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Characterization of cast iron and slag produced by jarosite sludges reduction via Arc Transferred Plasma (ATP) reactor

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ABSTRACT

Jarosite process is the most widely adopted method for zinc production via a hydro-metallurgical route. Jarosite sludges are classified as hazardous waste by the European Waste Catalogue. Up to now, jarosite sludges were stored in lined pounds within the zinc refinery, representing a pollutant source for subsurface and groundwater. Landfilling is possible only after a stabilization treatment that covers twice the amount of waste to be disposed of. In this paper, a new method to recover the residual iron content within jarosite sludges through an Arc Transferred Plasma (ATP) reactor is presented. Reduction of jarosite sludge leads to the production of cast iron, accompanied by the formation of a glassy inert slag that can be easily disposed of in inert waste landfills, or better, recovered as alternative to stone materials. This process results in the recovery of the whole amount of jarosite sludges, reducing to zero the waste to be disposed of.

1. Introduction

Worldwide, the refined zinc metal production accounts for 13 million tonnes (Mt), China being the world's largest producer with 5 Mt in 2014 [1,2]. Approximately, 50% of produced zinc is employed for steel galvanizing [3].

The most widely used ore in zinc production, commonly known as zinc blend, is zinc sulphide sphalerite ((Zn,Fe)S). Zinc can be produced by both pyro-metallurgical processes and hydro-metallurgical processes. About 85% of the world's total zinc output is produced through the conventional hydro-metallurgical route, i.e. the roast-leach-electrowin (RLE) route [4]. In order to maximise zinc extractions, leach residues (mainly zinc-ferrites, a by-product of leaching process) are treated to hydrolyse their iron content into disposable jarosite/goethite/hematite. Romero and Rincon [5] have estimated at 600,000 t/year the zinc waste produced in 1997 within European Union, though probably this value has risen by now [6].

Specifically, jarosite is a potassium-iron-sulphate-hydroxide mineral that can accommodate many other elements to produce chemically diverse varieties. Intermediate jarosites consist in mixtures of alkali-site cations (for example, K^+ and Na^+, or H_3O^+ and K^+) to form different end-members, namely, natrojarosite [$NaFe_3(SO_4)_2(OH)_6$], hydronium jarosite [$H_3OFe_3(SO_4)_2(OH)_6$], ammoniojarosite [$NH_4Fe_3(SO_4)_2(OH)_6$] and plumbojarosite [$PbFe_6(SO_4)_4(OH)_{12}$]. This material is deemed a hazardous waste (CER 110202*) because of the content of toxic elements such as Cd, Zn, Pb, As [7] and sludge acidity (pH 2); therefore, jarosite is usually stored in lined ponds close to the zinc refinery. With or without liners, pollution of the subsurface and groundwater with toxic metals is only a matter of time, because these liners are only guaranteed for a limited number of years [8]. Lined ponds are only a temporary solution, and the search for alternatives must continue. For example, washing jarosite can decrease its environmental threat and can improve the zinc recovery. Nevertheless, this operation is expensive and requires further water treatments to avoid groundwater pollution. In addition, jarosite must still be stored in lined ponds [8]. Thus, its worldwide disposal has become a major environmental concern.

As regards the Italian regulatory framework, hazardous waste must be disposed of in dedicated landfills, which are associated with high disposal costs due to their low number and limited size [9]. The possibility of stocking hazardous wastes in a non-hazardous waste landfill depends upon the leachability of specific substances, i.e. Zn, Cd, As, Pb. At present, jarosite waste needs to be subjected to a stabilization treatment that can limit the leaching of some metals (Cd, Cu, Pb, Zn, Hg) and soluble salts (sulphides, chlorides) in order to be disposed of as non-hazardous waste, since untreated sludge does not comply with the maximum allowable values [10]. Actually, as indicated in the European

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BAT (Best Available Technology), jarosite precipitates are stabilized with Portland cement, lime and water, and disposed of in non-hazardous waste landfills, exploiting the so called jarofix® process [11]. However, the amount of additives (lime and cement) affects the overall amount of waste to be disposed of, since they account for 15–20% wt. of the jarosite mass. In addition, a high amount of water (to reach an additive/water ratio equal to 1) is needed to start up the reaction, and almost all the added water remains fixed in the deactivation process, contributing to further increase the waste mass.

Several other attempts have been proposed to recycle jarosite and reduce its environmental impact. For example, jarosite can be used as a substitute for natural gypsum in cement production [12], mixed with granites to produce glass type materials [13–16], or it can be mixed with sand and coal combustion residue (CCR) for developing value added products, i.e. clay bricks [17,18]. The high fraction of residual iron oxide (close to 50% wt.) pushed the researcher to develop economically suitable methods to recover iron in the form of hematite or magnetite via alkali decomposition [19] or hydrothermal reduction [20]. However, no indications about the health risks associated with the waste residual were analysed.

