

**Key words** local smelting; heavy metal; tailings; sediment; water characterization

## Mineralogy, geochemistry and release of heavy metals in wastes from indigenous zinc smelting in Northwest Guizhou

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Environmental impact resulting from mining activities is serious and ubiquitous all over the world, and it has become one of the important aspects in environmental geochemistry. The environment was seriously damaged by wastes from historical zinc smelting in Northwest Guizhou. The geochemical distributions of Pb and Zn in the different grain-size fractions of wastes indicate that the coarser particles show similar or even higher heavy metal concentrations than finer ones in the samples, although the concentrations of heavy metals tend generally to increase as the size fractions get finer. The heavy metal contents are very high, with maximum values of 31631, 57178, 2367 and 311.5 mg/kg for Pb, Zn, Cu and Cd, respectively. It is also shown that the residual fraction of Pb is less than that of Zn, accounting for 0.39%–15.75% and 14.3%–46.2%, respectively, of the total, and this is likely relative to Zn-silicate minerals formed from smelting. Although the relative partitioning of Pb and Zn is very low (0.03%–1.3% for Pb; 0.03%–3.3% for Zn), the exchangeable fraction of the waste contains large amounts of heavy metals (1.5%–385 µg/g for Pb; 3–590 µg/g for Zn). Heavy metals in exchangeable forms have the highest solubility to give the highest potential bioavailability in contrast to other chemical forms. Mineralogical study indicates that the wastes were found to be highly heterogeneous materials, dominated by quartz, feldspar, carbonatite, iron or/and aluminum vitric compounds and a few secondary mineral phases, and their contents vary with the type of smelting wastes. The secondary minerals formed from smelting and sequentially weathering are the major chemical phase for heavy metals. Complex composition of many phases and substitution of elements suggested that many of the phases were found to be non-stoichiometric compounds. Pb was found to be the main Pb phase in the wastes by precipitation or/ and adsorption. The species Zn is more complex in the form of occurrence than Pb, and Zn-bearing minerals include willemite, tephrowillemite and zinalsite, and occasionally Zn can be found in the wastes, and this is a possible reason why the relative partitioning of Zn in residue fraction is higher than that of Pb. The natural releasing processes of Pb, Zn and Cd in the wastes can be primely described with minus-exponent equation and with prolongation of piling time, the contents of these heavy metals in the wastes decrease gradually. They are hazardous to environment because of their high total contents and long-time release.

**Key words** mining environment; environmental geochemistry; heavy metal; zinc smelting waste

## High exposure of Chinese mercury mine workers to elemental mercury vapor and their increased hair methylmercury levels: A preliminary report

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**Objectives:** To assess the exposure to elemental mercury (Hg<sup>0</sup>) vapor and methylmercury (MeHg) among mercury mine workers in an area of Guizhou Province, China. **Methods:** Urine total mercury (THg) and hair THg and MeHg were measured in 26 mercury miners and smelters (i.e., exposed group), and 52 control subjects (unexposed group). **Results:** The mine workers showed high geometric mean THg concentrations in urine (258 ng/mL, 226 µg/g creatinine) and hair (20.0 µg/g). The urine Hg level of smelters, in particular, was extremely high (338 µg/g creatinine in urine). The highest urine THg reached 4580 µg/g creatinine. THg concentrations in urine and hair showed a significant correlation in the exposed group ( $r=0.62$ ), indicating the adhesion of Hg<sup>0</sup> vapor to hair. However, no such significant correlation was found in the control group. Hair MeHg concentration in those exposed (1.97

$\mu\text{g/g}$ ) was about 3 times higher than in the control (0.60  $\mu\text{g/g}$ ). Conclusions: This study indicated that smelters in a Chinese mercury mine were exposed to extremely high levels of  $\text{Hg}^0$  vapor, and that miners were estimated to be also exposed to higher levels of MeHg than those in controls. Further study is needed to determine the origin of such the comparatively high hair MeHg concentrations in the exposed group.

