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By Email

October 30, 2020

Mr. Mark Purcell Superfund Division (6SF) U.S. Environmental Protection Agency - Region 6 1445 Ross Avenue, Suite 1200 Dallas, TX 75202 Email: (purcell.mark@epa.gov)

Re: Homestake Mining Company Superfund Site Technical review of the NMED report titled: "Geochemical Conceptual Site Model and Batch-Equilibrium Modelling of Alluvial Groundwater at Monitoring Well DD, Homestake National Priorities List Site"

Mark:

As discussed during the October 23, 2020 technical meeting with EPA and NMED, Homestake Mining Company of California hereby submits a written technical review of the NMED report authored by Patrick Longmire, titled "Geochemical Conceptual Site Model and Batch Equilibrium Modelling of Alluvial Groundwater at Monitoring Well DD, Homestake National Priorities List Site".

Please don't hesitate to contact me by phone (775) 397-7215 or by email <u>dlattin@barrick.com</u> if you have any questions.

Sincerely,

Daniel Lattin, P.E. Sr. Closure Program Manager Homestake Mining Company of California

Cc:

Adam Arguello, P.E. Brad Bingham Kurt Vollbrecht Ashlynne Winton Patrick Longmire file Review of Longmire 2020.

We have reviewed the report issued September 11, 2020 titled "Geochemical Conceptual Site Model and Batch-Equilibrium modeling of Alluvial Groundwater at Monitoring Well DD, Homestake National Priorities List Site, Cibola and McKinley Counties, New Mexico", authored by Patrick Longmire of the New Mexico Environment Department (NMED) (Longmire 2020).

The report summarizes a geochemical modeling study performed to present an alternate conceptual model for the presence of uranium in groundwater at monitoring well DD. The report provides an extensive discussion of this conceptual model including reference to historical data, along with geochemical modeling to support concepts presented in the report. We respect the effort associated with this work and its execution; but there are flaws in the approach, our review identified several areas that require comment, some of which are presented in this memo.

Monitoring well DD is one of the nine (9) wells located upgradient of the Grants Reclamation Project (GRP) (upgradient relative to groundwater flow), and in the alluvial aquifer, that were used to establish the background, upgradient water quality conditions for select constituents for the groundwater restoration program at the GRP (Arcadis 2018). Groundwater quality data from the 9 wells was evaluated during the period 1995 – 2004 to establish the site background standards for uranium, molybdenum, sulfate, chloride, total dissolved solids (TDS), nitrate and vanadium, as per Nuclear Regulatory Commission requirements for establishing background conditions at the GRP (NRC 2006). In 2016 – 2019, additional data was developed through a field sampling and analysis program, with collection of groundwater quality data as well as both saturated an unsaturated aquifer soil samples from numerous locations upgradient of the GRP, to further support the established background standards (Arcadis 2018, 2019). These studies were published in the open, peer-reviewed technical journal in 2019 (Ulrich et al. 2019). The body of work completed to establish background water quality standards for the GRP therefore includes the statistical evaluation of groundwater quality data in 2006 and acceptance by the NRC, NMED, and USEPA, followed by a four-year period of field sampling campaigns (initiated by EPA in 2016, and then later thoroughly reviewed by EPA in 2018 and 2019) and extensive laboratory analyses completed in 2019 to support the site background standards.

The field and laboratory work summarized in Arcadis 2018, 2019 and peer reviewed paper by Ulrich et al., 2019 provided site-specific data to support the natural occurrence of uranium and other constituents in groundwater due to the presence of these constituents in minerals present in the soil upgradient of the GRP. The GRP is located in a highly mineralized area, as evidenced by the occurrence of uranium ore in the Jurassic Morrison formation bedrock highlands to the north of the GRP. Eroded bedrock highlands are present in the alluvium at the GRP. Heterogeneity in the distribution of these minerals, and in the soil composition (a mix of coarse-grained and fine-grained sediments, derived from weathering of the bedrock highlands) was shown to be responsible for the range of concentrations of uranium observed in the alluvial groundwater system. Well DD, on the west side of the upgradient alluvial aquifer system, has naturally-derived uranium at concentrations higher than at wells in the middle and east side of the system, due to the different mineralogy in this area.

Longmire 2020 presents an alternate conceptual model for the presence of uranium at well DD, based upon geochemical modeling of historical data from the region going back to the late 1970s/early 1980s

in combination with the recent work. There are no new additional data provided to the current data set for the GRP, instead a set of assumptions about past conditions north of the GRP is outlined, (with the most significant assumption being an assumption associated with a means of conveying mine-water via surface flow to an area adjacent to well DD), along with quantitative geochemical modeling to explore hypothetical scenarios related to the introduction of other sources of uranium to the groundwater system near monitoring well DD.

The following assumptions are described in the report, and require further discussion, and in some cases, clarifying language or modification.

- 1) Hypothetical mine-water discharge was conveyed via surface flow directly to an area in the vicinity of well DD.
- Transient geochemical conditions, evidenced by variable uranium concentrations in groundwater measured at well DD, are due to movement of mine discharge water through the area.
- 3) Uranium is sourced to groundwater from somewhere other than through local, natural sources that reside in alluvial sediments.
- 4) Mixing ratios of mine water with background alluvial groundwater to match current uranium concentrations at well DD and are based upon the assumption that the alluvial aquifer is of uniform physical composition allowing complete mixing spatially.
- 5) A well (SMC-08/916) is presented as representative of "background".
- 6) Infiltration of mine water from the land surface to DD occurred without leaving a radionuclide signature.
- 7) Empirical data related to uranium leaching from soils does not support local, naturallysourced uranium to groundwater but suggests an alternate source of uranium.
- 8) Geochemical modeling, using the software PHREEQC, is used to support some aspects of the alternate conceptual model, but not all aspects of the model.

