

Evaluation of Zero Valent Iron and Other Iron-Based Media for Selenium Reduction in Water

ABSTRACT

Iron-based media, including zero valent iron (ZVI) and chemically modified iron, have found use for removal of selenium from contaminated aqueous streams such as found in coal ash ponds, flue gas desulfurization wastewater, mining, and refining applications. The iron-based media available in the market comes in a wide range of specifications that affect performance and cost, both capital and operating, for the end user. Envirogen has developed a versatile and flexible, upflow, fluidized, active water treatment system, the Advanced Metals Removal System (AMRS), that utilizes multiple iron-based media. The purpose of this study was to understand and compare the performance of several iron-based media, including their ability to remove selenium, fluidization characteristics that impact treatment vessel size, iron attrition rates, and the impact of high chloride and sulfate. The extensive data gathered in our pilot facility will benefit clients in the proper selection of media, that will ultimately make a critical difference in compliance and system lifecycle costs for each specific customer's application.

INTRODUCTION

Zero valent iron media is a granular product used for remediation to remove chemical constituents either via sequestration or reduction reactions. ZVI media has been used in situ as well as in active water treatment systems to remove selenate (SeO_4^{2-}) (selenium (Se)) from coal ash ponds, flue gas desulfurization, mining, and refining applications. The Envirogen AMRS is an upflow, active water treatment system designed specifically for use with fluidized, iron-based media to remove selenate, arsenate, chromate and other oxyanion contaminants. This unique system is engineered to operate optimally regardless of media size and density. The objective was to identify various zero valent iron or other iron-based media that could remove selenium in an effective and cost-efficient manner in the AMRS process.

Initial screening of a wide range of ZVI products showed appreciable differences in their ability to adsorb selenium, as well as fluidization properties which excluded them from further consideration. This led to a select group of media that were deemed viable and evaluated further. The testing protocol, test results, and learnings are presented in this paper.

TEST PROGRAM

Initial Screening

Initial screening of a broad spectrum of iron media was conducted to evaluate hydraulic characteristics in column studies and isotherm kinetics in batch testing. The media differed in basic composition, as well as in average and range of particle sizes.

Physical properties

Testing was conducted on various iron-based media identified throughout this report as Media A, B, C, D, E, and F. Physical characteristics of the media are contained in Table 1.

Table 1 - Physical Properties

Media	Particle Size Range Microns	Bulk Density LBS/ CF (\pm 5%)
A	Medium	Light
B	Fine	Heavy
C	Coarse	Heavy
D	Medium	Heavy
E	Coarse	Heavy
F	Fine	Medium

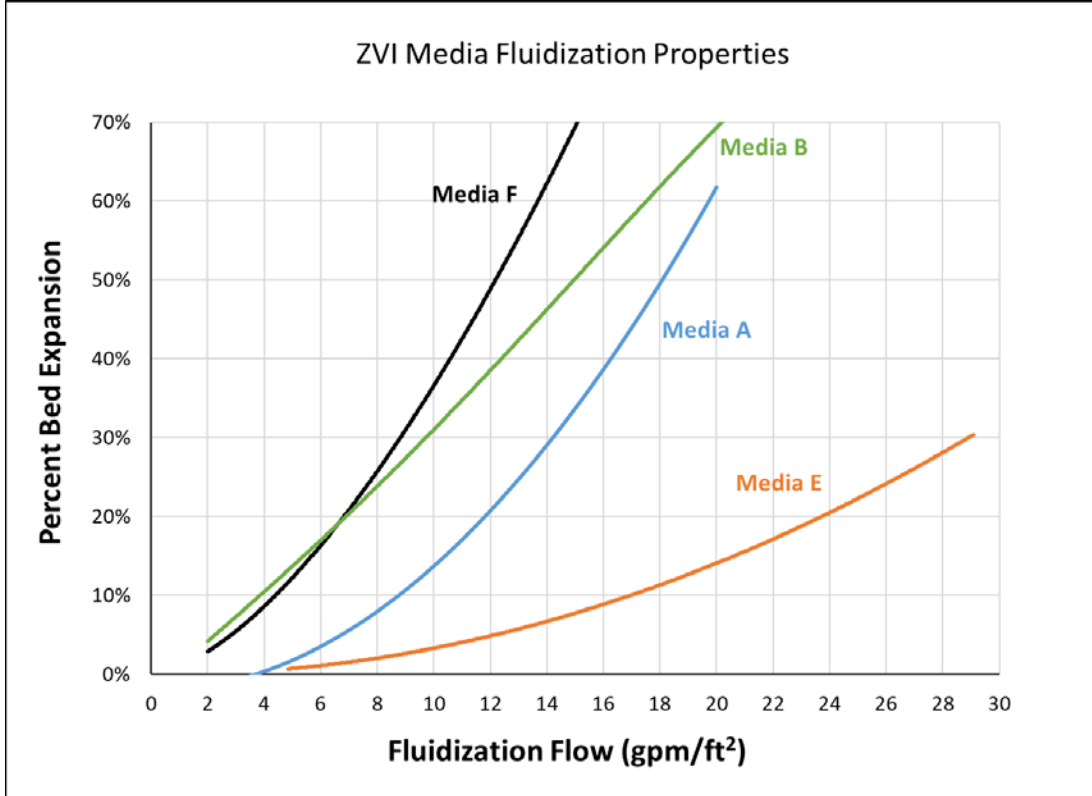
Hydraulics

Since the AMRS process is an upflow process, the fluidization characteristics of the media used in the process need to be known. The process must maintain a minimum bed expansion to keep the media separated and segregated with larger particles at the bottom and smaller particles at the top. In addition, the media needs to be expanded periodically to (1) “fluff” the bed to release trapped gases and small oxidized iron particles, and (2) “regenerate” iron active sites that are blocked by surface oxidized iron. Since fluidization is based on Stokes Law that considers the fluid viscosity, flow rate, size of the particle, buoyancy and gravitational force, larger more dense media requires more force (flow velocity) to fluidize the particles.

