



**Mobilization and secondary enrichment processes in the sulfide porphyry copper tailings of Cauquenes (El Teniente) and Piuquenes (La Andina), Chile.**

Bernhard Dold, Lluís Fontboté & Walter Wildi

Earth Sciences Department, University of Geneva, Rue des Maraîchers 13, 1211 Genève 4, Switzerland.  
(Bernhard.Dold@terre.unige.ch)

ABSTRACT

Preliminary results on mineralogical and geochemical changes at the transition between oxidation and primary (sulfide) zone in copper flotation tailings located in Chile are presented. The tailing Cauquenes (El Teniente) and Piuquenes (La Andina) were sampled down to a depth of 10,4 m with percussion drilling. In both tailings, results of sequential digestions analyses show a similar distribution. In the oxidation zone (jarosite zone) Cu, Ca, Co, Mg, Mn, Pb, Zn are almost completely leached out. Fe and Mo display relatively high values in the oxalic acid and H<sub>2</sub>O<sub>2</sub> fractions of the oxidation zone indicating that they have been fixed in Fe(III)hydroxides subsequently to the breakdown of sulfides. K is fixed in jarosite. As, Al, and Ba show relatively high values in the oxalic acid fraction in the oxidation zone. The underlying precipitation zone (gypsum zone) is characterized by enrichment of elements leached from the oxidation zone in particular Cu, Co, and Mo. In the basal primary zone, carbonates (e.g. siderite) and sulfides are still stable and no secondary mineral formation is recognized.

INTRODUCTION

Oxidation of pyrite, the most common sulfide mineral in sulfide copper mine tailings, leads to strong geochemical and mineralogical changes after operation ceased [5,8]. The net reaction of complete oxidation of pyrite, hydrolysis of Fe<sup>3+</sup> and precipitation of iron hydroxide produces 4H<sup>+</sup> per mol of pyrite, i.e., pyrite oxidation is an extremely efficient acid producer. The acid liberated in this process, and the resulting low pH in the oxidation zone (in the range of pH 1.5-4) is able to mobilize a great number of elements in the tailings [1,3,5,8]. The underlying material has the function of a retention zone for the acid and metal bearing solution through sorption and neutralization processes, which result in enrichment of some elements. Acid-neutralization reactions can occur along the ground water flowpath throughout the tailings impoundment and underlying aquifers, limited by the availability of acid-consuming mineral phases. The H<sup>+</sup>-consuming reactions result in the general increase in pH with increasing depth [1]. The adsorption of H<sup>+</sup> ions mainly at clay minerals is a second possible buffer reaction. Adsorption and absorption processes from metal ions at iron hydroxides, clay minerals, and calcite are well investigated in laboratory research [2,4,6]. Adsorption of metal ions at Fe(III)hydroxides is a function of pH (surface adsorption at Fe(III)hydroxides is not stable below pH 3), temperature, and reaction time. Long-term studies show that metal ions may incorporate by diffusion into the crystalline system of secondary Fe(III)hydroxides, which is a stable fixing also at lower pH [2,4]. Once the adsorption and acid-neutralization capacity of the underlying layers of tailing material is exceeded, the mobilized elements lead to the formation of a highly metal-bearing acid mine drainage (AMD), one of the main environmental problems of the mining industry.

In this paper preliminary results of the mineralogical and geochemical changes at the interface between the oxidation zone and the primary (sulfide) zone of two copper flotation tailings in Chile are presented. Parameters of climate, water budget, and original mineralogical composition are taken into account. The tailings are from porphyry copper deposits with ore parageneses relatively poor in pyrite and poor in carbonates with abundant hydrothermal clay minerals. The Piuquenes tailing from La Andina (CODELCO) was chosen as a representative tailing in a humid climate (mountain-humid, precipitation ca. 1000 mm/a). The Cauquenes tailing from El Teniente (CODELCO) represents a semi-arid climate with about 500 mm/a rainfall. Piuquenes stopped operation in 1980 and Cauquenes in 1975.

