Modeling and evaluation of local groundwater quality adjacent to a weathering porphyry copper system, USA[1]

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ABSTRACT
This study focuses on the geochemical processes affecting the water quality in a minesite and, identifying what processes may be controlling the solubility of metals in the regional aquifer. The study area is located in the southwestern United States and consists of a porphyry Cu-Mo characterized by a disseminated to veinlet-controlled mineralization deposited throughout large volumes of altered, intermediate-composition intrusive rocks. For years, copper has been recovered by leaching methods using acid solutions added to piled ore to extract copper as $CuSO_4$. 256 wells have been monitored for 28 years.

The pH values in the wells are circum-neutral, but are lower in a few wells in the open pits − stockpiles and cluster area. Geochemical modeling shows that calcite and ferrihydrite, tenorite, gibbsite, and talc among others, seems to be the mineral phases controlling the groundwater pH and hence, the metal availability and mobility in the aquifer. In addition, sorption/desorption, and aqueous complexation processes are controlling the availability of elements in solution. Also, the presence of dissolved iron can result in precipitation and attenuation of dissolved metals by sorption reactions. However, more research on sorption/desorption, ion pairs and aqueous complexation is recommended since they are an important part of the processes responsible for controlling the metal concentration in the mine site aquifer.

Additional Key words: Acid rock drainage, geochemical modeling,

INTRODUCTION

Mining activities, if not well managed, can produce significant environmental impact. Mineral extraction and processing activities expose and greatly increase the quantity of fresh rock surfaces as they produce crushed and milled waste. Sulfide-bearing mineralization, if oxidized, has the potential to produce sulfuric acid, a component of acid rock drainage (ARD) and thereby increase heavy-metal mobility in the mine environment. Significant contamination of surface and groundwater may result from these processes. At present in the western United States, essentially all copper ores are derived from porphyry-type deposits being mined by open pit methods. Copper is extracted via stockpile leaching, and by froth flotation methods. Because of oxidation due to weathering and to leaching waters within the mine area, the groundwater and surface water may eventually suffer water quality degradation. Monitoring and intercept wells are commonly installed in order to monitor the water quality and to control degradation, and may be

used to assess the nature and extent of metals and oxy-anions present in local and regional waters. This latter characteristic is the basis for this study.

This study focuses on the characterization of the geochemical processes affecting water quality adjacent to a western U.S. open pit porphyry copper mine, and in the identification of mineral precipitation, solubility, transport and/or other processes that may be controlling the solubility of metals in the regional aquifer of the study area.

STUDY AREA
The study area is located in the western United States. This mine was open in the late 60's as an open pit mine (Kolessar, 1982), with copper extraction using SX – EW leaching techniques initiated in the early 80's. The site orebody occurs within quartz monzonite and underlying Precambrian granite, and consists of a supergene blanket of erratic chalcocite coating on pyrite mineralization. Chalcocite is the most important ore mineral, and along with covellite are the supergene sulfide minerals that replace pyrite, chalcopyrite, and sphalerite (Kolessar, 1982). Chrysocolla is the most abundant copper mineral in the oxidized zone, with tenorite, malachite, azurite and scant cuprite, native copper, brochantite, and chalcantite.
At the mine area, there are two groundwater divides; which divert the flow either to the tailings area or to the main pits area. Between these two groundwater divides there are several smaller pits in the surroundings, and the bottom of these pits are above the local groundwater table (Figure 1).

Among the several stockpiles located surrounding the main and smaller pits, the stockpiles located to the northwest of the continental groundwater divide, have been leached since the early 1980's, which for the purpose of this study, this area is named the cluster area. The area located further northwest, immediately after the cluster area, where there are six tailings ponds, is named the tailings area. Thearea between the two groundwater divides, where the main pit is located, plus the area located to the southeast is named the open pits – stockpiles area (Figure 1) Kolessar, 1982). A major zone fault trends northwest – southeast through the mine area.Across this major fault, to the east, there is no groundwater flow coming from the mine area. Other minor faults are present in the open pits – stockpiles area, and are assumed to affect locally but not regionally to the groundwater flow (Kolessar, 1982).

Within the study area since the early 1980's, besides mining, copper has been recovered by leaching methods, in which acidic leach solutions are added to piled ore to extract copper as $CuSO_4$. The resulting pregnant leach solution (PLS) is piped to the solvent extraction / electro-winning plant for copper extraction. The former PLS solution is reused for leaching by pH adjustment.