We highlight some of the assumptions or theories presented that are not fully supported by the available data in the following discussion, with reference to statements in the Executive Summary (ES) in order to follow the sequence of items assembled to convey this alternate conceptual model.

We have also reviewed the input files for the PHREEQC geochemical modeling that was performed (item 8, above). The modeling work was done to support some of the theories presented and is therefore important to demonstrate the validity of statements about the cause for geochemical transients observed at well DD. We identified some aspects of the modeling work that can be improved upon and we provide these as well in the following discussion, at the conclusion of discussion of items 1-7.

1) Mine water is described as having been directed through a surface water diversion into the area of well DD.

The work by Gallaher and Cary 1986 is referenced relative on Page 1 (ES); this work discusses the discharge of 128 billion gallons of mine water over 26 years from 1952 to 1982 and surface-flow of this water into the San Mateo Creek floodplain. While this number is likely taken from Figure 6.1 in Gallaher and Cary (1986), the basis of this data is unclear. No references nor methodology is specified for the compilation of this data. In Table 6.1, Gallaher and Cary present averages discharges for 1979-1981 of 2300 and 1500 gpm for Arroyo Del Puerto and San Mateo Creek, respectively. The discrepancy between

the figure and table is not clarified in the report. The total discharge from the mines (yearly averages ranging from 6,000 to 13,000 gpm) correlates poorly with USGS stream gauges set on San Mateo Creek (SMC) & Arroyo Del Puerto (ADP). Combined flows reported at the stream gauges never accounted for more than half of the total discharge for those overlapping periods, and typically accounted for less than 25%. Gallaher and Cary (1986) estimated that surface flow persisted for 3 miles in San Mateo Creek and 5 miles in Arroyo Del Puerto. Perkins and Goad 1980 estimated that surface flow persisted 10 kilometers (6 miles) from the major facilities. Neither historical reports indicate that surface flow was readily present in the Lower San Mateo Creek Basin. In order to convey water to the area of well DD, a surface feature is discussed that shows up in historical aerial photographs and is suggested to be a ditch or diversion structure that diverted water from San Mateo Creek to a location to the north of well DD as early as 1958. There are not any specific details about this ditch, and it is assumed in the report to have conveyed mine water. Water quality data, and flow volumes through the ditch are not available. Based upon the USGS stream gauges it is not clear that there would be a significant volume of water conveyed through the ditch, and there is no information for surface water quality, with assumptions made about the possible composition of water in this ditch. A major assumption is that the flow would have to have persisted across approximately 8 additional miles beyond the USGS stream gauges in a poorly defined streambed in the Lower Basin to reach well DD.

2) "Transient geochemical conditions" at well DD is provided as a reason for investigating other, non-natural, and non-local sources of uranium to groundwater.

On page 2 (Executive Summary), the following statement is a theory that is provided as an explanation for the changing concentrations of constituents at well DD, however, it is too strong a statement to make based upon assumptions and without fully evaluating other possible causes for the transient conditions:

"Based on <u>transient aqueous geochemical conditions</u> observed at upgradient monitoring wells, such as DD and nearby DD2, dissolved concentrations of uranium, sulfate, and calcium are not representative of natural groundwater background in the alluvium at the Homestake NPL Site."

There are a number of possible reasons for the trend in the concentration of uranium, as follows

- The trend in concentrations of uranium at monitoring well DD and DD2 can be due to nearby
 groundwater extraction and injection at the GRP, leading to water level rises/declines and
 saturation/desaturation of the vadose zone (or a periodically-rewetted zone) mobilizing
 constituents associated with the aquifer sediment environment here (vadose zone), or
 attenuating concentrations of constituents due to the hydrogeological transient created by the
 GRP activities.
- Evidence of a vadose zone influence includes increasing nitrate, sulfate and selenium concentrations in groundwater at well DD, possibly leaching out of the soils that were previously unsaturated, along with a water level rise and decrease in uranium concentrations (there may be a lag in the effects of natural processes sourcing uranium to groundwater (from previously unsaturated sediments) as a new equilibrium is achieved with water level changes).
- A dynamic environment relative to gypsum and calcite precipitation and dissolution can be the result of these water level fluctuations leading to effects on uranium concentrations through incorporation into these solid phases and others. Mine-water discharge moving through

groundwater at well DD would likely be accompanied by an increase in concentration at this well (e.g., a greater proportion of mine-water mixing in with ambient groundwater), rather than a decrease.

In addition, it is not possible to definitively attribute "spikes" in uranium concentrations at well DD to mine-water discharge (Figure 9) and this could just as likely be due to sampling anomalies. Dissolved nitrate concentrations are increasing at well DD (Figure 13) and are suggested to be an indicator mine water working through the alluvial system. If mine-water discharge infiltrated beginning in 1976, and was associated with agricultural activity at this time, then nitrate concentrations should have peaked in the past and now with the cessation of infiltration, concentrations should be declining. Similarly, if mine-water discharge was introduced near DD through surface infiltration, and associated with agriculture, nitrate and uranium should be positively-correlated - that is, as more water flowed in from the surface along with nitrate and uranium, these two constituents should exhibit similar trends in the groundwater system - however, they are negatively-correlated as shown on Figure 14.

