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A Simulation of the Supergene Copper Enrichment Process

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ABSTRACT

A simplified simulation of copper precipitation during supergene enrichment processes was carried out to study the feedback behaviors of geochemical reaction and groundwater flow. Reevaluation of the pattern of formation was studied by means of the HYDROGEOCHEM code, wherein redox half reactions of covellite and chalcocite as reactants as well as precipitation reactions to form covellite and chalcocite were considered. The results indicate that the precipitation pattern is attributable to the redox-controlled process, wherein the electron potential is the key parameter for forming such a pattern. The quantities of precipitation are also related to the time span and initial aqueous copper ion concentration. This finding is in good agreement with field observations and gives a more physically-meaningful explanation of such phenomena compared to the non-selective equilibrium and/or kinetic controlled approaches reported in the literature.

Key Words: precipitation, reactive transport, redox half reactions, supergene enrichment

I. Introduction

The phenomenon of supergene enrichment, involving copper precipitation, is a remarkable case of a weathering process that takes place at and beneath the groundwater table under reducing conditions and is involved in a large number of minerals and complex encountering environments. It is also very valuable for the mining industry from the economic viewpoint due to its role in reprecipitating and enriching low-grade materials into high-grade secondary minerals (Guilbert and Park, 1986). However, unlike the oxidation processes for mobilizing primary minerals, the precipitation process for fixation of secondary minerals is much more complicated and not well understood so far although several mechanisms have been proposed experimentally, conceptually, or numerically in literature. Generally, it is considered to be an abiotic process that involves progressive replacement of pyrite or chalcopyrite to form copper-rich sulfides (Brimhall *et al.*, 1985). It has been proven that the presence of pyrite is a critical condition for the precipitation of copper-bearing minerals (Stokes, 1970). Pyrite with high solubility acts as a host for deposition of ores through replacement of ferric ions with copper ions. Sulfide interaction with copper also leads to precipitation of copper-bearing minerals, such as chalcocite or covellite (Guilbert and Park, 1986; Xu *et al.*, 1999a, 1999b, 2000). Chalcocite containing 79.8% Cu generally precipitates at the top of the blanket, where the Cu^{2+}/HS ratios are higher, while covellite containing 66.4% Cu precipitates at depths where the blanket is less rich and the Cu^{2+}/HS ratios are low (Guilbert and Park, 1986). Replacement of other metal-sulfide minerals also may take place during enrichment processes. Ague and Brimhall (1989) found that chalcocite was formed through the destruction of chalcopyrite by copper ions. They also concluded that oxygen fugacity is the key control in the system, and that the dominant source of sulfur for precipitation of secondary minerals is the primary minerals (hydrogen sulfide or chalcopyrite) in the reduced zone, not the sulfate migrating from the leached zone. Sulfur leached from the oxidation zone is highly mobile and leaves the flow region in the from of sulfate.

However, a recent study proposed that microbial fixation of copper at active replacement fronts between hypogene sulfides and chalcocite may be a critical kinetic factor in the enrichment process (Sillitoe *et al.*, 1996). The results from scanning electron microscope (SEM) examination indicated the presence of fossilized and metallized forms of bacteria or nanno-bacteria near the replacement interfaces that might promote the fixation of mobilized copper ions.

With regard to modeling of the enrichment behavior, several equilibrium and kinetic approaches have been proposed to describe the precipitation processes (Ague and

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Table 1. Summary of the Previous and Present Work of Modeling the Enrichment Process

Work	Module	Description
Ague and Brimhall (1989)	METASOM	Coupled fluid flow (TRUST), chemical compositions (EQ3NR) and water-rock interaction (EQ6) programs based on steady-state, local thermodynamic equilibrium to solve 1-D problem in a porous media.
Lichtner and Biino (1992)	MPATH	2-D simulation of the enrichment process by kinetic expressions for both precipitation and dissolution in a porous media.
Xu *et al.* (1999b)	TOUGHREACT	Coupled multiphase flow and mass transport code (TOUGH2) with speciation model (REACT) to simulate water-rock-gas interaction under equilibrium (precipitation) and kinetic (dissolution) conditions.
Xu *et al.* (2000)	MINC/TOUGHREACT	Coupled MIMC and TOUGHREACT model to resolve global flow and diffusion in a 2-D fracture system under equilibrium (precipitation) and kinetic (dissolution) conditions.
This Work	HYDROGEOCHEM	Incorporating selective redox half-reaction concept to the reactive-transport module to simulate the precipitation process in a porous media based on quasi-equilibrium.

