

ZEOLITE PROCESS TECHNOLOGY
URANIUM ADSORPTION AT HOMESTAKE MINING COMPANY –
GRANTS RECLAMATION PROJECT

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February, 2010

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1.0 BACKGROUND

Natural zeolites are alumino-silicate volcanic minerals with high cation exchange capacities (CEC). As such, they have the ability to adsorb cations from waste streams. The most common natural zeolite used for cation adsorption is clinoptilolite. Clinoptilolite generally has a CEC in the range of 0.8 to 1.25 milli-equivalents per gram (meq/g). Zeolites are used for adsorption of many cations and gasses, including potassium, ammonia, sodium, cadmium, cesium, strontium, radium, copper, mercury, carbon dioxide, and numerous other metals and gasses (St. Cloud Mining Company, 2010).

Numerous zeolite-based adsorption technologies have been developed in Europe, particularly in Belgium, Poland, and Japan. As an example, Polish scientists have used clinoptilolite to adsorb mercury from copper mine waste streams (Chojnacka, A., et al., 2004). As another example, RIMCON, LLC has developed a proprietary technology to treat developed water from Coal-Bed Methane fields in Wyoming. This technology was developed to reduce high sodium concentrations and resultant high sodium adsorption ratios and to reduce high electrical conductivity levels resulting from high bicarbonate waters (RIMCON, LLC, 2008). RIMCON has been working with natural zeolites since 1997 to develop cation adsorption technologies.

The Homestake Mining Company of California (HMC) is interested in determining if natural zeolites could remove uranium from alluvial and Upper Chinle aquifers located at the former HMC uranium mill site near Grants, New Mexico. Alluvial and Upper Chinle aquifer uranium concentrations range from about 0.40 to 1.50 mg/L depending on the sampled well and the sampling time. Their goal is to lower uranium levels down to, or below, the aquifer background concentration of 0.16 mg/L. At the request of HMC, RIMCON began bench testing HMC aquifer water using zeolites to adsorb uranium in early 2007. The bench testing data was used to set up a field pilot test of the proprietary process at the Grants site to further test the viability of using natural zeolites for uranium removal. This report summarizes the results to date, operational processes and problems, and plans to move ahead with the research and testing.

2.0 PROCESS TECHNOLOGY

A proprietary process was developed for using natural zeolites for uranium adsorption. The natural zeolite used for the bench and field testing was the mineral clinoptilolite. Clinoptilolite is an alumino-silicate mineral that exhibits a negative electrical charge on its crystalline structure. As such, high grade zeolite has a very high cation exchange capacity (CEC) in the range of 1.00 to 2.25 milli-equivalents per gram (meq/g).

Depending on mineral purity and CEC, the theoretical cation loading rate of the zeolite will range from 40 to 80 pounds of adsorbed cations per ton of zeolite.

Uranium generally behaves in water as an anion and, therefore, will not adsorb onto a cation exchange medium. The uranium is most likely to be in the form of uranium carbonate (UO_2CO_3) or calcium-uranium carbonate [$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$]. In the case of the alluvial or Upper Chinle aquifer water, the carbonate is likely to be in the bicarbonate form. Bicarbonate levels in the well water range from 180 to 240 mg/l.

Other uranium adsorption processes have focused on the use of synthetic anionic resins which are very expensive and costly to operate. In addition, the anionic resins also adsorb other anions, such as sulfate, that tend to load up the exchange sites quickly and compete preferentially for exchange sites. In the case of the Grants site aquifer water, sulfate levels tend to range from 600 to 900 mg/l.

The theory of the RIMCON process is to create the further dissolution of uranium carbonate (bicarbonate) molecular bonds with weak acid releasing the positively charged uranyl (UO_2^{+2} - uranium dioxide) ion. The uranyl ion would then be free to adsorb onto the cationic zeolite. Initially, weak hydrochloric acid (HCl) was selected for breaking up the uranium carbonate and freeing the uranyl ion. While uranium carbonate is soluble in HCl, the uranyl ion is not soluble in the acid and will retain its positive charge.

The operational key to the process is determining how much acid is needed to effectively release the uranyl ion from the bicarbonates. In addition, the type of acid used is also an important operational consideration. If the process requires too much acid, two significant problems occur. First, the zeolite will release cations from the exchange sites in the presence of high levels of acid. Instead of continuing to adsorb cations, including the uranyl ion, sodium, calcium, and others, the acid would remove the cations from the zeolite and release them back into the discharge waters. Secondly, the need for high concentrations of the acid would be cost prohibitive and would adversely affect the economics of the process.

