

Metals Removal in a Two Stage HDS Pilot Study on Concentrated Mine Water

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KEYWORDS: Mining, HDS, Acid Mine Drainage, Pilot

ABSTRACT

Abstract: The closure of inactive mine sites requires the management and disposal of water that has over time accumulated onsite. In the specific case that is the subject of this paper, a large volume of water had accumulated from mining operations. The water is characterized as being highly acidic, with a high sulfate and TDS concentration, and large concentrations of a variety of metals and metalloids. The volume of water is sufficiently large that treatment will take over a decade. A number of processes were evaluated for removal of the bulk of the wastewater constituents, including sulfate, fluoride, aluminum, copper, iron and host of metals and metalloids at lower concentrations. As an initial evaluation, the High Density Sludge (HDS) process was selected for lab scale pilot study. Lime was used as the neutralizing agent, due to cost considerations. Limestone was also evaluated. The study was conducted in HDR's process research lab in February and March 2021. An additional run was conducted in May 2021. The pilot system operated at a flowrate of nominally 100 ml/min, under a variety of operating conditions. The high strength of the wastewater and the resulting high solids formed in neutralization presented major challenges. This paper describes the wastewater characteristics, pilot system configuration, overall pilot system performance and the degree of removal of some of the specific metals present.

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INTRODUCTION

A mining company is in the process of closure of a non-operational copper mine site in the southwestern US, which has accumulated a substantial volume of wastewater. This water is acidic and contains high concentrations of sulfate, copper, aluminum, and other metals. The accumulated water volume along with the continuing inflow of groundwater and drainage must be treated prior to discharge or reuse. There are many options for handling this wastewater, including resources recovery options (recovery of metals), traditional treatment and disposal options (like HDS) and evaporative solutions.

One approach under consideration is the HDS Treatment. This process was initially developed by Bethlehem Steel in the 1960s to improve the treatment of acid mine drainage. HDS improves on simple hydroxide precipitation by modifying process conditions in such a way as to create a denser sludge and use chemicals most efficiently. This is critical because chemicals (lime) and sludge disposal are usually the two largest contributors to operating costs. These process conditions focus on driving the precipitation reaction for metal hydroxides and insoluble salts onto the surface of recycle solids as opposed to occurring in solution. This results in the formation of larger particles, and if done properly, generate more uniform particle sizes that thicken and dewater more effectively. Typically, this process is used on streams in which the precipitated solids total in the hundreds to low thousands of parts per million (ppm). In this case, the concentration of precipitated solids is over 70,000 ppm.

RAW WATER CHARACTERISTICS

Four totes of water from the site were used as raw wastewater during the HDS testing described in this paper. These four totes were collected in a single sample event from the larger of the two pits at the site, as the water quality in the pits was similar. Runs #1 through #4 were performed using pit water from Tote #1. Mid way through Run #4, the raw wastewater from Tote #2 was used. Run #7 was run on concentrated pit water from Tote #3. This tote was deliberately concentrated by blowing air through it to evaporate water. The concentration factor for this tote was approximately 15%. It is suspected that a sampling anomaly resulted in Tote 2 having higher concentrations than other totes for most parameters. The sampling was done using an existing pumping system and piping, and it is possible some material in the line originated at another pit and was in the line at the start of sampling. The analytical data for each tote is detailed in Table 1 below. It was expected that the water quality in the pit was relatively homogenous based on past studies.

The characteristics of the water in the totes varied to a greater degree than expected. This is evident in the data presented above, for example for aluminum data where the concentrated tote (Tote 3) was concentrated over Tote 1, but Tote 2, which was not concentrated prior to use, was higher still in aluminum and most other parameters. Also, it should be noted that tote 4 was much higher in several parameters, including sulfate, than the other totes.

The data in Table 1 reflects missing data for fluoride and sulfate in Totes 2-4. This results from analytical error on the part of the outside lab performing the analyses.

Table 1 – Raw Pit Water from Totes Used During Pilot

Analyte	Units	Tote 1	Tote 2	Tote 3	Tote 4
Aluminum	mg/L	6,400	7,800	7,200	11,000
Antimony	mg/L	0.0037	0.0042	ND	0.0046
Arsenic	mg/L	0.37	0.45	0.40	0.39
Beryllium	mg/L	2.1	2.3	2.2	2.5
Cadmium	mg/L	4.6	5.4	4.9	5.4
Calcium	mg/L	420	490	520	240
Chromium	mg/L	2.6	3.0	2.8	3.0
Cobalt	mg/L	10	12	11	12
Copper	mg/L	610	690	830	820
Fluoride	mg/L	840	-	-	-
Iron	mg/L	130	150	140	<0.39
Magnesium	mg/L	4,100	4,600	4,300	5,000
Manganese	mg/L	240	280	250	350
Mercury	ng/L	3.6	3.5	4.6	2.6
Molybdenum	mg/L	0.0042	0.0079	0.0099	0.0027
Nickel	mg/L	20	24	22	23
Potassium	mg/L	200	220	190	210
Selenium	mg/L	0.29	0.33	0.36	0.4
Silver	mg/L	<0.0041	<0.0082	<0.0082	<0.0041
Sodium	mg/L	300	310	310	320
Strontium	mg/L	3.5	4.0	3.8	3.2
Sulfate	mg/L	56,000	-	-	70,000
Thallium	mg/L	0.020	0.015	0.019	<0.010
Tin	mg/L	<0.042	<0.084	<0.084	<0.042
Total Dissolved Solids	mg/L	84,000	87,000	82,000	91,000
Total Suspended Solids	mg/L	170	210	96	26
Uranium	mg/L	2.8	2.3	3.0	2.6
Vanadium	mg/L	0.055	0.21	0.14	0.16
Zinc	mg/L	75	91	84	87

