SELENIUM AND URANIUM REMOVAL IN NITRATE-RICH GROUNDWATER

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ABSTRACT

Mallinckrodt Chemical Works (MCW) in St. Louis purified uranium from uranium black oxide and pitchblende ore as part of the Manhattan Project in the 1940's during the early days of the country's nuclear program. The radioactive waste material from MCW and other sites was captured and stored at a site near the St. Louis Airport (Lambert Field). The site is currently a Superfund site under the Formerly Utilized Sites Remedial Action Program (FUSRAP) called the St. Louis Airport Sites (SLAPS). In addition to uranium, significant levels of selenium were present in the feed material. Nitric acid, an oxidizing agent, was used in the extraction process, resulting in SLAPS groundwater contaminated with high levels of uranium, selenium, and nitrates. SLAPS groundwater contaminant concentrations ranges are as follows – uranium: 600 pCi/L to 5,700 pCi/L, selenium: non-detect to 5.20 mg/L, and nitrates: 600 mg/L to 2,800 mg/L as nitrogen.

A biological treatment system for the removal of uranium and selenium from water generated at SLAPS was designed and tested. Denitrification efficiency was of particular interest, as nitrate removal would likely be needed as a precursor to any chemical system developed for selenium removal. Activated sludge was used to inoculate the system and methanol utilized as an electron donor. The process was successful at treating site water to local sewage treatment system influent standards at bench (55 gallon), pilot (16,000 gallon) and full (120,000-450,000 gallon) scale batch volumes.

The biological process reaction rate, while consistent for uranium and nitrate removal, proved unreliable at times for complete selenium reduction. Plateauing selenium levels following periods of initial rapid selenium reduction led to the development of a chemical polishing process.

Bench tests were undertaken using SLAPS excavation water in order to determine the effectiveness of a copper/iron co-precipitation process. The pH of the water was lowered, aqueous copper added, and the water contacted with elemental iron. The pH of the water was then raised and the solids settled out. The process proved highly successful for the denitrified water and ineffective for non-pretreated water, with copper levels the limiting factor in the governing reaction. Continued success of this process will result in a treatment method that can be used at other radioactive clean up sites experiencing similar treatment situations, as well as projects solely requiring selenium removal.

INTRODUCTION

Selenium is both an essential and toxic element, with the variance in determinate concentrations relatively small. Selenium contamination from anthropogenic sources has been responsible for the devastation of entire aquatic systems [1, 2]. Most organisms demonstrate a tendency to bioaccumulate high levels of selenium, possibly due to being a nutrient. Biomagnification can result in organisms with selenium concentrations 100 to 30,000 times that found in their aquatic environment [3]. Whereas lower organisms experience elevated selenium concentrations resulting from aqueous and vegetative sources, the chief origin of selenium in fish and higher organisms is their food [4]. As a result, long after sources of selenium are eliminated and aqueous concentrations are low, rooted plants and food pathways can continue to be a source of selenium contamination to fish and wildlife in the system [5].

In 1942, during the early days of the country's nuclear program, Mallinckrodt Chemical Works (MCW) in St. Louis was contracted by the Atomic Energy Commission to purify uranium from uranium black oxide and pitchblende ore as part of the Manhattan Project. This continued through 1957, with the radioactive waste material from MCW captured and stored at a site adjacent to the St. Louis Airport (Lambert Field). The site, now referred to as the St. Louis Airport Sites (SLAPS), is currently a Superfund site under the Formerly Utilized Sites Remedial Action Program (FUSRAP). Currently, uranium levels in SLAPS groundwater range from 600 pCi/L to 5,700 pCi/L. The 10CFR20 Appendix B discharge limits for uranium is 300 pCi/L when releasing to Coldwater Creek - a stream bordering the site and for which its lower stretch is classified for livestock watering and recreation - and 3,000 pCi/L when releasing to the St. Louis Metropolitan Sewer District (MSD), a publicly owned treatment works. Ion exchange was utilized for groundwater uranium removal prior to the evaluation of nitrate and sulfate interference as well as characterization of selenium in excavation water.

