XIVCGPLP
Congresso de Geoquímica dos Países de Língua Portuguesa
XIX Semana de Geoquímica

Indicadores mineralógicos de drenagem ácida (ARD) em cortes de estrada em diferentes unidades litoestratigráficas

Mineralogical indicators of Acid rock drainage (ARD) in road cuts from different lithostratigraphic units

Valente, T.[1]*, Pamplona, J.[1], Gomes, P.[1], Rios, C.A.[2]

[1] Institute of earth sciences, Pole of University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal, *teresav@dct.uminho.pt

[1] Institute of earth sciences, Pole of University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal, jopamp@dct.uminho.pt

[1] Institute of earth sciences, Pole of University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal, patricia_s_gomes@hotmail.com

[2]Escuela de Geología, Universidad Industrial de Santander, Bucaramanga, Colombia, carlosalbertoriosreyes@yahoo.es

Abstract

Construction of highways in some particular geological conditions exposes pyrite and other associated sulfides to oxidative weathering. This generates a process known as acid rock drainage. As a consequence, typical properties of acid drainage may develop, such as precipitation of soluble salts efflorescences. Also, acidic and metal-rich runoff from the exposed road cuts may pose concerns about the surface and groundwater contamination as well as regarding the structural robustness and the safety of the road slopes.

In the North of Portugal, particularly in the Minho region there are geological conditions that promote the development of natural acidic and metal contamination. Such acid rock drainage appears as an exuberant phenomenon in several highway cuts, where the sulfide-rich exposed rocks are suffering oxidation. The present work reveals the occurence of acid rock drainage sites in road cuts in the north of Portugal, relating this process with the geology of the terrains. Thus, it describes the sources of acid and metals and the respective genesis conditions, and presents the mineralogical indicators of such a geochemical process, which are dominated by magnesium sulfates. Moreover, remediation measures are pointed out, some of them already implemented in some sites.

Resumo

A construção de infraestruturas viárias em certas condições geológicas pode expor minerais como os sulfuretos a mecanismos de dissolução oxidativa. A complexa cadeia de reacções que se desencadeia gera um processo de drenagem ácida, que na bibliografia anglo-saxónica é conhecida por “Acid Rock Drainage” (ARD). Como consequência, desenvolvem-se propriedades típicas de uma contaminação ácida, idêntica à que se observa em contexto mineiro, tais como a precipitação de sais solúveis. Para além desta manifestação mineralógica, as águas de escorrência criam preocupações ambientais, especificamente no que respeita à qualidade do meio hídrico, mas também quanto à estabilidade dos taludes sujeitos a uma meteorização química acelerada.

No Norte de Portugal, particularmente na região do Minho, existem condições geológicas favoráveis ao desenvolvimento deste processo, que se manifesta de forma exuberante nalguns cortes de auto-estrada. O presente trabalho revela a ocorrênca de sítios afectados, relacionando o processo com a geologia dos terrenos em que se implementaram estas vias. Descreve-se a origem da drenagem ácida e apresentam-se indicadores mineralógicos da evolução geoquímica das rochas mais reactivas, dominados pela presença de sulfatos de magnésio. Apontam-se ainda exemplos de medidas de remediação, algumas já implementadas em certos sectores das vias afectadas.

Palavras-chave: drenagem ácida, ARD, cortes de estrada, eflorescências salinas, contaminação.

Keywords: Acid rock drainage, ARD, raod cuts, salt efflorescences, water contamination.

Introduction

Contamination by acid, sulfate, and metals, through the process called acid mine drainage (AMD) is a global problem, occuring in most of the mining regions in the world, associated with the exploitation of coal and metals in sulfide-rich mines. However, this process is not exclusive to mining operations. It may occur in areas where there has never been mining. The required condiction for the development of acidic contamination is the presence of rocks with sulfide minerals, being excavated or exposed to weathering conditions. In such natural conditions, the process takes the denomination of Acid Rock Drainage (ARD).

