

1. INVERSE MASS-BALANCE MODELING OF GOATHILL ROCK-PILE WATER

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2. STATEMENT OF THE PROBLEM

What are the rates of mineral dissolution in the bulk Goathill North rock pile, based on water discharging from the base of the pile, and how are these relevant to understanding mineral and rock weathering as they may affect shear strength of the rock pile?

Objectives of the study include:

- Applying the principles of mass-balance modeling to the steady-state flow and chemistry observed in GH Spring.
- Calculating the rates at which pyrite, feldspars (alkali and plagioclase), phyllosilicates (sericite and chlorite), and epidote dissolve along flow paths integrated over the entire rock pile.
- Comparing the calculated rate of pyrite oxidation and alumino-silicate dissolution in the bulk rock pile to laboratory-measured value (including published values and values calculated by this project in its program of humidity-cell testing)
- Evaluating the modeled rates of bulk reaction integrated across the rock pile in terms of Project observations of petrography and in terms of implications for overall rates of mineral transformation that could affect shear strength.

3. PREVIOUS WORK

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. Rock-pile weathering was considered by URS (2002) in terms of equilibrium-constrained reactions (see DRA-30), but the simple equilibrium approach did not, of course, attempt to address rates of weathering or the implications of weathering rates on the evolution of the rock piles.

Mass-balance modeling of natural waters has a long geochemical history. The most well-known example is the classic analysis of Sierra Nevada spring waters by Garrels and Mackenzie (1967). A recent review article (Bricker et al., 2005) summarizes much of the relevant background work and theory, including the computerization of the calculational approaches pioneered by the USGS for groundwater studies and watershed investigations (e.g., Plummer et al., 1983; Bowser and Jones, 2002, Nordstrom, 2005).

Other DRAs related to aspects of water chemistry that are closely 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), and DRA-31 (Simple Models of Acid-Base Balance: Controls on Pyrite Oxidation and Neutralization by Carbonates and Silicates). The presentation and analysis in DRAs -28 and -29 of water chemistry from GH Spring and the conceptualization of those flows as

representing a steady-state condition that integrates a significant portion of the total flow through Goathill North rock pile is essential background to this DRA..

4. TECHNICAL APPROACH

This DRA uses the very simple approach pioneered by Garrels and Mackenzie (1967). We apply the approach to low-pH, high-TDS flows from Goathill Spring (GH Spring). Because empirical evidence all over the world shows that meteoric precipitation is very dilute, we infer that the currently observed water chemistry is the result of mass-transfer between infiltrating solutions and the minerals that are encountered along the flow path (DRAs -28, -29, and -31). The reactions may include both dissolution and secondary precipitation reactions (DRA-30 and -31). The focus of the Project's geochemistry is on reactions that could affect shear strength, especially reactions associated with the putative initiating reaction, pyrite oxidation and generation of acid-rock drainage. Therefore, for this mass-balance study, we concentrate on reactions that have the potential to (a) oxidize pyrite and generate acidity; (b) generate low shear-strength clay minerals, or (c) to precipitate secondary minerals that can act as cements to increase cohesion.

The mass-balance approach looks at observed solution chemistry in terms of the mass of specific components (e.g., Fe, SO₄, Mg, Al etc.) as related to the stoichiometries of specific minerals and their dissolution and/or precipitation reactions. The observed mass of Mg in effluent from rock pile, for example, must relate to the amount of Mg released by the dissolution of some Mg-bearing mineral(s), modified by the amount of Mg that may have precipitated, if any, as a component of a secondary Mg-bearing phase. The mass of Mg (per unit time, for example, per year) is taken to be the concentration of Mg in the discharging effluent (M.V⁻¹, e.g., mg/L) times the volume of fluid discharged (V, e.g., L/a). Physical mass of Mg is related to moles of Mg through the atomic weight of Mg, and mass of minerals to the moles of minerals through the gram-formula weight of the mineral. For example, one mole of Pyrite (FeS₂ – one mole of Fe and two moles of S) has a mass of 119.98 g. Finally, the moles of component species (Fe, SO₄, Mg, etc.) involved in reactions are related to the moles of those components through the relevant stoichiometric coefficients for the mineral(s) in question. The calculations are developed and applied in a very simple EXCEL spreadsheet, a modeling tool that we consider is at the appropriate level for the nature of the issues and the data.

The studies of this Project, following from the early considerations of environmental geochemistry that led to the Project, show that the most important factor to evaluate is the oxidation of Pyrite, as it is the release of H⁺ ions from this reaction that are able to hydrolyze the alumino-silicate minerals, potentially forming clay minerals. Because Al is an essential component in clay minerals, the rate and extent of hydrolysis of parent alumino-silicates is essential to an understanding of the rate at which any such clay formation could possibly occur. Therefore, this mass-balance study concentrates on pyrite oxidation (and its consequences) and on the dissolution as the major alumino-silicate minerals of the Questa rocks. Because we use observed effluent chemistry and flow (and include the effect of precipitated ferric hydroxysulfate that is now present as a secondary mineral) to estimate the amounts of minerals that are undergoing dissolution (and/or precipitation), the methodology is called an “inverse” model. A forward model, which would start with a mass of minerals

and a set of defined reactions would predict effluent chemistry. Examples of forward models are presented in DRAs -31 and -32.

