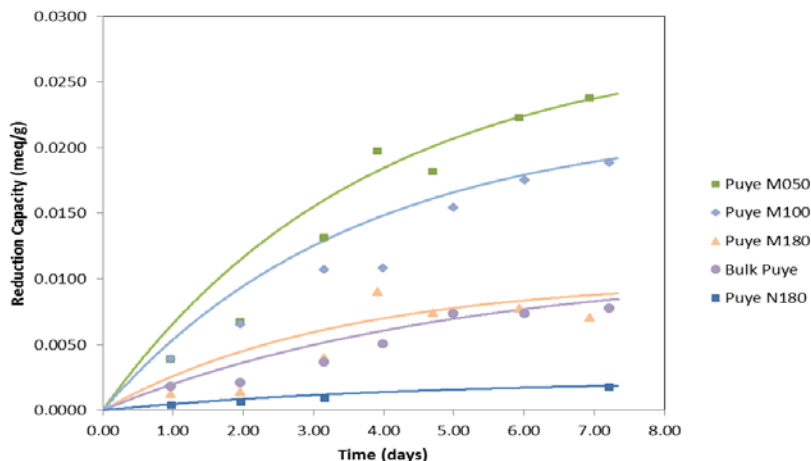


Figure 3. Reduction capacity (Equation) of ~1g of Puye formation sediments separated by magnetic amperage applied (either bulk sample, 0.5A, 1.0A, 1.80A, or non-magnetic at 1.80A). Puye bulk (reacted with 1 mL of chromate) and ~ 1g of M050 Puye (reacted with 1 mL of chromate), ~1g of M100 Puye (reacted with 1mL of chromate), ~1g of M180 Puye (reacted with 0.5 mL of chromate), and ~1g of N180 Puye (reacted with 0.5 mL of chromate) after 24-168 hours. All of the samples were treated with 2 mL sulfuric acid before addition of the chromate and the concentration of final chromate was measured using photometry following step dilutions.

Once the reducing capacities of zircon, rutile, silica sand, magnetic leucoxene, staurolite, magnetite, ilmenite, and the Puye formation sediments were plotted, the TRC was correlated to the magnetic susceptibility (Figure 4). Then, the TRC was plotted against the percentage of elemental iron within each mineral (Figure 5).

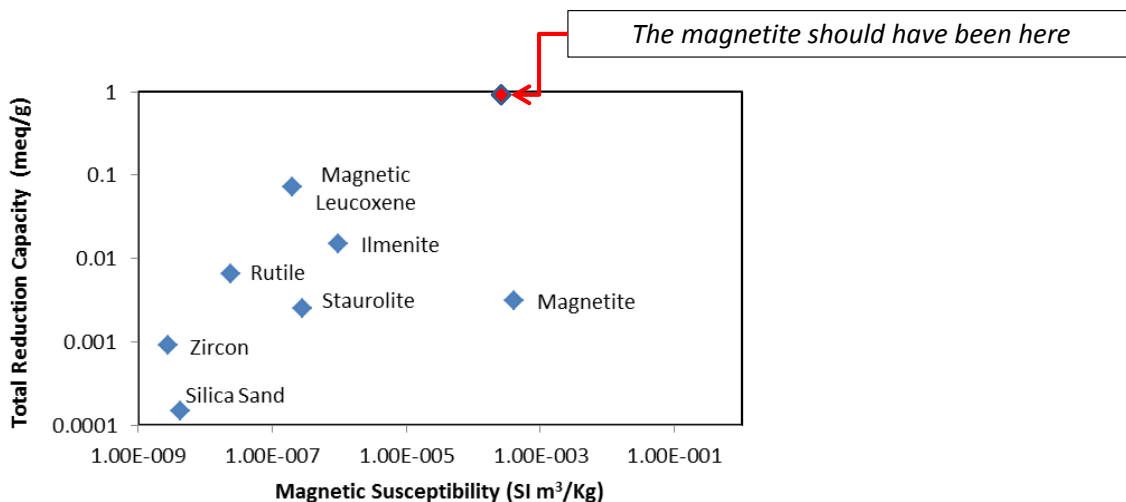


Figure 4. Measured magnetic susceptibility of reduced-iron containing minerals determined using a magnetic susceptometer versus the Total Reduction Capacity (TRC). The TRC for each mineral was determined by plotting the asymptote at which the reducing capacity leveled off.