Fluidization testing was conducted in Envirogen’s Memphis treatability facility. These experiments were conducted using a 2” diameter clear PVC column with a set volume of media. The media was loaded in the column and allowed to hydrate prior to initiating the testing. The upflow rate was varied and the bed expansion measured. The experiment for each media was repeated to verify consistency of expansion.

The hydraulic fluidization of all the media is shown in Figure 1 below. This graph shows that Media F required the lowest upflow velocity, while Media E required the highest. Media A, with medium particle size range and light density, required an upflow velocity of 4-8 gpm/ft² to prevent bed compaction and 8-10 gpm/ft² to maintain fluidization. Media B, with fine particle size range and much higher density, required 4-7 gpm/ft² to maintain fluidization. The fluidization data is consistent with the physical data provided in Table 1, when considering the combined effects of particle size and density as well as the ability for the particles to pack together (packing density). Relative performance reflected in Figure 1 is expected to apply to full-scale system design. In general, lower upflow velocity is desirable as it optimizes plug flow treatment kinetics, which improves the selenate reduction to selenite and finally to elemental selenium, resulting in smaller system size and reducing upfront capital costs for the system.

Figure 1 – Media Hydraulics



Phase 1 Isotherm Testing

The next phase of evaluation involved isotherm testing to measure the ability of the media to remove selenium (selenate). The isotherm data compares micrograms of selenium removed per gram of media. Initial testing was performed by adding media to a pH adjusted solution of selenate laden water. The media in each beaker was allowed to sorb selenium while stirred for a set period of time. The liquid was then extracted and the selenium concentration in solution determined.

For the first round of isotherm testing, only Media A, B, C, D, and E were evaluated.

Specifically, for this test, known amounts of ZVI media were placed in beakers with 250 µg/l of selenate (from sodium selenate crystal) in solution. The crystals were dissolved in Memphis city water which is typically ≤ 71 mg/l chloride and ≤ 35 mg/l sulfate. The following weights of ZVI media were used:

0.5 g, 2.5 g, 5.0 g ZVI

Each of the media at the three weights were stirred in the selenate solution and samples were extracted for analytical testing at the following times:

15 min, 30 min, 45 min, 60 min, 120 min, 240 min and 1440 min

The results of these tests (logarithmic fit of the data) are shown in Figures 2 to 4. As expected, the longer the media contact time, the more selenium was removed. Rates of selenium removal (i.e., the slopes of the curves) declined

over time as the concentration of selenium in solution dropped and available media adsorption sites were reduced. The inflection point, where rates dropped for all the ZVIs tested, is estimated to be between 30 and 45 minutes of reaction time.