Brimhall, 1989; Lichtner and Biino, 1992; Xu *et al.*, 1999a, 1999b, 2000). These studies and our work are listed and described in Table 1 for the purpose of comparison. These models apply quasi-equilibrium and/or kinetic approaches to describe the dissolution and/or precipitation processes that occur during enrichment based on consideration of the complicated geochemical reactions that involve numerous primary and secondary minerals. In this way, the formation of layered ore deposits can be partially explained based on specific given conditions and parameters. However, the physical meaning of the phenomena that naturally occur when covellite is sandwiched by chalcocite in the enrichment blanket has not been adequately explained because of the non-selective equations used in these equilibrium and kinetic approaches.

Sato (1992) summarized the precipitation processes related to geochemistry that might take place during the enrichment processes. The precipitation (concentration) of copper-bearing minerals, that is, supergene enrichment, near the groundwater table can be considered as including three processes: (1) fixation of oxidation products as insoluble minerals at or above the oxidation boundary; (2) reprecipitation of metal ions in a slightly reducing environment due to the change of the electronic potential; (3) replacement of a sulfide by another sulfide with higher sulfide affinity by means of cation-exchange reactions wherein the condition needs to be in a reduced zone but with slightly higher electronic potential to prevent the formation of native metals. Sato (1992) also described the complex supergene enrichment processes based on the construction of an Eh-pH diagram of the redox half-reactions. When the copper-rich water reaches the saturated zone under a slightly oxidized zone, Cu^{2+} reacts with sulfur or hydrogen sulfide to form CuS (covellite) or Cu_2S (chalcocite) according to the abundance of copper and the redox potential. When excess copper is present in the solution, chalcocite will predominately form due to the reaction between CuS and Cu^{2+}. This relationship explains why Cu_2S lies on top of CuS under slightly oxidized conditions. Beneath it and when there is no excess copper, covellite is the end product under slightly oxidized conditions. In a high reducing zone, reactions take place to form chalcocite.

Therefore, it is reasonable to hypothesize that the mechanisms of precipitation may vary according to the environmental conditions (*e.g.*, the redox potential) and mineral compositions that are encountered. As such, the use of redox half-reactions may be critical in modeling so as to reflect such a redox-controlled process and may lead to a more reasonable explanation of copper-mineral formation in an enrichment blanket.

In this study, the redox half-reaction concept and the quasi-equilibrium approach were both considered to evaluate supergene enrichment processes related to copper-bearing minerals. Redox half reactions and the corresponding reaction constants of covellite and chalcocite were obtained from Sato (1992), while other equilibrium reactions and their corresponding reaction constants were taken from the EQ3/6 database (Wolery, 1992) and from Stumm and Morgan (1970). The simulation was carried out using HYDROGEOCHEM (Yeh and Tripathi, 1990, 1991) for a simplified case, wherein only the interactions between copper and sulfur were considered. The results are in good agreement with those reported in the literature. The phenomena of covellite precipitation is fully considered in this approach.

II. Simulated Area and Initial Conditions

Simplified one-dimensional porous media (neglecting fractures) saturated with water 10 meters in height was selected for simulation (as shown in Fig. 1). The groundwater table was assumed to be placed on top of the column. Infiltration was assumed to be steady-state with a vertical flow rate of 70 mm/yr. The matrix in the saturated zone was considered to be inert with negligible change in porosity due to precipitation.