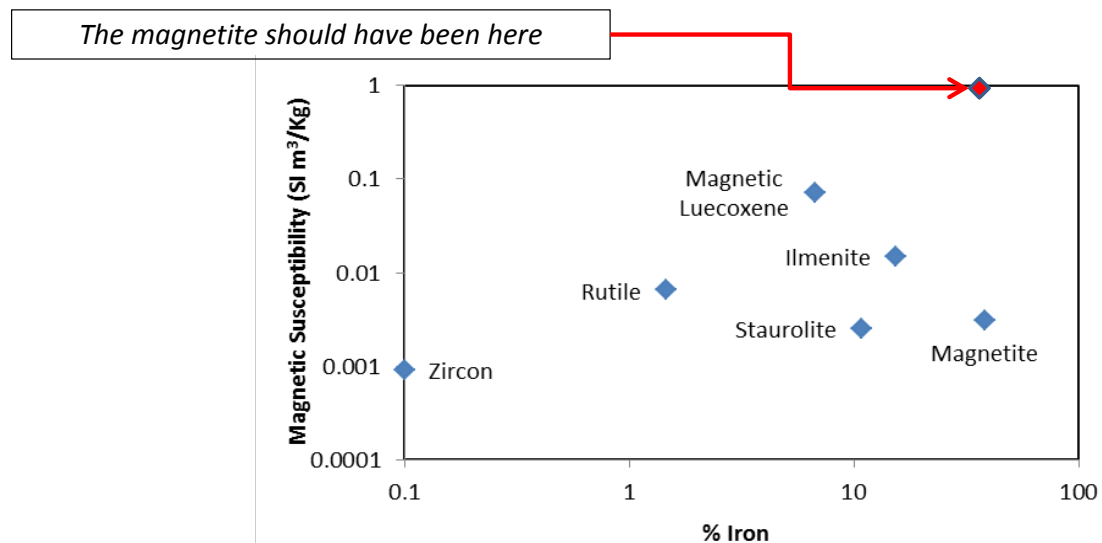


Figure 5. Elemental iron in reduced iron-containing minerals and relative magnetic susceptibilities. Percentage of iron in each element was determined using X-ray fluorescence (XRF) and then corrected using a standard calibration curve based on NIST standard reference materials.

IV. DISCUSSION

Both the Puye and the mineral samples effectively demonstrated an increasing level of reduction capacity with time with the data leveling off at later times. The decreasing rate is a function of using up the electrons from the active minerals. Figure 1 demonstrates that magnetic leucosene has the highest Cr(VI) reduction capacity 0.07 meq/g and zircon has the lowest with a total reduction capacity of 0.0009 meq/g.

Equation 1 plays an important role because it quantifies the total reduction capacity of a mineral. The TRC values of each mineral when compared among each other provide valuable tools for predicting the reduction capacity of an aquifer where reduced iron-bearing minerals or even Puye sediments are present.

Figure 2 introduces an important conceptual learning point that occurred when determining whether to treat the minerals and Puye sediments with either sulfuric or phosphoric acid before

adding chromate. The initial thought was to treat with phosphoric acid in order prevent Cr(VI) adsorption to the mineral surfaces.⁶ When chromate comes into contact with a mineral surface and the concentration after reaction is measured, if not treated with an acid beforehand, the concentration would not represent the true amount reacted because chromate can react with minerals but it can also adsorb to mineral sites. The phosphate therefore directly competes for the adsorption sites in the soil and mitigates the possibility for chromate to adsorb allowing us to measure only the amount of chromate reacted. Further, waiting for natural attenuation to occur at the rate parallel to nature would be impractical due to the time allotted for the research. Therefore, not only did the phosphate directly compete for adsorption sites, it also sped up the simulated natural attenuation of chromate process. Additionally, magnetite, when reacted with the same concentrations of phosphoric and sulfuric acid and chromate after 24 hours had a reduction capacity of 0.0003 but when reacted with sulfuric acid and chromate after 24 hours had a reduction capacity of 0.0014 demonstrating a 37% increase in reduction capacity.

Figure 4 demonstrates that minerals with higher magnetic susceptibilities have higher reducing potential in a generally increasing trend. Further, in the case of the ilmenite in Figure 5, it could be argued that a high amount of iron in a mineral also lends to a higher reducing potential of Cr(VI). Arguably however, in the case of magnetic leucoxene which consists of 6.7% iron and has less iron than ilmenite, magnetite, and staurolite, it has the greatest amount of reduction potential. This fact indicates that more components need to come into consideration when quantifying the total reduction capacity such as mineral elemental compositions. In both Figures 4 and 5, magnetite is the outlier and special case. Even though magnetite consists of 38.2% iron and has the largest magnitude of magnetic susceptibility, its total reduction capacity is comparable to that of zircon and staurolite.

During preliminary testing, the magnetite (which has the highest degree of iron) did not reduce the most amount of chromate which is contrary to what literature suggests.⁷ Even though both ilmenite and magnetite have a high degree of magnetic susceptibility, the reduction capacity of the ilmenite was almost 5 times greater than that of the magnetite. Thus, it can be reasoned that passivation played a role in preventing chromate reduction of magnetite due to the geologic history of where the magnetite sample was taken from. Passivation occurs when exposed iron valence atoms (such as in magnetite) react with the oxygen in air to form a tough layer of oxide, preventing the chromate from reacting. The passive layer can be damaged through mechanical and chemical means. Sulfuric acid was introduced as an alternative to phosphoric acid because it could have the potential to essentially burn through a passive layer and allow chromate reduction to occur. In conclusion, it is more robust and less sensitive to passivation.

Figure 3 also demonstrates passivation of the Puye formation sediments. Note that in the beginning of each set of data points, Equation 1 does not fit the data for the Puye as well as it did for the minerals (Figure 1). This is because the Puye sediments were taken from an environment (similar to that of the magnetite) where they were exposed to oxidizing conditions and thus a passivation layer was formed. By day 5 however, the sulfuric acid appears to have burned through the passivation layer and the Puye data finally fits a curve that can be fit.

In order to mitigate the occurrence of passivation, additional work is necessary with fresh mineral samples. A standard range for chromate reduction also needs to be calculated in order for the minerals to fully express a range of reduction capacity thus excess chromate was needed in order to keep the CHEMetric reading at or above approximately 1.7mg/L chromate.

V. Conclusion

This investigation found that minerals that contain a high amount reduced iron (> 3%) such as ilmenite , have high reducing capacities. Further, Puye formation sediments containing volcanic ash and pumice (which are not pure minerals), also have the potential to reduce chromate due to the presence of iron. The data indicated that sample history may impact reduction capacity tests due to surface passivation.

VI. Acknowledgments

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