METHODOLOGY
For the present study, only wells located in the regional aquifer, 256 out of more than 1000 thousand in total, were taken into account (Figure 2). Groundwater sampling was performed over twenty-eight years, beginning in the 1970's, with samples taken on a monthly basis, four times a year, or twice a year. For this study, the following chemical elements were taken into account: aluminum, cadmium, calcium, copper, bicarbonates, fluoride, iron, potassium, magnesium, sodium, lead, sulfates, zinc and, pH.
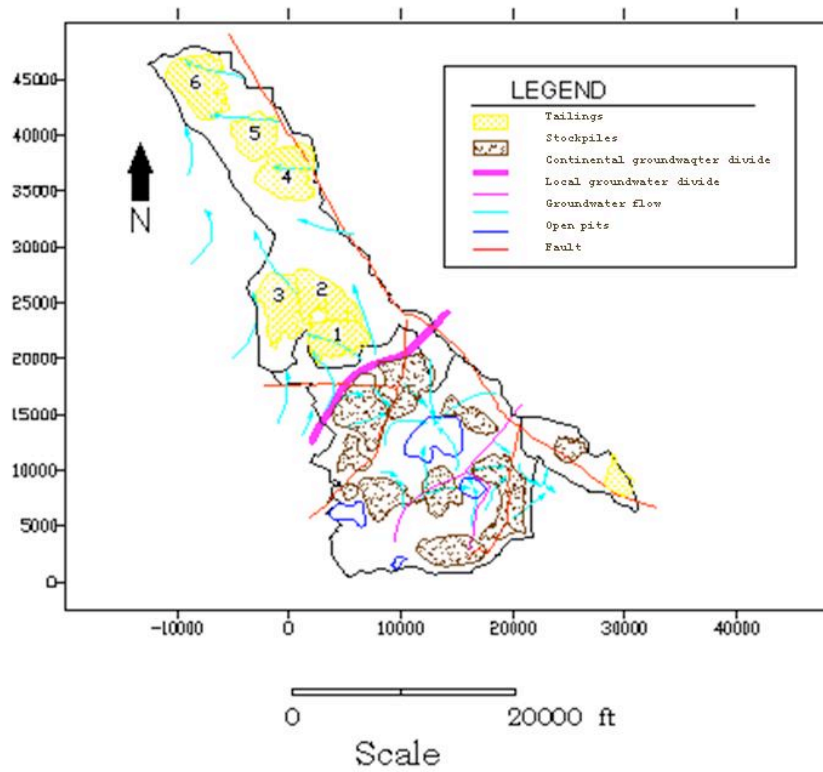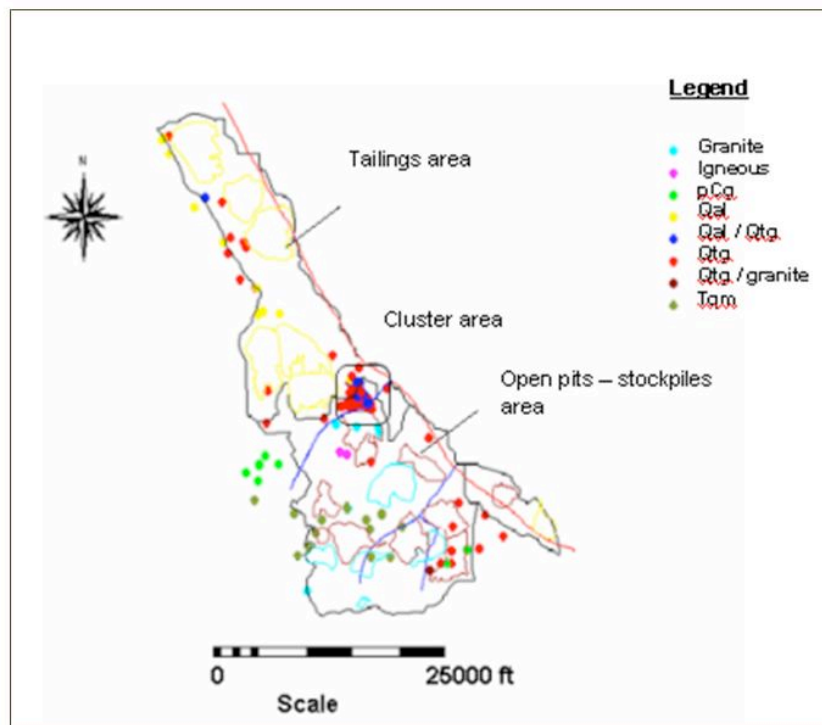
Figure 1. A. Location of tailing ponds, pit lakes, stockpiles and physiographic units in the site of study B. Wells location (256 wells sampled) and geologic units in the study area. pCg = precambrian granite, Qal = quaternary alluvium, Qtg = Undifferentiated Gila conglomerate, Tqm = tertiary quartz monzonite

