

Metal mobility in acid mine drainage-impacted waters: from rivers to oceans

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Abstract

The complete pathway to the oceans for metals contained in acid mine drainages (AMD), from their release to river courses by weathering of sulfide-rich mining wastes, can be elucidated in the Iberian Pyrite Belt (FPI). The Odiel and Tinto rivers drain this vast expanse of massive sulfides, exploited since historical times, discharging a large amount of acidity and pollutants into a common estuary, the so-called Estuary of Huelva. The mixing of acidic river water and alkaline seawater in the estuary leads to a series of geochemical reactions that control the residence time of pollutants along the estuarine transition. This manuscript focuses its attention on that set of geochemical processes that ultimately determine the amount of pollutants that are subsequently transferred to the Atlantic Ocean. In the estuary, a progressive increase in pH is observed from the fluvial to the marine domain due to the water mixing. During the AMD neutralization, flocculation of particulate material occurs: Fe firstly precipitates as schwertmannite and later Al in the form of basaluminite. Other non-conservative elements that are removed from the water column by precipitation processes are Cu, rare earth elements (REE) and Y. The precipitation of schwertmannite produces the retention of As by adsorption at pH below 5.0. However, when schwertmannite particulate matter reach waters with higher pH values, As desorption occurs, which is released back to solution. Arsenic adsorption/desorption processes are associated with the zero-charge point for schwertmannite. Other contaminants such as Zn, Mn, Ni and Co behave conservatively, remaining in solution throughout their estuarine transit and, hence, significantly threatening the environmental conditions of the coastal areas of the Gulf of Cadiz.

Resumen

El camino completo hasta el océano que siguen los metales contenidos en drenajes ácido de mina (AMD), desde su liberación a los cursos fluviales debido a la meteorización de residuos mineros ricos en sulfuros, puede ser dilucidado en la Faja Pirítica Ibérica (FPI). Los ríos Odiel y Tinto drenan esta vasta extensión de sulfuros masivos, explotados desde tiempos históricos, descargando una gran cantidad de acidez y contaminantes a un estuario común, el Estuario de Huelva. La mezcla de agua fluvial ácida y agua de mar alcalina en el estuario conduce a una serie de reacciones geoquímicas que controlan el tiempo de residencia de los contaminantes en la transición estuarina. El presente manuscrito focaliza su atención en ese conjunto de procesos geoquímicos que en definitiva determinan la cantidad de contaminantes que posteriormente se transfiere al Océano Atlántico. En el estuario, se observa un aumento progresivo del pH desde el dominio fluvial hasta el dominio marino debido a la mezcla de aguas. Durante la neutralización del AMD, se produce la floculación de material particulado: primero precipita el Fe como schwertmannita y posteriormente el Al en forma de basaluminita. Otros elementos no conservativos que son eliminados de la columna de agua por procesos de precipitación son Cu, elementos de tierras raras (REE) e Y. La precipitación de schwertmannita produce la retención por adsorción del As a pH inferiores a 5.0. Sin embargo, cuando el material particulado de schwertmannita entra en contacto con aguas de pH superior se produce la desorción del As que pasa de nuevo a solución. Los procesos de adsorción/desorción de arsénico están asociados al punto de carga cero de schwertmannita. Otros contaminantes tales como Zn, Mn, Ni y Co se comportan conservativamente, permaneciendo en solución durante todo su tránsito estuarino y, por tanto, amenazando significativamente las condiciones ambientales de las áreas costeras del Golfo de Cádiz.

Key-words: Acid mine drainage; Estuary of Huelva; Seawater mixing; Geochemical processes; Contaminants mobility

1. Introduction

Sulfide minerals have a high potential to react with oxygen and water, and their weathering under atmospheric conditions involves a series of chained geochemical and microbiological reactions that result in the generation of extremely acid drainage with high concentrations of sulfate, metals (Fe, Cu, Pb, Zn, etc.) and metalloids (As, Sb, etc.). Acid leachates originating from oxidation of sulfide minerals located in wastes and facilities from mining activities (e.g., waste piles, tailings ponds and open-pit mines) are called acid mine drainage (AMD). Human activities, especially related to abandoned mining facilities, cause important global environmental changes due to the release of significant concentrations of these metals into rivers that finally flow into the oceans. But before that, estuaries represent the transition zone between river water and seawater, regulating through a series of geochemical processes the flux of metals reaching the coastal areas.

The Estuary of Huelva is formed by the confluence of the Tinto and Odiel rivers (SW Spain). Both rivers cross a region known geologically as the Iberian Pyrite Belt (IPB), which is one of the most important massive sulfide provinces in the world with original reserves on the order of 1700 Mt (Sáez et al., 1999). Intense mining activity in the IPB dates back to about 5000 years (Leblanc et al., 2000). The main environmental problem in the IPB is the AMD from the surface oxidation of sulfides located in the abandoned mining districts. These acidic and metal-rich leachates are drained by the Tinto and Odiel rivers, causing their total degradation (e.g., Olías et al., 2006; Nieto et al., 2013). The transfer of acidity and toxic metals to the Estuary of Huelva has been the focus of numerous investigations (e.g., Elbaz-Poulichet et al., 2001; Borrego et al., 2002; Braungardt et al., 2003; Carro et al., 2011; Hierro et al., 2014). Pollution levels are so extreme that both rivers and their common estuary are considered one of the most polluted aquatic systems in the world. This manuscript focuses on the geochemical processes occurring in the Tinto and Odiel rivers as well as in the Huelva Estuary; however, it is extensible to other mining districts in the world where AMD-affected fluvial courses reach seawater such as King River (Tasmania, Australia; Augustinus et al., 2010), Chonam-ri Creek (Kwangyang, South Korea; Jung et al., 2012), Afon Goch (Anglesey, North Wales; Dean et al., 2013) or Gromolo Torrent (Liguria, North-West Italy; Consani et al., 2017).

