HYDROGEOLOGICAL AND GEOCHEMICAL CHARACTERIZATION OF A WASTE ROCK PILE FROM A PORPHYRY COPPER DEPOSIT IN THE SEMI-ARID SOUTH WEST USA

I.F. Walder[2], T., Stein, and T. Shelly Jr.

Abstract. Over the last 15-20 years, there has been a large emphasis on tailings geochemistry and hydrogeology. Waste rocks piles, on the other hand, have received much less attention. Especially in the porphyry copper mining industry, waste rock piles can represent a larger potential for groundwater and surface water contamination than tailings since the waste rocks are commonly unsaturated and coarse. This setting allows for greater oxygen availablility throughout the pile, thus increasing the oxidation potential. In general, there are three flow systems within waste rocks: macro flow (high flow); matrix flow (low flow) and micro flow (within particles) that together with waste rock composition effect seepage water quality. These systems have been investigated at the Tyrone Mine.

Continuous seepage water quality monitoring was performed at one of the stockpiles for approximately one year. The selected stockpile consisted primarily of oxide material with low sulfide content, and had never been leached. Seepage was observed throughout the year and seepage monitoring consisted of flow rate, pH and electric conductivity measurements. Waste rock samples were analyzed for acid base accounting and mineralogy, and kinetic tests were performed. The flow rate together with rainfall, hydrogeological data from the stockpile, stockpile infiltration and evaporation rates, and groundwater recharge rates were used to calculate macro/matrix components in the system using the kinematic wave theory. The results of this modeling indicated that only approximately 10 % of the infiltrating rainwater flowed through the macro pores all the way to the bottom. The majority of the water flowed through the matrix.

Water quality monitoring showed a pH increase during low flow periods and a rapid drop during heavy rainstorms. Electric conductivity had a slow decrease during the dry periods and a drastic increase shortly after heavy rainstorms. The geochemical data indicated a buildup of easily leachable secondary acid generating minerals during the dry periods that were being leached during heavy rain storms. The matrix also possessed a neutralizing effect from silicate mineral dissolution that was working effectively only in the slow matrix flow zones.

Additional Key Words: macro flow, micro flow, waste rock oxidation, silicate mineral neutralization

---

Introduction

Over the last 15-20 years, there has been a large emphasis on tailings geochemistry and hydrogeology (Boorman and Watson, 1976; Blowes and Ptacek, 1994; Jambor, 1994; Blowes, et al., 2003; Dold and Fontbote, 2001, Walder and Chavez, 1995.). Waste rocks piles, on the other hand, have received much less attention due to their complexity, e.g. large grain size variations, mineralogy and chemistry heterogeneity, convective airflow potential, and unsaturated conditions. This complexity has made researchers focus on individual issues such as the flow system (Smith and Beckie, 2003) and oxygen transport and consumption (Ritchie, 2003). Even low (< 2%) sulfide waste rock piles from porphyry Cu mines can represent a larger potential for groundwater and surface water contamination than tailings due to the material coarseness and unsaturated nature. This coarseness (from clay size to boulders) and unsaturated setting increase the possibility for convective air flow, therefore, enhancing oxidation in the waste rocks.

These waste rocks, even though low in sulfides, may still have a large potential for acid rock drainage with high metal concentrations. According to Ritchie (1994), covering waste rocks will have and immediate but temporary effect on mass loading due to reduced flow. With time, however, concentrations will increase and combined with lower flow rates will result in similar mass loading as before. However, if there are neutralizing minerals, the mass loading may be reduced with a cover (Walder and Stormont, 2004; Ritchie, 1994). An investigation evaluating these processes in waste rocks was performed at the Tyrone Mine. The paper is based on the findings from the investigation as reported in several hydrogeological and geochemical reports (Daniels B Stephens & Associates [DBS&A], 1999a; DBS&A, 1999b; SARB, 2000).

Background Data

The Tyrone Cu deposit is located approximately 10 miles southwest of Silver City in Grant County, New Mexico (Fig. 1). Several underground mines operated between 1879 and 1921. Phelps Dodge Corporation reopened the Tyrone Mine in 1967 as an open pit mine (Gillerman, 1964; Kolessar, 1982). The Cu mineralization at the Tyrone Mine is hosted within Precambrian granitic rocks and the Paleocene Tyrone stock (granodiorite and monzonite intrusions). These rocks are overlain by Tertiary volcanic and sedimentary rocks (Gila Conglomerate). A quartz monzonite porphyry dominates the southern half of the ore body, while the ore body is hosted by Precambrian granites in the northern half of the Tyrone deposit (Kolessar, 1982).

There are four general types of stockpiles at Tyrone: (1) overburden material that was not mineralized; (2) waste rocks with low grade mineralization; (3) leach rock stockpiles that primarily contain Cu oxides and can be leached with sulfuric acid; and (4) stockpiles that contain chalcocite/covellite needing an oxidizing agent in addition to H_2SO_4 for leaching. These four stockpile types will generate different tertiary mineralogy and, therefore, different seepage water quality.

To evaluate the seepage potential of poor quality water from the stockpiles having a large mix of mineral assemblages (MA; Table 1), material collected during exploration drilling of the deposit was geochemically characterized, including kinetic testing. The result of the testing indicated that none of the MA's would go acidic (or only slightly acidic) (DBSA, 1997a,b).

The focus of this investigation was to 1) present a geochemical evaluation of a stockpile at the Tyrone Mine that has not been leached and has been weathered for more than 10 years, 2) determine the potential for the release of acid rock drainage, and 3) evaluate the processes

controlling the quality of the water exiting the stockpiles. The west part of the Stockpile 2A (SP-2A) that has not been leached was used for this investigation.
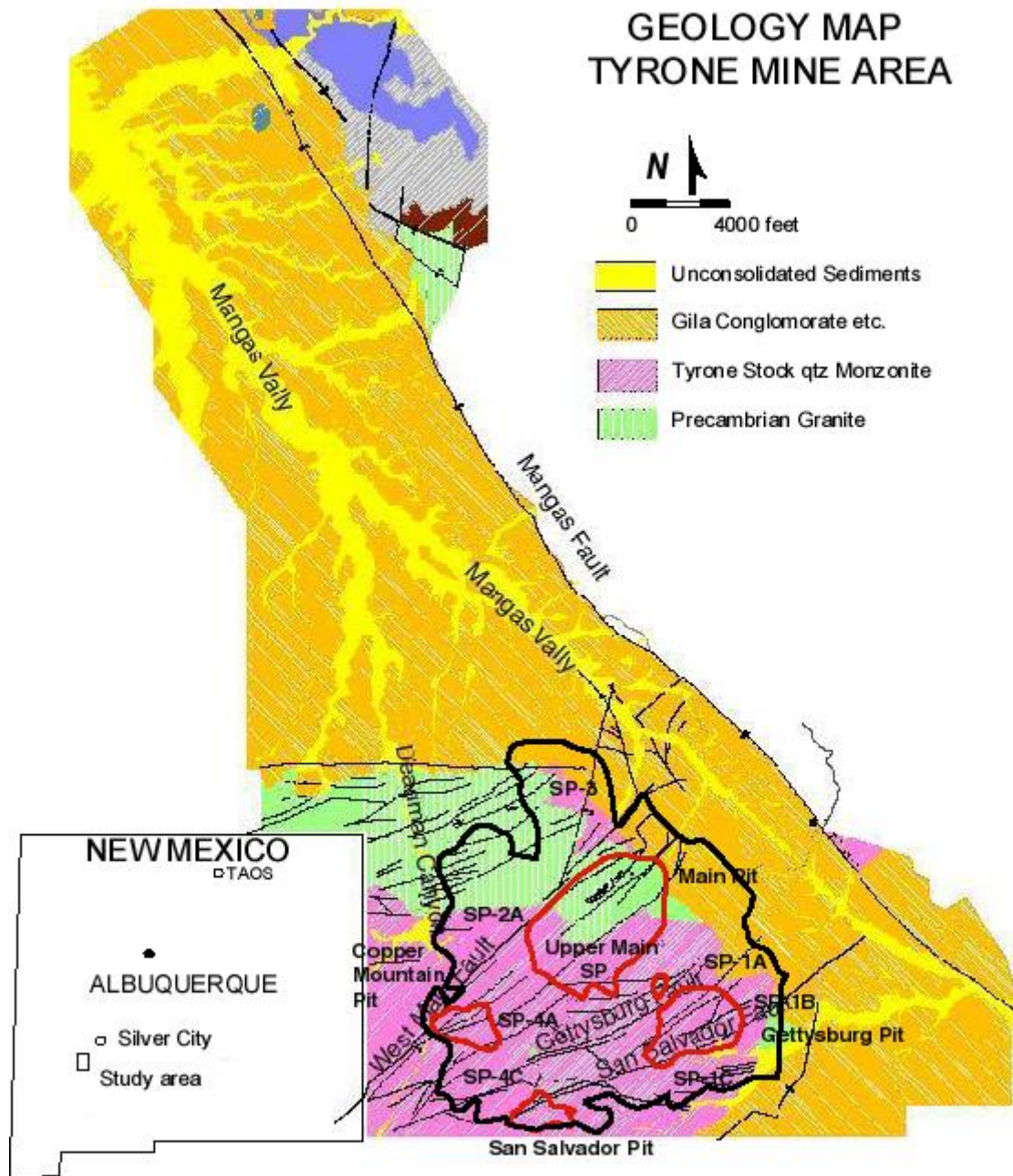

Figure 1. Geology map of Tyrone mine area. The map shows four pits marked with a red line, the active mining area in black and location of stockpiles (SP-) around these pits. Modified from Blandford et al., 2004.