We note that the uranium concentrations and water levels were relatively steady over the period (1995 – 2004) during which data was obtained from well DD for inclusion in the data set used to establish background water quality conditions; the transients described in the report occurred after this time period and could be caused by the mechanisms described above, namely a water level rise associated with hydraulic conditions induced at the GRP site, along with changing constituent concentrations recently and associated with this condition.

3) The source of uranium and isotopically depleted sulfate to groundwater is assumed to be something other than natural – but without definitive data to support other sources.

On page 3 (ES), the "original source" of sediment-bound uranium is acknowledged, and the mechanism for this local source of uranium to groundwater near well DD is stated to be "desorption of uranium(VI) and oxidative dissolution of uranium(IV) solid phases." We agree with this mechanism as it is based upon information developed from extensive field and laboratory work and published in Ulrich et al., 2019. However, this is indicated by the report to be a "secondary or minor source of dissolved uranium." The report goes on to state that "the majority of dissolved uranium measured at wells DD and DD2 is most likely sourced from historical mine- water discharges." That this statement is based on assumptions that are not fully supported by the field and laboratory data.

On page 2 (ES), the report states that "Depleted sulfur isotope signatures in sulfate in alluvial groundwater are consistent with most of the dissolved sulfate originally and dominantly source from ore zones. Oxidative dissolution of trace amounts of pyrite in alluvial sediments may have also produced depleted δ^{34} S-SO⁴ ratios in alluvial groundwater at the Homestake NPL Site."

The source of isotopically-depleted sulfur in sulfate is therefore assumed to be mine-water discharge without evidence, while the findings of the recent field and laboratory studies and associated data are dismissed as explaining another source from "trace amounts of pyrite in alluvial sediments." However, pyrite was found to be very commonly encountered in the mineralogical examination of the alluvial sediments near DD and DD2 (Arcadis 2019; Ulrich et al. 2019), with evidence of more oxidized pyrite, and originally of biogenic origin, on the west side of the alluvial system (near wells DD and DD2) and less oxidized pyrite on the east side. All of the soil samples examined by microscopy and collected in 2018 (8 samples) and 2019 (10 samples) by Arcadis contained metal sulfides, notably as pyrite. Iron (hydr)oxide-

replaced framboidal pyrite was observed in abundance at 3 boreholes in 2019 indicating that isotopically light biogenic sulfur was likely released to groundwater in the vicinity of well DD, with this pyrite likely serving as the local source of isotopically-depleted sulfur in sulfate measured in groundwater. In addition, a geochemically-reducing environment was encountered in groundwater screened in fine-grained material at well BK2f in 2019 (Arcadis, 2019) demonstrating that geochemical heterogeneity exists in the alluvial aquifer and sulfide is likely actively being oxidized locally in sediments, sourcing additional light sulfur to sulfate in groundwater.

4) The description of "plausible percentages" of mine water mixed with background groundwater in the alluvium today rely upon simplification of the groundwater flow conditions.

On page 2 of the ES, the report states that a mixture of 97.11% of alluvial groundwater at monitoring well P with 2.89% of infiltrated mine water produces an average concentration of uranium of 0.165 mg/L measured at well DD from 1997 to 2019. The report also mixes 89.85% of alluvial groundwater at well SMC-08/916 with 10.15% of infiltrated mine water to produce average dissolved concentrations measured at well DD. These mixing ratios are indicated to be "plausible percentages of native alluvial groundwater that are impacted from infiltrating mine water."

These percentages were derived in an attempt to match the average uranium concentration measured at well DD, assuming a highly simplified groundwater flow environment. The assumption of volumetric mixing of waters is useful for the batch mixing calculations, but the hydrogeological conditions in the alluvial aquifer system are much more complex with multiple groundwater flow paths due to heterogeneity in the aquifer properties. A more robust means of evaluating groundwater mixing would be through the use of a numerical groundwater flow model that includes the detailed hydrogeological complexity incorporated into the model.

The results of the mixing calculations (Table 7a) approximated reasonably well the current concentrations of major ions calcium, chloride and sulfate, along with trace elements uranium and selenium measured at well DD; however, the predicted concentrations of magnesium and sodium were not well approximated – sodium in particular is a concern because its concentration was underpredicted and owing to the conservative nature of this ion, its concentration would not be expected to change much along a groundwater flow path.

One of the endmembers of the mixing calculation is represented by water discharged from an ionexchange system in Ambrosia Lake and described in Perkins and Goad, 1980; there is not any information to support that the water quality detailed in the 1980 work would be representative of any water conveyed in the ditch and distributed into the area at the land surface near well DD. A <u>major</u> <u>assumption</u> is that this water chemistry would remain essentially unchanged during migration down the SMCB system and through the soil column.