The following tasks were performed to analyze the hydrogeochemical data:
- Interpolation of laboratory chemical analyses at five year interval using moving average – inverse distance method in order to show the water quality evolution with time.
- Geochemical modeling using MINTEQA2 V 3.11 (Allison, 1991), to calculate the saturation indexes values. Elements input was as Al^{3+}, Ca^{2+}, Cd^{2+}, Cu^{2+}, F^-, Fe^{2+}, K^+, Mg^{2+}, Mn^{2+}, Pb^{2+}, pH, SO^{2-}_4, Zn^{2+}, and bicarbonate.
- Plots of pH versus metal activity were constructed for several elements. Dissolution reaction of gibbsite, ferrihydrite, calcite, and gypsum were used to estimate if these mineral phases would control the availability of their corresponding elements.
- Correlation and determination coefficients were calculated
- Finally, travel time for calcium, iron and sulfate was calculated using the solution to the following equation:

RESULTS
Over the entire sampling period, the average pH of the wells sampled in the tailings area ranged from 5.34 to 8.1, whereas in the cluster area, where most of the wells are located, pH is near-neutral, with a few wells with pH values of 2.88 to 3.35, and in some cases, these wells are located as close as 7 meters to wells having a near-neutral pH. These few acidic wells have high concentration of metals that contrast with low metal concentration values of wells having near-neutral pH values, except for bicarbonates and lead. Bicarbonates have a rather low concentration in low pH conditions, while the behavior for lead is not as clear as for the other elements, since lead has high values both in acidic and near-neutral conditions.

Aluminum concentration has a strong dependency on the pH, since in the few acidic wells in the cluster area (pH = 3.23) present values in the range of 10 to 3000 mg/L, and a similar behavior in the only one well in the open pit - stockpile area; whereas most of the wells in the study area have aluminum concentrations in the range of 1 to 7 mg/L, where the pH is circumneutral. Both wells, with acidic and near-neutral pH values have an increasing tendency in aluminum concentration over time, from 0.5 mg/L in 1977 to > 2 mg/L in 1996 (Figure 2).

Iron has a low concentration (<0.01 mg/L) at the beginning of the sampling period in all the areas, but over time the concentration in the cluster and open pit – stockpile areas is higher (>100 mg/L). The well having an acidic pH (~3) presents the higher iron concentration (3500 mg/L in a few wells), whereas wells with a near neutral pH presents low concentration. Therefore, iron concentration is strongly controlled by the pH. In addition, there is an increasing iron concentration over the years (Figure 2).

The pattern just described for aluminum and iron applies for the other elements like lead, manganese, copper, fluorine, sulfate, calcium, magnesium and, sodium, that is, there is an increasing concentration over the years in the cluster areas and open pits – stockpile areas, whereas, the tailings area present lower concentrations. In addition, pH is correlated to the elements concentration in the mine area. Most of monitoring wells are located in the cluster and open pits – stockpiles area. The acidity, pH values < 4.5, in these wells was detected after about 10 years from the beginning of the sampling period.