3.0 PRELIMINARY BENCH TESTING

Columns were set up in the laboratory to test various quantities of HCl for breaking up of the uranium carbonate, releasing uranium for adsorption. Standard technical grade HCl with a concentration of 32% was diluted to various pH levels to see the direct effect of pH, and indirectly, the effect of dissolved bicarbonate on the adsorption of zeolite. Results are shown in Table 1.0 below.

Table 1.0 – pH Versus Uranium Adsorption

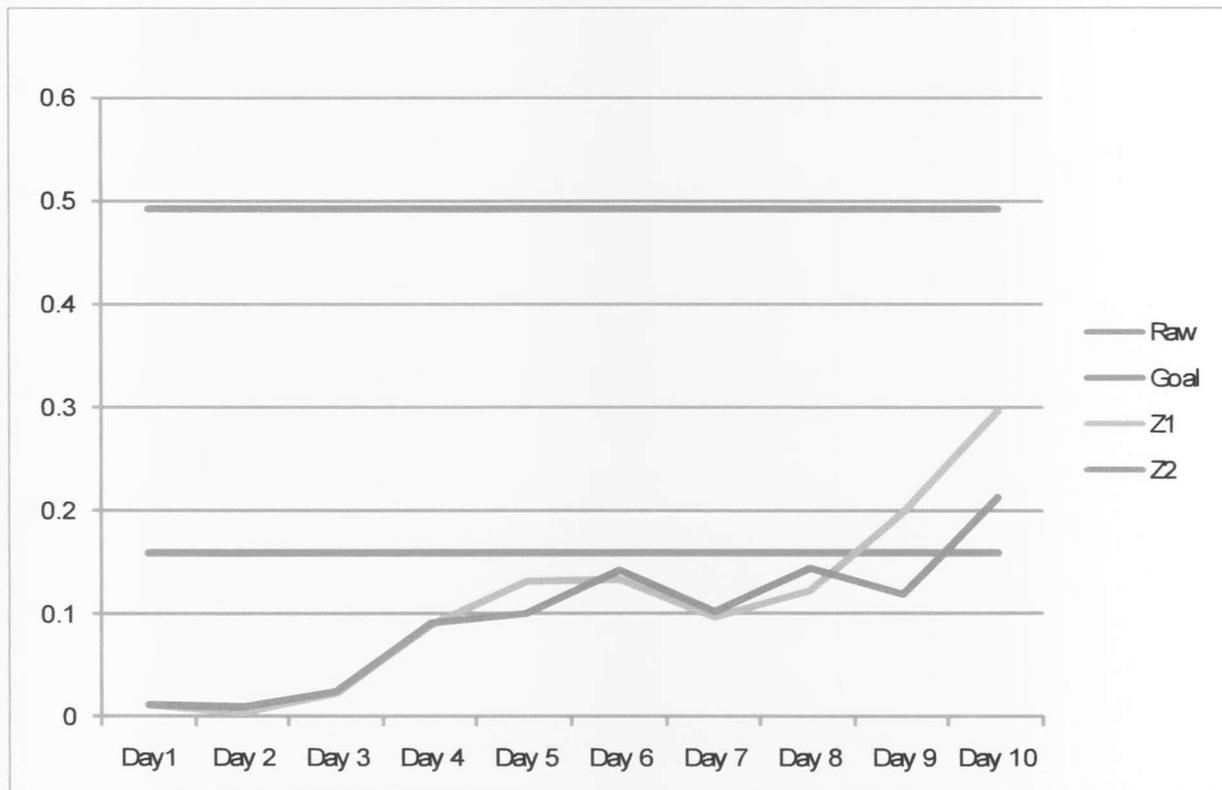
Sample ID	pH	HCO ₃ ⁻ – mg/L	Total U – mg/L
CE5 (raw water)	7.83	465	0.493
Z1	7.00	404	0.474
Z2	6.50	379	0.389
Z3	6.25	178	0.255
Z4	6.00	26	0.055
Z5	5.75	0	0.014
Z6	5.50	0	0.008

The raw water is denoted as CE5 representing the Upper Chinle aquifer. The concentration of uranium in that water was 0.493 mg/L and the bicarbonate level was 465 mg/L. When the pH was 6.5 or above, little, if any, uranium adsorption had occurred and the amount of bicarbonate was similar to aquifer concentrations. As expected, as the pH decreased, the amount of adsorbed uranium increased. Approximately one half of the uranium was adsorbed at a pH of 6.0 and the concentration of bicarbonate was significantly reduced. At a pH of 5.50, the uranium concentration in the effluent was near non-detect levels and all bicarbonate was dissolved. Based on this data, it appears that the optimum pH for the process is between 5.5 and 6.0.

