Geological, Hydrological, and Geochemical Framework for Questa

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Abstract

The Questa Weathering and Stability Study included detailed earth-science characterization of hydrothermally-altered igneous rock-pile and analog materials and associated groundwater. Radiometric dating demonstrates that natural weathering processes and their mineralogical outcomes have been active at Questa over a million years or more. Dissolution of pyrite, calcite, and silicate minerals is the predominant geochemical reaction that results in low-pH, high-TDS seepage and precipitation of gypsum, jarosite, and iron hydroxide minerals. Silicate minerals in the Questa rock piles dissolve congruently, without producing clay minerals.

Seepage waters are thermodynamically under-saturated with respect to all silicate minerals (including clay minerals), sulfides, and carbonates, but are saturated with respect to jarosite, ferric oxides, and gypsum. Clay minerals at Questa formed under hydrothermal, not weathering, conditions. Secondary precipitates predicted from water chemistry are directly observed, and locally they act to cement rock fragments in rock piles and debris flows.

Introduction

The Site

The Questa molybdenum mine (Chevron Mining Inc., formerly Molycorp, Inc.) is located in the Sangre de Cristo Mountains in north-central New Mexico and is on southward facing slopes at elevations of approximately 2290 to 3280 m (Fig. 1). During the period of open-pit mining (1969-1982), approximately 317.5 million metric tons of overburden rock was removed and deposited onto mountain slopes and into tributary valleys, forming nine rock piles surrounding the Questa open pit. Since the rock piles were emplaced, a number of shallow-seated failures, or slumps, have occurred at Questa, and a previous foundation failure occurred at Goathill North (GHN) rock pile that resulted in sliding of the rock pile. This slide was halted by unloading and buttressing of the rock pile, and GHN is now stable.

The Questa rock-pile materials are a mixture of different lithologies and hydrothermal-alteration mineral assemblages that existed in the mined zones prior to emplacement in the rock piles. The rock-pile material was blasted, transported by haul truck, and dumped subaerially down the existing slope, which is composed of locally-derived colluvium and weathered bedrock. The bedrock geology on which rock piles exist comprises the same lithologies and ranges of hydrothermal alteration as the mined overburden, differing only in molybdenum grade. Naturally occurring hydrothermal alteration scars (Figure 2), debris flows, and weathered bedrock adjacent to and in some cases beneath the Questa
Figure 1  Questa rock piles and other mine features, including location of trenches constructed in Goathill North (GHN) rock pile.

rock piles constitute natural analogs of the near-surface weathering of the Questa rocks and provide long-term (tens of thousands to more than one million years) geologic and geochemical control on the processes and products of weathering of the hydrothermally altered rocks.

Figure 2   Naturally occurring hydrothermal alteration scar, Southwest Hansen Scar, Red River Valley, New Mexico
Although the Questa rock piles are compositionally heterogeneous in their detailed geological, chemical, and mineralogical composition, they are similar to each other in construction, lithology, hydrothermal alteration, geotechnical properties, and extent of weathering. The rock-pile material has reached close to its final density and locally is incipiently cemented with secondary minerals.

The Questa Rock Pile Weathering and Stability Project

In 2004 Molycorp, Inc. (now Chevron Mining Inc.) commissioned the Questa Rock Pile Weathering and Stability Project as an independent, scientific research project. The work continued until early 2009. The purpose of the Weathering and Stability Study was to determine the technical basis for how and to what extent, considering geological, geochemical, mineralogical, hydrological, and geotechnical processes and rates, weathering would affect the gravitational stability of the Questa mine-rock piles in 100 and 1000 years. A central motivation for the research was a conjecture that acid-rock drainage within the rock piles would transform primary and hydrothermal silicate minerals to clay minerals. If there were a significant increase in clay mineral content compared to that when the rocks were first placed in the piles, then there would be an expectation that the shear strength of the rock piles would decrease, and the rock piles might become gravitationally unstable.