2. Geochemistry of AMD-impacted rivers

Numerous investigations have focused on the behavior of metals in AMD-affected streams. The AMD contains mostly high concentrations of sulfates and iron (from sulfide oxidation, mainly pyrite) and aluminum (from dissolution of host rock), in addition to other elements, some of them being potentially toxic pollutants. In AMD-affected streams, both hydrochemistry and mineralogy are controlled by the $\text{SO}_4\text{-Fe(III)}$ and $\text{SO}_4\text{-Al}$ systems in pH ranges between 2.5-4.0 and 4.5-6.0, respectively (Bigham et al., 1996; Nordstrom & Alpers, 1999). Hydrolysis of Fe and Al during pH increase in AMD results in the precipitation of schwertmannite $[\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)_n\cdot n\text{H}_2\text{O}]$ and basaluminite $[\text{Al}_4(\text{SO}_4)(\text{OH})_{10}\cdot 4\text{-}5\text{H}_2\text{O}]$, respectively. Both mineral phases are oxyhydroxysulfates of poorly-crystalline nature.

In mining environments, acid drainage often arises from underground shafts under oxygen-free reducing conditions, where all iron in solution is Fe(II) and the water is almost colorless (Fig. 1a). Under atmospheric conditions, the presence of oxygen and, mainly, the activity of extremophilic microorganisms catalyze the oxidation of Fe(II) to Fe(III). High concentrations of ferric iron and sulfate lead to the spontaneous precipitation of schwertmannite. Iron oxidation and precipitation of schwertmannite turn the water reddish in color (Fig. 1a). In the river network, Fe(III) is the main iron species and schwertmannite is commonly oversaturated in solution. In addition, the increase of pH induced by mixing with pristine waters along the drainage basin or by alkaline addition in passive treatment systems favors the enhanced precipitation of schwertmannite, a process that buffers the pH between 2.5 and 4.0. With the progressive increase in pH, once all the aqueous Fe(III) precipitates, basaluminite precipitation begins and the pH becomes buffered between 4.5 and 6.0. Both phases have high capacity to retain some trace elements in AMD; whereas schwertmannite has strong affinity for As and Cr, basaluminite has for Cu, Si, rare earth elements (REE) and Y. Therefore, their precipitation attenuates pollution naturally along river courses (Fig. 1b; Sarmiento et al., 2009) and artificially in passive treatment systems (Fig. 1c; Macías et al., 2012).

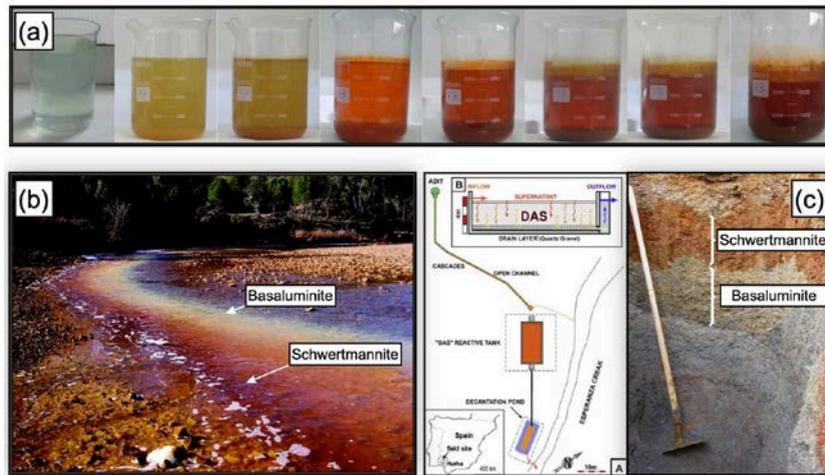


Fig. 1. (a) Oxidation of Fe(II) to Fe(III) and spontaneous precipitation of schwertmannite in an oxygen-free AMD sample. (b) Precipitation of schwertmannite and basaluminite by mixing of AMD and unpolluted Odiel river. (c) Reactive filling of a treatment system for AMD and detail of the precipitation horizons of both mineral phases.

In the AMD-affected fluvial systems of the IPB, Al precipitation as basaluminite is a minor process because Fe concentrations are so high that the system is controlled primarily by schwertmannite precipitation or even jarosite if acidic conditions are extreme. In fact, schwertmannite minerals cover the bed of most AMD-affected fluvial courses. The affinity of schwertmannite to retain preferentially oxyanions such as As and Cr and its ability to buffer pH lead to that other metal cations typically behave conservatively in streams at pH below 4.0; i.e., their concentrations mainly decrease by dilution instead of mineral precipitation (Braungardt et al., 2003). On the other hand, schwertmannite structure is metastable and recrystallizes spontaneously to more crystalline phases with time (Acero et al., 2006). In the IPB, iron precipitates capping riverbeds affected by AMD upon slight consolidation and ageing create terrace levels along the channels. The current terraces frequently define a laminated sequence where this recrystallization is observed gradually, from fresh schwertmannite at surface to goethite at depth (Fig. 2a). In addition, there are fossil analogues of current terraces that are isolated from the stream courses due to the river migration over time. In the older terraces, goethite, originating from precursor schwertmannite, has partially recrystallized to hematite by diagenetic processes (Fig. 2b; Pérez-López et al., 2011). The mineral transformation could be accompanied by the release of part of the contaminants, mainly arsenic, previously retained in the solid. Therefore, the search for stability in this poorly crystalline oxyhydroxysulfate could determine the flux of contaminants over time, and what is now considered a sink could become a source of contamination in the medium or long term.

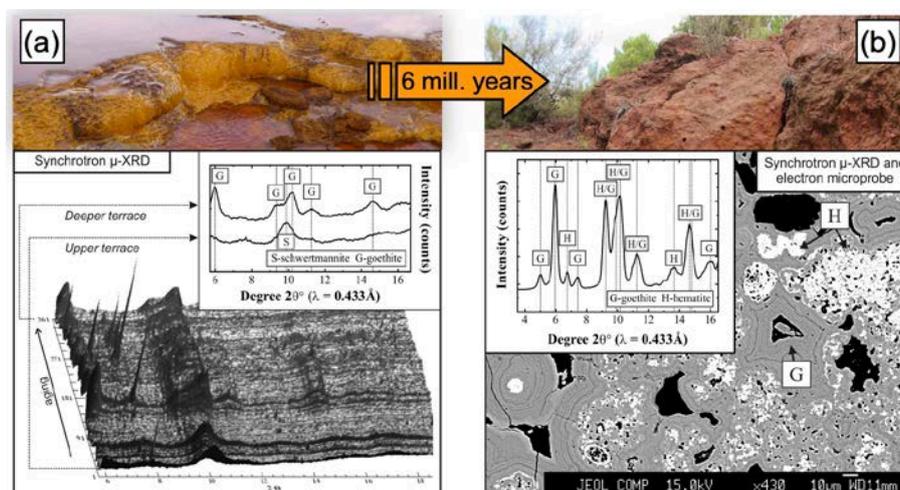


Fig. 2. Synchrotron μ -XRD analysis on samples from (a) current terrace and (b) fossil terrace of the Tinto-Odiel fluvial system affected by AMD.

