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**Title: “Novel Approach for Removing Selenium from Phillips 66 Ponca City, OK
Refinery Effluent”**

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ABSTRACT

The Phillips 66 Ponca City, OK Refinery (PCR) developed and implemented a novel, low-cost means of removing selenium (Se) from wastewater in order to meet new OPDES permit limits. It is well-known that Se, which is a component of the organic molecules in crude oil, is isomorphous with sulfur, is released in process units such as cokers, hydrotreaters, and fluid catalytic crackers, and hence is a constituent in refinery wastewater. After liberation from crude oil, Se accompanies the sour gas to the Sour Water Stripper (SWS), where it partitions and remains with the stripped sour water (SSW). Nearly all of the Se in a refinery wastewater is contained in the bottoms from the SWS. Because of new environmental permit requirements, PCR evaluated a number of candidate technologies for Se removal and selected co-precipitation for testing. The novelty of the approach is using co-precipitation in an existing, operating Activated Sludge Unit (ASU). Se from the SWS is oxidized in the ASU to selenite which sorbs onto the iron hydroxide created by adding (poly) ferric sulfate. Jar tests, short-term step tests, and two longer-term plant demonstration tests were conducted to determine the required dosage of ferric and poly ferric sulfate (PFS). Once sorbed onto the iron floc, the Se can be separated and managed with the biosludge. When iron sulfate is used as a coagulant aid, it improves the operation of the ASU by increasing the settleability of the sludge. The full-scale system was started up to meet a compliance date of Aug 1, 2014, and has now successfully operated below the new permit limits for more than a year.

1.0 INTRODUCTION

The Ponca City Refinery (PCR) received a new OPDES wastewater permit in August 2011, and for the first time the permit contained discharge limits for Se. Beginning August 1, 2011, the requirements were to sample the effluent and report only, but effective August 1, 2014, compliance for Se in wastewater began. Permit limits were to be based on the collection of a minimum of two samples/month and measurement of total Se. Total Se includes both soluble and particulate forms, so a chemical digestion step was required prior to analysis. The ODEQ (Oklahoma Department of Environmental Quality) load allocation for the permit was based on an in-stream Se standard of 5 ppb. The flow used for the Arkansas River was the USGS 7Q2 value, while the flow for PCR was the highest rolling 30-day average wastewater flow. 7Q2 is the 7-day, 2-year annual low-flow statistic which is based on an annual series of the smallest values of mean flow computed over each 7-consecutive days during the annual period. A probability distribution is fit to the annual series of 7-day minimums, and the 7Q2 statistic is the annual 7-day minimum flow with a 2-year recurrence interval. The approximate effluent flow rate linking the concentration (ppb) and mass loading limits (lbs/day) is 2,840 gpm. The OPDES concentration and mass loading limits for Se are shown in Table 1.

Table 1
OPDES Permit Requirements for Selenium in PCR Wastewater
Effective August 1, 2014

Permit Criteria	Concentration Limit (ppb)	Mass Loading Limit (lbs/day)
Monthly Average	77.5	2.64
Daily Maximum	100.4	3.42

2.0 BACKGROUND

The presence of Se in crude oil and refinery wastewater is well-known and was first addressed in refinery effluent on the San Francisco Bay beginning more than 20 years ago. Se, a metalloid which acts as an anion and is difficult to remove, is typically present as either selenite (SeO_3^{-2} , +IV) or selenate (SeO_4^{-2} , +VI) at normal environmental conditions. Numerous Se treatment approaches^{1,2} have been and are being developed and tested, and can be organized into 3 major groupings—physical, chemical, and biological. Individual methods include ion exchange, activated carbon adsorption, sorption on various media, numerous versions of co-precipitation, anaerobic biological reduction, and constructed wetlands. However, all suffer from similar problems found with refinery wastewaters. Either a few pounds of Se per day must be removed from large volumes of wastewater that are in the range of millions of gallons per day (MGD), or a smaller stream of a few hundred gallons per minute (gpm) from the SWS could be addressed. However, the water from the SWS must start with a unique form of Se, selenocyanate (SeCN^-), created by the very strongly reducing conditions in the Sour Water Stripper (SWS) at a high temperature. Either way, costs escalate quickly into millions of dollars for capital and then the system has a high operating cost with large amounts of sludge to manage.

PCR has two activated sludge units (ASUs). The Main ASU handles most of the process water, while, prior to the Se project, the Groundwater ASU (GWASU) treated groundwater from remediation wells; about 60% of the Refinery's stripped sour water (SSW); blowdown for the wet gas scrubbers (WGS) from two Fluid Catalytic Cracking Units (FCCU); and the wastewater from the sulfur plant. During peak groundwater extraction for hydrocarbon recovery in the mid-1990s, groundwater production was more than 1,000 gpm, but at present it has been reduced to 200 – 300 gpm, leaving the GWASU underutilized.

Traditional Se removal technology has usually been co-precipitation with iron salts to form ferric hydroxide [$\text{Fe}(\text{OH})_3$], or with other chemical additives. Since groundwater containing ferrous iron (Fe^{+2}) was already being treated in the GWASU, $\text{Fe}(\text{OH})_3$ was being formed, giving the water a characteristic reddish color. Sampling showed that 30% - 40% of the influent Se to the GWASU was already being removed, and the biosludge contained 3 – 5 times more Se than the sludge from the Main ASU. Inasmuch as the underutilized GWASU was already treating 60% of the Refinery's SSW, the idea was proposed to use the GWASU for Se co-precipitation and potentially avoid the capital and operating costs of much more expensive options.

During early 2012, a sampling campaign was conducted to develop a Se balance for the PCR wastewater system and to speciate the forms of Se. When combined with other 2010 - 2012 Se data, the analysis showed that approximately 64% of the Se left the refinery as a soluble constituent in treated wastewater; 7% was incorporated into the biosludge; and 29% was unaccounted and assumed to be volatilized as microbially-mediated methylated selenides, a process which is well documented in the literature². It was also learned that nearly all of the Se entering the wastewater comes from the SWS in the form SeCN^- . All of the SeCN^- entering either the Main or GW ASUs is oxidized and most of the Se leaves the units in the form of selenite (SeO_3^{-2}) with a small amount as selenate (SeO_4^{-2}). Selenite is the form necessary for co-precipitation and sorption onto

Fe(OH)₃, while selenate is difficult to remove with most current technologies. Essentially no Se was found in the effluent of the desalters.

The quality of stripped sour water (SSW) between refineries varies greatly, depending on whether water sources are segregated; how close to the design limit the SWS system is operated; and how effectively the SWS is operated, e.g. stripping steam ratio. In addition to some ammonia, sulfide, phenol, and organic acids, SSW can have significant amounts of oil and suspended solids, as well as chlorides which may affect the use of stainless steel and cause related stress cracking. The amount of each of these constituents as well as their concentration variability can have a great deal of influence about which Se removal process would be most appropriate for a specific location.

3.0 AMOUNT OF SELENIUM GENERATED & DISCHARGED

3.1 Se Generated

Between Jan 20, 2011 and July 31, 2015, 579 samples were collected from the two SWSs, which are effectively operated in parallel, and analyzed in the Refinery Control Lab. The two SWS samples for a given day were averaged, and then the entire data set was rank ordered as shown in Figure 1. The p50 (50th percentile or median) and p97 concentrations are approximately 0.77 and 1.13 mg/L (ppm), respectively. Mass loadings were generated by combining matched sets of concentration and flow rate for the unit for each day of sampling, which were then rank ordered as shown in Figure 2. The p50 and p97 mass values were approximately 3.0 and 4.6 lbs/day, respectively. Influent supply water contained ~0.5 µg/L Se, which translated to ~0.1 lb/day in the effluent. By observing several shutdowns of the Coker Unit for furnace decokes and a turnaround, it was also learned that about half of the Se was generated by the Coker.