Significant levels of selenium were present in the feed material. An initial step in the extraction process was the digestion of the feed material with nitric acid, an oxidizing agent. The selenium compounds were oxidized to the soluble forms selenate and selenite, the contamination source. Currently, over 95% of the selenium found in SLAPS groundwater is present as selenate. Aqueous selenium concentrations found at SLAPS range from non-detect to 5.20 mg/L. The default discharge limits for selenium are 0.005 mg/L when releasing to lower classified reach of Coldwater Creek and 0.200 mg/L when releasing to MSD.

Another consequence of the extraction process has been elevated nitrate levels in the groundwater, ranging from 600 mg/L to 2,800 mg/L as nitrogen. In addition to uranium, selenium, and nitrates, the presence of significant sulfates (50 mg/L to 250 mg/L as sulfur) merits consideration when evaluating potential treatment applications.

Uranium is normally removed without difficulty using ion exchange or pH adjustments. However, these methods are inadequate in removing selenium from SLAPS groundwater. Initially, a biological treatment approach was designed as a solution. Whereas the treatment goals were met using the biological process, selenium removal efficiency issues resulted in the pursuit of a chemical polishing step.

BIOLOGICAL TREATMENT APPROACH

Efforts initially focused on determining the applicability of a biological treatment system for the removal of nitrates, uranium, and selenium from water generated at SLAPS. Prior research identified these contaminants as candidates for biological reduction under certain conditions [6, 7]. Biological denitrification was a requisite goal as it would likely be needed as a precursor to any chemical system developed for selenium removal.

Biological reduction of nitrate and uranium individually has been demonstrated in the past. However, long-term removal of uranium has been complicated by the presence of nitrates [8]. Biological reduction of selenium is not as defined and has been explored in depth only recently.

In an attempt to minimize operating costs an activated sludge process was designed and tested. Return activated sludge from municipal water treatment plants was used as seed inoculates. Initial suspended solids concentrations following inoculation ranged from 500 ppm to 1,000 ppm. The target microbial population corresponded to a volatile suspended solids concentration between 1,000 ppm to 2,000 ppm. Once this level is achieved, means should be taken to waste sludge at a rate equivalent to that of generation. Methanol was utilized as an electron donor and BiChem Accelerator IV as a source of phosphorous. Sulfuric acid and sodium hydroxide were used for pH adjustments.

Testing Methodology

Initial bench tests were conducted using 50-gallon batches and focused on determining applicability of the process design to the specific site water, identifying competing ions, and optimizing reagent dosages and conditions. Parameters such as pH, reagent dosages, mixing rates, and number of stages were varied in order to determine the most advantageous operating conditions. After the seed inoculate and reagents were added, the process was closely monitored for pH, dissolved oxygen, nitrates, uranium, sulfates, selenium, and total organic carbon. Once treatment goals were met, the supernatant (~75%-85% of the total reactor volume) was decanted and filtered through a 1.0-micron nominal bag filter. Untreated groundwater was then added to the reactor and the process repeated.

Once process efficaciousness was established and ideal operating conditions were determined the process was scaled-up in order to confirm the bench test results and begin treating site groundwater. The treatment goals were subsequently met at pilot-scale (15,000 gallons) and full-scale (140,000 gallons to 400,000 gallons) batch volumes.

REDUCTION OF TARGET CONTAMINANTS VIA BIOLOGICAL TREATMENT

Uranium

Bench, pilot, and full-scale tests successfully reduced uranium to below the MSD discharge criteria of 3,000 pCi/L. There are a host of anaerobic bacteria known to reduce uranium, often resulting in the precipitation of uraninite [6]. In all cases, oxygen is reduced and the water turns anoxic. Once this has occurred, uranium was reduced preferentially to nitrate in some cases and

concomitantly in others. In the majority of tests, virtually all uranium was reduced (< 20 pCi/L) by the time denitrification was complete; in many cases this condition was met significantly earlier in the process. This is in contrast to prior research that had shown nitrates to be an inhibitor of uranium reduction [6, 8]. Rapid, complete uranium removal was observed under all conditions tested, including sequential batches within the same reactor. In-situ dissimilatory nitrate reduction has been associated with the mobilization of previously reduced uranium due to the oxidation of uranium by denitrification intermediates [8]. This unfavorable reaction was avoided by maintaining a highly reductive environment in the bioreactor.