The Weathering and Stability Study established and documented the geological, hydrogeological, and geochemical characteristics of the Questa rock piles, and studied the processes, rates of reaction, and products of water-rock interaction within the rock piles. From these studies, one can critically evaluate the geochemical conjecture of clay formation. The purpose of this paper is to summarize the critical earth-science studies relevant to establishing the nature and behavior of geochemical processes in the rock piles.

Acknowledgments

The work described in this paper was developed under contract between Molycorp, Inc. (now Chevron Resources Inc.) and a collaborative scientific team organized and managed by University of Utah. Although Molycorp/Chevron funded the Project and provided access and field support such as bulldozers and safety supervision, the Company provided no policy or technical direction to the research work and had no editorial control over Project findings and publications.

The Weathering and Stability Project team included multi-disciplinary specialists from universities and consultant firms in the U.S. and Canada, including New Mexico Institute of Mining and Technology (NMIMT), University of British Columbia (UBC), University of Nevada, Reno, University of California at Berkeley, Weber State University, Minnesota Department of Natural Resources, Spectral International, SoilVision Systems; R², Inc., and Geochimica, Inc. The twenty-one senior scientists and engineers were supported by an outstanding group of more than 100 graduate students and technicians. Principal investigators whose detailed technical work was especially critical to the geoscience studies discussed in this paper included Drs. Andrew Campbell, Nelia Dunbar, Virginia McLemore, and Virgil Lueth and Ms. Kelly Donahue (NMIMT), and Dr. Murray Fredlund (SoilVision Systems). I gratefully acknowledge all their contributions and critical discussions, and the collegial process of the entire University of Utah team, technical and management. The author alone is responsible for any errors that remain.

Introduction To The Geologic Framework And Context

The Questa rock piles are end-dumped, subaerial deposits of mixtures of plutonic, volcanic, and volcanioclastic rocks that have been hydrothermally altered to varying degrees and that existed in the mined zones prior to emplacement as rock piles. A typical rock composition [hydrothermally altered
andesite, with quartz-sericite-pyrite superimposed on a pre-existing propylitic alteration] in piles today would have a mineralogical composition of approximately:

40% Quartz – 12% K-feldspar - - 13% Plagioclase Feldspar (An90) – 4% Chlorite – 21% Sericite (2M1 Illite) – 1% Epidote – 1% Calcite – 1% Kaolinite – 3% Pyrite – 1% Fluorite – 1% Gypsum – 2% Jarosite – 1% Ferric hydroxide.

Equivalent compositions, including structurally identical clay minerals, are documented for the hydrothermal alteration scars of the Red River Valley. Argon-argon age dating of jarosite crystals by the Questa Weathering and Stability Project shows that local natural analogs have been undergoing weathering with mineralogical outcomes identical to those of the rock piles for periods ranging from about 30,000 to 1.5 million years.

The dumping process produces a generally stratified system of alternating coarse and fine layers. Layers coarsen down slope and are connected tortuously in three dimensions. The average dip of the layers is 36°, essentially parallel to the average slope of the paleo-surface on which they were deposited (Fig. 3).

Figure 3   Idealized cross-section of angle-of-repose waste-rock deposition, Goathill North rock pile, Questa.

In the Questa rock piles and local natural analogs, dissolution of pyrite, calcite, and to a much lesser extent, alumino-silicate minerals, is the predominant geochemical reaction that results in 1) the evolution of water chemistry seeping from the rock piles and analog sites and 2) the precipitation of gypsum, jarosite, soluble efflorescent salts, and iron oxide/hydroxide minerals. Petrographic observations and geochemical inference from solution chemistry indicate that the silicate phases in
Questa rock piles dissolve congruently (i.e., without producing clay minerals such as kaolinite as reaction products); this conclusion also has been reported by others in recent published studies of silicate-mineral dissolution. Argon-argon radiometric dating of secondary jarosite in the local natural analogs dates of 30,000 years to 1.5 million years, demonstrating that the natural weathering processes and their mineralogical outcomes have been active, though not necessarily continuously, over a million years or more. The ability to project current processes forward so far in time using analog-weathering data greatly enhances the reliability of the Weathering and Stability Study’s analysis and conclusions with respect to future conditions.

