Selenite and Selenate Removal by a Functionalized Alumina Adsorption Technology

NANCY SHERWOOD, MELISSA HAYES, REBECCA UNKEFER and GINA SACCO,
MAR Systems Inc. Solon, Ohio

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ABSTRACT

Selenium speciation presents unique challenges for removal to low ppb trace levels. The selenite oxyanion is reported to be much more readily removed from water by adsorption technology in flow-through column studies than the selenate oxyanion. Selenate removal however, is paramount to wastewater decontamination in the coal mine process and FGD scrubber water markets. The removal of both species is discussed as a function of water quality, pH and temperature. Water conditioning pretreatment options that improve selenate removal by adsorbent technology are discussed and treatment case histories providing selenium removal in coal mine process water ponds to very low levels of selenium are provided.

INTRODUCTION

Over the past two decades, treatments of reverse osmosis, ion exchange, reduction by iron, active and passive microbial reduction, *in situ* microbial reduction and wetlands have emerged as leading technologies for selenium removal (Golder, 2009). However the market continues to look for new innovation in selenium removal to mitigate issues of ease-of-use, capital cost, ancillary waste streams and the ability to reach low selenium levels discharge with these technologies.

Adsorbent technology has been identified that addresses many of these issues. Ongoing research utilizing a proprietary functionalized alumina adsorbent technology in a single pass through a standard filtration vessel with no ancillary waste stream, has found interesting variables that affect the removal of selenium oxyanions. This paper describes laboratory and field removal studies that examine selenite and selenate removal from synthetic and coal process waters and suggests ways to improve selenium removal. The findings indicate that removal is not necessarily species driven and that this adsorbent technology is highly capable of removing both selenite and selenate to achieve a reduction in total selenium applicable to both coal mines and FGD scrubber wastewaters.

FGD wastewater streams and coal mine process waters increasingly face discharge regulations regarding selenium sourced from coal. Selenium occurs naturally in coal and tracks with the sulfur content of the coal throughout the processes in coal fired power plants and coal mining operations, eventually ending up in the wastewater. The removal of selenium in both of its oxyanion forms, selenite and selenate, is highly pertinent to reducing contaminant levels in these wastewaters.

Environmental impact studies on the effects of coal mining in the Appalachian Plateau indicate that concentrations of selenium in sediment ponds and small streams frequently exceed the aquatic wildlife standard of 5 ppb. (Bevans, 2005). The selenium in these waters is generally present in a dissolved state and speciation studies report that the majority of this soluble selenium is present as the selenate (Se^{+6}, SeO_4) species. (Bevans, 2005). The University of West Virginia found that 90% of the selenium in the Mud River, West Virginia, was present as selenate, and selenate was measured at 70% levels in other West Virginia valley fill streams (Bevans, 2005). Selenate is the predominant species reported by coal companies to be present in their mining tailings ponds and other process waters. Selenate removal has typically been more difficult than the other common soluble species, selenite (Se^{+4}, SeO_3) because of its high oxidation state. To mitigate the selenium problem, the Appalachian region coal industry is actively seeking effective selenium removal technologies.

In flue gas desulfurization (FGD) systems, the newer forced oxidation units drive a majority of the selenium to the highest oxidation state. EPRI reports selenate levels up to 100% when high oxidation air rates are used for sulfur oxidation (Sandy,2010). Like the coal mining waters, selenate is the predominant species and the industry is seeking effective removal technologies.