Figure 1

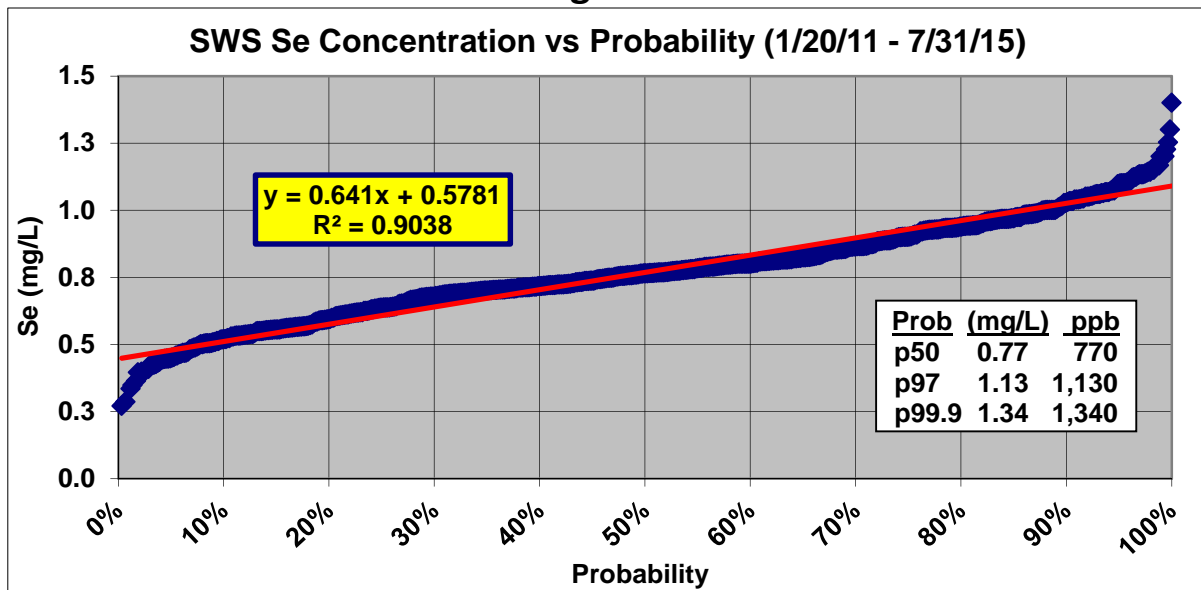
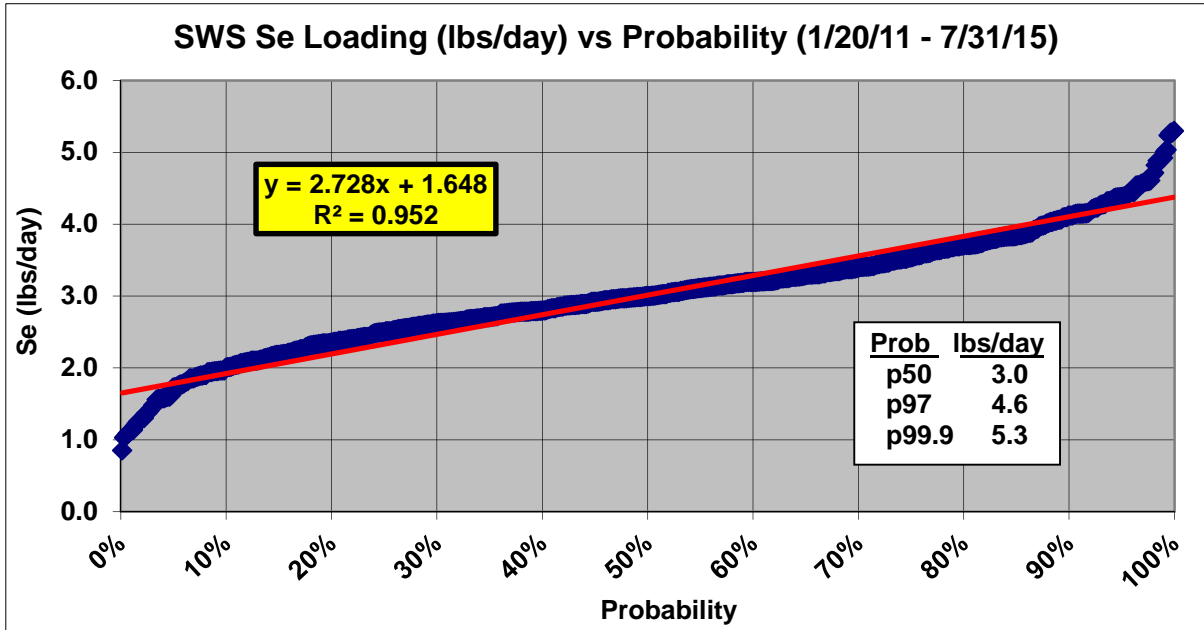


Figure 2



3.2 Se Discharged

Between Nov 29, 2010 and May 1, 2013, 70 samples were collected from the final refinery effluent at Outfall 001 and analyzed by TestAmerica. During this period there was no active Se removal process. The samples were rank ordered, as shown in Figure 3, yielding p50 and p97 concentrations of 79 and 103 $\mu\text{g/L}$ (ppb), respectively. Mass loadings were generated by combining matched sets of concentration and flow rate for the day of sampling, which were rank ordered as shown in Figure 4. The p50 and p97 values are 2.3 and 3.3 lbs/day, respectively. As can be seen by comparing the permit limits in Table 1 with the p50 values shown on Figures 3 and 4, 77.5 vs 79 ppb and 2.6 vs 2.3 lbs/day, the refinery wastewater would only be in compliance about 50% of the time without additional Se removal. Consequently, some type of Se removal process would be required to meet the new permit limits.

Figure 3

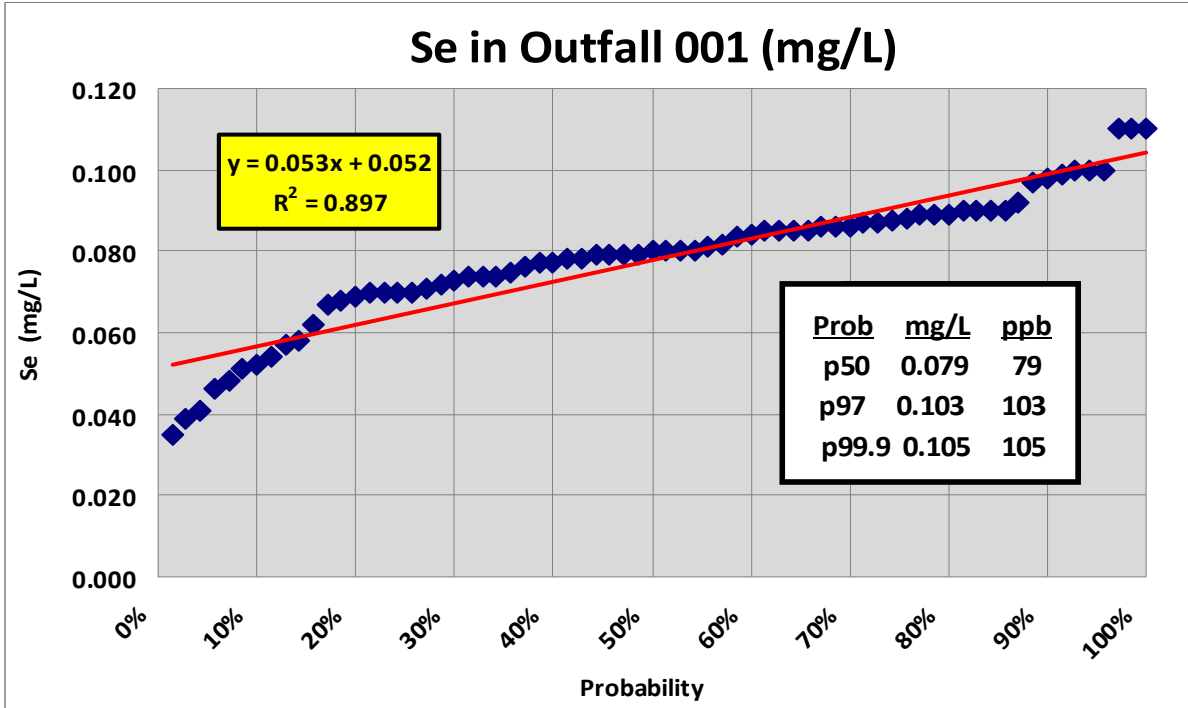
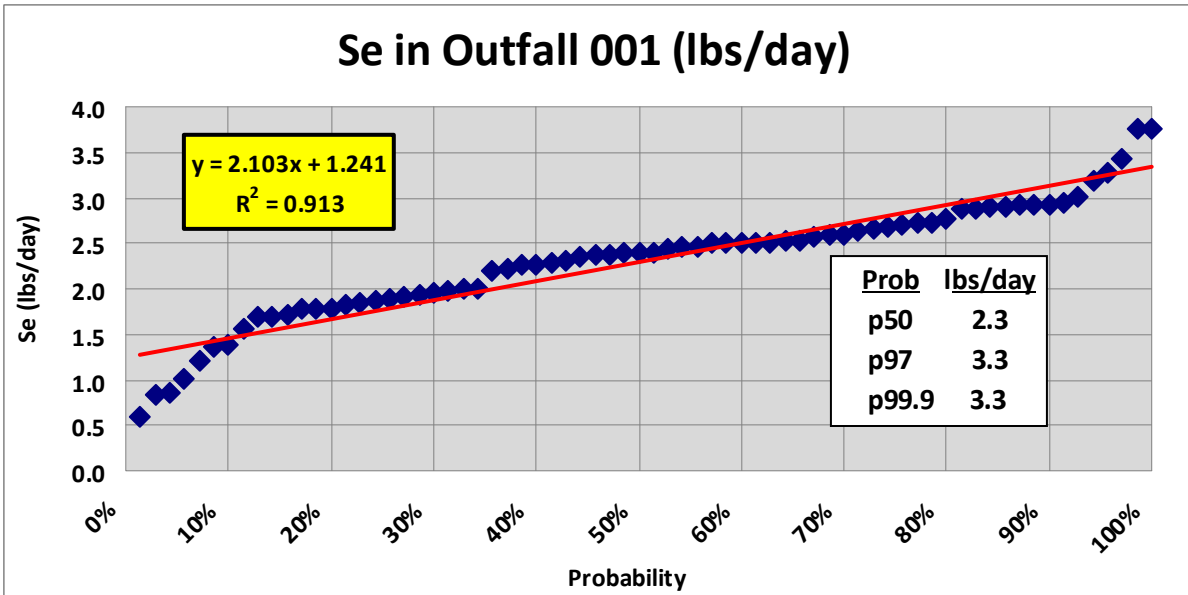


Figure 4



3.3 Treatment Target & Removal Required

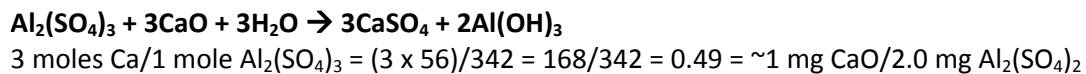
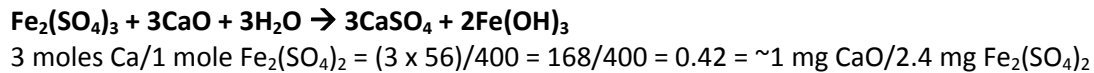
As shown in Table 1, permit limits were set by ODEQ at 77.5 and 100.4 ppb Se, respectively, for the monthly average and daily maximum concentrations. For planning, a treatment target of 50 ppb was set for the final effluent, which translated to ~1.5 lb/day. Since ~0.1 lb/day results from the ~0.5 ppb in the water supply, the amount of Se that could be contributed by the SWS would be 1.4 lb/day. Table 2 shows how much Se must be removed per day without considering any existing removal.

