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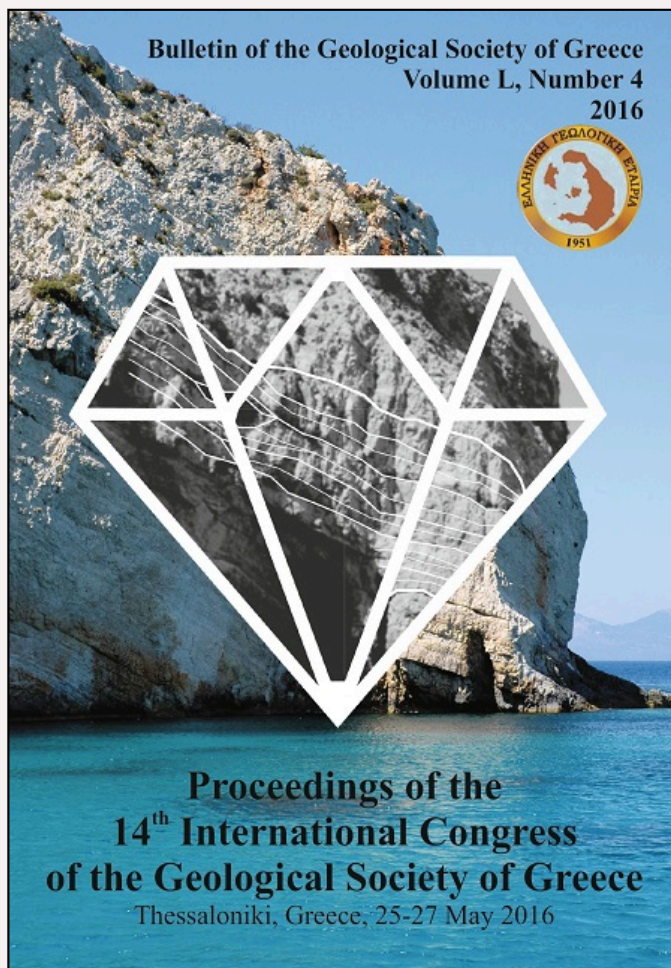
**GEOCHEMICAL MODELING OF ABANDONED SULFIDIC FLOTATION MILL TAILINGS: THE CASE OF KIRKI, NE GREECE**

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# GEOCHEMICAL MODELING OF ABANDONED SULFIDIC FLOTATION MILL TAILINGS: THE CASE OF KIRKI, NE GREECE

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## Abstract

*The Kirki flotation plant is located approximately 5 km south of the Agios Filippos open pit mine (Thrace, NE Greece), and unconfined mill tailings are exposed to atmospheric conditions. Rain water accumulates on the surface of the tailings and interacts with the solids, resulting in highly acidic and oxidative surface solutions with increased heavy metal content. The tailings material is dominated by gangue minerals with very low acid buffering capacity, including quartz, kaolinite/dickite, pyrophyllite and minor orthoclase. Secondary phases identified include mainly species of the jarosite group, gypsum and anglesite. No primary ore minerals besides pyrite are identified. The finegrained character of the tailings material favors fast reactions between the surface waters and the solids. The speciation/mass transfer computer code PHREEQC-2 and the MINTEQ database were employed for geochemical modeling of the acidic surface waters of the tailings dams T1 and T2. Three different scenarios were employed, "Direct Precipitation", "Mixing with Rainwater" and "Evaporation" to check the equilibrium between the developed surface solutions and the secondary minerals identified in the tailings. The purpose of this work is to understand the way heavy metals may be locked to the lattice of secondary minerals, or dispersed/dissolved after dissolution of unstable secondary phases.*