SAMPLING AND ANALYTICAL METHODS

Standard soil sampling equipment (percussion) was used and the obtained cores show no or low contamination. The length of the drillings range from 4 m to 12 m. In the oxidation zone and at the interface to the primary zone up to 5 samples of 20 cm length/meter were taken. In the primary zone only two samples/meter were taken. The samples, after description of mineralogical characteristics, color and grain size estimation, and pH measurement (paste pH according to MEND 1991), were sealed in plastic bags. Drying (< 40°C) and water content determination took place in the laboratory.

X-ray diffraction (XRD) is used to detect mineralogical changes in the tailings stratigraphy. Polished and thin sections are used to complement XRD data. A sequential digestion procedure was used for drill cores T/4 and A/5. It is based on a series of digestions on the same sample (1 g) which has been previously dried at low temperature (<40°C) to

avoid modification of the structure of minerals (e.g. clay minerals). Six digestion steps (fractions) have been chosen: 1. 1M NH<sub>4</sub>OAC, pH 4,5 ("adsorbed"), 2. 0,1M NaOAC, pH 5 ("carbonate"), 3. 0,25M hydroxylamine HCL, pH 2 ("Mn-oxides"), 4. 0,1M oxalic acid, pH 3 ("Fe(III)oxides"), 5. H<sub>2</sub>O<sub>2</sub> 35 % ("sulfide"), 6. HF, HNO<sub>3</sub>, HClO<sub>4</sub> ("residual"). The terms in quotation mark denote the main fraction leached at each step; they are only indicative as for instance significant amounts of Fe(III)oxide and sulfides survive the 0,1M oxalic acid and the H<sub>2</sub>O<sub>2</sub> steps, respectively. The digestion solutions were analyzed by ICP-EOS for 31 elements.

## RESULTS

### A) CAUQUENES TAILING FROM EL TENIENTE

At the studied tailing Cauquenes from El Teniente (725 m.a.s.l., semi-arid climate: temperatures from 33° to -4°C, precipitation of 540 mm/a) five drill cores down to a depth of 10,4 m were drilled. The main phases are quartz, muscovite, biotite, kaolinite, and plagioclases (andesine-labradorite, albite-oligoclase). Minor phases are pyrite, calcite, siderite and secondary minerals jarosite, gypsum, and Fe(III)hydroxides. One drilling (T/4) did cross the tailing to the bedrock of Upper Cretaceous clastic sediments of the Abanico Formation. On the top, the tailing shows an oxidation zone (1.05 to 4 m thickness) situated in the vadose zone (water table 2.4 - 4 m depth). Primary grain size differences, as a result of the deposition technique are still preserved (1 to 30 cm thick sandy layers interlayered with clay-size horizons). The oxidation zone is characterized by low pH (between 1.7 and 4), by the presence of secondary minerals, mainly jarosite (yellow brown) and Fe(III)hydroxides (red brown color), and by a finer grain size (between clay-size and fine sandy) than the original material (Fig.2). The smaller grain size in the oxidation zone is due to the dissolution of carbonate and aluminosilicate minerals and to the precipitation of fine grain-sized hydroxides. The contact to the underlying precipitation zone is sharp. The precipitation zone is characterized by an increase of the pH from 2.9 to 3.6 at the oxidation/precipitation zone interface, brown to dark grey color, and the precipitation of gypsum; pyrite is still stable. The primary zone is mainly characterized by an increase of pH at the precipitation/primary zone interface from 3.7 to 5.5, dark grey color, and coarser grain size than in the oxidation zone. The primary minerals including pyrite and the aluminosilicates are stable and not altered. The correlation of the three zones with mineralogy and geochemical parameters is mainly characterized by the formation of jarosite in the oxidation zone as result of pyrite oxidation, by precipitation of gypsum in the precipitation zone (pyrite is still stable), and by the presence of primary sulfides in the primary zone of the tailing (Fig. 1a). XRD and sequential digestion results show the breakdown of pyrite in the oxidation zone; iron is depleted in the residual fraction and, logically, enriched in the oxalic acid fraction (Fig. 1a). K content is high in the oxalic acid fraction in the oxidation zone due to precipitation of Fe(III)hydroxides and jarosite. Ca shows decreased values in the NH<sub>4</sub>OAC fraction of the oxidation zone, while the content increases in the precipitation zone (Fig. 1a). Cu, as the main element of economic interest, is almost completely leached out from the oxidation zone. High Cu contents in the NH<sub>4</sub>OAC fraction in clay-size horizons underlying the oxidation zone, may be explained by fixing at clay minerals and Fe(III)hydroxides. Mo, the main byproduct, shows a relatively constant value of 100 mg/kg through the three zones (not shown in Fig. 1b), but is distributed differently in the analyzed fractions. In the oxidation zone Mo is already leached by the oxalic acid and the H<sub>2</sub>O<sub>2</sub> attacks, indicating adsorption at Fe(III)hydroxides. In the precipitation and primary zone Mo still occurs as molybdenite as indicated by the high contents in the residual fraction (Fig. 1b). Ca, Co, Cu, Mn, Zn as well as Al (not shown) and As display lower total values in the oxidation zone and increasing contents in the basal part of the tailing, especially in the NH<sub>4</sub>OAC fraction and the oxalic acid fraction. Some elements, such as As, are enriched in the oxalic acid fraction in the oxidation zone (Fig. 1b) and are associated to secondary Fe(III)hydroxides (As, Mo) and jarosite (K, Ba).