Additional mixing calculations should be performed to evaluate mixtures required to predict concentrations of uranium at more of the wells in the vicinity of well DD in order to evaluate the range of mixing percentages between native alluvial aquifer groundwater and mine-water discharge; it is likely that a range of mixing percentages would be required to approximate the concentrations measured in groundwater. Without performing mixing calculations at each of the wells that are hypothesized to be affected by mine-water discharge, it is difficult to confidently state what is reasonable in terms of mixing

percentages, other than the end-members that were mixed were able to approximate concentrations of uranium and sulfate an well DD.

In summary, the alluvial system is assumed to be a "homogeneous and isotropic aquifer matrix;" this assumption is invoked in order to perform a simple volumetric mixing calculation. However, the alluvial aquifer system is known to be highly variable in aquifer sediment composition (particle size, lithology) and flow properties (Arcadis 2019) and this statement is an over-simplifying assumption.

There is no discussion in the report on lateral (saturated) and vertical (unsaturated) groundwater flux rates and how mine water may have moved out of the vadose zone and into the saturated zone. Likewise, there is no basis provided for the predictions about the time period over which water movement through the system may have occurred or may be occurring at present.

5) Statements about groundwater from SMC-08/916 being representative of background conditions are not supported by the data.

On page 18, top of the page, water quality at well SMC-08/916 is indicated to "likely represent background conditions in alluvial groundwater in lower San Mateo Creek Basin." We are concerned with this statement based upon the following:

- There is not ample justification to make this statement and simply because the groundwater here is a "sodium-bicarbonate" type does not justify this well as being representative of background; the majority of the groundwaters at the GRP, north and downgradient of major LTP influences of the site are "calcium-sulfate" type waters.
- The field and laboratory work conducted recently showed that the aquifer sediment on the east side of the alluvial system is very different than the middle and west side of the system, and that water quality at well ND, just to the south of SMC-08/916, exhibited significantly different water quality due to the differences in sediment lithology, mineralogy, and possible surface water recharge at this location.
- The source of sediments on the eastern side of the alluvial system was shown to be different than the source of sediments on the west (Ulrich et al. 2019).
- The reference to water quality at well SMC-08/916 in the text transitions from "likely represent(s) background conditions" to "background well SMC-08/916" (page 20, text above Figure 10). It appears that an assumption about the composition of background water quality has been arrived at, based upon this statement. This statement about background conditions at well SMC-08/916 should always be qualified given that it has not been determined to represent background conditions.
- Completion information indicates SMC-08/916 was potentially completed into underlying Chinle bedrock rather than in the alluvium. "Red clay" is noted in the well logs from 34 ft below ground surface (bgs) to 120 ft bgs. Historic driller's logs in the vicinity of the GRP periodically identified the Chinle bedrock as red clay. The screened interval of the well is logged from 45 to 70 feet bgs and the water bearing strata is identified as 60 to 85 feet bgs. Beyond the lithologic description and completion information, the presence of sodium as the major cation in the water quality is consistent with the Chinle water bearing units in the vicinity of the GRP, whereas calcium is typically the major cation in the alluvial water.

- The geology and hydrogeology of the alluvial aquifer system upgradient of the GRP is very complex and as noted in the recent field work (Arcadis 2018, 2019; Ulrich et al., 2019) even greater heterogeneity in lithology was observed than previously documented with significant variation in sand/silt/clay distribution in the alluvium. Based upon this recent information, designating one location in the alluvium as representative of background is not considered a valid approach and it is more appropriate to characterize background based upon a range of aquifer conditions, as is represented by the set of wells used in the 1995 2004 data set on upgradient background water quality.
- 6) Local recharge of surface water, consisting of mine-water discharge in the areas of wells DD and DD2, would likely have left a radionuclide signature in the soil column from the surface downward to the saturated zone.

Downhole geophysics work at DD-BK, DD2-BK, and BK1c did not reveal an elevated gamma radiation signature in the near-surface soil/vadose zone (as would be expected due to deposition of radionuclides in the soil during infiltration of mine-water discharge) and did not reveal an elevated concentration of uranium based upon spectral gamma signatures.

There is no evidence in this data, nor in the solid phase soil chemistry data, for the surface infiltration of mine-water discharge near DD and DD2.

7) The data from the evaluation of leaching of uranium from alluvial aquifer sediments are presented to reject the possibility of a local source of uranium to groundwater, however, these results support that uranium present in the sediments is able to be mobilized out of the sediments when contacted with water.

On page 45, the report presents the result of work that evaluated leaching of uranium from the sediments, using SPLP and selective extraction methods. The report points out that there is a 20:1 solution: solid ratio used in many of the leach tests, as per standard EPA methods. However, it does not point out that this ratio is in excess of what would be expected in a saturated alluvial sediment environment (there would be a lower solution: solid ratio) and therefore absolute concentrations evolved in the leach studies do not fully approximate what might be possible in a groundwater system, with dissolution of uranium from sediments from DD, DD2, etc.

- The report makes general statements that uranium concentrations in the sediments are too low, and the amount leached is too little, and therefore not supportive of locally sourced uranium to groundwater.
- Ulrich et al. 2019 references work done in a quaternary alluvial aquifer system in China where uranium in sediments ranged from 1.9 to 8.8 mg/kg (similar to concentrations measured in the alluvial system north of the HMC Mill) and groundwater concentrations ranged from 0.119 to 0.209 mg/L (Wu et al. 2019). This work pointed to oxidation and weathering of uranium-bearing minerals in the sediments, similar to processes that occur in the alluvial sediments at the GRP.