For example, if one had a steady effluent containing 200 mg/L SO₄ at 1 L/s, the total mass exported by the system would be 6.30E+06 g SO₄/a, or 6.56E+04 mol SO₄/a. Assume for the sample calculation that the source of SO₄ is exclusively from the dissolution of pyrite (FeS₂). One mole of pyrite yields two moles of SO₄, so the observed effluent system can be inferred to represent 3.28E+04 mol Pyrite oxidized. This is 3.96E+06 g (or 3.96 tonne) of Pyrite oxidized per year. Suppose now that the system for which the calculation is being done had a total mass of 1 million tonnes, with an average initial Pyrite concentration of 1 wt%. Then the initial Pyrite mass in the pile would be 1.00E+04 tonne Pyrite, and the apparent rate of pyrite depletion would be 3.96E-04 tonne/a, or 4 one-hundredths of one percent per year.

The initial mineralogy of the rock pile is taken, for the simple models in sequence DRA-28 to -33, to be that given in DRA-29 (repeated as Table 1 of this DRA). We further assume that in the current rock pile, the average concentrations of key secondary reaction products are as Jarosite and Gypsum; QRPWASP geochemists estimate, based on field observations of circum-neutral layers with little or no observable Jarosite or secondary Gypsum in the interior of the rock pile, that bulk concentrations of both secondary sulfate sinks is 0.5 wt% (V. Lueth, personal communication, September 2008). Effluent chemistry from the rock pile is taken to be a steady-state chemistry exemplified by GH Spring, with a steady flow of 0.6 L/s (7 gpm), as discussed in DRA-28. Other studies undertaken by this Project have shown that the current hydrogen-ion balance of the solutions in the rock pile is an essential control on the stability of minerals that are reasonable candidate models for the mass-balance considerations of this approach (DRA-29). We assume that the rock pile to be considered has the dimensions and characteristics of GHN. Therefore, the model pile has a total mass of 16 million tons (1.45 Mtonne) with a bulk density of 2E+03 kg/m³ (Chen and Wilson, 2006).

The calculations that support this DRA are presented in their entirety in Attachment 1. The initial chemical and physical assumptions are compiled in the first worksheet (“Basic”). Calculations of pyrite oxidation and its consequences for Fe and SO₄ are in the sheet called “Py_SO4_Fe”. The calculations for alumino-silicate dissolution leading to release of Al (directly relevant to clay formation) are in two sheets, “Mg” and “Al Balance_Other Minerals”. Calculation of the apparent rate of pyrite oxidation and comparison of that rate to laboratory rates is presented in sheet “Pyrite Reaction Rate”. Extrapolations of rate of pyrite depletion by different models are presented in the sheet “Py Leaching Models”.

The choice to use specific mass-balance calculations developed for this site rather than to use a general model developed by others was made to reflect the control of pH on silicate stabilities, as discussed in DRA-28 and-29. Because the mass-balance approach does not consider thermodynamic stability controls, an unconstrained mass-balance model will not recognize that some minerals cannot participate in dissolution or precipitation reactions in this specific system, and therefore returns results that, while mathematically plausible, are not empirically adequate for the solution chemistry and mineralogy of GHN.

5. CONCEPTUAL MODEL

The full-scale conceptual model for GH Spring in the model rock pile is presented and defended in DRA-28, illustrated as Figure 1. We consider GH Spring to represent a seepage zone at steady state chemically and physically, discharging at least 10% and probably 20% of the total annual precipitation on the catchment of Goathill North rock pile (GHN); this is a large proportion of the total infiltration through the pile (DRA-28). The model chemistry of the GH Spring outflow, derived in DRA-28, is summarized in Table 1. The mineralogy of the rock pile is taken for the model to be that of a hydrothermally altered andesite (QSP alteration superimposed on propylitic alteration) (DRA-29; see Table 2).

Table 1 Model Chemistry – Goathill Spring (See DRA-28). [Values in mg/L, except pH in s.u. and Alkalinity in mg CaCO₃eq/L. SO₄ adjusted for ion balance as explained in DRA-28. For full analyses, see DRA-28, Attachment A]