Fluvial contribution of metals to the Estuary of Huelva is currently well known for different periods and under different climatic conditions. For example, Olías et al. (2006) calculated the discharge for the period 1995 to 2003 and estimated that both rivers contribute to the estuary more than 50% of the Zn and 10% of the Cu of the total of these metals transferred globally from the continents to the oceans (Table 1). Thus, IPB is a local anomaly but with global repercussions from an environmental point of view.

Table 1. Average values of the pollutant load transported by the Tinto and Odiel rivers (Olías et al., 2006), and their comparison with the global flow transported by rivers to the oceans (GESAMP, 1987).

	Río Tinto ton/yr	Río Odiel ton/yr	Tinto-Odiel ton/yr	Global gross flux ton/yr	Fraction (%)
As	12	23	36	10,000	0.4
Cd	4	7	11	340	3.3
Cu	469	1252	1721	10,000	17.2
Fe	5075	2847	7922	1,400,000	0.6
Mn	163	1452	1615	280,000	0.6
Pb	15	12	27	2000	1.3
Zn	863	2612	3475	5800	59.9
Co	9	62	71	1700	4.2
Ni	2	34	36	11,000	0.3

In rivers affected by AMD, geochemical processes have been widely described in the scientific literature and, therefore, this section can be considered as background for this text. The following section aims to highlight an integrated study between river discharges and the geochemical processes that take place during mixing with seawater in the Estuary of Huelva. These processes will reveal the net flux of pollutants that really reaches the Atlantic Ocean. This information is novel in the scientific literature, and for that reason, these results will be explained in more detail.

3. Geochemistry of AMD-impacted estuaries

The geochemical processes controlling the mobility of contaminants in estuarine systems can be very complex, including removal from solution into newly-formed solid phases or release to solution by dissolution, desorption or even mineral transformation processes (Morris et al., 1986; Bowers & Yeats, 1989; Baeyens et al., 1998; Zhou et al., 2003). Freshwater inflows and oceanic saltwater mixing is addressed in typical estuaries as salt-induced mixing. However, other geochemical processes occur in estuaries receiving AMD-affected streams, as there is a gradient of pH from values between 2.5-3.5 at the mouth to values close to 8.0 in the marine domain. Such a wide variation in pH in a very short space can cause metals, which are mostly conservatives in fluvial courses, to undergo strong geochemical processes related to acid neutralization that can affect their mobility in marine environments. Such processes will be unpacked below from laboratory to a real field scale.

3.1. AMD - seawater mixing

Evaluation of the hydrochemical and mineralogical processes taking place during interaction of AMD with water of the Estuary of Huelva can be simplified at the laboratory scale by mixing experiments. The dropwise addition of seawater over AMD from the main course of Tinto and Odiel rivers just at the mouth to the estuary causes a progressive increase in pH, revealing the acid neutralization during estuarine mixing (Fig. 3a,b). The pH increases slowly even with large amounts of seawater. Approx. 8.8 mL and 11 mL of seawater were necessary to raise the pH to 7 for each 1 mL of AMD from Tinto and Odiel, respectively.

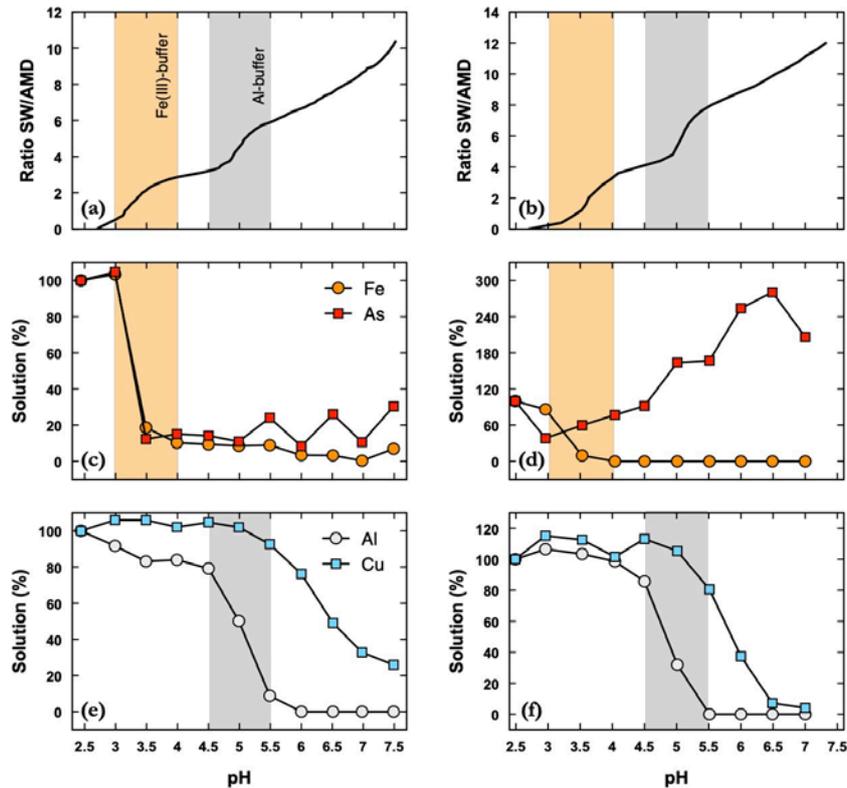


Fig. 3. Evolution of pH and percentages of Fe, As, Al and Cu during the addition of seawater to AMD from (a,c,e) Tinto and (b,d,f) Odiel rivers. Orange and grey areas represent different buffers for Fe(III) and Al, respectively. Percentages refer to the relationship between the experimental concentrations and the values calculated from the theoretical mixing of the end-members.