Table 2
Se Removal to Meet Compliance Objective

Location	Condition (lbs/day)	
	p50	p97
SWS Effluent	3.0	4.6
Outfall 001	2.6	3.4
Discharge Target (50 ppb) Less 0.1 Other	1.4	1.4
Removal Required in GWASU	1.6	3.2
Removal Required at Outfall 001	1.2	2.0

4.0 PROOF-OF-CONCEPT JAR TESTS

Once co-precipitation was deemed potentially viable, two phases of bench-scale, proof-of-concept testing were conducted. The first phase considered theoretical flocculation equations where lime was added to provide a source of hydroxide (OH⁻) to form Fe(OH)₃ and Al(OH)₃ floc according to the following equations:



Considering how little Se was removed in jar tests and in some cases the Se actually increased above the starting concentration due to desorption from the biosludge, the addition of lime was abandoned and those results are not presented. The work was repeated without lime addition as explained below.

GWASU mixed liquor samples were collected at the point of SSW influent entry and then treated with amendments at a series of dosages in jar tests. The approximate chemical dosages were pre-weighed into individually labeled Mason® jars with screw lids. Jars were filled with 400 – 500 mls of GWASU mixed liquor using a sample dipper. Since jars had been weighed empty, after chemical addition, and after water sample addition, the exact concentration of chemical dosage could be calculated. No pH adjustment was made.

To simulate the GWASU the jars were aerated in the lab for ~18 hrs at room temperature, the approximate residence time in the GWASU; centrifuged to separate solids; and then the supernatant was passed through a 0.45-micron filter to remove any remaining particulate-bound Se. The filtered soluble fraction was sent to the laboratory for Se analysis. Additives tested included lime (CaO); ferric sulfate [Fe₂(SO₄)₃]; ferrous sulfate (FeSO₄); ferric chloride (FeCl₃); aluminum sulfate [Al₂(SO₄)₃]; corn cob pellets; three activated carbons; and a commercial polymer designed for Se removal. Only the additives successful in removing Se are plotted in Figure 5 at the metal concentration for the dosing chemical used. The polymer is plotted at the concentration points for the accompanying FeSO₄ that was added. The results were very encouraging and showed that co-precipitation might be capable of achieving a 20-ppb effluent level of Se, or ~85% reduction.

Figure 5

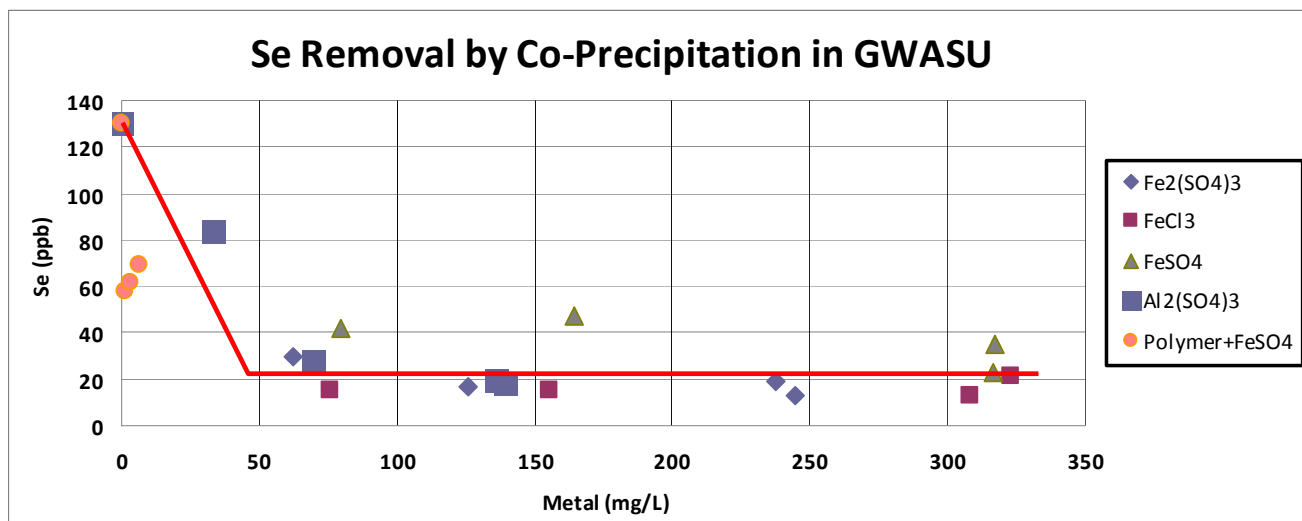


Table 3 shows a selected set of parameters for the GWASU. In as much as the GWASU received the blowdown from two WGS, the TDS concentration was 5,000 – 10,000 mg/L and was especially high in sulfate. However, based on the success of the jar tests, short-term tests were planned in the GWASU.

Table 3
Selected GWASU Mixed Liquor
Parameters (June – July 2012)

Parameter	Approximate Average (mg/L) or as noted
Temperature	97 °F
pH	7.1
Dissolved Oxygen	3.5
Oxidation-Reduction Potential	-31 mv
Conductivity	7,404 μS
Lab Total Dissolved Solids	5,901
TDS/Conductivity Ratio	0.80
Lab Total Suspended Solids	5,116
Sodium	1,600
Calcium	98
Magnesium	23
Potassium	11
Sulfate	3,400
Chloride	380
Nitrate	31

5.0 Step-Test in GWASU

The GWASU has two co-mingled influent streams which totaled ~400 gpm during the Step Test. The first influent stream of ~110 gpm was the blowdown from one of the WGS, which had a composition of about 1/3rd each of river well water, service water, and SSW. The second influent stream of ~290 gpm was composed of groundwater from remediation wells, the blowdown from a second WGS, all of the SSW from one of the SWS, a portion from the other SWS, and wastewater from the sulfur plant. The flow split of 110 and 290 gpm, 27.5% and 72.5%, was used to provide flow-weighted averages for influent Se.

The configuration of the GWASU is a rectangular in-ground basin with approximate dimensions of 200 ft x 40 ft x 7 ft with lift pumps in one corner of the basin pumping mixed liquor to an above-ground clarifier. Mixing and aeration are provided by six 30-hp and two 50-hp Aeromix Tornado aerators organized in two rows. The configuration of the aerators results in an elliptical flow pattern of the mixed liquor around the perimeter of the basin. Since the theoretical residence time of the GWASU basin and clarifier were ~18 and ~2 hrs, respectively, a complete turnover occurred every day.

Based on the laboratory success, short-term field step tests of three days each were conducted with four sequential concentrations of ferric sulfate [Fe₂(SO₄)₃] set at 25, 50, 75, and 100 mg/L Fe. The target dosing levels were chosen based on the results displayed in Figure 5. The actual dosing rates were set using the combined GWASU feed rate of 400 gpm and sufficient Fe₂(SO₄)₃ to achieve an instantaneous Fe concentration for each target level. Totes of ferric sulfate were used and had strength of 50%, density of 12.22 lbs/gal, and Fe content of ~10 wt%. LMI Milton Roy chemical pumps were used to deliver the necessary amount of chemical directly to the GWASU basin at a point downstream from the clarifier lift pumps so the Fe₂(SO₄)₃ added would be in the GWASU basin for the full residence time. Return activated sludge from the clarifier also enters the basin near the same point.

Grab samples were collected daily during the Step Test from the two influent streams and the effluent of the clarifier. Because of a communication issue, dosing was also conducted at 4, 6, and 11 mg/L Fe, so those results are included. The test periods were Aug 23 – Sep 8, and Sep 24 – Oct 6, 2012. Samples were analyzed for total and soluble Se after filtration through 0.45-micron filter. Since there was little difference between total and soluble Se, the values were averaged. During the first field trial a non-routine vendor lab as well as the Refinery's normal routine commercial lab both analyzed GWASU samples using EPA protocol methods. The total Se values from the non-routine lab were very high compared to the filtered samples, whereas the normal lab's Se values for the whole and filtered samples matched. Consequently, for the first test period, the total Se sample values were not used. Results for both test periods are shown in Tables 4 and 5.