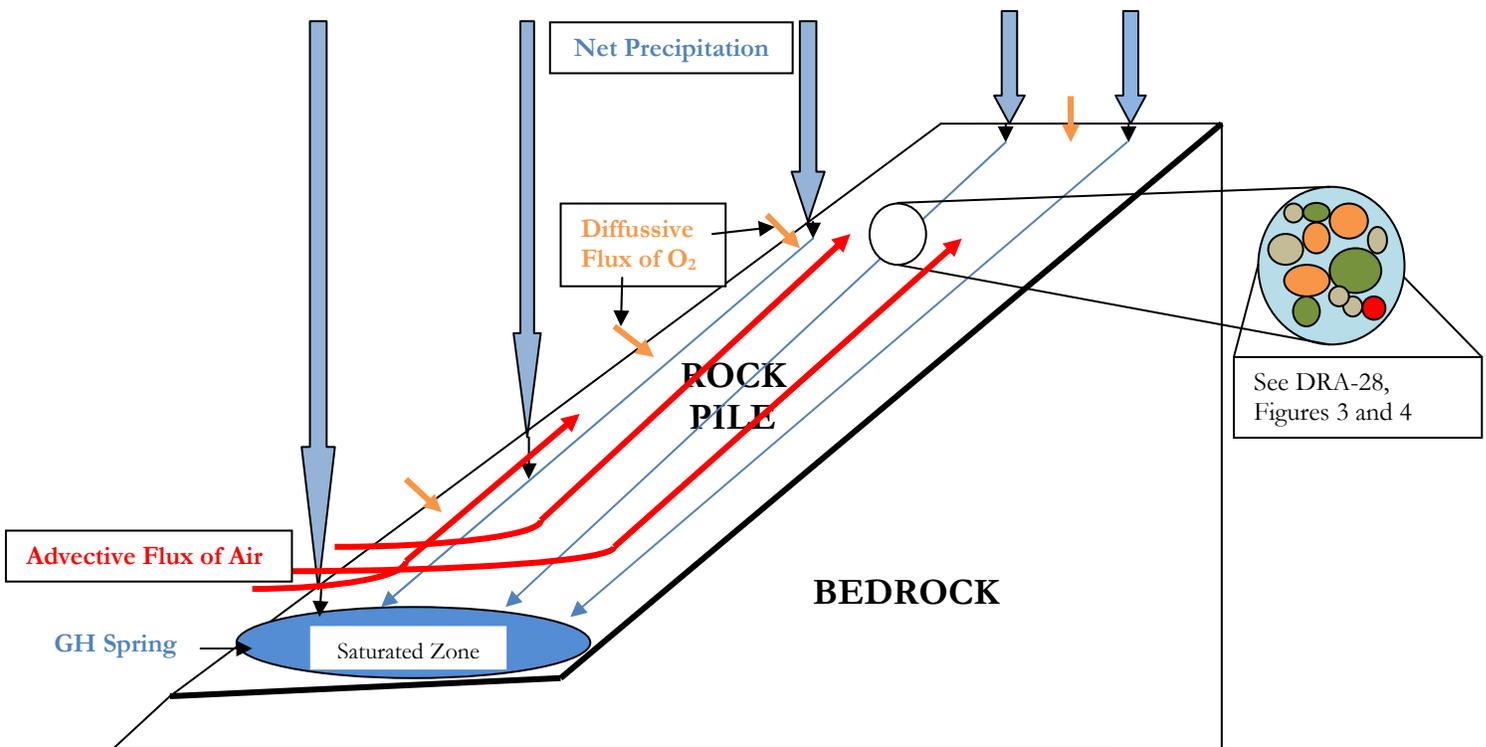
pH	Total Alkalinity	TDS	Si	Ca	Mg	Na	K
2.78	< 5	22000	50	370	740	9.4	2.1
Cl	F	SO ₄	Al	Cu	Fe (total)	Mn	Zn
29	91	13,750	1400	10	690	430	100

Table 2 Conceptual model mineralogy (see DRA-29, Table 1). Note low precision of estimates; all fractional values rounded to next highest percent. Values in the wt% column are re-normalized to 100% with addition of jarosite (Jar), Fe-hydroxide (Goe, goethite), and gypsum (Gyp).

Mineral	Model – Initial Rock – Vol%	Model – Initial Rock + Jar+Goe +Gyp Wt%
Quartz	41	40
K-feldspar	12	12
Plagioclase	13	13
Chlorite	4	4
Illite	21	21
Epidote		
Calcite	1	1
Kaolinite	1	1
Pyrite	1	1
Fluorite	5	3
Gypsum		
Jarosite	1	1
Fe-Hydroxide		1

The conceptual model for the mass-balance model is that GHN rock pile represents a small, unforested watershed, into which very dilute meteoric water enters as recharge and from which there is a steady, downgradient outflow, evaluated in terms of GH Spring. The upper boundary is atmosphere; the lower boundary is the underlying bedrock, taken for our purposes to be a no-flow boundary so that all net infiltration reports as toe seepage at steady-state flow. The flow system is considered to be a heterogeneous and anisotropic system that is unsaturated hydraulically. The unsaturated state of the interior of the pile is not relevant to conceptualization, except that it permits sufficient flow of air to well-oxygenate the pile. The state of saturation is sufficient to permit physical flow of liquid water downward under gravity along some pathways. The discharge water represents the net heterogeneous reactions of dissolution and precipitation between water and rock that have occurred along the flow paths.

Figure 1 Conceptual Model of Fluid Flow, Goathill North Rockpile, with Goathill Spring. Net Precipitation = [Ppt-(Runoff +Evap)] = Infiltration. Counter-current flow of water downward (gravity) and air upward (buoyancy). Additional O₂ flux by diffusion across surface.