The conclusions from the review of these data, on page 46 of the report, are that "Most of the dissolved uranium measured at wells DD and DD2 is most likely sourced from surface-water, containing mine-water discharges, which provided recharge to the alluvial aquifer in the area of wells DD and DD2 since

at least 1976. Solute transients observed at both wells are not representative of natural conditions in the alluvial aquifer north of the Homestake NPL Site."

Similarly: "This confirms that most of the sediment-bound uranium at boreholes DD-BK and DD2-BK is not soluble or leachable under the prevailing oxidizing and circumneutral pH conditions occurring in alluvial groundwater at wells DD and DD2."

 Work performed by Ulrich et al. 2019 revealed that the alluvial sedimentary system near DD and DD2 is dynamic in terms of grain size and hence groundwater movement into and out of sediment pore-space, and in terms of mineralogy, with varying amounts of oxidized and unoxidized materials. The dynamics of this system is discussed as the reason for transients in geochemistry (along with water level changes due to groundwater extraction and injection at the GRP) and for the presence of uranium in groundwater derived from sediments.

8) Review of the Geochemical Modeling Input Files and Model Execution

While no additional data were generated as part of the Longmire 2020 work, there was a significant effort related to geochemical modeling using the freely available software PHREEQC published by the USGS (Parkhurst and Appelo 2013). The modeling was performed to support the conceptual model described in the report. This review identifies some issues with the construction of model input files that should be considered and, in some cases, corrected. In addition, we comment on the model approach and results and applicability to validating the conceptual model presented.

In general, the modeling approaches are not entirely consistent with the conceptual model or across computational models. For example, the conceptual model describes mixing of upgradient waters and reactions with various minerals and adsorbing surfaces to create the water at Well DD; however, the initial modeling uses actual water from Well DD in a series of simulations designed to understand the genesis of water at Well DD. Displacement of uranium from sorption sites is discussed as a factor controlling uranium concentrations; however, only sorption (not desorption) of uranium at Well DD was simulated, and adsorption reactions were not included in subsequent models. The conceptual model is based, in part, on dissolution of gypsum as calcite precipitates; however, precipitation of calcite is an artifact of the model resulting from assigning a saturation index (SI) value of 0, which forces calcite to precipitate to a much larger extent than would occur naturally. Increases in calcium concentration from these reactions are attributed to desorption of uranium and formation of additional calcium-uranium solution complexes which enhance uranium mobility; however, the model results do not indicate an increase in dissolved or adsorbed calcium as proposed to be unique to this mechanism. Detailed comments are provided associated with each category of modeling work presented in Longmire 2020.

Well DD Speciation and Simulated Reaction With Calcite/Gypsum

Page 31 introduces the concept of gypsum dissolution and calcite precipitation, which becomes the foundation to explain increasing calcium concentrations and their effects on uranium concentrations at Well DD. However, the model simulation is inconsistent with the conceptual model because it uses an actual composition from Well DD in the calculation. There are additional observations related to defining which reactions are allowed to occur and which properties are to remain constant:

- It is stated that the PCO₂ was fixed to maintain the pH at the initial value of 7.15. The pH is a
 master variable which should be allowed to respond to the various geochemical reactions which
 occur. In natural groundwater, the pH is not fixed.
- The PCO₂ is a dynamic component which can be calculated from pH and alkalinity (Langmuir, 1997). In a system open to the atmosphere, the PCO₂ would be defined as 10^{-3.5} atm. However, the calculated PCO₂ is usually greater than atmospheric in the alluvial groundwater and should thus be treated as a closed system where the PCO₂ is allowed to vary. While the PCO₂ was fixed in the Well DD simulations, the PCO₂ was allowed to vary in the inverse modeling (Section 6.1). The initial well DD water is oversaturated with respect to calcite (SI = +0.13) and in equilibrium with gypsum (SI = -0.01). However, in the PHREEQC input file, calcite is being forced to precipitate to equilibrium by setting the SI value to 0 during the simulation. Due to various kinetic limitations on calcite precipitation, calcite oversaturation is commonly observed in groundwater¹, as was predicted for the initial groundwater at Well DD. Forcing calcite to equilibrium in the model is not consistent with the natural groundwater conditions. When calcite is allowed to remain oversaturated the model no longer predicts gypsum dissolution and calcite precipitation, but rather both calcite and gypsum are predicted to precipitate.

In PHREEQC, solid phases are input as moles/L of water (essentially the same as moles/kg water) of pore water (Parkhurst and Appelo 2013). However, it was stated (Page 31) that the molal concentration of calcite used in the model (0.2 molal) is based on 2 weight percent of calcite present in sediments. Converting 2 weight percent (20,000 mg/kg) to a molar basis (formula weight of calcite = 100 g/mole) results in 0.20 moles/kg. In PHREEQC, the required input unit (moles/L) is calculated by multiplying the concentration on a mass basis (moles/kg) by the ratio of the bulk density to the water filled porosity.² Using the particle density for quartz (2.65 g/cm³) and a reasonable water filled porosity of 0.30, the corresponding bulk density is 1.86 g/cm^3 . Multiplying the mass basis concentration (0.20 moles/kg) by the ratio of the bulk density correct value of 1.24 moles of calcite/L. It is unclear how the input concentration of 0.0135 molal for gypsum (Page 31) was derived. However, using the same approach for gypsum (formula weight = 172 g/mole) and assuming a content of 1% by weight (Page 31), a more approximate correct value would be 0.5 moles of gypsum/L.

