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# EFFLORESCENT SULFATE MINERALS OF THE KARABASH MINING/SMELTING AREA, URAL MOUNTAINS, RUSSIA

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Karabash is a copper smelting town in the Chelyabinsk district of the Southern Ural mountains of Russia. The town is in close proximity to a large copper deposit and resultant mining activities. Efflorescent minerals from tailings outwash were collected from the mining-impacted landscape. The efflorescent sulfates collected from a variety of sites on tailings outwash adjacent the streams downstream from the Karabash mining zone were dominated by hydrated Fe-Mg-Al sulfates (halotrichite-pickeringite series, melanterite, pentahydrite, magnesiocopiapite, and coquimbite). The efflorescents noted in the tailings outwash site in Karabash appear to be water-soluble salts that crystallized during evaporation of waste-water runoff from the tailings area. The oxidation of the mine wastes acts to liberate sulfur, creating an acidic drainage that leaches both the mine tailings (mobilizing iron and other potentially harmful metals) as well as elements from the rocks around the tailings site. Acid mine drainage, mine and smelter fallout pose a significant environmental concern to the Karabash region.

Figures 5. References 13.

Key words: efflorescent sulfates, tailings, weathering, XRD, SEM.

# СУЛЬФАТНЫЕ МИНЕРАЛЫ ВЫЦВЕТОВ В КАРАБАШСКОМ ГОРНОПРОМЫШЛЕННОМ РАЙОНЕ, УРАЛ, РОССИЯ

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Карабаш - город с медеплавильным производством в Челябинской области на Южном Урале. Город находится в непосредственной близости от крупного месторождения меди и связанных с ним горнопромышленных объектов. Сульфатные выцветы собраны с поверхности неорганизованного хвостохранилища, образованного в результате работы обогатительной фабрики. В выцветах, собранных в различных местах хвостохранилища, преобладали гидратированные сульфаты Fe-Mg-Al (галотрихит-пиккерингит, мелантерит, пентагидрит, магнезиокопиапит и кокимбит). Многочисленные выцветы, появляющиеся в результате поверхностного смыва хвостохранилищ в Карабаше, представляют собой водорастворимые соли, которые кристаллизовались во время испарения капиллярных вод на поверхности хвостохранилища. Выветривание горнопромышленных отходов способствует выделению серы, создавая кислотный дренаж, который выщелачивает как сами отходы (мобилизация железа и других металлов), так и элементы из горных пород вокруг хвостохранилища. Отходы добычи и переработки руд представляют серьезную экологическую проблему для Карабашского региона.

Илл. 5. Библ. 13.

Ключевые слова: Сульфатные выцветы, хвостохранилища, выветривание, XRD, SEM.

#### Introduction

Disposal of mine wastes is one of the most important environmental issues for any metal mining activity due to many hazardous substances they contain. One of the most serious problems of environmental contamination is the formation of acid mine drainage, globally known by the acronym AMD (Carro et al., 2011). Acid mine drainage (AMD) derives from weathering of sulfides, particularly iron sulfides, in mining areas. This process leads to the generation of highly acidic waters with huge amounts of dissolved SO<sub>4</sub><sup>2-</sup>, Al, Ca, Fe, Mg and other elements hosted by sulfide minerals such as Cu, Zn, Pb, As, Cd and Sb (Blowes et al., 2014). AMD is a global negative environmental event, with severe consequences in metallogenetic provinces with sulfides around the world. This process results from sulfide oxidation, in particular iron sulfides such as pyrite (FeS<sub>2</sub>). Detailed information about the complex chain of biotic and abiotic reactions that involve the oxidative dissolution of pyrite can be found in the classical references (Evangelou, Zhang, 1995; Nordstrom, Southam, 1997; Nordstrom, Alpers, 1999; Keith, Vaughan, 2000). Efflorescent sulfate minerals are common in base metal deposits, tailings and waste rock piles where they are frequently associated with oxidizing sulfide minerals. Knowledge of the sulfate mineralogy and paragenesis at an AMD site is important because different sulfate minerals carry different amounts of trace elements and produce different amounts of acid upon dissolution (Jerz, Rimstidt, 2003; Belogub et al., 2007). The dissolution of sulfate minerals during rain events can dramatically impact aquatic ecosystems.