***Keywords:*** *Acidic surface waters, secondary minerals, geochemical modelling.*

## Περίληψη

*Το εργοστάσιο εμπλουτισμού της Κίρκης εντοπίζεται περίπου 5 km νότια του μεταλλείου του Αγίου Φιλίππου. Τα απορρίμματα της επεξεργασίας του μεταλλεύματος είναι εκτεθειμένα στις ατμοσφαιρικές συνθήκες, με αποτέλεσμα τη συσσώρευση μετεωρικού νερού στην επιφάνειά τους. Τα επιφανειακά ρευστά αλληλεπιδρούν με το λεπτόκοκκο υλικό με υψηλό φορτίο βαρέων μετάλλων, με τελικό αποτέλεσμα τη δημιουργία όξινων και οξειδωτικών διαλυμάτων με υψηλό φορτίο μετάλλων στην επιφάνεια των απορριμμάτων. Τα απορρίμματα της επεξεργασίας αποτελούνται κυρίως από σύνδρομα ορυκτά της μεταλλοφορίας (χαλαζίας, δικίτης/καολινίτης, πυροφυλλίτης και άστριοι), ενώ τα κυριότερα δευτερογενή ορυκτά που εντοπίζονται αφορούν ορυκτά της ομάδας του γιαροσίτη, γύψο και αγκλεσίτη. Μοναδική πρωτογενής φάση της μεταλλοφορίας που εντοπίζεται στα απορρίμματα είναι ο σιδηροπυρίτης. Ο λεπτόκοκκος χαρακτήρας των απορριμμάτων της επεξεργασίας ευνοεί ταχύτατες αντιδράσεις μεταξύ των επιφανειακών ρευστών με το υλικό των απορριμμάτων. Το γεωχημικό πρόγραμμα PHREEQC, με χρήση της βάσης δεδομένων MINTEQ, εφαρμόσθηκε για τη διερεύνηση της λειτουργίας του συστήματος «επιφανειακό διάλυμα - δευτερογενή ορυκτά», με την*

*ανάπτυξη τριών διαφορετικών μοντέλων, «Άμεση Καθίζηση», «Ανάμιξη με Μετεωρικό Νερό» και «Εξάτμιση». Σε κάθε μοντέλο εξετάζεται ο μηχανισμός με τον οποίο βαρέα μέταλλα δεσμεύονται στο πλέγμα δευτερογενών ορυκτών, αλλά και αποδεσμεύονται/διαλυτοποιούνται μετά από διαλυτοποίηση μετασταθών φάσεων.*

***Λέξεις κλειδιά:*** *Όξινα επιφανειακά νερά, δευτερογενή ορυκτά, γεωχημικό μοντέλο.*

## 1. Introduction

A major issue the mining industry faces is the safe disposal of ore processing waste or tailings. Tailings are defined as the processing waste from a mill, washery or concentrator where the economic metals or minerals from the mined resource are removed (Lottermoser, 2010). During the early years of ore exploitation, the produced processing wastes were usually dumped in nearby streams or creeks without consideration of their environmental impact (Plumlee and Logsdon, 1999). In recent years and following processing, the tailings are usually disposed as slurry or paste to certain facilities and present unique environmental and physical characteristics. Mill tailings originating form sulfide ores present challenges namely because of the high oxidation potential of sulfides remaining in the tailings (Fergusson, 1990; Larsen *et al.*, 2001; Lacal *et al*., 2003) and possible generation of Acid Rock Drainage (ARD). The flow of meteoric water over sulfidic tailings may further increase the potential for metal leaching from tailings due to the fine to very fine-grained character of the tailings material (Mohamed *et al*., 2002) but also due to dissolution of heavy-metal bearing secondary phases that develop at the surface and near the surface of the tailings (Wray, 1998). Therefore, abandoned mine waste disposal sites containing sulfide minerals may pose significant environmental threats and may severely contaminate surface and groundwater as well as soils and ecosystems (Bigham and Nordstrom, 2000; Draves and Fox, 1998; Groudev *et al.* 1999; Hudson-Edwards *et al.*, 2003; Komnitsas *et al.* 1998; Adam, 2003).

