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Review

Perspectives regarding the use of metallurgical slags as secondary metal resources – A review of bioleaching approaches

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A B S T R A C T

Smelting activity by its very nature produces large amounts of metal-bearing waste, often called metallurgical slag(s). In the past, industry used to dispose of these waste products at dumping sites without the appropriate environmental oversight. Once there, ongoing biogeochemical processes affect the stability of the slags and cause the release of metallic contaminants. Rather than viewing metallurgical slags as waste, however, such deposits should be viewed as secondary metal resources. Metal bioleaching is a "green" treatment route for metallurgical slags, currently being studied under laboratory conditions. Metal-laden leachates obtained at the bioleaching stage have to be subjected to further recovery operations in order to obtain metal(s) of interest to achieve the highest levels of purity possible. This perspective paper considers the feasibility of the reuse of base-metal slags as secondary metal resources. Special focus is given to current laboratory bioleaching approaches and associated processing obstacles. Further directions of research for development of more efficient methods for waste slag treatment are also highlighted. The optimized procedure for slag treatment is defined as the result of this review and should include following steps: i) slag characterization (chemical and phase composition and buffering capacity) following the choice of initial pH, ii) the choice of particle size, iii) the choice of the liquid-to-solid ratio, iv) the choice of microorganisms, v) the choice of optimal nutrient supply (growth medium composition). An optimal combination of all these parameters will lead to efficient extraction and generation of metal-free solid residue.

Contents

1. Introduction

In modern production streams metals are routinely used as

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essential components for a broad array of consumer and industrial electric goods, indispensable for the functioning of modern societies (Hong et al., 1996; Radetzki, 2009; Themelis, 1994). Thus, the demand for metal commodities is increasing every year and metal production capacity needs to be guaranteed and, looking towards the future, expanded. Metal production is mainly achieved through mining, flotation, hydrometallurgical, pyrometallurgical and electrometallurgical processes (Norgate et al., 2007; Roy et al., 2015). Since pyrometallurgy processes account for a considerable percentage of the worldwide metal supply, pyrometallurgical ore processing rates are not expected to decrease in the coming years. Beyond the intentional acquisition of the desired metal(s), the pyrometallurgical industry also produces huge quantities of various waste products including ashes, residues, and slags (Ettler et al., 2009; Jarošíková et al., 2017a, 2017b). Hence, the rates of waste generation and its associated emissions are predictable for the years ahead, and consideration of ways to mitigate the possible environmental impacts and related uncertainties should be prioritized (Bridge, 2000; Dimitrijević et al., 2009; Gordon, 2002). An additional concern of the metal supply market lies in acquiring the resources, mainly because natural deposits of metals (raw metal-bearing ores) are finite and non-renewable. However, a strong contention to this idea has recently been raised by Arndt et al. (2017). Due to the development of new concepts and techniques in mining and processing mineral resources, the real, accessible volume of reserves may be larger than previously estimated (Arndt et al., 2017). Thus, the search for secondary metal resources has recently received increased attention, with the hope that it can help meet the growing demands of the world metal market (Gyurov et al., 2017).

Within the group of waste products generated by pyrometallurgical processing, metallurgical slags account for a significant volume. Generally, industrial activity generates two types of slags: non-ferrous (*i.e.* base metal) slags and ferrous slags. An important feature that differentiates non-ferrous slags from ferrous slags is a lower content of metals in the latter (Piatak et al., 2015). In addition, due to their durability, ferrous slags are commonly utilized in a variety of commercial products (Piatak, 2018). Numerous organizations currently operating on the market deal with the manufacture and application of these ferrous slags (*e.g.* Euroslag-The European Association representing metallurgical slag producers and processors http://www.euroslag.com/; National Slag Association http://www.nationalslag.org/). Due to their high demand, however, base metal slags (non-ferrous) are also produced in large quantities. For example, it is estimated that every ton of copper produced worldwide integrally entails the generation of a double volume equivalent of slags (*i.e.* 2 tons) (Gorai et al., 2003; Roy et al., 2015). Likewise, Sobanska et al. (2000) reported 0.6 ton of slags produced per ton of lead (Pb) in France. Scientific studies dedicated to the reconstruction of smelting conditions under which the ore has been processed also deliver profound information on the volume of slags disposed of in the area of interest (Manasse et al., 2001). Base metal slags have also recently been used commercially as construction materials for roads and buildings, as well as in hydraulic engineering applications (Al-Jabri et al., 2006; Moura et al., 2007; Piatak, 2018; Schmukat et al., 2012, 2016; Shi et al., 2008, 2008). However, there is potential bias against the use of these slags in hydraulic application due to a high risk of contaminant release. Therefore, an intense debate is currently ongoing among researchers as to how these slags should be viewed: as simply a waste product or rather as a metal resource (Duester et al., 2016; Piatak, 2018; Schmukat et al., 2012).