The same HFO content is being used interchangeably with different units: the input of 0.089 g HFO/kg H_2O (Page 31) and a "measured" content of 0.089 g HFO/kg sediment (Page 32). Assuming the starting point should be 0.089 g HFO/kg sediment, a more correct approximate HFO input (using the bulk density and porosity assumptions above) might be closer to 0.0052 moles HFO/L. This takes into account that ferrihydrite is defined as Fe(OH)₃ in the Minteqv4.dat database (106.85 g/mole) and used to represent HFO. The mass of HFO under the SURFACE keyword should represent grams of adsorbent (equal to g/L in PHREEQC), rather than g/kg sorbent. Therefore, the mass of adsorbent would be 0.089 g/kg x (1.86/0.3) = 0.55 g/L.

¹ See Amrhein et al. (1993); Doner and Pratt (1969); Inskeep and Bloom (1986); Kavanagh and Rayment (1990); Suarez (1977); Suarez and Rhoades (1982); Reddy et al. (1990); Suarez et al. (1992).

² See "Frequently Asked Questions for PHREEQC and Phreeqci" (Topic No. 182). https://water.usgs.gov/water-resources/software/PHREEQC/Frequently%20Asked%20Questions%20for%20PHREEQC%20and%20Phreeqcl.pdf

Adsorption Calculations

The report states (Page 33) that "Competition of adsorption sites between dissolved calcium and uranyl cation $(UO_2^{2^+})$ present on HFO is a viable exchange reaction that results in uranyl desorption from alluvial sediments at well DD", and that "variable concentrations of dissolved calcium..." are likely a combination of **both** the gypsum-calcite equilibria and groundwater mixing. Thus, it is recognized that calcium could increase even in the absence of the gypsum-calcite equilibria proposed. But while the model demonstrates the relative strengths of adsorption, it does not directly support a desorption mechanism for the release of uranium. The model uses water from Well DD which has already been geochemically modified, and then reacts the water with HFO in the presence of calcite and gypsum. It seems that a more appropriate input file would be to equilibrate native groundwater with HFO, then react that surface with the upgradient mixture to evaluate whether uranium desorption causes increased uranium in solution. In this manner, the competitive effects of the various constituents can be evaluated in a manner consistent with the conceptual model.

PHREEQC Mixing Simulations

- For the simulation using Well P, it is stated that the mixing fractions for Well P and mine discharge were determined from uranium measured at Well DD and Well P. It seems that using the uranium concentration from the well whose composition is being simulated would bias the resulting composition of the mixture itself.
- It is also stated that uranium is conservative and appropriate to determine fractions at Well P, which seems inconsistent with other statements regarding attenuation by calcite and HFO.
- Unlike the initial Well DD simulations, the mixing file does not specify the mineral contents (calcite and gypsum) which have been referenced throughout the report. Rather, they are unspecified, upon which PHREEQC defaults to an excess of mineral (10 moles/L) which is not consistent with the initial modeling approach. Both the mine water and Well P are oversaturated with respect to calcite, but in the model, calcite is forced to precipitate and the PCO₂ is arbitrarily fixed, rather than being allowed to vary with chemical reactions.

Section 6.1 Inverse Geochemical modeling

- While the report describes geochemical conditions in the groundwater system as being "dynamic and complex", it was stated that "chemical kinetics are not included as part of the inverse modeling presented in this report." On the contrary, chemical kinetics should be taken into account when modeling such a dynamic system, rather than use of a simple equilibrium model.
- Six of the twelve resulting models required dissolution of uranophane, but it was noted that groundwater is undersaturated with respect to uranophane and therefore the mineral is unstable. However, this does not confirm *"that mine water discharges are the dominant source of dissolved uranium"*. The fact that uranophane is undersaturated in the groundwater and consequently "unstable" indicates the mineral would dissolve rather than precipitate, which is consistent with 50% of the resulting models that included uranophane dissolution. Therefore, it seems possible that the dissolution of uranophane (or uraninite or other analogous phase) could be a source of uranium based on the inverse modeling results.

• The report acknowledges "It is reasonable to assume that trace concentrations of potential and assessable uranium(IV) solids have partly or completely oxidized and dissolved to form uranium(IV) aqueous species....that have become mobilized in oxidizing alluvial groundwater at wells DD, DD2, and at other monitoring well locations". If these minerals have only partially oxidized, then a portion of them could still remain. Additional discussion is warranted on the validity of the twelve models and why the results indicate mine water is the dominant source of uranium at Well DD.