## 2. Site description

The Kirki (Agios Filippos) high sulfidation deposit is hosted into the Eocene-Oligocene rock sequences of SE Evros county and is associated with orogenic calc-alkaline to high-potassium calc-alkaline magmatism. The epithermal mineralization is developed between two sub-parallel fault zones that form the western and the eastern part of the open pit. An advanced argillic alteration with alunite and pyrophyllite followed an early pervasive grey silicification of the rocks. The base metal sector has been exposed due to erosion of the upper part of the epithermal system (Skarpelis, 1999). The mineralization is characterized by complex mineralogy with several Pb-bearing and Pb-As-bearing sulfosalts (Moelo *et al.*, 1985; Moelo *et al.*, 1990).

The Kirki flotation plant and tailings ponds, built approximately 5 km south of the Agios Filippos mine (Fig. 1), are founded on Tertiary clastic sediments, including mainly breccio-conglomerates, sandstones, shales and marls (Michael and Dimadis, 2006). The flotation plant comprises eight tailings ponds in total (4 of them depicted in Fig.1) built in favorable locations that required minimum earthworks, while no measures to protect the environment were taken (Directives 2006/21/EC and 98/83/EC) (Triantafyllidis *et al.*, 2007). Sandstones, conglomerates and fine-grained tailings were used for the construction of the tailing dump walls with questionable results regarding their stability, as evident by the collapse of the walls at dumps T2, T3 and T4 (Triantafyllidis, 2006). Additionally, the dumps were constructed without consideration of a drainage system thus favoring accumulation of rain water on their surface (Loupasakis and Konstantopoulou, 2010).
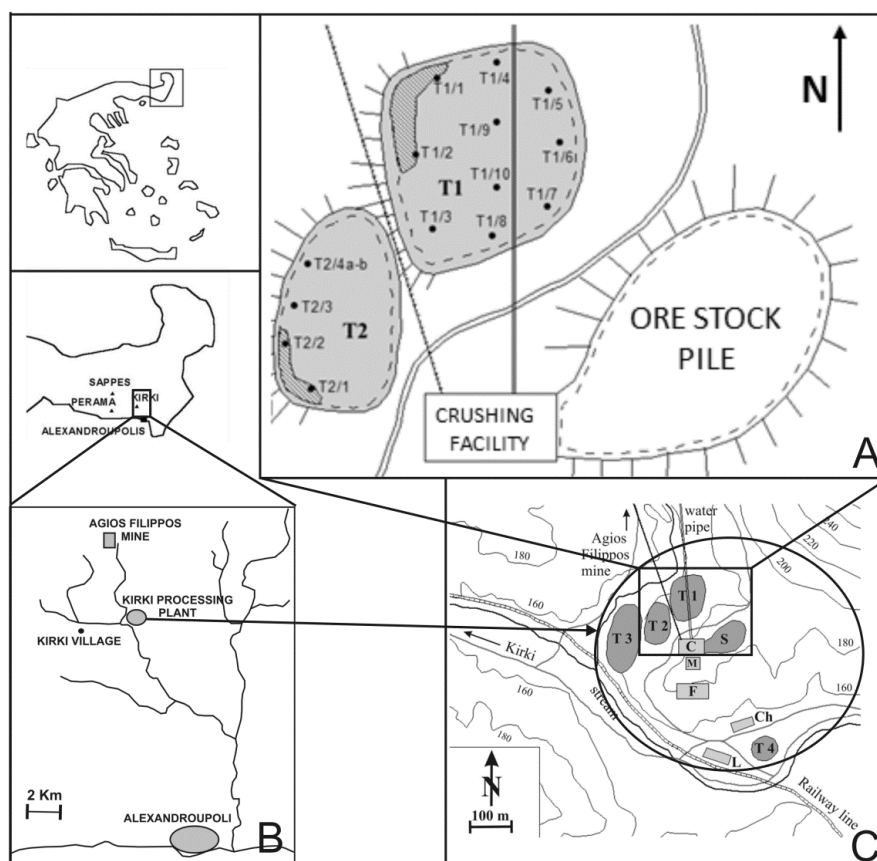
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**Figure 1 – Location map of the Kirki processing plant. A. Sampling points for tailings dams T1 and T2. Small water ponds formed on the surface of the dams appear with dashed lines. C. Kirki flotation plant.**

