



# 行政院國家科學委員會專題研究計畫成果報告

## 地化反應與地下水流自組反饋之研究(三)

### Study on Self-organization and Feedback of Geochemical Reaction and Groundwater Flow (III)

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#### 中文摘要

本研究乃利用一簡化之模式模擬銅礦富集過程中之沉澱現象以探討地化反應與地下水流自組反饋之行為，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之關係並藉由 HYDROGEOCHEM 模式分析模擬，結果顯示氧化還原電位為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，運用此模式更具物理意義來解釋此一現象。

**關鍵字：**沉澱、反應傳輸、氧化還原半反應、銅礦富集

#### Abstract

A simplified simulation of copper precipitation during supergene enrichment processes was carried out to study the self-organization and feedback behaviors of geochemical reaction and groundwater flow. Reevaluation of the pattern of formation was studied by 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 precipitation pattern can be 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 observation and gives a more physically-meaningful explanation to such phenomena compared to the non-selectively equilibrium and/or kinetic controlled approaches in literature.

**Keywords:** precipitation, reactive transport, redox half reactions, supergene enrichment.

#### Introduction

The phenomenon of supergene enrichment involving copper precipitation is a remarkable case of weathering processes that takes place at and beneath the groundwater table under reducing conditions and involves in a large body of minerals and complex encountering environments. It is also very valuable for mining industry in economic viewpoint by reprecipitating and enriching low-grade materials into high-grade secondary minerals at lower levels by several factors (Guilbert and Park, 1986). However, unlike the oxidation processes for mobilizing primary minerals, the precipitation process for fixation of secondary minerals is much more complicate and not well understood so far although several mechanisms have been proposed experimentally, conceptually, or numerically in literature. Generally, it is considered as an abiotic process with the involvement of progressive replacement of pyrite or chalcopyrite to form copper-rich sulfides (Brimhall *et al.*, 1985). It has been proved to be true that the presence of pyrite is a critical condition for the precipitation of

copper-bearing minerals (Stokes, 1907). Pyrite with high solubility acts as a host for deposition of the ores by 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,b; Xu *et al.*, 2000). Chalcocite containing 79.8% Cu generally precipitates at the top of the blanket where  $\text{Cu}^{2+}/\text{HS}$  ratios are higher while covellite containing 66.4% Cu precipitates at depth where the blanket becomes less enriched and  $\text{Cu}^{2+}/\text{HS}$  ratios are low (Guilbert and Park, 1986). Replacement of other metal-sulfide minerals also may take place during enrichment processes. Ague and Brimhall (1989) revealed the formation of chalcocite by the destruction of chalcopyrite by copper ions. Besides, they also concluded that the oxygen fugacity is the key control on the system and the dominant source of sulfur for precipitation of secondary minerals is the primary minerals (hydrogen sulfide or chalcopyrite) in the reduced zone but not the sulfate migrating from the leached zone. Sulfur leached from the oxidation zone is highly mobile and leaves from the flow region in the form of sulfate.

Nevertheless, 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 a scanning electron microscope (SEM) indicated the presence of fossilized and metallized forms of bacteria or nanobacteria near the replacement interfaces that might promote the fixation of mobilized copper ions.

With regards to modeling of the enrichment behavior, several equilibrium and kinetic approaches have been proposed for describing the precipitation processes in literature (Ague and Brimhall, 1989; Lichtner and Biino, 1992; Xu *et al.*, 1999a,b; Xu *et al.*, 2000). These models applied quasi-equilibrium and/or kinetic approaches

to describe the dissolution and/or precipitation processes during enrichment with the consideration of complicated geochemical reactions involving numbers of primary and secondary minerals. By this means, the formation of layered ore deposits is partially explained under specific given conditions and parameters. However, it is still of questions to explain the physical meaning of the phenomena that naturally occurs wherein covellite was sandwiched by chalcocite in enrichment blanket due to the unselected equations used in those equilibrium and kinetic approaches.

