1. FORMATION OF CRUSTS BY EVAPORATION OF GOATHILL ROCK-PILE WATER

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2. STATEMENT OF THE PROBLEM

What mineralogical reaction path would occur if pore water, such as that sampled at Goathill Spring evaporated in the capillary zone near the surface, how do the predicted minerals relate to the observed minerals in the crusts on Questa rock piles, and how are these relevant to evaluation of the hydrogeology of the rock-pile system?

Objectives of the study include:

- Developing a simple simulation of the evaporation of pore water that tracks the formation of secondary minerals that form during progressive evaporation in the shallow, soil-like rock near the surface of Questa rock piles.
- Consider the uncertainty in the results that are associated with the solution model.
- Relate the simulation outcomes to observed behavior of the shallow skin of the rock-pile system.

3. PREVIOUS WORK

There are two other DRAs in this series that address relevant aspects of the rock-pile crusts, DRA-8 and DRA-26.

Site-wide chemistry of ground and surface water has recently been evaluated in great detail by the U.S. Geological Survey (Nordstrom, 2007), but these studies did not address the rock piles in detail, nor did they consider the evaporative crusts that exist on rock-pile surfaces seasonally.

The geochemical processes and products that occur during evaporation have been the subject of geochemical research for many decades, beginning with questions about the formation of large-scale marine and non-marine evaporates (e.g., Holland, 1984, 2003; Veizer and Mackenzie, 2005). Quantitative modeling of the evaporation process and its mineralogical products was developed significantly by H.P. Eugster and his students and colleagues (e.g., Eugster and Jones, 1979; Eugster et al, 1980; Harvie et al., 1984; Hardie, 1991). The specific computer approach of this study is that set out by Bethke (1996), based on essentially on the Harvie et al. (1984) approach, which in turn is based conceptually on the Eugster and Jones (1979) work.

Other DRAs related to aspects of water chemistry that are related to this document include DRA-28 (Water Chemistry – Goathill Spring), DRA-29 (Conceptual Model of Hydrogeochemistry), DRA-30 (Simple Thermodynamic Models of Solution Chemistry), DRA-31 (Simple Models of Acid-Base Balance: Controls on pyrite oxidation and neutralization by carbonates and silicates), and DRA-33 (Inverse Mass-Balance Model - Goathill Spring).

4. TECHNICAL APPROACH

Based on data and arguments presented in DRA-28 and -29, this modeling task assumes that water infiltrating the Questa rock piles such as Goathill North quickly take on a pore-water chemistry characterized by low pH, high TDS, high SO_4, and elevated concentrations of Ca and Mg. The water also contains dissolved Fe, derived primarily from oxidation of pyrite and present overwhelmingly as Fe^{3+} because of a high flux of O_2 through the rock pile. Hydrolysis of alumino-silicate minerals in the rock pile yields Al and Si, as well as the Mg, Na, K and some of the Ca. Because $\boldsymbol{a}_{SO42-} >> \boldsymbol{a}_{Ca2+}$ (see DRA-30), there will be a "chemical divide" (Eugster and Jones, 1979). Precipitation of gypsum will deplete the residual solution of Ca but the evapo-concentration drives the $\boldsymbol{a}_{SO42-}$ yet higher, and ultimately saturates the solution in other salts, specifically Mg-sulfates for the solution chemistry of GH Spring. Because of observational evidence of crust formation at and near the surface, and because we are considering the processes to occur very near the surface, we model the solution as being in equilibrium with atmospheric CO_2 and O_2 at all times, and we hold the temperature at 25 C (the only temperature for which the selected numerical databases have valid virial coefficients).

This DRA uses a very simple, idealized model of evaporation of an aqueous solution by "reverse-titrating" water to progressively concentrate the solution. The model treats the evaporation process as if it were occurring in a system that is closed to all mass except H_2O; it is analogous to models for the evaporation of sea water to produce bedded evaporites (e.g., Eugster and Jones, 1979). The physical system in the rock pile that corresponds to the "basin" in seawater evaporation, is the 1-2 m thick zone of fine-grained, soil-like rock fragments near the surface of a Questa rock pile in which there is significant drying over annual and sub-annual cycles through capillary draw of solution and evaporation (DRA-15).