## 3. Sampling – Analytical methods

Water samples were collected from the surface of tailings dams T1 and T2 (Fig.1A) in September 2001 and June 2003, applying standard sampling techniques. Temperature, pH and Eh were measured on site using a WTW pH 320/Set-2 electronic pH-meter. Water samples were filtered through a 0.45 μm Millipore filter and acidified with 1 M $HNO_3$ for cation analyses. Concentrations of Pb, Cu, Zn, Fe, Cd, Ni, Co, As, Hg, Mn and Sb were measured commercially with an inductively coupled plasma atomic emission spectrometer (ICP-AES), whereas $SO_4$ concentrations using a Hach DR 2000 spectrophotometer. Bulk samples from successive tailings layers were collected up to a depth of 1.6 m (Fig.1A). Samples were dried at room temperature, and sieved to achieve collection of the finer-grained material for more reliable identification of the secondary phases with X-RAY diffraction. The samples were then pulverized, homogenized and split in two so that analyses were done in duplicate. Mineral identification was carried out at the Laboratory of Economic Geology and Geochemistry, University of Athens by X-ray Diffractometry and Scanning Electron Microscopy (SEM). X-ray diffractometry included the use of a SIEMENS D5005 X-ray

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Diffractometer with Cu(kα) radiation at 40kV/20mA operating conditions. Scanning Electron Microscopy involved the use of a Jeol JSM 5600 scanning electron microscope combined with energy dispersive X-ray spectrometry (EDS) (OXFORD ISIS Link electron microprobe) and equipped with a Jeol Analytical back scattered electron detector. Operating conditions for the SEM were 20kV accelerating voltage and 0.5 nA beam current. Counting time for each analysis was 50 sec, with 15 sec dead time.

## 4. Analytical data used

The geochemical characteristics of surface waters accumulated on the surface of tailings dams T1 and T2 are given in table 1. In table 2 selected major and trace elements analyses are given for tailings dams T1 and T2, whereas the secondary phases identified by X-ray Diffraction and Scanning Electron Microscopy are presented in table 3.

**Table 1 – Physicochemical characteristics of stagnant surface waters on tailings dams T1 and T2, after Triantafyllidis (2006) (dissolved ions in mg/L, Eh in mV).**

| | pH | Eh | SO$_4$ | As | Cd | Co | Cu |
|---|---|---|---|---|---|---|---|
| Tailings dam T1 | | | | | | | |
| **Min** | 3.1 | 160 | 2600 | b.d.l. | 1.9 | 0.12 | 1.0 |
| **Max** | 4.4 | 256 | 6300 | 0.12 | 14.7 | 1.10 | 18.0 |
| **Mean** | 3.7 | 239 | 4450 | - | 8.3 | 0.56 | 8.1 |
| **Stand. Dev.** | 0.6 | 37 | 1752 | - | 5.5 | 0.45 | 7.5 |
| Tailings dam T2 | | | | | | | |
| **Min** | 3.0 | 226 | 2450 | b.d.l. | 3.8 | 0.25 | 5.0 |
| **Max** | 3.4 | 235 | 17500 | 0.33 | 35.3 | 2.90 | 11.6 |
| **Mean** | 3.3 | 229 | 9975 | - | 19.6 | 1.61 | 8.3 |
| **Stand. Dev.** | 0.1 | 4 | 7261 | - | 15.5 | 1.25 | 3.0 |