### B) PIUQUENES TAILING FROM LA ANDINA

At the Piuquenes tailing of La Andina (2100 m.a.s.l., temperatures about 0 - 25°C, precipitations of 1000 mm/a), five drillings down to a depth of 10 m were performed. The mineralogy of this tailing consists mainly of the major phases quartz, muscovite, plagioclases (oligoclase-andesine, albite-andesine), ankerite, kaolinite, and siderite; and of the minor phases pyrite, calcite, and the secondary phases gypsum and jarosite. Like at Cauquenes, the Piuquenes tailing shows an oxidation zone at the top (50 - 100 cm thickness) with low pH (2.8), yellow brown (jarosite) and red brown (Fe(III)hydroxides) color, and finer grain size than in the primary zone. The primary stratigraphy in grain size is still observed. The oxidation zone is situated in the vadose zone (water table 2-5 m). Down section, the contact to the gypsum zone (50 - 500 cm, gray brown to brown) is continuous and corresponds to a pH increase to 3.5. The interface between the gypsum zone and the primary zone is characterized by the change from brown to dark gray color and a pH increase from 5.9 to 7.0 (Fig. 2a). Dissolution of siderite in the oxidation and precipitation zones is the main acid buffer in the Piuquenes tailing (Fig. 2a). A comparable development of pH-buffering zones (Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, and calcite -

siderite) is reported in [1]. The element distribution shows a similar behavior as at Cauquenes. Iron contents in the oxalic acid fraction of the oxidation zone are high due the formation of Fe(III)hydroxide. K is enriched in the oxalic acid fraction of the oxidation zone, while Ca is mobilized downwards. Cu is almost completely leached in the oxidation zone; contrasting with the high values of the precipitation zone, which are higher than in the primary zone. The highest values are found in the residual and NH<sub>4</sub>OAC fractions, possibly associated to secondary precipitation processes. Only a minor part of the mobilized Cu is fixed in the NH<sub>4</sub>OAC fraction. Mo shows similar behavior as described for the Cauquenes tailing (Fig.2b). Arsenic, as well as Al, Cr, Mg, Mn, Pb, Zn, are enriched in the oxalic acid fraction.