Table 4
Se Concentration Data (ppb) – 8/23/12 – 9/8/12

Sample Date	Test Phase	PTU Influent		East Influent		Wt. Avg.		GWASU Effl		% Removal			GWASU Effl – Lab 2	
		Total Se	Diss Se	Total Se	Diss Se	Total Se	Diss Se	Total Se	Diss Se	Total Se	Diss Se	Total + Diss Se	Total Se	Diss Se
8/23/2012	Background	2,510	534	1,160	323	1,531	381	1,190	224	22%	41%	26%	240	230
8/24/2012	Fe ₂ (SO ₄) ₃ 4 mg/L Fe	-	-	1,540	313	-	-	1,260	230	-	-	-	-	-
8/25/2012		-	-	1,530	380	-	-	1,130	194	-	-	-	-	-
8/26/2012		2,390	484	1,810	343	1,970	382	915	184	54%	52%	53%	190	190

8/27/2012	Fe ₂ (SO ₄) ₃ 6 mg/L Fe	-	-	399	370	-	-	162	123	-	-	-	-	-
8/28/2012		-	-	212	192	-	-	186	130	-	-	-	-	-
8/29/2012		396	406	337	292	353	323	188	150	47%	54%	50%	200	170
8/30/2012	Fe ₂ (SO ₄) ₃ 11 mg/L Fe	-	-	288	288	-	-	182	159	-	-	-	-	-
8/31/2012		-	-	334	334	-	-	192	174	-	-	-	-	-
9/1/2012		440	420	313	313	348	342	194	184	44%	46%	45%	220	200
9/8/2012	Background	718	661	234	220	367	341	206	195	44%	43%	43%	-	-
Average	-	1,434	461	742	306	1,050	357	-	-	-	-	-	-	-

Table 5
Se Concentration Data (ppb) – 9/24/12 – 10/6/12

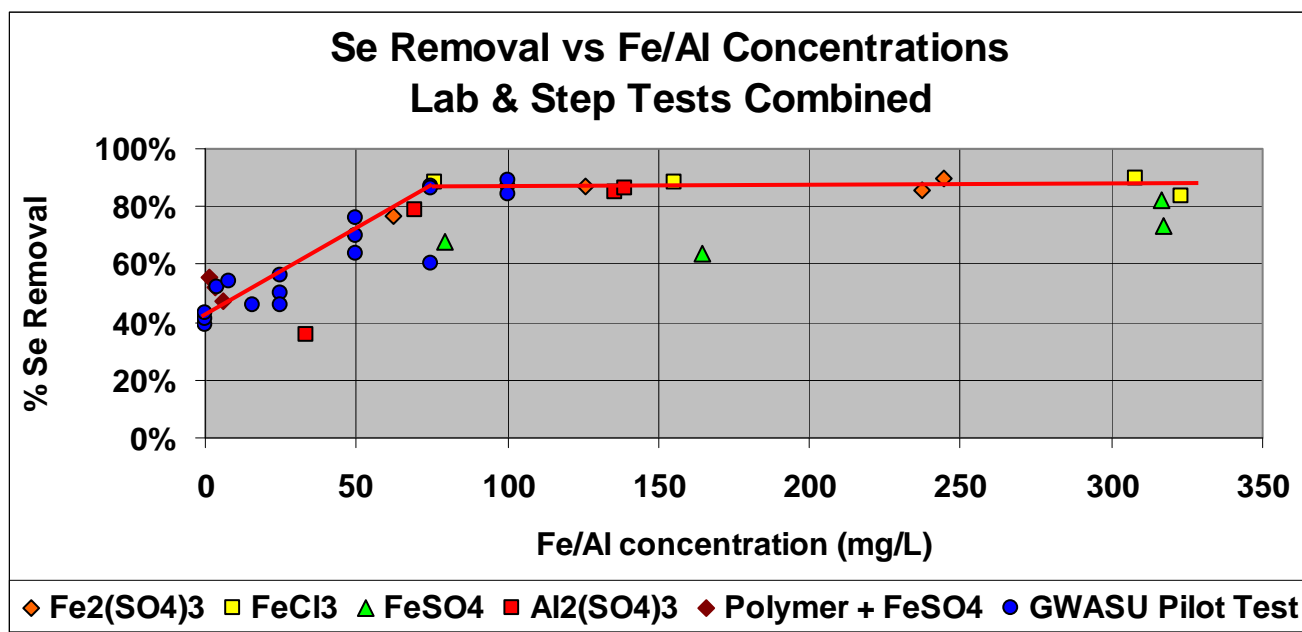
Sample Date	Test Phase	PTU Influent		East Influent		Wt. Avg. (ppb)		GWASU Effl		% Removal			
		Total Se	Diss Se	Total Se	Diss Se	Total Se	Diss Se	Total Se	Diss Se	Total Se	Diss Se	Total + Diss Se	Avg for Period
9/24/2012	Background	720	760	460	400	532	499	320	310	40%	38%	39%	39%
9/25/2012	Fe ₂ (SO ₄) ₃ 25 mg/L Fe	700	670	390	470	475	525	250	250	47%	52%	50%	51%
9/26/2012		710	680	370	280	464	390	230	230	50%	41%	46%	
9/27/2012		560	560	320	320	386	386	170	170	56%	56%	56%	
9/28/2012	Fe ₂ (SO ₄) ₃ 50 mg/L Fe	630	620	220	220	333	330	100	98	70%	70%	70%	70%
9/29/2012		610	560	250	240	349	328	74	87	79%	73%	76%	
9/30/2012		600	590	210	210	317	315	120	110	62%	65%	64%	
10/1/2012	Fe ₂ (SO ₄) ₃ 75 mg/L Fe	580	590	220	120	319	249	110	120	66%	52%	60%	78%
10/2/2012		440	430	380	360	397	379	45	52	89%	86%	88%	
10/3/2012		570	590	370	360	425	423	56	60	87%	86%	86%	
10/4/2012	Fe ₂ (SO ₄) ₃ 100 mg/L Fe	760	690	270	280	405	393	57	46	86%	88%	87%	87%
10/5/2012		680	690	240	290	361	400	62	60	83%	85%	84%	
10/6/2012		730	730	420	400	505	491	58	56	89%	89%	89%	
Average	-	638	628	317	304	405	393	-	-	-	-	-	-

The results from Tables 4 and 5 are summarized in Table 6 to show the % Se removal for a given Fe addition level as well as influent and effluent Se concentrations. The % removed data for both the laboratory jar tests and the field dosing step tests are plotted in Figure 6. The lab and step test show excellent correlation for % removal of Se.

Table 6
Summary of Se Removal in Step-Test Pilot

Fe Addition Level (mg/L)	~%Se Removal	Average Se (ppb)		
		Influent	Effluent	Reduction
0 (Background)	41%	413	245	168
3	52%	382	184	198
6	54%	323	150	173
11	46%	342	184	158
25	50%	438	217	221
50	70%	329	98	231
75	78%	365	74	291
100	87%	426	57	369

Figure 6



The % Se removal data for the step tests are plotted versus their respective Fe dosing concentrations in Figure 7, providing a good fit to the regressed equation. Figure 8 shows % Se removed vs. Fe:Se molar ratio. The 40% removal of Se noted at 0 mg/L Fe addition is attributed to the iron present in the groundwater that oxidizes to Fe(OH)₃ in the GWASU.