Figure 2 – 0.5 g ZVI Isotherm

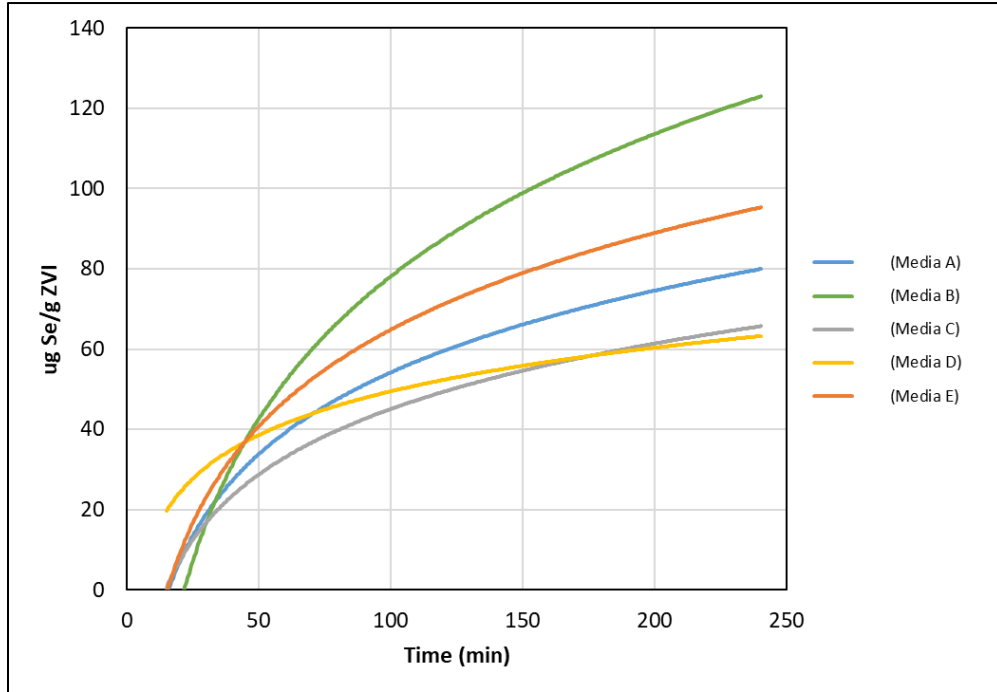


Figure 3 - 2.5 g ZVI Isotherm

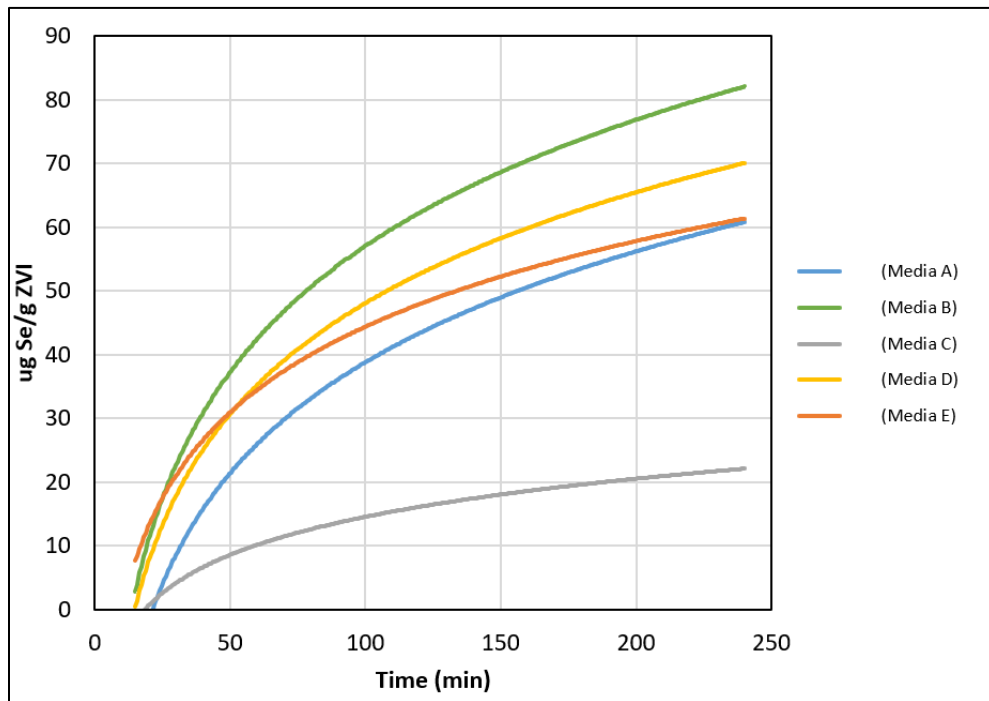
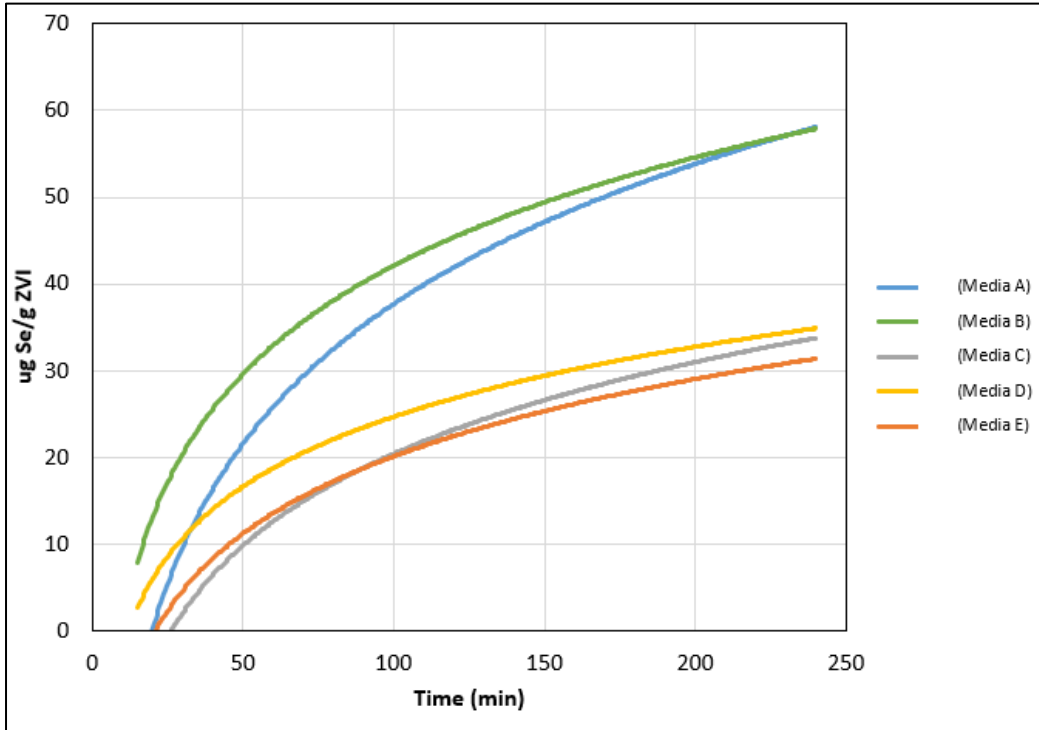


Figure 4 - 5.0 g ZVI Isotherm



Phase 1 Kinetics Testing

Next, ZVI kinetic rate evaluations were conducted, which examined the rate of selenium uptake for each media over a set time interval, measured in micrograms of selenium removed per gram of media per minute. Average removal rates over 30 and 45 minutes of contact time are presented in Table 2. Several factors are considered when designing a commercial AMRS system including the kinetics rate (g Se/cubic foot/min) and the life cycle cost of the system. In general, 30-minute EBRT is projected to deliver a lower life cycle cost versus 45 minute and so would be used as the basis of most system designs.