The relatively high residual metal content, combined with the large volumetric quantities of processed base metal (non-ferrous) slags necessitate a full understanding of their environmental and societal impacts. The environmental problems associated with the generation of metallurgical slags goes back many centuries. Until relatively recently, industry disposed of the slags at poorly protected dumping sites without any environmental monitoring from the moment of disposal onward (Ettler, 2016). This resulted in long-term slag exposure to a variety of chemical and biological factors (*e.g.* pH variations, the presence of inorganic and organic acids, microbial communities) collectively termed “Biogeochemical Weathering” (Ettler et al., 2009; Gee et al., 1997; Potysz et al., 2015, 2016a; 2016b; Tyszka et al., 2014; Seignez et al., 2006; Yin et al., 2014). Only recently has it been discovered that biogeochemical weathering may cause the release of metals from deposits of slag into the local environment. Due to a lack of environmental awareness and appropriate oversight, the presence of excessive metal concentrations is a shared characteristic of numerous dumping sites across Europe, and the world at large (Boularbah et al., 2006; Bunzl et al., 2001; Casper et al., 2004; Ettler et al., 2003, 2004; Ettler and Johan, 2014; Gee et al., 1997; Kierczak et al., 2013; Lottermoser, 2002; Manz and Castro, 1997; Morrison, 2003; Parsons et al., 2001; Piatak et al., 2004; Sobanska et al., 2000; Tyszka et al., 2014). Prime examples of European countries with historical metallurgical waste dumping sites include, but are not limited to: Poland, Germany, France, the Czech Republic, Belgium, Spain, Italy, and Portugal (Álvarez-Valero et al., 2009; Ash et al., 2014; Ettler et al., 2011, 2015; 2016; Ganne et al., 2006; Hudson-Edwards et al., 1999; Kierczak and Pietranik, 2011; Manasse et al., 2001; Mateus et al., 2011; Sāez et al., 2003; Scheinert et al., 2009; Seignez et al., 2006; Van Brempt and Kassianidou, 2016). Likewise, many industrialized nations around the world have slag disposal sites, including Australia, the USA, China, Turkey, Chille, some African countries (*e.g.* Zambia, Namibia) and Saudi Arabia (Çubukçu and Tüysüz, 2007; Gonzalez et al., 2005; Ettler et al., 2009; Lottermoser, 2002; Morrison and Gulson, 2007; Piatak and Seal, 2012; Surour, 2015). In such places, the presence of such sites with a lack of proper impermeable barriers designed to prevent metal migration may require remediation actions be taken in order to avoid further contamination. Therefore, sustainable waste management and proper handling methods that could prevent or at least mitigate the environmental inconveniences associated with disposal remain an open debate (Houben et al., 2013). The most reasonable solution to overcome the problem of contamination would be the waste's removal from dumping sites and their utilization in an environmentally friendly manner. The aim of slag reuse stems not only from the desire of the waste management sector to diminish the associated environmental risks, but also to pass on the unused metal resources within the waste to the civil engineering or metal production sector. Therefore, a strong emphasis is still placed on the development of a sustainable slag treatment flow-sheet standing in accordance with an environmentally friendly concept and delivering economic profit at the same time.

At the present time, it is widely known that suitable and sustainable slag application methodology requires critical appraisal of slag stability and its susceptibility to release metals given the right stimulus (Ettler et al., 2003; Khorasanipour and Esmaeilzadeh, 2016; Najimi et al., 2011; Piatak, 2018; Schmukat et al., 2012, 2016). At any point along the slag life-cycle, evaluative steps have to be followed (Fig. 1). These steps involve chemical and mineralogical characterization as well as a determination of slag leachability, all of which jointly determine a slag's properties and thus dictate the appropriate management method to be selected. A strong leachability rating suggests that slags may be successfully subjected to further metal leaching/recovery treatment, whereas poor metal leachability renders slags more suitable for engineering applications. The use of slags as a replacement for natural raw materials,