Nitrate

Successful denitrification was achieved in all tests. The *Pseudomonas* species is the predominant denitrifying bacteria found in activated sludge [9].

Only oxygen and uranium were reduced preferentially to nitrates in the process. Normally nitrates and uranium were reduced simultaneously. In most cases, uranium was completely reduced prior to total denitrification. As previously noted, nitrate reduction did not result in oxidation of insoluble uranium. Nitrate was reduced preferentially to selenium, but more often they were reduced simultaneously, with denitrification concluding prior to complete selenium removal.

A two-stage process was bench tested in which nitrate reduction was isolated in one reactor and the process completed (selenium removal) in another after denitrification. Nitrate removal exhibited increased efficiency with successive batches. This was expected as successive generations of bacteria grown on identical substrates are more effective at utilizing those particular substrates.

Figure 1 displays the nitrate achieved during the bench tests conducted. The disparity in reduction rates was useful in determining optimal operating conditions.



Fig. 1 Nitrate reduction rates

Selenium

Selenium removal was successful at varied levels at each tier of testing. Once anoxic, nitrate was reduced preferentially to selenium, but more often they were reduced simultaneously, with denitrification concluding prior to complete selenium removal. There were occasions in which total selenium removal occurred prior to the completion of denitrification. This presents no compliance issue and the water can be discharged without further treatment for nitrates.

The two-stage process did not result in increased efficiency of selenium removal; the second batch treated demonstrated lower selenium reduction rates than the initial batch. This can be attributed to the nature of the specific bacteria responsible for selenium reduction – many are unable to reduce selenate or selenite in the absence of nitrate or nitrite. The inability to effectively reduce selenate would have obvious detrimental effects. The inability to reduce selenite can lead to the accumulation of toxic selenite levels resulting in decreased performance.

Figure 2 displays the selenium reduction rates achieved during the bench tests conducted. The disparity in reduction rates was useful in determining optimal operating conditions.



Fig. 2 Selenium reduction rates

The most pertinent issue observed with respect to selenium was severe drop-off in reduction rate following rapid initial removal (discussed below).

OBSERVATIONS / DISCUSSION

Scalability

The process as described was successful in achieving selenium removal in batch volumes ranging from 50 gallons to over 400,000 gallons. The process challenges that are discussed herein were observed over the range of batch volumes treated. Despite any delays caused by problems encountered, all targeted excavation water has been successfully treated. The process is well suited for full-scale operation.

Optimal Process Conditions

Completion of the bench and pilot tests, as well as full-scale operation, has allowed for the determination optimal process conditions, displayed in Table I.

| Operating Parameter | Target Range |
|----------------------------|-----------------------|
| mixing | complete |
| pH | 7.00 to 7.75 |
| total organic carbon | 400 mg/L to 800 mg/L* |
| phosphorous | 25 mg/L to 50 mg/L |
| temperature | 80° F to 90° F |

Table I: Optimal operating conditions observed for slaps bioremediation

*target range when methanol is used and does not include non-methanol TOC which may be present, target concentration may vary with a different electron donor source

Observation of Figs. 1 and 2 reveal the highest reduction rates for nitrate and selenium can be found in the tests referred to as "mixed" that utilized an agitator to obtain complete mixing. Due to the urgency to commence treatment, process water was re-circulated by pumping within tanks and basins as opposed to purchasing and installing agitators. Re-circulating resulted in improved performance over conditions in which no means to improve biomass contact was utilized. Both conditions resulted in minimal biomass contact and did not compare to the efficiency observed in the "mixed" tests. SLAPS will install a floating mixer in the 210,000 gallon tank used for biological water treatment in spring of 2004.

Identification of Selenium Reducing Bacteria

Detailed microbiological analysis has not been performed on the SLAPS bioreactor water to determine the characteristics and growth dynamics of the microbial population. There are a broad range of bacteria which reduce uranium and nitrates; these are relatively common reactions and are well documented. Determining a microbe suitable for selenium reduction in a given system is more difficult. In addition, a vast array of bacteria is represented in an activated sludge inoculate. However, observations made to this point can narrow the field of responsible bacteria, aiding future process optimization.