5. STATUS OF MASS-BALANCE MODEL FOR GOATHILL NORTH

The calculations supporting this section are presented in their entirety in Attachment 1.

6.1 Pyrite Oxidation and the Balances for Fe and SO₄ (Sheet “Py-SO₄-Fe”)

6.1.1 Aqueous-Phase Balance

The observed SO₄ concentration, assumed to be due to pyrite oxidation, implies oxidation of 7.15E+02 moles Pyrite per liter of effluent (mol Py/L). At the measured steady-state discharge, the aqueous-phase sulfate concentration implies 1.19E+02 tonne of pyrite oxidized per year. If the measured discharge at the observed GH Spring chemistry actually represents only half the total discharge (see DRA-28), then 2.39E+02 tonne of pyrite oxidize per year.

If such quantities of pyrite dissolve, then stoichiometrically equivalent molar responses of Fe must have entered solution. However, the observed Fe concentration of GH Spring represents only 17% of the stoichiometrically expected Fe flux, implying that 83% of the Fe initially released has been retained in the pile. The effect of the retained iron on estimating total pyrite oxidation is considered next.

6.1.2 Jarosite and Gypsum Related to Pyrite

Jarosite and Gypsum are recognized as secondary mineral precipitates in GHN (DRA-petrography). [For purposes of this set of computations, we will treat all secondary ferric oxides as if they were Jarosite. The other recognized secondary ferric oxide is Goethite (FeOOH), and because both Jarosite and Goethite have one mole of Fe per mole of mineral, their relationships to Pyrite as a parent phase are equivalent in terms of the solid-phase sinks for iron.] On a stoichiometric basis (Attachment 1, sheet “Basic”) one mole of pyrite oxidation can produce one mole of Jarosite (on the Fe stoichiometry) or two moles of Gypsum (on the SO₄ stoichiometry). Assuming that Jarosite and secondary Gypsum, averaged over the whole of the rock pile, each represents 0.5 wt% and that the Jarosite and Gypsum currently observed accumulated over a 30 year (25-40 year) period formed at a constant rate (the steady-state model assumption), the inferred jarosite and gypsum values represent an additional 1.51E+02 tonne/a of Pyrite oxidation. This is essentially equivalent to the pyrite oxidation inferred from the aqueous chemistry (1.19-2.39 E+02 tonne/a).

6.2 Aluminum: A Simple Mass-Balance of Silicate Dissolution Reactions

For the assumed starting mineralogy (Table 1), there are five possible alumino-silicate minerals that could contribute to the observed aqueous concentration: Chlorite, K-feldspar, Plagioclase, Illite (as sericite), and Epidote (Attachment 1, Sheet “Basic”). The solution-chemistry analysis (DRA-30) shows that all five minerals are significantly under-saturated in GH Spring water, and no Al-bearing phases are calculated as possible products. Because there is no plausible solid-phase sink, we can calculate the Al balance strictly from the aqueous phase.

We develop a model for their contributions to the observed Al flux as follows:

- Assume that the only source of Mg from the model rock is from dissolution of Chlorite. Therefore, we use the observed Mg concentration and a specific stoichiometry of Chlorite (Sheet “Mg_Chlorite”) to calculate the number of moles of Al released during dissolution of Chlorite sufficient to account for the observed Mg. In this model, dissolution of Chlorite accounts for 29% of the total observed Al in GH Spring effluent.
- We assume that all four of the remaining alumino-silicates would dissolve in low-pH waters generated by pyrite oxidation (DRA-30). Two of the candidates (K-feldspar and Illite) are K-bearing minerals; mineralogical studies indicate that the plagioclase at Questa has a high Ab component (90% or more) and so would yield predominantly Na as an alkali product. Epidote and the small An component of Plagioclase could contribute to aqueous Ca, as also could dissolution of calcite during the fast initial reactions in the system (DRA-28, -29, -30). Ca is not conservative in the GHN system, given the precipitation of secondary Gypsum, and some K also reports to secondary Jarosite. Given the complexities of sources and sinks for Na-K-Ca, unique solutions are unlikely.
- Therefore, we built the model by assuming that all four candidates dissolve, and they dissolve in proportion to their kinetic dissolution rates, as determined at 25° C in laboratory experimental work (Sheet “Al balance_other minerals”). To keep those values as consistent as possible, we use dissolution rates from a single compiled source (White and Brantley, 1995). In this model the order of mineral contribution to Al in solution is Chlorite > Epidote >> K-feldspar > Plagioclase > Illite. This corresponds to the order of concentration of the cations, Mg > Ca >> Na > K seen in the GH Spring effluent, which is at least internally consistent and also does not diverge from interpretations of field-scale weathering in other systems.

6.3 Rates of Mineral Reaction Averaged Over Rock Pile (Sheets “Al balance other minerals” and “Pyrite Reaction Rates”)

Combining the apparent pyrite oxidation rates from both the aqueous and solid consideration, the pile is currently yielding 2.26 E+06 mol Py/a. In order to calculate a mineral oxidation rate in units that are equivalent to those used in laboratory studies and for the analysis of the site-specific humidity-cell columns (DRA-35), one must have a model for converting rock-pile mass to volume, and volume to effective surface area. The conversion of mass to volume is through the bulk density assumption (2.00E+03 kg/m³), and it is likely, based on field studies of rock piles all over the world, that this value is quite precise, probably ± 10%.