Figure 7

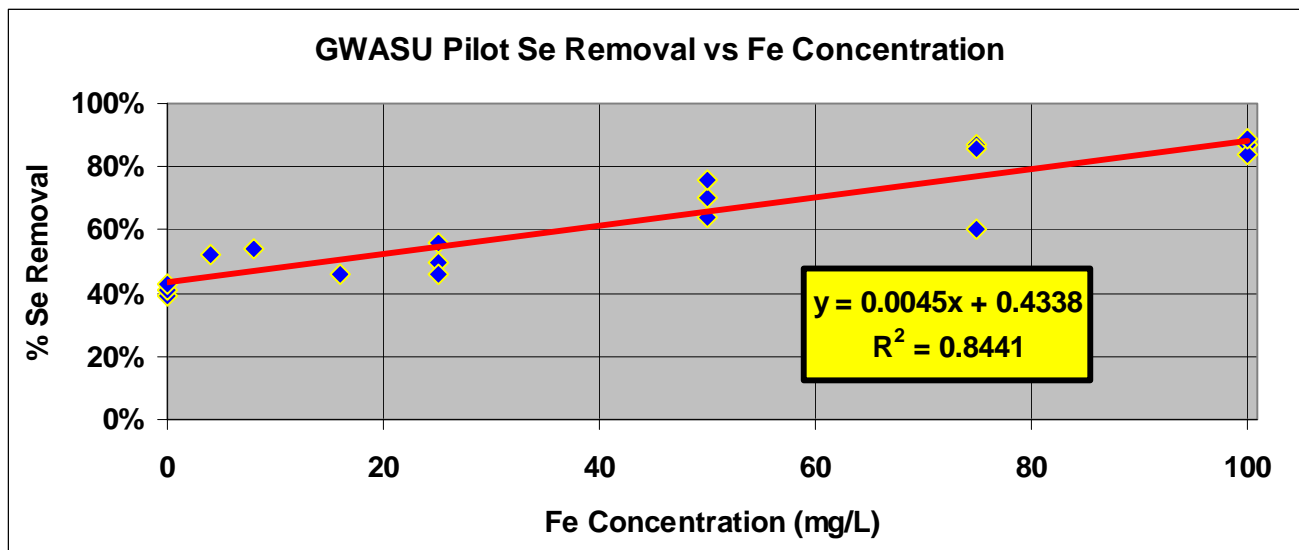


Figure 8

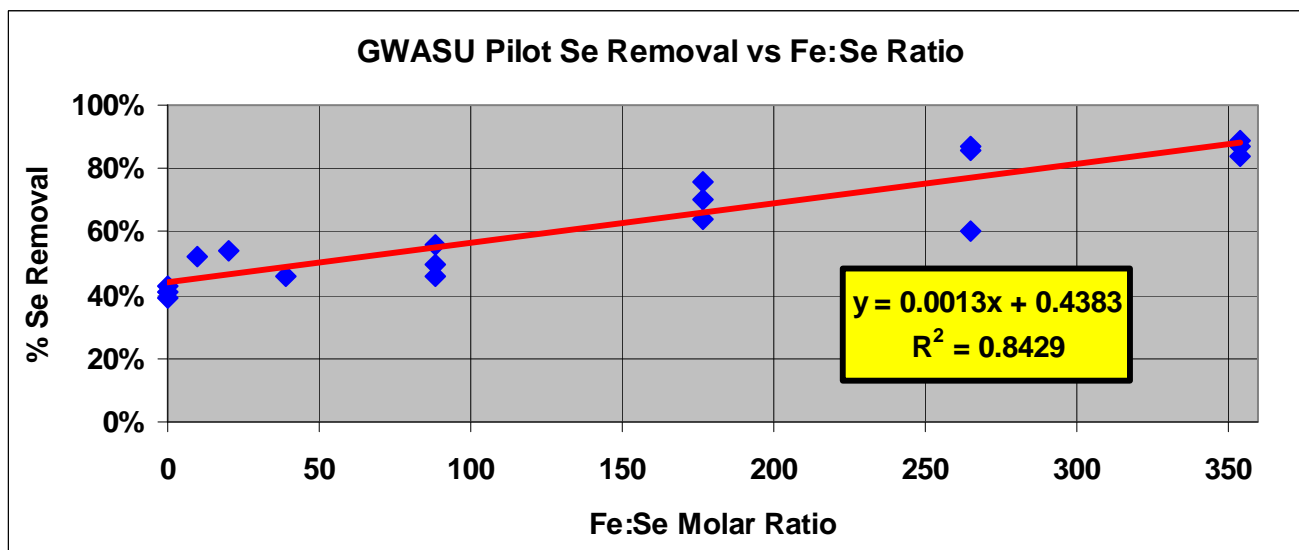
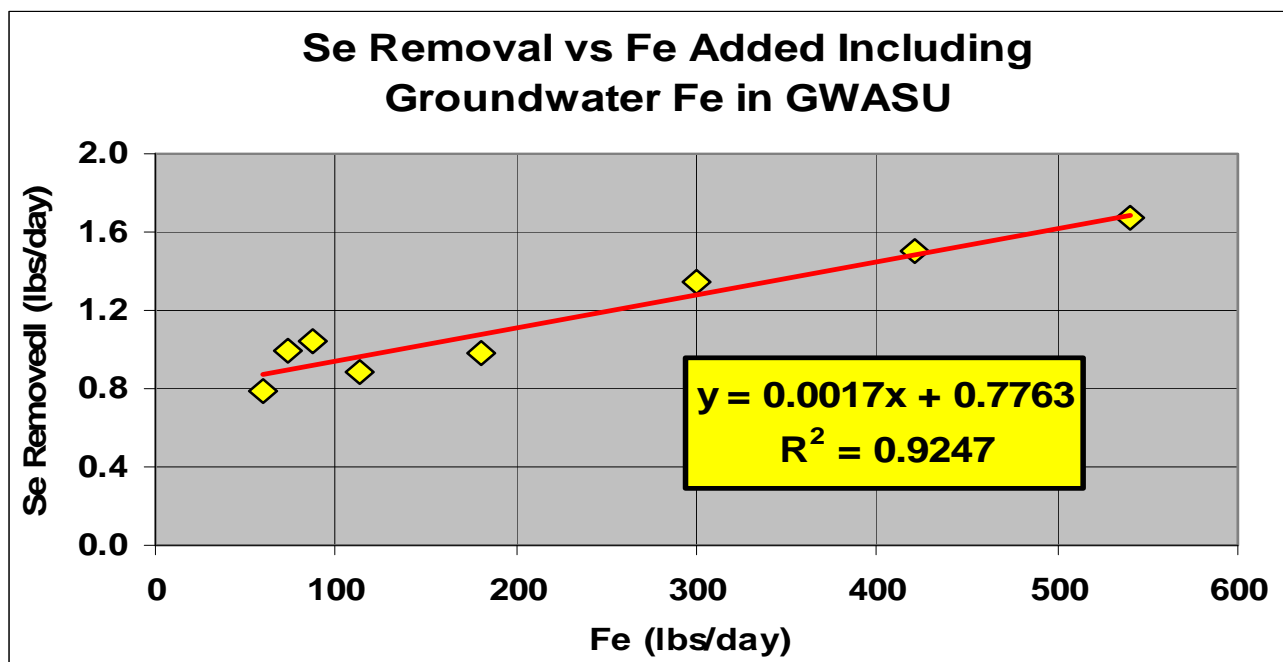


Figure 9 shows the amount of Se removed versus the amount of Fe added. It was estimated that the groundwater introduced about 60 lbs/day of ferrous iron, which oxidizes to form $Fe(OH)_3$. The 60 lbs/day was added to the amount of Fe dosed.

Figure 9



Co-precipitation of Se with ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$] was successfully demonstrated in PCR's underutilized Groundwater ASU (GWASU). Four sequential, 3-day step tests with successively increasing dosages of $\text{Fe}_2(\text{SO}_4)_3$ reduced an influent Se concentration of ~400 ppb by ~85% to an effluent level of 45 – 60 ppb. The results showed that it took ~200 pounds of Fe to sorb one pound of Se. During the pilot test biosludge samples were collected during each concentration step and TCLP tests conducted which demonstrated that the sludge is RCRA non-hazardous. Waste sludge was managed by normal once-per-week removal by vac truck and application to the permitted Land Treatment Unit (LTU). Finally, routine parameters used to monitor the GWASU were unaffected by the addition of $\text{Fe}_2(\text{SO}_4)_3$.

6.0 EQUIPMENT CHANGES MADE PRIOR TO DEMONSTRATION TESTS

As stated earlier, the SSW was split for treatment between the Main and GW ASUs. It was decided that it would be preferable to treat all of the SSW in the GWASU rather than trying to remove Se in both ASUs. The flow rate of the Main ASU is approximately four times greater than the GWASU.

To consolidate all of the SSW into the GWASU required a project. The project included installation of a new 1,000-ft 4" carbon steel line; appropriate valves, insulation, and heat tracing; upgrades to two effluent pumps; installation of a radar gauge for level control on the tank from which the GWASU effluent pumps take suction; installation of a 10,000-gal poly tank for (poly) ferric sulfate; addition of several flow meters; instrumentation to take signals into DCS; and other miscellaneous items. One significant point is that most of this cost would have been incurred with any Se removal technology, since all of the SSW would have to be combined for treatment. Several additional tasks were also completed to improve the operation of the entire wastewater system, such as replacing an existing steel line that was in poor condition with a larger poly line that allowed the entire effluent of the GWASU to be recycled to the fire/service water system.

7.0 FULL-SCALE DEMONSTRATION TESTS IN GWASU

Two full-scale demonstration tests were conducted in the GWASU, one during the Fall of 2013, and the second in early 2014. Baker frac tanks of 4,000 gal each were set to hold chemicals for dosage, one for $\text{Fe}_2(\text{SO}_4)_3$ and, later, another for poly ferric sulfate. There were number of uncertainties and many unexpected findings that presented challenges that would have to be solved to be commercially successful.

7.1 1st Demonstration Test

The first Se removal demonstration test was conducted in the GWASU by dosing with $\text{Fe}_2(\text{SO}_4)_3$ from Aug 5 – Sept 11, 2013. Due to the loss of nitrification early in the test, only ~64% of the SWS flow and Se were routed to the GWASU versus a target of 90%. Target iron dosage was 75 mg/L at a wastewater flow rate of ~700 gpm. Nitrification is the biological process that converts ammonia (NH_3) to nitrate (NO_3^-), and had been considered to be one of the purposes of the GWASU. In an attempt to restore nitrification, biosludge was not wasted until late in the test in an attempt to build up the population of nitrifiers. The sludge buildup also allowed Se to accumulate in the system. Two Se desorption events occurred, one due to a biological excursion to pH 5.4 and the other due to a mechanical failure of the PTU pH controller leading to caustic injection and a pH of 10 in the GWASU. Se removal was erratic, although an average removal of 72% was achieved for the days when removal was good. Because the results were less than expected, a second demonstration test was planned. However, there were uncertainties and several key findings that needed to be addressed.

- The high TDS, especially the sulfate (SO_4^{-2}), contributed by the WGSs interfered with Se sorption and increased the amount of $\text{Fe}_2(\text{SO}_4)_3$ required.
- pH excursions <6 were believed to be due to the introduction of thiosulfate ($\text{S}_2\text{O}_3^{-2}$), which was then biologically degraded to make acid, lowering the pH.
- Loss of nitrification was due to near complete consumption of alkalinity.

7.1.1 Lineup Changes for WGS

Lineup changes would eventually be made so that the effluent from the two WGSs would be routed directly to the Main ASU for treatment rather than to the GWASU. This change required the completion of a line replacement for wastewater pumped from the Main Lift Station to the Main ASU. The lineup change eliminated ~20 tons of TDS, ~15 tons of which was sulfate, reducing the TDS in the GWASU from 5,000 – 10,000 mg/L to 500 – 750 mg/L. The lineup change from one of the WGSs also eliminated a significant amount of NH_3 from the GWASU. The NH_3 was the result of slip from the ENSCR unit (enhanced non-selective catalytic reduction), which was located on the tail gas of the FCCU where NH_3 is injected to convert NO_x to N_2 gas. The excess NH_3 dissolved into the circulation fluid of the WGS to become a constituent in the WGS blowdown to wastewater.