DISCHARGE CRITERIA

There are several options for discharge of the water after treatment and all have different discharge criteria. One attractive option is partial treatment and conveyance to an adjacent active mine site. Other options include discharge to groundwater, discharge to surface water, and use for livestock watering. Table 2 below summarizes critical parameters of the potential discharge criteria versus the characteristics of the pit water. Based on these data, the parameters of greatest concern include aluminum, arsenic, cadmium, chromium, copper, fluoride, iron, manganese, nickel, selenium, sulfate, total dissolved solids, total suspended solids, uranium, and zinc. The option of sending water to a neighboring mine is attractive, as only pH and Total Suspended Solids (TSS) requirements need to be met. However, most of the lime demand has to be satisfied to increase the pH to safely over 6, and to do this economically still requires treatment and solids/liquid separation. Of the other options, livestock watering is the most

attractive set of criteria, but any of the discharge criteria may require polishing treatment beyond the HDS process.

Table 2 – Potential Effluent Concentration Requirements

Analyte	Units	Tote 1	Adjacent Facility	Groundwater	Surface Water	Livestock Watering
pH	Std units	2.0	>6			
Aluminum	mg/L	6,400			0.243	
Arsenic	mg/L	0.37		0.01	0.15	0.2
Boron	mg/L	<0.025		0.6	187	
Cadmium	mg/L	4.6		0.005	0.00147	0.05
Chromium	mg/L	2.6		0.1	0.23	1
Cobalt	mg/L	10		0.875	0.042	
Copper	mg/L	610		1.3	0.0291	0.05
Fluoride	mg/L	840		4	140	
Iron	mg/L	110			1	
Manganese	mg/L	240		1.6	3.39	
Molybdenum	mg/L	0.0042		0.04		
Nickel	mg/L	20		0.1	0.168	
Selenium	mg/L	0.29		0.05	0.002	0.05
Sulfate	mg/L	56,000				
Total Dissolved Solids	mg/L	84,000				
Total Suspended Solids	mg/L	170	500			
Uranium	mg/L	2.8		0.02	2.8	
Zinc	mg/L	75		2	0.38	25

HDS System Configuration

There were several concerns with the raw water characteristics that made the configuration of the pilot critical. These included:

1. The very high sulfate concentration >56 grams/Liter (g/L). Given the pH below 3, a large amount of lime is required, and this potentially represented the production of as much as 76.5 g/L of calcium sulfate. The HDS process has some limitations in this area, and with the other precipitates present, the potential to reach 100 g/L solids formed exists, which is high for effective treatment. The limiting factor here is solids recycle, the homogeneity of the reaction tank contents and the solids flux limitation on thickening. To counter this, effluent recycle was provided as well as solids recycle, so that the solids level was diluted.
2. Aluminum was the highest concentration metal present at over 6,400 mg/L. Precipitated as aluminum hydroxide, this would yield a solids-formed concentration of about 14.5 g/L TSS. Aluminum hydroxide is more difficult than other metals to form HDS solids. Improvement in solids characteristics is achievable, but the solids produced are smaller, and less dense than other metals. Aluminum hydroxide is amphoteric, starting to increase in solubility above pH 6.5. To remove the optimal amount of aluminum, solids liquid separation should occur near that pH.
3. A number of metalloids are effectively removed by coprecipitation at a pH below 7. These include arsenate, molybdenum, and selenite.
4. Magnesium is present at over 4,000 mg/L. The conventional wisdom is that magnesium hydroxide doesn't precipitate until a pH of over 10, and that's true when the concentration of

magnesium is small. The solubility curve for magnesium hydroxide is steep, but at a pH of 9, a review of published solubility curves for magnesium hydroxide indicates a solubility as magnesium in the vicinity 3,400 mg/L at a pH of 9.4, and slightly over 4,000 mg/L at a pH of about 9. On a theoretical basis, some amount of magnesium hydroxide would precipitate in a second stage operated at about 9.

- Most of the lime demand and most of the solids formed are generated at a pH below 6. This includes most of the calcium sulfate (from neutralization of the bulk of the free acidity plus that associated with aluminum, iron and copper sulfates). The metals precipitating at higher pH levels (zinc, nickel, cadmium) are low in concentration compared to aluminum, iron and copper.