Two new columns were set up for testing the zeolites ability to adsorb uranium over time. The columns were 2 inches in diameter by 8 inches long. They were packed with 14 x 30 mesh zeolite from the St. Cloud Mining Company in New Mexico. Raw water from the CE5 well was utilized as the column feed water. The pH of the feed water was adjusted with HCl to a pH level of 5.75. Approximately 4 ml of 32% HCl per gallon of raw water was needed for this adjustment. The zeolite was then soaked with a 5% solution of HCl to remove the cations naturally occurring on the zeolite. The columns were then rinsed twice to remove the majority of the acid rinse. This process frees up most of the cation exchange sites on the zeolite for adsorption.

Both columns were then run for 10 days to test the adsorption of the uranium. Columns were configured in an up flow direction to achieve more uniform contact with the zeolite; influent retention time in the columns was one hour. Results of this testing are shown in Figure 1.0 below.

Figure 1.0 - Column Uranium Adsorption Over Time



As can be seen from the chart, the adsorption of uranium stayed below the upper goal of 0.16 mg/l through Day 8 for column Z1 and through Day 9 for Column Z2. At Day 10, effluent uranium concentrations in both columns exceeded the goal concentration. The column loading data resembles typical loading curves for cations on zeolite, although longer loading times are desirable. As the zeolite becomes loaded with cations, the adsorption starts to decline rapidly. Keep in mind that the zeolite was also adsorbing other cations in the water, particularly sodium and calcium. It is expected, that by Day 11 or 12, the column would have been fully loaded with cations and further adsorption would not occur. Based on these results, and other testing in the laboratory, it was decided to proceed with a field test of the process.

4.0 INITIAL FIELD PILOT TESTING

Based on the results of the bench testing, a five gallon per minute pilot test was designed for field evaluation of the process. The system was designed to have two 4 ton zeolite tanks operated in sequence. The raw water used in the test was from the

CE5 Upper Chinle well. The first zeolite tank (Z1) was elevated above the second tank (Z2) to create enough head differential to allow for gravity flow from one tank to the other. Zeolite used was again 14 x 30 mesh size provided by St. Cloud Mining Company. Running the tanks in sequence allowed the lower tank to operate as a polishing system.

Based upon laboratory data, the CE5 well had an average pH of 7.8 and an average uranium content of 0.453 mg/L. Sodium, calcium, magnesium, and potassium content averaged 285, 235, 55, and 18 mg/L, respectively during the first phase of testing. As the test proceeded, the sodium concentration dropped over time to about 250 mg/L and the calcium content dropped to 220 mg/L. Bicarbonate levels ranged from 185 to 240 mg/L over the testing period.

The zeolite was soaked with a 5% HCl solution and rinsed two times with site RO water to free up all available cation exchange sites. HCl was added by a Pulsatron metering pump to the influent water at a rate of 4 mg per gallon of influent to produce a pH ranging from 5.6 to 5.9. The addition of the acid did not alter the concentration of dissolved sodium and calcium, but, as expected, did significantly reduce the level of bicarbonate in the feed water.

Results of the initial testing were mixed, but encouraging. Data from the time period March 14, 2007 thru March 26, 2007 (Table 2.0) shows the range of operating conditions for the system as it was initially operated. Reviewing the March 14 data, the pH of the feed water was adjusted down to only 6.26. The pH of the Z1 (2.76) and Z2 (3.21) data showed that the pH of the feed water had been too low for a period before this date since the excess acid had not cleared the zeolite system yet. While the bicarbonate level was non-detect, the uranium adsorption had ceased and was being stripped from the zeolite exchange sites. This low acid condition in the tanks remained through March 16 and uranium continued to be stripped.

By the following Monday (March 19) the pH of tank Z1 was approaching that of the feed water, but, tank Z2 still had a low pH. By March 21, the pH of the feed water had been properly adjusted and the pH of both tanks was similar to the feed water, a condition that is desirable. As can be seen during this time, the acid was sufficient to reduce most of the bicarbonate, generally down to 20 mg/L or less. At the same time, the uranium was adsorbed to levels significantly below the goal of 0.16 mg/L with tank Z1 averaging 0.13 mg/L and polishing tank Z2 averaging 0.023 mg/L. However, over the next weekend, the March 26 pH was again very low in the feed water (2.90) as was the pH leaving the zeolite tanks, 3.68 and 2.63, respectively. The tanks were again going through a slow regeneration with the acid and the zeolite was being stripped of uranium.