Analytical Methods

Mineralogical analyses were performed using standard microscopic analysis on epoxy mounted rock chip material at the University of Geneva, Switzerland. X-ray diffraction analyses were performed at the New Mexico Bureau of Mines, USA.

Acid Base Accounting (ABA) was performed by SVL Analytical of Kellog, Idaho using the sulfur species method for Acid Producing Potential (APP) following the modified Sobek method (Sobek et al., 1978) and the gross neutralizing potential method Acid Neutralizing Potential (ANP). The APP method gives the SO_4^{-2} sulfur, sulfide sulfur, organic sulfur (non reactive sulfur) and total sulfur all recalculated as $CaCO_3$ tons/1000 tons equivalents using the sum of non reactive and sulfide sulfur.

Water quality analyses were performed by Inter-Mountain Laboratories of Farmington, New Mexico, following standard EPA methods. Samples were analyzed for major and trace elements, bi-carbonates, SO_4^{-2}, alkalinity, total dissolved solids and pH.

Table 1. Mineral assemblages at Tyrone Mine. Mineral assemblages MA 1 to MA 6 were included in the column tests analysis for both stockpile samples and un-mined material.

Mineral Assemblage	Name	Description
0	Not Mineralized	Gila Conglomerate, younger alluvium, and soils
1	Leach Capping	Iron oxide dominant mineralogy, copper grades less than 0.15%, no sulfide minerals
2	Green Oxide Copper	Chrysocolla, malachite minerals with accessory azurite, copper grades of 0.15 to 0.5%, no sulfide minerals
3	Oxide/Chalcocite	mixed mineralogy of oxide copper minerals with chalcocite and pyrite, copper grades of 0.15-0.60%
4	Chalcocite-Pyrite	Chalcocite dominant copper mineral, pyrite present, copper grades of 0.15-0.80%, no oxide minerals
5	Chalcocite/ Chalcopyrite	Chalcocite dominant over chalcopyrite with accessory covellite, bornite and pyrite, copper grades of 0.10-0.30%
6	Chalcopyrite/Pyrite	Chalcopyrite with pyrite and bornite, no chalcocite or covellite, copper grades less than 0.15%
7	Mixed Oxide and Chalcopyrite	Copper oxide, carbonate and silicate minerals with chalcopyrite, pyrite present, volumetrically minor mineral assemblage
8	Native Copper/Cuprite	Native copper and cuprite, no sulfide associated, copper grades of 0.15-0.35%
10	Stockpile/tailings	Stockpiles and tailings material. If the mineral assemblage is known, as described above, the logged number will be 10X, where X may be 0-8.

Water quality analyses were performed by Inter-Mountain Laboratories of Farmington, New Mexico, following standard EPA methods. Samples were analyzed for major and trace elements, bi-carbonates, SO_4^{-2}, alkalinity, total dissolved solids and pH.

Kinetic tests for ten stockpile samples were run in 4 inch diameter columns at the University of New Mexico, Engineering Department, Albuquerque, New Mexico. The columns were designed with drain and filter at the bottom, and humidified air was pumped into the top of the columns at a constant rate. Once every 1-3 weeks, the samples were rinsed with 150 ml distilled water to extract soluble SO_4^{-2} minerals precipitated since the previous rinse. Sulfate, pH, and Fe were analyzed for the extracted samples, while Cu and alkalis were analyzed in a few of the extractions.

Core samples of un-mined material collected during exploration drilling (15-20 years ago) were selected and run for Kinetic tests by DBS&A Hydrological Testing Laboratory (DBS&A, 1997b). The tests were performed with a seven day wetting a drying cycle with a rinse at the end of each weekly cycle. The tests were run for approximately 30-50 weeks. The weekly rinse was analyzed for pH, electric conductivity (EC), acidity, alkalinity and SO_4^{-2}.

Waste rock samples may contain several minerals which release the same constituents. Therefore, weathering rates for specific minerals cannot be calculated using kinetic tests. However, release rates for SO_4^{-2} were calculated based on the following equation (Morin and Hutt, 1997):

$$\frac{C_i x V_i}{M_s x T} = \text{ rate of release [mg/(kg x week)]} \tag{1}$$

where C_i is concentration of constituent i in the solution in mg/l; V_i is the volume in ml of the extracted rinse solution, M_s is the mass in kg of solid material used for the kinetic tests, and T is the time in weeks elapsed since last rinse.

The field hydraulic testing performed by DBS&A of Albuquerque, New Mexico, was done using small scale tension infiltrometers. These tests measured the hydraulic conductivity of an 80 cm^2 area. Two large scale falling head field tests were performed in order to estimate hydraulic conductivity on the surface of the stockpile and at ½ - 1 meter depth.

Physical and hydraulic parameters were measured on two core samples from Stockpile 2A consisting of uncompacted and compacted colluvium material at the DBS&A laboratory. Parameters included; porosity, water content, particle-size distribution, saturated hydraulic conductivity using Falling Head (uncompacted colluvium) and Constant Head (compacted colluvium), and moisture retention characteristics. In addition, 8 grab samples were collected from various lifts within Stockpile 2A and analyzed for particle distribution at the DBS&A laboratory.

Results

The central and southern part of SP-2A (Fig. 1) was emplaced during the period from 1973 to 1978. Since that time, no additional material was added to this portion of SP-2A. The southern and central portions contained a mixture of all mineral assemblages; MA-0 - MA-6.

Historically, SP-2A has been considered a waste stockpile receiving predominately MA-0, MA-1, and MA-2.

Mineralogy and Mineral Assemblage

The majority (>95%) of SP-2A, determined by the Tyrone Mine drilling program, consisted of MA 1 (leach cap) and MA 2 (green oxide). These zones were logged MA 101 and MA 102, respectively, the number 10 placed in front of the mineral assemblage indicating "stockpile". Stockpile material was collected and combined into 10 foot intervals and stored. A few zones in the stockpile were logged as 104, 105, and 106. Samples from these zones, as well as samples from MA 101 and MA 102, were selected (6 samples from 20 ft. intervals [MIX 1-6], 3 samples from 10 ft. intervals [MIX 7-9] and one sample from a 30 ft. interval [MIX 10]) and analyzed. Thin sections and polished thin sections were analyzed using optical microscopy, and XRD analysis was performed on sub-samples.

The microscopy analyses indicated that all samples contained some pyrite. Pyrite was found to be less abundant (trace 0.5 vol.%) in the four samples of MA 101 and MA 102, than in the other six samples (0.5 to 1.5). Traces of chalcopyrite and covellite were observed in five of the samples. No other sulfide minerals were observed. Red hematite and goethite were observed in all samples, however, in slightly greater abundance in the MA 101 and 102 samples. Quartz and alkali feldspar were observed in all samples as the major minerals occupying 30-50% by volume.

The feldspar, to a large extent was altered to sericite. Jarosite was observed in all samples, occupying 5-15 vol.% of the samples. Biotite and chlorite were observed in most of the samples, occupying 1-4 vol.% of the mineral assemblages.

Hydrogeology

The stockpile seepage investigation focused on 1) monitoring the water quality and flow rates (weekly to monthly) of a seep (5E Seep) located on the west side of the Tyrone Mine since 1997; 2) field hydraulic testing, hydraulic and physical parameter testing of stockpile material, and particle distribution analysis of grab samples; and 3) modeling the flow system in the stockpiles.

There were no historic springs in the area of SP-2A. However, drilling of the stockpile determined that the western portion of SP-2A filled the top of an ancestral drainage area in which water was collecting and generating a seep that exited the base of the stockpile. This seep, referred to as 5E Seep, was assumed, therefore, to be representing water leaching through the western portion of SP-2A.

With the use of automated seep monitoring systems, 5E Seep was continuously monitored for flow rate, pH and conductivity. A summary of the seep collection data is listed in Table 2.

The small scale field hydrologic testing performed on various stockpiles at Tyrone resulted in calculated hydraulic conductivities ranging between 10^{-4} and 10^{-5} centimeters per second (cm/s). The large scale field tests were performed on Stockpile 1A (SP-1A) and the western portion of SP-2A. The resulting hydraulic conductivities ranged from 1.5×10^{-4} to 2.0×10^{-4} cm/s. Large scale tests performed 2-3 feet below the stockpile surface resulted in estimated conductivities between 2.3×10^{-3} and 1.2×10^{-2} cm/s.