As the solution becomes more concentrated by evaporation, one approaches saturation of the solution in mineral phases as the calculated activities of the mineral components increase. In the modeling, we consider two models for thermodynamic activity. We use a virial model to account for very high ionic strengths of major ions (Harvie a et al., 2004; Bethke, 1996), however, the data for this model are restricted to the major solutes, and do not include parameters for Fe and Al. This model is expected to better simulate the precipitation of major evaporative minerals such as gypsum and one of the hydrated Mg-sulfates. We also have run the model using the Debye-Huckel solution model, in order to evaluate the effects of evaporation on precipitation of iron minerals, which can be observed in the field (DRA-8) and to consider clay minerals (alumino-silcates).

The modeling approach used in this study is based on the approach and uses the methods described by Bethke (1996, p. 270-276). The calculations were made with the computer program React in the Geochemist's Workbench suite of computer programs, release 6.0.4 (Bethke, 2006). For the virial-model case, we use the PHRQPITZ database, and for the unconstrained Debye-Huckel model, we use the WATEQ4F database that is the default database for React. The sub-models and their stepwise development are:

- Define a hypothetical reference volume (conceptually, pore space in the fine-grained sediment near the rock-pile surface). The volume is sufficient to encompass 1 kg of initial solution. The initial solution is the nominal solution chemistry form GH Spring (Table 1 below).

- In 100 equal increments, remove a total of 996 g of water. The remaining mass of water will be tied up in hydrated minerals, so this is equivalent to mapping the solution – solid chemistry to complete dryness.
- At each step, the computer revaluates the solution composition, determines the distribution of species, calculates the saturation indices, removes mass that would expected to precipitate at equilibrium, and transports the residual solution onward without back-reaction.
- A post-processor integral to the GWB software plots the volume or mass of minerals precipitated as a function of the changing mass of water in the system. Additional computations track the residual fluid chemistry, and those also can be plotted if wished.
- The modeling process is run twice, once with the PHREEQPITZ database for major components, and again with the standard database to allow evaluation of Al, Si, Fe and other components.

5. CONCEPTUAL MODEL

The conceptual model for these numerical experiments is extremely simple: a system with no specific, real-world boundaries contains 1 kg of water with specified initial chemistry of GH Spring water. This is taken to be equivalent to shallow pore water, of which QRPWASP has no samples for which analytical chemistry was determined. Oxygen and carbon dioxide arte present in the air phase of pore space in the shallow soil near the rock-pile surface. The gases are assumed to exchanges rapidly with water (relative to modeling periods on the order of years), so that the dissolved oxygen concentration of the water is set by the average fugacities of O_2 and CO_2 in the atmosphere. Pure water, as H2O, is numerically titrated out of the solution at a steady rate, effectively concentrating the residual solution. We assume that the minerals, once precipitated are irreversibly removed from the residual solution, as the fluid phase is continually drawn upward by capillary force driven by high evaporation rates at the ground-air interface (DRA-15). Reactions are controlled by the thermodynamic potentials of the relevant components for the designated systems as evapo-concentration advances. When, and so long as, plausible minerals[1] reach saturation indices of 0 (as calculated within the numerical model), the mineral is considered to precipitate

The conceptual model of water chemistry in Goathill North is presented in detail in companion DRAs-28 and -29. Please consider DRA-29 for a detailed analysis of the general hydrogeochemical setting of the rock piles. In this simple modeling study, we consider only the relatively fine-grained, soil-like sediment present at and near the rock-pile surface. Hydrogeological modeling identifies a zone, 1 to 2 m deep, over which expensive drying occurs across annual and subannual cycles, as water under less than atmospheric pressure ("unsaturated") is pulled toward the drier surface, where high evaporation rates exist (DRA-15). The calculations conducted here do not depend on the 1 to 2 m depth or that the

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[1] It is modeler's responsibility to designate mineral phases that can be considered. For example, at temperature near 25 C, if silica precipitates, it will be as a poorly ordered or amorphous SiO_2 phase, not as quartz. The modeler (in the React model) "suppresses" (that is, disallows) quartz and other polymers that do not form from low-temperature solutions.

solution reside sin pore space, only that there is a zone in which high rates of evaporation occur. Because QRPWASP and others routinely observe the precipitation of evaporite minerals on and immediately below the ground surface, it is clear that such evaporation does occur.

