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Review

Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review

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ABSTRACT

The supply risk for some critical rare-earth elements (REEs), which are instrumental in many cleantech applications, has sparked the development of innovative recycling schemes for End-of-Life fluorescent lamps, permanent magnets and nickel metal hydride batteries. These waste fractions represent relatively small volumes, albeit with relatively high rare-earth contents. Rare earths are also present in lower concentrations in a multitude of industrial process residues, such as phosphogypsum, bauxite residue (red mud), mine tailings, metallurgical slags, coal ash, incinerator ash and waste water streams. This review discusses the possibilities to recover rare earths from these "secondary resources", which have in common that they contain only low concentrations of rare-earth elements, but are available in very large volumes and could provide significant amounts of rare earths. The success rate is set to increase if the rare-earth recovery from these industrial waste streams is part of a comprehensive, zero-waste, "product-centric" valorisation scheme, in which applications are found for the residual fractions that are obtained after removal of not only the rare earths but also other valuable (base) metals.

1. Introduction

For more than two decades, at least 95% of the annual global supply of the rare-earth elements (REEs) has been provided by Chinese rare-earth producers. The tightening of rare-earth export quotas has caused supply risks outside China, as evidenced by the rare-earth crisis of 2011 with record high prices. This situation endangers the secure and sustainable supply of these critical (clean) technology metals, in particular the heavy rare earths, to many economies in the world. Paradoxically, on the positive side, this situation has also stimulated other countries to look for alternative rare-earth resources and to develop their own rare-earth industry. To tackle the rare-earth supply challenge, a threefold approach can be proposed. This strategy is particularly relevant for the heavy rare earths for which the supply risk is far greater than for light rare earths such as lanthanum and cerium. A first component of this strategy is to substitute critical rare earths by less critical metals. Secondly, the supply risk can be mitigated by investing in sustainable primary mining from old or new rare-earth deposits. Mining companies are now actively seeking for new exploitable rare-earth deposits, while old mines are being reopened. A good example is the Mountain Pass Mine in California, which restarted production in 2012. Nevertheless, many non-Chinese mines, such as the Mountain Pass mine, are mostly light rare earth mines and, hence, do not deliver a meaningful stream of the most critical heavy rare earths. Furthermore, many countries such as Japan and most EU Member States do not possess any type of primary rare-earth deposits on their territory. Consequently, they will have to invest in *technospheric mining* (Johansson et al., 2013) of secondary rare-earth containing resources in order to obtain a source of both light rare earths and, particularly, heavy rare earths. This is the third component of the strategy.

Technospheric mining, however, can take many forms. With respect to (critical) metal containing streams, such mining incorporates (1) the direct (preconsumer) recycling of metal scrap and swarf generated during the production of metal based (intermediate) products (as for instance NdFeB magnets) and (2) the (postconsumer) recycling and/or urban mining of, respectively,

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flows and stocks of complex, multi-material, metal-containing products (as for instance a hybrid electric vehicle), (3) landfill mining of historic urban solid waste (Jones et al., 2011), (4) metal recovery from flows of industrial process residues from primary and secondary metal production and, finally, (5) metal recovery from stocks of landfilled industrial process residues, as shown in Fig. 1. When considering the potential for rare-earth recovery from these five secondary sources, it is clear that at present most attention is going out to the direct recycling of scrap and the recycling/urban mining of End-of-Life rare-earth containing products. The state-of-the-art in this domain has been described in detail in recent review papers (Binnemans et al., 2013a; Binnemans and Jones, 2014; Tanaka et al., 2013; Anderson et al., 2013; Innocenzi et al., 2014). The most interesting (heavy) rare earths sources intended for recycling/urban mining are permanent magnets and lamp phosphors (Binnemans et al., 2013a).

In contrast to recycling of rare earths from End-of-Life products, much less attention has been devoted to previously landfilled *stocks* and freshly produced *flows* of rare-earth-containing industrial process residues (Binnemans et al., 2013c) (top part in Fig. 1). In general, these secondary resources contain much lower concentrations of rare earths than the End-of-Life consumer goods that are considered for direct recycling or postconsumer recycling/urban mining activities. Nevertheless, the volumes of these residues are enormous so that the total amounts of rare earths locked in these residues are also very large and may secure an independent source of rare earths as well as shield resource-poor countries from export quotas and price fluctuations. This review paper gives on overview of the possibilities to recover rare earths from the most important industrial process residues. These include residues from metal production (as shown in Fig. 1) – phosphogypsum, bauxite residue (red mud), mine tailings, metallurgical slags – and industrial process residues from thermal treatment facilities (coal ash, incinerator ash). Likewise, it is investigated if waste water streams may be a source of rare earths as well. In all cases the zero-waste valorisation concept is promoted. For more background on the extractive metallurgy of rare earths, the reader is referred to general references (Gupta and Krishnamurthy, 1992, 2004; Habashi, 2013; Xie et al., 2014).