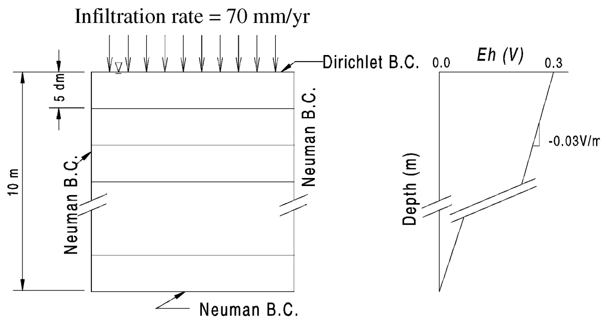

Fig. 1. Schematic presentation of the simulated field and the redox conditions.

The column was evenly divided into 20 vertical elements with a height of 5 dm in each element. Other geological and hydraulic parameters in assumed in this simulation were: porosity: 0.2; permeability: 10^{-14} m^2; molecular diffusion coefficient: 3.6×10^{-4} dm^2/hr; tortuosity: 0.1; and diffusivities for all elements in the longitudinal direction: 7.6 dm; those in the transverse direction: 0.0 dm. The initial concentrations of the chemicals of interest in the column were assumed to be zero. The amounts of dissolved minerals and the chemical compositions of the infiltration water released from the leached zone into the saturated zone at steady state were kinetic controlled according to the basic kinetic dissolution law, wherein the volumetric dissolution rate of a mineral is assumed to be constant and to be governed by the kinetic rate constant and the surface area of the mineral. Therefore, it can be expressed as

$$r = k \times \mathit{Surface\ area}\ [\mathrm{mol/dm^3/s}].$$

The kinetic rate constant and the surface area of each mineral reactant have been given by Xu *et al.* (1999a). In this manner, the flux of dissolved minerals from the leached zone into the saturated zone in steady-state can be calculated as

$$\mathit{Flux} = r \times d \times \mathit{Volume\ fraction},$$

where d = the depth of the protore zone (assumed to be 10 m in depth). The dissolution of minerals into ions was assumed to be instantaneous and to follow the stoichiometrics of reactions listed by Xu *et al.* (2000). Therefore, the composition of the water leached from the top of the column is shown in Table 2 with an initial pH of 2.0 assumed. The electronic characteristics of the column was hypothesized to change from slightly oxidation conditions just beneath the water table and to more reduced conditions when the water was descending due to chemical and biochemical activities. However, these processes are complicated and not well understood at present time. As such, the electron potential in this column was simplified and assumed to be linear decreasing from an *Eh* value of 0.3 V at the top to one of 0.0 V at the bottom with a descending rate of −0.03 V/m.

Table 2. Concentrations of Ions in the Source Leached from the Top at Initial pH of 2.0

Ion	Concentration (mole/dm^3)
$HSO_4^- + SO_4^{2-}$	0.028544747
H^+	0.01
Cu^{2+}	0.004757458
$H_2S + HS^- + S^{2-}$	0.01

Table 3. Species Considered in the Simulation of Supergene Copper Precipitation

Primary cation species	Primary anion species	Secondary species
H^+	OH^-	H_2O
Cu^{2+}	SO_4^{2-}	$CuS_{(s)}$
Cu^+	S^{2-}	$Cu_2S_{(s)}$
	e^-	HSO_4^-
		H_2S
		HS^-

Note: Secondary species can be expressed with combinations of the primary species.

III. Boundary Conditions

Based on the assumption of constant dissolved ion concentrations in inflow as the only source of input, the upper boundary of the simulation area was a water table with constant flux, a constant flow rate and, therefore, a constant input concentration, in other words, a Dirichlet boundary condition. The lower and the right and left boundaries were set to be a Neumann boundary condition since the flux (concentration gradient) perpendicular to the boundary was zero.

