Sorbster® Media Removes Selenium from Coal Mine Tailings Ponds and Process Waters

BACKGROUND

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. 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. The University of West Virginia① found that 90% of the selenium in the Mud River, WVA was present as selenate and selenate was measured at 70% levels in other WVA valley fill streams. The coal companies in these studies reported selenate as the species 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.

SORBSTER® Se-1 MEDIA

A specialized adsorbent technology, Sorbster® media, can be effective in solving coal mine selenium contamination and achieves a high level of selenium removal from coal mining waters. Sorbster® media is produced from an activated alumina substrate upon which various proprietary chemistries are reacted throughout the high porosity. These varied 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.

COAL MINING POND WATER PERFORMANCE

Field waters from ten different mining sites were treated by Sorbster® 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%, with an increase in the water-to-media contact time providing some additional removal. The waters were evaluated through packed beds of Sorbster® 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 received span a broad concentration range for selenium and are summarized in Table 1.

Table 1 – Selenium Removal from Coal Mine Pond Waters by Sorbster® Media
Water Evaluated As Received in Flow-Through Vessels @ Ambient Temperature, EPA 200.7 & SM3114C-M Methods Used

Coal Mining Pond	Speciation Reported By Customer	Se, ppb In Pond	Se, ppb, after Sorbster® Treatment	% Se Removal	CT, Minutes	Pond Water pH	Bed Volumes Treated*
A	significant selenate	8.8	Not Detected	**>95%**	23	7.1	12
B	mostly selenate	14.1	Not Detected	**>95%**	21	7.0	13
C	unknown	48.1	Not Detected	**>95%**	21	1.5	15
D	unknown	48	Not Detected	**>95%**	21	8.0	15
E	selenate	13	Not Detected	**>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 with extended contact time		389	253	**35%**	51	7.7	4
*Bed volumes treated limited to amount of available water							

The factors in coal mining waters that influence percent selenium removal by Sorbster® media are not yet fully understood but selenium speciation alone does not foretell removal efficiency, as evidenced by these ten different waters. The waters supplied by the coal companies for this study were reported to contain significant levels of selenate, yet removal performance was varied. Other water quality parameters were checked for a correlation to performance however, no correlation between % removal and other common water chemistry parameters, such as sulfate, are evident in this data set, Table 2.

Table 2 - Additional Coal Pond Water Quality Parameters

Coal Mining Pond	% Se Removal	Total Fe, ppm	Total Ni, ppm	Chloride, ppm	Sulfate, ppm	Nitrate, ppm	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	0.700	6.1	1,370	0.3	NA	NA
ND = Not Detected NA = Not Analyzed For								

One water quality parameter that may trend and correlate with performance is the calcium-to-magnesium ratio. In the majority of the cases where >95% removal was achieved, the water contained more magnesium than calcium. Overall, the average magnesium to calcium for these five waters was 155 ppm magnesium to 137 ppm calcium. Three of the waters contained significantly more magnesium than calcium, Table 3. This suggests that the selenium is present in a water flowing through or sourced from dolomitic limestone and/or other magnesium based ores such as mica, talc, vermiculite, brucite, serpentine or magnesite. Or that the water was sampled at a place in the coal processing that adds magnesium. In the case of all the sites where selenium removal was significantly less than 95%, every site contained a typical water calcium-to-magnesium ratio, where the magnesium was less than the calcium level. The calcium averaged 236 ppm and the magnesium averaged 120 ppm for these five waters. This finding presents the possibility for a magnesium salt pretreatment of the water to be treated by Sorbster® media to maximize selenium removal.