Sato (1992) summarized precipitation processes that might take place with respect to geochemistry during the enrichment processes. The precipitation (concentration) of copper-bearing minerals, supergene enrichment, near the groundwater table can be considered as three processes, where (1) fixation of oxidation produces 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 cation-exchange reactions wherein the condition needs to be in reduced zone but with slight higher electronic potential to prevent the formation of native metals. Sato (1992) also described the complex supergene enrichment processes based on the construction of Eh-pH diagram of the redox half-reactions. When the copper-rich water reaches the saturated zone under a slightly oxidized zone,  $\text{Cu}^{2+}$  react with sulfur or hydrogen sulfide to form CuS (covellite) or  $\text{Cu}_2\text{S}$  (chalcocite) according to the abundance of copper and redox potential. When excess copper present in solution, chalcocite will predominately form from the reaction between CuS and  $\text{Cu}^{2+}$ . This relationships give the explanation that why  $\text{Cu}_2\text{S}$  is lying on the top of CuS in the slightly oxidizing condition. Beneath that and when no excess copper, the covellite will be the end product in the slightly oxidized condition. In a much 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., redox potential) and mineral compositions that encountered. As such, the use of redox half-reactions may be critical in modeling to reflex such a redox-controlled process and may lead to a more reasonable explanation for copper-mineral formation in enrichment blanket.

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

### Simulated Area and Initial Conditions

Simplified one-dimensional porous media (neglecting fractures) saturated with water with 10 meter in height was selected for simulation. Groundwater table was assumed to be placed on the top of the column. Infiltration is assumed to be steady-state with a vertical flow rate of 70 mm/yr. The column was evenly divided into 20 vertical elements with a height of 5 dm in each element. Other geological and hydraulic parameters in assumption used in this simulation are: porosity of 0.2, permeability of  $10^{-14}$  m<sup>2</sup>, molecular diffusion coefficient of  $3.6 \times 10^{-4}$  dm<sup>2</sup>/hr, tortuosity of 0.1, and diffusivities for all elements in longitudinal direction of 7.6 dm and in transverse direction of 0.0 dm. The initial

concentrations of chemicals of interest in the column are assumed to be zero. The amounts of dissolved minerals and chemical compositions in the infiltration water released from leached zone to the saturated zone at steady state are kinetic controlled according to basic kinetic dissolution law wherein the volumetric dissolution rate of a mineral is assumed to be constant and governed by the kinetic rate constant and the surface area of such mineral. Therefore, it can be expressed as:

$$r = k \times \text{Surface Area} [\text{mol} / \text{dm}^3 / \text{s}]$$

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

$$\text{Flux} = r \times d \times \text{Volume fraction}$$

where d = depth of the protore zone (assumed to be 10 m in height). The dissolution of mineral into ions was assumed to be instantaneous and follows the stoichiometrics of reactions listed in Xu (1999). Therefore, the compositions of water leached from the top of the column are listed in Table 1 with initial pH of 2.0 in assumption. The electronic characteristics of the column was hypothesized to changes from a slightly oxidation condition just beneath the water table and moves to a more reduced condition when water was descending due to chemical and biochemical activities. However, the processes are complicate and not well known at present time. As such, the electron potential in this column is simplified and assumed to be linear decreasing from Eh of 0.3 volt at the top to 0.0 volt at the bottom with a descending rate of -0.03 volt/m.

Table 1. Concentrations of ions in the source leached from the top at initial pH of 2.0.

Ion	Concentration (mole/dm <sup>3</sup> )
H <sub>2</sub> SO <sub>4</sub> + SO <sub>4</sub> <sup>2-</sup>	0.028544747
H <sup>+</sup>	0.01
Cu <sup>2+</sup>	0.004757458
H <sub>2</sub> S + HS <sup>-</sup> + S <sup>2-</sup>	0.01

## Boundary Conditions

With the assumption of constant dissolved ion concentrations in inflow as the only source of input, the upper boundary of the simulation area is the water table with a constant flux and a constant flow rate thereby a constant input concentration, in other word, a Dirichlet B.C.. The lower and the right and the left boundaries are set to be a Neumann B.C. since the flux (concentration gradient) perpendicular to the boundary is zero.