Table 2 - Average Selenium Removal Rates

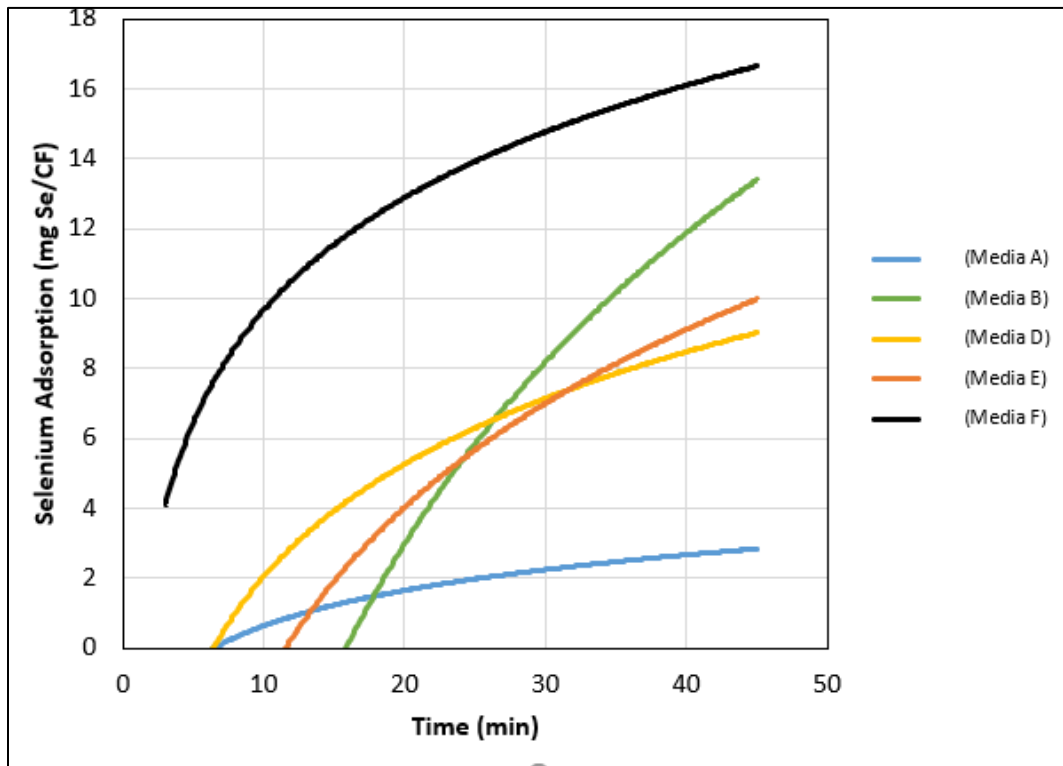
	ug Se/g/min				
	Media A	Media B	Media C	Media D	Media E
	0.5 g ZVI				
30 minutes	0.53	0.66	1.23	1.13	0.89
45 minutes	0.58	0.66	0.49	0.58	0.70
	2.5 g ZVI				
30 minutes	0.25	0.33	0.26	1.13	0.33
45 minutes	0.16	0.94	0.12	0.58	0.94
	5.0 g ZVI				
30 minutes	0.18	0.55	0.33	0.34	0.03
45 minutes	0.31	0.64	0.32	0.30	0.39

Based on Phase 1 Isotherm and Kinetic testing, it was determined that Medias B, D and E were the top performers.

Phase 2 Isotherm Testing

Following the completion of Phase 1, an additional interesting chemically modified iron media was identified for testing – labeled as Media F. Because the ZVI density differs greatly from one media to the other, isotherm testing in Phase 2 was evaluated on a unit volume (cubic foot) of media basis. Results of that testing are presented in Figure 5 (logarithmic fit of the data), which shows selenium sorption over time from tap water.

Figure 5 - Selenate Redox/Adsorption per Cubic Foot of Media



The data shows that Media F had the highest capacity per unit of media volume and the shortest required contact time to be effective. Conversely, Media A had the lowest capacity per unit of volume. Medias B, D and E were relatively similar with Media B slightly outperforming Media D and E. This may be due to the smaller particle size of Media B or the amount of highly reactive ZVI in the media.

Phase 2 Kinetics Testing

The data generated in the isotherm testing above were evaluated to determine average removal rates in batch on a mg of selenate per cubic foot per minute basis for all the media tested. The results of this evaluation are in Table 3 below.