Table 2.0 – Initial Pilot Test Results

Date	Sample ID	pH	HCO ₃ – mg/l	Total U – mg/l
3/14/2007	Feed	6.26	211	0.427
	Z1	2.76	0	0.348
	Z2	3.21	0	0.529
3/15/2007	Feed	6.32	249	0.352
	Z1	2.83	0	0.453
	Z2	3.18	0	0.568
3/16/2007	Feed	3.26	0	0.354
	Z1	3.09	0	0.523
	Z2	3.08	0	0.292
3/19/2007	Feed	7.31	518	0.432
	Z1	6.30	179	0.332
	Z2	3.38	0	0.130
3/21/2007	Z1	5.26	16.3	0.128
	Z2	5.96	47.5	0.012
3/22/2007	Z1	5.05	0	0.212
	Z2	5.60	28.5	0.012
3/23/2007	Z1	5.63	21	0.061
	Z2	5.57	28.8	0.046
3/26/2007	Feed	2.90	0	0.411
	Z1	3.68	0	0.615
	Z2	2.63	0	0.829

Feed = acid modified well water; Z1 = zeolite tank 1; Z2 = zeolite tank 2

This problem continued with further testing and it was apparent that, as expected, when the pH was out of the 5.6 to 5.9 range, the adsorption of uranium did not occur. When the pH was too high, not enough acid was present to break up the uranium bicarbonate to free up the uranyl ion for adsorption. When the pH was too low, the system went through a slow regeneration process, stripping cations, including uranium, from the zeolite exchange complex.

5.0 MODIFIED FIELD PILOT TESTING

It was decided to further automate the acid feed system to try to achieve more consistent results. A new Pulsatron Series MP electronic acid metering pump was ordered to replace the original pump. An inline electronic pH electrode was

purchased as was a GF controller and readout unit to set upper and lower limits on acid feed based on the pH readout from the electrode.

The system was operated for a few days, however, observation of the pH data showed that large swings in the pH were still occurring over short time frames. An inline mixer was then purchased and placed in the water feed line between the acid injection site and the pH electrode. The feed pH appeared to be much more stable over short time periods after this installation.

The system was operated over longer periods of time but the data was still variable for consistent uranium removal and the uranium concentration averaged more than the goal of 0.16 mg/L. The system was designed to have between three and four weeks of loading capacity. Immediately following system regeneration, the process would remove the uranium to levels below the goal concentration, then, the adsorption would stop very quickly.

Review of the influent calcium and sodium data showed that when the uranium was being adsorbed, sodium and calcium were also being adsorbed. This function of the process was as expected. However, review of the data also showed that after a few days, the sodium and calcium were no longer being adsorbed with the influent sodium and calcium concentration equaling the effluent concentrations. This data suggested that the zeolite exchange sites were fully loaded and could not adsorb additional cations.

Zeolites can be regenerated to remove adsorbed cations. The ability to continually reuse zeolites is attractive from an operational standpoint. The regeneration process consists of soaking the zeolite exchange sites with a 5% solution of HCl. The hydrogen from the HCl is very efficient at exchanging for the other cations, including uranium, sodium, calcium, and magnesium. An acid soak is usually followed by at least two fresh water rinses. Measurement of the cation concentrations in the regeneration reject and the rinse water allows for computation of the amount of cations stripped from the zeolite as compared to the known exchange site loading rate.

During the first few months of operation, the cations present in the regeneration reject and rinse water totaled about two-thirds of the exchange site loading rate. Additional acid soakings would likely have freed up more exchange sites. However, as time went on, the zeolite appeared to be loading much more quickly than previous load rates. In fact, following a thorough regeneration, the system would operate as designed with uranium, sodium, calcium, and other cations being adsorbed, but only for a short period. By the summer of 2008, the system would operate for only 2 to 3 days before adsorption would stop.

Calculation of the cation concentrations in the regeneration and rinse solutions showed that the measured cations stripped from the zeolite could not account for the rapid loading rates of the zeolite. That is, the measured cations were much less than the total loading capacity but the zeolite exchange sites were clearly loaded to capacity.