Infiltrating groundwater percolates downward through the irregularly layered rock piles under unsaturated flow conditions that involve both vapor- and liquid-flow (Fig. 4). Water chemistry in the piles evolves due to air-water-rock chemical interactions in pore spaces along the flow paths. Springs and seeps in the rock piles represent the flow over years to decades of seepage of infiltrating meteoric water that has accumulated in perched, saturated zones in various horizons stratigraphically above the base of the piles. Waters seeping near the toe of Goathill North are well oxygenated, low-pH, high dissolved-solids, high acidity solutions containing high concentrations of Al, Ca, Fe, Mg, SO$_4$ and other solutes (Table 1).

![Figure 4](image)

Figure 4  Schematic dynamic section through rock pile, showing flow, under variably saturated hydraulic conditions of both air (upward) and water (downward). From Cathles and Apps, 1975, Figure 1.
Table 1  Typical water chemistry of Goathill Spring (2001-2007) in mg/L, except pH is in standard units; Total Alkalinity is in mg CaCO$_3$/L; T (temperature) is in °C; Q (flow) is in L/s; DO is dissolved oxygen, in mg/L.

<table>
<thead>
<tr>
<th>pH</th>
<th>Total Alkalinity</th>
<th>TDS</th>
<th>Si</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
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<td>50</td>
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<td>740</td>
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<th>F</th>
<th>SO$_4$</th>
<th>Al</th>
<th>Cu</th>
<th>Fe (total)</th>
<th>Mn</th>
<th>Q</th>
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<td>1400</td>
<td>10</td>
<td>690</td>
<td>430</td>
<td>0.63</td>
<td>7.5</td>
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The water chemistry implies a range of water-rock reactions, including simple dissolution, redox, acid-base, and silicate hydrolysis. Incongruent dissolution of silicates to produce kaolinite (or other clay minerals) is inconsistent with the observed solution chemistry and is thermodynamically impermissible.

**Rock-Pile Weathering**

**Geologic and Physical Framework**

The likely stability of the geologic and physical framework of the rock piles over 100 to 1,000 years is described in detail in the final Project Report of Investigations and in van Zyl, 2011 (this volume). Observation of the field-scale behavior of rock piles around the world shows that one can reliably assume that the observed layering will be a very long-term feature of the system. Within the scope of our study, both the mechanical framework that affects the permeability of the layered structure and the gravitational stress (i.e., the stresses derived from the mass of the solids in the rock pile) will be steady for periods on the order of 100 to 1000 years.

**Hydrogeochemistry of the Model Rock Pile: Implications for Chemical Weathering**

Hydrogeological modeling of a two-dimensional flow system similar to GHN, using the boundary conditions and parametric data developed for this Project, indicates that the mean transit times from recharge to discharge zones near the base of such a rock piles would be on the order of a few to a few tens of years, depending on specific location of recharge and local distributions of permeability. Local, perched zones that achieve saturation, allowing small springs (e.g., Goathill Spring) show that hydrogeochemical evolution of GHN over its 25-40 year history has produced a flow and transport system in the unsaturated rock piles that approximates steady state from 2001-2008, the full period of record. Laboratory experiments of the leaching of GHN rock with de-ionized water (as a surrogate for dilute natural precipitation) show that the effluent chemistry evolves to a quasi-steady-state composition in only a few hours, largely through the dissolution of soluble salts that have accumulated on rock-fragment surfaces. The field and laboratory data and numerical modeling results all suggest that flow systems with chemistry such as that seen at field scale at GHN can develop in rock piles in a matter of a few years and perhaps less, once a flow path is established.