The results for the physical and hydraulic properties of the core samples indicated a distinct difference between the uncompacted and compacted colluvium. The results are as follows:

* Measured saturated hydraulic conductivity of the uncompacted and compacted colluvium was 2.4×10^{-3} cm/s and 1.9×10^{-6} cm/s, respectively;

* The dry bulk density of the uncompacted and compacted colluvium ranged from 1.69 to 1.99 grams per cubic centimeter, respectively;

* The initial moisture content of the colluvium ranged from 20.2 (uncompacted) to 24.4 (compacted) percent (%);

* Particle size analyses indicated a large variation in texture of the stockpile material, from cobble-size rocks to clay-size particles;

* The uniformity coefficient of the material ranged between 330 and 1500, and the curvature coefficient ranges from 1.9 to 6.7.

Field observations indicated that the following four types of materials could be found in almost all stockpile lifts: 1) compacted zone near the stockpile surface, 2) clastic unit comprised of cobbles/boulders, 3) matrix supported unit consisting of coarse sands and gravels, and 4) a matrix-supported coarse unit of sands and gravels mixed with clay. The last three of these units lie at the angle of repose.

Seepage Properties and Analysis

In the fall of 1998, Tyrone Mine installed an automatic pH, EC and flow meter as a part of the seepage investigation. The data is included in the January and July, 1999 seepage investigation reports. The data indicated (Table 2) that the pH could drop several units as a result of heavy rain fall and high seep flow. Most of the water seeping almost immediately after high rainfall is due to macro-pore flow. The 5E Seep was also sampled quarterly, and the average water quality is given in Table 3.

Table 2. Summary of seepage monitoring results for the different monitoring periods, including pH and electrical conductivity (EC) measurements, gpm- gallons per minute.

PROPERTIES		SEEP 5E	
Monitoring Period		Sept.-Dec. 1998	Jan.-May 1999
Precipitation		6.7 inches	1.3 inches
Average Flow		13 gpm	6 gpm
Measured pH	Low (precipitation events)	3.3 to 3.7	
	High (dry periods)	4.0 to 4.5	

EC	3,750 to 5,340 umhos/cm
Measurements	(between Sept-Jan. 1999)

Acid Base Accounting

The APP for the ten stockpile mix samples were within the range 2-16.5 t/kt $CaCO_3$ eq. The ANP was zero for all analyzed samples. 10-20% of the APP consisted of residual sulfur (SO_4^{-2} sulfur had not been included in the APP even though this SO_4^{-2} sulfur seemed to be from jarosite). As a comparison, the APP reported for surface samples had a range of 5-70 t/kt $CaCO_3$ eq., and were much higher than the samples selected from the drill holes.

Table 3. The average water quality of five samples collected at the 5E-Seep. The element concentrations are in mg/l.

5E-Seep

Date collected	97-98	Cond.	2,786	Mn	59
Na	54	pH	3.74	Mo	na
K	11	Al	203	Ni	0.35
Ca	294	As	Na	Pb	0.1
Mg	184	Cd	0.14	Se	na
Cl	71	Co	1.55	Zn	25.5
F	18.5	Cr	0.02	CO_3^{-2}	<1
HCO_3	<1	Cu	506	Temp	14.2
SO_4	3,644	Fe	1.88	Field pH	3.7
TDS	5,686	Hg	Na		

Table 4. Mineral type mix and ABA data for the Stockpile 2A used in kinetic tests. AGP –acid generation potential includes pyritic sulfur and non-extractable sulfur.

	Mineral Assemb.	Total Sulfur	Oxidized Sulfur	Py+Non S	AGP	AVG. MA AGP
MIX 1	101	0.19	0.12	0.07	2.3	9.1
MIX 2	102	0.26	0.09	0.17	5.2	3.2
MIX 3	101	0.42	0.07	0.35	10.8	9.1
MIX 4	101/105	0.76	0.24	0.52	16.1	79.4

MIX 5	102	0.34	0.16	0.18	5.7	3.2
MIX 6	101/106	0.34	0.1	0.25	7.8	57.1
MIX 7	104	0.93	0.41	0.52	16.2	66.2
MIX 8	101/105	0.8	0.4	0.4	12.5	79.4
MIX 9	101/106	0.37	0.04	0.33	10.4	57.1
MIX 10	101/106	0.64	0.38	0.26	8.1	57.1

Grain Size Analysis

The samples were analyzed for grain size distribution prior to kinetic testing. These tests indicated that 30-70% of the particles in these samples had a grain size of less than 1 millimeter. This resulted in a much higher surface area exposed in the tests than in the stockpiles. These small grain sizes were due to drilling method used, reverse circulation.

Column Tests

Kinetic (column) tests were performed on the ten stockpile mix samples (MIX 1-10) as listed in Table 4. The rinse solutions were analyzed for electrical conductivity and pH immediately after collection. In addition to the above mentioned parameters, the rinse solutions were also analyzed for SO_4^{-2} and Cu throughout the test period and for Fe in the first 6 sampling periods,

The pH was relatively stable for all tested samples with approximately ½ a log unit drop over the test period (Fig. 4 and Fig. 5). However, the pH level was higher (3.5-5.5) for the samples with only leach cap or Cu oxides mineralization (MIX 1, 2 ,3, and 5), than for the samples with sulfide mineral assemblages (2-4.5) (Fig. 4). The two highest recorded SO_4^{-2} concentrations in these tests were approximately 80,000 mg/l and 33,000 mg/l for Mix 7 and Mix 8, respectively, for the first week's rinse (Fig. 5). The SO_4^{-2} increased for most of the samples after 3-4 rinse periods, then dropped again. The SO_4^{-2} increase coincided with the decrease in pH. Even after 25 weeks of rinsing, the SO_4^{-2} concentration was one half to one order of magnitude higher than for the kinetic tests run on un-mined material (Fig. 6).

The Cu concentration was high for the first few rinse periods, dropped down and increased slightly for the next few rinse periods then dropped again (Fig. 4 and Fig. 5). The Cu increase was taking place at the same time or slightly prior to the increase in pH and release of SO_4^{-2}.

Iron concentrations were high for the samples Mix 7, Mix 8 and Mix 10 (Table 5). These were the samples that had the highest SO_4^{-2} concentrations. The SO_4^{-2} released per week for the stockpile samples was one half to one order of magnitude higher than for the un-mined material. The pH was 1-3 units lower for these stockpile samples than for the un-mined material (Fig. 6).

Table 5. Iron concentrations in mg/l for rinse solutions for the first six sampling times.

	March 23	April 9	April 28	May 26	June 16	July 1
Mix 1	0.8	0.8	0.8	nd	nd	nd
Mix 2	0.8	0.8	0.8	nd	nd	nd

