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## TECHNICAL MEMORANDUM

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**TO:** ADAM ARGUELLO, P.E., SENIOR HYDROGEOLOGIST, HOMESTAKE MINING COMPANY  
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**SUBJECT:** PRELIMINARY ASSESSMENT OF POTENTIAL URANIUM REMOVAL AND STABILITY OF A HYDROXYAPATITE PERMEABLE REACTIVE BARRIER FOR TREATMENT OF ALLUVIAL GROUNDWATER AT THE GRANTS RECLAMATION PROJECT  
**DATE:** OCTOBER 6, 2020

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### 1.0 INTRODUCTION

Uranium and other metals can be removed from groundwater by inducing their precipitation as metal phosphates (Hafsteinsdottir et al., 2015). In particular, the mineral hydroxyapatite (HA)  $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$  has been shown effective in removing U from groundwater through a number of mechanisms: (1) Release of structural  $\text{PO}_4$  followed by precipitation of U-phosphate minerals, (2) adsorption to the HA mineral surface, and (3) substitution/coprecipitation within the mineral structure (Bostick et al., 2003; Lammers et al., 2017; Simon et al., 2004). Sources of HA which have been used to this extent include both synthetic HA and various biogenic products (fish bone, Apatite II™, apatite char). Synthetic HA can be formed *in situ* through injection of solutions containing Ca and  $\text{PO}_4$  which precipitate within the pore space and on the surface of mineral grains. Injection of Ca-citrate and  $\text{Na}_3\text{PO}_4$  significantly reduced U concentrations in column tests conducted at Rifle, Colorado (Szecsody et al., 2016). Analogous field pilot tests were conducted at the Grants Reclamation Project (GRP) during 2013-2014 (small-scale field pilot test) and 2015-2016 (large-scale field pilot test), where solutions of tripolyphosphate (TPP) and  $\text{CaCl}_2$  were injected into the alluvial aquifer. Reductions in groundwater U concentrations were achieved through the direct formation of U-phosphates and also HA-type minerals which provide an additional sink for U adsorption and coprecipitation (Arcadis, 2014; 2016).

Utilization of a full-scale *in situ* HA permeable reactive barrier (PRB) is currently being considered for future long-term U removal from alluvial groundwater in the On-site area near the Large Tailings Pile (LTP) at the Grants Reclamation Project (GRP). The objective of this memorandum is to provide practical information that can be used to assess the potential effectiveness of the On-site PRB. This technical memorandum evaluates the potential U removal capacity and longevity of the PRB, and addresses the expected level of treatability, utilizing information from the scientific literature and from the GRP site-specific studies.

### 2.0 PREVIOUSLY DEMONSTRATED URANIUM TREATABILITY

A small-scale TPP pilot study was performed in the alluvial aquifer at the GRP in August 2013 with monitoring that continued for 180 days (6 months) past the injection period (Arcadis, 2014). The pilot test consisted of two injection wells (a shallow (screened at 55-70 ft bgs) and deep (screened at 75-95 ft bgs) injection well) and 10 monitoring wells up to 40 ft downgradient of the injection wells. This pilot test was located to the north of the large-scale TPP transect (described below) in the "S-area" (a cluster of injection

and monitoring wells just to the north of GRP monitoring well S25). In addition to the injection of TPP (at 1,000 mg/L total P),  $\text{CaCl}_2$  was added to bring the concentration of Ca higher than the natural concentration in groundwater (to 13,000 mg/L dissolved calcium). The Ca:P molar ratio in the injected reagent for this pilot test was 25. A Ca:P molar ratio of approximately 10 was maintained in the aqueous phase at the injection wells for the entire monitoring period, with consistent treatment performance during this time period. Studies have shown optimal Ca:P molar ratios for U removal with TPP to be greater than 2 (Wellman et al., 2007). Note that the Ca:P molar ratio in HA is 1.62, at lower ratios TPP can form soluble Ca complexes that may remain stable and limit precipitation of  $\text{PO}_4$  minerals (Omelson et al., 2009). Groundwater flow direction was relatively constant during this test, and U treatment persisted out to the 180-day monitoring period. The average treatment efficiency was calculated from the monitoring data for wells SDR-1S, SMW-1, and SMW-3D, and SMW-4S (all locations where elevated concentrations of Ca and P were achieved, and downgradient of the injection wells) out to 180 days post-injection (see Arcadis, 2014, Table 4). The treatment efficiency based upon these wells averaged 75.7%. Note that injected tracer rapidly washed out of the target injection area and U treatment persisted with this washout, indicating that treatment was due reaction between U and  $\text{PO}_4$  phases (through precipitation and sorption) rather than dilution.

Data from the large-scale TPP pilot study (750 ft long transect with 34 injection wells; Arcadis, 2016) were evaluated to calculate an average U treatment efficiency of the *in situ* PRB. Performance monitoring was conducted downgradient of the PRB from a series of 16 wells which demonstrated variable groundwater U removal percentages. Wells which displayed irregular treatment trends were either installed outside of the radius of influence of the injection wells, or were located at either end of the TPP transect, where changes in groundwater flow directions induced by ongoing Site restoration activities had a greater effect on successful treatability (Arcadis, 2016). However, four of the wells (PMW-2S, TDR-1S, TDR-1D, TDR-2D) displayed consistent U treatment, with an average U treatability corresponding to 39.4% removal over the 9-month monitoring period (Table 4 in Arcadis, 2016).

