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Geochemistry of rare earth elements in a passive treatment system built for acid mine drainage remediation

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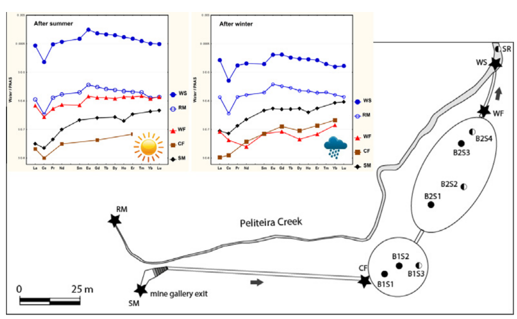
HIGHLIGHTS

- First detailed study of REE in a passive treatment system for AMD (Jales, Portugal).
- REE are sequestered by ochre sludge, particularly the LREE after winter.
- REE are significantly released by soil particles to the water after summer.
- Water dynamics favors lower REE contents and lower MREE/LREE ratio in effluent.
- REE fractionation indicates selective sequestration/release to the effluent.

GRAPHICAL ABSTRACT



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ABSTRACT

Rare earth elements (REE) were used to assess attenuation processes in a passive system for acid mine drainage treatment (Jales, Portugal). Hydrochemical parameters and REE contents in water, soils and sediments were obtained along the treatment system, after summer and winter. A decrease of REE contents in the water resulting from the interaction with limestone after summer occurs; in the wetlands REE are significantly released by the soil particles to the water. After winter, a higher water dynamics favors the AMD treatment effectiveness and performance since REE contents decrease along the system; La and Ce are preferentially sequestered by ochre sludge but released to the water in the wetlands, influencing the REE pattern of the creek water. Thus, REE fractionation occurs in the passive treatment systems and can be used as tracer to follow up and understand the geochemical processes that promote the remediation of AMD.

1. Introduction

Acid mine drainage (AMD) is an environmental problem that typically impairs water resources in mining regions. As a consequence of sulfide oxidation in mines, dumps and tailings impoundments, AMD poses often long-term threat to the aquatic environment. Thus, outflow from mining operations, it is common to observe high loads of suspended solids, low pH values and high contents of metals and sulfate. In order to deal with this type of contamination and to protect the surrounding aquatic environment there are several type of strategies (Younger et al., 2002; Balintova et al., 2009; Zipper et al., 2011).

Passive systems with wetlands have been widely used, especially in abandoned mining sites, because of their cost-effectiveness and low maintenance demands (Younger, 1997; Skousen et al., 1998; Zipper et al., 2011; Peer et al., 2015). In the course of the treatment system, a complex chain of physical,

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chemical and biological processes is acting to remove pollutants and to promote attenuation of the mining contamination. However, the pollutants sequestered by ochre sludge formed by neutralization as well as by soil particles of wetlands can be released to the water column with slight changes in hydrobiological and physico-chemical conditions, such as pH and redox potential (Hakansson et al., 1989; Kruopiene, 2007; Lizama et al., 2011; Balintova et al., 2012). Moreover, mobility and bioavailability of the elements, including metals, in soils and sediments depend also on their chemical form. There are numerous studies about the effect of physicochemical conditions on the speciation of metals in sediments. Most of them are based on laboratory experiments carried out under specific pH, redox or salinity conditions (Balintova et al., 2009; Calmano et al., 1993).

The abandoned Jales mining area is located near Vila Pouca de Aguiar (north of Portugal) and is a sulfide-rich deposit. Mining activities were performed in an uncontrolled way, originating erosion and serious environmental contamination, namely related with AMD processes. The main pollutants identified by Oliveira and Àvila (1995) were heavy metals, particularly elevated concentrations of manganese, cadmium, lead and arsenic. The impact on community health was also previously reported by Coelho et al. (2007). A rehabilitation project has been implemented including procedures for closing mine adits and shafts, measures for containing mine wastes and bioremediation. Some measures have been taken to diminish soil erosion and dispersion of contaminants (Bleeker et al., 2003; EDM, 2006). A passive system was built to collect and treat the drainage that flows from an old adit into the Peliteira creek. The treatment system includes a biological unit process composed by two wetlands, and a pre-treatment unit devoted to chemical processes using the water–limestone interaction. A previous study performed by Valente et al. (2012), on the role of mineralogical attenuation for metallic remediation in this passive system, showed that iron, arsenic, barium, cobalt, manganese and zinc are mainly controlled by iron oxides and clay minerals among other phases. It was also shown that the ochre-precipitates formed as waste products from neutralization process are mainly poorly ordered iron-rich materials, such as ferrihydrite.