Conclusion Statements Associated with the Geochemical Modeling

- Page 23 states (with similar discussion on Page 37) "Dissolution of gypsum in equilibrium with calcite provides additional dissolved concentrations of calcium that drives precipitation of fresh calcite that can potentially sequester stoichiometric concentrations of the uranyl cation (UO₂²+) through coprecipitation". In addition, Page 48 states "Dissolution of gypsum in equilibrium with calcite is the major source of increasing dissolved concentrations of calcium and sulfate measured at several alluvial monitoring wells". However, these statements are not supported by the modeling, which does not predict an increase in dissolved calcium or an increase in adsorbed calcium in the presence of calcite and gypsum. Evaluation of the original Well DD output file shows that gypsum dissolves, calcite precipitates, and some calcium becomes adsorbed. The final dissolved calcium concentration is slightly lower due to adsorption and precipitation, where the adsorbed calcium can potentially displace adsorbed uranium into solution. Much of the calcium released by gypsum dissolution is consumed by calcite precipitation and to a lesser extent by adsorption. When the file is run in the absence of calcite and gypsum, the adsorbed and dissolved calcium fractions are actually greater. Therefore, the system behaves almost identically with respect to dissolved and adsorbed calcium concentrations, whether gypsum dissolution in the presence of calcite is simulated or not.
- All geochemical modeling calculations assume chemical equilibrium and ignore chemical kinetics, which is not consistent with the groundwater system being described as demonstrating "transient" and "dynamic" geochemical conditions (Page 48).
- The report states "Either desorption of uranium(VI) complexes or oxidative dissolution of uranium(IV) minerals is a minor or secondary process contributing soluble uranium to groundwater at well DD and DD2". Additional discussion is warranted regarding the relative contribution of uranium mass to groundwater from mine water versus native solids, especially with respect to the inverse models which included uranophane dissolution.
- Page 50 states "Results of PHREEQC simulations confirm that partial dissolution of gypsum in equilibrium with calcite contribute increasing concentrations of dissolved calcium and sulfate to alluvial groundwater at wells DD, DD2, and other monitoring wells completed in the alluvium". As discussed above, the PHREEQC model does not confirm this; rather calcite was forced to precipitate in the models, and regardless, the model does not predict an increase in dissolved calcium or an increase in adsorbed calcium in the presence of calcite and gypsum.
- Page 50 states "Based on results of PHREEQC simulations, calcium (Ca²⁺) concentrated in alluvial groundwater effectively exchanges with weakly adsorbed uranyl cation (UO₂²⁺) associated with strong-binding sites present on HFO, which provides a secondary or minor source of dissolved uranium at well DD". The PHREEQC modeling did not simulate exchange or desorption of constituents from

natural sediments upon reaction with groundwater-mine water mixtures. Rather, only a single equilibration will Well DD onto fresh HFO was simulated. The results indicated more adsorption of calcium compared to uranium, but does not evaluate the overall competitive effects between dissolved constituents in the inflowing groundwater and those already present on the surface of the HFO from long-term equilibration with natural groundwater. More importantly, the model uses water from Well DD in a series of reactions to explain the genesis of water in Well DD, which is counter-intuitive. Results from additional mixing models and inverse models also cannot be used to support this statement because adsorption reactions were not included in those model simulations.

- Page 50 states "Results of PHREEQC simulations, mixing mine-water discharges with wells P and SMC-08/916 groundwater, confirm that precipitation of calcite drives partial dissolution of gypsum under equilibrium conditions". In the models, calcite was forced to precipitate from a naturally-occurring oversaturated condition to an equilibrium condition by arbitrarily changing the saturation index value to 0. Some inconsistency was also observed where the Well DD simulation considered the actual measured mineral contents (which do not seem to be calculated correctly), and the mixing calculations assumed an excess of mineral content. The proposed precipitation of calcite which drives gypsum dissolution is stated to occur "under equilibrium conditions" in the model, whereas the report states that the actual groundwater system being simulated is "dynamic and transient".
- Page 50 states "Results of inverse modeling using PHREEQC to produce groundwater chemistry measured at well DD are considered relevant for the purpose of confirming that mine-water discharges are most likely the dominant source of dissolved uranium present in alluvial well DD". Previous discussion acknowledges the desorption of uranium from sediments as a potential source to groundwater, and the Well DD simulation included adsorption to HFO, yet those adsorption reactions were not included in the inverse modeling. In 50% of the models, dissolution of a solid phase uranium mineral was required for mass balance of uranium. Additional detailed discussion and presentation of the mass balance from the inverse models are needed to support the statement that mine water discharges are "most likely the dominant source of dissolved uranium present in Well DD".

Review Summary

There are a number of conclusions made about the occurrence of uranium in groundwater at well DD that are based upon assumptions that should be further clarified in the report. As such, we suggest that the following be considered and the language in the report be adjusted to address these concerns about uncertainties and assumptions in the report:

- The conveyance ditch is observed in the aerial photographs, however its role in transport of water from San Mateo Creek to the area adjacent to well DD is not known. While the report discusses the total volume associated with the mine water discharge, no analysis is provided on the hydrology to support the assumption of surface flow in the Lower Basin.
- 2. There are other possible explanations for the transient geochemical conditions observed at well DD, including recent changes to hydraulic conditions at the well and interaction of groundwater with the vadose zone, and these transient geochemical conditions were not evident prior to 2004 when the groundwater quality data here was used in the background data set.