Mix 3	2	0.8	0.8	nd	nd	nd
Mix 4	8.4	3.3	1.6	nd	nd	nd
Mix 5	0.8	0.8	0.8	nd	nd	nd
Mix 6	1.8	0.8	0.8	nd	nd	nd
Mix 7	532	398	228	227	ns	178
Mix 8	26.8	3.3	2	42	nd	nd
Mix 9	0.8	0.8	0.8	nd	nd	nd
Mix 10	206	10.5	1.8	38	63	66
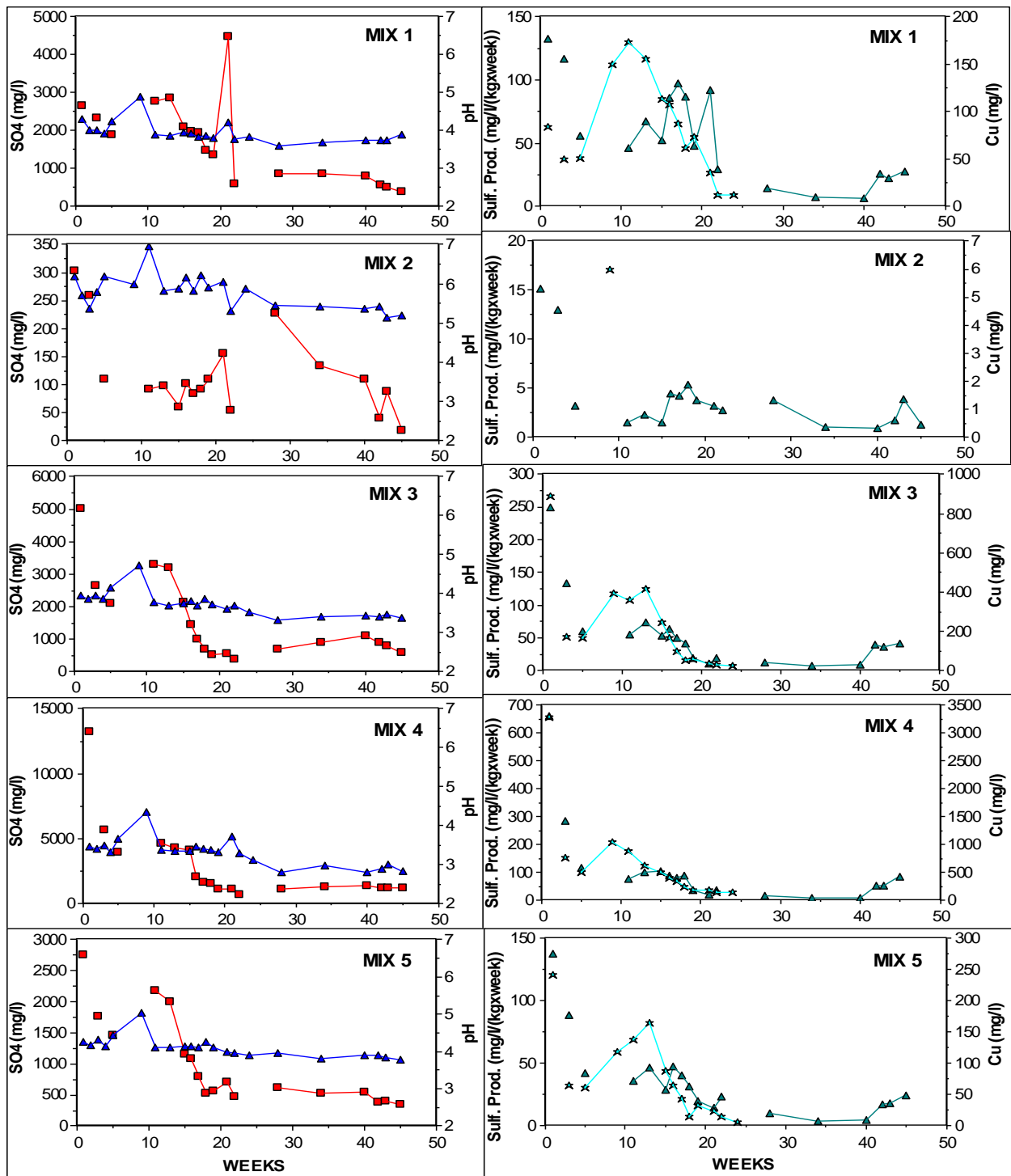
Figure 4. Kinetic tests for waste rock samples Mix 1 to Mix 5. Red squares are SO_4^{-2}; blue triangles are pH; green triangles in figures to the right are SO_4^{-2} production; and stars are Cu.
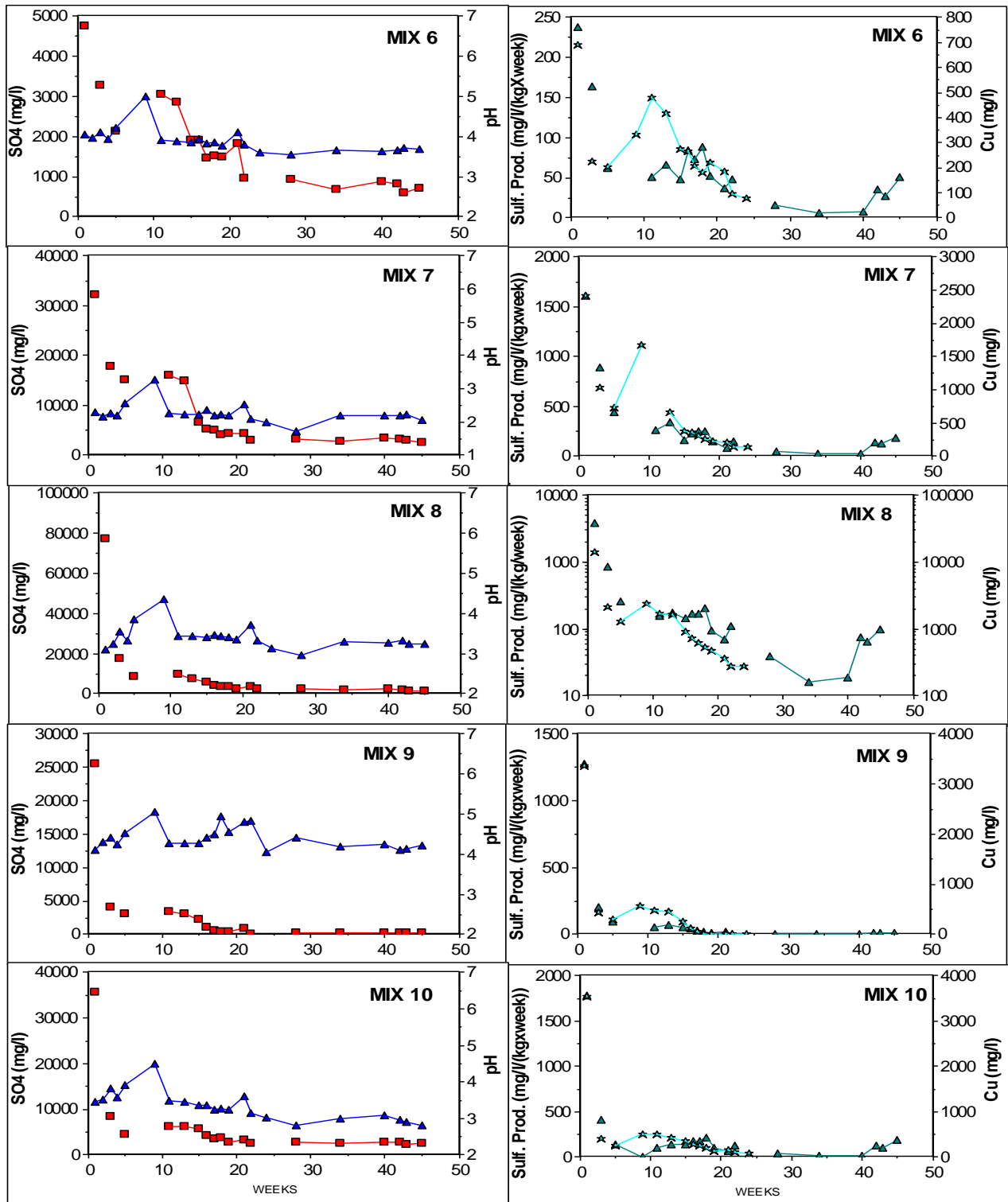
Figure 5. Kinetic tests for waste rock samples Mix 6 to Mix 10. Red squares are SO_4^{-2}; blue triangles are pH; Green triangles in figures to the right are SO_4^{-2} production; and stars are Cu.

The kinetic tests of the leach cap, oxide ore, and oxide-chalcocite mineral assemblages (MA1, MA2, and MA3, respectively) in the un-mined material indicated an alkalinity production of 1 mg $CaCO_3$/(kg x week) and SO_4^{-2} production of less than 1 mg/(kg x week) throughout the 35-50 weeks of testing. The pH was stable around 6-7.

Four of the five kinetic tests of the sulfide mineral assemblages, MA4 (two tests), MA5, and MA6, in the un-mined material, indicated a drop in pH, which was 7.5-8 in the initial rinse, stabilizing to pH values in the range of 5.5-6.5. The alkalinity production was less than 1 mg $CaCO_3$ /(kg x week) throughout the test period. The alkalinity production was slightly higher in the beginning of the tests than at the end of the tests.

Discussion

The stockpile flow modeling involved calculating the macro-pore flow by using the kinematic wave theory applied to stockpiles (Smith et al., 1995). Using this method, the macro-pore flow is modeled as channels through the stockpiles. The matrix flow is assumed to be the rock matrix, everything outside the macro-pore flow.

The kinematic wave theory was developed by Germann and Beven (1985) to model water movement in macro-pore systems. Germann and Beven derived the analytical solution to calculate the wetting fronts and drying tails in macro-pore and porous matrix. This theory interprets the macro flow as boundary-layer flow instead of preferential flow and was originally used to explain saturated flow through fissures and worm holes in soils.

In order to predict the water quality of the seepage exiting a stockpile having a variable grain size composition (from clay size to boulder size), it is necessary to know the following (Smith et al., 1995): 1) the flow system and reactions within the stockpile void spaces, and 2) the flow system and reactions within the stockpile matrix. Reaction time can be quite different in these two systems. DBS&A (1999) modeled the flow system in Stockpile 2A based on field observations, rainfall measurements, evaporation measurements, stockpile toe flow measurements, water content of stockpile material, and a conceptual model of the structure of the stockpile. This input data (as described in the result section) was then used to perform reactive transport modeling of water flowing through the macro-pores and the matrix.