The conceptualization of the computational computer model for calculating the virial coefficients (for the PREEQPITZ model) and general activity coefficients for the Debye-Huckel model needed to establish the distribution of species and saturation indices at each computational strep are described in great detail in Bethke, 1996.

6. STATUS OF EVAPORATION EVALUATIONS

6.1 Data

The initial pore water, subject to evaporation at and near the rock-pile surface, is considered for this model to be equivalent to the best-estimate derived form consideration of Goathill Spring (DRA-28, -29).

Table 1 Typical Water Chemistry, Goathill Spring (2001-2007) [mg/L, except pH in su; Alkalinity in mg $CaCO_3$/L; T in °C; Q in L/s] – See DRA-28, -29. Note that for this modeling, temperature is assumed to be 25 C, so Table 1 has been modified from Table 3 in DRA-29.

pH	**Total Alkalinity**	**TDS**	**Si**	**Ca**	**Mg**	**Na**	**K**	**T**
2.78	***< 5***	***20,000***	***50***	***370***	***740***	***9.4***	**2.1**	**25**
Cl	**F**	**SO_4**	**Al**	**Cu**	**Fe (total)**	**Mn**	**Q**	**DO**
29	***91***	***13,750***	***1400***	***10***	***690***	***430***	**0.63**	**7.5**

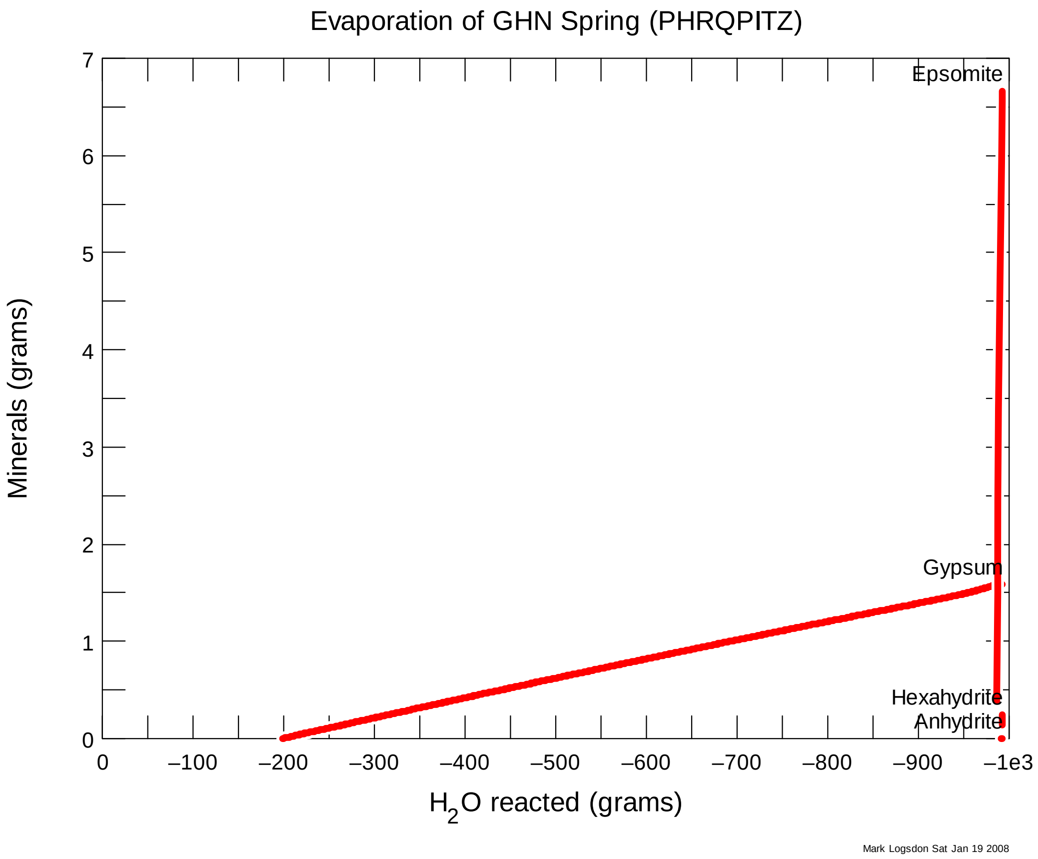
6.2 Results

6.2.1 Virial Models (PHRQPITZ) – Major Components

Modeling results for the virial model of aqueous activities are compiled in Attachment A.