The coupled air and water flows produce acidic waters due to the oxidation of pyrite in a system that has locally exceeded its bulk ability to neutralize the available acidity budget. The oxidation of pyrite, with coupled dissolution of calcite in a well-oxygenated system, is expected to precipitate ferric sulfates (e.g., jarosite) and oxides (e.g., goethite) and gypsum. As is known also from many other porphyry-style deposits, the (pyrite + calcite) → (ferric oxides + gypsum) system is a reaction
sequence that is rapid at the scale of the rock piles, presenting clear petrographic evidence in the observed rock pile system (that is, in time frames of years to a few decades). The same geochemical products can be observed in alteration scars and other local natural analogs, and because the products, both aqueous and solid, are consistent, we conclude that the same weathering processes exist in both the young rock piles and the very old natural analogs.

The most significant geochemical outcomes of a rapid reaction that can be schematically represented as (pyrite + calcite) → (ferric oxides + gypsum) are:

- Pore waters in the rock piles have pH < 3, that is, below the first hydrolysis constant for aluminum. In a system characterized by such a pH, Al-bearing minerals (including clay minerals) cannot precipitate, but instead are subject to dissolution. Waters such as that listed in Table 1 would be under-saturated by 3.5 to > 60 orders of magnitude for all common alumino-silicates, including kaolinite, pyrophyllite, smectites, feldspars, illite, muscovite, and the entire range of chlorites.

- There are secondary reaction products (e.g., gypsum, ferric hydroxides, jarosite, and perhaps amorphous silica) that form in the heterogeneous geochemical system of the rock piles. Because the solution chemistry is saturated with such minerals, they can form, but will not dissolve unless fresh water replaces the existing pore water, and even then, dissolution would be slow under well-aerated conditions for poorly pH-buffered infiltrating waters.

The rapid response of the hydrogeochemical system and its evolution imply that there is a bimodal distribution of permeability in the flow system that allows preferential flow paths for both (a) air transport (leading to heterogeneous and in part anisotropic distribution of incipient oxidation) and (b) through-flowing aqueous infiltration (leading to rapid flow and transport of secondary reaction products of mineral weathering). We observe the gypsum, ferric hydroxides, and jarosite as macroscopic evidence for rapid reaction in the (pyrite + calcite) → (ferric oxides + gypsum) in an open system (i.e., one in which mass and energy are mobile), but the average bulk reaction rate for pyrite oxidation is actually 2-3 orders of magnitude lower than values calculated from laboratory experiments with pure pyrite. The bulk chemical kinetics is best reconciled with small-scale evidence for rapid pyrite oxidation by recognizing that the surface coatings represent the redistribution of only a very small total mass compared to the mass of pyrite present in the rock piles. The redistributed ferric iron as jarosite plus goethite is a minute fraction of the total mass of the rock piles.

The mineralogical effect of the fast-reacting weathering system is to produce precipitates of secondary reaction minerals on the surface of existing rock fragments. These secondary precipitates are typically yellow to orange, reflecting the role of ferric ion in the mineral structures; gypsum may be white or buff, or may take on a colored cast when intergrown with the ferric precipitates. Where those rock fragments are small, the secondary precipitates can cause or increase the adhesion between mineral or rock-fragment grains. On larger rock fragments, the secondary precipitates form coatings on exterior surfaces and along microfractures, but typically do not infiltrate more than a few microns into the rock matrix, except along fractures. Thus, the macro-scale, visual impression of weathering, caused by the discoloration from the secondary precipitates, is greatly exaggerated compared to the volumetric or mass effect.