Stockpile Flow Modeling

A numerical model was developed to simulate flow through the Tyrone Mine stockpiles. The western portion of Stockpile 2A was modeled as a representative case. The flow system within the stockpiles was divided into two types: macro-pore flow, the rapid but short duration flow of water through the top surfaces of the stockpiles; and matrix flow, the base flow conditions within a stockpile. The following are the general characteristics/assumptions used in modeling the western portion of the 2A stockpile:

* Two lifts present: The top lift, approximately 33 feet (10 meters) thick; and the lower lift, varying from 50 to 230 feet (15-80 meters) thick,

* A compacted zone on the top of each lift (due to heavy equipment traffic),

* A layered system within each lift (due to the end-dump construction process),

* Outslopes of 2A rest at an angle of approximately 33.7 degrees;

* Seep 5E, outflow from the western portion of stockpile 2A, an average flow rate of approximately 8.8 gallons per minute (gpm);

* The 5E Seep watershed covers an area of approximately 97.5 acres (394,596 m^2). Approximately 80% of this watershed covered by the western portion of 2A Stockpile;

* The depth to the regional groundwater table ranges between approximately 89 feet and 630 feet bgs of the pre-mining watershed;

* An average annual precipitation of 16 inches per year, and

* No vegetation on Stockpile 2A.

The preferential flow through the stockpile was analyzed by evaluating the seep flow variation at the base of the western portion of the stockpile following precipitation events. The matrix flow was simulated using the finite element code SWMS-2D, developed by the U.S. Salinity Laboratory, Riverside, California (Šimúnek et al., 1996).
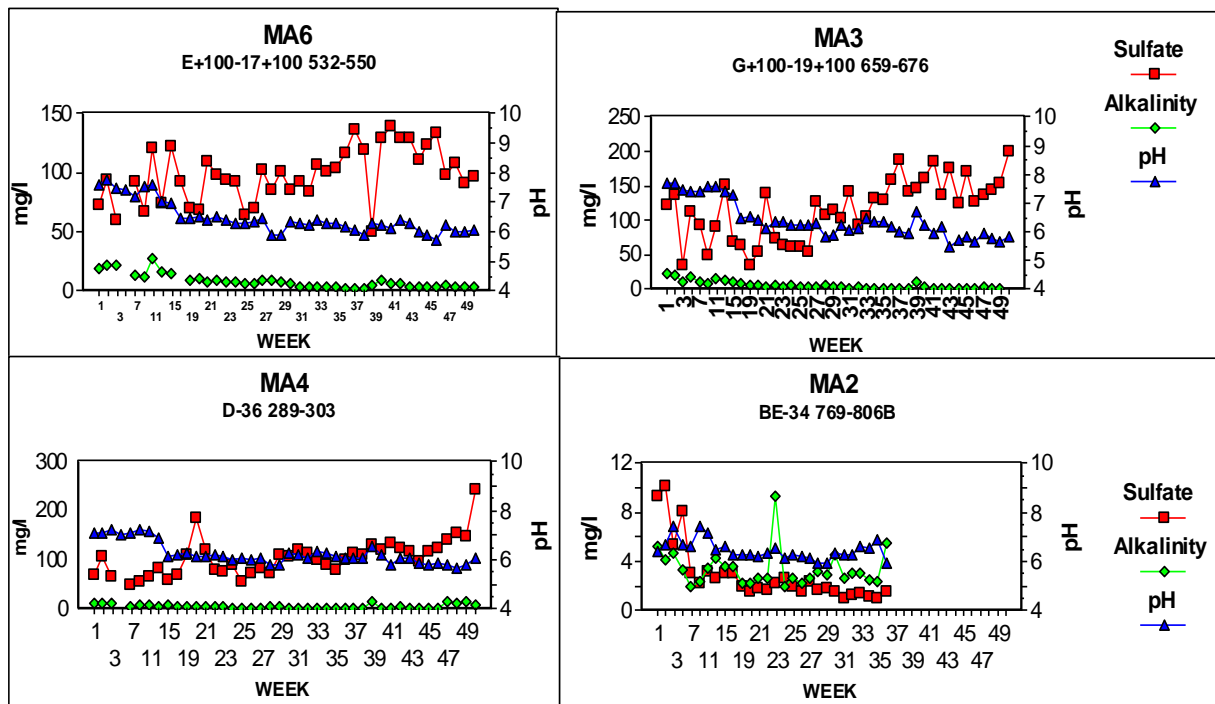

Figure 6. Kinetic tests results for MA 6, MA3, MA 4 and MA 2 for un-mined material selected from stored core samples.

Boundary Conditions.   A constant recharge rate equal to 15% of the average annual precipitation, was initially applied to the top and the outslope of the stockpile to simulate water infiltration from precipitation. Sensitivity analyses, using infiltration equivalent to between 12 and 50% of the average annual precipitation, were also performed to evaluate the effect of various constant recharge rates.

Material Properties. The following eight different material types were applied to the numerical modeling: 1) three material types within the main body of the stockpile (referred to as layers A, B, and C), 2) upper and lower compacted zone at the top of each stockpile lift, 3) thin colluvium layer at the base of the stockpile, 4) bedrock unit beneath the colluvium layer, and 5) alluvium within drainage emanating from stockpile toe. In addition, a layered system, with individual layers varying in thickness between 3.3 and 13 feet (1 and 4 meters), was applied to each stockpile lift. The layers were made up of the following three repeating material types: 1) clastic unit consisting of cobbles/boulders, 2) matrix-supported unit consisting of course sands and gravels, and 3) matrix-supported unit consisting of sands and gravels mixed with clay. Table 4 summarizes three parameters associated with the calibration of the model, based on field and laboratory physical and hydraulic properties measured and used for the matrix flow simulations.

Macro-pore Flow Simulations. Three precipitation events were evaluated: 1) a 2.29 inch rainfall event (between October 25 and 27, 1998) that produced a peak flow of approximately 21 gallons per minute (gpm), 2) a 0.91 inch rainfall event (between November 9 and 11, 1998) that produced a peak flow of about 36 gpm, and 3) a 0.33 inch rainfall event (January 21, 1999) that produced a peak flow of approximately 14 gpm.

Results of these three separate precipitation events indicate that between 0.9 and 3.6% of precipitation during these storm events resulted in preferential flow through the western portion of the stockpile. The results of the analysis suggest that for precipitation events between approximately 0.3 and 2.3 inches, most of the water infiltrating the stockpile does not migrate as macropore flow. Only approximately 0.9 to 3.6 percent of the precipitation that occurred during the three storm events resulted in preferential flow (macro pore flow) (Fig. 7).

Ancestral Drainage Seepage Estimations. There are two pathways by which water seeping from Stockpile 2A eventually exits the stockpile: 1) draining directly downward into the underlying bedrock unit, and 2) flowing laterally within ancestral drainages underlying the stockpiles into the 5E Seep collection system, with a small portion possibly infiltrating the underlying bedrock unit. The Green-Ampt infiltration model (Rawls et al., 1993) was used to estimate water seepage from the ancestral drainages to the underlying bedrock. For the analysis, a channel width of 4 meters was assumed for the drainage beneath the stockpile. A vertical saturated hydraulic conductivity of 7.9 x 10^{-8} cm/s was assigned to the bedrock unit. This calculation indicates that only <0.5 of the seepage at the base of the stockpiles recharges the stockpiles from the ancestral drainage.

Matrix Flow Simulations. Eight flow simulations were run for the western portion of the 2A stockpile using vertical bedrock conductivity, horizontal colluvium hydraulic conductivity and infiltration rate as the variables. After 8 years simulation time, two of the runs gave 9.5 and 9 gpm as base flow, while the measured base flow was 8.8 gpm. These two runs where, by far, the closest to seep measurements. Based on the modeling simulation from these two of the runs, it is estimated that 67 to 70% of the total infiltrating precipitation flows into Seep 5E collection system. The remaining 30 to 33% infiltrate the underlying bedrock. Therefore, of the average annual precipitation, 10.1 to 10.5% flow to the Seep 5E collection system and 4.5 to 4.9% infiltrates the underlying bedrock.

Table 6. Parameters for material types used to calibrate model; K_s - horizontal saturated hydraulic conductivity, θ_r - residual and θ_s - saturated moisture content.