Examination of other possible cations in the well water, such as iron and aluminum, that could account for the loading of the zeolite were not in sufficient quantities to load the zeolite. So, another cation source for exchange site loading had to be found. Field measurement of the well pH indicated the pH was around 6.80, as confirmed by three separate pH electrodes. However, by the time the sample got to the laboratory the pH was 7.80. This type of pH rise was accounted for by the off-gassing of carbon dioxide (CO₂). Clinoptilolite is very efficient at adsorbing CO₂. This quantity of CO₂ accounts for the difference in cations necessary to load the zeolite to capacity.

Finally, the simple dissolution of the uranium bicarbonate with the acid results in the production of additional CO₂ that enters the zeolite tanks and is adsorbed. Given an average bicarbonate concentration of +/-200 mg/L, approximately 100 mg/L of CO₂ is generated upon dissolution. Ideally, preventing the CO₂ from entering the zeolite is the preferred mechanism for avoiding excessive loading of the zeolite.

During the late summer months, an attempt was made to off-gas CO₂ using an air relief tower. The influent water was first passed through a venturi device to inject high volumes of oxygen into the water. The water then would proceed to the air relief tower so the CO₂ could be released through the valve. When the water temperatures were warmer, the air venturi and the air relief valve were successful in releasing around half of the CO₂ from the water. However, as outside temperatures, and subsequently water temperatures cooled, the venturi/air relief system was not efficient.

Since warming the water appears to be a reasonable method for decreasing the CO₂ to keep it in gas form to be released from the water, it was decided to purchase an inline water heater capable of warming the water to around 60°C. A Bosch AE125 inline continuous heater was purchased and installed. In addition, the incoming water line was re-plumbed so that the acid used to dissolve the uranium bicarbonate could be added before the water moves through the inline heater. This allows for the off-gassing of the CO₂ produced by dissolving the bicarbonate. After the influent water passes through the heater, it goes through the venturi and then passes on to the air relief towers. Because the inline heater, venturi, and air relief towers were installed after the acid injection line, the acid feed pump could no longer overcome the backpressure from the water lines and would not feed acid to the water consistently. A new pump has been ordered that can overcome the backpressure.

Following is a discussion on the CO₂ effects on the zeolite adsorption process.

6.0 CARBON DIOXIDE LOADING

The presence of the CO₂ has hindered the pilot testing process since the amount of loading capacity for the uranium was limited. Several concerns exist for the presence of the high concentration of CO₂ in the well water. First, as mentioned above, the CO₂ is loading valuable exchange sites for the uranium and significantly limits the time the system is able to operate efficiently. The effective adsorption of uranium has been limited to only a few days after regeneration with adsorption ceasing very quickly.

Carbon dioxide is more soluble in cold water. The normal well water temperature is around 15° C. As the temperatures dropped, the pipelines became colder and the incoming water to the system had a temperature around 5°C. This increased the soluble CO₂ and more CO₂ was available for adsorption. This phenomenon explained why the time it took to load the zeolite in the fall and winter decreased significantly over summer loading times. In fact, significant differences were observed between cold nighttime hours and warm daytime hours. This problem made it difficult to maintain a constant pH throughout the day and night since the soluble CO₂ concentrations varied significantly over that time.

Secondly, the CO₂ has proven to be difficult to remove from the exchange sites. An attempt to strip the CO₂ using caustic soda (NaOH) was less than successful. And, precipitated caustic soda made it difficult to keep the pH in the zeolite tanks at the correct level since the sodium hydroxide buffered a significant portion of the added acid. Repeated regenerations with 5% HCl appears to be somewhat more efficient at removing the CO₂ but additional work needs to be done on the removal of CO₂ during regeneration and the removal of CO₂ from the influent stream prior to reporting to zeolite beds.

