

Detailed slag characterization relevance in environmental and economic assessments; the example of São Domingos (Iberian Pyrite Belt, Portugal)

Relevância da caracterização detalhada de escórias em avaliações económicas e ambientais; o exemplo de São Domingos (Faixa Piritosa Ibérica, Portugal)

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Abstract

Slag piles at São Domingos represent $\approx 8\%$ of the mine residues accumulated in that place, recording discarded outputs of the ore smelting carried out in different periods of the massive sulphide and its iron hat exploitation. The major constituents of modern slag (produced between 1934 and 1962) are crystalline silicates (mostly olivine and pyroxene), magnetite and glass; accessory amounts of sulphides and metal alloys are also present, sometimes coupled by sulphosalts. The modern slag is typically Fe-rich (30-40%) and contains up to 1.7% Zn, 0.9% Pb and 0.5% Cu, besides minor to trace contents in many other metals (e.g. Mn, Sb, Co, As, In, Ag, Bi, Ge). Weathering effects are observed in many slag fragments, denoting significant chemical reactivity of their glassy component and providing support for interpreting slag piles as potential sources of some metal pollutants. Further use of this slag as an economical by-product for the manufacture of aggregates must not ignore its compositional features; the needed previous re-smelting or other alternative chemical handling for this purpose may, additionally, offer the possibility to obtain subsidiary amounts of valuable and diverse metal concentrates.

Keywords: Metal-rich slag, Recycling and recovery, São Domingos, Iberian Pyrite Belt

Resumo

O acervo de escórias em São Domingos constitui $\approx 8\%$ dos resíduos mineiros acumulados naquele local, representando rejeitados pirometalúrgicos obtidos em diferentes períodos da exploração dos sulfuretos maciços e produtos resultantes da sua alteração supergénica. Os principais constituintes das escórias modernas (produzidas entre 1934 e 1962) são silicatos cristalinos (essencialmente olivina e piroxena), magnetite e vidro; as fases acessórias compreendem sulfuretos e ligas metálicas, por vezes acompanhadas por sulfossais. As escórias modernas são tipicamente ricas em Fe (30-40%) e contêm até 1.7% Zn, 0.9% Pb e 0.5% Cu, para além de concentrações traço em diversos outros metais (e.g. Mn, Sb, Co, As, In, Ag, Bi, Ge). Os efeitos da meteorização são observáveis em muitos fragmentos de escória, denotando reactividade química significativa da sua componente vítrea e fornecendo argumentos que substanciam a possibilidade das acumulações de escórias serem fontes potenciais de alguns poluentes metálicos. O uso destas escórias como matéria-prima na manufactura de agregados não pode ignorar as suas características composicionais; a necessidade de recorrer a processos pirometalúrgicos ou a outros tratamentos químicos prévios, poderá permitir a obtenção de quantidades subsidiárias de diversos concentrados metalíferos com valor económico.

Palavras-chave: Escórias metalíferas, Reciclagem e recuperação, São Domingos, Faixa Piritosa Ibérica

Introduction

São Domingos is a volcanogenic massive sulphide deposit located in the Portuguese segment of the Iberian Pyrite Belt that was subjected to intermittent but significant exploitation since Roman times till 1966 (Matos *et al.*, 2006, and references therein). Mining activity led to the production of large volumes of residues ($\leq 15 \text{ km}^3$) that were dumped near different mining facilities. Comprehensive mapping of these mining residues (Matos, 2004) enabled to delimit different types of piles which, according to their compositional nature and internal organisation, record the advance of the exploitation work and of the ore treatment / benefiting through distinct processing stages (e.g. physical refining, roasting and smelting). All these piles have significant amounts of metals (e.g. Matos *et al.*, 2003) that reflect primarily the efficiency of the methods used in ore exploitation and processing along time. The slag piles are just a small part ($\approx 8\%$) of the total mine residues accumulated at São Domingos; yet they put many challenges concerning their management either as a source of pollution (of soils, surface and ground-waters), or as a potentially valuable by-product (*i.e.* a residue that can be reprocessed in accordance with environmental best practices). The modern slag piles represent $\approx 7.4\%$ of the total slag accumulation at São Domingos and are an output of the Orkla metallurgic process used by the company Mason & Barry between 1934 and 1962 (Vara, 1963; INETI-Beja Technical Reports).

In this work, data concerning modern slag are reported and discussed with a twofold objective: (i) to identify the metals present and their distribution in the slag-forming phases; and (ii) to assess slag stability when weathered over a long period of time.

Sampling and analytical methods

At São Domingos, two distinct modern slag piles were sampled: one adjoining the abandoned open pit, the other near the smelter facility at Achada do Gamo (3 km downstream). The collected samples were comprehensively examined by means of optical microscopy, X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray spectroscopy, and particle induced X-ray emission microanalysis. Additional quantitative data were obtained by image analysis techniques, using the Leica QWin V3 software coupled to an optical microscopy digital image acquisition system.