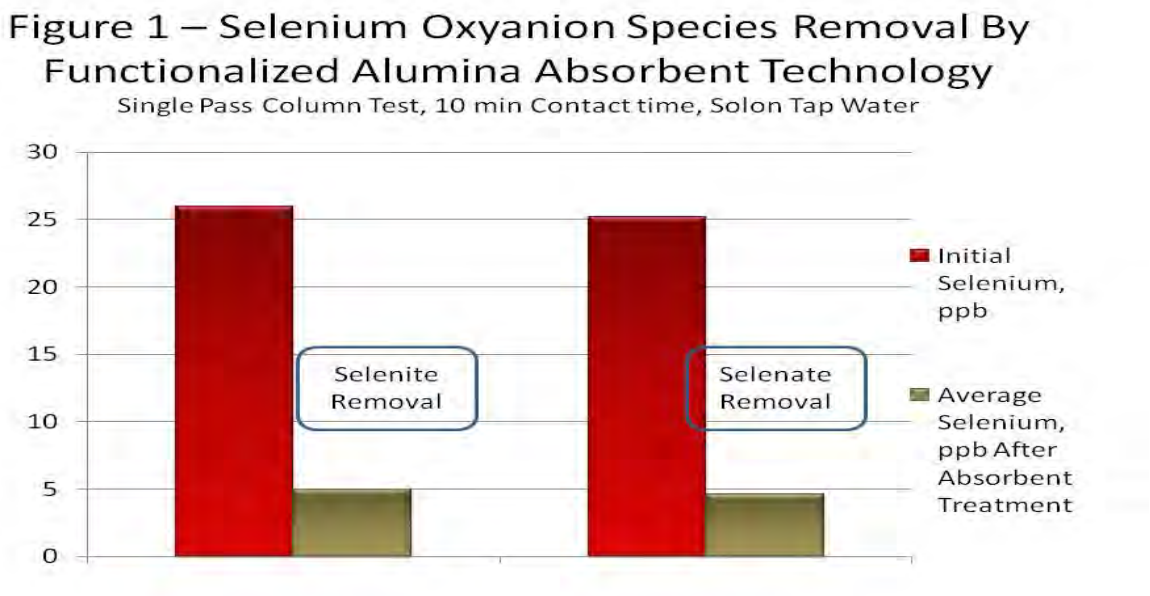
THE ADSORPTION TECHNOLOGY - A specialized adsorbent media can be effective in solving coal mine and FGD selenium contamination. The media is produced from

an activated alumina substrate upon which various proprietary chemistries are reacted throughout the high porosity. These varied inorganic chemistries form functionalized sites in the media for selected soluble metals to covalently bond and be removed from aqueous streams. At least three of the chemistry components forming these functionalized sites are known to complex with soluble selenium in the selenate and selenite oxyanion forms. The removal is accomplished by the formation of various selenite and selenate complexes such as aluminum selenite, aluminum selenate and others.

SPECIATION STUDIES

The adsorbent technology was evaluated for the removal of both selenite and selenate species in packed bed flow-through columns of adsorbent media. Traditionally, plain un-functionalized alumina is known to have a high adsorption capacity for the selenite species only (Kapoor, 1994). However, because this media contains reacted chemistries throughout the alumina that are capable of attracting selenium oxyanions and other metals, performance for both species was anticipated. The tests were conducted using commercially available selenite and selenate standards diluted in Solon, Ohio, tap water to provide a water with ionic strength for speciation comparative studies. Selenium removal of the two species was studied separately by flowing 25 ppb selenium containing water through a packed bed of the adsorbent media at a 10 minute water-to-media contact time for 100 bed volumes of treatment at a hydraulic loading typical of adsorbent treatment vessels (1 to 6 gpm/ft^2). The removal of both species by the media was high, sustained and nearly identical, Figure 1.

EXPERIMENTAL PROCEDURE and RESULTS FOR COLUMN TESTS USING WATER PREPARED FROM SELENIUM STANDARDS - The selenite standard was purchased commercially and contained selenium (+4) oxide in a 2% nitric acid in low TOC water (<50 ppb). As prepared, the standard contained 1000 µg Se (+4) per



milliliter of solution. The selenate standard was purchased commercially and contained anhydrous sodium selenate in ACS reagent grade water. The standard contained 1000 µg Se (+6) per one milliliter of solution. Both standards had valid expiration dates still in effect.

Solon, Ohio, tap water is a moderate hardness water characteristic of the Great Lakes region. It nominally contains 31 ppm calcium, 8 ppm magnesium, 25 ppm chloride, 27 ppm sulfate, 0.5 ppm phosphorus, 0.03 ppm iron, pH of 6.9 and 4 ppm suspended solids. It is consistent in quality and other metals removal studies using this water have been reproducible.