Table 3 - Average Selenium Removal Rates on a Volume of Media Basis

	Average mg Se/CF/min				
	Media A	Media B	Media D	Media E	Media F
15 minutes	18.7	44.5	67.9	33.5	141.9
30 minutes	12.9	45.1	72.9	42.9	97.5
45 minutes	14.0	65.8	40.5	47.4	80.2

As can be seen from Table 3, Media A had the lowest rate of selenium adsorption while Media F had the highest, mimicking the isotherm testing results. Media B, D and E had similar rates of adsorption, with Medias B and E outperforming Media D at higher contact times. As the selenium concentration in solution drops over time, adsorption rates were expected to drop over time in batch experiments such as these.

As stated previously, the kinetic rate on a cubic foot basis is used to help determine the appropriate AMRS system design and EBRT for the lowest life cycle cost.

Sulfate Effect on Selenium Adsorption

Having established Media A, B, E and F to be of most interest, additional testing was conducted to measure the effects of sulfate on selenium reduction.

For this evaluation, tests were conducted by adding a known amount of Se and various amounts of sulfate, from 250 to 2,500 mg/l, to the City of Memphis tap water containing base levels of ~ 71mg/l chloride and ~ 35 mg/l sulfate. The pH was adjusted to 5.0 ± 0.5 , and measurements were taken to determine selenate loss and iron gain (from/to the solution) at two time points after adding the media.

Specifically, aliquots of the solutions were removed for analysis of selenium, iron, sulfate, and chloride. The solution containing the added media was stirred for the duration of the test. After 30 minutes, the pH of the mixture was measured, and aliquots were removed for analysis. Note that two sets of samples were sent for testing – filtered through a 0.45 um membrane disc and unfiltered to retain particulate material. Sampling was repeated after 45 minutes of contact time. Media F was tested at 5 minutes and 10 minutes due to its faster kinetics.

The effect of sulfate on selenium adsorption (logarithmic fit of the data) are shown in Figures 6 and 7 below for Media A, B and E, and in Figure 8 for Media F.

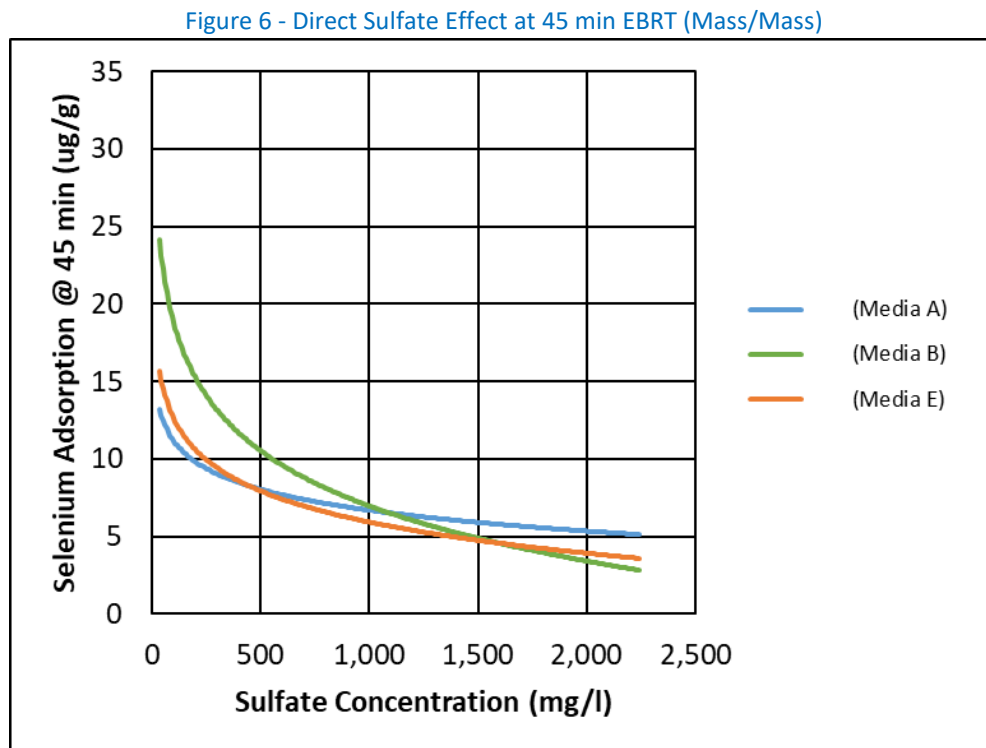


Figure 7 – Direct Sulfate Effect at 45 min EBRT (Mass per Unit Volume)