Figure 1 shows the expected mineral-precipitation sequence for the flow-through model evaporation of the GH Spring water, using the PHRQPITZ database. Note that the PHRQPITZ database does not include Al, Cu, F Fe, Mn Si, or F and does not address redox chemistry. It does, however, better represent the interactions in solution between dissolved components for the major ions, and therefore is expected to give a better representation of the timing of precipitation (i.e., with respect to degree of evaporation) and better reflect proportions, too, than would be accomplished with a Debye-Huckel solution model.

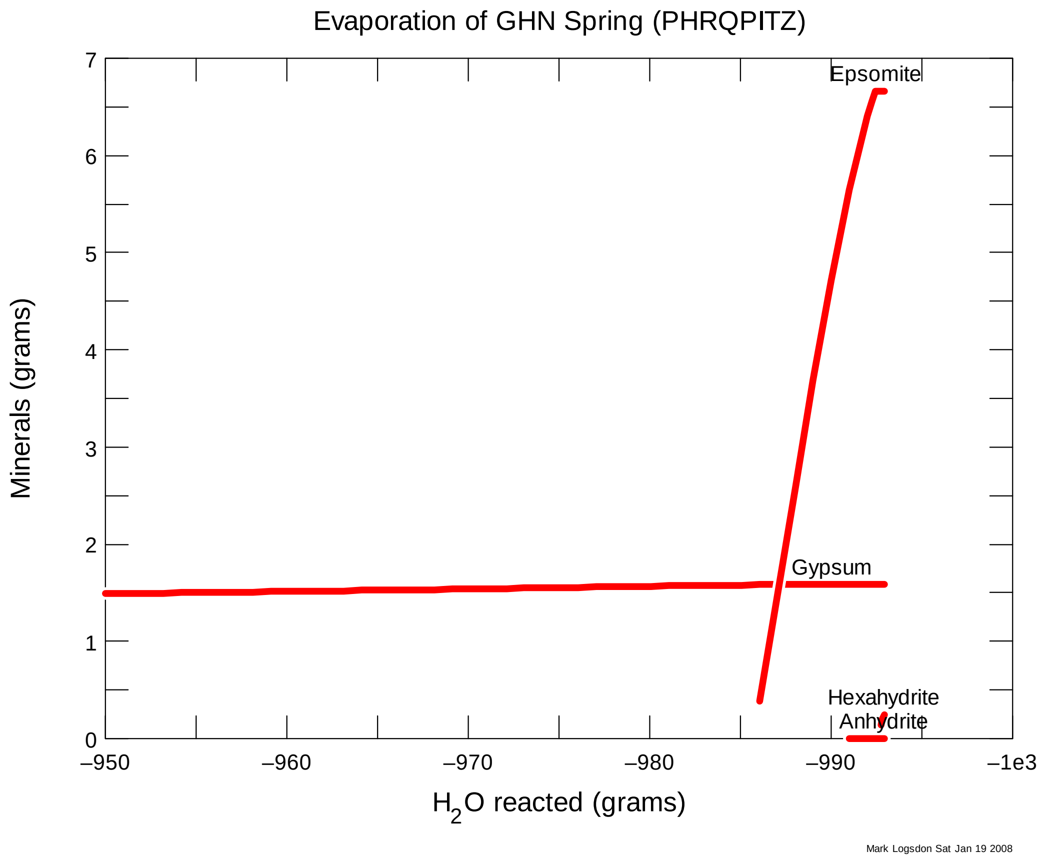
Figure 1 Minerals Precipitated (grams) During Progressive Evaporation of GH Spring Water [PHRQPITZ database]



The model produces a simple projected mineralogy. When the Goathill Spring water is about 20% evaporated (200 grams of the original 1000 grams have been removed), the solution achieves saturation with gypsum. The water continues to precipitate gypsum ($CaSO_4.2H_2O$) to nearly complete dryness. At very high evaporation rates, additional phases (the multi-hydrated Mg sulfates, epsomite and hexahydrite) reach saturation, and very large masses of Mg sulfate are precipitated if evaporation continues to completion. Note that anhydrite, the anhydrous equivalent of gypsum is predicted.

In order to better understand the late-stage products, Figure 2 expands the scale of the highly-evaporated portion of Figure 1.