As the pH increases, two buffer zones are observed which are closely related to the formation of two newly-formed mineral phases whose precipitation involves the release of protons. The first buffer, at pH between 3.0 and 4.0, corresponds with the precipitation of Fe(III) as schwertmannite; while the second buffer, at pH between 4.5 and 5.5, corresponds with the precipitation of Al as basaluminite (Fig. 4).

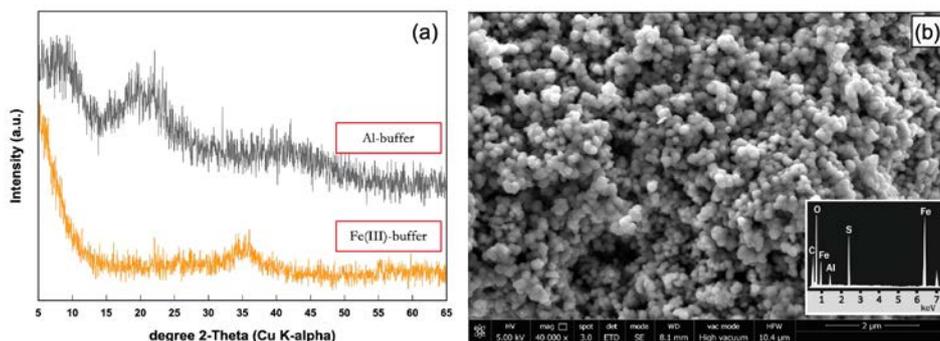


Fig. 4. (a) XRD spectra revealing schwertmannite precipitation in Fe(III)-buffer and basaluminite in Al-buffer. (b) SEM image and EDS analysis of schwertmannite. Note the poorly-crystalline nature of both schwertmannite and basaluminite, as suggested by their typical XRD spectra. For comparison purposes, XRD spectra for pure schwertmannite and basaluminite can be found in Sánchez-España et al. (2011).

These findings show for the first time the progressive sequential precipitation of schwertmannite and basaluminite during the mixing of an AMD with seawater, as also observed in fluvial systems. Schwertmannite precipitation, at pH between 3.0 and 4.0, removes Fe(III) from solution. Concomitant with the removal of Fe(III) is the depletion of As (Fig. 3c,d). On the other hand, basaluminite precipitation, at pH between 4.5 and 5.5, removes Al from solution, in addition to Cu (Fig. 3e,f), REE and Y. Hence, both mineral phases also exert a control on the same

elements as in fluvial courses. However, in the estuary there is a wide pH range so that Al precipitation as basaluminite is expected to be of greater importance than in AMD-affected rivers. Moreover, the affinity of schwertmannite for As is only observable at low pH values during the estuarine mixing since an increase in As concentration is observed at higher pH (Fig. 3c,d). This As increase could be associated with possible changes in the superficial properties of schwertmannite in the marine environment, as will be discussed in the next subsection. Other contaminants such as S, Zn, Cd, Ni and Co reveal a conservative behavior throughout the experiments, i.e., their experimental concentrations can be deduced from the theoretical mixing of the end-members (Fig. 5).

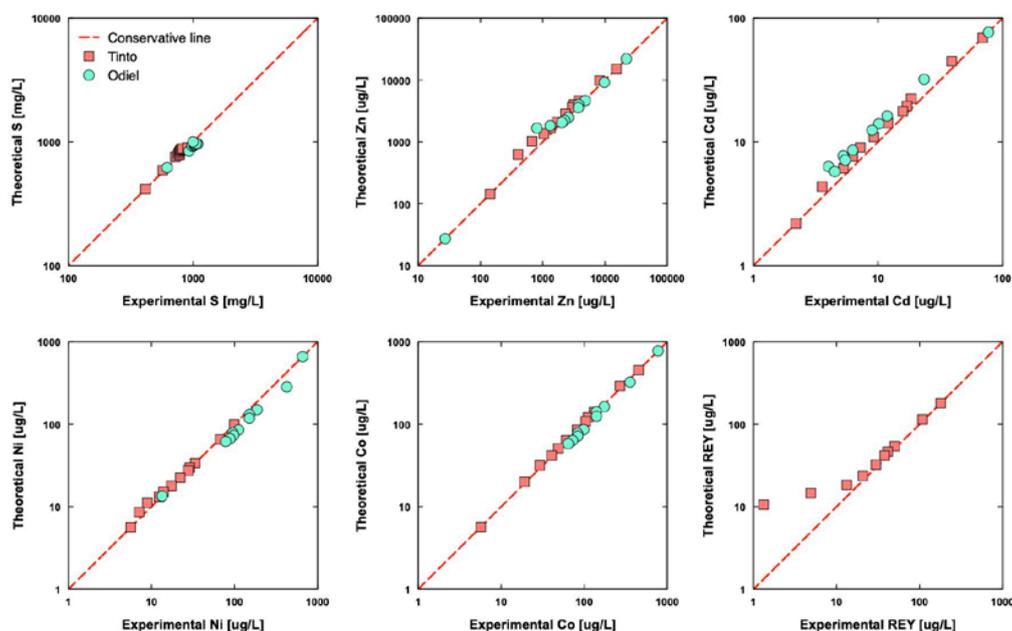


Fig. 5. Comparison between experimental concentrations and values calculated from the theoretical mixing of end-members for AMD from Tinto and Odiel rivers. Red line marks the conservative behavior, i.e., those elements plotting on the conservative line do not precipitate during acid neutralization.

3.2. The role of particulate matter

According to the previous experiments, high amounts of schwertmannite should flocculate in the Estuary of Huelva during the neutralization of the Tinto and Odiel rivers by seawater mixing. In addition, elevated concentrations of suspended particulate matter consisting mainly of schwertmannite must be transported by both rivers to the estuary, especially during flood events associated with strong rainfalls. The stability of schwertmannite under estuarine conditions, as well as its role on contaminant mobility, can also be simplified in the laboratory. The continuous schwertmannite-seawater interaction at different contact times (from 0 to 336 h) causes a decrease in pH from seawater values (pH = 7.7) to values of around 2.7, 3.7 and 4.6 for the solid:liquid ratios of 1:40, 1:200 and 1:400, respectively (Fig. 6). The higher the amount of schwertmannite, the lower pH values are reached. This response confirms the high potential of schwertmannite to buffer pH.