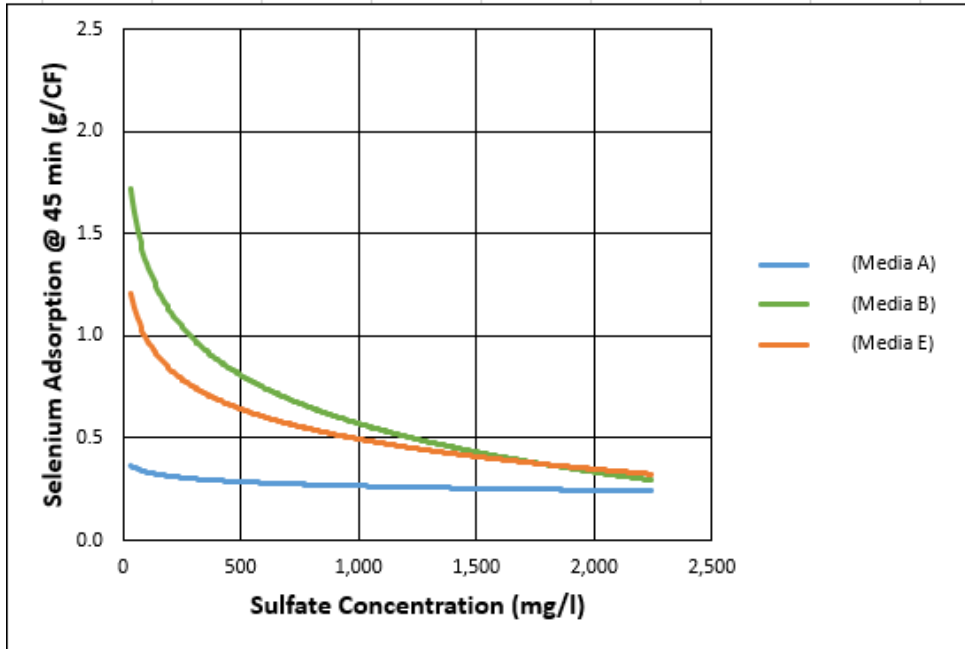
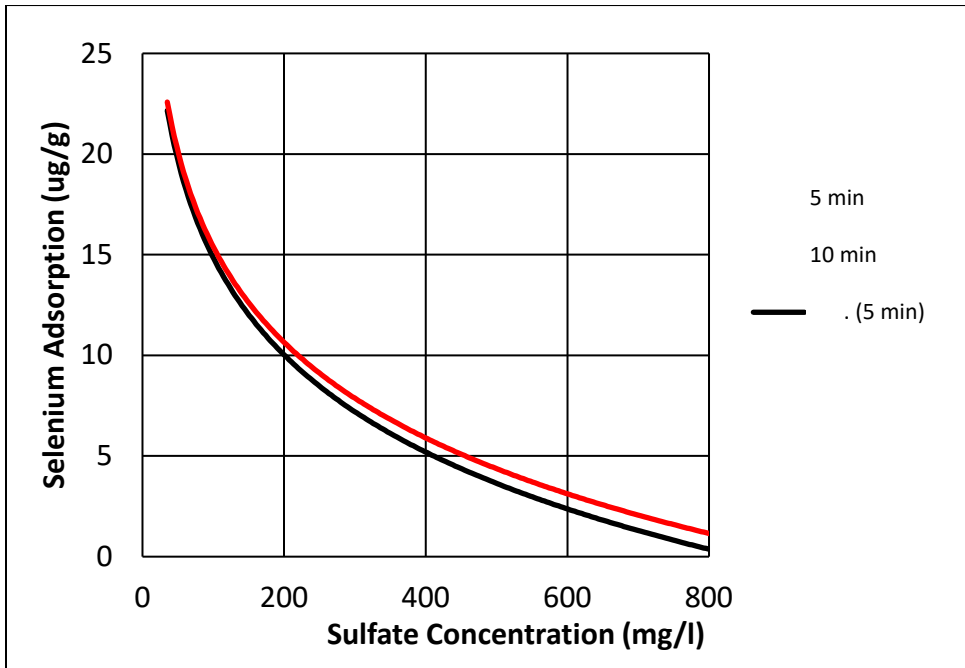


Figure 8 - Direct Sulfate Effect Media F (Mass/Mass)



The data illustrates that in general, the ability of iron media to adsorb selenium decreases with increasing levels of sulfate in the solution. Sulfate at concentrations above 250 mg/l impacted the capacity of selenate reduction and adsorption for all the ZVIs tested. The reduction appears to be in the range of 50-90% on a g Se/CF basis (>250 mg/l). It should be noted that Media A's selenium capacity changed the least as sulfate concentrations increased, showing sulfate had a lesser impact on this particular media. Conversely, Media B and E show a higher selenium uptake in clean water per cubic foot but drop off drastically as sulfate levels increased. Thus, it can be concluded that Media A appears to be "less affected" by sulfate. However, even though Media A is less impacted by sulfate, the volumetric

selenium adsorption capacities for Media B and E are approximately 2x or more than the capacity of Media A at sulfate levels up to 1,000 mg/l.

Note that Media F was not fully evaluated for sulfate effects, as it has been established by the manufacturer that this media does not perform well in high sulfate concentrations. Limited testing by Envirogen has confirmed this fact (see Figure 8). General guidance suggests that Media F is good for low sulfate applications up to approximately 500 mg/l, and other alternative media should be selected if the application contains sulfate above that level.

Sulfate Effect on Kinetics

The data were evaluated to determine the effect of sulfate on the rate of selenium sorption.