Figure 2 Minerals Precipitated (grams) Between 95% and Full Evaporation of GH Spring Water [PHRQPITZ database]



The appearance of anhydrite ($CaSO4$) in place of gypsum ($CaSO4.2H2O$) and hexahydrite ($MgSO4.6H2O$) in place of epsomite ($MgSO4.7H2O$) at the extreme right-hand side of the figure is due to the decrease in the calculated activity of water (a_{H2O}) in the late-stage. When the model finds that a_{H2O} is too low, the higher hydration-state mineral becomes unsaturated, and the next-lowest hydration state takes its place in the computations.

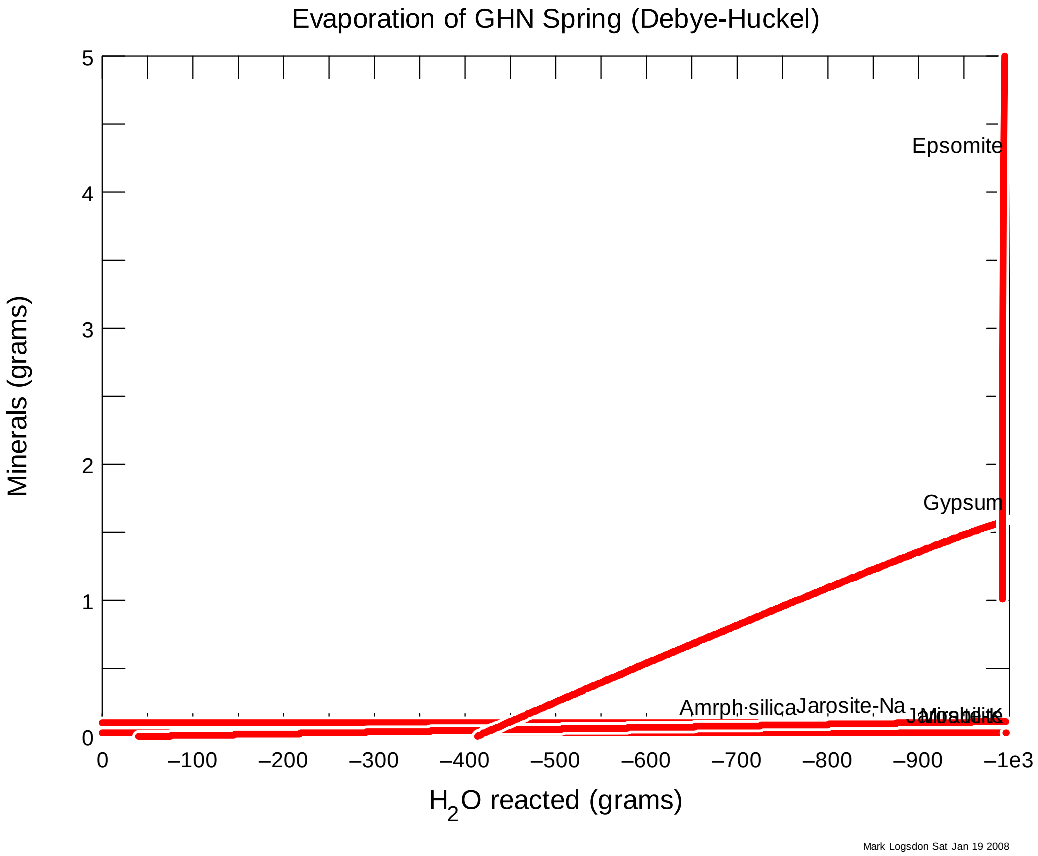
The essential outcome of the PRQPITZ model is that that crusts formed on Questa rock piles should be dominated by gypsum, which begins to precipitate at low rates of evaporation, and a magnesium sulfate when evaporation rates are very high.

6.2.2 Debye-Huckel Model (WATEQ4F) – Including Si, Al, F and Fe

Modeling results for the Debye-Huckel solution model are compiled in Attachment B.

Figure shows the predicted precipitation sequence of the GH Spring water is evaporated to dryness, using the thermodynamic data from WATEQ4F. The second model is presented both to show the comparability and differences based on how the activity coefficients are handled, and also to examine possible phases that cannot be modeled with PHRQPITZ data

Figure 3



Note that the Debye-Huckel model also predicts precipitation of gypsum, with precipiutation of epsomite in very late-stage evaporation. However, using the Debye-Huckel activity model, precipitation of gypsum does not begin until approximately 40% of the solution has evaporated.

