Potential of reuse and environmental behaviour of ochre-precipitates from passive mine treatment

Marcel Antunes[1], Ricardo Fernandes[1], Avelino Pinheiro[1], Teresa Valente[1], Sérgio Nascimento[2]

[1]*Centro de Investigação Geológica, Ordenamento e Valorização de Recursos (CIG-R) – Universidade do Minho, Campus de Gualtar, 4710—057 Braga, Portugal, teresav@dct.uminho.pt*
[2]*Centro de Física – Universidade do Minho, Campus de Gualtar, 4710—057 Braga, Portugal*

Abstract This work aims to characterize the waste sludge formed by neutralization in a passive mine water treatment system (Jales plant, Portugal). These waste materials were designated as ochre-precipitates, since they are mainly iron oxyhydroxide, specifically ferrihydrite, in accordance with the mineralogical study by X-ray diffraction. Other properties, such as colour parameters in the colour space L*a*b*, thermal behaviour and metal content are presented. The obtained results help to evaluate the ochre potential for reuse as industrial pigments. They also give information about the toxic behaviour, in order to assist the waste management process of this passive system.

Key Words Mine water, passive treatment, ochre-precipitates, colorimetric parameters, Jales, Portugal

Introduction

Passive systems for mine water treatment are especially appropriated to deal with acid mine drainage (AMD) from abandoned mines. Low-cost, particularly important in such long-term operations, low and infrequent maintenance and less production of waste sludge are major advantages of passive treatment over the conventional active systems. These last demand the constant supply of chemicals and energy. The advantages of the passive strategies arise from the principle of natural attenuation, as they simulate and take advantage of a variety of processes that normally run on Nature. Other considerations about the different types of passive systems, as well as respective advantages and limitations were reviewed by Johnson and Hallberg (2003), Younger et al. (2002) and López-Pamo et al. (2002). The present work deals with data obtained in a passive system for mine water treatment (Jales mining site, Portugal), regarding the properties of the resulted waste sludge.

The Jales plant was planned as part of the rehabilitation project of the Jales mining site (Northern Portugal; www.edm.pt), in order to treat the acid mine drainage (AMD) that flows from an old adit. The general properties of the effluent may be consulted at Loureiro (2007). The layout of the system includes two wetlands planted with typha and an initial inorganic stage. This comprises a reception basin, a cascade aeration facility and a limestone channel (Fig. 1). In conjunction, they promote neutralization and precipitation of metals as ferric hydroxide sludge, generating the ochre-precipitates under study. Eq. (1) illustrates the generic combined process that involves iron oxidation, hydrolysis and sedimentation of ochre-precipitates.

$$Fe^{2+} + 1/4O_2 + 2HCO_3^- \longleftrightarrow FeOOH + 2CO_2 + 1/2H_2O \tag{1}$$

The potential of these kind of precipitates as economic resource, for instance as industrial pigments, has been subject of extensive investigation in the last few years (Batty and Younger, 2004; Hedin, 2002, 2007; Kirby et al., 1999; Fenton et al., 2009). This paper is focused on the ochre-precipitates from Jales plant. Properties such as colorimetric features, thermal behaviour and metal contents are presented, in order to evaluate their potential for reuse, to deduce their pollution potential and, therefore, to assist the waste management process.

Methods

Samples were taken from the limestone channel (Fig. 1) in three consecutive years: 2007 (April and August), 2008 (February) and 2009 (July). This sampling program intents to represent several hydrological and seasonal conditions. The samples were collected as suspended matter at the water surface (CFL) and as coatings on the limestone gravel (C1). Sampling sites are presented in Fig. 1.