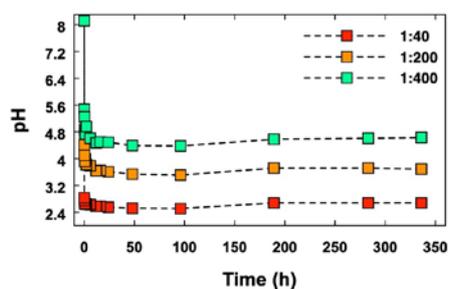


Fig. 6. Time evolution of pH in the schwertmannite-seawater interaction experiments.

During the interaction time of schwertmannite with seawater, other contaminants are increasingly released into solution until reaching a steady-state. In addition, the concentrations reached at the steady-state are higher at increasing amounts of starting schwertmannite. Figure 7 shows, as an example, the behavior of Fe, Zn and Mn, although it can be extended to other metals studied such as Al, Cu, REE or Y.

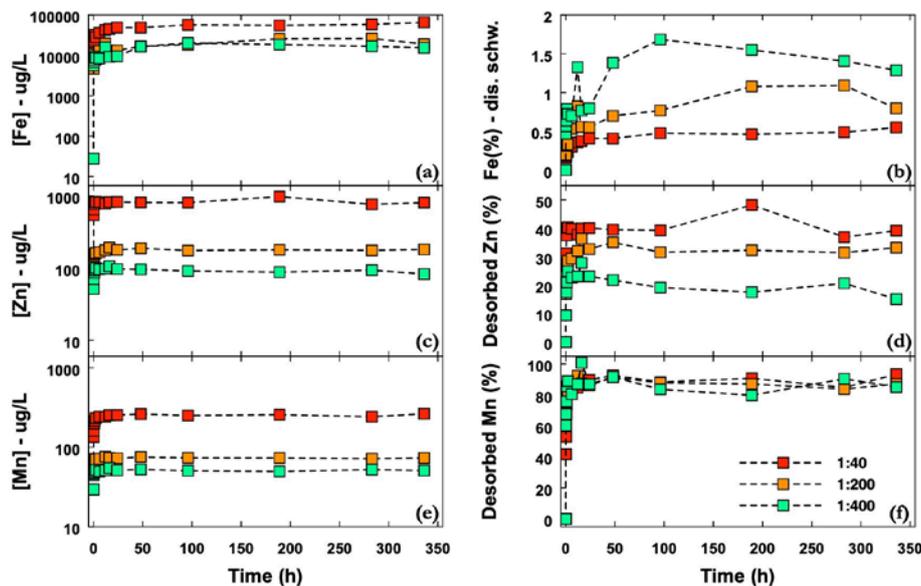


Fig. 7. Time evolution of Fe, Zn and Mn: (a,c,e) concentrations in solution and (b,d,f) percentages exclusively released by desorption in the schwertmannite-seawater interaction experiments. In the case of Fe, the percentage would indicate the amount of schwertmannite dissolved in the experiments.

Considering the following assumptions as starting points: (1) the initial sample consists only of schwertmannite, (2) the release of Fe is due exclusively to schwertmannite dissolution during the interaction with seawater and (3) the rest of the metals are also hosted in the schwertmannite by the same structural mechanism, it is possible to calculate the amount of metals released to solution by desorption using the following equation:

$$[M]_{desorbed} = ([M]_{solution} - [M]_{seawater}) - \frac{[M]_{schw}}{[Fe]_{schw}} \times ([Fe]_{solution} - [Fe]_{seawater})$$

The metal concentrations released by desorption ($[M]_{desorbed}$) would correspond to the concentrations in solution ($[M]_{solution}$) minus those in the initial seawater ($[M]_{seawater}$) and minus the concentrations theoretically released by mineral dissolution. The latter concentrations can be calculated from the ratio of metal/Fe in the starting solid ($[M]_{schw}/[Fe]_{schw}$) by the concentration of Fe in solution released only by mineral dissolution, i.e., by deducting the Fe in solution ($[Fe]_{solution}$) minus the Fe in the initial seawater ($[Fe]_{seawater}$). The concentrations released by desorption with respect to the total concentrations that the solid could release by complete dissolution, expressed as a percentage, can be also seen in Figure 7.

As shown in Figure 7, the metals define a positive desorption isotherm with higher percentages released at higher amounts of initial schwertmannite. The contact of schwertmannite with seawater causes the release by desorption of up to 40% of Zn and 100% of Mn with respect to the total existing in the solid; in addition to other elements such as 30% of Al, 20% of Cu and 100% of La. This behavior demonstrates the potential of this mineral to easily release the previously retained elements. The amount of schwertmannite dissolved in the experiments ranges from 0.5% for the 1:40 ratio to 1.5% for the 1:400 ratio. However, the behavior of As is different from that of the other elements previously indicated. Although the total concentrations of As in solution increase with time (Fig. 8a), the percentage released by desorption does not define a positive isotherm as with the other elements. At pH values of 2.7 (1:40 ratio), the percentage of desorbed As defines negative values as an “inverse desorption isotherm” (Fig. 8b). This inverse isotherm reflects the ability of schwertmannite at extremely acidic pH to re-adsorb the As that is

released to solution during the dissolution of the mineral itself. At pH values of 3.7 (ratio 1:200), the As concentrations released by desorption are still slightly negative; however at pH values of 4.6 (ratio 1:400), some As release by desorption is already observed (Fig. 8c). This behavior could indicate that the zero-charge point for schwertmannite in seawater is found at pH values close to 4.6.

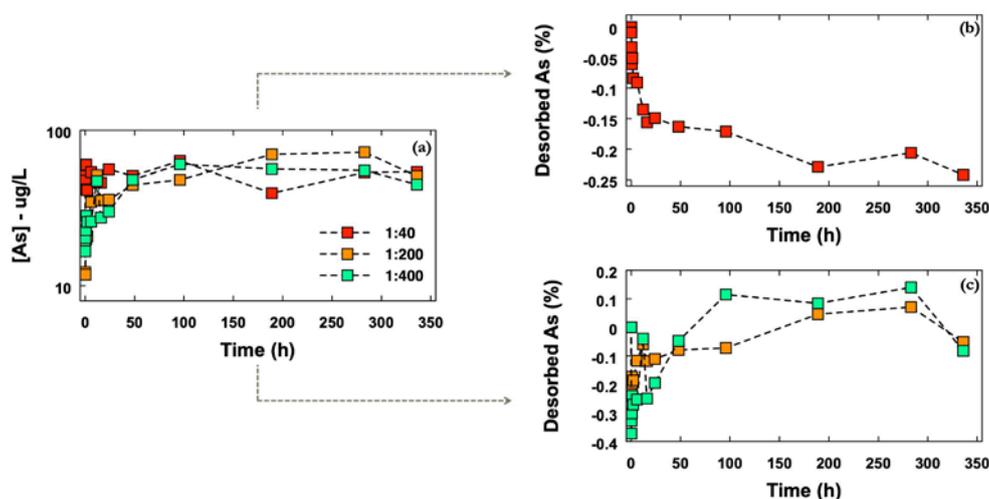


Fig. 8. Time evolution of As: (a) concentration in solution, (b) percentage exclusively released by desorption for the ratio 1:40 and (c) percentage exclusively released by desorption for the ratios 1:200 and 1:400 in the schwertmannite-seawater interaction experiments.