Because the database for the Debye-Huckel model (WATEQ4F) includes Fe, Si, Na, and K, and can handle redox reactions, the Debye-Huckel model predicts additional phases that cannot be calculated using PHRQPITZ and its underlying solution model. Specifically, the Debye-Huckel – based model predicts precipitation of jarosite [$(K,Na)Fe_3(SO_4)_2(OH)_6$] and amorphous silica. These minerals are consistent with the saturation-index predictions for GH Spring calculated in DRA-30. Because the modeled pH is low and the activity of SO_4 is very high (and rising as evaporation proceeds), jarosite, rather than goethite, is predicted as the sink for ferric iron. As with the raw GH Spring ca;lculations, the pH of the solution during evaporation remians below 4, and no Al-bearing phases are predicted as stable. As the solutioon evapo-concentarted, compexation between F and Al (and other residual cations) woulkd increase, and no fluoride-bearing mineral is predicted to precipitate. In such waters, the analytical concentration of F, were it measured, would be extremely high.

6.3 Consistency of the Modeling Results with the Conceptual Model

Water flowing from the rock pile at GH Spring is a low-pH solution, high in SO_4^{2-} (and balancing cations, mostly Ca and Mg). It also contains high concentrations of Fe, Si, Al and other dissolved components.

During dry periods, crusts form over large portions of the surface of the rock piles (DRA-8). As evaporation proceeds during extended dry periods, especially when the air also is warm, the crusts become harder and extend to greater thickness, indicating a progressive change in texture. Field observations and mineralogical examination (MSC, 2008) clearly identify gypsum precipitation, and a simple "taste test" of white alkaline crusts that appear in high-evaporation periods shows the characteristic bitter taste of magnesium sulfates such as epsomite. The orange to yellow caste commonly observed in portions of the crusts indicates ferric hydroxides or hydroxysulfates such as jarosite. These ferric phases are confirmed in thin section and X-ray diffraction analysis (DRA-8; MSC, 2008).

Therefore, the modeled results of this study are very consistent with respect to the empirically documented evaporative crusts, the modeled results. The presence of evaporative crusts is consistent with the numerical modeling results of a shallow zone of high evaporation (DRA-15). It should be noted that the presence of such crusts, which – because they formed by high evaporation - also can be readily dissolved during precipitation events, is an essential element of the modeling of the upper boundary condition of the hydrogeologic model. The modeled behavior of the crusts is essential to the water balance of the modeled rock pile, and therefore to all subsequent evaluations of the amount of infiltration and the moisture content/pore pressure conditions throughout the rock pile (DRA-15). Only a rapidly reversible chemical precipitation process such as that modeled here has the capacity to represent the changes over short time periods during annual cycles that is needed to produce a plausible flow model for the rock piles. The seasonality and correlation with meteorology of the observation formation and break-up of the crusts essential guarantees that the driving chemical potential in the processes is related to changing the activity of water, through evaporation or re-dissolution.

The detailed mineralogical analysis by thin-section petrography and supportive X-ray diffraction is supportive of this model in most respects, as described above. However, the detailed petrography identifies discernible quantities of smectitic clay in the crusts (MSC, 2008). There is abundant petrographic evidence for smectite (and other clays) in the hydrothermal assemblages at Questa (DRTAs-1,-3,-4, and -5), and other alumino-silicate minerals identified in the rock fragments that are assimilated into the crusts are certainly primary igneous or hydrothermal phases. However, the amount of smectite observed in the crust samples is distinctly higher than in most other petrographic descriptions for other parts of the rock pile (DRA-5).