Selenium analysis for all testing was done by an outside EPA certified laboratory using ICP method E200.7. When results were near the method detection limit of 5 ppb, the EPA certified lab implemented a check standard procedure to report numbers below 5 ppb and/or samples were sent for low level selenium analysis by method SM3114C-M gaseous hydride atomic fluorescence.

All columns used in these studies were packed with commercial Sorbster™ dry media in a standard pellet form, supplied by MAR Systems Inc. The beds were then backwashed with Solon tap water to wet the media, rinse off fines and remove entrapped air prior to introduction of the test selenium water.

SELENITE PACKED BED TEST #1: FUNCTIONALIZED ALUMINA THAT REMOVES SELENITE - Selenite water was prepared at 25 ppb by diluting a one milliliter aliquot of the 1000 ppm selenite standard to 1000 ml with tap water to produce an intermediate water containing 1000 ppb Se. The 25 ppb test water was then prepared by diluting 50 ml of the intermediate standard to 2000 ml with tap water.

The functionalized alumina media was packed into two fixed-bed glass columns. Each column had an effective length of 30 cm and an inner diameter of 1 cm. A screen distributor was placed into the bottom of the column and a small piece of glass wool was inserted on top of the fitting to act as a water distributor. Media sized to 1680 µm x 420 µm was packed into the columns and back-flushed to remove fines prior to use. 47.5 bed volumes or 2.0 liters of the selenite water was pumped up-flow through the column at 4.2 ml/min in series. These conditions allowed for a 10 minute contact time and a flow flux of 1.35 gpm/ft^2. A similar experiment was performed in a down-flow configuration with the same selenite water. No difference was observed in selenium removal between the water in an up-flow or down-flow direction. Since no apparent difference was evident between up-flow and down-flow modes, all subsequent testing was performed in the up-flow configuration. A removal of >90% of the selenite was found. Inlet value of 25 ppb was reduced to less than 2 ppb, Figure 2.

SELENATE PACKED BED TEST #1: FUNCTIONALIZED ALUMINA ALSO REMOVES SELENATE - The 25 ppb selenate water was prepared with the same procedure as the selenite water however, 1.81 ml of the stock standard was diluted to 1000 ml in order to prepare an intermediate containing 1000 ppb Se as selenate. The 25 ppb Se water containing selenate was tested in the same column configuration as the selenite test in the up-flow direction. A removal of >90% of the selenate was found. An analyzed value of 22 ppb selenate was reduced to below 2 ppb, Figure 3.