Macroscopic features

The modern slag piles show distinct macroscopic features: (1) the pile preserved in the vicinity of the abandoned open pit (**S1**) comprises fine (and oxidised) fragments of granular slag and coarse fragments of massive black-greyish slag that display discontinuous weathering coatings (either consisting of Fe-hydroxides or of Cu and Fe sulphates); (2) the piles located near the old smelter (**S2**) are more homogeneous in granularity and include coarse-grained, massive black slag fragments with glassy appearance that rarely display macroscopic evidence of significant weathering effects and,

locally, occur along with vitreous material of grey-greenish colour.

According to the available technical data, molten slag was dumped into a pit and simply allowed to air cool, solidifying under ambient conditions. Thus, a significant part of the **S1** pile records a relatively late operation of slag disposal and management (1950-1960), leading to heterogeneous mixing of air-cooled slag (the most abundant) and granular slag. The latter, more porous and apparently more reactive, prevails in the northern domain of the **S1** pile and is a result of sporadic rapid water and air quenching; this slag displays typically a lower specific gravity and is composed of angular fragments that show variable degrees of oxidation.

Slag chemical composition

Chemically, **S1** and **S2** are quite similar, the granular and massive sub-types showing the most significant (although slight) variations. The samples analysed display a characteristic Fe-Si(-Ca) composition, with Fe contents ranging from 34 to 43 wt.% and Ca values up to 5 wt.%. The Zn, Pb and Cu concentrations ($\leq 1.7 \text{ wt.}\%$, $0.9 \text{ wt.}\%$ and $0.5 \text{ wt.}\%$, respectively) show this is a metal-rich slag with high S contents ($\leq 3 \text{ wt.}\%$). Other chemical elements, such as Mn, Sb and Co (showing concentrations up to 800 ppm, 538 ppm and 370 ppm, respectively) reinforce that metal-rich signature, which furthermore includes minor amounts of Cr ($\leq 50 \text{ ppm}$), V ($\leq 40 \text{ ppm}$), As ($\leq 20 \text{ ppm}$), In ($\leq 10 \text{ ppm}$), Ag ($\leq 5 \text{ ppm}$), Bi ($\leq 3 \text{ ppm}$), Cd ($\leq 2.5 \text{ ppm}$), Tl ($\leq 2 \text{ ppm}$), Ge ($\leq 0.6 \text{ ppm}$) and Au ($\leq 113 \text{ ppb}$).

A straight comparison between the available chemical data for the modern slag at São Domingos and the grades reported for the dominant metals in the massive sulphide ores here exploited (Cu < 1.5%, Zn < 3%, Pb < 2% and 45-48% S), strongly suggests that the smelting processes used were relatively efficient ($\geq 70\%$) for Cu removal, but much less effective for Zn and Pb.

Slag petrography

On average, the silicate phases (including glass) in massive **S1** occupy nearly 81 vol.%; oxides correspond to $\approx 2 \text{ vol.}\%$ and, together, the sulphides and alloys to $\approx 1 \text{ vol.}\%$. Porosity is of the order of 7 % and the majority of the voids ($\approx 71\%$) presents an average diameter ranging from 5 to 20 μm . Crystalline silicates belong mainly to the olivine- and pyroxene-group minerals and occur as (sub-)euhedral grains together with tiny (sub-)euhedral Fe-spinel grains in the inner parts of slag fragments. Irregular millimetre oxide / sulphide mixed clusters are abundant, showing wormy intergrowth of spinel in sulphides and, rarely, in silicate glass; occasionally, these mixed clusters encircle (sub-)euhedral magnetite grains. The prevailing sulphide is marcassite, often coupled with pyrite or pyrrhotite, and containing accessory amounts of other sulphide phases. Among the latter phases, the Cu-bearing sulphides (chalcopyrite, chalcocite) are the most noteworthy, although Zn-rich phases (sphalerite and/or wurtzite) can be locally important, sometimes together with rare Pb-rich phases (galena and/or sulphosalts). In these mixed aggregates, metal alloys are also common and classified as three types of brass: (1) relatively large (and yellowish) particles that occur associated with sulphide

Cu-phases; (2) tiny and quasi-globular light-greyish particles that seem to occur in close association with Cu- and Zn-phases, most of the times forming textural relationships that are alike to those generated through exsolution processes; and (3) minute white-bluish particles that develop very fine myrmekitic textures in (or adjoining) galena, clearly related to a non-complete decomposition of existing Cu- and Pb-phases. Particles of the former two brass types may occur also within late fractures cross-cutting the sulphide-rich aggregates. The borders of massive **S1** fragments are glassy and display usually fine to very fine disseminations of oxides (magnetite and / or wustite?), rarely accompanied by marmatite; sporadic silicate micro-crystallites can also be observed in this surface domain, showing textures of rapid growth with characteristic dendritic shapes. Late hematite (and/or lepidocrocite?) polyphasic masses, often developing botryoidal textures and sealing the most external voids and fractures, represent the most obvious products of slag weathering.

