Sorbster® Media Column Studies for Removal of Selenium from Northwestern USA Refinery Effluent Water

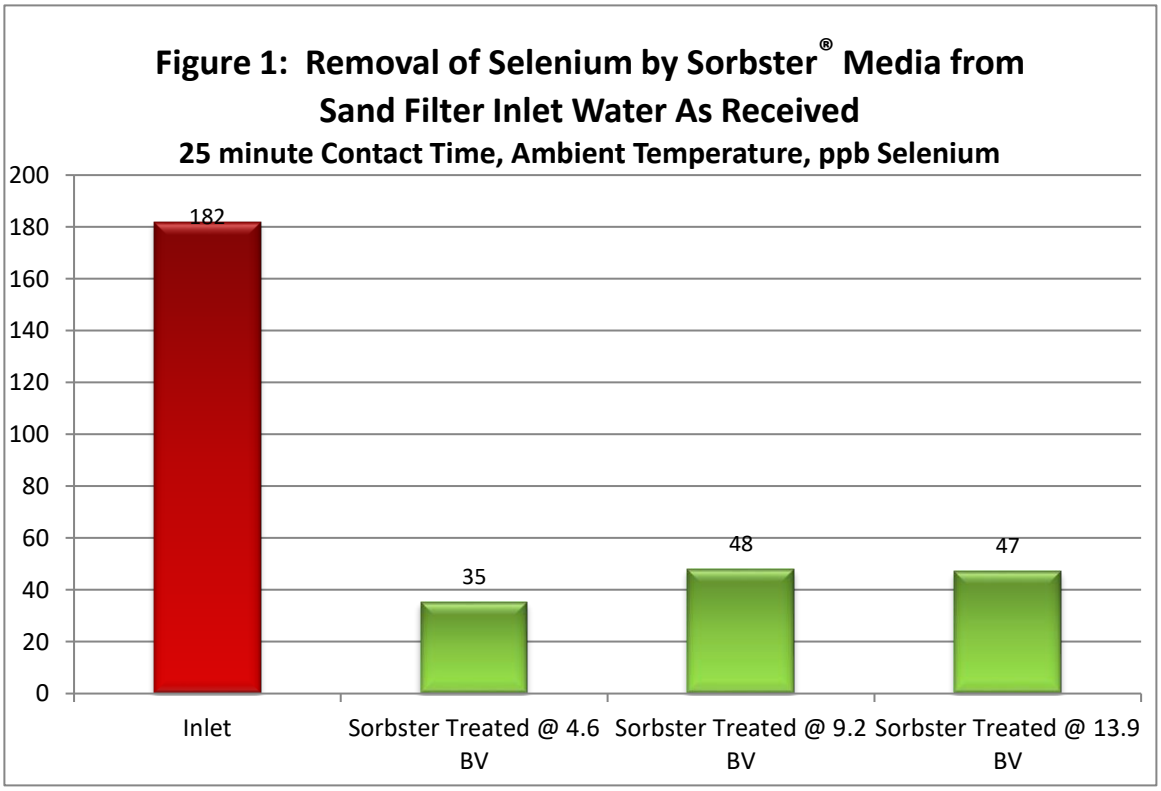
Summary

Effluent water from client containing 184 ppb total and 182 ppb dissolved selenium at pH 7.62 was sampled for investigation of chemisorption removal by Sorbster® media. Selenium in this water was reduced an average of 76% by Sorbster® media to levels as low as 35 ppb at a 25 minute water-to-media contact time. In addition, the media provided significant removal of fluoride, mercury, barium and ammonia, and the complete removal of arsenic and orthophosphate to below standard detection limits.

Oxidation and bentonite clay pretreatment options were investigated to further boost the selenium removal by oxidizing any selenocyanate to selenite and by removing oils and greases which might coat the Sorbster® media. With clay pretreatment ahead of Sorbster® media, the selenium eventually was reduced to below a detection level of <0.25 ppb.

Sand Filter Inlet Water "As Received"

Sorbster® media reduced the selenium in the water by an average of 76% with a 25 minute contact time. Selenium levels of 35 to 48 ppb were obtained and maintained in the water through 14 bed volumes (BV) treated, Figure 1. This removal was achieved for the water as received with no pretreatment.