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The following pairs Ca-Mg, Ca-Na, Mg-SO$^{2-}_4$, in the three areas show a high correlation ($R^2>0.90$), suggesting that the same factor is controlling the solubility of these elements in the mine regional aquifer. In the tailings area the pairs SO$^{2-}_4$-Ca, SO$^{2-}_4$-Mg, SO$^{2-}_4$-Na and Ca-Mg have a $R^2>0.90$, whereas in the cluster area the pairs Mn-Zn, Al-F, Cu-Mn, Cu-Zn and Cu-F have a $R^2>0.90$, conversely, the open pits-stockpile areas present no correlation between elements.
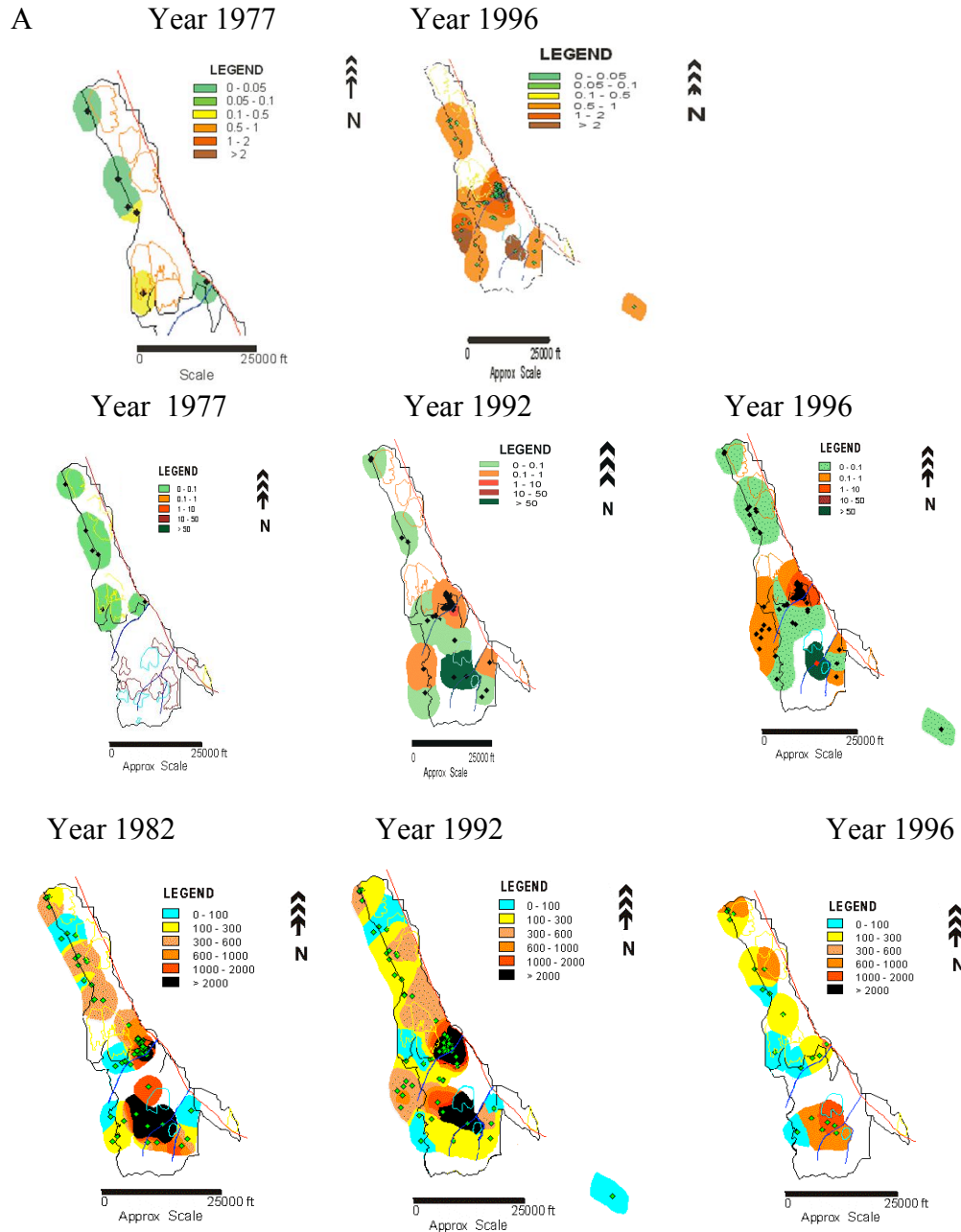
A

Year 1977   Year 1996

Year 1977   Year 1992   Year 1996

Year 1982   Year 1992   Year 1996

Figure 2. Chemical elements concentration over time A. Aluminum, B. Iron C. Sulfate

DISCUSSION
The water quality parameters considered in this study provide important information for understanding the geochemistry of the mine site and setting the baseline for further studies to accurately identify the factors (geochemical, microbiological, geological, climatic) that may be controlling the presence of metals in the regional mine site aquifers.

Geochemical modeling and chemical elements behavior
The abundance of metals in solution is closely related to the pH of the regional aquifer. In the open pits – stockpile and cluster area, wells that have low pH values (about 3), also have high metal concentrations. In the cluster area, the "acidic" wells are located in between or as close as 1.5 – 3 m to wells with near-neutral pH values. Modeling results show that gibbsite has saturation index (SI) values of 0.91 and 0.82 in the tailings area at the beginning of the sampling period, but later, according to SI values, SI values > 10, there is no precipitation of aluminum phases. Wells in the tailings area have near-neutral pH values; therefore, the presence of gibbsite is reasonable. Saturation index values close to equilibrium, SI = 0.3 – 1.3, in some other wells may be an additional indication that this phase, to some extent, is controlling the aluminum concentration in the northernmost part of the tailings area and in some wells (well 6-4) in the open pit – stockpiles area.