The granular **S1** is composed of an irregular mixture of heterometric fragments of slag (including glass) and unprocessed ores. These fragments are packed together and incipiently cemented by a poor matrix of fine-grained glass particles. Compositionally, the slag fragments are similar to massive **S1**, enclosing: (i) silicates (olivine and pyroxene-group minerals); (ii) Fe-spinels; (iii) marcassite, often coupled with pyrite; and (iv) accessory amounts of other sulphide phases (Cu-bearing sulphides, yellowish brass particles, galena group and/or Pb-rich sulphosalts phases). As in massive **S1**, tiny and quasi-globular light-greyish particles seem to occur in close association with Cu- and Zn-phases, forming textures generated through exsolution processes. The outer part of slag fragments is mostly formed by glass, which could be the source of the very fine glass particles that cements the pile. The presence of unprocessed ores mixed in the slag, suggests a blending process resulting from the transportation and deposition of larger volumes of residues. Particles of unprocessed ores are rare and their mineralogical composition is mainly pyrite, arsenopyrite, chalcopyrite and sphalerite (showing "chalcopyrite disease" textures), coupled by minor tetrahedrite-tennantite.

Fragments of **S2** are composed of roughly 24 vol.% silicates, as elongated prisms with variable aspect ratios, in a dappled silicate glass which may well be inhomogeneous. Accessory phases include Fe-bearing oxides (≈ 4 vol.%) and sulphides; metal alloys are rare but invariably yellowish brass particles. Total voids make, on average, less than 1 vol.%, showing diameters $\leq 18 \mu\text{m}$. In the inner parts of **S2** fragments, silicate grains are coarse and (sub-)euhedral, showing often optical features suggestive of strong chemical zoning. In this textural context, pyroxene grains are larger than those of olivine and coexist with euhedral to sub-euhedral Fe-spinel grains. In the vicinity of the fragment glassy borders, pyroxene is missing and olivine grains are very elongated, displaying textural arrangements similar to those commonly described as spinifex; this textural feature reflects rapid crystallisation from a significantly under-cooled melt, thus justifying either the absence of pyroxene and/or the sudden break of olivine growth immediately adjoining the chilled borders. In these slag domains, the oxide phase (mostly magnetite)

represents, on average, 5 vol.% and develops either micro-cruciform habits or fine dendrites (from several micrometers to tens of micrometers in size), which are also typical of rapid growth under a fast cooling rate. The outer glassy domains of **S2** contain, in addition, abundant sulphide-rich droplets (about 4 vol.%) with variable size (< 2 to $20 \mu\text{m}$), representing metal-rich phases unable to decant in time during the smelting process and reflecting immiscibility of sulphide and silicate liquids. Detailed characterisation of the larger droplets reveals different Fe- and Cu-rich phases whose textural relationships allow inferring a pre-existing higher-temperature homogeneous phase subjected to a rapid cooling rate. The Cu-rich assemblage typical of many droplets is made of mauve bornite with tawny chalcopyrite exsolutions, occasionally displaying pyrite and chalcocite and showing late fringes of covellite / digenite; occasionally, tiny grains of sphalerite are present, as well as minute brass particles. Galena is rare but represents a significant accessory phase in some larger droplets, occurring with another phase that develops very fine myrmekitic or dendritic textures and was tentatively classified as a member of the galena-clausthalite solid solution. The majority of the small sulphide droplets are composed of pyrite (\pm pyrrhotite), although accessory amounts of chalcopyrite occur usually along their outer domains. Similar sulphide droplets are randomly distributed in the glassy matrix of the slag inner domains and represent, on average, 0.5 vol.%.