**Key words** elemental mercury vapor; smelter; urine; hair; mercury mine

### **Dispersion and immobilization of pollutants in Cretaceous sandstones where U ore was mined by sulfuric acid leaching**

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The uranium deposit Straz pod Ralskem in the northern part of the Czech Republic was exploited by underground acidic leaching between 1968 and 1996. More than 14000 tons of uranium were produced during this period. More than 4 million tons of  $\text{H}_2\text{SO}_4$ , 300 thousand tons of  $\text{HNO}_3$ , 120 thousand tons of  $\text{NH}_3$  and other chemicals were injected in Cenomanian sandstones. The mining has resulted in a large contamination of ground waters. Lateral hydrodynamic dispersion of the pollutants and migration of pollutants across aquitard are a potential hazard to drinking water supply and to surface aquatic environment. Chemical leaching was done by forced circulation of a technological acid solution introduced to the sandstones through injection drill holes and withdrawal of the enriched resulting solution by production wells. The solution is reacting not only with uranium ore, but also with minerals of the rock environment. Hydrogen ions are replaced by uranium and other cations leached from the rock, especially Fe, Al, Be and As. Ammonia remaining after the precipitation of the yellow cake (ammonium diuranate) was rejected underground in spite of that it serves no purpose in the underground leaching. High concentrations of Al, Be, As and ammonium ions in ground water became the most serious ecological pollutant. Modelling of the hydrodynamic dispersion of the pollutants predicts the future risks to local water supplies in 200 to 500 years. A possible way to reduce the risk is an immobilization of the pollutants in deeper parts of the sandstone aquifer. We found that modeling of the geochemical reactions using classical hydrochemical models give unrealistic results because of formation of colloidal particles. Mineralogy of the particles is complex with a precipitation and crystallization sequence, which will be demonstrated using microscopic images of mobility experiments.

**Key words** uranium mining; acid leaching; dispersion of pollutants; underground immobilization; colloid

### **Distribution of uranium and thorium in Irtysh River and the upriver wastewater from a rare metal mine impact on it**

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Uranium and Th are important radioactive elements. Most studies were focused on their environmental impact from uranium deposits and mining sites. But other sorts of mines such as rare metals mines are associated highly with uranium and thorium, too. In China, the Irtysh River is the only river that runs into the Arctic Ocean. The famous Koktokay rare metal pegmatite deposit is located in the headwater region of this river and has been exploited for several decades. The waste ore piled along the riverside as long as several kilometers. The wastewater from the concentrating plant is discharged into the river directly. In addition, uranium and thorium can be leached from the waste ore into the river in the weathering process. So it is necessary to study the uranium and thorium distribution in the branch and trunk streams of the Irtysh River and the wastewater from the mining site impact on it. In this study, the contents of uranium and thorium in water samples from the Irtysh River and rare metal mine wastewater have been detected directly with ICP-MS. Uranium and thorium distribution and geochemical behaviors in the Irtysh River basin have been studied. The environmental uranium and thorium pollution status in the Irtysh River and wastewater from a rare metal mine impact on it have also been evaluated. The study shows that uranium and thorium contents in wastewater from a rare metal mine are as high as 78.311  $\mu\text{g/L}$  and 0.627  $\mu\text{g/L}$ , respectively, so we should also pay attention to the radioactive pollution from the rare metal mine. The average contents of U and Th in the branch streams of the Irtysh River are 0.572  $\mu\text{g/L}$  and 0.015  $\mu\text{g/L}$ , respectively. At the mean time, in the trunk of the Irtysh River, average thorium content is 0.019  $\mu\text{g/L}$  while U is up to 2.234  $\mu\text{g/L}$ , much higher than the average content (0.0309  $\mu\text{g/L}$ ) of the world rivers. From upstream to downstream in the trunk of the Irtysh River, thorium content declines gradually due to dilution by other branches and deposition itself. But uranium content increases steadily. This should be the ascribed to the