## Redox Chemistry Considered

The precipitation reactions involved in saturated zone are assumed to be equilibrium controlled and the environment is controlled by the electron potential ( $E_H$ ) that is gradually descending with the increase of water depth as mentioned before. In this simplified case, reactions associated only with copper ions with a total of 13 species (as shown in Table 2) for secondary mineral precipitation were considered. As cited from literature, acid-base, substitution, and redox reactions may all take place in the slightly oxidizing to reducing conditions. Table 3 lists all the reactions considered in this study. The acid-base reactions include the dissolution of sulfide and sulfate according to pH (Eqns (1)-(3)). The substitution reactions include the replacement of hydrogen ion with copper ( $Cu^+$  and  $Cu^{2+}$ ) to form covellite and chalcocite (Eqns (4) and (5)). The redox reactions include the reduction of  $Cu^{2+}$  to  $Cu^+$  (Eqn. (6)), the reduction of covellite to form chalcocite vice versa when conditions are favorable (Eqns (7)-(12)), and the reduction of  $Cu^{2+}$  by sulfate to form covellite (Eqns (13) and (14)) are also included. Assuming solid phase reactions will take place by instantaneous dissolution followed by ionic reactions, then the reactions involve solids ((7)-(14)) as reactants can be rewritten as ((7)\*-(14)\*) with back-calculated log K. As such, the simulation will use reactions

(1)-(6), (7)\*-(12)\*, and (13)-(14).

Table 2. Species considered in the simulation of supergene copper precipitation. (Secondary species can be expressed with combinations of the primary species.)

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

Table 3. Reactions involved for secondary mineral precipitation

Reactions	Log K (25°C)	Eqn.
$HS^- = H^+ + S^{2-}$	-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	(11)*
$2Cu^+ + H_2S + SO_4^{2-} + 6H^+ + 6e^- = 2CuS_{(s)} + 4H_2O$	38.23	(11-2)*
$2Cu^{2+} + HS^- + 2e^- = Cu_2S_{(s)} + H^+$	18.18	(12-1)*
$2Cu^{2+} + H_2S + 2e^- = Cu_2S_{(s)} + 2H^+$	18.18	(12-2)*

## HYDROGEOCHEM

The simulation was carried out by the use of an existing equilibrium-based model, HYDROGEOCHEM (Yeh and Tripathi, 1990 and 1991), wherein coupled reactive multicomponent systems for both hydrologic transport and geochemical equilibria were

sequentially and iteratively solved by the use of finite element method (FEM). This code is designed for application to heterogeneous, anisotropic, saturated-unsaturated media under transient or steady state flow conditions in 2-dimensional domain. It is able to model redox half reactions by defining and calculating the concentration (activity) of "operational" electrons as a component. Same as other components, the principle of conservation of electrons must also be ensured so that all electrons donated by chemical species must be accepted by another species. Detailed description of the code can be referred to the original manual (Yeh and Tripathi, 1990).

### Results and Discussion

The simulation was first carried out by applying the pre-described conditions to the field wherein the infiltration rate and concentration of leached copper were set as 70 mm/yr and  $4.76 \times 10^{-3} \text{M}$ , respectively. Figure 1 presents the simulated results. It is evident that only covellite was precipitated under these conditions and the concentration of covellite precipitation increased with the increase of time span. Nevertheless, the precipitation profile of covellite stays relatively unchanged with no extension to a deeper zone with the increase of time span.

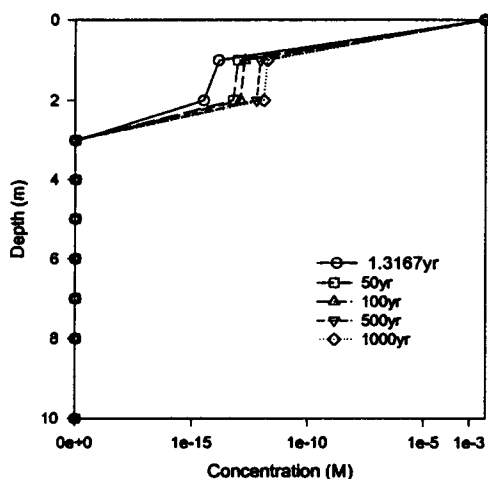


Figure 1. Covellite precipitation at various time spans and  $[\text{Cu}^{2+}]_{\text{initial}} = 4.76 \times 10^{-3} \text{M}$ , Infiltration rate = 70mm/yr.