The average treatment efficiency for U at the four monitoring wells where consistent decreases in concentration were noted over the monitoring period (9 months) was measured when groundwater flow directions were continuously changing across the treatment transect. In order to best determine treatment performance, groundwater should have maintained a consistent flow direction during the monitoring period, such that groundwater flowed from upgradient, through the treatment zone where the  $\text{PO}_4$  amendment was injected and distributed, and then downgradient to treatment performance monitoring wells on the opposite side of the treatment transect (this was the case for the small-scale pilot test). However, the groundwater potentiometric surface varied widely during the large-scale pilot test performed in 2015-2016 due to the location of the treatment zone. The pilot test goal was to demonstrate the ability of the TPP technology to treat U within the groundwater system where U concentrations and groundwater flow velocities were highest. This area, at the southwestern corner of the LTP, was also where hydraulic capture was focused and where groundwater extraction rates were optimal for effective capture. Although an effort was made to limit groundwater extraction on the upgradient side of the treatment zone, there were many times during the course of the 12-month performance monitoring period that groundwater flow reversals were observed, and also where groundwater was shown to move parallel to the treatment transect, rather than perpendicular to the transect. The width of the treatment

zone was effectively decreased in this arrangement. When the full width of the treatment transect was accessed, the removal efficiency was greater than 80%. This was shown at TDR-2D, a location approximately 200 ft from the northern end of the transect and therefore within the length of the transect rather than at the edge of the transect (Figure 1). A higher U removal efficiency was noted here in August 2015 (approximately 4 months after the TPP injections were completed), with a decrease in U concentrations from 2.28 mg/L to 0.327 mg/L (85.7%). The groundwater flow direction in late August 2015 shifted such that flow was optimal through the treatment transect, switching from parallel to the transect to directly perpendicular. Higher removal efficiencies were noted at TDR-1D (69.3%) in April 2016 when groundwater flow crossed through the treatment transect upgradient of the monitoring well, such that TDR-1D was downgradient of the PO<sub>4</sub> barrier that was established. These higher treatment efficiencies were therefore seen during periods where groundwater flow wasn't reversed or shifted significantly relative to the orientation of the treatment transect and monitoring wells.

Three additional factors limited optimal injection and distribution of the TPP amendment in the large-scale pilot study: 1) the Ca:P molar ratio was sub-optimal for uranium treatment, and was less than 1 in the injected reagent and measured in groundwater for the duration of the pilot study; 2) the TPP formed a Ca polyphosphate "gel" (an amorphous, non-crystalline, hydrated phase) upon injection into the groundwater and 3) the alluvial aquifer sediments exhibited greater variability in lithology than originally expected, with many more lenses of fine-grained materials throughout the area where the TPP transect was constructed. The gel that formed limited the radius of influence that could be achieved by the injected reagent, and therefore the treatment zone was likely established over a smaller area within the aquifer than could be achieved with a fully-soluble reagent. Soluble PO<sub>4</sub> was seldom detected and the treatment zone was therefore limited in areal extent. The lithologic variability also presented challenges for injectability of the gel, with some injection wells screened directly within a significant amount of silts and clays (see Figure 3 in Arcadis, 2016), limiting the volume of reagent that could be injected.

In summary, the pilot test performed in 2015-2016 demonstrated the ability to implement the TPP technology on a large scale in a practical manner in the field, however the evaluation of treatment performance was hindered by continual changes in groundwater flow direction. These changes were due to extensive extraction and re-injection associated with ongoing groundwater restoration efforts at the time. In addition, the formation of a Ca-TPP gel limited the solubility of the TPP, and without the addition of Ca in the injected amendment, the Ca:P molar ratios were never optimal for treatment. Finally, the variability in the alluvial aquifer lithology (with some wells screened in excessive fine-grained materials) limited injection performance at some of the wells. These four factors led to sub-optimal performance of the technology with an average treatment efficiency of 39.4% determined based upon data from monitoring wells located up to 40 ft away from the injection wells and subject to variable groundwater flow conditions. Within the treatment transect at an injection well, the treatment efficiency was greater than 90%. A smaller-scale pilot test completed in 2013–2014 introduced Ca as well as TPP, with Ca:P molar ratios >2 and approximately 10 for the majority of the pilot test period, showed an average treatment efficiency of 75.7%. Under optimal hydraulic and chemical conditions, the U treatment efficiency of an injected PO<sub>4</sub> PRB should therefore be closer to what was observed in the small-scale pilot test.

### **3.0 URANIUM REMOVAL CAPACITY OF THE PRB**

The demonstrated U treatment efficiency from the small-scale pilot test was used in conjunction with the known U removal capacity of HA and the computed flux of U through the PRB over time to assess the longevity of U removal. First, the available literature regarding the U removal capacity of HA from both batch and column tests conducted using similar groundwater were summarized (Table 1). Each of the studies utilized a synthetic carbonate groundwater that was either near-neutral pH or only slightly acidic, with the exception of the Simon et al. (2004) study where the solution composition was not specified. The batch test studies reported a range in U removal capacity for HA, which varied depending on initial U concentrations. A number of the initial U concentrations were much higher than observed in GRP groundwater, hence for batch tests the measured U removal capacities corresponding to the lowest U concentrations were chosen. Based on the summary in Table 1, a range in U removal capacity for the HA PRB was selected to be 2.5 to 6.2 g/kg.