The well-studied AMD has normally higher magnitude, due the grinding and milling for ore extraction. Nevertheless, ARD has similar genesis, properties and effects. It begins with the oxidation of sulfides, promoting liberation of acidity, sulfate and trace elements, as described by the following equations for pyrite (1) and arsenopyrite (2):

$$FeS_{2(s)}+15/4O_{2(g)}+7/2H_2O_{(l)}\rightarrow Fe(OH)_{3(s)}+ 2SO_4{}^{2-}{}_{(aq)}+4H^+{}_{(aq)} \quad (1)$$

$$FeAsS_{(s)}+7/2O_{2(g)}+3H_2O_{(l)}\rightarrow FeAsO_4 2H_2O_{(s)} +SO_4{}^{2-}{}_{(aq)}+ 2H^+{}_{(aq)} \quad (2)$$

When the geology is propitious to the appearance of ARD, the same effects that of AMD are expected to occur. So, the pH of runoff water is usually below 4 and newly formed minerals are commonly to develop. Specifically, sulfates, iron hydroxides and arsenates, as described in equations (1) and (2), are typical mineralogical indicators of both processes.

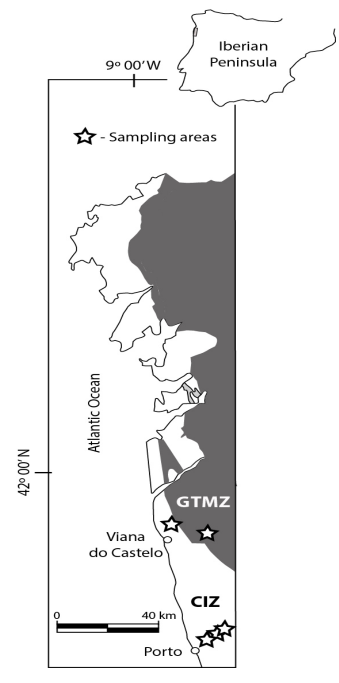
One of the most typical and problematic contexts of ARD arises from the rock excavation for road constructions. Therefore, exposition of road cuts presents the appropriate conditions for the process, directly revealed by the presence of soluble salts and iron oxyhydroxides, as well as acid contamination of surface runoff.

The present study shows evidences of ARD in different road sectors in the North of Portugal: A27 and A28, in the Minho region, IP4 and A3 near Porto. The main objectives of the present work are to: (i) show evidences of ARD in road cuts, relating them with specific lithostratigraphic units; (ii) describe the mineralogical indicators, dominated by soluble salts; (iii) to propose long term rock storage measures to prevent environmental contamination.

Geological setting

The lithologies of the studied sectors belong to different lithostratigraphic units of the Central Iberian Zone (CIZ) and of the Galiza-Trás-os-Montes Zone (GTMZ) (Fig. 1). The CIZ lithologies comprise following units/formations: (i) *Valongo Formation*, characterized by black shales, metassiltites and metapellytes with levels of iron-oxides; (ii) *Xistos Carbonosos Inferiores Unit*, with black shales with intercalations of ampelites and lydites; (iii) *Sobrado Formation* with alternation of psammites and pelites sometimes black (Pereira, 1989). In carbonaceous rocks of these formations there are intense dessimination of sulfide minerals.

Fig. 1 – Location of sampling sites in sectors of Central Iberian Zone (CIZ) and Galiza-Trás-os-Montes Zone (GTMZ).



The GTMZ lithologies belong to two different units: (i) Torre-Amonde unit (Parautochthonous), which contains carbonaceous and black shales with rare lenticules of lydites and gray quartzites (Silurian); (ii) Arga unit (Allochthonous), characterized by millimetric alternations of metassiltites and metapellytes with intercalations of quartz-phyllites and volcanic to volcanoclastic rocks of different chemism, with abundant disseminated sulfides (Meireles et al., 2014).