Figure 2 - Selenite Removal

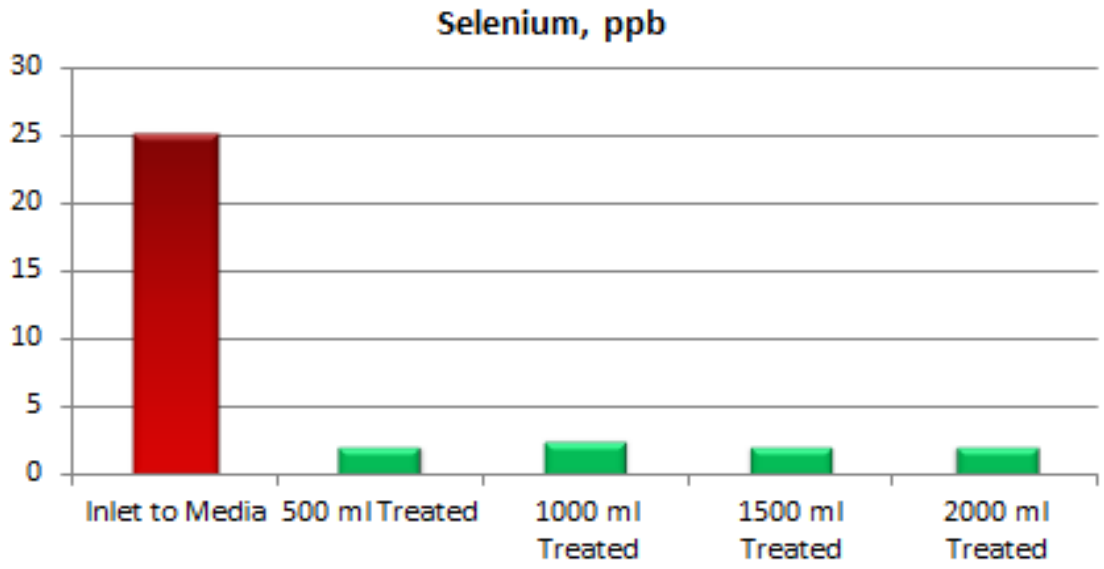
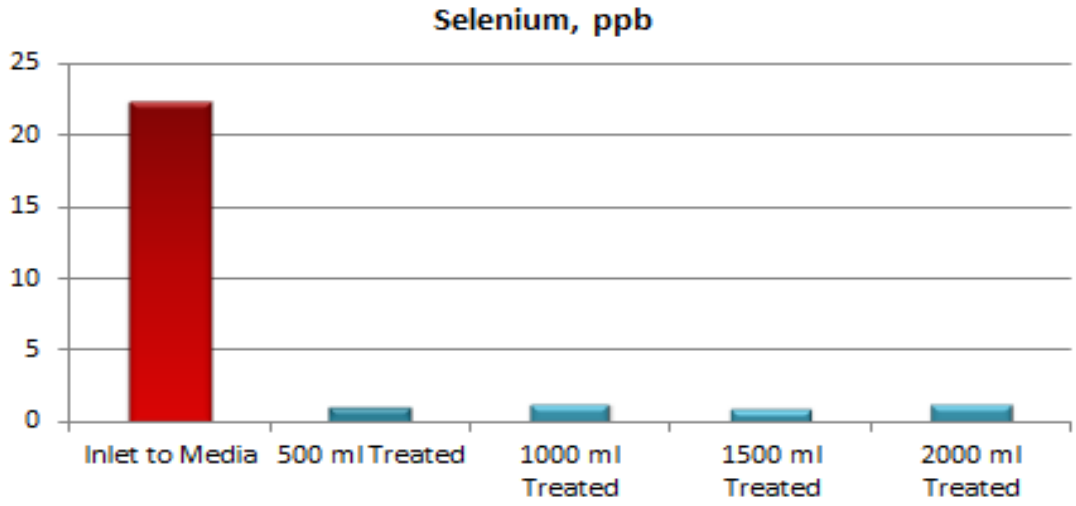


Figure 3 – Selenate Removal



SELENITE AND SELENATE REMOVAL IN LARGER COLUMNS WITH HIGHER VOLUME OF TREATMENT- Confirming tests using larger packed bed columns and higher treatment volumes were run that achieved the same results as the packed bed. The average removal of both species of selenium was >80%, Figures 4 and 5.

These column tests were run in 36" long by 1" internal diameter glass columns. In place of glass wool, a screen supplied with the fitting was used as a distributor and to eliminate any plugging of the tubing by the media. 25 ppb selenite and 25 ppb selenate waters were prepared as noted in the Experimental Section description in a