Previously, most cases of biological selenium reduction were considered incidental – attributable to non-growth supporting reactions catalyzed by non-specific enzymes [3, 7, 10, 11]. These reactions are responsible for the reduction of selenium oxyanions in ideal environments and are often associated with sulfate or nitrate reducing bacteria. However, further study has revealed a class of microorganisms capable of conserving energy and sustaining growth through specific enzyme reduction of selenate. Four have been specifically identified with other potential bacteria awaiting characterization [12]. Certain bacteria from either of these classes may be responsible for the reactions occurring in the SLAPS bioreactor.

The simultaneous reduction of selenium and nitrate observed at SLAPS is characteristic of the bacterium *Thauera selenatis*, one of a small group of bacteria capable of utilizing selenate as a terminal electron donor [13]. *T. selenatis* is capable of growth-supporting reduction of selenate to selenite and nitrate to nitrite utilizing distinct reductases; as a result, selenate and nitrate are not competitive inhibitors and will be reduced simultaneously when both oxyanions are present. *T. selenatis* catalyzes the reduction of selenite to elemental selenium using its nitrite reductase, although this reaction is not growth-supporting. The nitrite reductase is present/active during

denitrification and, consequently, significant reduction of selenite will only occur with active denitrification; selenate is reduced to selenite with no further reduction in the absence of denitrification [14].

Enterobacter cloacae strain SLD1a-1 also reduces selenate to selenite concomitantly with nitrate, but cannot do so to support growth; a separate mechanism is responsible for the subsequent reduction to elemental selenium which is deposited extracellularly [15]. The second step, dissimilar selenite reduction to elemental selenium, will not take place unless nitrate is present, possibly implicating the nitrate or nitrite reductases in selenite reduction [16]. The optimum pH and temperature ranges for selenate reduction by *E. cloacae* strain SLD1a-1 are similar to those typically found at SLAPS: 6.5 < pH < 7.0 and $86^{\circ} F < T < 95^{\circ} F$ [17].

Selenium reduction following nitrate reduction was also observed at SLAPS. This may be indicative of the nitrate reductases found in bacteria such as *Rhodobacter sphaeroides*, *Escherichia coli, Ralstonia eutropha, Paracoccus denitrificans*, and *Paracoccus pantotrophus* which, like *E. cloacae* strain SLD1a-1, catalyze the reduction of selenate through a non-specific enzyme [14, 18, 19]. Selenate reduction by bacteria of this type normally requires active denitrification; unlike *T. selenatis*, though, the reduction of nitrate and selenate may happen consecutively [20]. Whereas the presence of these bacteria may be responsible in part for the reduction of selenium oxyanions at SLAPS, in most cases significant selenium reduction was observed before complete denitrification was achieved.

In some cases, the efficiency of selenium reduction increased with subsequent batches in the same reactor. In general, most bacteria capable of selenium reduction demonstrate greater efficiency in carrying out the reaction when they are grown on the substrate. In particular, *Wolinella succinogenes* appears to adapt to the presence of selenium oxyanions, with efficient reduction occurring only after an initial growth period [21].

There are many bacteria capable of contributing to the selenium reduction occurring at SLAPS. More than likely the actions of a number of bacteria are responsible. The bacteria whose characteristic behavior most closely mirrors the treatment patterns observed in the SLAPS bioreactors are *T. selenatis* and *E. cloacae* strain SLD1a-1.

Process Challenges

The most critical problem encountered has been a drop-off in selenium reduction rates after efficient removal in the initial treatment period. This results in a plateau in which the selenium levels are significantly reduced, yet remain above discharge criteria. This has occurred mainly in bioreactors which had treated three or more batches. This circumstance is demonstrated in Figure 3, which displays the results of consecutive batches treated in the pilot reactor.

The drop-off in efficiency may have resulted from inadequate sludge wasting. The tanks and lined basins used for treatment are not traditional bioreactors and are subsequently absent of an ideal means to waste sludge. In addition, the lack of complete mixing made measuring the volatile suspended solids concentration difficult and prone to error, resulting in unreliable

indications of when wasting was necessitated. These issues will be addressed with the addition of a floating mixer system in spring of 2004.