A new process for treating jarosite has been recently developed. This by-product was used as raw material in an arc transferred plasma (ATP) furnace, with the aim of recovering the iron oxide fraction and transforming it into valuable Fe-base product. Moreover, through the use of a plasma furnace, the vitrification of residual oxide fraction is possible. Firstly, jarosite sludges were dehydrated and calcined up to 1000 °C in a rotary kiln, in an attempt to remove imbibition and crystallization water, and to reduce the total sulphur content by decomposition of metal sulphates. Formed SO_x were recovered to produce sulphuric acid. The resulting fraction (calcine) was reduced in an arc transferred plasma (ATP) reactor at 1600–1700 °C by the addition of metallurgical coke (as reducing agent) and limestone (to adjust the basicity to $BI_2 = 0.3$) acting as flux. The reduction reaction led to a separation among a metallic magnetic fraction, a non-magnetic fraction (indicated as slag) and a dust fraction, obtained from the exhaust gases treatment. The process flow-sheet is reported in Fig. 1.

The overall process energy consumption is estimated at 1.3 MWh per ton of treated jarosite. After the first step (dehydration and calcining), the fed mass of jarosite sludge is more than halved, leading it to transform approximately 20% of weight into sulphuric acid. The dehydrated and calcined jarosite, mainly formed by hematite [22], is then milled to homogenize its size and, mixed with metallurgical coke and limestone, to obtain the desired FeO_x/C ratio and basicity ($BI_2 = CaO/SiO_2$). This compound is charged into the arc transferred plasma furnace leading to the production of cast iron, slag and dust.

For these experiments, the calcine reduction treatment was performed in semi-continuous mode (semi-batch) in a 15 l volume laboratory furnace, equipped with graphite electrodes and an installed power of 40 kW. Each batch consists of about 10 kg of feeding material (calcine plus additives). The whole study involved the treatment of about 300 kg of jarosite. The tap-to-tap time of a single batch was about 30–35 min. The ATP was lined with acidic refractories to prevent any interaction with the slag. The external structure of the reactor is built in stainless steel, with cooling system and temperature control devices. The safety refractory linings (between stainless steel case and reaction chamber) is built in high aluminous refractory.

The extracted dusts represent 6% of the material charged in the ATP; they contain mainly Zn, Pb and Ag, and can be internally recovered by being inserted at the beginning of RLE route as raw material or used in the Waelz process to recover Zn, Pb and Cd [23,24].

The metallic fraction extracted from ATP is nearly half of the charged material, as well as the slag.

In this paper, the produced cast iron and the associated slag were characterized from a metallurgical and environmental point of view to highlights the quality of the obtained by-products and to estimate the benefits of the proposed method. The main goal of the proposed approach is to cancel the waste amount associated with zinc hydrometallurgy, producing a valuable Fe-based metallic product, recirculating the dust at the beginning of the RLE process and managing the slag fraction as inert material for civil purposes.

2. Experimental procedure

2.1. Jarosite characterisation

Jarosite were collected from two European plants, the former,

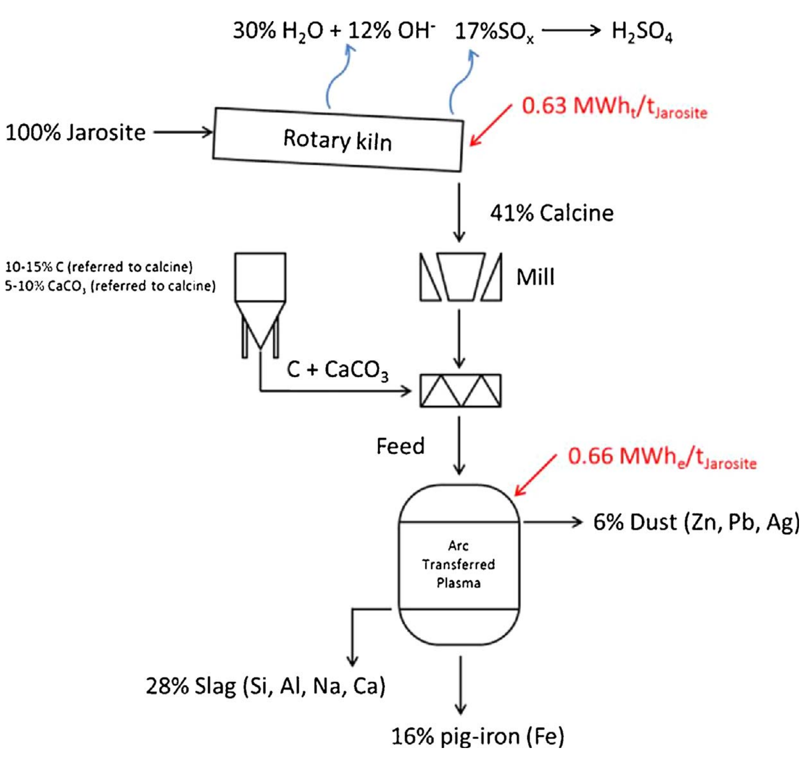

Fig. 1. Schematic ATP process flow-sheet [21].