Figure 4 – Long Term Selenite Removal By Functionalized Alumina Adsorbent

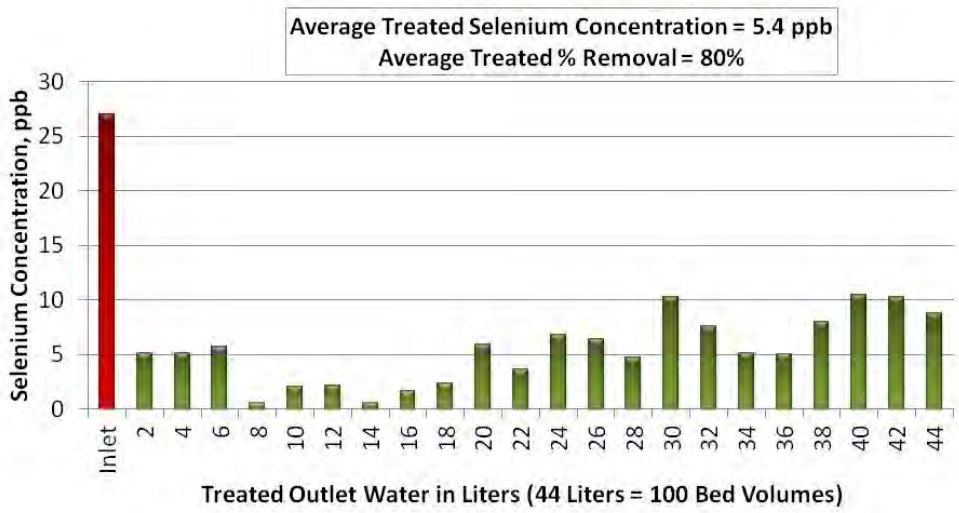
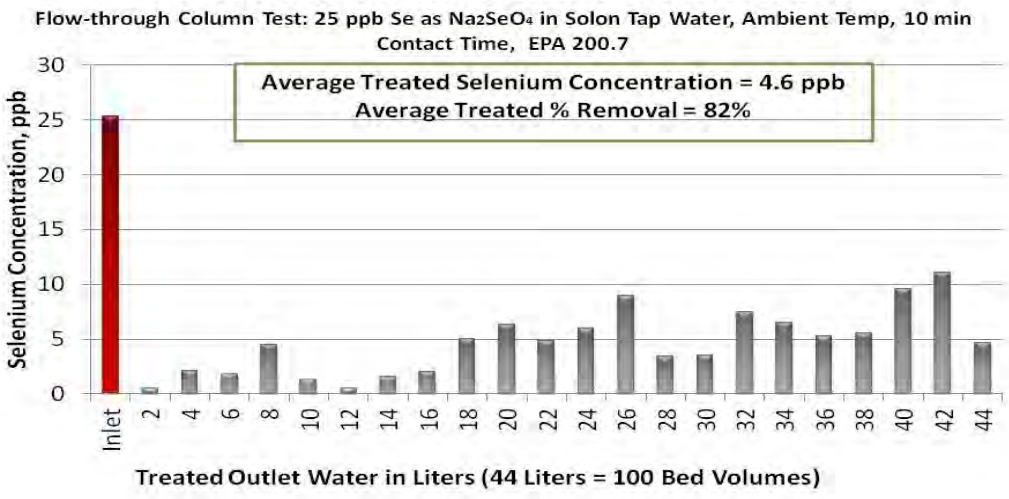


Figure 5 – Long Term Selenate Removal By Functionalized Alumina Adsorbent



sufficient quantity for the test. 100 bed volumes of selenite and selenate containing water was treated through the columns over a period of days. Samples of treated water at the column outlet were collected at 2000 ml intervals or every 4.7 bed volumes. The media-to-water contact time was 10 minutes and the flow flux was 2.2 gpm/ft^2. As in the first tests, the media demonstrated a high and sustained removal of both species.

SPECIATION CONFIRMATION - To insure that there was no change in the speciation of the inlet selenate water upon dilution, speciation analyses were run. Unpreserved samples of both the 1000 ppb standard and the 25 ppb selenate water were analyzed for speciation. Total selenium was determined by isotope dilution mass spectrometry (IDMS) and selenite (+4) and selenate (+6) were quantified by speciated isotope dilution mass spectrometry (SIDMS) techniques and cross-checked with IC-ICP-MS by standard calibration curve technique. Both isotope analyses, IDMS and SIDMS, are EPA RCRA Method 6800 compliant. The analysis confirmed the presence of selenate^{+6} in the test water, Table 1.

Table 1
Speciation Analysis of Selenate Column Test Water

Sample ID	Se $^{+4}$ (ng/g)	Se $^{+6}$ (ng/g)
25ppb Selenate Water	.0614+0.0079	31.5604+0.4934
1000 ppb Selenate Standard	<DL	1225.83+25.07

No reversion to selenite or other species was evident in the selenate water tested in the column studies.