Next, the range in total U removal capacity (kg) for the PRB was calculated using the minimum and maximum HA removal capacity values from the literature (Table 1), in conjunction with the properties of the PRB. Inputs to the calculation (Table 2) include the HA density, aquifer particle density, total porosity, effective porosity, allowable reduction in porosity, estimated PRB dimensions, and U removal capacity values. To calculate the maximum amount of HA that could precipitate in the alluvium, it was assumed that a maximum of 10% of the effective porosity would be allowed to be occupied by HA, so as not to significantly reduce the permeability of the PRB. The proposed PRB is 2,750 ft (838 m) long across the saturated extent of the alluvium, and 41 ft (12.5 m) deep based on the average saturated thickness. The estimated width (40 ft or 12.2 m) of the PRB is calculated as 2x the spacing between injection wells (20 ft). The resulting range in calculated total U removal capacity (kg U) is  $2.34 \times 10^4$  to  $5.00 \times 10^4$  (Table 2).

Finally, the remaining U removal capacity of the PRB over time was calculated using the range in total U removal capacity, the demonstrated U removal efficiency of 75.7% (Section 2.0), and the annual flux of U (kg/year) across the PRB from the Site groundwater model. Because the saturated groundwater thickness is predicted to decrease significantly in the first 50 years, the available removal capacity of the PRB was reduced accordingly based on the fractional area of the saturated thickness at the PRB-groundwater interface (Figure 2). The calculated U removal capacity remaining over time is shown in comparison to cumulative U loading to the PRB on Figure 3. The resulting U removal lifetimes for the PRB range from 38 to 55 years when using the minimum and maximum U removal capacities for HA, respectively, at a 75.7% U treatment efficiency (Table 2).

### **4.0 LONG-TERM GEOCHEMICAL STABILITY OF THE PRB**

The PRB technology relies on the precipitation of metal phosphates in conjunction with metal adsorption to the hydroxyapatite (HA) mineral surface. Hydroxyapatite is very insoluble and therefore no loss of PRB effectiveness is expected to occur from mineral dissolution or precipitation of secondary minerals within the PRB pore space. In addition, metals loading to the PRB is likely within the range of reported metal capacity of HA, such that the U removal capacity of the PRB is not expected to be compromised. To demonstrate these concepts, the geochemical reactive transport model PHREEQC was used to evaluate the expected degree of HA dissolution for a 1,000-year timeframe. The dissolved metal concentrations from alluvial monitoring wells were used to calculate expected future metal loading to the PRB, to

evaluate their effects on the duration of its capacity for metals and U removal. Potential secondary geochemical effects are also discussed.

#### 4.1. Hydroxyapatite Stability and Mineral Precipitation

The 1D geochemical model (Attachment A) simulates transport of representative groundwater through a single cell 40 ft. in length to be consistent with the dimensions of the PRB. The modeled PRB is assumed to consist of pure HA solid (100%, or  $10^6$  mg/kg), which precipitates upon injection of Ca and  $\text{PO}_4$  into the alluvium. An alluvium bulk density of  $1.72 \text{ g/cm}^3$  and a minimum *in situ* effective porosity of 20% was assumed. The geochemical model requires that mineral contents be input as moles per liter of water (mol/L), which is calculated by multiplying the solids-based concentration (mg/kg) by the density:porosity ratio. Using the molecular weight for HA of 502.3 g/mol, the resulting HA content is 17.1 mol/L and was assigned a target saturation index (SI) value  $\text{SI} = -0.5$  to conservatively maintain a slight degree of undersaturation with respect to HA:



The influent composition is represented by the 2019 average concentrations from selected wells in the vicinity of the proposed PRB (Table 3) from which general water quality data were available (HMC and HE, 2020). Because dissolved  $\text{PO}_4$  is primarily below detection (WME, 2020), the groundwater is infinitely undersaturated with respect to HA, which consequently dissolves while maintaining a SI value of -0.5 in the model. Results from the Site groundwater model indicate a flux of 61,702 pore volumes through the PRB in 1,000 years. In the 1D geochemical transport model, a conservative total of 65,000 pore volumes of the groundwater were passed through the simulated PRB and a dispersivity = 0 was assumed. The amount of HA present at each time step was used to calculate the percent HA remaining based on the initial content of 17.1 mol/L. Dissolution of HA releases low concentrations of Ca and  $\text{PO}_4$ , which could potentially combine with other solutes to precipitate secondary minerals and consume reactive pore space. Therefore, the potential for secondary mineral precipitation was also evaluated from the SI values for some common  $\text{CO}_3$ ,  $\text{SO}_4$ , and  $\text{PO}_4$  minerals.

The model results (Figure 4) show that virtually all (99.984%) of the HA is predicted to remain after 1,000 years due to its extremely low solubility ( $K_{\text{sp}} = 10^{-44.33}$ ). As a consequence, very little Ca or  $\text{PO}_4$  is released from the HA, and some of the common major minerals which could potentially precipitate remain undersaturated. Calcite is the only mineral predicted to be slightly oversaturated, but maintains the same degree of oversaturation as calculated for the initial groundwater ( $\text{SI} = +0.40$ ). Therefore, no additional calcite would be expected to precipitate within the PRB.

Note that there are a number of natural analogs that demonstrate the long-term stability of U associated with  $\text{PO}_4$  minerals. The unmined Coles Hill U deposit of south central Virginia is a natural setting where U is stabilized by  $\text{PO}_4$  mineral precipitation in an oxidizing bedrock aquifer (Jerden and Sinha, 2003). Analysis of groundwater here shows that U solubility is controlled by  $\text{PO}_4$  in the deposit, and that the oxidized U- $\text{PO}_4$  mineral assemblages have been stable for up to 150,000 years. A study of the geochemistry of the Sela granite in the south Eastern Desert of Egypt, showed that natural U mineralization was dominated by autunite with apatite in the rock as the source of  $\text{PO}_4$  for the formation of this low solubility U phase (Abd

El-Naby and Dawood, 2008). This process is theorized to have been occurring for the past 200,000 years limiting uranium migration. Finally, at the DOE Hanford site, column studies of PO<sub>4</sub>-amended U contaminated sediments show leaching decreased by 1-2 orders of magnitude as compared to unamended sediments (Shi et al., 2009).