Several other dissolved metals and contaminants were removed simultaneously with the selenium, Table 1. The chemistry on the media allows for the simultaneous removal of both cationic and anionic contaminants as a function of the amount of oxyanion selenium in the water and the overall water quality. For this water, concentrations of arsenic, orthophosphate, fluoride, ammonia, barium and mercury were reduced along with the selenium. Mercury removal was less than typical for Sorbster® media because less than half of the mercury was in the soluble form that bonds with Sorbster® media (inlet water contained 45 ppt total mercury and only 25 ppt was dissolved/soluble.)

Table 1: Contaminant Removal Summary by Sorbster® Media for Water "As Received"

Contaminant	Inlet Concentration	After 14 BV of Sorbster® Media Treatment	% Removed
Selenium	182	47	**74%**
Arsenic	9.4 ppb	Not detected	**>95%**
Barium	224 ppb	137 ppb	**39%**
Fluoride	3.2 ppm	0.7 ppm	**78%**
Mercury	44 ppt	28 ppt	**36%**
Nitrate	4.2 ppm	3.9 ppm	**<10%**
Orthophosphate	1.05 ppm	Not detected	**>95%**
Vanadium	3.1 ppb	4.9 ppb	**0%**
Zinc	21 ppb	21 ppb	**0%**
Ammonia	1.23 ppm	0.7 ppm	**43%**
Sulfate	334 ppm	373 ppm	**0%**
Chloride	541 ppm	529 ppm	**<10%**

The Effect of Pretreatment

Bleach Oxidation

All of the pretreatment results are summarized in Figure 2 and are compared to the effluent water "as received" selenium removal results. The Oxidation Study (red bars in Figure 2) did not improve selenium removal for this water. This would indicate that carryover of selenocyanate from upstream separation of selenium from the crude oil was not occurring and that the selenocyanate species likely was not the form of selenium remaining in the water.

Activated Bentonite Clay

The oxidized water with added clay pretreatment (green bars in Figure 2) was pumped through the same Sorbster® media column used in the bleach oxidization study. This column had been stored wet with no flow for about 10 days prior to the clay study.

The complete removal profile for the clay pretreatment study is shown in Figure 3. Initially, clay pretreatment did not appear to improve selenium removal. (The two initial reductions in selenium to 27 and 45 ppb in the first 1.2 bed volumes of water pumped through the media are typical for Sorbster® media that has rested. Resting allows for increased diffusion of selenium into the porous media and higher removal for the water resting in the column. Once flow was started and the rested

water began exiting the column, selenium removal through 5.8 bed volumes treated leveled off at the selenium level measured for the oxidization pretreatment study of 79 ppb Se.)

However by 8.2 bed volumes treated, no selenium was detected in the water (method 200.8 with CRC has a reporting limit of < 5 ppb by Sorbster. Unfortunately, this test could not be extended beyond 8.2 bed volumes (4 Liters) due to a lack of water. It is assumed that the drop in selenium occurred after the oxidized water present in the column was significantly flushed out with clay pretreated water.