Methodology

A review of geological information allowed selecting highway sectors potentially affected by ARD. Field surveys were performed in dry season (July-September), in order to assess the presence of ARD and to refine the geological mapping of each area. Then, sampling campaingns were performed to collect samples of salt efflorescences and ochre products. The location of the sampling areas is indicated in Fig. 1.

Samples were collected with plastic tweezers and spatulas and stored in plastic containers. At the laboratory, they were observed and separated under a binocular microscope, based on color and textural differences. Mineralogical identification was performed by x-ray diffraction, by using X-ray powder diffraction (XRD) (Philips PW 1710, APD), using CuKα radiation. This type of sample poses particular problems, which imply the use of an iterative procedure, including scanning electron mycroscopy (SEM) for accomplishing mineralogical identification (Valente et al., 2013).

Salts and ochre crusts were carbon-coated and examined by scanning electron microscope (SEM) equipped with a secondary electron (SE) detector, which gave images of crystal morphology. In turn, an energy-dispersive system (EDS) allowed obtaining spectra with semi-quantitative analysis of mineral compositions.

Results and discussion

The development of ARD is evidentiated in the field by the presence of salt efflorescences with whitish colors and different ocurrences, such as powder, reticulated, globular or rosaseous efflorescences and dry crusts. Also, ochreous colors, associated with iron oxyhydroxides are common observations.

Even representing different lithostratigraphic units, all the sampling sites are covering sectors with sulfide-rich rocks, specifically carbonaceous rocks.

The soluble salts, resulted from the evaporation of the acidic solutions, may occur over extensive sectors of the road cuts, overllaping the extent of the sulfide-rich rocks. Fig. 2 shows a field image of an affected sector.

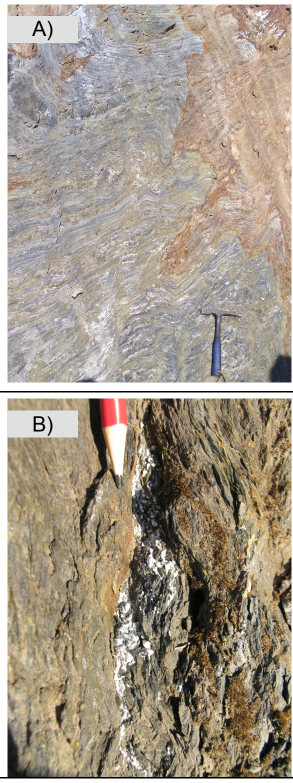


Fig. 2 – Field image of cut roads. A) Illustration of the Arga unit with banded levels with sulfide dessimination; B) Detail of white efflorescence of epsomite in rocks of Valongo formation.

Strongest salinization is usually observed on the slopes exposed to south, as a consequence of higher insolation and evaporation.

XRD analyses revealed that soluble salts are dominated by magnesium sulfates, particularly hexahydrite and epsomite. There are also aluminum sulfates, with dominance of pickeringite (Table 1).

Table 1 – Secondary minerals identified in the road cutsand relative abundance

Mineral	Ideal Formula	Abundance
Epsomite	$MgSO_47H_2O$	(++)
Hexahydrite	$MgSO_46H_2O$	(+++)
Gypsum	$CaSO_42H_2O$	(+)
Pickeringite	$MgAl_2(SO_4)_422H_2O$	(+++)
Alunogen	$Al_2(SO4)_317H_2O$	(++)
Rozenite	$FeSO_47H_2O$	(+)
Jarosite	$KFe(SO_4)_2(OH)_6$	(++++)
Goethite	FeOOH	(++++)

SEM study allowed refining XRD identifications through chemical morphology and compositional data. Fig. 3 presents one of the most typical mineral assemblages, composed by hexahydrite and pickeringite. Composition of hexahydrite includes trace amounts of Al, Si, Mn, Ni, and Fe. The secondary morphology is monotonous and the rareness of iron sulfates, except jarosite, is noteworthy.

The relevance of this salinization relies on potential environmental and geotechnical implications. So, it is important to avoid the use of the excavated rocks for geotechnical proposes, such as paving. Also, these sulfide-rich materials must be carefully stored in appropriate landfills.