#### **4.2. Total Metals Loading to Hydroxyapatite**

Hydroxyapatite has the capacity to attenuate other metals in addition to U, primarily a large number of divalent metal ions (Hafsteinsdottir et al., 2015) . Therefore, the potential total metals loading to the PRB was calculated to evaluate the potential effects of additional metals removal on U treatment longevity. Historic data provided by HMC were used to calculate the average dissolved metals concentrations (Al, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Zn) in the alluvial groundwater. As shown in Table 4, their average concentrations were summed to obtain a total average (3.27 mg/L). This value was then used in conjunction with predicted flows through the PRB (L/d) from the Site groundwater model to calculate the total metals flux into the PRB (kg) for a 60-year period (the sum of average divalent metals loading was added to the predicted U loading from Section 3.0 calculations to obtain the total metals loading). The mass of available HA was conservatively reduced to 70% of the total HA mass for the entire 60-year period, based on the fractional area of the saturated thickness (Figure 2). The resulting total average metals flux into the PRB (including U) is 71,031 kg and the assumed mass of HA available is 5.65 x 10<sup>6</sup> kg, which equates to a HA metals content of 1.26% by weight. The upper limit of reported metal capacities for analogous materials range from 20 to 50% depending on the types of metals and environmental conditions (Conca and Wright, 2003; Wright et al., 2004). Therefore, it is reasonable to expect that the U removal capacity of the PRB would not be significantly reduced by additional metals removal.

#### **4.3. Secondary Geochemical Effects**

The addition of PO<sub>4</sub> to the aquifer has the potential to release adsorbed As present in alluvial sediments into groundwater (Arcadis, 2014; 2016). The USNRC subsequently requested that HMC "*Provide the following additional information on the environmental impacts of...the potential for release of other COCs, such as arsenic displacement that was observed with the TPP injections*". During the small-scale and large-scale pilot test injections, As permit standards were set to ≤ 0.2 mg/L within the radius of influence during the period of injection, and As was specified not to exceed the MCL (0.01 mg/L) within 60 ft downgradient. These As concentration limits were not exceeded, and As concentrations were not significantly elevated above baseline concentrations outside of the treatment zone.

With respect to additional COCs, their relative strength of adsorption compared to PO<sub>4</sub> is shown in the lyotropic series presented by Wakatsuki et al. (1974):

Arsenic > Phosphate > Molybdenum >> Selenium > Sulfate > Nitrate ≈ Chloride

Note that while As is more strongly adsorbed to alluvial sediments compared to PO<sub>4</sub>, it is effectively displaced by the mass-action effect of elevated PO<sub>4</sub> concentrations during injection. Molybdenum is more weakly adsorbed compared to PO<sub>4</sub>, and consequently followed the same trends as, with concentrations in downgradient wells decreasing or remaining stable at the end of the monitoring period (Arcadis, 2014).

As indicated by Wakatsuki's lyotropic series which includes four additional COCs (Se, SO<sub>4</sub>, NO<sub>3</sub>, Cl), these constituents are only very weakly adsorbed compared to As, PO<sub>4</sub>, and Mo. Thermodynamic data used to

model constituent adsorption to Fe oxide surfaces are also consistent with the relative strengths of adsorption shown in the lyotropic series. Representative log K values from Dzombak and Morel (1990) which are used in the USEPA Minteq.v4 database are shown in Table 5. The relative strength of adsorption as indicated by the log K values is significantly higher for As, PO<sub>4</sub>, and Mo compared to Se, SO<sub>4</sub>, and V (NO<sub>3</sub> and Cl typically only exhibit conservative behavior in groundwater). The native alluvial sediments would thus contain insignificant quantities of these additional COCs available for desorption, and therefore their concentrations in groundwater would not be expected to increase from PO<sub>4</sub> injection.

Selenium concentrations were monitored during small-scale testing and no increases were observed due to its low strength of adsorption. Because the alluvial solids have an even lower capacity to adsorb and subsequently release SO<sub>4</sub>, NO<sub>3</sub>, Cl, and V, their concentrations would also remain protective in the alluvial groundwater. However, increases in TDS and Cl were observed due to the injection of TPP and CaCl<sub>2</sub>, but their concentrations had returned to near-baseline values by the end of monitoring. Overall, increases in As and other COC concentrations associated with the TPP and CaCl<sub>2</sub> injections were shown to be minor, temporary, and limited only to areas immediately proximal to injection wells (Arcadis, 2014; 2016).

