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**THE RELEASE OF METALLIC TRACE ELEMENTS  
FROM FORMER METALLIC MINES.  
MAIN MECHANISMS AND ENVIRONMENTAL IMPLICATIONS**

Mining exploitations create galleries and fissures which modify underground water circulation. They also produce great quantities of solid waste falsely called “barren” : after the recovery of valuable elements it still contains up to 1-5% of sulphur, metalloids (As, Sb...) and metallic elements such as Pb, Zn, Ni (...) according to the composition of the primary ore. Until recently, these waste and galleries were abandoned when the extraction activity ended. Today, for most of the developed countries, the concerned administrations require specific treatments including for solid materials, recovering of the dump or their inclusion in cements. Concerning the groundwaters the treatments consist of water gathering in few dewatering points allowing the installation of chemical purification plants. For the galleries, the objective is to lower the permeability by their filling with appropriate solid material. However, the inheritance of the past remains significant for all the former mining districts, witnessed by numerous sites which are still untouched since the ending of the exploitation.

One of the most important impact of these activities is the release from the waste and/or galleries of metallic or metalloid (trace) elements (MTE) generally known as pollutants (As, Pb, Cr...). The crushing of primary ore materials to sandy or silty granulometry as well as the creation of fissures in the rocks surrounding the exploited zones, highly favour water circulation and as a consequence the exchanges between rocks and water. The release of MTE occurs in several ways such as acid mine drainage due to sulphide oxidation or as solid particles exportation to the neighbouring rivers and to estuaries. Depending on the local physico-chemical conditions, these particles can keep or release their metallic content during the different stages of their journey to the sea. As a result, pollutants can be transferred to hydrophere or biosphere (plants or animals).

Since seven years, our team in Limoges deals with the different aspects of the behaviour of MTE, after mining (or industrial) activities. I will present some parts of our work in order to illustrate the different ways of the MTE release.

**METHODS**

Significant conclusions can be made only if these studies are carried out considering the physico-chemical records in the field as well as in the laboratory. It

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is also necessary to consider in conjunction the liquid and the solid parts and to complete the analyses of natural products by laboratory experiments. For the liquid fraction, accurate analyses need liquid and gas chromatography for anions, ICP or AAS for (trace) cations. Solid phases are usually very small ; they can be studied only by SEM, electron microprobe, XRD and/or microXRD, (micro)infrared spectroscopy and TEM. Furthermore oxidation state and some structural data can be determined at the atomic scale using (micro)X-ray absorption spectroscopy.

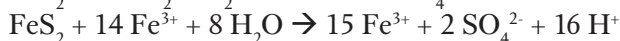
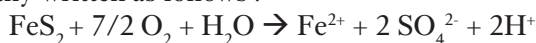
Classical solution chemistry allow to study the interactions between solid phases and water such as *appropriate* selective or sequential extraction followed by careful examination of the solid residue with the above-cited methods.

Finally the future behaviour of MTE on the sites and downstream could be forecast using geochemical calculation models (MINETEQ, CHESS...).

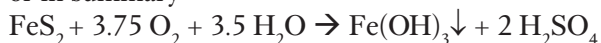
#### THE INITIAL MECHANISM OF RELEASE: SULPHIDE OXIDATION

Metalliferous ores mainly contain sulphides which are very reactive when they are subject to weathering in highly oxidising conditions such as those prevailing in tailings impoundments. As a result, major cations, but also associated trace elements (Cd or Ge in sphalerite for example), are released and generate acid drainage water.

For pyrite, the most common sulphide, this instability depends on the partial pressure of oxygen and the quantities of water. The alteration reactions are classically written as follows :



or in summary



Nevertheless, other sulphides present different relative reactivity. For example, in most impoundments Jambor and Blowes (1994) pointed out that the increasing resistance of sulphides seems to be :

*Pyrrhotite < sphalerite < pyrite - arsenopyrite < chalcopyrite.*

Then this susceptibility to weathering processes depends on parameters concerning the minerals such as mineralogy, grain size, fracturation, as well as local environmental conditions (e.g. Dold and Fontboté 2002) : whole mineralogy, sulphide quantities, pH and Eh at microscale, climate, microbial activity, permeability, water / rocks ratio etc.