**Table 1 continued**

| | Fe | Mn | Ni | Pb | Zn | Sb |
|---|---|---|---|---|---|---|
| Tailings dam T1 | | | | | | |
| **Min** | 0.1 | 121 | 0.9 | 1.0 | 193 | b.d.l. |
| **Max** | 130 | 613 | 5.2 | 3.7 | 1398 | b.d.l. |
| **Mean** | 64.6 | 385 | 3.1 | 2.4 | 798 | - |
| **Stand. Dev.** | 64.1 | 230 | 2.1 | 1.2 | 575 | - |
| Tailings dam T2 | | | | | | |
| **Min** | 1.0 | 188 | 1.6 | 2.8 | 278 | b.d.l. |
| **Max** | 4.8 | 2852 | 17.5 | 4.8 | 4298 | 0.15 |
| **Mean** | 2.7 | 1518 | 8.8 | 3.4 | 2223 | - |
| **Stand. Dev.** | 1.3 | 1166 | 7.3 | 0.7 | 1955 | - |
| b.d.l.: below detection limit As< 0.01 mg/lt Sb< 0.002 mg/lt Hg< 0.001 mg/lt (Hydride/cold vapor technique) Ag< 0.002 mg/lt | | | | | | |

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**Table 2 – Selected major and trace elements analyses of tailings dam material in wt % and ppm respectively, after Triantafyllidis (2006).**

|            | $SiO_2$ | $Al_2O_3$ | CaO  | $Na_2O$ | $Fe_2O_3$ | $K_2O$ | $TiO_2$ | L.O.I. |
|------------|---------|-----------|------|---------|-----------|--------|---------|--------|
| **Min**        | 63,0    | 9.12      | 0.27 | 0.09    | 2.77      | 0.74   | 0.44    | 5.6    |
| **Max**        | 84.1    | 20.95     | 0.54 | 0.31    | 3.61      | 1.82   | 0.49    | 10.9   |
| **Mean**       | 73.9    | 14.5      | 0.43 | 0.15    | 3.1       | 0.84   | 0.46    | 7.7    |
| **Stand. Dev.** | 8.5     | 5.0       | 0.11 | 0.07    | 0.3       | 0.39   | 0.02    | 2.2    |
|            | **Pb**  | **Zn**    | **Cu** | **Cd** | **As**   | **Mn** | **Bi**  | **Sb** |
| **Min**        | 2597    | 2082      | 57   | 14      | 92        | 200    | 38      | 13     |
| **Max**        | 13991   | 11013     | 526  | 122     | 238       | 6828   | 339     | 60     |
| **Mean**       | 4465    | 6086      | 109  | 45      | 127       | 1545   | 60      | 16.5   |
| **Stand. Dev.** | 3818    | 3285      | 149.6 | 38.8   | 46.8      | 2002   | 101     | 15.8   |
| L.O.I. Loss on Ignition | | | | | | | | |

**Table 3 – Secondary phases identified in the tailings material of dumps T1 and T2.**

| Mineral phase | Empirical Formula | Tailing dump T1 | Tailing dump T2 |
|---------------|-------------------|-----------------|-----------------|
| Jarosite group* | $(K,Na,Pb,H_3O)Fe^{+3}{}_3(SO_4)_2(OH)_6$ | +++++ | +++++ |
| Gypsum | $CaSO_4 \times 2H_2O$ | +++++ | +++++ |
| Anglesite | $PbSO_4$ | +++ | + |
| Butlerite | $Fe^{+3}(SO_4)(OH) \times 2H_2O$ | + | + |
| Ktenasite | $Zn(Cu,Zn)_4(SO_4)_2(OH)_6 \times 6H_2O$ | | + |
| Giniite | $Fe^{2+}Fe^{3+}{}_4(PO_4)_4(OH)_2 \times 2(H_2O)$ | + | |
| Zykaite | $Fe^{3+}{}_4(AsO_4)_3(SO_4)(OH) \times 15(H_2O)$ | + | |
| Osarizawaite | $PbCuAl_2(SO_4)_2(OH)_6$ | + | |
| * Namely K-jarosite with minor Pb-jarosite, Na-jarosite and Hydronium-jarosite<br>Mineral abundances: +++++ major, +++ minor, + trace | | | |