Calculation of total surface surface area of rock fragments within a rock pile is very difficult, because the particle-size distribution of the rock that was placed is not known and quite surely was not constant over the life of the construction of the pile. Cathles (personal communication, 2006) developed a methodology for calculating the effective surface area of rock based on knowledge of the permeability and a recognition that the coefficient of permeability must be related to the effective surface area, because it is the surface area that

provides the resistance to flow. For a range of permeabilities from 25 to 100 darcy (approximately 10^{-2} to 10^{-1} cm/s when liquid water is the fluid phase), Cathles shows that the ratio of surface area to volume must be close to $50 \text{ cm}^2/\text{cm}^3$ of total volume. Robertson GeoConsultants estimated rock-pile hydraulic conductivity at $3\text{E-}02$ cm/s (in Chen and Wilson, 2006), or 30 darcy. Therefore, for this calculation we use the Cathles estimate of $50 \text{ cm}^2/\text{cm}^3$. Based on the calculated bulk rates of pyrite oxidation and the inferred surface area, we calculate a bulk oxidation rate of pyrite in GHN of $1.3\text{E-}12$ mol Py/ $\text{m}^2\cdot\text{s}$

The best estimate we know for pyrite oxidation under unsaturated conditions (96% relative humidity) is due to Jerz and Rimstidt (2000), $10^{-8.5}$ mol Py/ $\text{m}^2\cdot\text{sec} = 3.16\text{E-}09$ mol Py/ $\text{m}^2\cdot\text{sec}$. Recently determine empirical oxidation rates for Questa rocks return apparent pyrite oxidation rates that are very similar to those of Jerz and Rimstidt, ranging from $10^{-8.9}$ at circum-neutral pH to $10^{-8.2}$ at pH 3 when corrected to reactive surface area (DRA-35, Fig. 2)

The estimated field-scale rate for the entire rock pile is a factor of approximately 1,000 lower than the laboratory rate measured on pyrite as a single phase. Other studies of rock weathering typically show watershed scale values for weathering rates that are 100 to 10,000 times slower than laboratory-derived values for single minerals (e.g., White, 1995, 2005), and a recent study that calculated rates based on a whole rock and also on minerals separated (though imperfectly) from that rock found the rock-scale values to be at least 100 times slower than the single mineral values (Ganor et al., 2005). The results of this study for pyrite therefore are not unreasonable. There is no clear consensus among researchers as to why the large-scale values are so different from carefully controlled values for aluminosilicates.

There are two factors, probably related to each other in field-scale systems, that seem most likely to represent the majority of the difference: (1) laboratory methodology and (2) reactive surface area. The experimental technique used to determine pyrite oxidation rates is designed to produce a maximum oxidation rate, that is one for which neither oxygen nor water is a limiting reagent (e.g., Ritchie, 2003). Unlike a laboratory experiment set up with continuous flow of air past a surface area of essentially pure pyrite, the field system allows air to flow through the rock mass differentially, with some high-permeability zones (e.g., low-moisture, coarse layers with clast-supported rocks) dominated by high advective fluxes of air and other lower-permeability zones (e.g. high-moisture, fine layers of matrix-supported rock fragments) through which O_2 must migrate from high-flow zones by diffusion. The result is that some portions of the rock pile may not receive a flux of O_2 sufficient to allow the oxidation rate to be established at the maximum-rate observed in the laboratory. Secondly, the rock piles are made up of rock fragments, not individual mineral grains, so some portion of the total surface area of pyrite (which itself is only present at about 6 vol% in the original rock fragments) is occluded from surfaces to which O_2 and H_2O have ready access as they flow through the rock pile. Given that pyrite is present at percent levels, it is reasonable to infer that only percent-levels of the total surface area of the pile expose pyrite. If, further, only about 10% of the rock pile is well-connected high-permeability material, then the combined factors would argue for field-scale pyrite oxidation rates that are on the order of 1,000 less than the minerals-specific rates seen in controlled laboratory tests.

Regardless of the details of why the rates may be lower in the field than in the lab, the currently available data for GHN indicate that for a rock pile containing approximately 3 wt% pyrite, the pyrite dissolution in the pile amounts to only about 0.05% of the total pyrite

present per year (0.3%/a if the pyrite concentration were as low as 0.5 wt%). For the Pyrite reaction rate to reach 1%/a, the production of secondary ferric minerals also would have to reach approximately 1%/a, and this rate, integrated over a 25-40 year life of the rock pile, is completely incompatible with the observed petrography of the rock pile. Pyrite weathering, integrated over the whole of GHN, must be slow or the mineralogical response, and degree of subsequent cementation by secondary iron precipitates, would be very different.