Figure 9- Direct Sulfate Effect Kinetics (mg Se/CF/min)

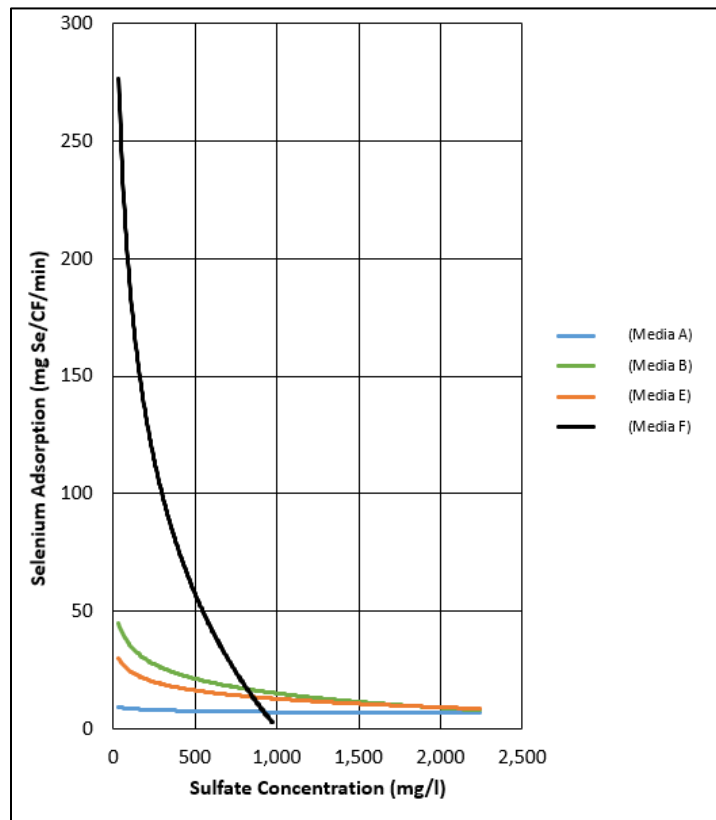


Figure 9 shows the rate of selenium sorption at various sulfate levels and reaction times (logarithmic fit of the data) and demonstrates that Media F is significantly affected by the sulfate levels in the feed water. The data also show that the performance of Media F, while initially higher than the others, dropped below the other media at or near 1,000 mg/l sulfate. Although Media A, B and E all displayed different adsorption rates at lower sulfate concentrations, they approach the same kinetic rate at around 2,500 mg/l sulfate.

Chloride Effect on Selenium Adsorption

Unlike for sulfate, it was not expected that the chloride would affect selenium capacity or the sorption rate. The concern with chloride instead centers on ZVI media loss in the form of particulate or dissolved iron. Nonetheless, tests were conducted and confirmed that chloride has little effect on the ability of the ZVI media to adsorb selenium. Sulfate concentrations for these tests were held constant at 450 mg/l. In particular, the data showed that selenium adsorption of Media A and E did not appear to be overly affected by the chloride concentration. Media B did show

a small reduction in selenium adsorption as chloride levels rose. Media B, with a higher selenium capacity at low chloride, approached Media A's capacity at chloride concentrations of about 400 mg/l. This indicates that Media B's morphology is impacted by chloride but it is still a viable media for selenium removal. Testing indicated Media E may be the best choice for high chloride applications.

Chloride and Sulfate Effect on Iron Loss

As the ZVI media exhausts and/or oxidizes, a portion of the media is released as either particulate iron or as soluble iron. The amount of iron released may be dependent on the morphology of the ZVI and/or on the concentration of chloride in the water. The pH of the feed water may also be a contributing factor.

To evaluate the effect of chloride and sulfate on iron loss, the same testing protocol and aliquots used for the sulfate and chloride effect on selenium adsorption were used. The aliquots were filtered and unfiltered and analyzed for iron after being preserved for shipment.

Sulfate Effect on Iron Loss

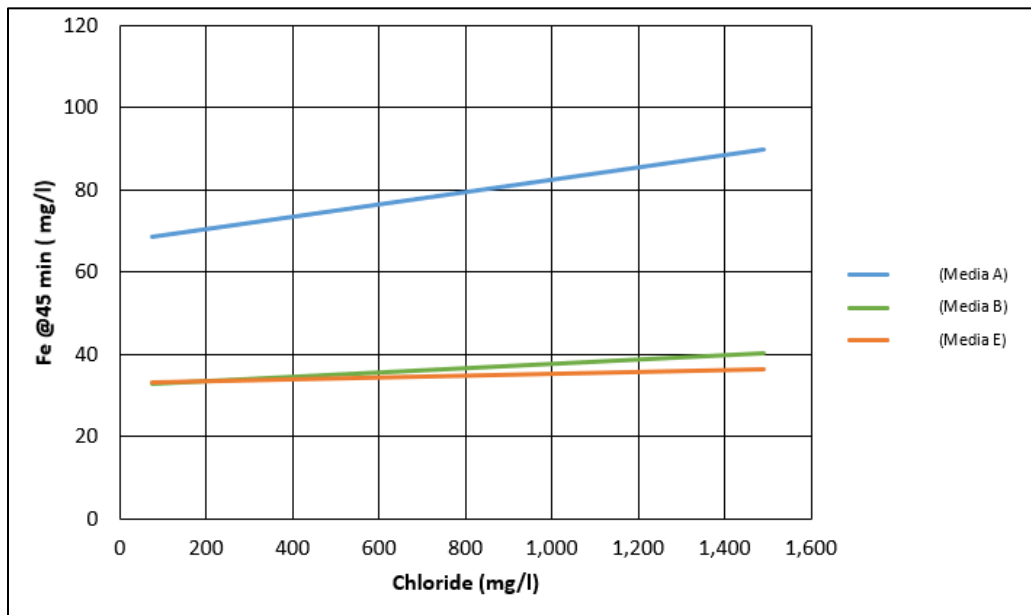
Testing showed that sulfate concentration did not appear to have much effect on the total loss of iron for Media B or E, and only a minor effect on Media A.