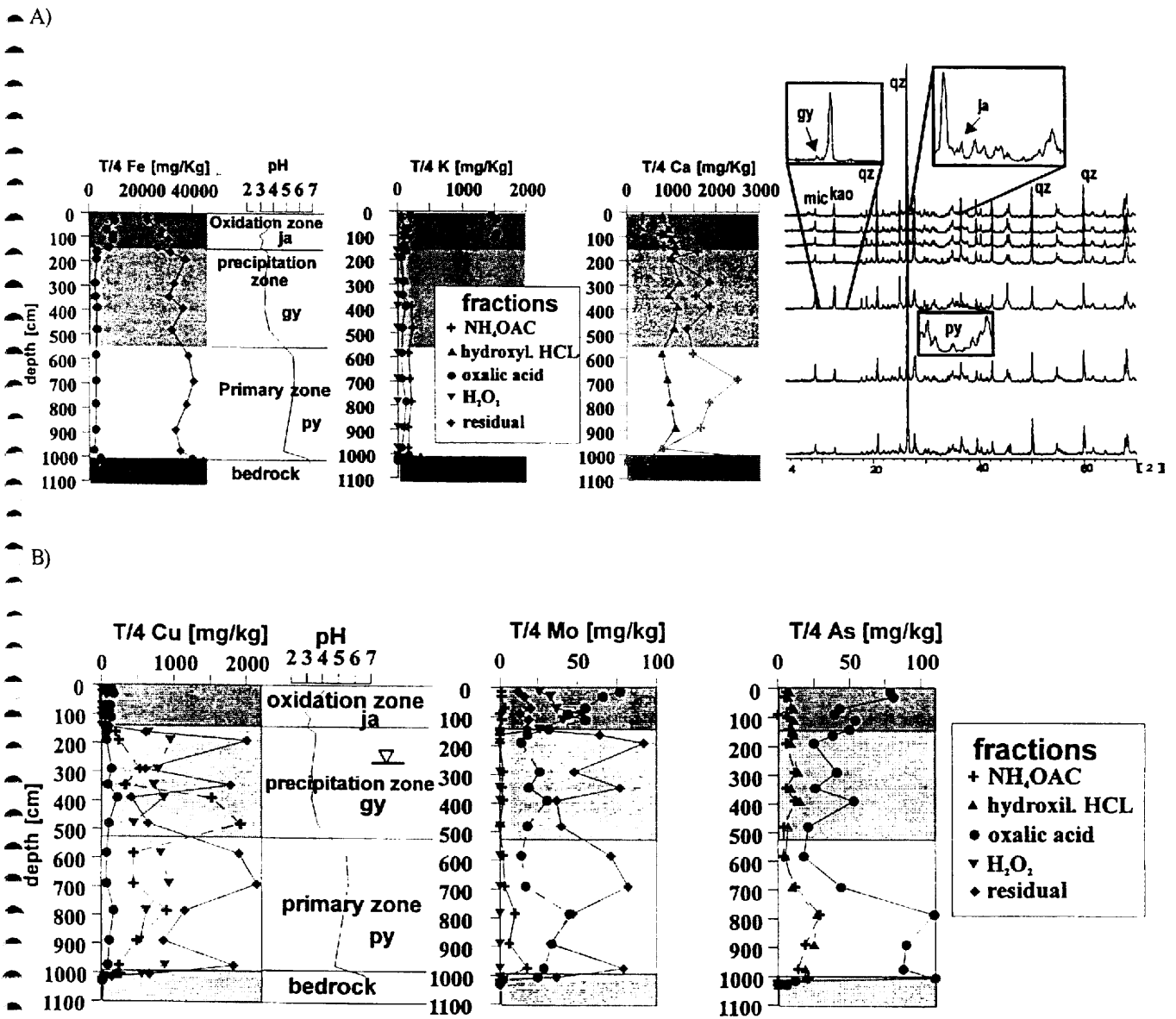
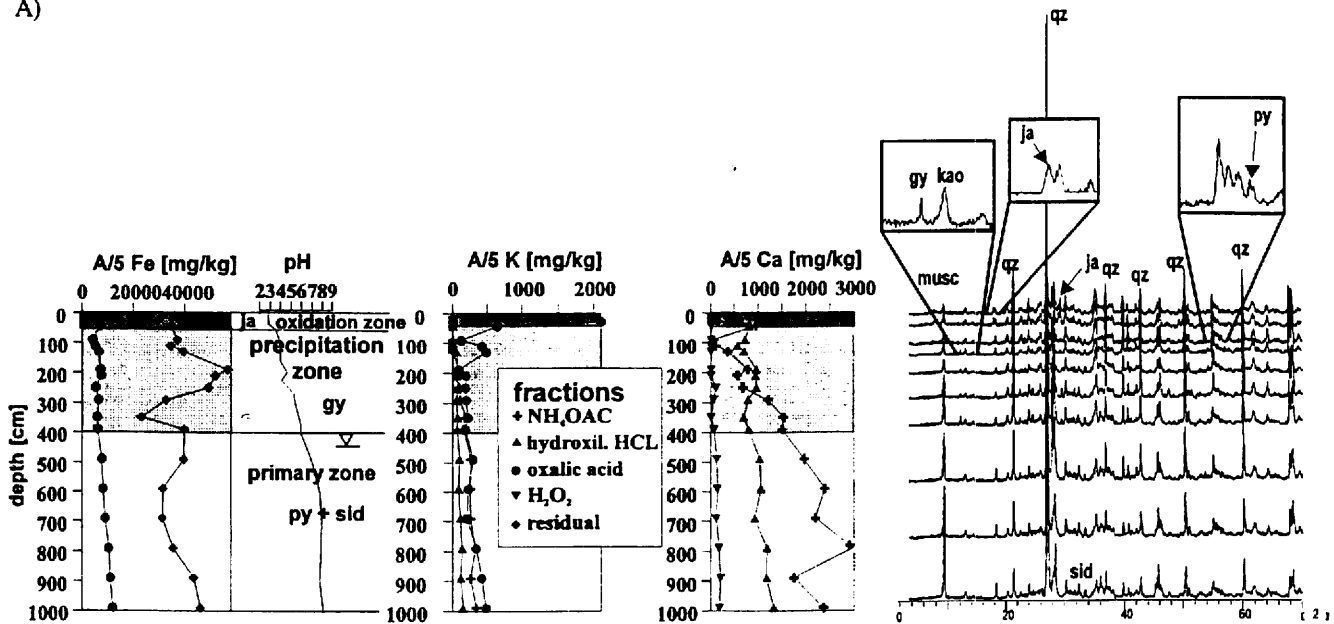