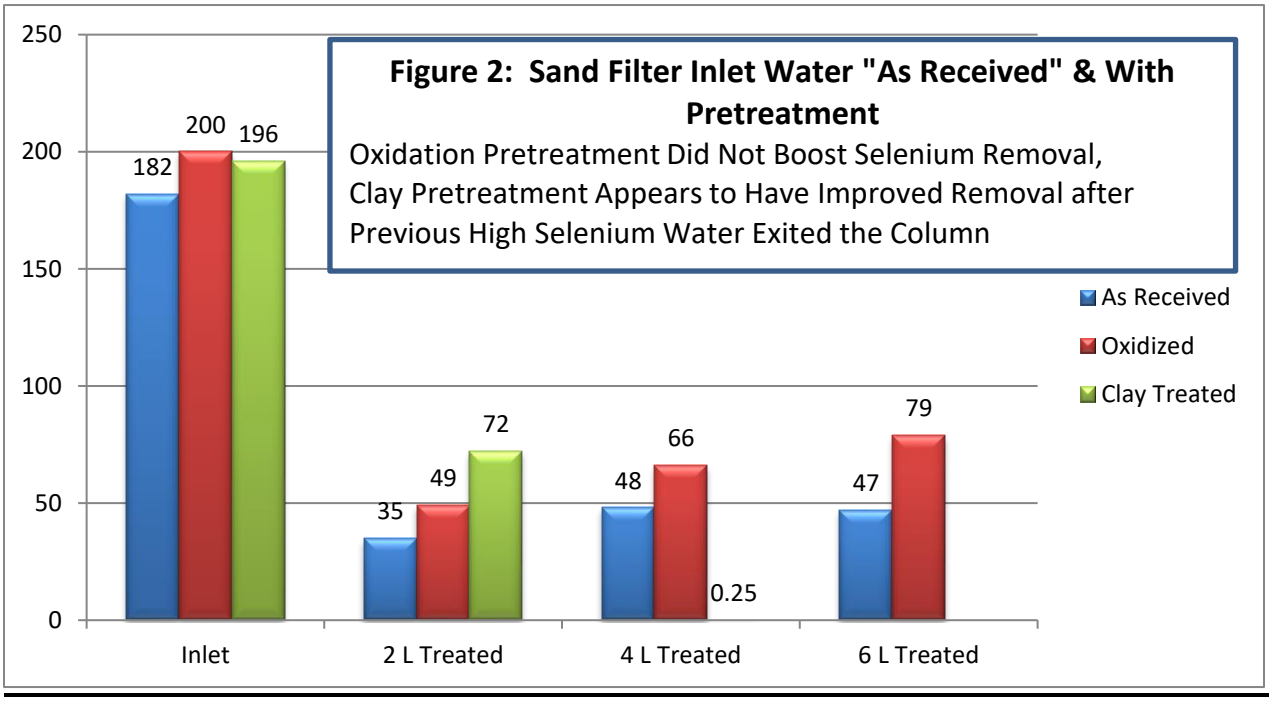


Figure 2: Sand Filter Inlet Water "As Received" & With Pretreatment
Oxidation Pretreatment Did Not Boost Selenium Removal, Clay Pretreatment Appears to Have Improved Removal after Previous High Selenium Water Exited the Column

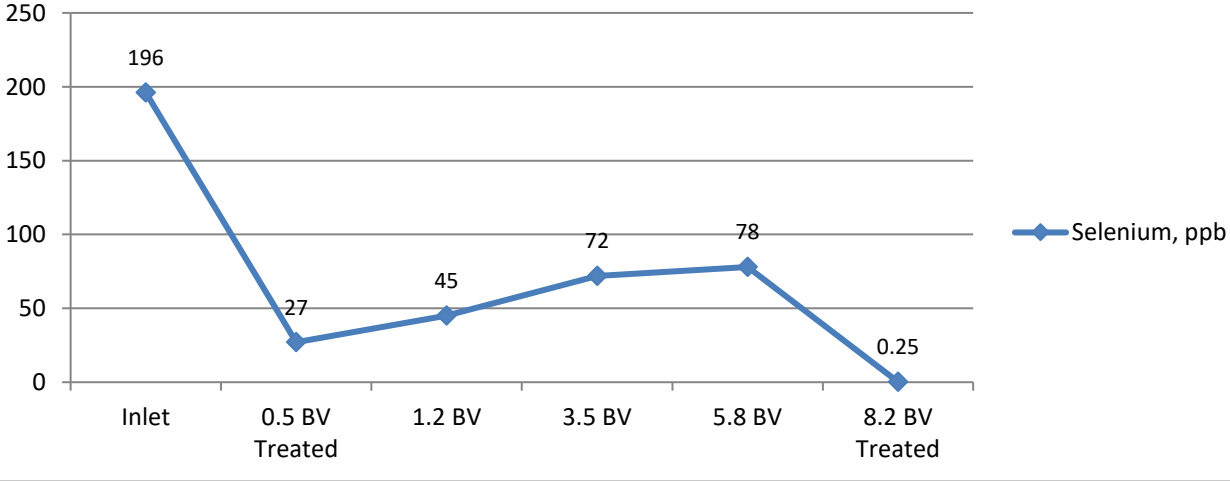


Figure 3: Sorbster® Media Selenium Removal Following an Activated Clay Pretreatment in a Column Containing Oxidized Water