The surface of schwertmannite is found positively charged at acid pH values; while the main aqueous As species for the entire pH range is a negatively-charged oxyanion ($H_2AsO_4^-$) according to thermodynamic models. Both aspects would explain the high affinity of As for schwertmannite through adsorption in acid environments. The remaining elements present as positively-charged metal cations would undergo electrostatic repulsion with the mineral surface and thus be released easily into solution. At pH values above the zero-charge point (ca. 4.6 in seawater), the schwertmannite surface becomes negatively charged and desorption of As is also expected (Fig. 9). This desorption process would also explain the increase in the As concentration observed at high pH values in the mixing experiments of the previous section (Fig. 3c,d). Moreover, schwertmannite controls in the same way as for arsenic the mobility of other elements such as Cr, V, Mo or Sb occurring as oxyanions as the main species in solution.

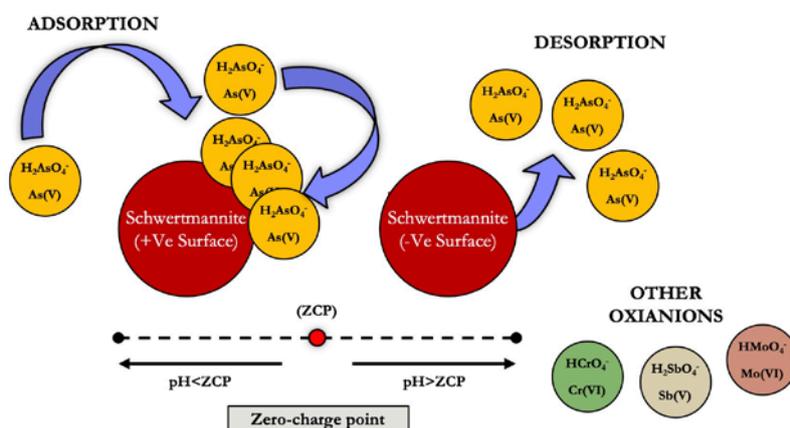


Fig. 9. Illustration of adsorption-desorption processes associated with the zero-charge point in schwertmannite.

3.3. Hydrochemical study of the Estuary of Huelva

A field study was required to provide a complete picture of the geochemical processes controlling metal mobility during mixing of AMD solutions and particulate matter with seawater observed in the laboratory. Thus, water samples during several sampling campaigns were collected by boat through the Estuary of Huelva, from the fluvial to the marine environment (Fig. 10). Samplings in the estuarine zone allowed us to locate the areas of neutralization

of the acid discharges and flocculation of precipitates. Water samplings were carried out using a Van Dorn bottle at 10 m depth to avoid possible contamination by the ship, except for surface waters where the sampling depth was around 5 m. To understand the behavior of metals during mixing, both total and dissolved contaminants were analyzed through the analysis of both filtered and unfiltered samples, the difference being those associated with particulate matter. Note that a non-conservative element tends to precipitate, and its concentration would pass from dissolved to particulate fraction; while a conservative element does not precipitate, so the concentrations in the particulate fraction would be negligible.

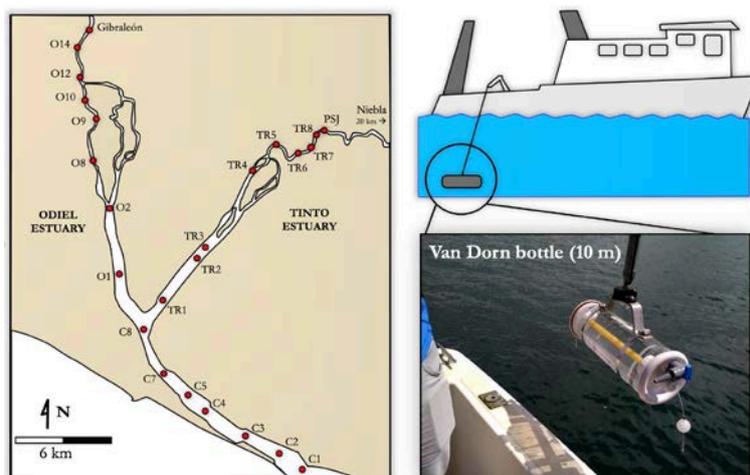


Fig. 10. Location of sampling points in the Estuary of Huelva: O points refer to Odíel river estuary, TR points to Tinto river estuary, and C points to the common estuarine channel, which is directed until the Atlantic Ocean.

In the Estuary of Huelva, an increase in pH from acidic fluvial values to alkaline values typical of the sea was observed. In the mixing zone (orange band; Fig. 11), the increase in pH is accompanied by a decrease in dissolved Fe concentrations. Arsenic concentrations first tend to decrease along with the decrease in Fe concentration. However, at pH values above 5.0-6.0 (vertical green dashed line), As concentrations again increase in solution while Fe continues to decrease. The concentration of Fe in solution decreases by mineral precipitation since Fe passes from being 100% in the dissolved fraction to 100% in the particulate fraction. Arsenic first precipitates together with Fe; however, at pH values close to neutrality the percentage of As associated with the dissolved fraction begins to increase until reaching 100% (Fig. 11).