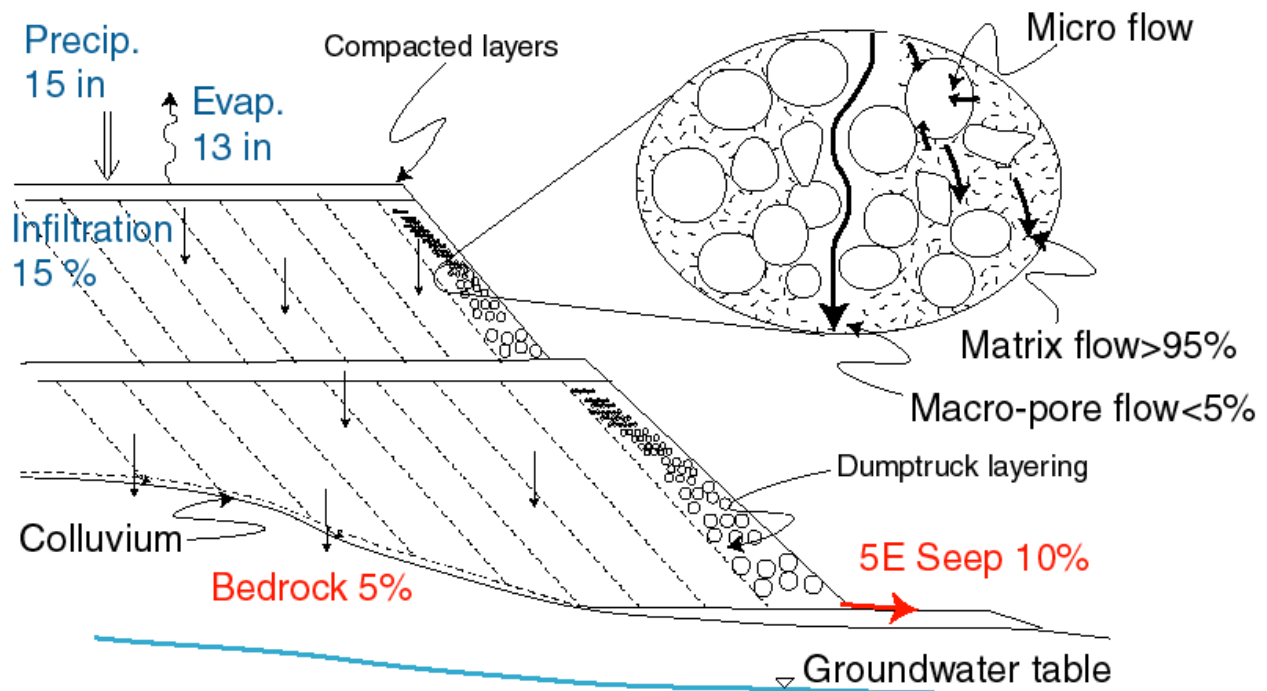| Property	K_s (cm/s)	θ_r (% cm^3/cm^3)	θ_s(% cm^3/cm^3)
Lift layer A	1.0×10^{-2}	0.01	0.350
Lift layer B	1.00×10^{-1}	0.02	0.300
Lift Layer C	1.00×10^{-3}	0.05	0.250
Bedrock	7.90×10^{-7}	0.0025	0.015
Top compacted zone, upper	1.00×10^{-5}	0.06	0.150
Top compacted zone, lower	1.00×10^{-4}	0.06	0.200
Alluvium	3.47×10^{-2}	0.05	0.360
Colluvium	2.40×10^{-2}	0.01	0.360

Figure 7. Conceptual model of the stockpile showing a compact horizontal layering due to dump truck traffic and an angular layering from the dumping. The dumping results in coarse material gradation. The figure also includes results from the flow modeling where 15% of the rainfall infilltrates; 5% of this rainfall recharges the groundwater; and 10% reaches 5E seep. >95% of infiltrating water moves through the matrix, while <5% moves through the macro pores.

During dry periods the macro pores dry out more rapidly than the matrix. During a heavy rainfall, the macro pores in the upper parts (near surface) of the stockpiles fill with water. When this water spreads over a larger part of the macro pores, the hydraulic conductivity in the matrix becomes higher than that in the macro pores, and the water will move into the matrix instead of reporting to the base of the stockpile (Walder and Stormont, 2004). Only when the matrix is near saturation will water move from the matrix into the macro pores.

Residence Time Estimates. Residence times were estimated for steady state matrix flow within the following units: 1) main body of stockpile, 2) colluvium unit beneath stockpile, and 3) and underlying bedrock unit. Flow paths were constructed by releasing particles on the surface of the simulated steady state flow field and recording the trajectories. Results indicate that flow is predominantly in a downward direction within the stockpile. Pore water exits the stockpile either via the drainage or infiltrating the underlying bedrock. For each flow path, the residence time was calculated by summing the estimated travel in each unit, results are as follows:

 * Average residence time for steady-state water flow through the main stockpile body is approximately 47 years. The longest estimated residence time is 62 years.

 * Residence time within the colluvium depends on the location where water moves down from the base of the stockpile to the colluvium contact. The longest estimated time for water particles draining from within the colluvium to the underlying alluvium channel is approximately 3.1 years.

 * The residence time estimates for the bedrock unit are between approximately 10 to 70 years, averaging 37 years.

Geochemistry

The ABA test results show no ANP and low APP. The analyzed rock material contains less than 1 % sulfides. The stockpile samples Mix 1 - Mix 10 from Stockpile 2A were from material that was mined more than 10 years ago. The material was only blasted in the pit and moved, which resulted in a large grain size variation. The ABA results indicate that a large portion of the pyrite has already oxidized, if using the data from the Materials Characterization (DBS&A, 1997c) as the original baseline AGP, about one half of the samples collected from the stockpile drilling material was logged as mixed material, having characteristics of the leach cap mixed with other mineral assemblage types.

The kinetic tests results indicate that these rocks, that have been available for oxidation for 20-30 years, produce sulfuric acid, most likely leaching SO_4^{-2} (acidity) from iron SO_4^{-2} minerals. This could be because there are still more SO_4^{-2} minerals left in the stockpile material and/or Fe^{+3} iron is available for sulfide oxidation. The results also indicate much higher sulfide oxidation rates in the mined than the un-mined material. Secondary precipitates may include Fe^{+3} iron, indicating a relatively high rate of sulfide oxidation (Nicholson, 1994). These conditions were not produced in the drill cores from un-mined material.

Simple reactive transport modeling was performed on the waste rock system using MPATH (Lichtner, 1998), modeling the matrix and macro flow systems separately using feldspar, chalcopyrite, and pyrite as the reacting minerals, with sericite, kaolinite, gibbsite, tenorite, bochentite, chalcocite, ferrihydrite and jarosite, as secondary minerals (Walder and Stormont, 2004). Reaction rates for the minerals used in the modeling were based on field observations and published data (Walder et al., in prep).

The model calibration for the stockpile modeling included the following: 1) within 20 years of oxidation/weathering, the tertiary SO_4^{-2} minerals such as jarosite and brochantite should appear, 2) within 20 years oxidation/weathering, a pH of 2.5-3 should be generated somewhere along the flow path, and 3) a total sulfide oxidation of a 0.2 meter diameter particle should occur within 300 years.

The thrid criteria was based on the individual particles representing a matrix flow that is much slower than the macro-pore flow, each of the particles had an oxidation front moving towards its center. This oxidation front can be expressed by the shrinking core model, developed to describe a time scale for the oxidation of a particle (t_p) (Davis and Ritchie, 1986 and 1987):

$$t_p = \frac{\rho_s a^2}{3 c_0 D_2},$$
(2)

where is mass of oxygen per mass of reactant; ρ_s is initial bulk density of reactant; a is particle radius; is a proportionality constant (0.3); is volume fraction of the solid phase; c_0 is concentration of oxygen in air; and D_2 is diffusion of oxygen in the particle.

The matrix-flow geochemistry simulation was performed assuming the oxidation, with high flux of oxygen, was the same in the upper 40 meters. The program does not directly compute with unsaturated and saturated conditions, and therefore, some adjustment to the modeling was made to compensate for this. This adjustment was done by spiking the incoming water with 160 mg/l oxygen. Water can dissolve approximately 10 mg/l oxygen. This large amount of oxygen is equal to a 20% saturation.

Predictive modeling for the matrix flow was performed for the first 100 years from the start of the stockpile development, assuming that the stockpile is approximately 20 years old. The input data included the infiltrating water quality (Table 7) and the initial water quality in equilibrium with the minerals used in the modeling under reducing conditions.

After 100 years of reaction time, the pyrite oxidation front has moved to approximately 6 cm. At particle depth 0 to 0.5 cm, pH is a high 5.5 to 7.5 (Fig. 8), while pH is higher when Cu minerals are not included. The pH appears to be controlled by the Cu minerals in the oxidized zone and by pyrite oxidation near the oxidation front with tenorite in the higest pH area, replaced by brochentite and chalcocite towards the oxidation front.

At particle depth 0.5 – 6 cm, the environment is acidic (Fig. 8). As goethite dissolves, there is a slow increase in the pH. When Cu mineral are not include in the modeling, jarosite becomes stable, and the pH drops drastically.