The differences in ionic radius, oxidation state and bonding of the rare earth elements (REE) drive fractionation of these elements in natural systems. Hence, REE have been largely used as fingerprints in the understanding of surficial environments (Prudêncio and Cabral, 1988; Prudêncio, 2007; Prudêncio et al., 2007, 2010, 2011; Marques et al., 2012, 2014), and of recharge processes and inter-aquifer mixing conducting seasonal sampling campaigns (Duvert et al., 2015). Also, in mining environments, REE may behave as tracers of AMD contamination. In fact numerous investigations on the identification of the water–rock interactions mechanisms that govern the chemistry of acidic drainage have been done, and several publications have reported the REE geochemistry of acidic sulphate in the last two decades (Johannesson et al., 1996; Johannesson and Zhou, 1999; Verplanck et al., 1999; Marchand, 2002; Borrego et al., 2005; Gammons et al., 2005a,b; Merten et al., 2005; Olias et al., 2005; Wood et al., 2006; Ferreira da Silva et al., 2009; Pérez-Lopez et al., 2010; Delgado et al., 2012; López-González et al., 2012). These works have reported a shale-normalized pattern enriched in MREE relative to LREE and HREE. More recently Grawunder et al. (2014) explain that MREE enrichment in water sampled in AMD impacted areas is due to their preferential release from the widespread pyrite. According to these authors most probably complexation to sulphite (SO_3^{2-}) or another intermediate S-species during pyrite oxidation is the reason for the MREE enrichment in the normalized REE patterns. Despite the REE have largely been considered of minor environmental concern, some toxicological studies have suggested that REE may have significant pathogenic potential (Wu et al., 1983; Haley, 1991; Hirano and Suzuki, 1996; Zhu et al., 1997; Protano and Riccobono, 2002; Pagano et al., 2015). These works focus mainly on the REE mobility in host minerals typically in affected AMD regions. Rare earth element patterns in AMD remediation processes have been less studied. Furthermore only a few studies concerning their behavior in mining contexts and especially in mine water treatment systems exist. Nevertheless, they may suite as a tool for understanding the processes that occur in the course of the treatment, such as dissolution, precipitation, complexation and sorption (Merten et al., 2005). In this work special attention is provided to the behavior of REE in the course of a passive treatment system, constructed for AMD remediation (in Jales mine, north of Portugal).

The specific objectives of the present study are: (i) to evaluate the seasonal behavior of rare earth elements in the water along the treatment system; (ii) to evaluate the contribution of the main mining focus (AMD and mine wastes) to the behavior of REE in the fluvial system; (iii) to evaluate the distribution of REE in the fine fractions of the wetland soils and sediments; and (iv) to assess the REE patterns in the water/soil system in the constructed wetlands and their role as tracers of the remediation processes. Thus, a detailed study of the REE distribution is performed aiming better understand the complexity of hydrogeochemical processes that occur in the course of passive treatment systems constructed to improve water properties.

1.1. Site description

Jales mining site is an inactive gold mining area located in the Vila Real district, in the Northeast of Portugal (Fig. 1). This sulfide-rich deposit has been exploited since Roman times. In the XX century it was mined for gold and silver between 1933 and 1992 (Rosa and Romberger, 1997).

The study site has a temperate warm climate with highest rainfall values in winter (mainly in January), being July the driest month. The average annual temperature and rainfall are 12.5 °C and 1214 mm, respectively.

The Jales treatment plant was part of the rehabilitation project planned to the abandoned mining site of Jales (EDM, 2006). The passive system was built to collect and treat the drainage that flows from an old adit into the nearby watercourse (Peliteira creek) (Fig. 1) and is fully operating since the end of the summer of 2006.

The mine water can be generically described as an acid ($pH < 4.5$) and sulphate-rich solution. General properties of the untreated mine water are described in Pedrosa et al. (1998), and Loureiro (2007).

The mouth of the mine was littered with limestone. After this first contact with limestone (first stage of pre-treatment), follows an open limestone (OLC) system devoted to chemical processes, especially oxidation and neutralization, comprising a reception basin (of which the bottom is filled with limestone), a cascade aeration facility and a limestone channel (inorganic stage). This pre-treated effluent enters into a typical aerobic wetland system planted with *Typha* sp. to aid wetland performance (see Fig. 1). The all system promotes oxygenation, pH raise, alkalinity increase and subsequent precipitation of metals as ferric hydroxide sludge (ochre-precipitates) as well as fixation of metals by plants.

2. Methods

2.1. Sampling and sample preparation

The sampling sites were selected taking into account the different environmental conditions of the treatment system (see Fig. 1);