Conclusion

The present work showed evidences of ARD in several highway cuts. Goethite, jarosite and and Mg-Al sulfates are the most abundant minerals. Abundance of Mg-Al sulfates indicates dissolution of sulfide host rocks with high contents of minerals, like micas, namely chlorite. The same sulfates were found independently of the lithostratigraphic unit. This can be explained by the common occurrence of carbonaceous rocks and volcanic to volcanoclastic rocks, both with sulfides. The presence of sulfide-rich black shales seems to be the triggering factor for higher magnitude of ARD. Protection of water and structural safety of the road cuts must be considered, namely through encapsulation of the affected sectors.

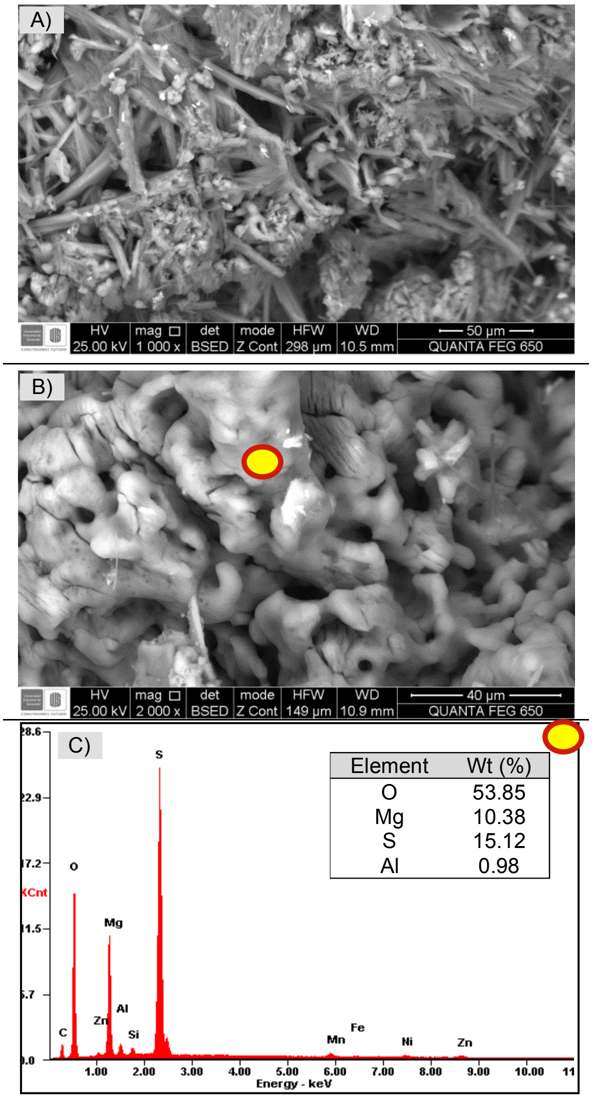


Fig. 4 – SEM data of salt efflorescences. A) hexahydrite and pickeringite (acicular); B) Detail of hexahydrite; C) EDS spectra for chemical composition of hexaydrite.

Acknowledgements

This work was co-funded by the EU, based on COMPETE 2020, project ICT (UID/GEO/04683/2013), reference POCI-01-0145-FEDER-007690, national funds provided by FCT.

Referências

Meireles C, Pamplona J, Castro P., 2014. Lito e tectono-estratigrafia da Unidade do Minho Central e Ocidental: uma proposta de reclassificação. Comum. Serv. Geol., 101, 269-273.

Pereira, coord., 1989. Carta Geológica de Portugal, Folha 1, escala 1:200.000; Serv. Geol. Portugal, Lisboa.

Valente, T., Grande, J., de la Torre, L., Santisteban, M., Cerón, J., 2013. Mineralogy and environmental relevance of AMD-precipitates from the Tharsis mines, Iberian Pyrite Belt (SW, Spain). Appl. Geochem. 39, 11–25.