The models calculated here do not show smectites or any other clay minerals as stable in the projected solution chemistry. As discussed here and also in DRAs-28, 29, and 30, the modeled instability of clays is driven significantly by the low pH of the modeled solutions (as well as by high proportions of Al^{3+} complexed with SO_4 and F). However, as can be seen from the large masses of "epsomite" projected for high evaporation rates, the solutions in the shallow zone during evaporation will have very high $\boldsymbol{a}_{Mg2+}$, and it is imaginable that there could be a diagenetic transformation of clay minerals through some process of ion-exchange. In addition, if there were micro-environments in the shallow soil in which the pH locally was buffered to > 5, then the Al-Si-Mg of the concentrating waters would be entirely compatible with the local precipitation of a clay-like mineral. Because any such mineral formed in this environment at low temperature likely would be amorphous or very finely crystalline, it would be hard to identify, except perhaps by the kind of high-resolution X-ray analysis performed by MSC (using the University of British Columbia facilities). Because the crusts form in only the shallowest part of the rock pile, even if clay minerals such as smectite can form (by precipitation or exchange), that would not affect the intermediate and deep portions of the rock piles, which are the focus of the geotechnical evaluation of the QRPWASP. Evaluation of this petrographic hypothesis for smectite formation would require extensive study, experimentation, and analysis

6.4 Assumptions

The major assumptions of this analysis are that the water analyses form GH Spring and the petrographic analyses of the rock-pile and scar samples are sufficiently accurate and precise to be useful. We also assume that the thermodynamic data used in the computer calculations are reliable. The water chemistry has been developed under established quality-assurance and quality control programs at laboratories that have records of reliable analytical chemistry. The databases used (PRQPITZ and WATEQ4F) are carefully peer-reviewed and widely applied, and are considered entirely sound for the simple nature of this model.

6.5 Major Results Affecting Understanding of Mineral Stabilities in the Rock Pile

The results of the very simple heuristic model strongly supports a dynamic environment for formation and dissolution of evaporative crusts on rock piles. The projected mineralogies – gypsum dominant during initial evaporation, with small quantities of jarosite and amorphous silica, and magnesium sulfate in late stages - is very consistent with the field petrography and laboratory mineralogy. If pore water were much more dilute than GH Spring, precipitation of gypsum and late-stage salts would not occur to the extent and with the early onset observed. Leaching crusts with de-ionized water produces a low-pH solution (DRA-26), consistent qualitatively with the use of the GH Spring water, and the absence of clear evidence for newly-formed clay minerals is generally supportive of a low-pH pre water environment undergoing evaporation.

Note that for a nominal annual evaporation across the rock pile of about 60% (DRA-15), the expected evaporative mineral would be gypsum, with jarosite also precipitating to provide the orange-yellow caste common in the crusts. Under especially dry conditions, annually or over longer cycles, Mg sulfates could be expected; under wetter than average conditions, the amount of gypsum precipitation would decrease and locally gypsum would dissolve. These generalities correspond well with site experience.

The hydrogeologic implications of such evaporative crusts is evaluated in DRA-15.

7. RELIABILITY ANALYSIS

The principal technical uncertainty in this analysis is the extent to which the water chemistry obtained from a saturated zone deep in the pile represents the unsaturated-zone pore water in shallower parts of the rock pile. Please see DRAs 28 and 29 for further discussions of this matter. At this time, we consider that the balance of the geochemical evidence is that the geochemical results of open-system oxidation and transport of reaction products calculated in DRA-31 apply to almost all of the rock pile for all times beyond a few years to perhaps a decade.

The best approach to resolving the residual uncertainty about vadose-zone water chemistry for use as a starting water for evaporation calculations would be to develop a technique for sampling unsaturated-zone water (for example via suction lysimeters in fine-grained zones) for direct chemical analysis. This could only be done plausibly during wet conditions, as under the dry-end of the soil moisture that corresponds with these calculations of evaporation it would be impossible to extract sufficient water to analyze form reasonably sized samples of sediment.

Additional modeling is very unlikely to change the general results of this study, and the general nature of the projected mineralogy is not sensitive to the choices of thermodynamic databases.

8. CURRENT CONCLUSION

Based on current thermodynamic calculations, it is highly likely that water chemistry in a mined rock pile such as that at Goathill North will evolve rapidly (over periods of a few years to a few decades) to low-pH, high sulfate solutions that would dissolve, not precipitate clay minerals. These reactions arise because of the rapid oxidation of pyrite in a system that is open to oxygen, for all rock types (such as the Questa rock piles) that have a relatively small reservoir of carbonate minerals. Such waters have the potential to precipitate secondary cements (ferric hydroxides and hydroxysulfates and silica). Such mineralogical outcomes would be unlikely to reduce internal friction by producing new clay minerals.

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