IV. Redox Chemistry Considered

The precipitation reactions involved in the saturated zone were assumed to be equilibrium controlled, and the environment was assumed to be controlled by the electron potential (E_H) that was gradually descending with the increase of the water depth as mentioned above. In this simplified case, reactions associated only with copper ions with a total of 13 species (as shown in Table 3) for secondary mineral precipitation were considered. As reported in the literature, acid-base, substitution, and redox reactions may all take place under slightly oxidizing to reducing conditions. Table 4 lists all the reactions considered in this study. The acid-base reactions include the dissolution of sulfide and sulfate according to pH (Eqs. (1) – (3)). The substitution reactions include the replacement of hydrogen ion with copper (Cu^+ and Cu^{2+}) to form covellite and chalcocite (Eqs. (4) and (5)). The redox reactions,

Table 4. Reactions Involved for Secondary Mineral Precipitation

Reaction	Log *K* (25°C)	Equation
$HS^- = H^+ + S^{2-}$	–14	(1)
$H_2S = 2H^+ + S^{2-}$	–21.1	(2)
$HSO_4^- = SO_4^{2-} + H^+$	–2	(3)
$Cu^{2+} + HS^- = CuS_{(s)} + H^+$	22.83	(4)
$2Cu^+ + HS^- = Cu_2S_{(s)} + H^+$	34.73	(5)
$Cu^{2+} + e^- = Cu^+$	2.7	(6)
$2CuS_{(s)} + 2H^+ + 2e^- = Cu_2S_{(s)} + H_2S$	2.80	(7)
$2CuS_{(s)} + H^+ + 2e^- = Cu_2S_{(s)} + HS^-$	–4.19	(8)
$2CuS_{(s)} + 2e^- = Cu_2S_{(s)} + S^{2-}$	–18.18	(9)
$Cu_2S_{(s)} + HSO_4^- + 7H^+ + 6e^- = 2CuS_{(s)} + 4H_2O$	36.3	(10)
$Cu_2S_{(s)} + SO_4^{2-} + 8H^+ + 6e^- = 2CuS_{(s)} + 4H_2O$	38.23	(11)
$CuS_{(s)} + Cu^{2+} + 2e^- = Cu_2S_{(s)}$	18.18	(12)
$2Cu^{2+} + HSO_4^- + 7H^+ + 10e^- = Cu_2S_{(s)} + 4H_2O$	72.33	(13)
$2Cu^{2+} + SO_4^{2-} + 8H^+ + 10e^- = Cu_2S_{(s)} + 4H_2O$	74.19	(14)
$2Cu^{2+} + H_2S + 2e^- = Cu_2S_{(s)} + 2H^+$	2.80	(7)*
$2Cu^{2+} + HS^- + 2e^- = Cu_2S_{(s)} + H^+$	–4.19	(8)*
$2Cu^{2+} + S^{2-} + 2e^- = Cu_2S_{(s)}$	–18.18	(9)*
$2Cu^+ + H_2S_{(aq)} + HSO_4^- + 5H^+ + 6e^- = 2CuS_{(s)} + 4H_2O$	36.3	(10)*
$2Cu^+ + HS^- + SO_4^{2-} + 7H^+ + 6e^- = 2CuS_{(s)} + 4H_2O$	38.23	(11a)*
$2Cu^+ + H_2S + SO_4^{2-} + 6H^+ + 6e^- = 2CuS_{(s)} + 4H_2O$	38.23	(11b)*
$2Cu^{2+} + HS^- + 2e^- = Cu_2S_{(s)} + H^+$	18.18	(12a)*
$2Cu^{2+} + H_2S + 2e^- = Cu_2S_{(s)} + 2H^+$	18.18	(12b)*

including the reduction of Cu^{2+} to Cu^+ (Eq. (6)), the reduction of covellite to form chalcocite and vice versa when conditions are favorable (Eqs. (7) – (12)), and the reduction of Cu^{2+} by sulfate to form covellite (Eqs. (13) and (14)), were also included. Assuming that solid phase reactions take place through instantaneous dissolution followed by ionic reactions, reactions that involve solids (Eqs. (7) – (14)) as reactants can be rewritten as Eqs. $(7)^*$ – $(14)^*$ with back-calculated log K. In this case, the simulation used reactions Eqs. (1) – (6), $(7)^*$ – $(12)^*$, and (13) – (14).