There are chemical components in the Goathill Spring water other than those associated with the (pyrite + calcite) → (ferric oxides + gypsum) subsystem that also are significantly elevated with respect to most natural waters draining areas of intermediate igneous rocks. The elevated
concentrations and covariance of Al, Si and Mg with low pH only can be explained by hydrolysis reactions of alumino-silicate minerals. There are substantial kinetic barriers to the dissolution of feldspars, phyllosilicates (including hydrothermal clays), epidote, and quartz. Consequently, these slow-reacting minerals remain easily identified in the rock pile fragments, although in the bulk rock piles, they are undergoing dissolution due to the weathering under low-pH. The apparent contradiction of low rates of reaction with high aqueous concentrations is easily resolved. The aqueous concentrations are considered high for natural waters because most natural waters are associated with circum-neutral to slightly alkaline pH, in which silicate dissolution reactions are several orders of magnitude lower than they are at pH 3, as appears to be the typical pH for pore waters in the rock piles. Secondly, although the reaction rates are low, there is a very large mass (and therefore exposed surface area) of silicate minerals along flow paths in the rock piles. Given the low net mass infiltration of water through the rock piles, the low water-rock ratio will produce relatively high concentrations because of the mass-action effect of chemical reactions.

The Weathering and Stability Study developed an inverse mass-balance model, calculating the amount of minerals that needed to dissolve to produce the observed mass concentrations in solution. That modeling indicates that the highest reaction rates for silicates are associated with chlorite (the major source of Mg and Al) and epidote (a discernible source of Ca to solution), but even these are low rates on an absolute basis. The very low concentration of sodium implies very low reaction rates for the high-albite plagioclase. The low concentration of potassium in solution reflects not only slow reaction kinetics for K-feldspar and illite, but also the existence of a sink for K in the secondary precipitation of jarosite. Although rocks of the Questa area are known to contain fluorite, in the Questa rock piles it is very rarely observed and typically is present only in trace amounts. This is consistent with the inference developed by U.S. Geological Survey modelers that the principal source of high F in groundwater is dissolution of fluorite.

The effluent water chemistry at Goathill Spring and other discharge zones near the toe of GHN and from alteration scars shows clear evidence of silicate weathering. The major silicate minerals of the hydrothermally altered andesites and rhyolites either always undergo congruent dissolution because aluminum will not hydrolyze sufficiently to stabilize solid Al-forming minerals. Reaction rates of the dissolution of silicates, based on both field- and laboratory-scale data from this Project, are multiple orders of magnitude lower than the observed reaction rates for the fast-reacting system; this is fully consistent with literature studies published in the last 5 to 10 year. Because of the low reaction rates for silicate dissolution, the mass of silicate minerals dissolved per unit time is extremely low (small fractions of 1 weight-% per year). Because the silicate dissolution reactions are congruent, the mechanism, in any event, would be removal of mineral mass, not formation of new silicate (specifically clay) minerals (Fig. 5). Given these geochemical conditions, it is not reasonable to expect petrographic evidence of recent weathering of silicate minerals.
Extensive efforts to characterize the clay minerals in the rock piles material found no petrographic or X-ray mineralogic evidence of neo-formation of clay minerals. Clay minerals present in both rock piles and natural analogs are fully consistent in terms of their crystallography and detailed chemistry (including the oxygen-isotope chemistry of the solid phases) with formation under hydrothermal conditions. The empirical petrographic, mineralogic, and rock-chemistry results are consistent with the thermodynamic expectations derived from the solution chemistry and the geochemical modeling of the bulk hydrogeochemical evolution of the rock piles. It is a central finding of the Weathering and Stability Study that there is no evidence of formation of new clay minerals even in the old (tens of thousands to more than one million year-old) local natural analogs.
Long-Term Extrapolation Of Rock Pile Weathering

Site-specific, bench-scale weathering experiments conducted by the Weathering and Stability Study produce ranges of kinetic rates of pyrite oxidation under the weathering-cell conditions near those developed from laboratory experiments on pure pyrite systems under unsaturated conditions. Laboratory rates are for experiments that are designed to optimize pyrite oxidation, by ensuring that neither oxygen nor water is a limiting reactant, and leading researchers in the U.S., Canada, Australia and Europe now concur that the fundamental procedures of single-mineral dissolution experiments produce maximum dissolution rates that rarely, if ever, exist in natural systems. Differences between the Project’s bench-scale experimental rates and the field-scale rates calculated from the inverse-mass-balance model from Goathill Spring solution chemistry imply that there are constraints on pyrite oxidation in the GHN rock pile. As is seen in many comparisons of laboratory-scale and field-scale weathering rates (e.g., White, 1995; 2005), we infer bulk weathering reactions that are 100 to 10,000 times slower than the single-mineral reaction rates found in carefully controlled laboratory experiments, including our own. We consider that the differences are due to factors that also control the preferential flow of fluids (i.e., $O_2$ and $H_2O$) in the rock piles and the limited availability of reactive surfaces in rock fragments (compared to cleaned, single minerals). These relationships in the real, full-scale rock piles reflect the physical heterogeneity of the rock pile environment, including permeability and porosity, and the range and depositional history of mined rocks in a large rock piles.