7.1.2 Reroute of Sulfur Recovery Unit Wastewater

A new line was installed that allowed the sulfur plant wastewater to be routed directly to the Main ASU rather than to the GWASU. Since the recovered sulfur is used to produce agricultural chemicals, including ammonium thiosulfate, the source of the $\text{S}_2\text{O}_3^{-2}$ was eventually eliminated as were the very low pH excursions.

7.1.3 Loss of Nitrification

Biological nitrification requires a large amount of bicarbonate alkalinity. Since the influent to the GWASU is SSW, the makeup of which is mostly steam condensate, and some groundwater, the alkalinity is already low. Alkalinity is then depleted by the acid formed due to the degradation of some compounds, e.g. sulfide; Fe^{+2} from groundwater that is oxidized to Fe^{+3} ; and $\text{Fe}_2(\text{SO}_4)_3$ that reacts to form $\text{Fe}(\text{OH})_3$. A conscious decision was made to forego nitrification in the GWASU, since the NH_3 contribution from the GWASU was still well under permit limits at the final outfall.

7.2 2nd Demonstration Test

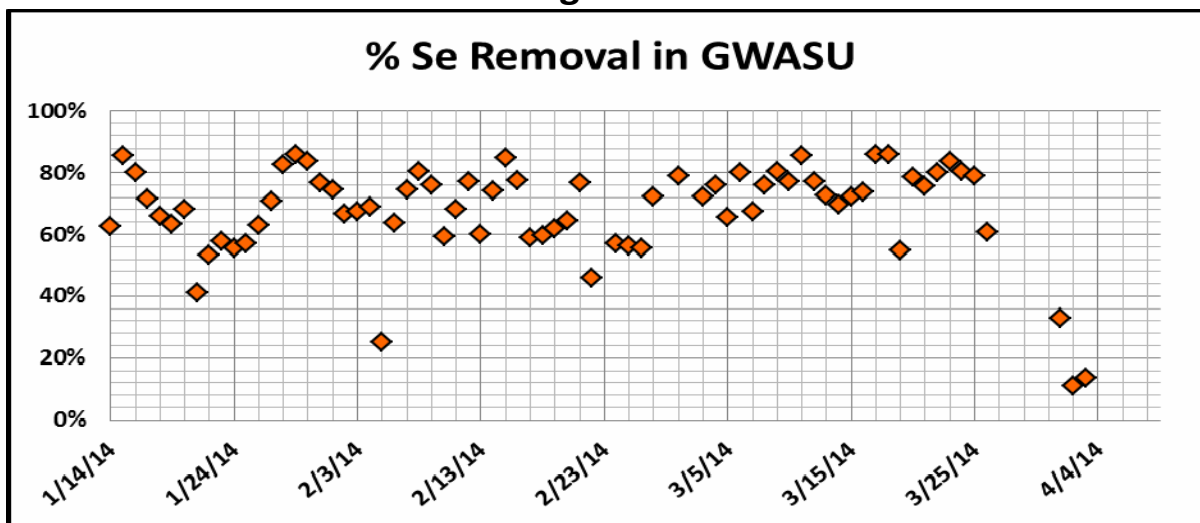
For the 2nd demonstration test the WGS effluent was diverted to the Main ASU, but flow from the sulfur plant continued since the new line was not yet in place. GWASU influent consisted of approximately 250 gpm of SSW, 150 gpm of groundwater from remediation recovery wells, and 100 gpm from the sulfur plant for a total of ~500 gpm. The test was conducted from Jan 14 – Mar 25, 2014, and included separate Fe₂(SO₄)₃ dosages of 10, 20, and 30 mg/L Fe and PFS dosages of 5, 10, and 20 mg/L Fe.

PFS is polymerized Fe₂(SO₄)₃, manufactured by Kemira, and has slightly higher iron content than ferric sulfate. See Table 7 for a comparison of Fe₂(SO₄)₃ and PFS. Recall that a 75-mg/L Fe target was used for the jar and step tests. Much lower chemical dosages were possible because of the removal of the TDS, especially sulfate. The % Se removal across the GWASU for all conditions is shown in Figure 10. As can be seen, when chemical injection ceased on Mar 25, removal fell off quickly. Because of the variability of parameters all Fe₂(SO₄)₃ and all PFS data were averaged as groups, yielding, 72% and 78% Se removal, respectively.

Table 7
Comparison of Key Properties for Ferric Sulfate & PFS

Property	Ferric Sulfate	Poly Ferric Sulfate
Strength	50%	50%
Density	12.2 lbs/gal	12.4 lbs/gal
Fe Content	10 wt%	13 wt%
Viscosity @ 60°F	~44 cp	~71 cp
Viscosity @ 0°F	~102 cp	~1,032 cp

Figure 10



8.0 COMMERCIAL IMPLEMENTATION

Based on the accumulated successes of the jar, step, and demonstration tests, the decision was made to proceed with commercial implementation of co-precipitation. In addition to the equipment changes described in Section 6.0, the line from the Main Lift Station to the Main ASU was debottlenecked so that the wastewater

from the two WGSs and the sulfur plant could be permanently removed from the GWASU. With the lineup changes the influent flow rate to the GWASU was ~550 gpm. An injection rate of 50 ml/min of $\text{Fe}_2(\text{SO}_4)_3$ or PFS was chosen for an iron content of 10 mg/L in the GWASU. This injection level was an 85% reduction from the dosages used in jars and step tests. 50 ml/min equals about 19 gal/day or 232 lbs/day. At a cost of \$0.17/lb the chemical cost is \$39/day or \$14,400/yr.

Prior to injection of $\text{Fe}_2(\text{SO}_4)_3$ or PFS a vac truck was used to waste sludge once/week from the GWASU clarifier. With $\text{Fe}_2(\text{SO}_4)_3$ or PFS injection two vac truck loads/day are wasted five days/week. At \$75/hr for a vac truck and operator, the increased sludge wasting costs are about ~\$33,000/yr. Combining the chemical and vac truck charges shows that the annual operating cost for co-precipitation gives an incredibly low operating cost of ~\$47,000/year. Since the sludge is spread on the Land Treatment Unit (LTU), there are no incremental costs for disposal. Figures 11 and 12 show the daily concentration and mass loading of Se measured in the refinery outfall.