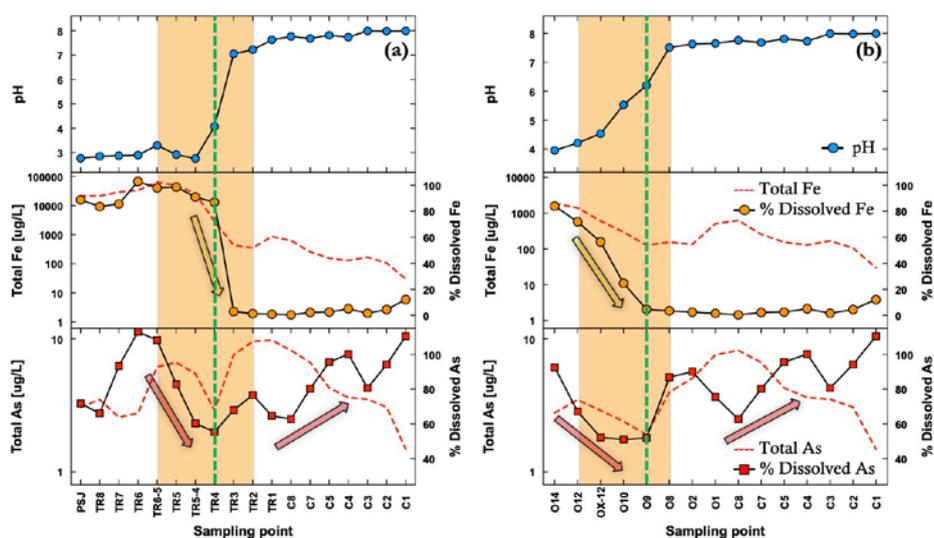


Fig. 11. Evolution of pH and total concentrations (principal Y-axis) and dissolved percentages (secondary Y-axis) of Fe and As along the estuaries of (a) Tinto and (b) Odíel rivers in a sampling conducted in May 2018.

Elements such as Al, REE, Y and, to a lesser extent, Cu seem to have also a non-conservative behavior in the estuary. The decrease in their total concentrations (dashed lines; Fig. 12) is due not only to dilution by seawater but also to mineral precipitation. This non-conservative behavior due to mineral precipitation is deduced since the percentages associated with the dissolved fraction with respect to the total (gray columns; Fig. 12) decrease during water mixing because these elements precipitate passing to the particulate matter fraction.

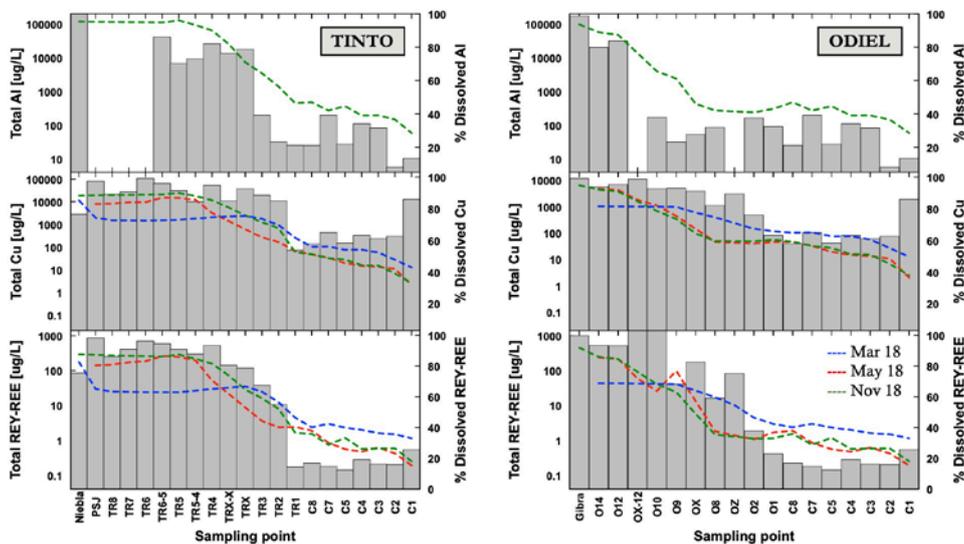


Fig. 12. Evolution of total concentrations (principal Y-axis) and dissolved percentages (secondary Y-axis) of Al, Cu, REE and Y along the estuaries of Tinto and Odiel rivers in three samplings conducted in March, May and November 2018 upon different hydrological conditions.

Iron chiefly precipitates during water mixing as schwertmannite; whereas Al precipitates as basaluminite (Fig. 13). However, the increase in dissolved As concentrations seems to be related to the release of As retained originally in schwertmannite precipitates at acidic conditions when pH values above their zero-charge point are reached in the estuary. These results support and further confirm previous laboratory results.

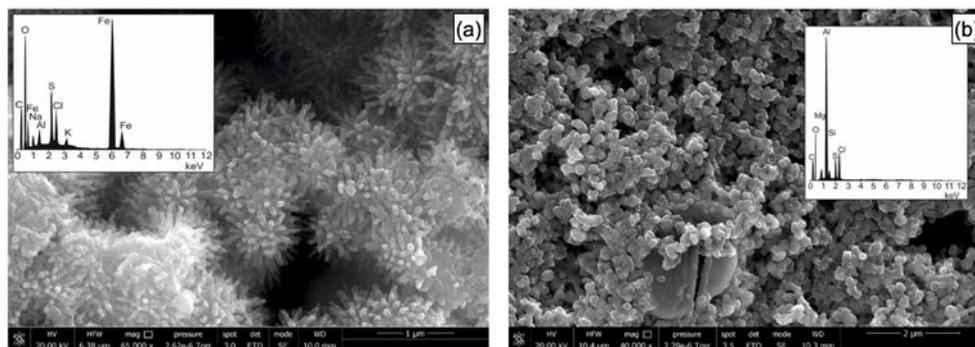


Fig. 13. SEM images and EDS analyses of (a) schwertmannite and (b) basaluminite precipitates found in particulate material from the Estuary of Huebra.

Other elements such as Zn, Cd, Co and Ni seem to have a quasi-conservative behavior in the estuary. The decrease in their total concentrations may be exclusively due to a dilution effect by seawater. No precipitation occurs during estuarine mixing as most of the total concentration of these elements is dominated by the dissolved fraction throughout the estuary (Fig. 14), also confirming the processes deduced in the laboratory.