The plot of pH versus logarithm aluminum activity (Figure 3) shows that, in the tailings area, the slope of aluminum activities is quite similar to the slope of gibbsite dissolution. However, in the other zones, the slope of aluminum activity is quite different than that of the ideal gibbsite dissolution.

When acid mine drainage is diluted by neutral surface water or groundwater; the pH and aluminum concentrations will eventually reach the gibbsite solubility curve and aluminum concentrations will become controlled by one of three possibilities: solubility of a solid phase (Fig. 3), a surface coating control with a stoichiometry similar to gibbsite, or a common alumino-silicate mineral with a exchange ratio of Al^{3+} to H^+ of 1:3 (Nordstrom and Alpers, 1999). More investigation is needed to determine which of these phases may be controlling the aluminum solubility in the mine site area.

For iron, the modeling results indicate that SI values are similar for all the mine areas in some wells, indicating that ferrihydrite, K and Na jarosite are the mineral phases with SI values close to equilibrium (Fig. 4). The ferrihydrite SI values may be an indication that this phase eventually may precipitate in some parts of the tailings area. In addition, a decreasing trend of SI values was observed over time and distance suggesting a distance-attenuation effect. The apparent supersaturation of ferric hydroxide or ferrihydrite, which in the mine site occurs at pH values above five, may be explained by the substitution of sulfate for hydroxide ions in the ferrihydrite and the formation of a schwertmannite-like phase, which starts to occurs at pH of 3 to 4.5 and may continue until reaching pH values of 5 - 5.5 (Nordstrom and Alpers, 1999).

The iron ion-activity figure indicates similar behavior to the one encountered by plotting iron concentrations (Figure 3). If ferric hydroxide controls the availability of Fe^{3+} in solution, the slope would be –3. The different slopes in the three areas suggest that pure ferrihydrite (ferric hydroxide) is not the only phase controlling the iron concentration in solution.

The fluctuating values in space in copper concentration in the mine site suggest transport and leaching process, which began in the early 1970's. The modeling results indicate that only tenorite is likely to be precipitating in the mine site. An explanation for the presence of Cu^{2+} in the aquifers is the fact that copper and other metals like lead tend to desorb at near-neutral or higher pH values due, mainly, to the increasing competition from complexing agents such as aqueous carbonates, which help keeping copper in solution (Plumlee et al., 1999).

For lead, according to the modeling results, there are no lead phases precipitating in the mine site area during the sampling period. The evidence found through the modeling results suggests that a more detailed analysis is necessary to determine what processes and factor / mineral phases would be involved in controlling the lead concentration in solution. Desorption may be one of the processes explaining the presence of lead in solution, given that when the pH is acidic, ~ 4, lead is strongly sorbed onto particulates. However, lead is desorbed at near-neutral or higher pH values (Plumlee et al., 1999; Smith et al, 1999).

For calcium, the modeling results indicate that calcite is near equilibrium in most of the wells analyzed in the tailings area. Other calcium phases, such as dolomite and Ca-nontronite, are far from equilibrium. The dissolution of calcite is an indication of the natural attenuation has been taking place in the mine site. Given that calcite is the most reactive carbonate, its dissolution by the acidity produced by the pyrite oxidation may be one of the reasons explaining the near-neutral pH values found in the mine site aquifers.

In the open pit – stockpiles area, from 1982 to 1997, K and Na jarosite had SI values closer to equilibrium, SI = 0.8 – 1.1. A value of SI = 0, indicates that the mineral phase is in equilibrium. In the cluster area, there were no potassium phases with SI values close to equilibrium. The dissolution of acid-neutralizing minerals like carbonates, feldspar, plagioclase, and felsic minerals release calcium, sodium, potassium, and magnesium ions, increase the buffering capacity of the solution. Therefore, the presence of cations, such as calcium, sodium, potassium and magnesium indicates that the buffering process is taking place in the mine site. For all areas under consideration, sodium activity vs. pH plots as horizontal line, suggesting that sodium solubility seems to be unaffected by pH changes.