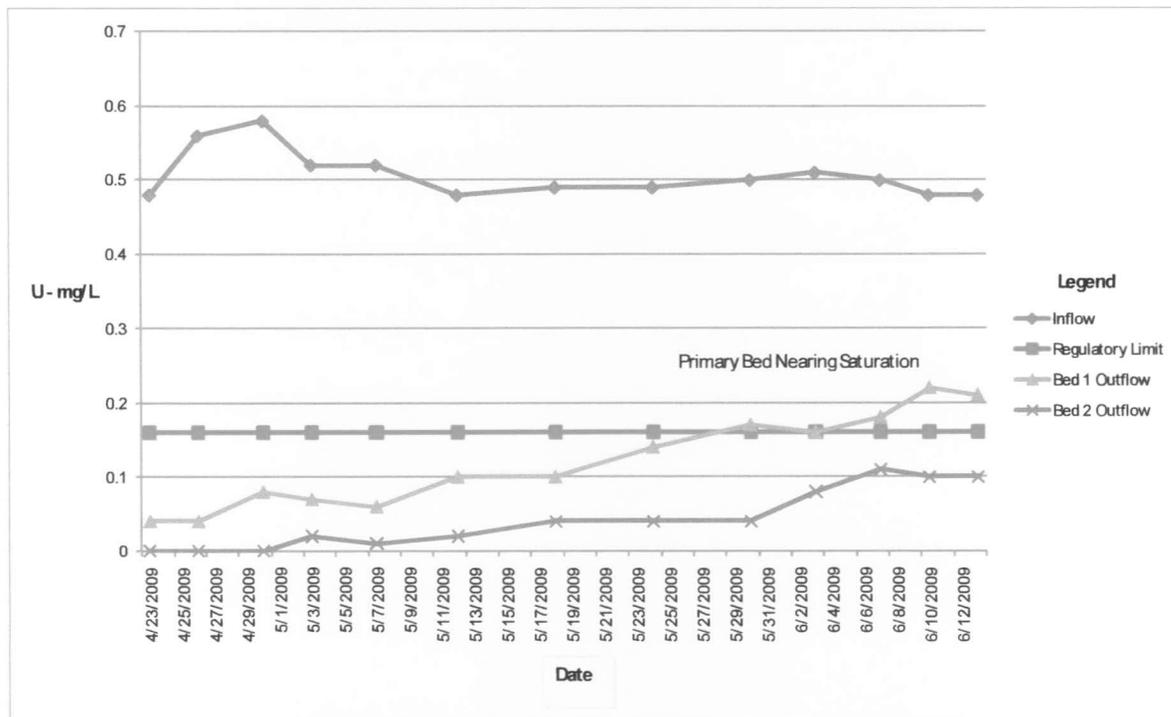
7.0 ONGOING PILOT TESTING

A new acid metering pump has been installed and observations of the effectiveness of the attempts to remove CO₂ through repeated regeneration soakings has been ongoing. In addition, attempts have been made to off-gas CO₂ using a combination of a venturi to change the in-line water pressure and two in-line air relief towers to release the gas from the water before it reaches the zeolite. The removal of the CO₂ has been indirectly measured in the field by observing the changes in the water pH.

The system has been completely regenerated with 5% HCl acid and after several acid regenerations, more of the cations have been removed from the zeolite. It is unclear in the field how much of the CO₂ has been removed since it cannot be measured effectively. However, the acid stripping of other cations on the zeolite was measured directly to judge the effectiveness of the HCl acid for regeneration.

Further modifications of the pilot testing process and operation of the system has shown that the system has been running more efficiently and can be effective in removing uranium from the aquifer well water. Figure 2.0 shows a period of time from April 2009 through early June 2009 when the system operated as designed and theorized.

Figure 2.0 - Uranium Adsorption From Modified Field Testing



In addition to evaluating the effectiveness of CO₂ removal, the pilot testing has been altered to test the use of sulfuric acid to break up the uranium carbonate and to regenerate the system. Potential advantages of sulfuric acid are reduced acid quantities, reduced overall operational costs, and significant reductions in chloride concentrations in discharge waters.

While this testing is in progress, preliminary results are encouraging. The system has had problems with acid quality, freezing of acid, and pump metering. However, both bench testing and pilot testing have shown that when the pH is adjusted between 5.75 and 6.0, the H₂SO₄ can be effective in allowing for the adsorption of uranium. In

addition, H₂SO₄ appears to do a much superior job of stripping cations and freeing exchange sites through the regeneration process. However, pilot testing needs to continue to develop a database of successful uranium adsorption before the use of H₂SO₄ can be determined to be a better choice than HCl.

8.0 LARGER SCALE TESTING

Moving ahead with the technology development, the plan is to construct larger (50 gpm) systems to further test the process at higher flow rates and potentially higher uranium concentrations. Carbon dioxide off-gassing will continue to be part of the larger system and the cost of CO₂ removal, along with other operating parameter costs, will need to be determined to evaluate the economic benefits of the process. The selection of either HCl or H₂SO₄ for the process will be determined from results obtained from the current 5 gpm pilot testing. In addition, one of the issues with the current system is the manpower required to make sure the pH feed adjustments are correct. The larger system would be equipped with computer automation to allow for remote monitoring of flow rates and pH via a computer.

9.0 REFERENCES

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