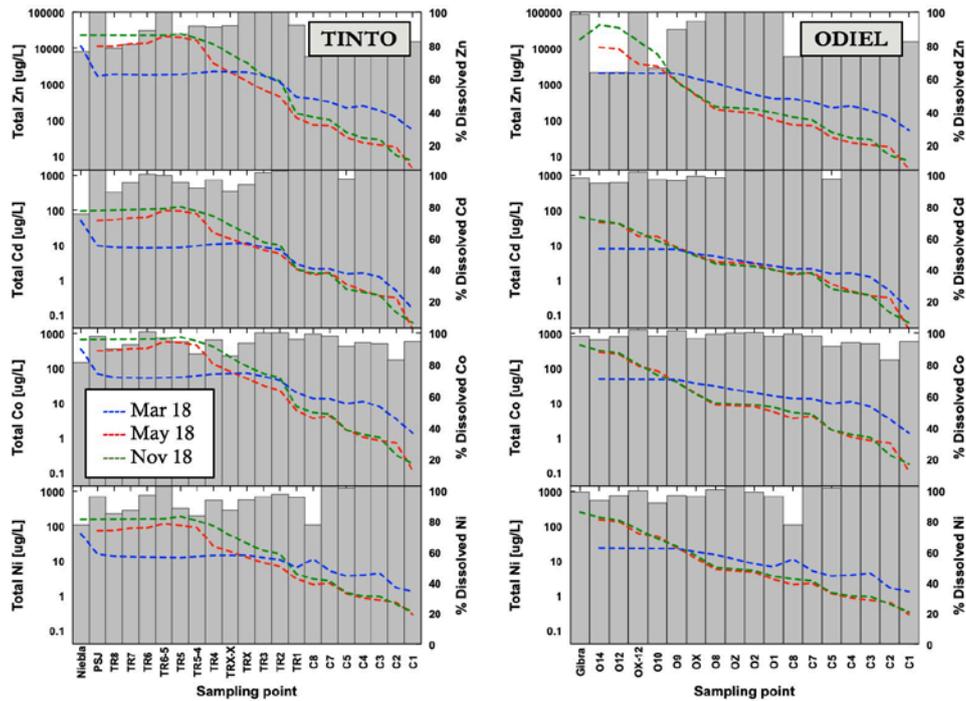


Fig. 14. Evolution of total concentrations (principal Y-axis) and dissolved percentages (secondary Y-axis) of Zn, Cd, Co and Ni along the estuaries of Tinto and Odiel rivers in three samplings conducted in March, May and November 2018 upon different hydrological conditions.

4. Transference of potentially toxic elements to oceans

The seawater of the Gulf of Cadiz shelf is particularly enriched in dissolved metals, mainly Zn, Cd, As and Cu, compared to other coastal waters. These enrichments were first observed and analyzed during the 1980s by an oceanographic expedition organized by the Woods Hole Oceanographic Institution of Massachusetts (Spivack et al., 1983; Boyle et al., 1985; Sherrell & Boyle, 1988). In fact, the pollution plume circulates and dominates the chemical composition of the Atlantic entrance to the Mediterranean Sea through the Strait of Gibraltar (Van Geen et al., 1988). Initially, after analyzing the main rivers draining this part of the region (e.g., Guadalquivir and Guadiana rivers), these authors ruled out the fluvial input and explained this enrichment by a process of upwelling from deep ocean areas and sequestration of metals in the Gulf of Cadiz (Van Geen et al., 1991). Some years later, Elbaz-Poulichet & Leblanc (1996) were the first authors to focus the source of the metals in two secondary fluvial courses in relation to the rest: the Tinto and Odiel rivers, which was confirmed a year later by the same authors who detected the anomaly in the ocean (Van Geen et al., 1997).

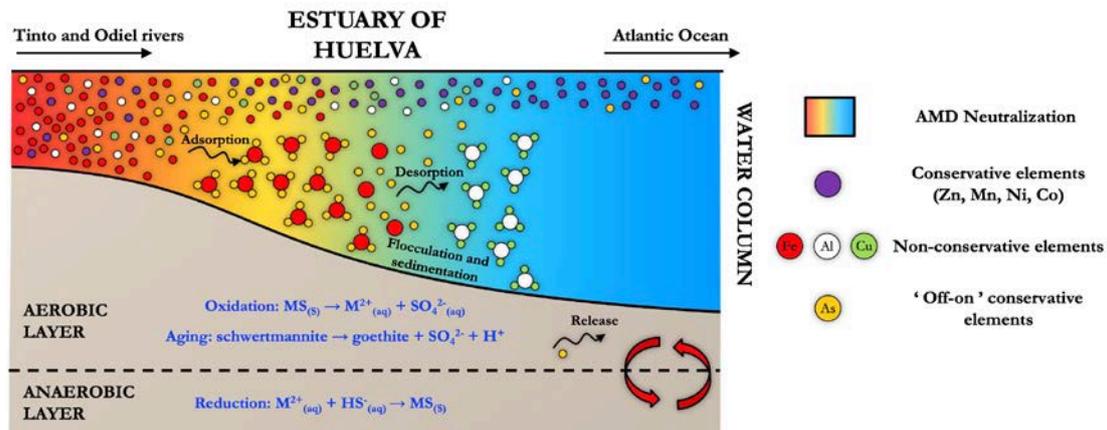


Fig. 15. Conceptual model of metal partitioning, indicating the processes that affect particulate matter from its flocculation to its sedimentation in the Estuary of Huelva during the mixing between AMD and seawater.

Currently, there is no scientific dispute regarding the fact that the metals circulating through the Gulf of Cadiz are discharged by the Tinto and Odiel rivers. This manuscript is dedicated to the geochemical processes that take place in the Estuary of Huelva, since it is the transition zone between the acidic fluvial discharges and the Atlantic Ocean. These processes would reveal the behavior of metals that are discharged into the Estuary of Huelva through the Tinto and Odiel rivers (Table 1). Special attention should be paid to conservative elements such as Cd, Zn, Co or Ni since the total amount discharged by both rivers would practically reach oceanic waters. Other elements such as As would have an OFF-ON behavior; that is, the schwertmannite that flocculates in the estuary adsorbs As (OFF) below a pH value close to 5.0, however, the As would be desorbed (ON), passing again to solution, when these precipitates reach the estuarine zones with pH values above 5.0. All these geochemical processes have been represented as conclusions in the conceptual model shown in Figure 15.

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