Since the functionalized alumina media demonstrated both the capability and capacity to remove selenium contamination from water and it is equally effective for both of the prevalent species found in coal mine and FGD waters, it was further tested using plant waters.

COAL MINING WATER SELENIUM REMOVAL – FIELD APPLICATIONS

Field waters from ten different mining sites were treated with the functionalized alumina media and in all cases, a reduction in selenium occurred. In five of the ten coal pond sites, the selenium removal attained was to less than 5ppb or > 95%. Removal was rapid and sustained. In the other five sites, selenium removal ranged from 16% to 50%. Increasing the water-to-media contact time provided some additional removal. The waters were evaluated through packed beds of media for selenium removal as soon as received to minimize any biological reduction of selenate to selenite or other changes in the water. Selenium removal for the waters as they were received, covered a broad concentration range for selenium, Table 2.

Table 2
Selenium Removal from Coal Mine Pond Waters by Sorbster™ Media
Water Evaluated As Received in Flow-Through Vessels and Ambient Temperature, EPA 200.7 & SM3114C-M Methods Used

Pond		Selenium (ppb)		Removal	Contact Time	Pond Water	
Pond ID	**Speciation****	**In Pond**	**After Treatment**	**%**	**Minutes**	**pH**	**Bed Volumes Treated***
A	significant selenate	8.8	ND***	**>95%**	23	7.1	12
B	mostly selenate	14.1	ND	**>95%**	21	7.0	13
C	unknown	48.1	ND	**>95%**	21	1.5	15
D	unknown	48	ND	**>95%**	21	8.0	15
E	selenate	13	ND	**>95%**	10	7.8	48
G	mostly selenate	11.8	6.2	**47%**	21	7.5	12
H	selenate	54.6	28.2	**48%**	22	7.5	13
I	mostly selenate	12	7.5	**38%**	21	7.5	12
J	selenate	37.6	31.5	**16%**	25	6.8	20
K	selenate	389	305	**20%**	21	7.7	13
K	selenate	389	253	**35%**	51	7.7	4

***Bed volumes treated limited to amount of available water**
**** Suggested by customer**
*****Detection limit <5ppb**

THE EFFECT OF WATER QUALITY - Factors affecting the percentage of selenium removal by the adsorbent media in coal mining waters are not yet fully understood. Selenium speciation alone does not foretell removal efficiency, as evidenced by these ten different waters. Water quality and temperature variables may influence total selenium removal. Table 3 summarizes the water quality parameters that were measured for the various coal mining sites. These included iron, nickel, chloride, sulfate, nitrate, silica and total suspended solids.

No strong correlation of water quality parameters to percent selenium removal is apparent but there are interesting trends that need to be followed further including the calcium to magnesium ratio, the nitrate to iron ratio and the sulfate plus nitrate as percent of the total ionic strength. It seems logical to expect that competing anions to the selenium oxyanions play a role in selenium removal. The trend of the calcium-to-magnesium ratio in this data set of ten coal mining waters is the most apparent. In the majority of cases where greater than 95% removal was achieved, the water contained more magnesium than calcium, Table 4. In the case of all the sites where selenium removal was significantly less than 95%, every site contained the typical water calcium-to-magnesium ratio, where the magnesium was less than the calcium.