## 5.0 SUMMARY AND CONCLUSIONS

This memorandum was prepared to provide practical information that can be used to assess the potential effectiveness of a full-scale *in situ* HA PRB currently being considered for U removal from groundwater in the On-site area at the GRP. In summary:

- In a variety of forms (synthetic, biogenic, precipitated), HA has proven effective in removing U from water in both laboratory and field tests.
- Pilot results from small- and large-scale tests indicate that under optimal hydraulic and chemical conditions, the U treatment efficiency of an injected PO<sub>4</sub> PRB should approximate that observed in the small-scale pilot test (75.7%).
- Calculations indicate the U removal lifetimes for the PRB range from 38 to 55 years when using the minimum and maximum U removal capacities for HA, respectively.
- The HA PRB is expected to remain stable as long as 1,000 years with no significant loss of functionality due to dissolution of the HA by groundwater or secondary mineral precipitation.
- Consideration of additional metals removal by the PRB from groundwater indicates that the U removal capacity would not be significantly reduced.
- Secondary geochemical effects resulting from TPP and CaCl<sub>2</sub> injection, such as increases COC concentrations caused by desorption from native alluvial materials, would be minor, temporary, and limited only to areas immediately proximal to injection wells based on pilot test monitoring.

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**Table 1. Literature Summary of Uranium Removal by Hydroxyapatite (HA).**

Type of Test	Reference	HA Source	Initial [U] (mg/L)	U Removal Capacity (g/kg)	Comments
Batch	Fuller et al. (2002)	Reagent grade synthetic HA	23.8 - 1,420	3.6 to 278	Synthetic carbonate groundwater. pH = 6.3 to 6.8. 3.6 g/kg removal at lowest U (23.8 mg/L).
	Fuller et al. (2003)	Various bone meal, bone charcoal, and reagent grade synthetic HA	12 - 60	0.2 to 12	Synthetic carbonate groundwater. 2.5 g/kg removal at lowest U (5.95 mg/L) and pH = 6.8.
Column	Bostick et al. (2003)	Apatite II™	10.4 - 130	~6.2	Synthetic carbonate groundwater. pH = 5.5 to 7.7.
	Simon et al. (2004)	Synthetic food grade quality HA	3.1	2.9	Solution composition not specified.

**Table 2. Total U Removal Capacities Calculated for the On-Site PRB.**

Parameter	Value <sup>1</sup>	Units
Hydroxyapatite Density	<b>3.16</b>	g/cm <sup>3</sup>
Q <sub>al</sub> Particle Density	<b>2.65</b>	g/cm <sup>3</sup>
Q <sub>al</sub> Porosity	<b>0.35</b>	-----
Q <sub>al</sub> Effective Porosity	<b>0.20</b>	-----
Q <sub>al</sub> Bulk Density	1.72	g/cm <sup>3</sup>
Max. Allowable Reduction in Porosity	<b>10</b>	%
Available Effective Pore Space	116	cm <sup>3</sup> /kg
Maximum Allowable HA Volume	11.6	cm <sup>3</sup> /kg
Maximum Allowable HA Mass	36.7	g/kg
Length of PRB	<b>838</b>	m
Width of PRB	<b>12.2</b>	m
Height of PRB	<b>12.5</b>	m
Upgradient Area of PRB	10,474	m <sup>2</sup>
Bulk Q <sub>al</sub> Volume	127,709	m <sup>3</sup>
Bulk Q <sub>al</sub> Mass	2.20 x 10 <sup>8</sup>	kg
Maximum Mass of Hydroxyapatite (HA)	8.07 x 10 <sup>6</sup>	kg
U Removal Capacity of HA (min)	<b>2.5</b>	g/kg
U Removal Capacity of HA (max)	<b>6.2</b>	g/kg
Total U Removal Capacity of PRB (min)	2.34 x 10 <sup>4</sup>	kg
Total U Removal Capacity of PRB (max)	5.00 x 10 <sup>4</sup>	kg
U Removal Lifetime (min)	38	yr
U Removal Lifetime (max)	55	yr

<sup>1</sup> Bold values are inputs and all other values are calculated.

**Table 3. Average Groundwater Composition (2019) Used as Model influent.**

Parameter (mg/L)	Well MQ	Well MR	Well S2	Well S4	Average
Ca	370	280	247	183	270
Mg	92	73.5	67.3	45.5	69.6
Na	390	307	459	251	352
K	8.4	8.6	6.1	4.4	6.9
Cl	191	186	208	137	182
SO <sub>4</sub>	1,010	953	1,100	633	924
HCO <sub>3</sub>	465	463	647	503	520
pH (s.u.)	6.99	7.03	7.06	7.36	7.11

**Table 4. Average Metal Concentrations in GRP Alluvial Groundwater.**

Metal	Average Concentration (mg/L)
Ag	ND <sup>1</sup>
Al	0.051
Ba	0.021
Cd	ND
Cr	0.012
Co	0.0013
Cu	0.026
Fe	1.95
Hg	ND
Ni	0.0025
Pb	0.017
Mn	1.14
Zn	0.054
<b>Total</b>	<b>3.27</b>

ND = All values were below detection.

**Table 5: Comparison of log K Values Indicating Relative Adsorption Strength of Various COCs.**

Reaction	log K <sup>1</sup>
$\text{HAsO}_4^{2-} + \text{Hfo\_wOH} + 2\text{H}^+ \rightleftharpoons \text{Hfo\_wH}_2\text{AsO}_4 + \text{H}_2\text{O}$	17.8
$\text{HPO}_4^{2-} + \text{Hfo\_wOH} + \text{H}^+ \rightleftharpoons \text{Hfo\_wHPO}_4^- + \text{H}_2\text{O}$	13.0
$\text{MoO}_4^{2-} + \text{Hfo\_wOH} + \text{H}^+ \rightleftharpoons \text{Hfo\_wMoO}_4^- + \text{H}_2\text{O}$	9.50
$\text{SeO}_4^{2-} + \text{Hfo\_wOH} \rightleftharpoons \text{Hfo\_wOHSeO}_4^{2-}$	0.80
$\text{SO}_4^{2-} + \text{Hfo\_wOH} \rightleftharpoons \text{Hfo\_wOHSO}_4^{2-}$	0.79
$\text{HVO}_4^{2-} + \text{Hfo\_wOH} \rightleftharpoons \text{Hfo\_wOHVO}_4^{3-} + \text{H}^+$	0.27

<sup>1</sup> The reactions and log K values for As, P, and V are normalized to their divalent species.