The SO_4^{-2} minerals are moving with the oxidation front occupying the area behind the front where the pH is low and SO_4^{-2} concentration is high (particle depth 3-6 cm) (Fig. 8). Alluminum concentration is high near the oxidation front in the low pH environment. Iron is in reduced form, at particle depth +6 cm. Whereas high SO_4^{-2} occurs behind and in front of the oxidation front (+3 cm depth).
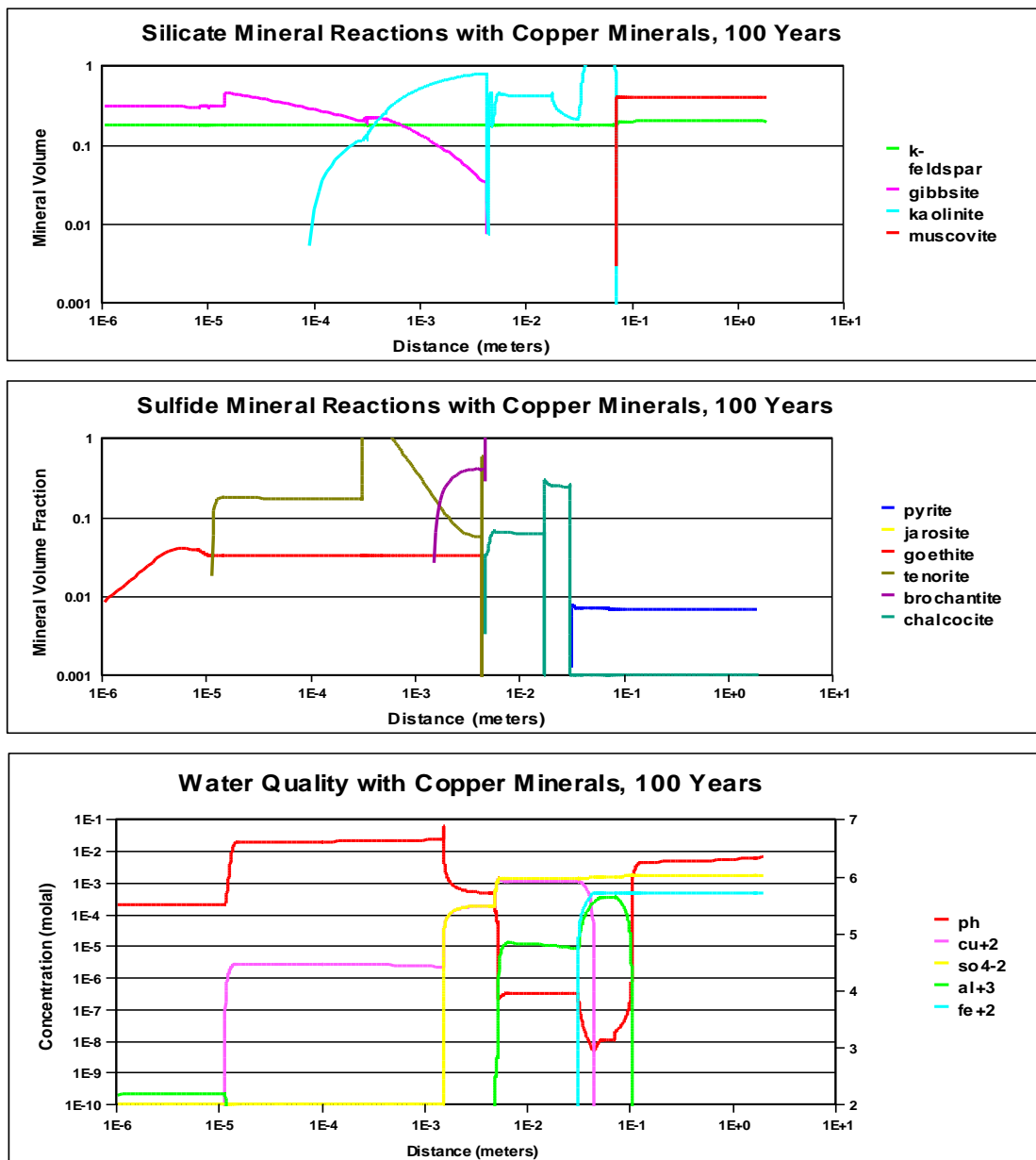
Figure 8. Mineral distribution during reactive transport modeling of stockpile material for two meters of material. Note that the pyrite oxidation has reacted to a depth of 10 cm, indicating that a particle with 20 cm diameter would be totally oxidized after 300 years.

Table 7. Initial water quality for the matrix flow predictive modeling. Atm - atmosphere pressure.

Parameters	Matrix Flow
pH	5.5
SO_4	0.1 mg/l
Al	3×10^{-6} mg/l
Cu	6×10^{-6} mg/l
K	4×10^{-6} mg/l
Si	6×10^{-6} mg/l
O_2	160 mg/l
CO_2	0.0032 atm

The modeling indicates that the matrix flow water quality can be modeled as a whole with oxygen being transported through the system If modeling the matrix separately, the water quality will stabilize at an almost neutral pH within a few years. However, as long as there is still oxidation in the matrix, the matrix reactions will control the macro-pore water quality.

Based on the modeling results, it is likely that as the water flows through the matrix, it moves through the oxidizing front increasing in SO_4^{-2}, Fe^{+2} iron and Cu content and becoming lower in pH (Fig. 9). On the way out of the matrix, towards the macro-pore channel walls, it goes through the oxidizing zone and into oxidized material, picking up more SO_4^{-2} and Cu. Ferrous iron oxidizes and possibly precipitates as goethite/ferrihydrite.

The deeper and inner parts of the stockpiles may have less influx of oxygen and thereby, less pyrite oxidation. In these areas, the pH is likely controlled by the feldspar-muscovite mineralogy as indicated by the 20 years, 100 years and 300 years modeling, in which a pH of 5.5 to 6 with low metals content results. There is sufficient amount of reactive silicate minerals to neutralize all acid generated from the small amount of pyrite within the stockpile, as long as, the flow is through the matrix.

 These stockpile reactive transport simulations, therefore, indicate that if most of the flow through the stockpiles can be as matrix flow, the water quality leaving the stockpile as seeps and possibly infiltrating to the groundwater will be of better quality than that observed at the 5E Seep collection, since the seep is a mix of matrix and macro-pore flow waters. As long as the matrix is weathering (pyrite oxidation and silicate mineral alteration), the matrix flow water quality is well represented by modeling the matrix flow as a whole.

If a cover is designed for the stockpile, it should take the infiltration rates into consideration such that the infiltrating water trickles into the stockpile over an extended period of time, without the rainstorm water flushing through.

In general, stockpiles have a long-term neutralizing capacity, through feldspars, that exceeds the acid producing potential. As long as the flow within or through the material is slow, the rate of neutralization is fast enough to neutralize the acid being produced by the sulfides. With this in mind, a closure cover should be designed to optimize a slow flow environment.
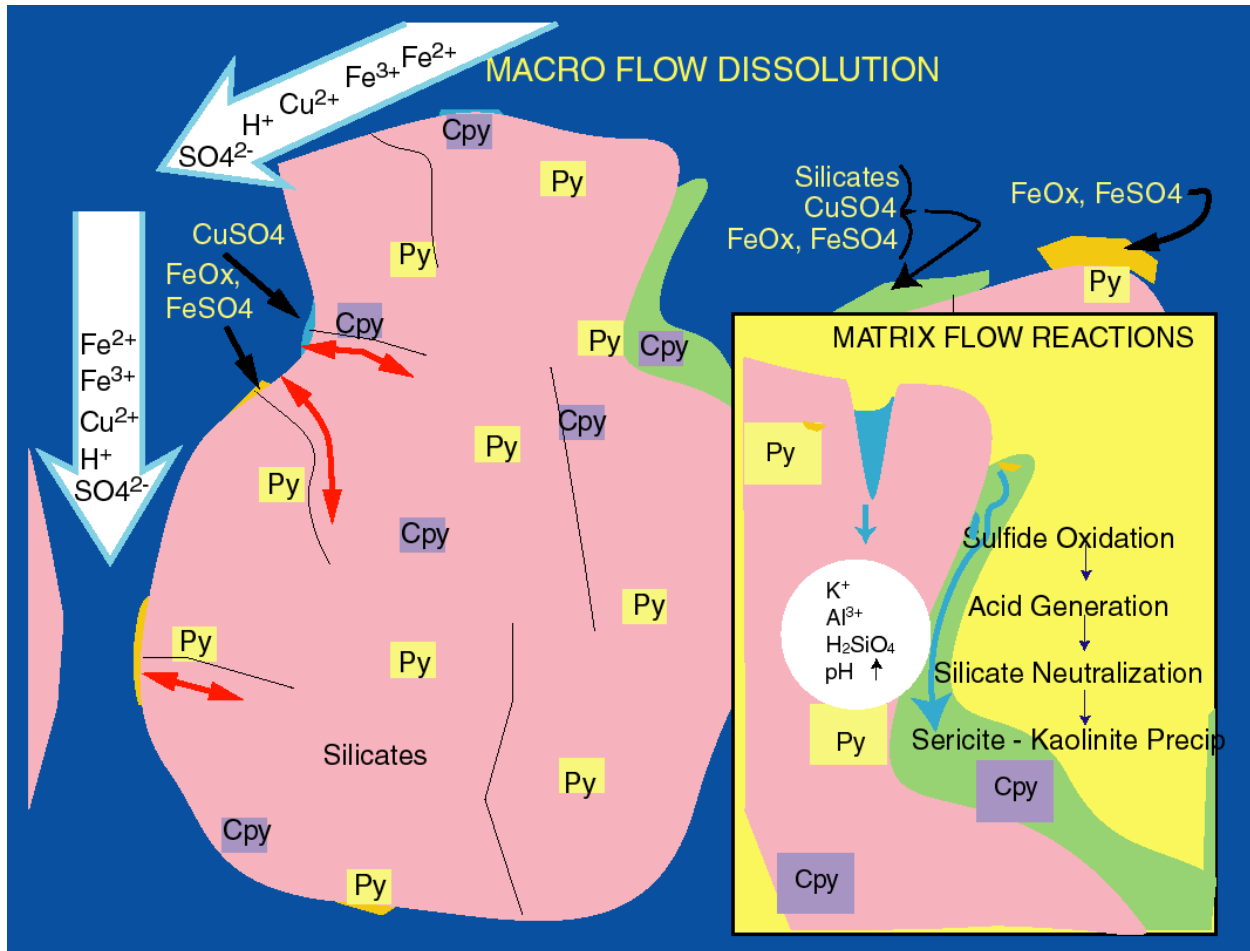