Fig. 1. Drill core T/4 from the Cauquenes tailing, El Teniente. A) Major elements (Fe, K, Ca) contents in sequential digestion fractions and the corresponding XRD spectra on bulk samples versus depth (qz-quartz, mic-micas, kao-kaolinite, py-pyrite, gy-gypsum, ja-jarosite). B) Cu, Mo, and As contents in sequential digestion fractions versus depth.

A)



B)

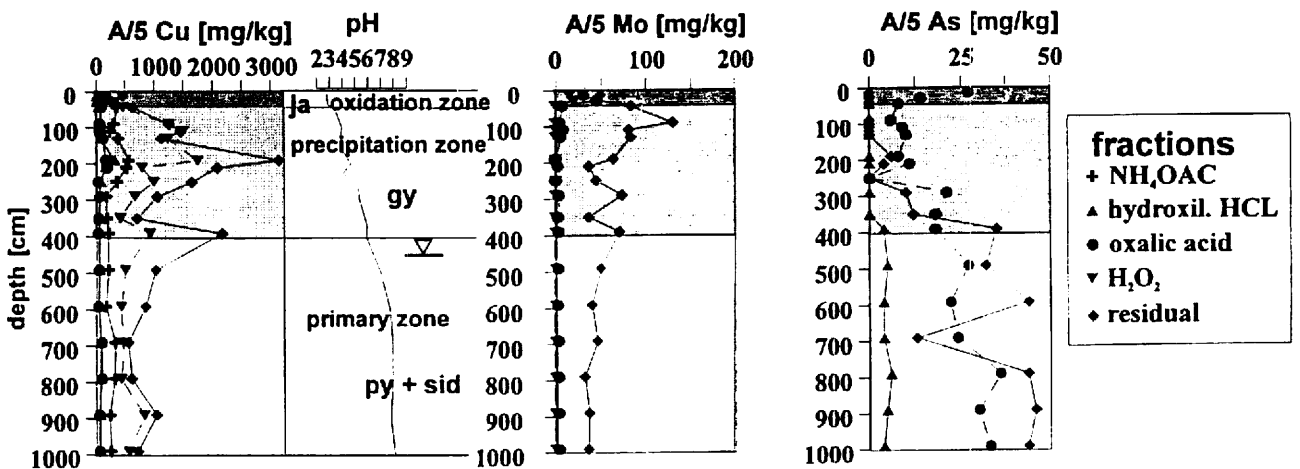


Fig. 2. Drill core A/5 from Piuquenes, La Andina. A) Major elements (Fe, K, Ca) contents in sequential digestion fractions and the corresponding XRD spectra (sid-siderite, other abbreviations as in Fig.1) on bulk samples versus depth. B) Cu, Mo, and As contents in sequential digestion fractions versus depth.