Observations from previous studies (single stage HDS) indicated that a two-stage process was needed to effectively remove aluminum and other metals. The pilot HDS system was a two-stage system, consisting of reaction tanks and a clarifier operated at a pH of about 6, and reaction tanks and a clarifier operated at a pH of 9. The configuration of the pilot system is shown below as Figure 1.

Recycle solids are initially mixed with lime slurry in an alkalization tank. The alkalization tank discharges to the neutralization tank, where it mixes with the influent water and recycle effluent for dilution. The neutralization tank overflows to an aging tank, which allows completion of calcium sulfate precipitation. The aging tank overflows to a vessel we've termed a sand trap. Our preference would have been a hydrocyclone, but the flows were too low. Heavier solids settle out in the sand trap and are pumped from the bottom. The intent is to remove some of the larger solids so that the recycle solids would be finer, and more opportunity for growth. The sand trap overflows to a flocc tank, and then on to the clarifier. The first stage normally operated at a pH of about 6. The clarifier effluent was then pumped to the second stage, which essentially duplicated the first stage without a sand trap.

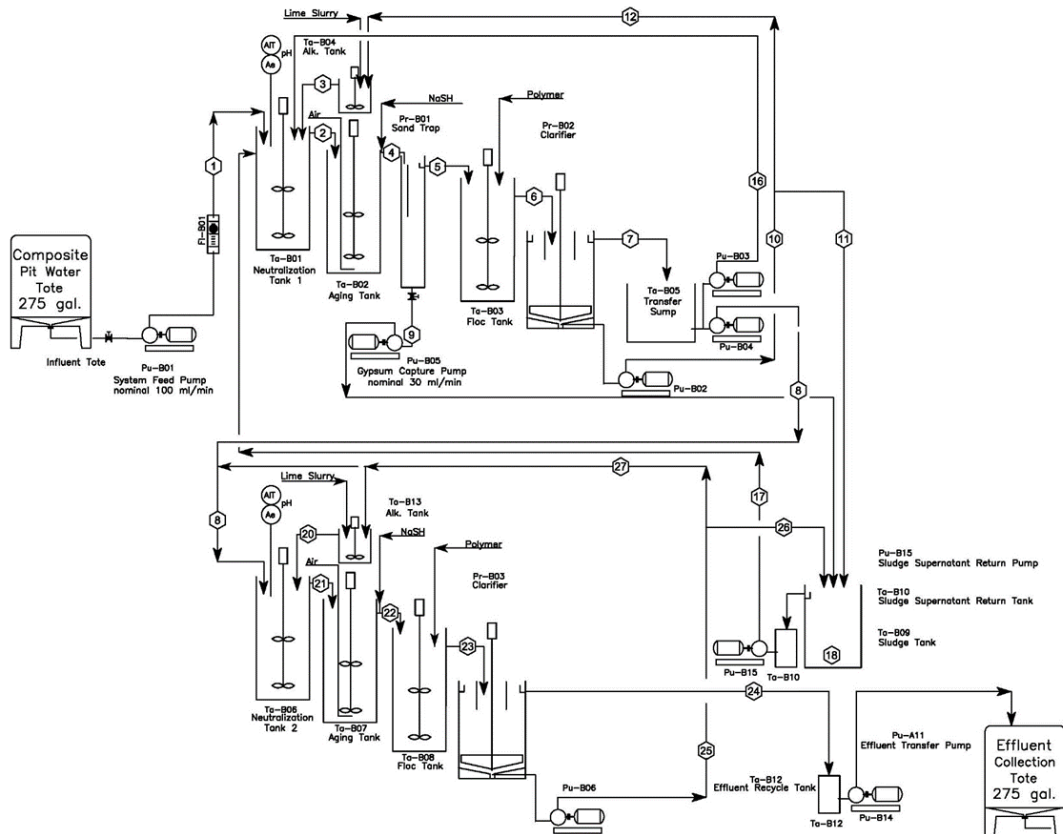


Figure 1: Flow Diagram

CHRONOLOGY

Rather than a detailed operating chronology, which would take more space than available in the rest of the paper, the table below shows the test runs that were conducted and their key parameters. Operationally, there were several issues that affected the outcome of the study. In no particular order, these were:

1. The solids-formed was measured on most runs, and was found to vary with minor modification of test conditions, including time between additions, mixing intensity and amount of reagent added at a time. The method was standardized using an intensely stirred 2 Liter beaker with a reaction tank mixer to produce very aggressive mixing, and adding lime in relatively small increments, allowing typically 5 minutes between additions. All solids formed values measured were higher than expected. It's possible that unreacted lime could have contributed to the solids formed measurement, but the mixing in the beaker was very aggressive.