As shown in the lowermost calculations of sheet “Al balance_other minerals”, the proportions of alumino-silicate minerals dissolved, according to this model, are extremely small, ranging from 0.05%/a for Epidote and 0.01%/a for Chlorite to 0.000X%/a for K-feldspar [X = 6.5], Plagioclase [X = 1.5] and Illite [X = 0.5]. The rate for the Epidote reaction, when integrated over a nominal 30-year period is sufficiently high (>1% of the Epidote taken to be initially present in the mineralogical model of Table 1) that it is plausible that there would be petrographic evidence. Indeed, the Project petrographers have identified evidence of epidote depletion in some samples (V. Lueth, personal communication, 2008). Based on the high concentration of Mg in the GH Spring water, especially compare to other major cations, it is reasonable that the relative rate of Chlorite dissolution is high relative to the other alumino-silicates. The low rates of reaction for feldspars and illite implies that petrographic evidence for loss will be very low, even over 25 to 40 years, and that also matches the Project’s petrographic results.

6.4 Projecting Mineral Reaction into the Future (Attachment 1, all sheets, especially “Pyrite Leaching Models”)

We have argued here and originally elsewhere (DRAs-28, -29) that the flow and chemistry of GH Spring is at “steady state” over the observational period from 2001 to 2008. If the rate of Pyrite oxidation calculate here were maintained into the future, pyrite oxidation in GHN could continue for approximately 3,600 years. However, experience with leaching, from laboratory to field scale, shows that the rate of leaching in almost all systems declines over time, usually as a function with a form dependent on $1/\sqrt{\text{time}}$, presumably because the reaction depends on double diffusion of O_2 into the pyrite and SO_4 and Fe back out. If pyrite oxidation (and the hydrolysis reactions driven by it) vary in such a way in the mined rock piles, then the time to depletion of pyrite in the rock pile would be on the order of hundreds of thousands to millions of years. Absolute-age dating of jarosite from local natural analog sites (DRAs-18, -19) range from tens of thousands to more than a million years, and petrography of the alteration scars shows abundant residual pyrite in portions of the scar that have undergone physical and chemical weathering (based on particle-size reduction and discoloration of rock-fragment surfaces).

GHN, our model rock pile, no longer has calcite readily available in the rock in zones for which secondary ferric minerals have precipitated on the surfaces and interstices of rock fragments. Experimental work, and common geological experience, is that calcite is very soluble in acidic conditions, with reaction rates several orders of magnitude faster than those of pyrite oxidation and many orders of magnitude faster than dissolution of silicate minerals. So rapid and quantitative removal of calcite from the Questa rocks is expected where pyrite oxidation has produced low-pH pore waters. There is no thermodynamically plausible way for calcite to be re-introduced into the rocks. Therefore, a flow system that is currently producing low-pH water will continue to do at least so long as pyrite oxidation continues,

even if the rate of pyrite oxidation decreases over time. Even after pyrite oxidation ceases, the recovery of pH will be slow (as H^+ ions by then sorbed on mineral surfaces desorb), and there will be no thermodynamic driving source to force pH higher, at any time, in the bulk pile than that of the infiltrating meteoric precipitation.

Because we anticipate that pyrite oxidation will continue for more than 1,000 years (and probably very much longer), there is no plausible geochemical pathway to increase the pH into a domain where Al-bearing secondary minerals would be stable. Therefore generation of clay minerals is not geochemically plausible for the Questa rock piles over time frames of 100 to 1,000 years. Similarly, for the low rates of bulk mineral dissolution, there must be similarly low rates of formation of mass and volume of secondary reaction products, because they are tied to the moles of reactants from which their components were generated. Therefore, it is reasonable to expect that, while we can observe secondary ferric oxides and gypsum precipitating, in the interior of the rock pile, the mass of these precipitating must be small. (See DRAs-8 and -32 for an evaluation of gypsum formation in the high evapo-concentration regime of the surficial crusts of rock piles. In the crusts, the major geochemical reactions differ from those in the pile's interior.) Furthermore, with the likelihood that dissolution reaction rates will fall over time, the possible rates of cementation also will fall over time. The effects of small amounts of cementation on rock-pile cohesion is outside the scope of this geochemical evaluation, although secondary cements need fill only pore space, so their effects could be disproportionate to the absolute value of mass

6.5 Consistency of the Modeling Results with the Conceptual Model

The mass-balance model depends on the underlying conceptual model for the hydrogeochemistry of GHN. The low rates of reaction inferred for the bulk rock pile from the mass-balance modeling are consistent with a flow system in which there is substantial preferential flow, both of air and also of water. The result of the low rates is that, on a mass and volumetric basis there has been very little chemical weathering of the rock pile as a whole. Even the fast reacting Pyrite system has oxidized only a few tenths of 1% of the total Pyrite present in the rock pile in a nominal 30-year period. The secondary reaction products, especially the ferric minerals and gypsum that provide light colors on the surfaces of the rock fragments, redistribute mass that has entered the flow system in one zone (energetically upgradient) and deposited it in another, but this represents a very small fraction of the mass and volume of the initial rock. The mass-balance calculations show that there cannot be significant alteration of the bulk rock fragments, and that is supported by available petrographic analysis.