- 3. Use of the data from and IX system in Ambrosia Lake, from the Perkins and Goad, 1980, report to represent water quality that possibly infiltrated into the alluvium near well DD is not based upon any measurement taken of water quality by well DD in 1976; the data is therefore used for to represent "hypothetical" water quality for the purpose of the geochemical modeling exercises.
- 4. Mixing ratios for hypothetical mine water with hypothetical background water quality were performed to match concentrations of uranium and sulfate currently observed at well DD, but do not have any basis in groundwater hydrogeological conditions.
- 5. Groundwater monitoring well SMC-08/916 was selected for use in the geochemical modeling work as representing water quality with low concentrations of uranium as compared to well DD, however, there is not any basis to assign this well as being representative of background due to the heterogeneous nature of the alluvial aquifer geological/lithological and hydrogeological conditions.
- 6. Prior work reported by Arcadis (2018, 2019) on leaching of uranium from aquifer sediments collected near well DD and DD2 was used to demonstrate that uranium is present in the sediments and is leachable, however, the leach tests were not performed to simulate the solid-solution ratio relevant to a fully-saturated aquifer system and therefore the concentrations that were noted from the leach tests do not indicate that other sources of uranium other than natural sources are required to produce the uranium concentrations in groundwater observed at well DD.
- 7. The well DD PHREEQC input file contain errors in the definition of mineral contents and erroneous assumptions regarding certain geochemical constraints (pH, PCO₂, and calcite saturation). Upon revision of these inputs to more accurately reflect Site-specific conditions, the model results do not support the conceptual model of gypsum dissolution in the presence of calcite. Calcium concentrations are not predicted to increase, nor is the resulting desorption of uranium from alluvial sediments by calcium demonstrated by the model. Some inconsistencies were observed between all PHREEQC models with respect to mineral content, simulation of adsorption, and other geochemical constraints.

Finally, due to the heterogeneity of the alluvial aquifer at the GRP, it is essential that groundwater quality data associated with well DD, representing the western side of the alluvial system upgradient of the GRP, be included in the background data set. The background data set currently includes monitoring well locations spaced across the upgradient alluvial aquifer system, from west to east across a highly complex, heterogeneous system in terms of lithology and water quality. Exclusion of the water quality data from west side of the alluvial system in the background data set will result in flawed background water quality standards and will not represent the range of conditions associated with background encountered upgradient of the GRP, and ultimately on-site at the GRP.

References

Amrhein, C.A., M.F. Zahow, and D.L. Suarez, 1993. Calcite supersaturation in soil suspensions. Soil Science. 156:163-170.

- Arcadis, 2018. Evaluation of Water Quality in Regard to Site Background Standards at the Grants Reclamation Project. Prepared by Arcadis on behalf of Homestake Mining Company of California. September, 2018.
- Arcadis, 2019. Draft Supplemental Background Soil and Groundwater Investigation Report. Prepared by Arcadis on behalf of Homestake Mining Company of California. August 2, 2019.
- Doner, H.E. and P.F. Pratt, 1969. Solubility of calcium carbonate precipitated in aqueous solutions of magnesium and sulfate salts. Soil Science Society of America Proceedings. 33:690-693.
- Inskeep, W.P. and P.R. Bloom, 1986. Calcium carbonate supersaturation in soil solutions of Calciaquolls. Soil Science Society of America Journal. 50:1431-1437.
- Gallaher, B.M., and S.J. Cary, 1986. Impacts of uranium mining on surface and shallow ground waters, Grants Mineral Belt, New Mexico. New Mexico Environment Improvement Division, New Mexico Health and Environment Department, Santa Fe, New Mexico. 180 pp.
- Kavanagh, A.M. and T. Rayment, 1990. Inhibition effects on calcite growth at low supersaturations. J. Chem. Soc. Faraday Trans. 86:965-972.
- Langmuir, D.L., 1997. Aqueous Environmental Chemistry. Prentice-Hall, Inc. New Jersey. 600 pp.
- Longmire, P., 2020. Geochemical Conceptual Site Model and Batch-Equilibrium modeling of Alluvial Groundwater at Monitoring Well DD, Homestake National Priorities List Site, Cibola and McKinley Counties, New Mexico. Ground Water Quality Bureau, New Mexico Environment Department. September 11.
- NRC, 2006, Correspondence from Gary Janosko (U.S. Nuclear Regulatory Commission) to Alan D. Cox (HMC), Re: Grants, New Mexico – License Amendment No. 39 to Materials License No. SUA-1471 (TAC LU0122). July 10, 2006 [ADAMS Accession No. ML061710354]
- Parkhurst, D.L and C.A.J. Appelo, 2013. Description of Input and Examples for PHREEQC Version 3 A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43.
- Perkins, B.L., and M.S. Goad, 1980. Water quality data for discharges from uranium mines and mills in New Mexico. NM Health and Environment Department, Environmental Improvement Division, Water Pollution Control Bureau, 87 pp.
- Reddy, K.J., W.L. Lindsay, S.W. Workman, and J.I. Drever, 1990. Measurement of calcite ion activity products in soils. Soil Science Society of America Journal. 54:67-71.
- Suarez, D.L., 1977. Ion activity products of calcium carbonate in waters below the root zone. Soil Science Society of America Journal. 41:310-315.
- Suarez, D.L. and J.D. Rhoades. 1982. The apparent solubility of calcium carbonate in soils. Soil Science Society of America Journal. 46:716-722.
- Suarez, D.L. J.D. Wood, and I. Abrahim, 1992. Reevaluation of calcite supersaturation in soils. Soil Science Society of America Journal. 56:1776-1784.

Ulrich, S., Gillow, J., Roberts, S., Byer, G., Sueker, J., and Farris, K., 2019. Hydrogeochemical and mineralogical factors influencing uranium in background area groundwater wells: Grants, New Mexico. Journal of Hydrology: Regional Studies 26, 100636.

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