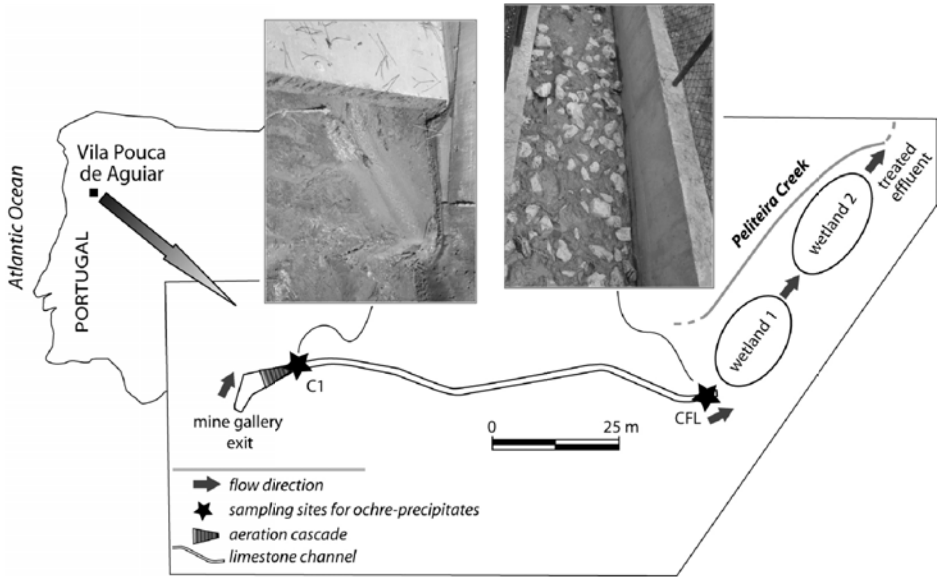

Figure 1 *Location and layout of the passive system under study*

After air-drying at room temperature and sieving to < 63 µm, samples were submitted to colorimetric, geochemical and mineralogical analyses. Loss on ignition at 900 ºC was also determined.

Colorimetric analysis was performed qualitatively, using the Munsell colour system (recording the hue, value and chroma), and quantitatively through the determination of the L*a*b* parameters from the Comission Internationale d'Eclairage (CIE, 1976). According to this notation, L* is a measure of lightness, while a* and b* are two colour channels. The channel a* extends from green to red and the b* channel goes from blue to yellow. These measures were carried out with a SpectraMagic Minolta CM2600D, assuming the following conditions: three consecutive measurements, absence of fluorescence, observer at 10º, Illuminant D65 and absence of specularity.

The mineralogy of the samples was provided by X-ray powder diffraction (XRD), in a Philips PW1710, using Cu-Ka radiation. Scanning electron microscopy (SEM, LEICA S360) allowed to describe the morphology and composition. SEM analyses were conducted on carbon and gold coated samples. Inductively coupled plasma-optical emission spectrometry (ICP/OES) was used for chemical analyses, after an extraction with Aqua Regia.

Samples from the year 2008 were selected to perform heating experiments in a muffle furnace, accordingly with procedure described by Brindley and Brown (1980). This included sequential heating, with mineralogical control by XRD, at the temperatures 280°C, 350°C and 850°C.

Results

Mineralogy and chemical composition

The results obtained by XRD indicate that ochre-precipitates are typical ferrihydrite, mixed with amorphous ferric arsenate. Upon heating, these initial phases transform firstly to goethite (280 °C) and then to hematite and a crystalline arsenate. Hematite and the arsenate appear well-discriminated at 850°C.

Table 1 *Loss on ignition (LOI) and elemental composition of ochre-precipitates (average of four sampling campaigns)*

	LOI (%)	S (%)	Al (%)	Fe (%)	As (%)	Cd (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
CFL sample	27	0.05	0.21	30.6	5.19	13.7	821	13.3	33	1213

Regarding chemical composition, iron and arsenic are major components, with concentrations around 30% and 5% respectively (Table 1). Follows, by decreasing order of abundance, the elements zinc, manganese, lead, cadmium and nickel.

Colorimetric properties

Macroscopically, the visual attributes of the ochre-precipitates are relatively homogeneous as the water flows through the limestone channel. They show mainly yellowish red and strong brown colours. Table 2 presents the colour properties in the Munsell system for dry samples (CFL/08 and C1/08) and for C1/08 sample after heating at 350°C and 850°C. The results of quantitative colorimetric analysis are shown in table 3, considering the space CIE L*a*b*.

The samples from Jales present colorimetric features that are comparable with the synthetic pigments used as reference (Kirby et al., 1999). The dry samples are in the colour range of the yellow synthetic pigment. Upon heating, the samples became more red, in the range of the Bayer red pigment. This result is in agreement with the mineralogical study, since at 350°C and 850°C prevails goethite and hematite, respectively.