V. Hydrogeochem

The simulation was carried out using an existing equilibrium-based model, HYDROGEOCHEM (Yeh and Tripathi, 1990, 1991), with coupled reactive multicomponent systems for both hydrologic transport and geochemical equilibria sequentially and iteratively solved using the finite element method (FEM). This code is designed for application to heterogeneous, anisotropic, and saturated-unsaturated media under transient or steady state flow conditions in a 2-dimensional domain. It is able to model redox half reactions by defining and calculating the concentration (activity) of "operational" electrons as a component. As is the case for other components, the principle of conservation of electrons must also be ensured so that all electrons donated by chemical species will be accepted by other species. A detailed description of the code can be found in the original manual (Yeh and Tripathi, 1990).

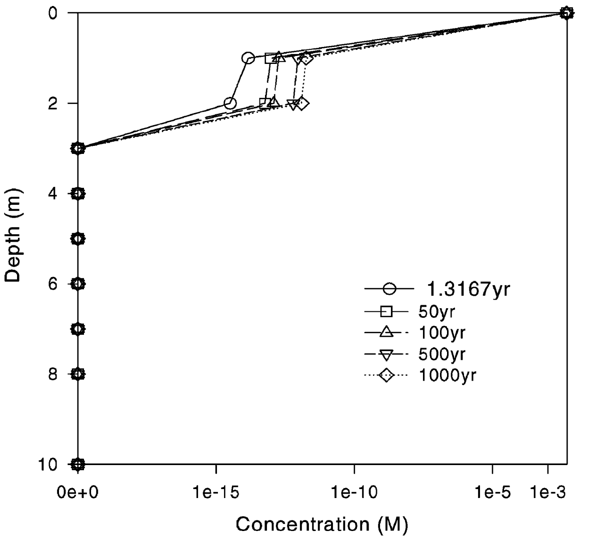

Fig. 2. Covellite precipitation at various time spans and $[Cu^{2+}]_{initial} = 4.76 \times 10^{-3}$ M, Infiltration rate = 70 mm/yr.

VI. Results and Discussion

The simulation was first carried out by applying the prescribed conditions to the field, where the infiltration rate and the concentration of leached copper were set as 70 mm/yr and 4.76×10^{-3} M, respectively. Figure 2 presents the simulation results. The concentrations of covellite are presented in log scale in Figs. 2 – 4. It is evident that only covellite was precipitated under these conditions, and that the concen-

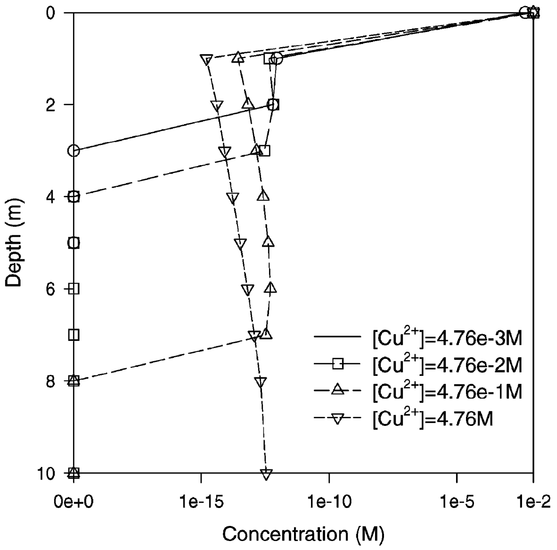

Fig. 3. Covellite precipitation at various initial [Cu^{2+}]. Time = 500 yr, Infiltration rate = 70 mm/yr.