Table 3: Study Operating Conditions

Run	Days	Configuration	Recycle Ratio		Clarifier Effl pH		Lime stone	Aeration	NaSH
			#1	#2	#1	#2			
1	6	Startup-maximize recycle	1.2	69	6.67	9.28	no	Both	No
2	5	Maximize recycle rate	5.75	91.3	6.85	9.33	no	Both	No
3	5	Limestone to first stage Alkalization Tank	3.98	215	6.59	9.46	yes	Both	Stage 1
4	5	Impact of aeration	3.38	271	6.23	9.22	no	no	Stage 2
5	5	Maximize sludge from Sand Trap	4.05	298	6.65	9.14	no	Stage 2	Stage 2
6	5	Lower pH setpoint	4.39	208	6.0	8.63	no	Stage 2	Stage 2
7	5	Concentrated influent	4.75	175	6.35	8.91	no	Stage 2	Only last day
8	5	Single Stage	2.7	XX	9.1	XX	no	Yes	No

2. Because of the higher than expected solids-formed, it was not possible to get the recycle ratio high enough in stage 1 to produce very dense particles.
3. Sludge recycle and high suspended solids in the stage 1 reaction tanks also presented problems related to plugging during startup. Plugging dropped off with routine operation, which may reflect on the particle size distribution or operational adjustments.
4. Stage 2 exhibited much lower than expected lime demand, and much lower than expected solids formed. It was very rare to waste solids from this system. Lime demand in some runs was managed manually with a dropper as pumping on a timer caused overshooting of the pH setpoint.

Summary of Solids Characteristics By Runs

A total of 8 runs were conducted, each with over 40 hours of operating time. As would be expected, the first run exhibited continually improving Stage 1 and Stage 2 Clarifier Underflow (CU) concentrations. A critical parameter in this study is that of Ultimate Density (UD). The UD test is done by gravity settling a sample of sludge for a period of 24 hours, and determination of the solids concentration of the thickened sludge. Stage 1 exhibited continued improvement in UD and CU in Run 2, but saw a decrease in both parameters in Run 3, in which limestone was added to the influent. As a point of comparison, UD at the end of Run 2 was about 220 g/L, but dropped to under 150 g/L at the end of Run 3. CU at the end of Run 2 was 150 g/L, and also dropped in Run 3 to a final value of about 75 g/L. CU and UD improved in Run 4, with the UD once again reaching 200 g/L. CU and UD continued to improve in Run 5, with a peak UD of 250 g/L at the end of Run 5. Note that in Run 5, all sludge was wasted from the sand trap, whereas in other runs the sand trap flow was set and excess solids were also wasted intermittently from

the clarifier underflow. Run 6 involved reducing the pH setpoints for both Stages. The impact on Stage 1 was a rapid decrease in both CU and UD, with some improvement during the week. At the end of Run 6, CU improved to 100 g/L, well below the 175 g/L value at the end of Run 5. UD at the end of Run 6 was 180 g/L. Run 7 reflected improvement to near Run 5 levels for both CU and UD. Run 8 was the single stage run. At the higher pH in the initial stage, there was greater lime demand and higher solids formed. As a result the recycle rate was lower, which may account for the lower CU (about 130 g/L at the end of the run) and UD (about 160 g/L). As shown in Table 3, recycle ratios were between 3/1 and 6/1. This range is not ideal, but the limitation on maintaining a reasonable solids concentration in the reaction tanks while trying to achieve a recycle ratio of 15/1 or 20/1 would have resulted in a huge upsizing of treatment equipment due to the need for substantial effluent recycle, and performance at this level was thought to be adequate in terms of indicating reagent utilization efficiency and overall removal of the various components.

The second stage of the process, which increased the pH from 6 to 9, experienced a lower-than-expected solids production. Lime demand was so low that even using a timer to control lime addition for a few seconds every few minutes could not provide a consistent pH level in the reaction tanks. At times, lime slurry was manually added using a dropper. The solids-formed level was much lower than expected in Stage 2. In terms of Clarifier Underflow and Ultimate Density, there was a consistent upward trend from startup through the end of Run 5, which peaked at about 200 g/L CU and 380 g/L UD. Run 6 (lower pH setpoints) exhibited a drop in CU to about 100 g/L, with an associated UD of under 200 g/L. These parameters trended up in Run 7, but due to the low solids formed, the rate of change was limited. There was no second stage in Run 8. Because of the lower-than-expected solids formed, and the need to maintain velocity in sludge tubing, the recycle ratio in Stage 2 was consistently above 100/1.

Removal of Major Contaminants

Aluminum, sulfate and magnesium were the three parameters with the greatest concentrations in the influent wastewater.

Aluminum: Aluminum removal was typically to under 2 mg/L as dissolved aluminum in the effluent from Stage 1, and slightly better in Stage 2. Given the initial concentration of over 6,400 mg/L this represents greater than 99.97% removal. Although the theoretical solubility of aluminum in Stage 1 is lower than this, given the matrix of soluble components, this still represents a high level of removal. The Single Stage effluent in run 8 was an order of magnitude higher at an average of 16 mg/L for days 4 and 5 of the run. This is in agreement with past studies using a single stage HDS pilot, which saw effluent concentrations of 10.6 mg/L aluminum at pH 9.0 and 15.0 mg/L at pH 9.6, both with an influent concentration of under 5,000 mg/L aluminum.