Figure 9. Illustration of geochemistry reactions along macro and matrix flow paths. The large white arrows illustrate water in the macro pore (blue) dissolving easily soluble minerals like Cu and iron SO_4^{-2}. Red arrows illustrate water transported by capillary forces in factures in particles (pink) and transporting constituents to the surface during drying (micro flow). The matrix flow in fine grained material (green) shows sequential reactions from sulfide oxidation to silicate weathering, with an increase in potassium (Na and Ca), aluminum, silica and pH. Py –pyrite; Cpy - Chalcopyrite.

Conclusions

The flow modeling of the stockpile at Tyrone Mine indicates that 15 % of rainfall infiltrates the stockpile. Greater than 95 % of that flows through the matrix (with a 47 year average residence time) and less than 5 % flows through the macro-pore channels (2 ½ days average residence time).

The different residence times for the macro-pore and the matrix flow systems will result in different water chemistry for these two flow systems. The macro-pore flow water will dissolve only highly reactive minerals on its quick flow path, while the matrix flow water will have a long time to react with slow reacting minerals. The matrix flow system is primarily feeding the mineralogy into the flow path of the macro-pore flow system, controlling the chemistry of the flow path.

This rapid flowing water dissolves the highly soluble secondary products (iron-sulfate minerals) left behind on the surface of particles within the stockpile, after sulfide oxidation. These SO_4^{-2} minerals do generate a high SO_4^{-2} - low pH environment when dissolving. The water has no time to react with silicate minerals, and as seen in the results, the seep flows have low pH.

Acknowledgement

Literature Cited

Blandford, T.N., Ronayne, M.J., Earley, D., and Shelley, T., 2004; lake formation at multiple pits: model development, verification, and application for closure. Abstract and poster for US EPA Pit lake workshop. Reno , Nevada, December 2004.

Blowes, D.W., Ptacek, C.J., Jurjovec, J., 2003: Mill tailings: Hydrogeology and geochemistry. *In Jambor, J.L., Blowes, D.W., and Ritchie, A.I.M. (Eds.) Environmental Aspects of Mine. Wastes Min. Assoc. Can Short course Vol 31,* 95-116.

Blowes, D.W. and Ptacek, C.J., 1994: Acid neutralizing mechanisms in inactivew mine tailings. In Jambor, J.L. and Blowes, D.W. (Eds.) Environmnetal geochemistry of sulfide mine-wastes, Min. Assoc. canada short course hand book, Vol. 22, 271-292.

Boorman, R.S. and Watson, D.M., 1976: Chemical processes in aboandoned sulfide tailings dumps and environmental implications for north eastern Brunswick. CIM Bull 69, No 772, 86-96.

Daniel B. Stephens &Associates (DBS&A), 1999a. Stockpile and Tailing Pond Seepage Investigation Interim Report, Tyrone Mine. Prepared for Phelps Dodge Tyrone, Inc., Tyrone, New Mexico. February 1, 1999.

DBS&A, 1999b. Stockpile and Tailing Pond Seepage Investigation, Tyrone Mine. Prepared for Phelps Dodge Tyrone, Inc., Tyrone, New Mexico. July 31, 1999.

DBS&A, 1997a: Preliminary Materials Characterization: Tyrone Mine Closure/Closeout. Prepared for Phelps Dodge Tyrone Inc., Tyrone, New Mexico, April 30, 1997.

DBS&A, 1997b: Supplemental Materials Characterization: Tyrone Mine Closure/Closeout. Prepared for Phelps Dodge Tyrone Inc., Tyrone, New Mexico, October, 1997.

Davis, G.B. and Ritchie, A.I.M., 1987: A model of oxidation in pyritic mine wastes. Part III Import of particle size distribution. Applied Math. Modelling. 10, 417-422 http://dx.doi.org/10.1016/0307-904X(87)90166-1

Davis, G.B. and Ritchie, A.I.M., 1986: A model of oxidation in pyritic mine wastes. Part II. *Applied Math. Modelling*. 10,

Dold, B. and Fontbote, L., 2001: Element cycling and secondary mineralogy in porphyry copper tailings as a function of climate, primary mineralogy, and mineral processing. *Special issue Geochemical studies of mining and the environment, Jour. Geochem. Explor. 74*, 3-55

Germann, P. and Beven, K., 1985: Kinematic wave approximation to infiltration into soils with sorbing macropores. Water Resourc. Res. 21: 990-996.

Gillermann, E., 1964: Mineral deposits of the Western Grant County, New Mexico. New Mexico Bureau of Mines and Mineral Resources Bull. 83.

Kolessar, J., 1982: The Tyrone Copper deposit, Grant County, New Mexico. In: Titley, S.R. (Ed.) Advances in geology of porphyry copper deposits in the southwestern North America. Tucson. Univ. Arizona Press. 327-333.

Lichtner, P., 1998: MPATH, Multiple reaction path model, User manual and programmer's guide. Univ. Bern, Switzerland. 48 pp.

Morin, K.A. and Hutt, N.M., (1997): Environmental geochemistry of mine site drainage, practical therory and case studies. *MDAG Publishing*, Canada. 330 pp.

Nicholson, R.V., 1994: Iron-sulfide oxidation mechanisms: Laboratory studies. *In: Jambor, J.L. and Blowes, D.W. (Eds.) Environmental Geochemistry of sulfide mine-wastes. Mineralogical Association of Canada, short course handbook.* 163-183.

Rawl, W.J., L.R. Uhuja, D.L. Brakensiek, and A. Shirmohammmadi, 1993. Chapter 5 in Handbook of Hydrology, D.R. Maidment (ed.) McGraw-Hill, Inc.

Ritchie, A.I.M., 2003: Oxidation and gas trasport in piles of sulfide material. In Jambor, J.L., Blowes, D.W., and Ritchie, A.I.M. (Eds.) Environmental Aspects of Mine. Wastes Min. Assoc. Can Short course Vol 31, 73-94.

Ritchie, A.I.M., 1994: Sulfide oxidation mechanisms: Controls and rates of oxygen transport. In: Jambor, J.L. and Blowes, D.W. (Eds.) Environmental geochemistry of sulfide mine-waste, Short Course Handbook, Vol. 22. Mineral. Assoc. Canada. 201-246.

SARB Consulting, Inc., 2000: Geochemical evaluation of tailings and stockpiles, Tyrone Mine. Report prepared for Phelps Dodge Tyrone, Inc., 183 pp.

Šimúnek et al., 1996

Smith, L and Beckie, R. 2003: Hydrologic and geochemical transport processes in mine waste rocks. *In Jambor, J.L., Blowes, D.W., and Ritchie, A.I.M. (Eds.) Environmental Aspects of Mine. Wastes Min. Assoc. Can Short course Vol 31,* 51-72.

Smith, L., Lopez, D.L., Beckie, R., Morin, K., Dawson, R., and Price, W., 1995: Hydrogeology of waste rock dumps. Contract No 23440-4-1317/01-SQ. MEND Report -1995

Walder, I.F. and Lichtner, P., In Prep.: Reactive transport modeling of Tyrone porphyry copper tailings.

Walder, I.F. and Chavez, Jr., W.X., 1995: Mineralogical and geochemical behavior of mill tailing material produced from lead-zinc skarn mineralization, Hanover, Grant County, New Mexico, USA. Environ. Geol., pp. 1-18. http://dx.doi.org/10.1007/BF00776027.

Walder, I.F. and Stormont, J., 2004: Thorough characterization of the hydrogeological and geochemical processes in waste rocks are essential for effective reclamation. Abstract and Article Mining Environ. Technology Conference, Concepcion, Chile, April 2004, 14 pp.