This finding is in agreement with field observation wherein accumulation of copper mineral precipitation takes place to form enriched copper mine at and just beneath groundwater table.

Similar simulations with variation in initial leached copper ion concentrations and infiltration flow rates were also performed to evaluate the influences of these two potential control factors. The results were illustrated in Figures 2 and 3. In Figure 2, it is evident that the changes in initial copper ion concentrations will significant influence the precipitation profile of covellite. The amount of precipitation will increase and extend downward with the increase of initial copper ion concentrations. This finding indicates the increase of copper ion can provide extra copper sources for formation of covellite. At lower copper concentration up to  $4.76 \times 10^{-1} \text{M}$ , copper leached from above was used-up at a shallow zone while at the highest copper concentration, the copper can leach to a deeper zone to form covellite precipitation according to the redox potential. Besides, the precipitation profile is also evidently related to the redox potential as shown in Figure 2.

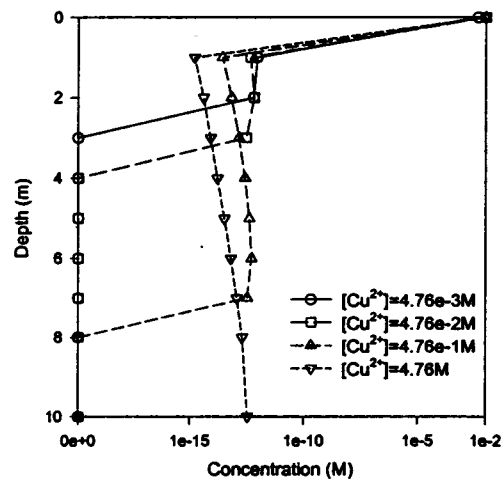


Figure 2. Covellite precipitation at various initial  $[\text{Cu}^{2+}]$ . Time = 500yr, Infiltration rate = 70mm/yr.

Figure 3 presents covellite precipitation at various infiltration rates while other factors remain unchanged. It is obvious that slight difference was observed when the

infiltration rate was changed to 10000 time higher than the initial value. This finding indicates that the increase of infiltration rate washes out the copper ion in water thereby preventing the formation of covellite precipitation in deeper zones as shown in Figure 3.

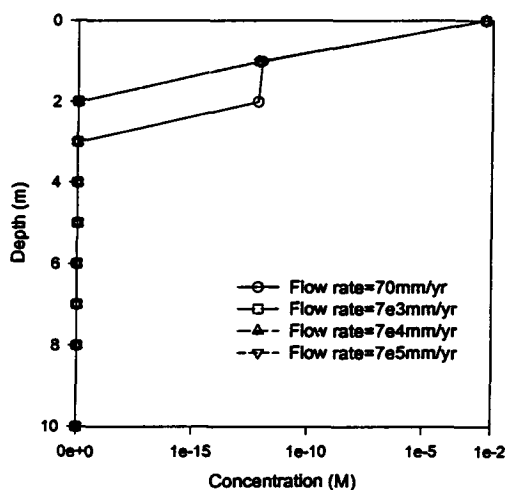


Figure 3. Covellite precipitation at various Infiltration rate and Time=500yr,  $[Cu^{2+}]_{initial}=4.76 \times 10^{-3}$ .

## Conclusion

A simplified simulation of copper precipitation during supergene enrichment processes was carried out by use 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 precipitation pattern can be 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 observation and gives a more physically-meaningful explanation to such phenomena compared to the non-selectively equilibrium and/or kinetic controlled approaches in literature.

## Self-Evaluation

This study is well in agreement with the proposal with respects to the contents and objectives. A preliminary evaluation of the application of self-organization and feedback of geochemical reaction and groundwater flow theories to simulate and explain field observation was achieved. The finding of this study can be applied to geological field, hydrological field, and environmentally-related field as well to study the coupled reaction-transport problems. Besides, the study is of great worth for publication in world-class journals. However, it requires further and extensive work with regard to refining the model and evaluating other factors. Submission of the manuscript will be subjected to the time availability and the success in extensive study.

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