At the end of the sampling period, high element concentrations were observed related to the beginning of the sampling period. The high concentrations - in the acidic wells- of Ca (200 mg/L), K (~ 52 mg/l), Na (100 mg/L), Mg (2115 mg/L) cations in the open pit – stockpiles and cluster areas indicate higher acid production in these areas. Acidity dissolves more acid neutralizing minerals; releasing therefore, more calcium, sodium, potassium, and magnesium into solution. Counteracting this behavior, there are sulfate ions, which are being released as a byproduct of sulfide oxidation or leaching processes. The comparatively low concentrations of these cations (Ca, Mg, K, and Na) in the tailings area, suggest a combined effect of little or no acidity produced in this area. Gypsum and K-jarosite are the phases with SI values indicating an over-saturation, thus suggesting precipitation in the tailings area. However, gypsum is the only phase that has SI values close to equilibrium in the other areas.

The activity of sulfate ions in all the three areas gradually decreases as pH increases. In the tailings and open pits – stockpiles areas, besides the regression line showing the same behavior as for the cluster area, there is a variation in the activity values in a short range of pH. By plotting ion activity figures for wells with acidic and circum-neutral pH values separately, it can be seen that sulfate ions follow an almost straight line, suggesting a pH independent behavior (Fig. 3-5). In addition, the tailings points are clustered in two groups, under the same pH range but with different activities. Each of these clusters have an almost pH independent activity behavior.
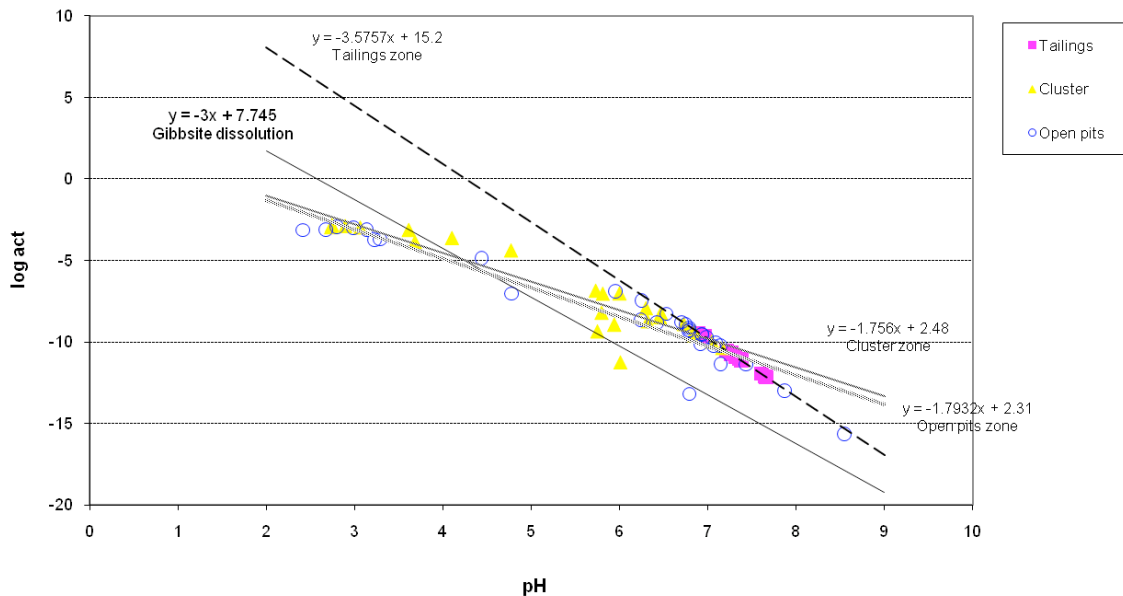

Fig. 3. Aluminum concentration relative to pH with solubility line for gibbsite and correlation lines for the aluminum in the different sampling areas.