Sulfate: Effluent sulfate concentrations in the Stage 2 effluent were ranged between 12,000 and 14,000 mg/L for the two-stage process. The run using a single stage configuration showed an effluent sulfate concentration of about 2500 mg/L. This run also exhibited a higher lime demand, and the reduced sulfate concentration likely results from the additional calcium added.

Magnesium: Magnesium removal, expected to be negligible, was observed to drop from an influent of over 4,000 mg/L to a Stage 1 effluent ranging from 2,700 to 3,600 mg/L. A slight decrease was observed across Stage 2.

Removal Mechanisms for Trace Contaminants

When discussing individual components of the wastewater, several factors must be kept in mind:

1. The amount of calcium sulfate formed is massive. The solids formed measurements indicated a solids production rate of 80 to 100 g/L. The aluminum hydroxide contribution to this total was typically about 14.5 g/L, which is the only other major component of the solids besides calcium sulfate. The sheer mass of precipitation occurring would be expected to trap some of the metals present in the precipitation solids matrix.
2. Coprecipitation with iron and aluminum is commonly seen to remove small amounts of other metals that would not be expected to precipitate at the pH levels used here.
3. The weak adsorption of alkali on the surface of recycle particles, which is the core mechanism for development of dense solids in HDS, causes precipitation of metal oxides and hydroxides at the surface of the particle instead of in solution. At the particle surface the pH close to the particle is thus higher than the pH in the bulk solution. Typically, metal precipitation in a well-designed HDS process exhibits removal characteristic of a higher pH than indicated by pH measurement.

This study did not make an attempt to investigate which of the aforementioned mechanisms was responsible for removal of a specific wastewater component. It is expected that the net effect of all three results in the observed removals as identified below. It should also be noted that the effluent from the Stage 1 Clarifier normally had a relatively high TSS, over 50 mg/L. While total and soluble concentrations were measured for the various parameters listed below, the use of soluble concentrations is more useful in evaluating performance, as the carryover solids would be expected to have trace contaminants present that contribute to the total but not soluble values.

Removal of Trace Contaminants

Antimony:

Influent values were all near 0.004 mg/L. Effluent values from Stage 1 all were near or below detection limit (nominally 0.000043 or 0.000086 mg/L).

Arsenic: Shown below as Table 4 is the data summary for arsenic for the various runs.

Table 4: Arsenic Removal

Date	Run	Day	Raw	Stage 1 Effluent		Stage 2 Effluent		Units
			TJ Pit	Total	Dissolved	Total	Dissolved	
2/22/2021	1	6	0.37	0.0072	0.009	0.0083	0.0076	mg/L
3/1/2021	2	5		0.008	0.006	0.009	0.0079	mg/L
3/8/2021	3	5		0.0063	0.0073	0.0064	0.0052	mg/L
3/15/2021	4	5	0.45	<0.0049	<0.0025	<0.0025	0.0052	mg/L
3/22/2021	5	5		0.0048	0.0046	0.0049	0.0049	mg/L
3/26/2021	6	4		0.0041	0.0028	0.0035	0.003	mg/L
3/27/2021	6	5		<0.0049	<0.0049	<0.0049	<0.0049	mg/L
4/1/2021	7	4	0.4	<0.0049	<0.0049	<0.0049	<0.0049	mg/L
4/2/2021	7	5		<0.0049	<0.0049	<0.0049	<0.0049	mg/L
5/26/2021	8	3	0.39	NA	NA	0.07	0.0073	mg/L
5/27/2021	8	4		NA	NA	0.093	0.0079	mg/L
5/28/2021	8	5		NA	NA	0.0084	0.008	mg/L

Table 4 indicates influent arsenic concentrations were in the range of 0.37 to 0.45 mg/L. Arsenic in the arsenate form can be co-precipitated with iron below pH 7. The best removals observed in Stage 1 were in runs 4, 6 and 7. None of these runs had aeration in Stage 1, but the only aeration in Stage 1 was in Run 3. These three runs achieved the lowest Stage 1 pH, as they operated between pH 6.0 and 6.35. The other runs all operated between pH 6.5 and 7.0. This would fit with iron (or possibly aluminum) hydroxide coprecipitation. The worst performance was observed in the single stage run (Run 8). The soluble arsenic in Run 8 was about 0.008 mg/L, which isn't that far from the best performance of <0.0025 mg/L soluble arsenic in Run 4. The difference in performance is likely not significant.

Beryllium: Shown in Table 5 are the data for beryllium in the study. As shown, the influent beryllium ranged between 2.1 and 2.5 mg/L. Effluent dissolved concentrations were below detection limits for both stages in all runs. Total beryllium was measurable in the first stage effluent as part of the solids carried over from the clarifier.