## 5. Application of PHREEQC geochemical code

The correlation between the chemistry of the surface waters on tailing dumps T1 and T2 (examined separately) and the mineralogy and geochemistry of the tailings material from each dam was investigated with the use of the geochemical code PHREEQC-V2 (Parkhurst and Appelo, 1999). Thermodynamic data was taken from MINTEQ database (Allison *et al.*, 1991). Saturation Indices were calculated only for jarosite group species, anglesite and gypsum, since thermodynamic data for ktenasite, butlerite, giniite, zykaite and osarizawaite are not included in the MINTEQ database. Imported parameters in the system (Table 4) include: Eh (as pe), pH, As, Ag, Cd, Cu, Fe (total), K, Na, Ni, Mn, Pb, Sb, Zn, Cu and $SO_4^{-2}$. The dissolved concentrations for Ca, Na, K for the PHREEQC models were based on estimate after geochemical analyses performed on acid mine drainage samples from the Agios Filippos mine (Liakopoulos, 2009). The pe (Eh) values employed in the PHREEQC tests are changed relative to those measured during sampling. At a center point surface stagnant waters are not equilibrated with atmosphere, thus preserving significantly higher pe conditions than normal measured values (Heikkinen *et al.*, 2009). As stated by Manchester *et al.* (2008), near the surface of sulfide tailings disposal facilities pe values may be high and approach the theoretical maximum of 13.75 for $O_2$ at pH=7. Several different scenarios were employed for the system "tailings surface waters – tailings secondary mineralogy" (Fig. 2), including:

- "Direct Precipitation"
- "Mixing with Rainwater"
- "Evaporation".

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**Table 4 – Physicochemical characteristics of solutions applied for PHREEQC modelling.**

| Parameter added to the program | Meteoric water* (applied on model "Mixing with Rainwater") | Tailings dam T1 surface water | Tailings dam T2 surface water |
|---|---|---|---|
| Temperature | 25 | 28.2 | 29.4 |
| pH | 5.5 | 3.7 | 3.3 |
| Eh | 4 | 6 | 9 |
| Density | 1 | 1 | 1 |
| Ca | 0.2 | 100 | 100 |
| K | 0.35 | 10 | 10 |
| Na | 0.6 | 20 | 20 |
| SO₄ | 0.18 | 4450 | 9975 |
| Ag | | 0.002 | 0.002 |
| As | | 0.063 | 0.168 |
| Cd | | 8.3 | 19.6 |
| Co | | 0.6 | 1.6 |
| Cu | | 8 | 8.3 |
| Fe | | 65 | 2.7 |
| Hg | | 0.005 | 0.005 |
| Mn | | 385 | 1520 |
| Ni | | 3.1 | 8.8 |
| Pb | | 2.4 | 3.4 |
| Sb | | 0.02 | 0.08 |
| Zn | | 798 | 2212 |
| * After Carroll (1962)<br>Temperature in °C<br>Density in gr/cm³<br>Eh in pε<br>All ions in mg/lt | | | |
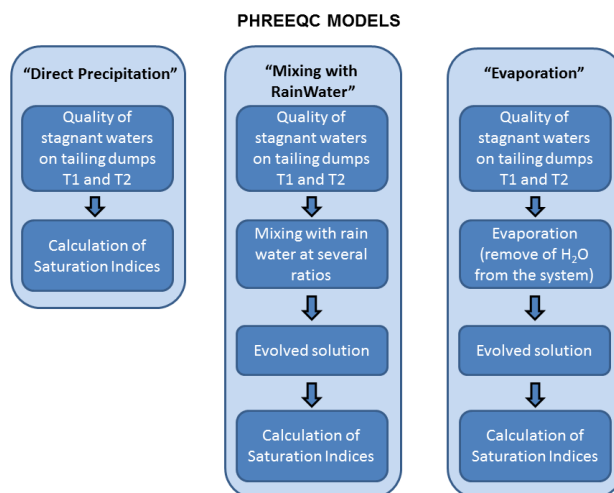