Karabash is a copper mining/smelting town in the Chelyabinsk district of the Southern Ural Mountains of Russia. The town is in close proximity to a large copper deposit and resultant mining activities. A copper smelter was built in the center of town in 1910, and has produced an estimated 30 million tons of slag and other related wastes. In 1934, a benefication mill was built in the eastern part of town. The mill produced copper concentrates by froth flotation, and as of 1954, also produced zinc and pyrite concentrates (Udachin et al., 2003). 1989 saw the closure of the last mine and the mill. The smelter continues operations processing ore from other mining towns.

The town and surrounding areas are affected by sulphur dioxide emissions, deposition of metal-rich particulates from the smelter, acid drainage from old mine workings, and leachates from waste dumps and tailings dams (Brooks et al., 2005; Williamson et al., 2004). Recently, several samples efflorescent minerals were collected in an effort to further characterize the weathering product mineralogy in the Karabash area.

## Sampling and analytical procedures

In the summer of 2010, samples were collected from the Karabash tailings impoundment. Efflorescent sulfates being collected from the surface of a mine tailings spill on the banks of a regional outwash stream below a dam fracture (Fig. 1).

A sub-sample efflorescent minerals were pulverized using an agate mortar and pestle, with a smear being placed on a silicon disc and analyzed on a PANalytical X ' Pert PRO XRD system equipped with a PIXcel detector. Samples were run with Co radiation, at 40 kV and 45 mA. Peak search results were obtained with both PANalytical HighScorePlus and MDI Jade software (Geo Labs, Laurentian University).

Sub-samples of efflorescent sulfates were placed on carbon tape, carbon coated, and analyzed on a Zeiss EVO-50 Scanning Electron Microprobe (Geo Labs, Laurentian University). Electron (backscatter and secondary electron) images were collected. Compositions were obtained using an Oxford Energy Dispersive (ED) Spectrometer for analysis with INCA software data.



*Fig. 1.* Efflorescent minerals on the surface of a Karabash mine tailings – postmining minerals that form due to evaporation, as surface encrustations.

*Рис. 1.* Минеральные выцветы на поверхности хвостохранилища в Карабаше – новообразованные минеральные формы, в виде поверхностных инкрустаций, образующиеся в результате испарения.



*Fig. 2.* XRD spectra for sample KA(M)930 with halotrichite-pickeringite, pentahydrite and melanterite. *Puc. 2.* Рентгеновские спектры образца KA(M)930, содержащего галотрихит-пиккерингит, пентагидрит и мелантерит.



Fig. 3. XRD spectra for sample KA(M)931 with dominant magnesiocopiapite, coquimbite and minor halotrichitepickeringite.

*Рис. 3.* Рентгеновские спектры образца КА(М)931, содержащего преимущественно магнезиокопиапит с кокимбитом и галотрихитом-пиккерингитом.

### **Results**

Efflorescent sulfates. The minerals appear to be hydrated sulfates (various combinations of Fe-Mg-Al phases):

- Halotrichite-Pickeringite series  $\text{FeAl}_2(\text{SO}_4)_4$ .  $22H_2O - MgAl_2(SO_4)_4 \cdot 22H_2O$
- Melanterite  $FeSO_4 \cdot 7H_2O$
- Pentahydrite  $MgSO_4 \cdot 5H_2O$
- Magnesiocopiapite  $MgFe^{3+}_{4}(SO_{4})_{6}(OH)_{2} \cdot 20(H_{2}O)$
- Coquimbite  $\operatorname{Fe}^{3+}_{2}(\operatorname{SO}_{4})_{3}$  · 9(H<sub>2</sub>O).