Besides the neutralizing effects of the acid-consuming minerals, it is important to consider another process that diminishes the metal concentration in groundwater like sorption, desorption, formation of ion pairs and aqueous complexes that need to be evaluated in order to assess the total natural neutralizing capacity of the country and/or gangue minerals in the mine site. Furthermore, it must be taken into account that an active form of a compound (i.e., a very fine crystalline precipitate with a disordered lattice) is generally formed incipiently from strongly supersaturated solutions and may persist in meta-stable equilibrium with the solution and slowly age into a more stable, inactive form. Measurements of the solubility of active forms give solubility products higher than those of inactive forms. In heterogeneous equilibrium of natural water systems, the more stable and inactive solids are frequently more pertinent (Stumm and Morgan, 1996). Therefore, the variability of SI values of the mineral phases likely precipitating may be a good indication that, given enough time, these phases, along with sorption and formation of aqueous complexes processes, will become effective controlling phases of metals in solution.
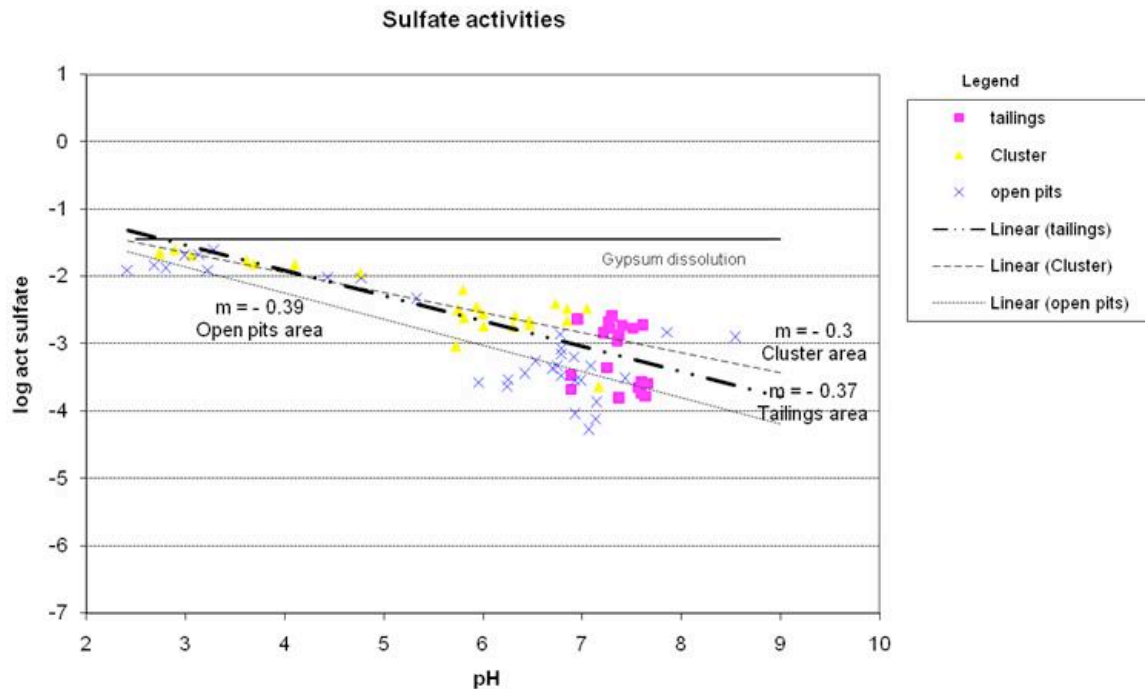
Sulfate activities

Fig. 4. Sulfate concentration relative to pH with solubility line for gypsum and correlation lines for the sulfate in the different sampling areas.