**Figure 2 – Schematic representation of PHREEQC models applied in the study.**

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## 6. Results of PHREEQC tests

### 6.1. Direct precipitation

The first model (*Direct Precipitation*) examines the equilibrium between the stagnant surface waters on the tailing ponds and the secondary phases identified in the tailings material, and calculates the Saturation Indices (SI) of specific phases based on the MINTEQ database (Fig. 2, Table 5). This model showed that anglesite is saturated and slightly undersaturated for dams T2 and T1 respectively, whereas only in dam T2 K-jarosite precipitates (SI > 0). All other secondary phases identified by XRD and SEM are undersaturated (SI < 0).

**Table 5 – Calculated Saturation Indices for model "Direct Precipitation" for tailings dams T1 and T2.**

| Mineral phase | Tailings dump T1 | Tailings dump T2 |
|---|---|---|
| Anglesite | -0.11 | **0.03** |
| H-jarosite | -4.43 | -1.61 |
| Na-jarosite | -4.96 | -2.66 |
| K-Jarosite | -1.95 | **0.32** |
| Gypsum | -0.60 | -0.57 |

### 6.2. Mixing with rainwater

The second model (*Mixing with Rainwater*) examines mixing of the surface stagnant waters with rain water (geochemical data for rain water were taken from Carroll, 1962) at several ratios, and checks the equilibrium between the solution produced after mixing and the secondary phases developed in the tailings material (Fig.2, Table 6). This model revealed that if surface solutions mix with rain water, at any ratio, all secondary phases identified show negative SI values (Table 6), indicating possible dissolution and release of heavy metals to solution.

**Table 6 – Calculated Saturation Indices for model "Mixing with Rainwater" for tailings dams T1 and T2 for several Rainwater/Surface water ratios.**

| Mineral phase | Tailings dump T1 (1/1 ratio) | Tailings dump T2 (1/1 ratio) | Tailings dump T1 (4/1 ratio) | Tailings dump T2 (4/1 ratio) |
|---|---|---|---|---|
| Anglesite | -0.41 | -0.25 | -0.85 | -0.66 |
| H-jarosite | -5.36 | -1.74 | -6.30 | --2.11 |
| Na-jarosite | -5.89 | -2.60 | -6.85 | -2.99 |
| K-Jarosite | -2.86 | **0.25** | -3.79 | -0.10 |
| Gypsum | -0.96 | -0.91 | -1.47 | -1.38 |

### 6.3. Evaporation

The third model (*Evaporation*) examines the evolution of the system and the possible secondary phases resulting from evaporation, at several ratios, of the sampled surface waters and may control the solubility of several toxic metals (Fig.2, Table 7). If the surface waters become more condensed, then the resulting solutions are highly acidic and oxidative with increased metal content. In such conditions precipitation of anglesite, K-jarosite and gypsum is favored, as evident by the positive SI values (Table 7).

**Table 7 – Calculated Saturation Indices for model "Evaporation" for tailings dams T1 and T2 for several evaporation ratios.**

| Mineral phase | Tailings dump T1 (x10) | Tailings dump T2 (x10) | Tailings dump T1 (x40) | Tailings dump T2 (x40) |
|---|---|---|---|---|
| Anglesite | **0.89** | **1.24** | **1.96** | **3.04** |
| H-jarosite | -1.14 | -2.28 | -0.99 | -2.01 |

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| | | | | |
|---|---|---|---|---|
| Na-jarosite | -1.35 | -2.94 | -0.86 | -2.15 |
| K-Jarosite | **0.38** | -0.08 | **1.94** | **0.39** |
| Gypsum | **0.56** | **0.69** | **1.49** | **2.35** |