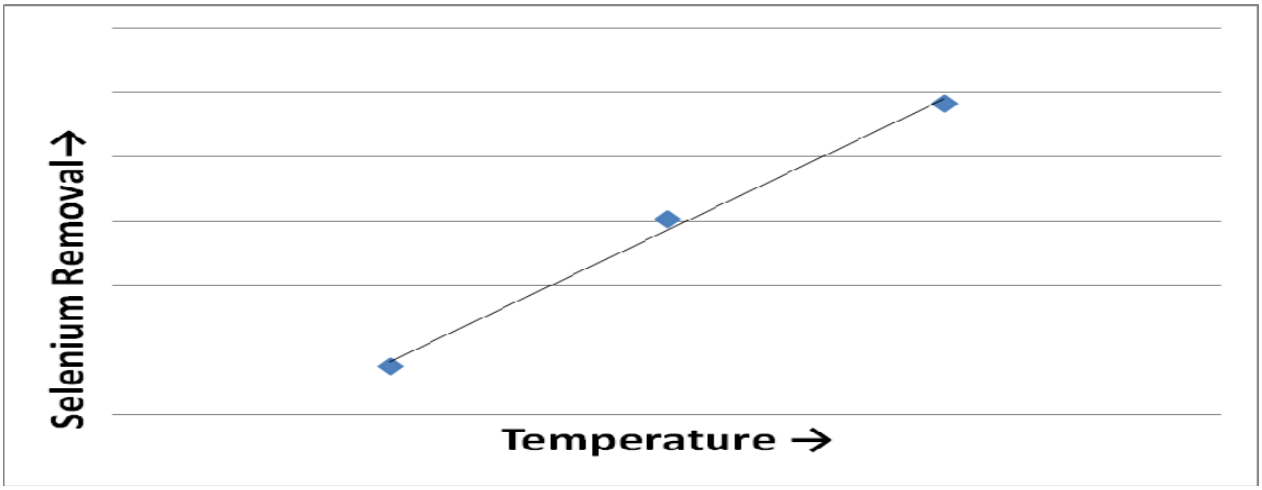
Table 3- Additional Coal Pond Water Quality Parameters								
Measured in ppb								
Pond ID	**% Se Removal**	**Total Fe**	**Total Ni**	**Cl**	**SO**	**NO**	**Silica ppm**	**TSS**
A	**>95%**	0.103	ND	NA	129	0.44	NA	ND
B	**>95%**	0.043	0.008	NA	1,570	5.06	NA	7
C	**>95%**	0.117	0.003	17	855	674	2.5	7
D	**>95%**	0.24	0.011	14	890	1740	2.4	16
E	**>95%**	NA	NA	NA	245	NA	NA	NA
G	**47%**	0.065	0.003	NA	1,040	6.07	NA	20
H	**48%**	0.234	ND	NA	315	1.43	NA	17
I	**38%**	0.094	ND	NA	879	3.69	2.1	ND
J	**16%**	ND	0.003	32.5	718	18.6	6.8	NA
K	**20%**	0.022	0.70	6.1	1,370	0.3	NA	NA
ND = Not Detected NA = Not Analyzed								

Table 4 – The Calcium and Magnesium Influence on Selenium Removal			
Waters With > 95% Se Removal			
Pond	Calcium, ppm	Magnesium, ppm	Δ Ca from Mg
A	38	11	+27
B	179	210	-31
C	209	246	-37
D	181	281	-100
E	76	27	+49
Average	137	155	- 18
Waters with < 50% Se Removal			
Pond	Calcium, ppm	Magnesium, ppm	Δ Ca from Mg
G	196	184	+12
H	78	29	+49
I	206	106	+100
J	205	187	+18
K	497	95	+402
Average	236	120	+116.2

THE EFFECT OF TEMPERATURE – The removal of selenite and selenate can be influenced by temperature. Static jar testing at various temperatures indicates increasing removal as a function of increasing temperature. Twenty-four hour temperature studies were conducted with 50 ppb selenium water prepared in Solon tap water from the 1000 ppm selenite and selenate standards. Two grams of adsorbent media were added to a beaker containing 500 ml of standard selenium. Samples in triplicate were tested at three temperature conditions: ambient, ice-bath (32°F) and heated (120°F).

After 24 hours, the selenium level in each beaker was determined. The results indicate an increase in selenium removal with increasing temperature, Figure 6. Typically a 5-30% increase in selenium removal was observed with temperature increases to 120°F.