Slag-forming phases chemistry

Olivine grains are Fe-rich (≈ 68 wt.%), containing minor amounts of MgO, ZnO, CaO and CuO (up to 0.75, 1.74, 1.16 and 0.40 wt.%, respectively); they are, thus, quasi-pure fayalite displaying limited deviations towards the end-members kirschsteinite (CaFeSiO_4) and willemite (Zn_2SiO_4). Large pyroxene grains are close to hedenbergite composition, although slightly enriched in Fe along with minor Zn (≤ 1 wt.% ZnO). The Fe-spinel shows, as well, significant Zn contents (≤ 1.36 wt.% ZnO) and traces of Pb and Cu (≤ 0.16 wt.% PbO and ≤ 0.08 wt.% CuO), being compositionally equivalent to magnetite with slight deviations towards the franklinite end-member. The Fe-sulphides (marcassite/pyrite and pyrrhotite) display traces (< 1 wt.%) of Zn, Cu and Pb. Sphalerite and/or wurtzite may reveal significant Cu contents (≤ 3 wt.%). The Cu-bearing sulphides show a relatively wide spectrum of compositions, from quasi-pure chalcopyrite, bornite or chalcocite to inhomogeneous sulphide masses interpreted as the result of incipient decomposition of unstable high-temperature phases. These masses record rapid cooling and possibly attest to the former presence of Cu-rich "iss" (intermediate solid solution; e.g. Craig, 2001). Late fringes of covellite/digenite (due to local oxidation of pre-existent Cu-rich phases) display quasi-ideal compositions. The Pb-rich phases are more difficult to characterise given their fine dimension and textural framework; nonetheless, galena chemically close to the ideal composition is present, as well as a Pb-bearing brass with ≈ 11 wt.% Cu (often coexisting with another alloy mainly composed of Zn and Cu).

The SiO_2 -glass component is Fe-rich, displaying relatively high contents of Ca, Zn and Pb (in comparison with the crystalline silicates). In many

surface borders, the glass show evident compositional zoning, the outer bands being characterised by lower contents of Ca, Zn and Pb. This chemical leaching is often coupled by the development of an Fe(-Mn) rich coating, which is compositionally indistinct from the hematite / lepidocrocite zoned masses due to weathering.

Discussion and conclusions

Slag characteristics reflect mainly the chemical composition of the ores and additives used in smelting, being also strongly influenced by the temperature and cooling rates of the melts produced and, subsequently, discarded. During the smelting process, however, the density and viscosity of the molten slag had to be kept low enough to ensure the gravity separation of metal-rich liquids (*sulphide matte*). Under ideal conditions, silicate slag should float on the surface of the *sulphide matte*, concentrating the oxide components of the silicate gangue and additives. Nonetheless, metal-rich droplets unable to decant in time will be incorporated in slag, as observed.

The relative abundance of Fe-olivine (theoretically formed at 1100-1177°C) strongly suggests that the temperature reached in the furnace must have been no less than 1200°C. The melts produced should not have been very rich in Ca, the available Ca being incorporated in the early formed pyroxene; subsequent olivine, coeval with magnetite, is therefore Ca-poor. The prevalence of these crystalline silicates together with the absence of melilite, indicate also that the slag was cooled and quenched quickly or under a fairly fast rate; this is consistent with the observed textures. When the cooling rate is too fast, pyroxene crystallisation is inhibited and olivine crystallises with spinifex texture and the dominant spinel develops a dendritic habit.

As crystallization of the silicate melt proceeds, the available base-metal content will be redistributed among several crystalline phases and residual glass. The *sulphide matte* should have fixed the greater part of the existing Cu, but not the Zn and Pb. Zinc, being vaporized or dissolved in silicate melt (Gilchrist, 1989, quoted by Ettler *et al.*, 2001), can be afterwards condensed as oxides or ZnS globules trapped by the molten slag (Chaudhuri and Newesely, 1993), or further incorporated into the early mineral structures. However, since the formation of melilite and of large amounts of pyroxene is prevented, the amount of Zn in the early mineral structures will be very limited, thus remaining in the glassy matrix; note also the low Zn contents in olivine and magnetite. Lead, on the contrary, behaves as an "incompatible element" and will be concentrated either in residual glass or in Pb-rich phases trapped in glass.

Slag is typically porous and chemically reactive, forming secondary mineral phases by reaction with air and surface waters. The surface-deposition zone probably results from the dissolution of the nearby metallic fraction (massive matte or sulfide-metallic inclusions trapped within the glass), succeeded by precipitation of secondary phases from the metal-rich solutions. The chemical composition of these precipitates, as well as those filling late fractures, is variable, although clearly dominated by a complex mixture of Fe oxy-hydroxides locally enriched in Cu-, Fe- (and Pb-) sulphates. Slag with

high glass content is potentially environmentally more hazardous (Eusden *et al.* 1999, quoted by Ettler *et al.*, 2001). The hazard quantification is at present impossible but is not very intense, as shown by the slight development of the alteration rims, provided the slag accumulations are left undisturbed. In the long run, or if subject to continuous mechanical disturbance, the slag will release considerable amounts of metals; therefore the slag should not be put to use without a previous programme of re-smelting or other alternative chemical handling in order to reduce its metal release ability. During this treatment, economic recovery of metals cannot be ruled out.

Finally, it should be noted that the São Domingos slag (like many other Fe-rich and air-cooled processed slag) shows favourable mechanical properties for aggregate use, including excellent sound characteristics, good abrasion resistance, and good stability (high friction angle due to the sharp fragment shapes).

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