Table 3 – The Calcium and Magnesium Influence on Sorbster® Media Selenium Removal

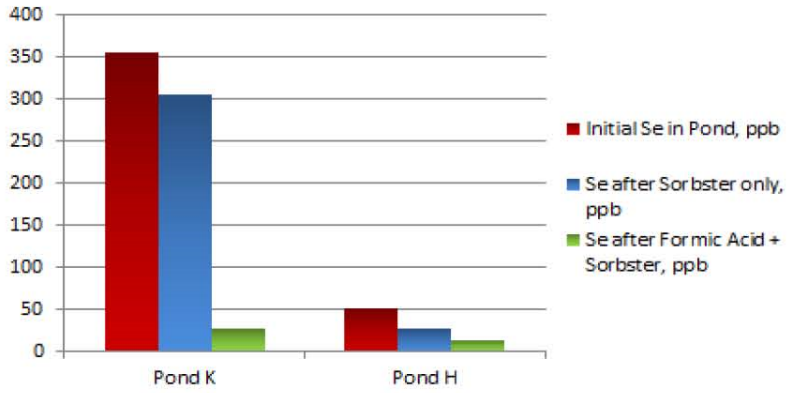
Waters With > 95% Se Removal				**Waters with < 50% Se Removal**			
Coal Pond	**Calcium, ppm**	**Magnesium, ppm**	**Δ Ca from Mg**	**Coal Pond**	**Calcium, ppm**	**Magnesium, ppm**	**Δ Ca from Mg**
A	**38**	**11**	+27	G	**196**	**184**	+12
B	**179**	**210**	-31	H	**78**	**29**	+49
C	**209**	**246**	-37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

While we are excited about this finding, the coincidence of higher magnesium and strong removal performance could be artificial. We are continuing to investigate the magnesium phenomena.

PERFORMANCE PRETREATMENT FOR WATERS WITH LESS THAN 90% REMOVAL

The strong removal of selenite by Sorbster® media has been well documented②. The mining data in this study suggests that Sorbster® media also has a proficiency for selenate removal. The results can be varied and the key removal parameters are perhaps factors other than speciation. Until all factors are well understood, one approach to overcome the variability and consistently achieve high selenium removal is to pretreat the water.

Figure 1 - Organic Acid Pretreatment Coupled with Sorbster Media Improves Selenium Removal



Currently many selenate treatment/pretreatment approaches are under investigation by government, private business and academic groups in a search for commercially viable methods that will consistently enable selenium removal to non-detection limits (<2 ppb.) Since selenite removal maybe accomplished more readily than selenate, an approach that reduces the oxygen content of selenate should be effective in increasing removal. The use of organic acids to accomplish the reduction to selenite is an approach investigated by Sorbster on two mining waters that without pretreatment, had given 16% and 48% removal with initial Sorbster® media treatment.

Waters from Pond water H and pond water K were pretreated with a reducing acid chemistry to lower the pH prior to flow through Sorbster® media and selenium removal improved significantly. Ascorbic acid, formic acid and other organic acids are known to reduce selenate to a lower oxidation state③. Using an organic acid to reduce the pH to 3 to 4 and allowing the pH adjusted water to sit for a minimum of one hour before pumping the water through a Sorbster® vessel raised the selenium removal from 20% to 92% in the water from mining Pond K and from 48% to 72% in the water from Pond H, Figure 1.

The pH reduction to 4 is a simple method to apply the acid and in the case of these waters, it provided an adequate amount of organic acid for interaction with selenate. The acid/water hold time is also a critical factor and commercial applications would require systems to accomplish a hold time prior to pumping the pretreated water through Sorbster® media. Formic acid is readily available in commercial quantities and when used as a pretreatment coupled with Sorbster® media enables the total removal system to achieve target selenium goals.

① *A Framework For Selenium Studies In The Appalachian Plateaus*, H. Bevans, S. Parsons, P. Ziemkiewicz, B. Winters, Topic WQ-4, Prediction and Treatment of Selenium, October 21, 2005.

② *Sorbster® Media Adsoprtion Technology For The Treatment of Selenium And Other Contaminants In Refinery Wastewaters*, internal white paper, MAR Systems Inc., February 2012.

③ *Relative Stability of Selenites And Selenates In Feed Premixes As A Function of Water Activity*, Eisenberg, Journal of AOAC International, March 1, 2007