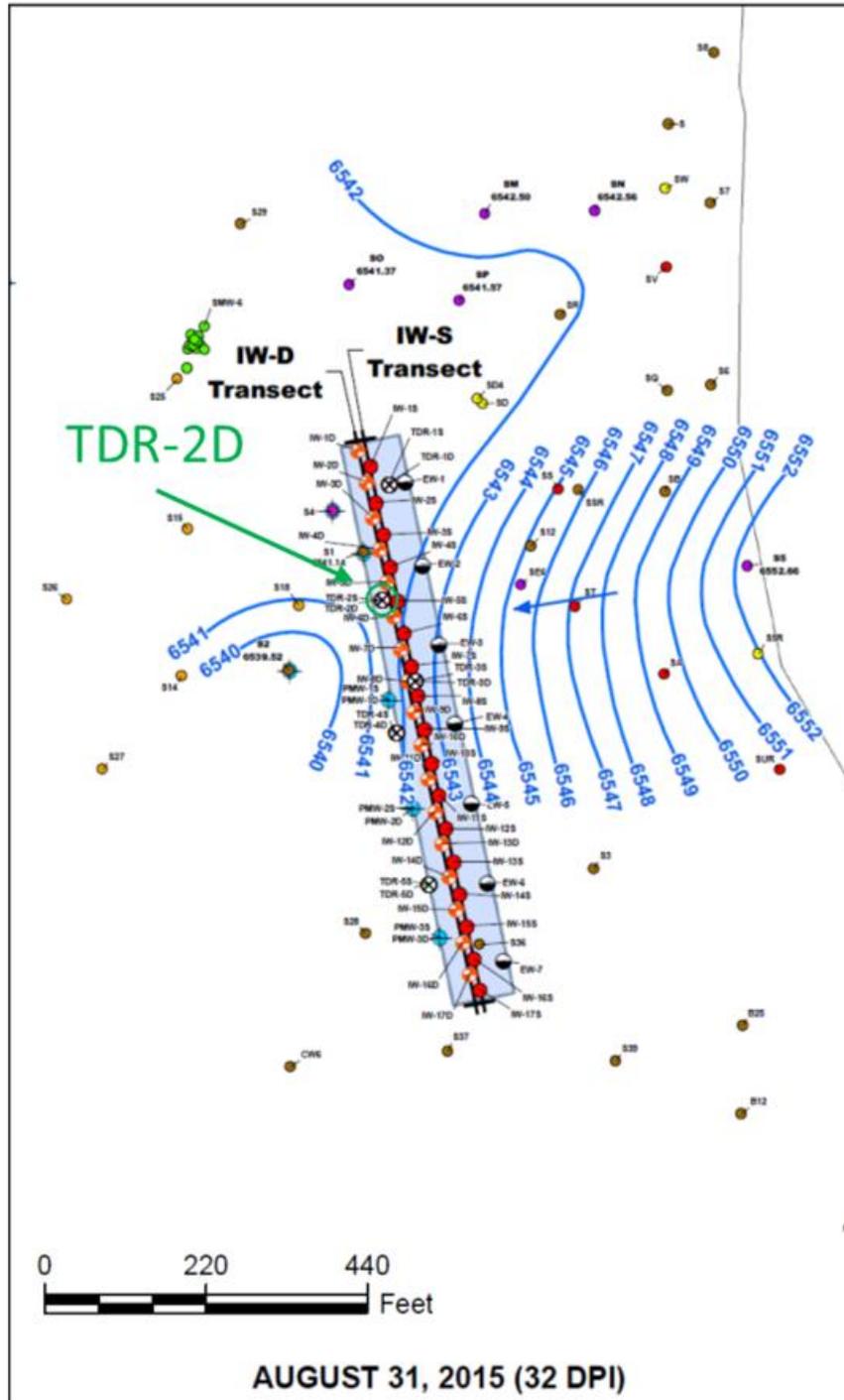
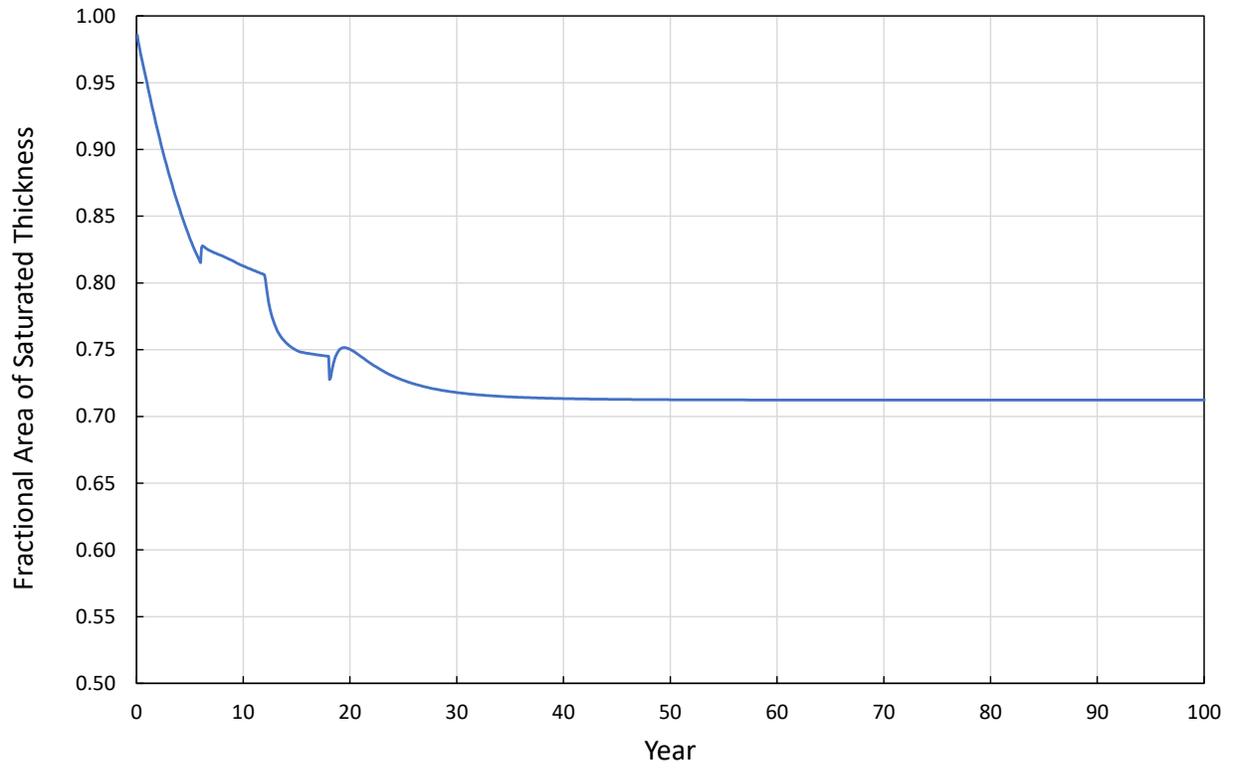
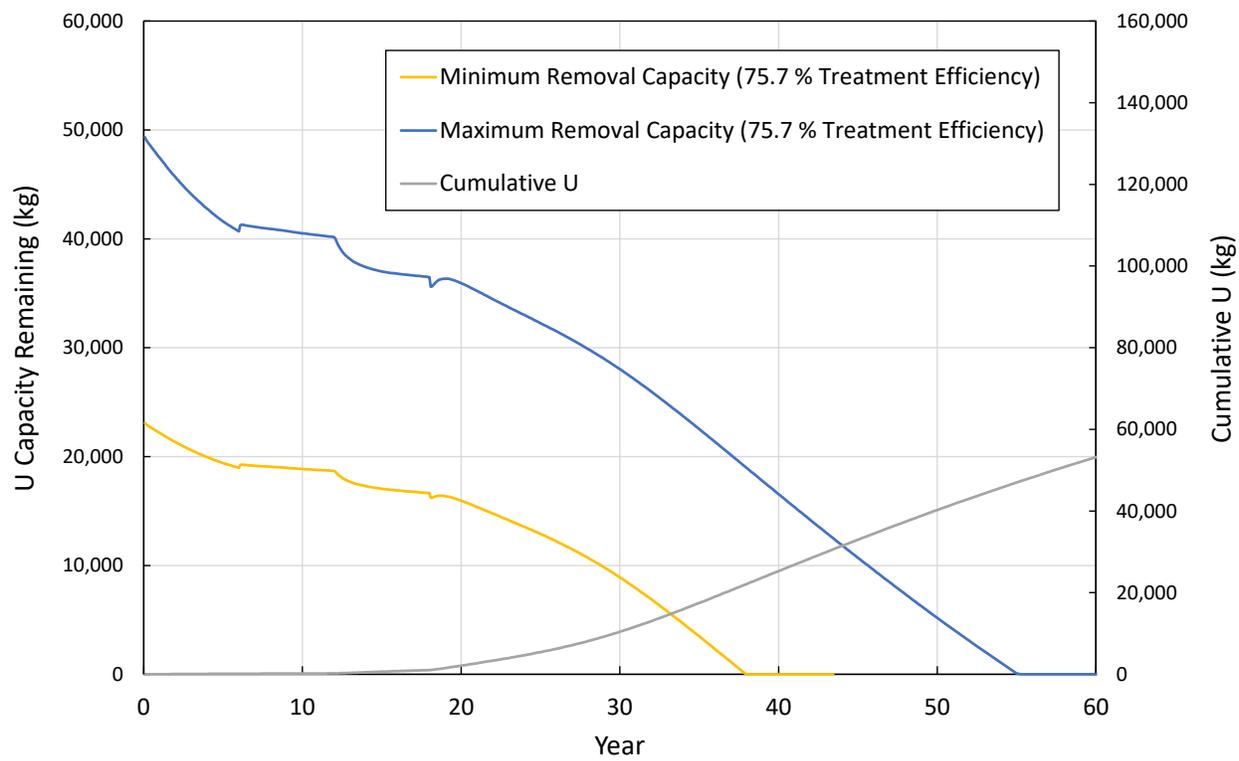