Table 5: Beryllium Removal

Date	Run	Day	Raw	Stage 1 Effluent		Stage 2 Effluent		Units
			TJ Pit	Total	Dissolved	Total	Dissolved	
2/22/2021	1	6	2.1000	0.0029	<0.000067	<0.000067	<0.000067	mg/L
3/1/2021	2	5		0.0027	<0.000067	<0.000067	<0.000067	mg/L
3/8/2021	3	5		0.0031	<0.000067	<0.000067	<0.000067	mg/L
3/15/2021	4	5	2.3000	0.000067	<0.000067	<0.000067	<0.000067	mg/L
3/22/2021	5	5		0.0011	<0.000067	<0.000067	<0.000067	mg/L
3/26/2021	6	4		0.0077	<0.000067	<0.000067	<0.000067	mg/L
3/27/2021	6	5		0.0036	<0.000067	<0.000067	<0.000067	mg/L
4/1/2021	7	4	2.2	0.0033	<0.000067	<0.000067	<0.000067	mg/L
4/2/2021	7	5		0.0041	<0.000067	<0.000067	<0.000067	mg/L
5/26/2021	8	3	2.50000	NA	NA	<0.000067	<0.000067	mg/L
5/27/2021	8	4		NA	NA	<0.000067	<0.000067	mg/L
5/28/2021	8	5		NA	NA	0.0016	<0.000067	mg/L

Beryllium is commonly precipitated at pH 6.5 as an hydroxide, but like aluminum the solubility increases with increasing pH above that point.

Cadmium: Shown below as Table 6 are the analytical results for cadmium. Cadmium is present in this water in concentrations of 4.6 to 5.4 mg/L. Cadmium is theoretically soluble at neutral pH levels to about 8 mg/L as an hydroxide, and as cadmium sulfide is soluble to less than 0.0001 mg/L. For Stage 1 removals, the best performance was found in Run 7, with a soluble cadmium of 0.05 mg/L. Runs 1,2,4 and 5 had Stage 1 soluble effluent concentrations of 0.14 to 0.20. Runs 3,6, and 7 had higher effluent cadmium values. Sulfide was added to the first stage in Run 3 only, and cadmium removal was not exceptional. No other variables were identified linking either the low values or high values related to first stage performance.

Stage 2 on the other hand, provides more insight. Note that in Run 7, there are values shown for day 4 and day 5. Days 1 through 4 of Run 7 had no sulfide addition to the second stage. Day 5 did have sulfide addition to the second stage. As shown, the cadmium concentration decreased by an order of magnitude due to sulfide addition as the only variable change. Other comparably low values were seen in Runs 4,5,6

and 8. Runs 4,5 and 6 all included sulfide addition to Stage 2. Runs 1, 2, most of 7 and Run 8 had no sulfide addition. Sulfide precipitation of cadmium would be viewed as less than optimal compared to lab data, and likely indicates the sulfide dosage was low. The worst Stage 1 removal was about 90%, and the worst Stage 2 effluent provided 98% removal. However, the lowest values produced were from the final run, single stage operation, with no sulfide addition. The only possible explanation is that the additional solids formed helped remove cadmium.

Table 6: Cadmium Removal

Date	Run	Day	Raw	Stage 1 Effluent		Stage 2 Effluent		Units
			TJ Pit	Total	Dissolved	Total	Dissolved	
2/22/2021	1	6	4.6	0.2	0.2	0.026	0.025	mg/L
3/1/2021	2	5		0.2	0.2	0.021	0.02	mg/L
3/8/2021	3	5		0.46	0.46	0.023	0.024	mg/L
3/15/2021	4	5	5.4	0.14	0.14	0.0068	0.0057	mg/L
3/22/2021	5	5		0.27	0.2	0.032	0.0058	mg/L
3/26/2021	6	4		1.2	1.3	0.039	0.0076	mg/L
3/27/2021	6	5		1.1	1.0	0.026	0.0057	mg/L
4/1/2021	7	4	4.9	0.52	0.54	0.094	0.08	mg/L
4/2/2021	7	5		0.5	0.5	0.025	0.0083	mg/L
5/26/2021	8	3	5.4	NA	NA	0.01	0.0099	mg/L
5/27/2021	8	4		NA	NA	0.0026	0.00066	mg/L
5/28/2021	8	5		NA	NA	0.0038	0.00066	mg/L

Chromium: Chromium in the influent varied between 2.8 and 3.0 mg/L. Based on hydroxide precipitation curves, chromium should not precipitate in the first stage, but in all runs the Stage 1 effluent was below 0.1 mg/L. This must be from coprecipitation. Chromium was observed to be near or below the analytical laboratory reported detection limit (typically 0.00085 mg/L, lower for Run 8) for all runs except Run 8 (single stage operation).