Figure 6 -Effect of Temperature on Selenium Removal

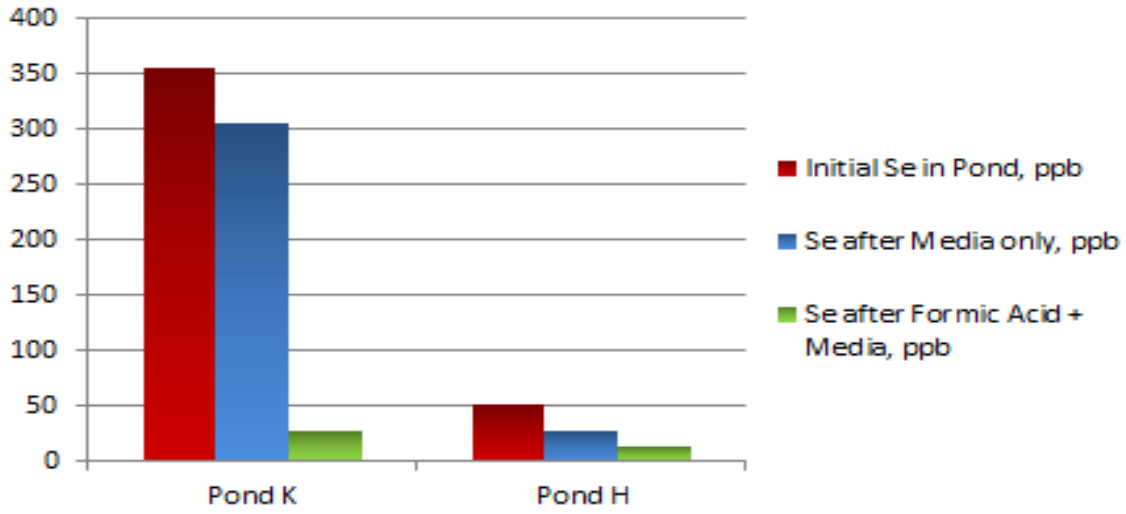


PRETREATMENT OPTION TO BOOST SELENIUM REMOVAL

The use of organic acids to accomplish the reduction to selenite is an approach investigated on two of the mining waters that without pretreatment, had given 20% and 48% removal with the initial functionalized alumina adsorbent treatment. Ascorbic acid, formic acid and other organic acids are known to reduce selenate to a lower oxidation state (Eisenberg, 2007). The addition of the organic acid to the water to achieve a pH of 4 and holding the pH adjusted water for a minimum of one hour prior to treatment with adsorbent in a flow-through column increased the selenium removal from 20% to 92% in the water from mining Pond K and 48% to 72% in Pond H, Figure 7.

This pretreatment has been found to be effective when the initial selenium removal is less than 50%. It has not been found to boost selenium removal when the initial removal is 80% or better. Since the functionalized alumina is effective over a broad pH range, it is capable of treating water to remove selenium from pH 4 water. The amount of organic acid, the pH and the hold time may require optimization for each system to achieve maximum removal.

Figure 7 - Organic Acid Pretreatment Coupled with Functionalized Alumina Media Improves Selenium Removal



CONCLUSIONS

A functionalized alumina adsorbent means to mitigate selenium contamination has been identified. The functionalized aluminum absorbent used in this study removes both forms of selenium oxyanions. The removal of selenite and selenate was found to be strong and sustained in column tests where large amounts of water were treated.

There are factors other than speciation that appear to have an influence on the amount of removal and they are continuing to be investigated. The temperature removal profile provides the opportunity for removal upstream when water is hot and at the source point prior to dilution. Work is continuing on the influence of water quality, competing anions and particulate selenium.

The technology has applicability to many industries, (Sherwood, 2012). Greater than 95% selenium removal was demonstrated at high sulfate levels. The sulfate in Ponds B, C and D ranged from 800 ppm to 1500 ppm sulfate. The reacted chemistry on the alumina provides the opportunity for the simultaneous removal of the selenium oxyanions, as well as mercury and other contaminants in a single pass. Currently, optimization to handle FGD particulates and FGD multi-metal removals is in progress. Preliminary results indicate significant removal of selenium and other contaminants in FGD wastewaters.

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