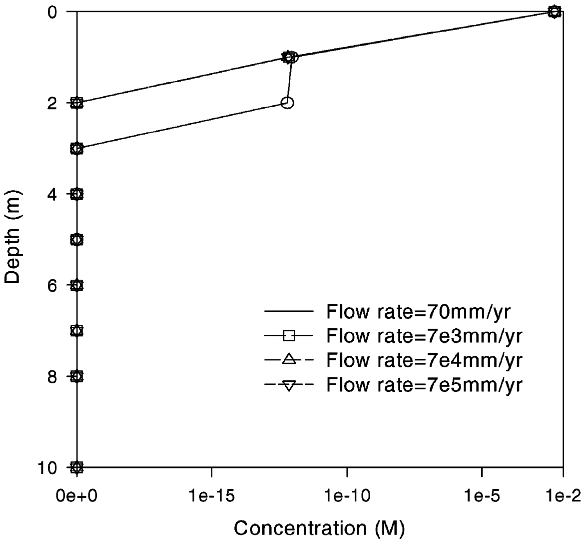

Fig. 4. Covellite precipitation at various Infiltration rate and Time = 500 yr, $[Cu^{2+}]_{initial} = 4.76 \times 10^{-3}$ M.

tration of covellite precipitation increased with the increase of the time span. Nevertheless, the precipitation profile of covellite stayed relatively unchanged with no extension to a deeper zone with the increase of the time span. This simulated result is in agreement with field observations, in which the accumulation of copper mineral precipitation took place to form enriched copper mine at and just beneath the groundwater table.

Similar simulations with variation in the initial leached copper ion concentration and infiltration flow rate were also performed to evaluate the influence of these two potential control factors. The results were illustrated in Figs. 3 and 4. In Fig. 3, it is evident that the change in the initial copper ion concentration significant influenced the precipitation profile of covellite. The amount of precipitation increased and extended downward with the increase of the initial copper ion concentration. This finding indicates that the increase of copper ion can provide additional copper sources for the formation of covellite. At copper concentrations as low as 4.76×10^{-1} M, copper leached from above was used up in a shallow zone while at the highest copper concentration, the copper could leach into a deeper zone to form covellite precipitation according to the redox potential. The precipitation profile was also related to the redox potential as shown in Fig. 3.

Figure 4 presents the covellite precipitation for various infiltration rates while the other factors remain unchanged. It is obvious that a slight difference was observed when the infiltration rate was changed to 10000 times higher than the initial value. This finding indicates that the increase of the infiltration rate washed out the copper ion in water, thereby preventing the formation of covellite precipitation in deeper zones as shown in Fig. 4.

VII. Conclusion

A simplified simulation of copper precipitation during supergene enrichment processes was carried out using the HYDROGEOCHEM code. Redox half reactions of covellite and chalcocite as reactants as well as precipitation reactions that form covellite and chalcocite were considered. The results indicate that the precipitation pattern is attributable to the redox-controlled process, wherein the electron potential is the key parameter for forming such a pattern. The precipitation amounts are also related to the time span and initial aqueous copper ion concentration. This finding is in good agreement with field observations, in which large amounts of Cu grade minerals within a narrow zone just beneath the water table were observed and the enriched blanket zone grew indefinitely with time. It also provides a more physically-meaningful explanation for such phenomena than do the non-selectively equilibrium and/or kinetic controlled approaches reported in the literature.

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A Simulation of Supergene Copper Enrichment

模擬銅礦富集之地化反應過程

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摘　要

本研究乃利用一簡化模式模擬銅礦富集過程中的沉澱現象以探討地化反應與地下水流之自組反饋行爲，研究中同時考量銅礦物生成及轉變之氧化還原半反應與水流的關係，並藉由HYDROGEOCHEM模式分析模擬，結果顯示氧化還原電位爲銅沉澱形成剖面之主要控制因子，沉澱之生成量並與時間及初始濃度有關。此發現符合現場調查結果；相較於其他非選擇性之平衡或動力模式，運用此模式解釋此一現象更具物理意義。