### CONCLUSION

- The soil sampling method, the mineralogical determination and the sequential digestions used in this study are shown to be powerful tools to detect mobilization and secondary enrichment in sulfide copper tailings as a product of sulfides (mainly pyrite) oxidation. The behavior of elements of economic interest as well as environmentally hazardous can be monitored.
- In the Cauquenes and Piuquenes tailings, three zones (oxidation zone, precipitation zone, and primary zone) are characterized by pH, mineralogical and geochemical composition and distribution. Elemental, mineralogical, and pH zonations can be correlated.

- In the oxidation zone (jarosite zone) most elements are leached out (Cu, Ca, Co, Mg, Mn, Pb, Zn). Fe and Mo display relatively high values in the oxalic acid and H<sub>2</sub>O<sub>2</sub> fractions of the oxidation zone indicating that they have been fixed in Fe(III)hydroxides subsequently to sulfide breakdown. K is fixed in jarosite. As, Al, and Ba show relatively high values in the oxalic acid fraction in the oxidation zone.
- The underlying chemical precipitation zone (gypsum zone) is characterized by enrichment of elements mobilized in the oxidation zone (Cu, Co, Mo).
- The primary material underlying the oxidation zone acts presently as a retention zone for the mobilized elements by adsorption and neutralizing processes.
- The thickness of the oxidation zone is 50-100 cm in the Piuquenes tailing and 105-400 cm in the Cauquenes tailing. This may be explained by the high altitude of the Piuquenes tailing (2100 m) and low temperatures, lower than the temperature of 30°C needed for the optimum development of *thiobacillus ferrooxidans* resulting in lower oxidation rates.

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#### REFERENCES

- [1] Blowes, D.W. & Ptacek, C.J. (1994): Acid-neutralization mechanisms in inactive mine tailings.- Short Course Handbook on Environmental Geochemistry of Sulfide Mine Waste. Mineralogical Association of Canada, Vol.22:271-291; Waterloo.
- [2] Davis, J.A., Fuller, C.C. & Cook, A.D. (1987): A model for trace metal sorption at the calcite surface: Adsorption of Cd<sup>2+</sup> and subsequent solid solution formation.- *Geochimica et Cosmochimica Acta*, 51: 1477-1490.
- [3] Dold, B., Eppinger, K.J. & Kölling, M. (1996): Pyrite oxidation and the associated geochemical processes in tailings in the Atacama desert/Chile: The influence of man controlled water input after disuse. - in *Clean Technology for the Mining Industry* (Sanchez, M.A., Vergara, F. & Castro, S.H., Eds.): 417-427; Concepción.
- [4] Donnert, D., Eberle, S.H. & Horst, J. (1990): Kinetic studies on the interaction of metal between water and clay minerals.- NATO ASI Series, Vol. G 23, Springer; Heidelberg.
- [5] Jambor, J.L. (1994): Mineralogy of sulfide-rich tailings and their oxidations products. - Short Course Handbook on Environmental Geochemistry of Sulfide Mine Waste. Mineralogical Association of Canada, Vol.22: 59-102; Waterloo.
- [6] Leckie, J.O., Benjamin, M.M., Hayes, K., Kaufman, G. & Altman, S. (1980): Adsorption and coprecipitation of trace elements from water with iron oxyhydroxides. Stanford University.
- [7] MEND, Mine Environment Neutral Drainage Program (1990): Acid rock drainage prediction manual, Report 1.16.1b. CANMET, Dept. Natural Resources Canada, Ottawa.
- [8] Moses, C.O., Nordstrom, D.K., Herman, J.S. & Mills, A.L. (1987): Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. - *Geochimica et Cosmochimica Acta*, 51: 1561-1571.