2. Phosphogypsum

2.1. Formation and composition of phosphogypsum

Phosphogypsum is the main by-product of the production of phosphoric acid (H_3PO_4) by sulphuric acid (H_2SO_4) digestion of a concentrated slurry of pulverised phosphate ores (Koopman and Witkamp, 2000). Phosphoric acid is an important raw material for the manufacturing of phosphate fertilisers. Phosphate ores can be divided into two main types according to their origin: sedimentary and igneous phosphate rock (Habashi, 1998). Sedimentary phosphate rock (also known as *phosphorite*) represents about 85–90% of the world reserves and is found in Florida, Morocco and the Middle East. Igneous phosphate rock represents the remaining 10–15% of the world reserves. It is found in the Kola Peninsula (Russia) and Brazil. Phosphate rock varies widely in composition (Becker, 1989). Apatite is the main phosphate mineral in most phosphate deposits (Rutherford et al., 1994). In sedimentary phosphate rock, apatite occurs in an amorphous form: *francolite*. Francolite has a complex chemical composition and can be represented by the formula $(Ca,Mg,Sr,Na)_{10}(PO_4,SO_4,CO_3)_6F_{2-3}$ (Benmore et al., 1983). In igneous phosphate rock, apatite occurs as the variety *fluorapatite*, $Ca_{10}(PO_4)_6F_2$. Phosphate rock also contains trace amounts of many other elements, including thorium, uranium and rare earths. The rare-earth content depends on the type of phosphate rock (Habashi, 1985, 1998) (Table 1). Sedimentary phosphate rock contains 0.01–0.1 wt% of rare earths, but also about 0.01 wt% of uranium. Igneous phosphate rock is much richer in rare earths than sedimentary phosphate rock (1–2 wt%) and contains only very small amounts of uranium. The potential of phosphate rock as a source of rare earths has already been recognised in the 1960s (Anon., 1966). Analysis of phosphate rock from Florida gave a total rare-earth content of 0.059%, with the main elements being lanthanum (0.015 wt%), cerium (0.012 wt%), yttrium (0.011 wt%)

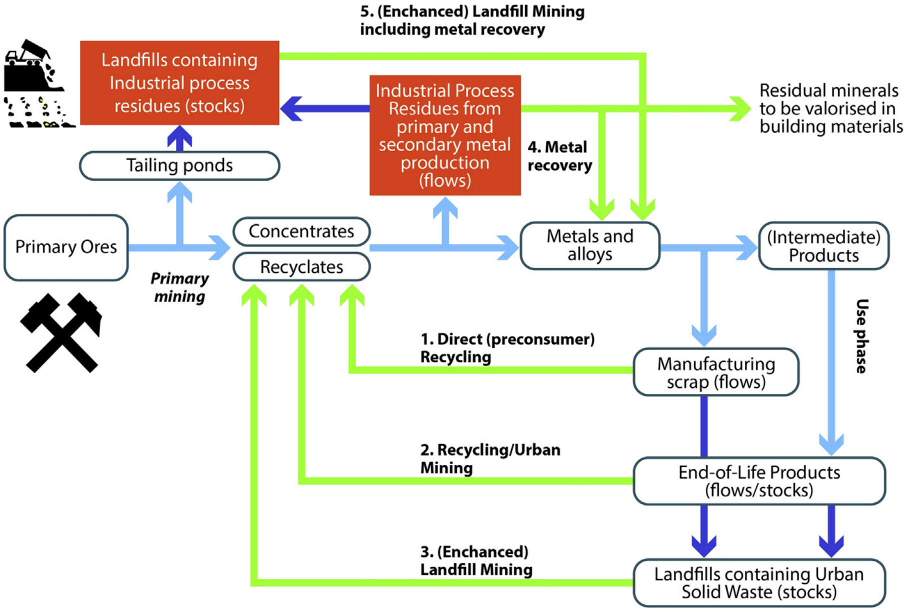

Fig. 1. Closing the loop through technospheric mining, revealing the importance of metal recovery from both flows and stocks of industrial process residues from primary and secondary metal production.