Figure 11

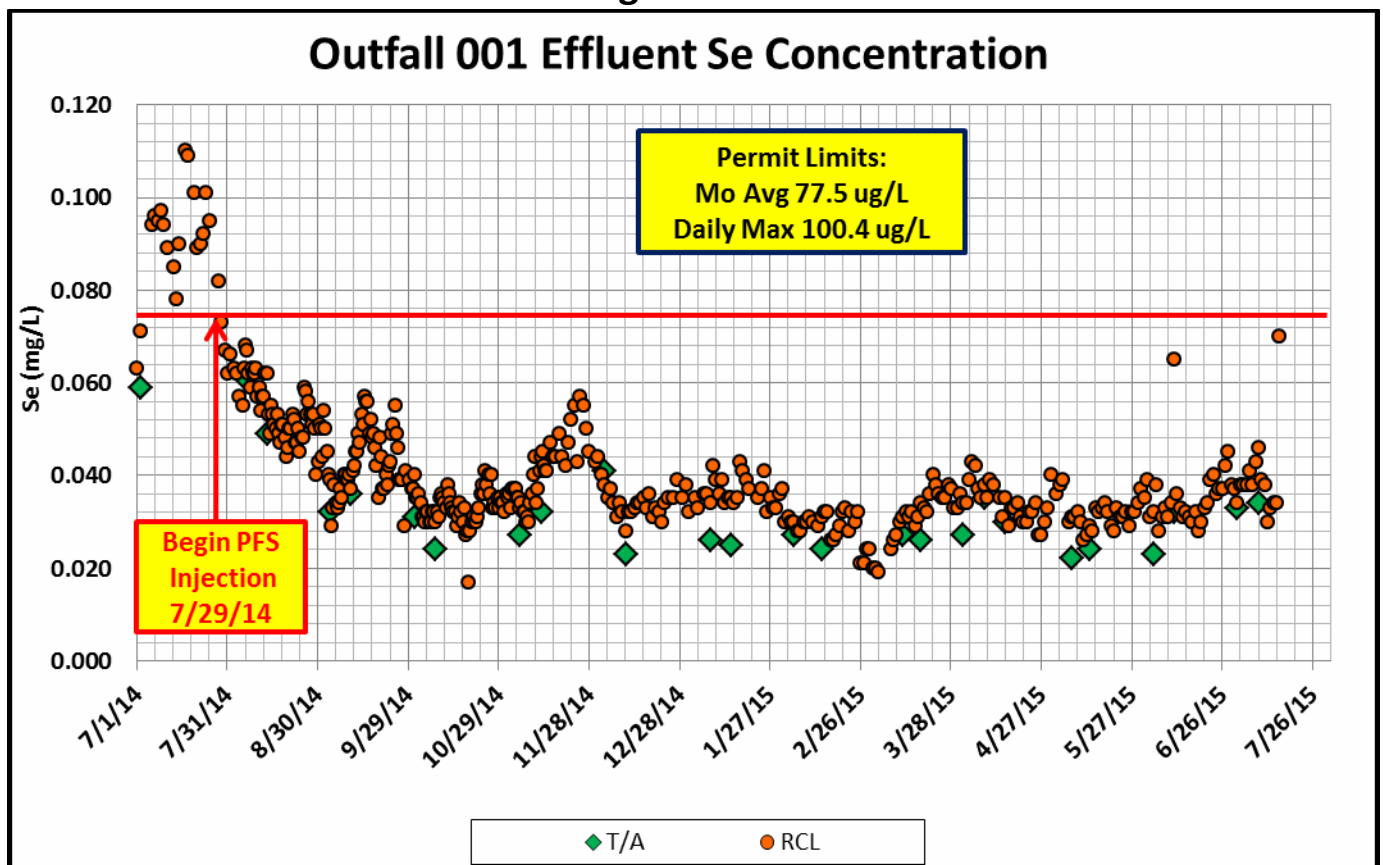
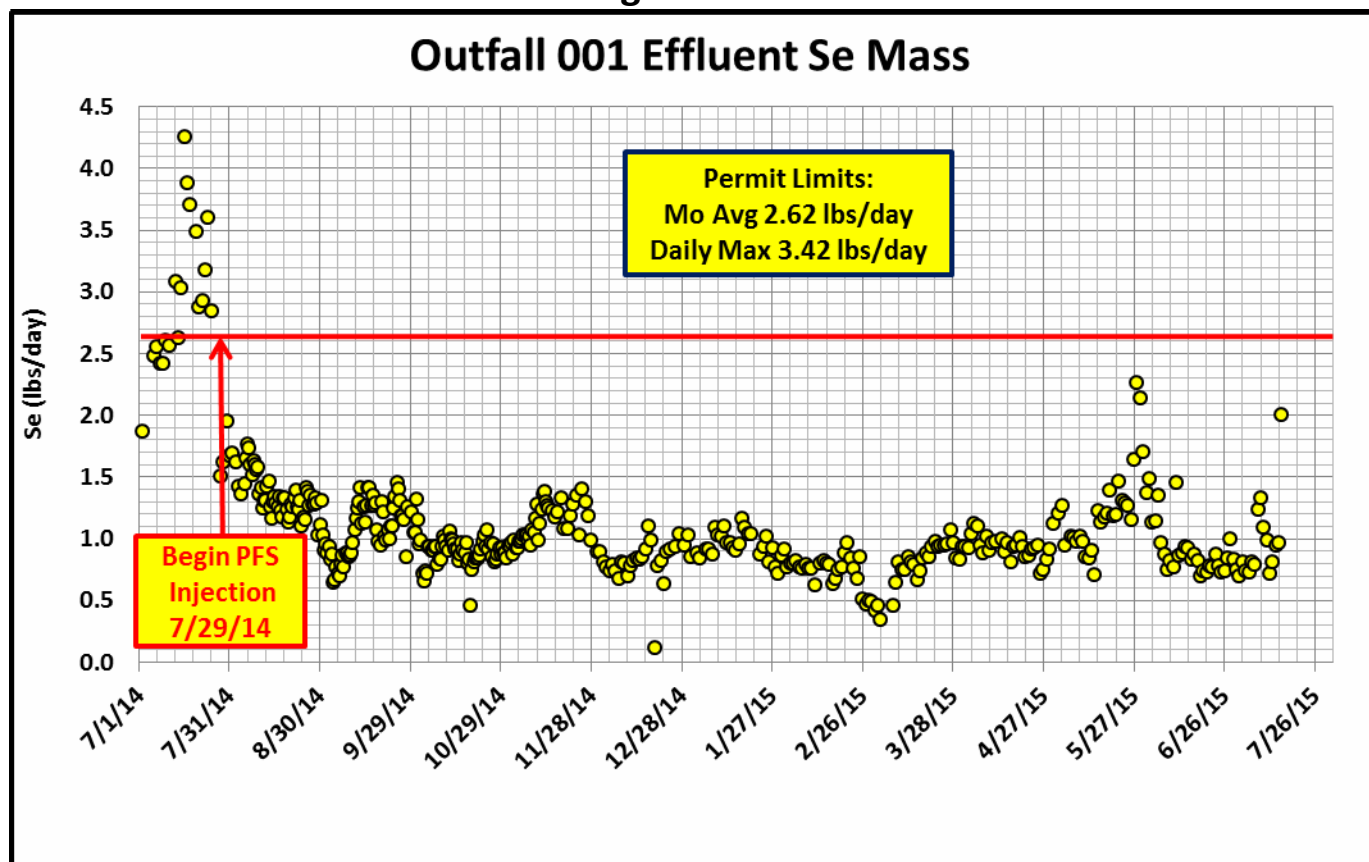


Figure 12



8.1 Analytical Issues Resolved

To save money and ensure quick turnaround, water samples were sent to the Refinery Control Lab (RCL) for Se analysis using a non-EPA protocol method. During the course of this project it was determined that the RCL analyses were giving erroneous elevated values. After an audit by the 3rd party lab that used the EPA methodology, a number of changes were made, e.g. aqua regia digestion. Since the goal was to provide analyses for daily operational guidance, implementing full compliance methodology to become a protocol lab was not deemed to be necessary. Compliance samples are sent to an outside certified lab. As can be seen in Figure 11, based on a year's worth of monthly matched pairs, RCL Se values are ~25% higher than TestAmerica (T/A) at Outfall 001. This difference provided an acceptable cushion of conservatism, since the commercial compliance lab had the lower concentrations.

Recall that Figures 3 and 4 provided results for Outfall 001 using T/A data that were based on rigorous EPA methodology, so there were no issues or concerns. However, RCL data had been used to develop the Se being generated in the SWS as shown in Figures 1 and 2. Since all RCL lab changes had been made by the time that co-precipitation went commercial, the period of Aug 1, 2014 – July 31, 2015 was evaluated as shown in Figures 13 and 14, based on 256 sets of samples for the SWS. The results show that ~13% less Se was being generated than previously thought based on a comparison of p50 values, 0.77 vs 0.67 mg/L and 3.0 vs 2.6 lbs/day.

Figure 13

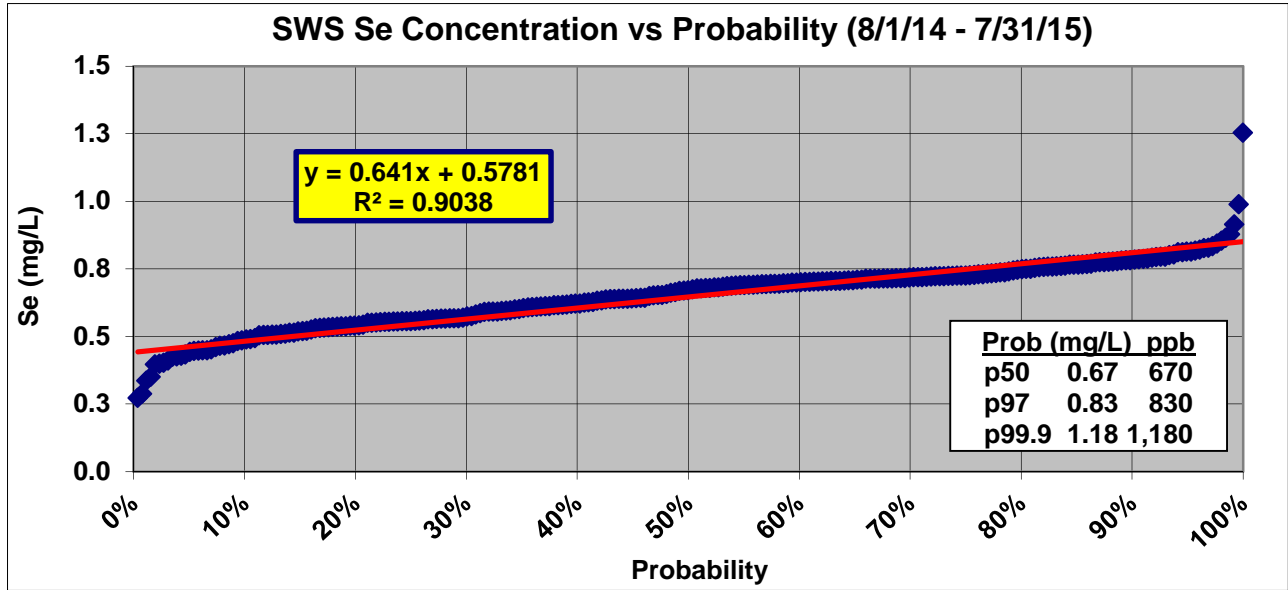
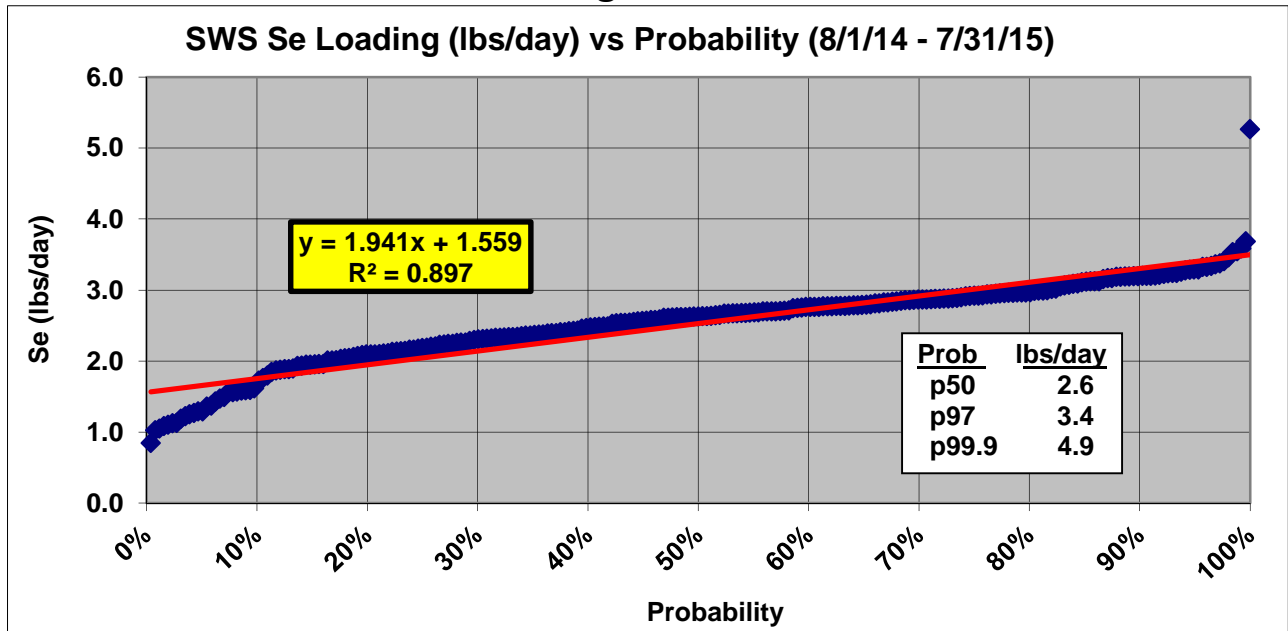