Fig. 3 Bioremediation pilot timeline

Another potential cause for the decline in reduction is the bacteria responsible for carrying out selenium reduction. It is important to note that selenite is toxic to most bacteria. There is only a single bacterium identified as capable of reductase-specific selenite reduction - *Bacillus selenitireducens*, a haloalkaliphile requiring high pH and salinity to thrive [22, 23]. The reduction of selenite is catalyzed by non-specific reductases and in many cases is considered a means of detoxification. It is possible that the bacteria present display diminished selenite reducing capabilities once the denitrification has completed. This condition could lead to the build-up of toxic levels of selenite, eroding the ability to reduce selenium oxyanions. Bacteria such as *Sulfurospirillum barnesii* – an anaerobe capable of conserving energy through selenate reduction to selenite – reduce selenite to elemental selenium as a detoxification function but often cannot sustain long-term selenite exposure [22, 24, 25].

In most cases the plateauing occurs following denitrification. Bacteria such as *T. selenatis* and *E. cloacae* strain SLD1a-1, previously identified as sharing treatment characteristics observed at SLAPS, cannot carry out dissimilar reduction of selenite to elemental selenium without active denitrification.

CONCLUSIONS ON THE BIOGICAL PROCESS

The biological treatment process is a cost-effective and efficient method to remove nitrates and uranium from contaminated groundwater. While further optimization remains, the activated sludge process has successfully treated SLAPS site water for selenium and uranium at a fraction of the cost of alternative options such as reverse osmosis, ion exchange, and evaporation. Issues

concerning reaction rate decreases may make the process inappropriate for some projects. Process improvements scheduled for spring of 2004 should overcome this hurdle.

SLAPS used the biological process to treat selenium contaminated water in 2002 and 2003. Plateauing selenium levels led to the investigation of a chemical polishing process capable of quickly completing selenium reduction in such cases.

CHEMICAL TREATMENT APPROACH

After researching treatment alternatives, bench tests were undertaken using SLAPS excavation water in order to determine the effectiveness of a copper/iron co-precipitation process for the removal of selenium.

Testing Methodology

Both untreated excavation water (hereafter referred to as "raw" water) and excavation water denitrified at SLAPS using the aforementioned biological process were used. All water was filtered through 1.0-micron nominal bag filters prior to testing. The pH of the water was lowered, soluble copper added, and the water was contacted with solid elemental iron for thirty minutes. The water was then adjusted to pH 9.0-10.0 and the solids allowed to settle. The bench tests focused on determining the process efficiency for selenium removal and optimizing the initial pH adjustment, level of soluble copper, the concentration of iron present during contact time, and the contact time duration.

CHEMICAL TREATMENT RESULTS

The process performed poorly under all operating conditions in the raw water. The raw water had initial concentrations of 484.34 pCi/L of uranium, 1.24 mg/L of selenium, and 1005.00 mg/L of nitrate-N. Fourteen different sets of operating conditions were tested using the raw water, with selenium reduction ranging from 5% to 19%. The process did, however, result in the uranium reduction of 98% to 99%.

The copper/iron co-precipitation process bench tests produced excellent results under all operating conditions in the denitrified water, with increasing removal efficiency generally correlating with lower pH, longer residence time, and higher initial copper concentrations. The denitrified water had initial concentrations of 0.74 pCi/L of uranium (the uranium was removed in the initial biological treatment step), 1.06 mg/L of selenium, and 3.30 mg/L of nitrate-N. The denitrified water was tested using thirty-three different operating conditions. All of these tests resulted in significant selenium reduction, with 26 of the 33 operating conditions tested resulting in selenium reduction below the 0.200 mg/L discharge requirements. Of the seven trials not reduced below 0.200 mg/L, six were tested at the lower limit of aqueous copper tested and the results led to the conclusion that copper was the limiting factor.

Critical parameters were tested at levels estimated to represent their potential operating range, including copper (10 ppm, 30 ppm, 50 ppm), pH (3.0, 3.5, 4.0), and elemental iron (5 g/L, 10

g/L, 15 g/L). The water was analyzed for selenium after it was allowed to settle. The results are presented in Tables 2, 3, and 4.