However, Media F behaved differently than the other ZVI media. The sulfate level had a significant impact on the amount of iron released from Media F. It appears the iron released (soluble and colloidal) from Media F coagulates and precipitates with time. This may be beneficial and influence the design and size of the downstream filtration system.

Chloride Effect on Iron Loss

Increasing chloride levels appeared to have only a slight impact on the iron release for most of the media tested. Figure 10 (linear fit of the data) shows that Media B and E had flat to slightly increasing amount of iron release. However, Media A had a significantly greater release of iron, 30-50 mg/l more than the other two media with a steeper increase. Media F has not been tested for chloride effect on iron release.

Figure 10 - Iron Release Versus Chloride Level at 45 minutes



Iron Release Observations

The feed water conditions can impact the iron release rate and amount released, depending on the media. This can have a significant impact on the economics since, in general, the higher the media leaching attrition rate the more frequently the media will need to be topped off or replaced. This may be a significant factor in ongoing operating costs. However, based on the nature of the media and the upflow process design of the AMRS, there is iron lost through attrition regardless of the water composition.

A summary of the iron loss due to sulfate and chloride is shown in Table 4 below.

Table 4 - Iron Generation Evaluation

Media	Sulfate Effect			Chloride Effect		
	Total Fe (Average mg/L)	Soluble Fe (Average mg/L)	Particulate Fe (Average mg/L)	Total Fe (Average mg/L)	Soluble Fe (Average mg/L)	Particulate Fe (Average mg/L)
A	43.6	0.38	43.2	68.9	0.68	68.2
E	33.6	2.49	31.1	29.2	2.97	26.2
B	24.3	2.78	20.5	28.5	2.97	25.5
F	44.7	9.49	35.3	-	-	-

For all media, the iron released was both particulate and soluble. At the extreme was Media A, where the iron generated was almost entirely in the form of particulate iron, indicating the media was breaking apart versus being dissolved. The other three media showed predominantly particulate but also some soluble iron.

For all media, the amount of soluble iron was consistent and appeared to be independent of the reaction time. This may indicate a portion of Media B, E, and F was solubilized upon initial wetting, but stabilized over time. The amount of particulate iron also appeared to be fairly consistent for Media B and E indicating that these two media are more stable and less likely to break apart versus Media A. Media F had a high release rate of soluble iron that decreased over time. Therefore, it is suspected that it may not have a high iron release rate in a dynamic flow condition.

RESULTS AND DISCUSSION

The various iron-based media that were evaluated demonstrate substantially different behavior and performance when used in an active water treatment system. Applying these media in real world applications requires a knowledge of the strengths and weaknesses of each to allow selection of the best performer for the given situation.

Table 5 illustrates the varied performance of the media across the range of parameters evaluated during this test program.

Table 5 – ZVI Comparison Across Parameters

Parameter	Media A	Media B	Media C	Media D	Media E	Media F
Bulk Density	Low	High	High	High	High	Medium
Particle Size Average	Medium	Fine	Coarse	Medium	Coarse	Fine
Particle Size Range	Wide	Medium	Narrow	Narrow	Narrow	Wide
Flow Required for Fluidization (Hydraulics)	Medium flow	Low Flow	High Flow	High Flow	High Flow	Low Flow
Selenium Absorption Ability (Isotherm)	Good	Better	Good	Better	Better	Best
Rate of Selenium Uptake (Kinetics)	Good	Better	Good	Better	Better	Best
Appropriateness for High Sulfate	Some	Best	N/A	N/A	Best	Least
Media Degraded by Chloride	Most	Some	N/A	N/A	Some	N/A
Media Cost per Unit Volume	\$\$	\$	\$	\$	\$	\$\$\$\$

Legend	Good	Better	Best
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Depending on the customer's objective, the engineer will weigh the various performance characteristics to deliver the best media choice. For example:

- For lowest upfront capital cost, the lower fluidization flow media (B and F) would be preferred as the system can be sized smaller. Note that this comes with some tradeoffs as it removes flexibility to switch to some of the alternatives at a later date.
- For a high sulfate concentration, Media B or E are preferred, and Media F would be avoided.
- For applications with high chlorides, Media B or E would also be preferred over Media A to minimize media loss and recurring media replacement costs.

CONCLUSIONS

A comprehensive testing program was conducted on a variety of iron-based media including zero valent iron and chemically modified iron. After evaluating for physical characteristics, selenium absorption ability and rate of absorption, as well as impact of sulfate and chloride on the media, it became clear that the media differ greatly on all parameters tested. In the end, there was no single top performer that excelled in each area. Instead, each media exhibited better performance in one or two areas over the others.

The conclusion to be drawn is that there is no "one-size-fits-all" media for every application. Instead, the engineer/system designer, aided by the knowledge of these performance nuances, will evaluate the application parameters and recommend the ideal media for the application and size the system accordingly.

Envirogen's Advanced Metals Removal System is inherently flexible in its' design concept, incorporating the best performing iron based adsorptive media for the customer's application and desired upfront and long-term economics and efficacy. Pilot units are available for onsite customer evaluations.

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