Figure 14



9.0 Se MATERIAL BALANCE

A material balance for the year between Aug 1, 2014 and July 31, 2015 was developed based on daily average mass loading values, as shown in Table 8. A total of 63% of the Se generated in the SWS and the small amount contained in the supply water was removed. Recall that the supply water contained 0.5 ppb Se, which would translate to 0.1 lb/day. As noted in Section 2.0, there was 29% unaccounted for Se; a portion of that amount was due to the overestimation of Se generated. Some methylation of Se may also occur, but that cannot be confirmed by these data. To remove the 1.4 lbs of Se/day in the GWASU, 232 lbs/day of $Fe_2(SO_4)_3$ was added which contained 10% Fe, or ~23.2 lbs/day. The amount of iron added was then ~17 lbs Fe/lb Se removed, versus the 200 lbs/lb mentioned earlier. The significant reduction is attributed to the removal of TDS, and especially sulfate, from the WGS.

Table 8
1-Yr Material Balance for Se Removal

Source	Average lbs Se/day	Comment
Generated in SWS	2.54	Total Se except for supply water
Bypassed to WGS	0.29	11% of SWS Se
GWASU Influent	2.25	By difference = SWS - WGS
GWASU Influent	2.23	By sample & flow
Se Removed in GWASU	1.40	To biosludge by difference
Removal in Main ASU	0.13	To biosludge = bypass + GWASU effluent - O/F 001
Se from Water Supply	0.10	By sample & flow
Outfall 001	0.99	By sample & flow
Total Se Removed	1.65	63%
Total Se Discharged	0.99	37%

10.0 SECONDARY BENEFIT--ARSENIC (As) REMOVAL

Although Se was the focus of this study, since samples were already being collected, the incremental cost of measuring As was low. Total and soluble As were measured for both SWS Units, showing the effluent concentrations to be less than the method detection limit (MDL) of 0.010 mg/L or “J” values just above the MDL for nearly every sample. Consequently, there was little As loading from the PCR SWS.

During both demonstration tests daily grab samples were collected and analyzed for total and soluble As by T/A for the 2 GWASU influent streams and the GWASU effluent. The first influent stream was from the WGS Purge Treatment Unit (PTU) for one of the FCCUs, while the other stream was the East Influent, which consisted mostly of remediation groundwater, the PTU from the other FCCU, and the sulfur plant wastewater. Arsenic is a well-known constituent of remediation groundwater. The As is liberated from the aquifer sediments when ferric iron is used as an alternative electron acceptor by in-situ microorganisms. For the second Demonstration Test the PTU was diverted to the Main ASU, but the As data are still included. Figure 15 shows Total As for PTU, East Influent, and GWASU Effluent, while Figure 16 shows soluble As. Note that analyses less than the MDL of 0.010 mg/L were plotted at zero, while the “J” values were plotted at their actual estimated concentrations. As can be seen, total concentrations are usually higher than their soluble counterparts, since filtration through a 0.45-micron filter removed solids onto which As was sorbed. Using the MDL of 0.010 mg/L to establish the maximum As that could have been present in the effluent shows that the As removal across the GWASU during ferric sulfate dosing >75%.

Figure 15

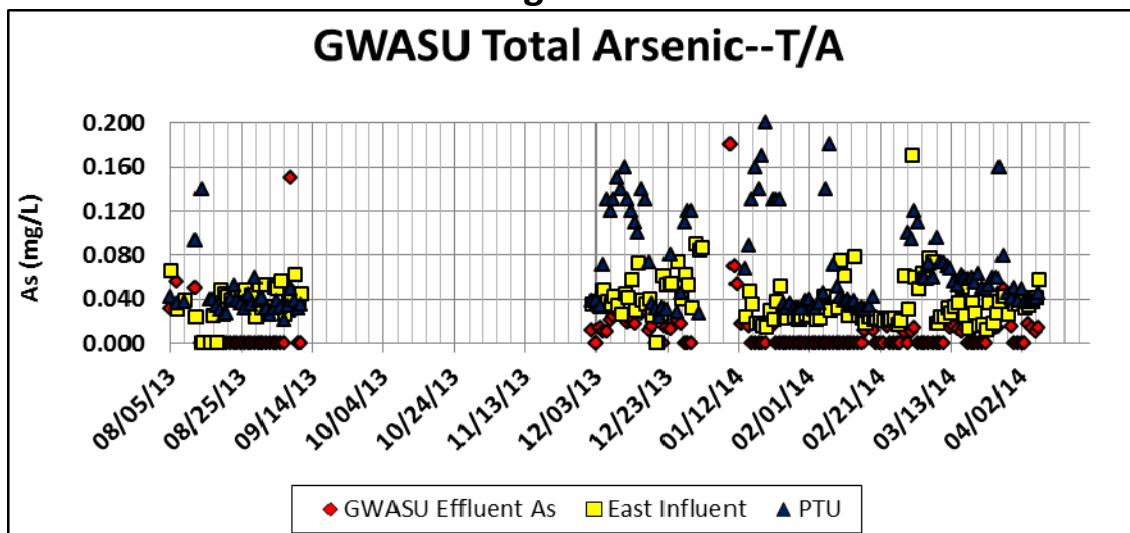
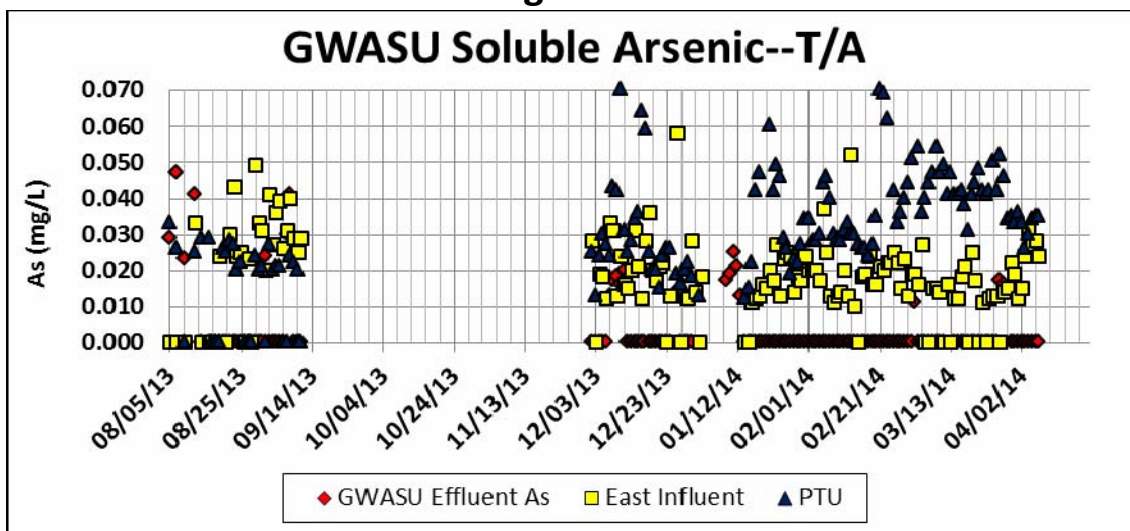


Figure 16



11.0 CONCLUSIONS

1. An operating ASU was successfully used to remove Se by adding a continuous small dose of $\text{Fe}_2(\text{SO}_4)_3$ or poly ferric sulfate, and managing the precipitate along with the biosludge.
2. The presence of high TDS and sulfate concentrations interfere with the sorption of Se on iron hydroxide. Chemical dosages of $\text{Fe}_2(\text{SO}_4)_3$ and poly ferric sulfate were reduced by ~85% due to changing the lineups of the high TDS streams.
3. Due to low alkalinity, nitrification could not be sustained in the GWASU. However, because the GWASU only treated 20 – 25% of the total wastewater flow, loss of nitrification was acceptable.
4. For one year of commercial operation, the material balance showed an average Se removal of 63%.
5. Arsenic removal of ~75% was achieved as a secondary benefit of this treatment.
6. Consistent Se removal is possible for a final effluent concentration of 50 ppb.
7. Numerous technical and logistical challenges arose during the project, but persistence, creativity, and patience prevailed.

8. A project such as Se removal included a significant amount of discovery and problem solving to ensure that the right project would get installed, which is quite different than following a predetermined procedure.

12.0 REFERENCES

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