Cobalt: Influent Cobalt varied between 10 and 12 mg/L. Stage 1 effluent Cobalt was lowest in Runs 1,2 and 4, and highest in Runs 3 and 6. All values from the second stage were less than <0.00066 mg/L, except Runs 6 and 7. Run 6 was the run at lower pH setpoints. In run 7, day 4, without sulfide addition, was less than detectable, but day 5, with sulfide addition, had a soluble cobalt concentration of 0.013. All values from single stage operation were <0.00066 mg/L. Runs 1,2, part of 7 and 8 had no sulfide addition to the second stage. Runs 3 and 6 both had sulfide addition.

Manganese: The influent manganese concentration ranged between 240 and 280 mg/L, except for the feed to run 8, which was 350 mg/L. Manganese is typically removed either by precipitation as an hydroxide at pH 10+, or by reaction with an oxidant at pH 8. Most of the manganese is removed in Stage 1, with an average soluble manganese in the Stage 1 effluent of 42 mg/L. In stage 2, the average across all runs was 16.6 mg/L soluble manganese. There were 5 values for dissolved manganese that were above 10 mg/L, and 10 that were single digits. The best stage 2 performance came from Run 8, where the final two days effluent soluble manganese were 0.053 and 0.026 mg/L. The worst performance was in Run 6 (lower pH setpoints) where the average effluent was 46 mg/L. It should be noted that aeration in Stage 1 was provided in Run 3 only, which did not offset the impact of limestone addition and the resulting loss in solids density and recycle ratio. Run 4 had no aeration in Stage 2, and the effluent manganese concentration was not appreciably higher. This indicates that removal via coprecipitation may have been more significant than oxidation and precipitation mechanisms.

Table 7: Manganese Data

Date	Run	Day	Raw	Stage 1 Effluent		Stage 2 Effluent		Units
			Total	Total	Dissolved	Total	Dissolved	
2/19/2021	1	5	240		0.58		31	mg/L
2/22/2021	1	6		37	38	7.7	7.8	mg/L
2/26/2021	2	4			21		5.5	mg/L
3/1/2021	2	5		36	36	1.9	1.7	mg/L
3/4/2021	3	3			66		0.28	mg/L
3/5/2021	3	4			72		2.4	mg/L
3/8/2021	3	5		73	74	4.7	4.5	mg/L
3/12/2021	4	4			3.3		50	mg/L
3/15/2021	4	5	280	33	34	6.8	6.8	mg/L
3/19/2021	5	4			47		1.2	mg/L
3/22/2021	5	5		32	33	9.5	6.4	mg/L
3/26/2021	6	4		68	72	38	36	mg/L
3/27/2021	6	5		59	57	43	61	mg/L
4/1/2021	7	4	250	50	49	9.9	9.1	mg/L
4/2/2021	7	5		49	49	20	18	mg/L
5/26/2021	8	3	350	NA	NA	2.6	1.9	mg/L
5/27/2021	8	4		NA	NA	0.099	0.053	mg/L
5/28/2021	8	5		NA	NA	0.17	0.026	mg/L

Nickel: Shown below in Table 8 is the accumulated data for Nickel. Influent nickel concentrations ranged between 20 and 24 mg/L. Effluent dissolved nickel concentrations for Stage 1 were lowest in Runs 4 and 5 (0.23 and 0.33 mg/L respectively) and highest in Runs 3 and 6 (1.6 and 1.9/1.3 mg/L respectively). Effluent soluble nickel from Stage 2 was lowest in Runs 2, 4, 5 and 8. Runs 2,4,5 and 8 had Stage 2 pH levels greater than 9.1, whereas Run 6 Stage 2 pH was 8.63, and Run 3 was the run using limestone. The

Table 8: Nickel Data

Date	Run	Day	Raw	Stage 1 Effluent		Stage 2 Effluent		Units
			TJ Pit	Total	Dissolved	Total	Dissolved	
2/22/2021	1	6	20	0.46	0.46	0.0052	0.011	mg/L
3/1/2021	2	5		0.56	0.54	0.01	0.0052	mg/L
3/8/2021	3	5		1.5	1.6	0.01	0.015	mg/L
3/15/2021	4	5	24	0.24	0.23	0.0052	0.0052	mg/L
3/22/2021	5	5		0.48	0.33	0.07	0.0052	mg/L
3/26/2021	6	4		1.9	1.9	0.074	0.037	mg/L
3/27/2021	6	5		1.4	1.3	0.056	0.032	mg/L
4/1/2021	7	4	22	0.71	0.71	0.022	0.011	mg/L
4/2/2021	7	5		0.62	0.62	0.053	0.02	mg/L
5/26/2021	8	3	23	NA	NA	0.0052	0.015	mg/L
5/27/2021	8	4		NA	NA	0.0052	0.0052	mg/L
5/28/2021	8	5		NA	NA	0.012	0.0052	mg/L

results seem to indicate that sulfide had some benefit, as it was used in Stage 2 on Runs 4,5 and 6. Note that run 6 had the lower pH setpoints. Run 8 also produced very low Stage 2 effluent soluble nickel concentrations. The theoretical solubility of nickel sulfide at pH 9 is less than 0.0001 mg/L. As before, this seems to indicate that the sulfide added was either not used efficiently or insufficient in dosage for the metals which can be precipitated as sulfides.