Chemical elements correlations

The high correlation between calcium and magnesium (R^2=0.93), calcium and sodium (R^2=0.93), and magnesium and sulfates (R^2=0.93) in the three areas of the mine site support the idea that phases and/or complexes containing these elements, besides possible cation sorption processes, especially involving divalent cations, are effectively controlling the solubility of metals in solution. On the other hand, the high correlation between sulfate and calcium, sulfate and magnesium, and sulfate and sodium in the tailings area, where there is little pH variability, suggest that sulfate bearing components (*i.e.,* gypsum, and possibly clay having in its composition calcium and/or magnesium) play a combined role in limiting the availability of metals in the mine site aquifer.
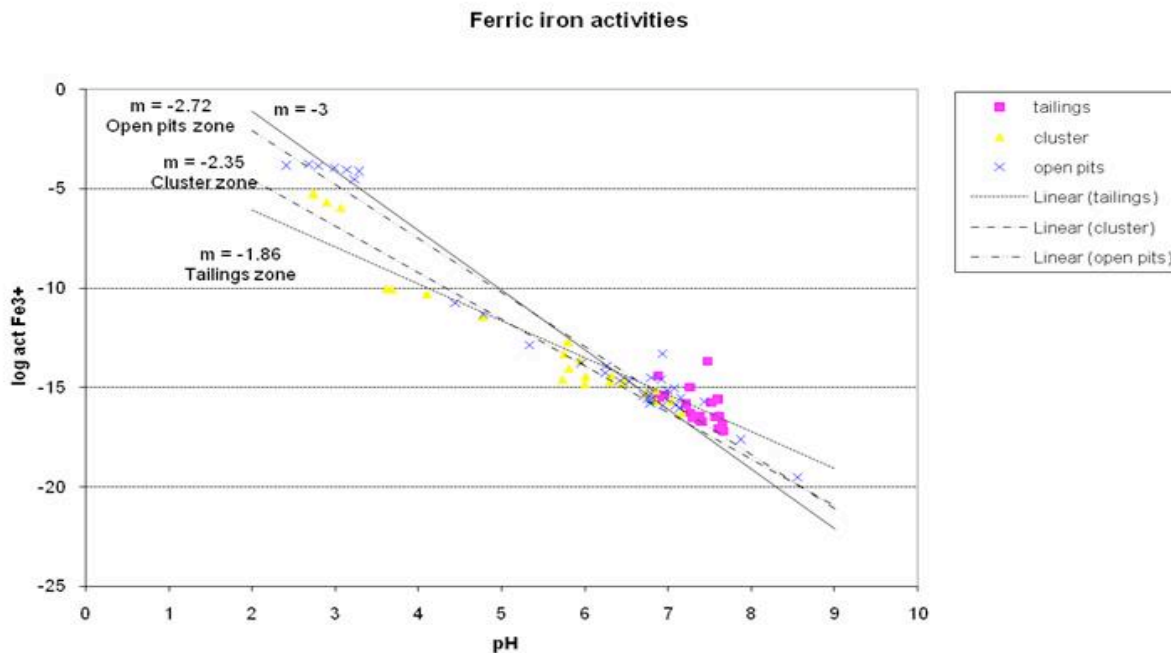
Ferric iron activities

Fig. 5.
Iron

concentration relative to pH with correlation lines for the sulfate in the different sampling areas

CONCLUSIONS

The pH values of most of the regional aquifer wells are circum-neutral, except in few wells in the open pits – stockpiles and cluster area where there are wells with low pH (~ 3) values; in these acidic wells the metal and anion concentrations are comparatively high in the cluster and open pits – stockpiles area, whereas in the tailings area the metal and anion concentrations are low.

Calcite seems to be the main carbonate mineral phase controlling the pH and hence, the metal availability and mobility in the mine site aquifer; whereas other phases like ferrihydrite, tenorite, gibbsite, K and Na jarosite, talc,, plagioclases and feldspars are the possible mineral phases, besides calcite, probably controlling the availability of its respective forming elements in solution.

Aquifer parameters, such as hydraulic conductivity and porosity, need to be accurately determined for the different parts of the mine site regional aquifer in order to estimate the rate of transport of metals in the tailings area.

It is recommend that more research be conducted to investigate the geochemical processes, like sorption/desorption, ion pairs and aqueous complexes, taking place in the mine site, particularly in the tailings area, since they are important parts of the processes responsible for controlling the metal concentration in the mine site aquifer.

REFERENCES

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0 users manual. US Environmental Protection Agency, Athens, Ga. EPA/600/3-91021, 106pp

Fetter, C.W. 1999. Contaminant hydrogeology. 2nd ed. Prentice-Hall, Inc. New Jersey, USA. 500 p.

Kolessar Joseph. 1982. The Tyrone copper deposit: Grant County, New Mexico; in Spencer R. Titley (ed). Advances in geology of the porphyry copper deposits: southwestern North America. The University of Arizona Press. Tucson, Arizona. pp 327 – 333.

Nordstrom, D. Kirk, and Alpers, C.N. 1999. Geochemistry of acid mine waters; *in* Plumlee, G. S., and Logsdon, M.J. (eds), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 133 - 154.

Plumlee., G.S., Smith, K.S., Montour, M.R, Ficklin, W.H., and Mosier, E.L. 1999. Geologic controls of natural waters and mine waters draining diverse mineral-deposit types; *in* Plumlee, G. S., and Logsdon, M.J. (eds), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6B, pp. 373 - 407.

Smith, Kathleen S., and Holly, L.O. Huyck. 1999. An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals; *in* Plumlee, G. S., and Logsdon, M.J. (eds), The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, pp. 29 - 64.

Stumm, W., and Morgan, J.J. 1996. Aquatic chemistry: An introduction emphasizing chemical equilibria in natural waters. 3rd ed. John Wiley & Sons, Inc., New York, USA. 1044 p