Conclusions

The general properties of ochre-precipitates from Jales are similar to other sludge from passive mine water treatment that proved to have potential for industrial use (Kirby et al., 1999). The colour parameters as well as the iron content are in the range of synthetic pigments, in accordance with the values presented by the cited authors. This suggests that ochre-precipitates could be recoverable as pigments, minimizing the costs and the environmental effect associated with waste disposal. This possibility could be economically interesting for the Portuguese market (e.g. pigments for coloured bricks), specially because at the moment there is no indication of other passive systems that are recovering ochre-precipitates. Nevertheless, if this option will be considered for Jales plant, their potential toxic behaviour should be taken into account. The high arsenic content (mean 5,1%) will not probably affect the value of the precipitates as pigments (Manasse and Mellini, 2006) since colour is more dependent on other parameters such as crystallinity (Schwertmann and Cornell, 2000). However, such enrichment in arsenic strongly affects the environmental properties of the ochre-precipitates and may control the options for reuse or final waste disposal. Since ochre-precipitates are key materials in this type of treatment systems, their properties, namely

Table 2 *Colour properties in the Munsell colour system*

Samples	Munsell color reference	Munsell color name
CFL/08	7.5YR 5/6	Strong brown
C1/08	7.5YR 5/8	Strong brown
C1/08-350ºC	5YR 4/6	Yellowish red
C1/08-850ºC	10R 3/6	Dark red

Table 3 *Colour parameters in the space L*a*b* (average of three consecutive measures). §Parameters of reference industrial pigments are provided by Kirby et al (1999)*

Samples	L*	a*	b*
CFL/08	51.0424	16.0499	37.324
C1/08	50.7344	18.808	38.6903
C1/08-350	44.8983	20.5878	36.2744
C1/08-850ºC	34.880	34.6599	28.080
Reference Pigments			
Syntetic pigment§ (Bayer red 130M)	38.98	31.80	24.75
Syntetic pigment§ (Bayer yellow 940)	64.05	13.74	62.66

the hazardous potential highlighted by the high metal contents, and the influence of the heating products for industrial re-use will be worthy of further research.

Acknowledgements

The authors thank to EDM (Empresa de Desenvolvimento Mineiro, S.A) for providing access to the water treatment plant. The Centro de Investigação Geológica, Ordenamento e Valorização de Recursos (CIG-R) is supported by the Pluriannual program of the Fundação para a Ciência e a Tecnologia, funded by the European Union (FEDER program) and the national budget of the Portuguese Republic.

References

Batty L, Younger P (2004) The use of waste materials in the passive remediation of mine water pollution. Surveys in Geophysics 25:55—67

Brindley GW, Brown G (1980) Crystal Structure of Clay Minerals and Their X-Ray Identification. The Mineralogical Society, London

CIE (1976) Colorometry L*a*b* scale, Commission Internationale de L'Eclairage, Publication No. 15, Supplement No. 2, Paris

Fenton O, Healy MG, Rodgers M, Huallacháin DO (2009) Site-specific P absorbency of ochre from acid mine-drainage near an abandoned Cu-S mine in the Avoca-Avonmore catchment, Ireland. Clay Minerals 44:113—123

Hedin RS (2002) Recovery of marketable iron oxide from mine drainage. Proceedings of the National Meeting of the American Society of Mining and Reclamation – Lexington, p 517—526

Hedin RS (2007) Self-sustaining mine drainage treatment through the passive production of marketable iron oxide sludge. Proceedings of Engineering Sustainability Pittsburg PA (extended abstract).

Johnson, DB, Hallberg, KB (2003) Acid mine drainage remediation options: a review. Science of the Total Environment 338:3—14

Loureiro C (2007) Sítios mineiros abandonados – monitorização de efluentes e acompanhamento de uma obra de reabilitação. BSc Thesis, Universidade do Minho, Portugal

Kirby CS, Decker SM, Macander NK (1999) Comparison of color, chemical and mineralogical compositions of mine drainage sediments to pigment. Environmental Geology 37:243—253

López-Pamo E, Aduvire O, Barettino D (2002) Tratamientos pasivos de drenajes ácidos de mina: estado actual y perspectivas de futuro. Boletín Geológico Y Minero 113:3—21

Manasse A, Mellini M (2006) Iron(hydr)oxide nanocrystals in raw and burnt sienna pigments. European Journal of Mineralogy 18:845—853

Schwertmann U, Cornell RM (2000) Iron oxides in the laboratory – preparation and characterization. 2nd ed., Wiley-VCH, Weinheim

Younger P, Banwart S, Hedin R (2002) Mine water: hydrology, pollution, remediation. Kluwer Academic Publishers, Dordrecht