Selenium: Selenium in the influent ranged between 0.29 and 0.4 mg/L. First stage removal typically achieved soluble and total selenium concentrations in the range of 0.13 to 0.11 mg/L. Run 7 was the outlier, with a final day dissolved selenium concentration of 0.061 mg/L. Run 8 averaged 0.042 mg/L over the last two days. In Run 7 there was not a substantial difference between the days without sulfide addition and the single day there was sulfide addition. Run 7 did benefit from a higher recycle ratio than any of the two stage runs except Run 2. There is an indication from the literature that a small amount of selenium can be removed in the precipitation of calcium sulfate.

Uranium: The Uranium concentration in the influent ranged between 2.3 and 3 mg/L, as shown in Table 9 below. Most removal occurred in the first stage, with the dissolved uranium concentration ranging between 0.015 and 0.037 mg/L. Greatest removal in Stage 1 occurred in Runs 6 and 7, which averaged under 0.016 mg/L. Poorest removal occurred in Runs 4 and 5. Runs 6 and 7 had slightly lower pH levels and slightly higher recycle ratios. Uranium, like aluminum, has a low solubility as an hydroxide at pH 5.5 to 6, and as pH increases from that point, solubility does as well. It should be noted that uranium behaves consistently from a chemical standpoint regardless of which isotope it is. The data reflects limited removal in the second stage, as one would expect. The single stage system (Run 8) achieved the lowest uranium concentration, with the final two days of Run 8 averaging 0.0025 mg/L. This is unusual, given that the solubility of uranium hydroxide at pH 9 is much greater than at pH 6. This likely results from the additional solids produced in the single stage process, and the greater impact of adsorption/coprecipitation on uranium removal.

Table 9: Uranium Data

Date	Run	Day	Raw	Stage 1 Effluent		Stage 2 Effluent		Units
			TJ Pit	Total	Dissolved	Total	Dissolved	
2/22/2021	1	6	2.800	0.028	0.024	0.012	0.012	mg/L
3/1/2021	2	5		0.04	0.037	0.015	0.016	mg/L
3/8/2021	3	5		0.028	0.026	0.02	0.018	mg/L
3/15/2021	4	5	2.300	0.038	0.0350	0.023	0.024	mg/L
3/22/2021	5	5		0.029	0.029	0.025	0.02	mg/L
3/26/2021	6	4		0.026	0.017	0.022	0.021	mg/L
3/27/2021	6	5		0.020	0.0150	0.021	0.02	mg/L
4/1/2021	7	4	3.000	0.024	0.015	0.019	0.018	mg/L
4/2/2021	7	5		0.02	0.016	0.019	0.018	mg/L
5/26/2021	8	3	2.600	NA	NA	0.0099	0.0096	mg/L
5/27/2021	8	4		NA	NA	0.0041	0.0036	mg/L
5/28/2021	8	5		NA	NA	0.0035	0.0014	mg/L

Zinc: The influent zinc concentration during the study were between 75 and 91 mg/L. The theoretical solubility of zinc hydroxide at pH 7.5 is over 100 mg/L. And yet, in the first stage of the two-stage process, the zinc is almost completely removed. Nearly all effluent zinc values were less than or equal to 0.0019 mg/L, including Run 8. Similar results were seen for nickel and cadmium. The sizing of the lime feed for the second stage reaction was based on a lime demand for these metals. It is apparent that they were

coprecipitated to a great extent in the first stage, which limited the solids formed and lime demand in the second stage.

Observations and Conclusions

Based on the previous descriptions and data, the following conclusions are drawn:

1. The removal of aluminum in stage 1 was less than hoped for, but still greater than 99.95% for two-stage operation. The clarifier effluent from the first stage was cloudy, and solids carryover resulted in higher aluminum concentrations entering stage 2, which would then be solubilized at the higher pH levels and exit the second stage clarifier. Effluent aluminum concentrations were an order of magnitude higher in the single-stage process.
2. Lime demand and solids production was much higher in the single-stage process, but some metals concentrations were lower. The reduction in lime consumption is significant, and an important economic driver for the increased cost of a two stage HDS process.
3. Magnesium removal was greater than expected in the first stage of the two-stage process and negligible in the second stage.
4. Metals that precipitate at high pH tend to coprecipitate in the first stage to a greater extent than anticipated. It might be desirable to operate the pH of the first stage lower or the second stage slightly higher to force more lime demand in the second stage.
5. Of the metals and metalloids evaluated, cadmium, manganese, selenium and uranium were more effectively removed in a single stage HDS process, whereas arsenic and chromium were more effectively removed in the two-stage process. There was no appreciable difference between one stage and two stage processes for antimony, beryllium, nickel and zinc. Aluminum was more effectively removed in the two-stage process, whereas magnesium achieved much lower effluent concentrations in the single stage process.

Overall, the benefits of the two stage HDS process in this instance involve savings in lime consumption over conventional neutralization approaches, and greater removal of some metals.