 Table II: Selenium Concentrations at 50 mg/L Copper (variable iron & pH)

| | pH = 3.0 | pH = 3.5 | pH = 4.0 |
|-------------------------|----------|----------|----------|
| Iron = 5 g/L | 0.036 | 0.097 | 0.147 |
| Iron = 10 g/L | 0.092 | 0.093 | 0.100 |
| Iron = 15 g/L | 0.091 | 0.074 | 0.234 |

Table III: Selenium Concentrations at 30 mg/L Copper (variable iron & pH)

| | pH = 3.0 | pH = 3.5 | pH = 4.0 |
|-------------------------|----------|----------|----------|
| Iron = 5 g/L | 0.137 | 0.136 | 0.191 |
| Iron = 10 g/L | 0.139 | 0.189 | 0.160 |
| Iron = 15 g/L | 0.146 | 0.156 | 0.169 |

Table IV: Selenium Concentrations at 10 mg/L Copper (variable iron & pH)

| | pH = 3.0 | pH = 3.5 | pH = 4.0 |
|-------------------------|----------|----------|----------|
| Iron = 5 g/L | 0.243 | 0.162 | 0.227 |
| Iron = 10 g/L | 0.319 | 0.137 | 0.266 |
| Iron = 15 g/L | 0.244 | 0.162 | 0.226 |

Copper

All series show improved selenium removal with the increase of initial copper levels. Effective selenium removal was achieved at all three copper concentration tested except for the lowest level (10 mg/L), where six of the nine tests did not reach discharge limits. These six tests did, however, achieve selenium reduction of 69% to 88%, indicating that copper levels were the limiting factor in the governing reaction. Initial aqueous copper concentrations are the most critical parameter in achieving the desired level of selenium reduction.

pН

All series except for copper at 10 mg/L produced its best results when operating at a pH of 3.0. Effective selenium removal was achieved at all three pH levels tested. However, the bench tests revealed a correlation between lower pH and increased removal efficiency of the process. A small change in pH can have a significant affect on the redox chemistry and, consequently, the process performance.

Iron

None of the bench tests indicate significant improvement when iron loading variations are made within the range tested. Adding higher levels of iron to the vessels resulted in minimal gains. In

fact, many of the lowest selenium levels achieved were using the lowest iron loading value tested, 5 mg/L.

Iron Contact Time

Varying iron contact times were also tested for denitrified and raw water at 50 mg/L copper and 15 g/L iron. In addition to the normal 30-minute contact time, 60 and 90 minute contact times were also tested.

Increased residence times in the denitrified water resulted in greater selenium reduction, especially at the higher pH levels. The 60-minute residence time resulted in an additional average selenium reduction of 32%. The 90-minute residence time further reduced selenium by an average of 46%, or an average additional reduction of 63% compared to the 30-minute values. No significant improvements in selenium removal were observed in the raw water samples as a result of increased residence times.

Figure 4 illustrates final selenium concentrations for denitrified water (initial selenium concentration = 1.06 mg/L) versus iron contact time with pH isograms. Inspection of the graph reveals increased selenium removal efficiency with increased iron contact time throughout the range tested. At a 90-minute residence time, all the pH levels had reduced selenium to nearly identical levels, indicating that shortcomings in process operating conditions can be overcome with increased iron contact time.



Fig. 4 Final Se vs. Fe contact time (denitrified water, Cu=50 mg/L, Fe=15 g/L)

CONCLUSIONS

The copper-iron co-precipitation process is applicable at SLAPS. Denitrification and an acidic medium are required prior to co-precipitation. Based on these bench test results, optimum operating conditions are a pH of 3.0, an initial copper concentration of 50 mg/L, and an elemental iron loading of 5 g/L to 10 g/L.

The design of a full scale treatment plant to utilize the copper-iron reduction process has been completed. A subcontract for the fabrication of the necessary controls and equipment has been awarded. Once the plant is operational, scheduled in spring of 2004, it will be used in conjunction with the biological process developed, resulting in an affordable, reliable water treatment method for uranium and selenium at SLAPS. Continued success of this method will result in a treatment method that can be used at other radioactive clean up sites experiencing similar treatment situations, as well as projects solely in need of selenium removal.

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