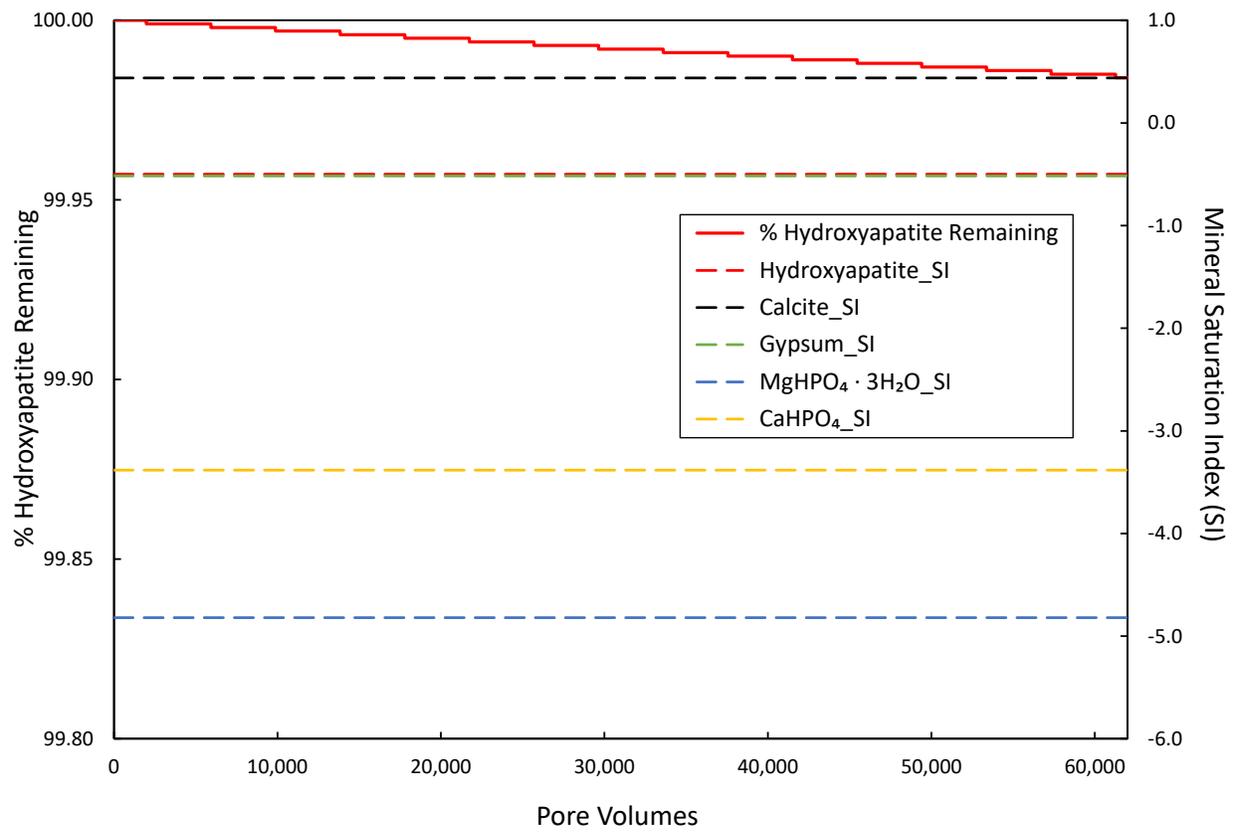
Figure 1. Injection, extraction, and monitoring wells associated with the 2015-2016 TPP pilot test (large-scale test), with groundwater potentiometric surface measured at the end of August, 2015 showing groundwater flow through the treatment transect. The location of monitoring well TDR-2D is highlighted.