Although long-term, field-scale numerical simulations of coupled flow and chemical transport have not yet been completed, the Weathering and Stability Study undertaken forward modeling of humidity-cell tests (HCTs) conducted by others for Questa. The best-fit projections for the HCTs shows a time-dependent behavior of the general form rate, $R = k/\sqrt{\text{time}}$, that is that reaction rates fall as the square root of time, consistent with a diffusion-dominated reaction system. This behavior, which is very commonly observed in leaching of rocks and minerals (e.g., Cathles and Apps, 1975; Berner, 1981; Brantley, 2002) implies that, absent a change in boundary conditions or initiation of a catalyzing process (presumably microbiological) that has not been documented through the Weathering Study work, leaching rates will decrease with time. Extrapolation of the currently inferred field-scale rate for pyrite oxidation indicate that more than 3000 years would be needed to deplete the system of pyrite; if the leaching rate is actually dependent on $1/\sqrt{\text{time}}$, depletion times would be on the order of $10^3$ to $10^6$ years. Local natural analogs have radiometric ages for secondary jarosite consistent with such long periods, and they contain abundant fresh pyrite, which is consistent with the very-long-term persistence of the weathering environment in terms of the sorts of reactions observed in the existing rock piles.

Geochemical Summary And Conclusions

Infiltrating groundwater percolates downward through the irregularly layered rock piles under unsaturated flow conditions that involve both vapor- and liquid-flow. Water chemistry in the pile evolves due to air-water-rock chemical interactions in pore spaces along the flow paths. Springs and seeps in the rock pile represent the flow over years to decades of seepage of infiltrating meteoric water that has accumulated in perched, saturated zones in various horizons stratigraphically above the base of the pile. Waters seeping near the toe of Goathill North are low-pH, high dissolved-solids solutions that are under-saturated with respect to all alumino-silicate minerals (including clay minerals), sulfides, and carbonates, but are saturated with respect to jarosite, ferric oxides, and gypsum. Because the pore waters are very far under-saturated with respect to clay minerals, new clay minerals cannot form by precipitation, and the existing clay minerals of hydrothermal origin are subject to dissolution. Slow rates of silicate weathering, based on both field- and laboratory-scale data from this Project and other published studies, cause the mass of silicate minerals dissolved per unit time to be sufficiently low that
petrographic evidence of recent weathering of silicate minerals in the rock piles is not observable. Given congruent silicate- dissolution reactions, the mechanism, in any event, would be removal of mineral mass, not formation of new silicate (specifically clay) minerals. Extensive efforts on a large suite of samples from major proto-lithologies and stages of alteration to find petrographic, chemical, or isotopic evidence of neo-formation of clay minerals in both rock-pile and natural-analog materials were uniformly unsuccessful. The secondary precipitates – jarosite, ferric oxide, and gypsum - predicted from water chemistry are observed petrographically and even visually, and locally they act to cement rock fragments in rock piles and debris flows.

Weathering of Questa rock piles over times from 100 to 1,000 years, including attack of acid-rock drainage on primary and hydrothermal minerals, will not produce new clay minerals. Therefore, reduction in shear strength due to increased clay-mineral content is not possible, and gravitational instability based on a mechanism that weathering, including by acid-rock drainage, will generate enough new clay minerals to reduce shear strength is not technically plausible.

References