Usually, these oxidation processes are very fast : after only < 10 years, most of metallic or metalloids elements are no longer present in sulphide forms. The only remaining sulphides are found in very low permeability environments, several meters below the surface of the dump. Sulphur is more mobile : the greatest part has been exported and the remaining part is present in gypsum or epsomite forms, more rarely as metal sulphates.

## ACID MINE DRAINAGE AND THE EXPORTATION OF DISSOLVED As AND MTE BY ACIDIC WATERS

The above-cited reactions leads to the production of important quantities of sulphuric acid, a change in the speciation form of MTE initially present as sulphides in the waste and to the production of iron-rich, coloured products.

One example is the medium-sized former gold mine studied by Roussel et al. (2000), which display a 600,000 metric tons of waste constituted by auriferous quartz crushed to 80µm and containing up to 0.8% As. Tailings, spread out on more than 7 hectares consist of a 30 meters high heap and settling basins. Only few arsenopyrite and other sulphides (pyrite or galena...) are still present throughout the waste. Therefore we have concluded that the sulphide oxidation induced in only several years, a change in the speciation of 4800 metric tons of As, more than ten thousands tons of iron and hundreds tons of other MTE.

However the rate of these changes as well as the nature of the secondary products strongly depend on environmental conditions defined at the microscale. The monitoring of the sites allow to distinguish different environments regarding to the physico-chemical conditions. For the previous example, within the heap Eh conditions are always oxidising and pH in the range 4-6. In the settling basins successive saturation-desaturation stages are observed in some parts whereas other zones are always submitted to saturated conditions.

Water analyses (13 water samples, two times a month, one year, ground and surface waters in relation to the rainfall and temperatures) show arsenic concentration 10 to 1000 times more than regional waters. They also show for a given sampling point a highly variable total dissolved As and other elements (1-100 times) and also a good correlation between total dissolved As and Fe in the water.

## TEMPORARY TRAPPING OF ARSENIC BY IRON OXIDES AND OTHER SECONDARY PHASES

These reactions are highlighted by the emission of yellow to brown effluents in the water corresponding to the presence of numerous iron-rich secondary phases; these products are constituted by a mixture of iron - Fe(III) - hydroxides, oxyhydroxides, and sometimes, by sulphates and other minerals. All these phases are initially highly hydrated and do not present well defined composition nor well-ordered structure.

They can precipitate in situ leading to the formation of MTE-rich specific levels within the tailings. They constitute natural immobilisation of potentially toxic elements issued from the sulphide oxidation and can be indurated as crusts or cements. Chemical and mineralogical analyses performed on this material show that some of them are constituted by low-crystallised material (1) containing high percentages of MTE and numerous different solid phases whereas others (2) present a lower content in toxic elements and are constituted by more crystallised and stable mineral species such as goethite, hematite, jarosite... The transformation

from (1) to (2) is due to local conditions such as instability of the local thermodynamic conditions, heavy runoff etc. (Courtin-Nomade et al., 2003) and is accompanied by a progressive release of MTE.

#### EXPORTATION OF MTE-BEARING SUSPENDED MATERIAL

These coloured effluents and MTE-rich secondary phases can also be exported from the sites as suspended material by erosion, for example during high rainfalls.

Artificial alteration, selective or sequential extractions in the laboratory help to appreciate the potential mobility of MTE from such materials. For example, As and iron species are frequently linked but these relationships occur in different ways (adsorption, co-precipitation or both). Nevertheless, such links are not exclusive : As can also be trapped by organic matter etc. As a consequence, in new conditions (river sediments...) only a part of arsenic is mobile, the adsorbed fraction for example.

#### REMEDIATION

A precise knowledge of the pollutants, their current and possible speciation in the future require to plan an adapted, effective and long-term remediation. Thermodynamic conditions prevailing on the different parts of the concerned sites and in the neighbourhood as well as possible modifications induced by the future remediation works must be taken into account.

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