**Figure 2: Fractional Area of the PRB Saturated Thickness Over Time.**



**Figure 3: Predicted PRB U Removal Capacity Over Time.**



**Figure 4: Predicted Amount of Hydroxyapatite Remaining and Calculated Mineral Saturation Index Values for the 1,000 Year Simulation.**

**ATTACHMENT A**

**PHREEQC INPUT FILE – Hydroxyapatite Dissolution**

```

PRINT
-reset false
SOLUTION 0 # Average from Wells MQ, MR, S2, S4 (2019)
-units      mg/L
pH          7.11
Alkalinity 520 as HCO3
Ca          270
Mg          69.6
Na          352
K           6.9
Cl          182
S(6)       924

SOLUTION 1 # Average from Wells MQ, MR, S2, S4 (2019)
-units      mg/L
pH          7.11
Alkalinity 520 as HCO3
Ca          270
Mg          69.6
Na          352
K           6.9
Cl          182
S(6)       924

EQUILIBRIUM_PHASES 1
Hydroxylapatite    -0.5  17.1

TRANSPORT
-cells            1
-lengths          1*12.2 #40 ft
-shifts           62000
-punch_cells     1

SELECTED_OUTPUT
-file             c:\output\Homestake_PRB_Dissolution_With_Transport.dat
-reset false
-step            true

USER_PUNCH
-headings %_Remaining moles_HA Calcite_SI Gypsum_SI MgHPO4:3H2O_SI CaHPO4_SI HA_SI
10 PUNCH (EQUI("Hydroxylapatite")/17.1)*100
20 PUNCH EQUI("Hydroxylapatite")
30 PUNCH SI("Calcite")
40 PUNCH SI("Gypsum")
50 PUNCH SI("MgHPO4:3H2O")
60 PUNCH SI("CaHPO4")
70 PUNCH SI("Hydroxylapatite")

USER_GRAPH
-headings          %HA_Remaining
-axis_titles      Pore Volumes \ %HA_Remaining
-axis_scale       x_axis 0 62000
-axis_scale       y_axis 0 100
-start
10 GRAPH_X       STEP_NO +0.5
20 GRAPH_Y (EQUI("Hydroxylapatite")/17.1)*100
end

```