## 7. Conclusions

The Kirki flotation dams T1 and T2 show high Pb and Zn content, and lower Mn, As, Cu and Cd load (Table 2). On site observations revealed that the tailings material is weakly cemented, with alternations of reddish-brown with grayish layers. The secondary phases identified with X-ray Diffraction are only identified in the reddish-brown layers, whereas only gangue and minor gypsum and pyrite are present in the grayish layers. The tailings material is fine-grained with particle size ranging from fine sand to fine silt (Triantafyllidis *et al.*, 2007), thus favoring high rates of reaction between surface waters and tailings solids. Oxidation reactions result in the development of a surface reddish-brown layer prior to the deposition of the next slurry layer in the dams.

The three PHREEQC models employed in this study are focused on the major secondary phases identified in the tailings material of the dams T1 and T2, and in particular jarosite group species, anglesite and gypsum (Table 3). The models showed that interaction between surface solutions and tailings material plays a very important role in the fate and transport of certain pollutants.

Jarosite group phases, and in particular K-jarosite, are the major secondary phases identified in the reddish-brown layers of the tailings dams T1 and T2. Jarosite is stable in highly acidic and oxidative conditions (especially after significant degree of evaporation - Table 7), and plays a key role in controlling dissolved metal concentration when it precipitates. On the other hand, if the geochemical environment becomes less acidic (e.g. mixing with rain water - Table 6), jarosite is metastable and dissolves (Lottermoser, 2010). Jarosite dissolution after mixing of surface solutions with rainwater favors metal mobility in two ways:

- Direct release of heavy metals and sulfates to solution (e.g. $Pb^{+2}$ from plumbojarosite in the case of dam T1).

- The dissolved Fe (III) may hydrolyze and precipitate as ferric hydroxide (e.g. goethite). Goethite precipitation causes solution pH to decrease (production of $H^+$), enhancing heavy metal mobility. Although goethite was not identified by XRD or SEM studies, employed PHREEQC models showed that after mixing with rainwater at any ratio, goethite is supersaturated relative to the developed solution (SI > 0).

Anglesite is also identified in the reddish-brown layers of dams T1 and T2, in lower content relative to jarosite (Table 3). Anglesite may control dissolved concentrations of Pb more effectively than plumbojarosite (minor secondary phase in tailings dam T1). Anglesite is rather insoluble in the Kirki tailings dams, since it is metastable to cerussite and hydrocerussite only in mildly acidic to alkaline environments with increased $CO_2$ content (Krauskopf and Bird, 1995). No cerussite or hydrocerussite are identified in the tailings material by XRD or SEM, so it is reasonable to assume that such conditions are not developed in the surface environment of the Kirki tailings dams.

Gypsum behaves in a similar manner as anglesite and jarosite. During mixing with rainwater, gypsum is undersaturated relative to the produced solutions, whereas it precipitates when surface solutions become more condensed. Moreover, based on the results of the PHREEQC models applied, hematite and goethite precipitation is favored when conditions turn less acidic, especially after mixing of surface solutions with rainwater, although none of these phases were identified by XRD and SEM in dams T1 and T2.

Finally, it is very important to state that the PHREEQC models applied for the Kirki flotation plant tailings dams T1 and T2 are based on several critical limitations:

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- Systematic sampling is required to focus on the geochemical conditions of the solid-water interface.
- Limited thermodynamic data for other secondary minerals identified in the tailings material.
- Microbial and organic activity within the tailings material. It is known that the role of aerobic bacteria is critical in the initial oxidation/weathering of primary sulfides and sulfosalts (Stokes, 1954; Walsh and Mitchell, 1972; Evangelou, 1983), as well as their catalytic behavior in the formation of secondary phases present in tailings dams.

## 8. Acknowledgements

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