6.6 Assumptions

The major chemical assumptions of this analysis are that the water analyses from 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 that are background for this analysis (DRA-30 and -31) are reliable, so that we can focus on pyrite oxidation and congruent dissolution of alumino-silicates as the dominant processes of reactive geochemistry. The mass-balance constraints are derived from standard mineral stoichiometries, well-known atomic weights, and simple algebra. The water chemistry has been developed under established quality-assurance and quality control

programs at laboratories that have records of reliable analytical chemistry. There is substantial consistency in petrographic descriptions between different petrographers, and at the level of these models, there is little question that the mineral identifications cited here (goethite, jarosite, gypsum) are accurate.

The major physical assumption of the analysis is that seepage at Goathill Spring represents infiltration of meteoric water and percolation of that water, with chemical reaction, under unsaturated flow that accumulates at the perched zone that feeds the spring. The model also assumes that the measured spring flow represents a large fraction of the total seepage through the rock pile, and that no significantly different water types discharge. The arguments for the hydrogeologic interpretation are presented in DRAs-28 and -29.

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

Mineral dissolution rates are very low, small fractions of 1% per year, and the system appears to require that there be preferential flow of air and water through the pile in order to explain the observed rates. At such low reaction rates, in a heterogeneous and anisotropic system, the total amount of weathering that has taken place is very small. Most of the measureable alteration involves the “fast-reacting” subsystem Pyrite + Calcite → Jarosite + Gypsum; alteration of alumino-silicates appears to be entirely by congruent dissolution at very low rates.

The current geochemical conditions in the rock pile, specifically the low-pH condition that prevents precipitation of Al in any known mineral, is expected to last substantially beyond 1,000 years. Therefore, no change in the geochemistry that would lead to production of clay minerals is foreseen, and generation of cohesion by precipitation of secondary-mineral cements also is expected to remain minor.

5. RELIABILITY ANALYSIS

The principal technical uncertainties in this analysis are (1) the extent to which the water chemistry and flow rates of GH Spring represent a “steady-state” discharge of much of the water flowing through GHN, and (2) the mass of secondary minerals (jarosite + goethite + gypsum) that have precipitated in the pile. Given the eight-year history of chemistry and flow at GH Spring, the “steady-state” assumption for the aqueous system seems quite robust. The mass of secondary jarosite plus gypsum may be low (or high) by a factor of 2 to 5, but it cannot be too low by a factor of 10 or more, or the petrographic evidence for secondary cements would be much greater, and the in-situ shear-box tests would show consistently higher values for bulk cohesion.

The reliability of our fundamental understanding of the detailed flow mechanisms within the rock pile is less clear. The QRPWASP Team has consistently considered that water that initially infiltrates into the rock pile (past about 2 m depth) moves continuously through the rock in a manner that can be described by Richard’s equations for fluid flow, although the rock pile is unsaturated and the coarse- and fine-zones of the rock pile have substantially different hydraulic properties. The available analysis (DRA-15) indicates that the upper 2 to 5 m of the rock pile are subject to substantial cycles of drying under the climatic conditions of the Questa site, leading to seasonal formation of evaporative salts on as much as 75% of

the rock-pile surfaces (DRA-8). During wet periods, there is substantial, variable wetting of the rock pile down to depths of approximately 10 m. Below 10 m, the QRPWASP analysis infers from numerical modeling and limited field measurements that moisture contents do not vary substantially over periods on the order of a year. There is compelling evidence from field observations and the large-scale behavior of the rock pile that, in three dimensions, there is tortuous connectivity of both the fine (water transmitting) and coarse (air transmitting) layers, so that the system behaves continuously with respect to fluid flow at the scale of the entire rock pile.

That is not to say that the system behaves as, or has been modeled as, a single equivalent porous medium. There is substantial evidence, from the Questa rock piles (Sections 4.2, 4.4, 4.6.2, and 5.2; also DRA-29) and other rock piles (e.g., Smith and Beckie, 2003; Ritchie, 2003), that there are zones of preferential flow, both upward of air and downward of water. At the scale of whole rock piles, essentially all applied models use the Richard's equation approach, not only because it produces plausible results, but also because it is the only approach to modeling for which practicable programs of data collection are possible. The best connection between field observations and modeling as to the physics of flow in GHN is the observation of the establishment of a steady flow regime at GH Spring in something less than 40 years (the rock pile age is 25 to 40 years), along with the recently computed particle-tracking model that shows transit times from recharge to discharge in the modeled rock pile ranging from a few to a few tens of years when tested against the best estimate range of Questa modeling boundary conditions and hydraulic properties (SVS, 2008).

However, not all project data are consistent with this approach. The most significant anomaly known now is that water collected from GH Spring and other seeps near the toe of the rock pile do not show a stable-isotope signature indicating substantial evaporation from local meteoric water, although their solution chemistry implies significant exposure to rock-pile materials. Hydrogeologic modeling and water-balance considerations require that up to 60% of ambient precipitation does not infiltrate into the pile. There is little evidence of overland flow or other runoff beyond small-scale gullying, and the QRPWASP model assumes that the overwhelming majority of the water that does not flow into and through the rock pile has been evaporated. Additionally, small samples of pore water collected in the upper third of the rock pile have stable-isotope signatures for hydrogen and oxygen that indicate evaporation, although not to levels of 60% (DRA-12).