The five samples appear to be in two primary groupings: 1) samples KA(M)930, KA(M)932 and KA(M)934 (halotrichite-pickeringite series, melanterite?, and pentahydrite?), and 2) samples KA(M)931 and KA(M)935 (dominantly magnesiocopiapite with coquimbite and minor halotrichite-pickeringite). Figure 2 shows a typical XRD spectrum for the first mineral grouping, and Figure 3 shows a typical XRD spectrum for the second mineral grouping.

SEM-EDS findings support the above XRD mineral identifications. The efflorescent minerals



Fig. 4. Sample KA(M)934 (A), KA(M)930 (B), KA(M)932 (C), KA(M)931 (D) showing blocky Fe-Mg sulfates (varying Mg-Fe ratios, melanterite? pentahydrite?) and a fibrous «bearded» Al-Fe-Mg sulfate (halotrichite-pickeringite). Рис. 4. Образцы КА(М)934 (А), КА(М)930 (В), КА(М)932 (С), КА(М)931 (D) с блочными Fe-Mg сульфатами (с варьирующими Mg-Fe соотношениями, мелантерит?, пентагидрит?) и волокнистым «бородатым» Al-Fe-Mg суль-

фатом (галотрихит-пиккерингит).



*Fig. 5.* Sample KA(M)935 (A) showing bladed crystals of Fe-Mg sulfate (magnesiocopiapite) and sample KA(M)935 (B) showing blocky rosettes of Fe-Al sulfate (coquimbite) and a fibrous Al-Fe sulfate (halotrichite?).

*Puc.* 5. Образец КА(М)935 (А) с пластинчатыми кристаллами сульфата Fe-Mg (магнезиокопиапит) и образец КА(М)935 (В) с блочными розетками Fe-Al сульфата (кокимбита) и волокнистого Al-Fe сульфата (галотрихита?).

often occur as blocky to bladed crusts (melanterite, pentahydrite, and magnesiocopiapite) held together by fibrous crystals (halotrichite-pickeringite) (Fig. 4A). The fibrous halotrichite-pickeringite crystals occur mostly as twisted bundles or «bearded» habit (Fig. 4B, C) and occasionally acicular (Fig. 4D). Spherical iron oxide smelter particles (Fig. 4E), similar to those found in the smelter impacted landscape of Sudbury, Ontario, Canada (Adamo et al., 1996), were also noted. These were found on the surface of the efflorescent minerals, likely deposited from aerial smelter fallout.

The magnesiocopiapite and coquimbite (Fig. 5A, B) display a bladed to blocky habit, often forming in small rosettes similar to that of classic gypsum rosettes.

The efflorescent sulfates noted in the tailings outwash site in Karabash appear to be water-soluble salts that crystallized during evaporation of wastewater runoff from the tailings area. The oxidation of the mine wastes acts to liberate sulfur, creating an acidic drainage that leaches both the mine tailings (mobilizing iron and other potentially harmful metals) as well as elements from the rocks around the tailings site. Evaporation of this resultant acid mine drainage can lead to the formation of secondary and tertiary minerals (Blowes et al., 2003) as seen in the efflorescent minerals from Karabash.

### Conclusions

The Karabash area is a landscape heavily impacted by mining and smelter activities. The efflorescent minerals collected from the surface of the outwash areas adjacent to the mine tailings area consist of hydrated sulfate salts of various combinations of Fe-Mg-Al phases. The mineralogy of the efflorescent salts appears in two group: 1) halotrichite-pickeringite series, melanterite and pentahydrite and 2) magnesiocopiapite with coquimbite and minor halotrichite-pickeringite.

The acid mine drainage from the tailings areas, as well as the areal deposition of smelter and tailings dusts is an environmental concern to the Karabash region.

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