Pretreatment of the water with activated clay also indicated some changes in the removal of other contaminants. Table 2 summarizes contaminant removal by Sorbster® media for water pretreated with clay and compares it to the % removal without a clay pretreatment. Several different contaminants were monitored in this study. In addition to selenium, it appears that clay pretreatment may also have helped condition this water for greater removal by Sorbster® media of vanadium and zinc.

Table 2: Contaminant Removal Summary for Sorbster® Media with Clay Pretreatment

	Inlet after Oxidation & Clay Pretreatment	Sorbster® Media Treated Effluent @ 8.2 Bed Volumes (4 Liters)	% Removal by Sorbster® Media with Clay Pretreatment	% Removal by Sorbster® Media for Water "As Received"
Selenium	196 ppb	Not detected	**>95%**	76%
Arsenic	8.2 ppb	Not detected	**>95%**	>95%
Mercury	39 ppt	21 ppt	**46%**	36%
Boron	411 ppb	346 ppb	**16%**	-
Vanadium	2.4 ppb	Not detected	**>95%**	0%
Zinc	25.2 ppb	4.8 ppb	**81%**	0%
Silica	11.8 ppm	6 ppm	**49%**	-
Fluoride	1.8 ppm	0.7 ppm	**61%**	78%
Nitrate	2.4 ppm	Not detected	**>95%**	<10%
Orthophosphate	1.1 ppm	0.1 ppm	**91%**	>95%
Sulfate	433 ppm	306 ppm	**29%**	0%
Chloride	532 ppm	531 ppm	**0%**	0%

Test Methods

Sand Filter Inlet Water "As Received":

6843 milliliters (15.8 bed volumes) of effluent water was pumped as received upflow at 17.5 mL/minute through a 1"x36" high packed bed containing 350 grams of commercial Sorbster® media pellets (lot SP-A042412-1-P.) This flow provided a water-to-media contact time of 24.7 minutes. The inlet water and Sorbster® media treated water samples after 2, 4 and 6 liters of column flow were analyzed for selenium by Precision Analytical, Inc., Cleveland, OH using EPA method 200.8 CRC (ICP-MS with CRC, reporting limit of 0.25 ppb.) Precision Analytical also analyzed the samples for metals (method E200.7), mercury (method E245.1) and anions (method E300.0) and provided the analysis for the two subsequent pretreatment studies.

Sand Filter Inlet Water Pretreated with Bleach Oxidation:

Three gallons of as received effluent water was oxidized with sodium hypochlorite/bleach in an effort to see if the 35 -47 ppb of selenium not removed by Sorbster® media in the “as received” study could be present as organic selenocyanate. Selenocyanate is typically responsive to oxidation for conversion of the organic species to the oxyanion selenium species, which are more readily removed by Sorbster® media. 1.0 mL of Chlorox was added to 3 gallons of effluent water to a level of 0.2 to 0.3 ppm free chlorine. The oxidized water was held overnight (0.2 ppm free chlorine remained after overnight) and then 5480 milliliters were pumped upflow at 16.25 mL/minute through a new 1” x 36” high packed bed containing 385 grams of Sorbster® media pellets (lot SP-A103012-1-P.) This flow provided a water-to-media contact time of 26.3 minutes.

Oxidized Sand Filter Inlet Water Pretreated with ET-1 Activated Bentonite Clay:

Following the oxidation study, all remaining unused oxidized water that had not been pumped through the Sorbster® media column was subjected to further pretreatment by ET-1, an activated bentonite clay supplied by Aqua Technologies, Inc. 50 g of ET-1 Mix and 50 g of ET-1 Size D were added to about 1 gallon of oxidized Sand Filter Inlet water, mixed well and allowed to sit overnight. With the bentonite clay settled to the bottom, 4000 mL of the water was pumped upflow at 17.1 mL/minute through the same column used in the oxidation study. This flow provided a contact time of 25 minutes.