If the spring flow at GH Spring represents a well-integrated sample of steady-state flow through the rock pile, the lack of an evaporated isotope signature is hard to reconcile with a continuum flow model for deep infiltration through the rock pile. The stable-isotope signature can be explained if waters rapidly infiltrate along preferential pathways in the shallow system, bypassing the portion of the flow domain sampled in the shallow isotope studies, then coalesce to form the saturated flow that discharge at the GH Spring. Although this is a physically plausible recharge scenario, it has not been demonstrated or observed at GHN and so remains speculative. While other information and inference (DRA-28 and -29; SRK, 2007) supports the interpretation of GH Spring as consistent with a dual-porosity modeled continuum flow system, the isotopic anomaly needs resolution before the flow modeling and geochemistry of GHN can be fully coordinated.

QRPWASP also has considered the possibility of micro-environments within the rock pile that differ from the bulk properties inferred in this and in other Component DRAs. Evidence summarized DRA-2, -6, -7, -8 indicate that the geological and geochemical system of GHN, and to the extent they have been characterized also other Questa rock piles, is heterogeneous. For example, whereas paste-pH of some zones and layers is low (paste pH <4), there are other samples collected deeper in the rock pile that have circum-neutral paste pH (DRA-6), indicating that acidic solutions are unlikely to have contacted those rocks in significant fluxes. Also, there are some rock samples that continue to contain calcite, although others have essentially all calcite removed and only acidic secondary hydroxysulfates present, and we have concluded that the low-pH water of GH Spring (pH 2.8) is representative of solutions draining much of the entire rock pile. Furthermore, the heterogeneity of the bacteria, from obligate aerobes to sulfate reducing bacteria, requires heterogeneous fluid flow conditions. Finally, the column-leaching experiments (DRA-35) have shown that in some locations within the rock mass of the columns after 52 weeks of leaching, there are accumulations of fines that contain undissolved carbonate minerals, although column effluents have been low-pH for many weeks.

The most likely explanation for these observations is related to the issues discussed in Section 6 above and in DRA-29: there must be zones or pathways of preferential flow of liquid water through the rock pile. Additionally, the observation of jarostic coating on large clasts in clast-supported, low moisture-content layers strongly supports the notion that there also are zones of preferential flow of air where, necessarily, there must be little water flowing (DRA-28 and -29). The very high concentration of dissolved oxygen and the plentiful evidence for ferric iron as the dominant form in solutions producing secondary minerals such as jarosite and goethite requires that there be an active high-flux system to transport oxygen through the rock pile. The chemistry of both GH Spring water and also the discharge effluent from acid-generating column-leach experiments is certainly representative of the preferential liquid pathway, and the high sulfate concentrations and abundant evidence for mobile ferric ion strongly imply that there has been sufficient flow of O₂ through the materials to oxidize pyrite. However, the inferential evidence of multiple-porosity flow paths and the local persistence of calcite that would rapidly and quantitatively dissolve at the pH of the GH spring water, implies that GH Spring discharge is not representative of all pore domains in the system.

Based on such ranges in large-scale conditions and uncertainties at small scale within the rock pile, we consider that the estimated mineral-dissolution rates based on the full volume of the rock pile are probably underestimates for specific flow paths. How large that underestimation is depends on how much of the total porosity of the rock pile is represented by waters like those sampled at GH Spring, and at this time that is not known. It seems entirely possible that the mass-based dissolution estimates may be off by a factor of two to five, but they cannot reasonably be off by factors of more than 10, or there would be much greater evidence of neutral drainage within the rock pile, and much more evidence of mineral dissolution (particularly near-complete removal of chlorite, which is not seen) in some zones.

6. CURRENT CONCLUSION

Oxidation of Pyrite in the bulk rock pile occurs at rates that are approximately 1,000 times slower than laboratory-derived rates. This is probably due to a combination of limited reactive surface area in the bulk pile and the effects of differential oxidation due to preferential pathways for air transport. Although the rates appear low compared to laboratory values, they are high enough to significantly affect water chemistry and to have quantitatively depleted the available calcite along active flow paths.

The system has irreversibly moved to one of low pH ($\text{pH} < 3$), which is below the first hydrolysis constant for Al^{3+} . This means that Al-bearing minerals, including clay minerals, will not be stable in the water-rock system. As with pyrite dissolution, the rates of dissolution for alumino-silicates are extremely slow, so slow that petrographic evidence for dissolution can hardly be expected, and in fact is not seen.

The major geochemical processes currently controlling water-rock interactions in GHN are expected to continue for thousands of years, though probably at gradually falling rates over long periods. Thus, there is no prospect for changes in the system geochemistry that would (a) cause clay minerals to begin to form; (b) increase the rates of mineral dissolution so that particle-size reduction or rounding accelerated; or (c) significantly increased the low rate of formation of secondary cements.

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