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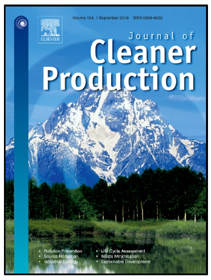

Recovery of rare earth elements from phosphogypsum

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Recovery of rare earth elements from phosphogypsum

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Abstract:
Phosphogypsum is a common large-tonnage waste of phosphoric fertilizers industry. The article describes a technology for complex treatment of a phosphogypsum Sredneuralsky Copper Smelting Plant (Sverdlovsk region, Russia) containing 0.43 - 0.52% of rare earth elements (REE). Joint co-crystallization of REE with gypsum provided a low degree of REE leaching in the direct leaching process. It was shown that combination of mechanical grinding treatment, ultrasonic impact and resin-in-pulp process provided significantly higher degrees of REE leaching from the phosphogypsum (from 15 – 17% to more than 70%). In addition, it was shown that the products after phosphogypsum treatment can be successfully used instead of natural gypsum as an addition for cements in the production of building materials.

Keywords:
Phosphogypsum, Rare earth elements, Acidic leaching, Grinding treatment effect, Ultrasound effect, Waste reprocessing.

Highlights:
- A technology of treatment of phosphogypsum containing 0.4 - 0.5% of REE is described
- 97 – 99% REE concentrate was separated from the phosphogypsum
- Product after phosphogypsum treatment is suitable for building materials production

1. Introduction

At present, raw materials and wastes containing rare earth elements (REE) in EU are considered as critically important materials (EC, 2010; EC, 2014). In contrast to many other countries, Russia has its own sources of raw REE materials and developed technologies for REE recovery (Russia, 2017). Apatite concentrate is considered as the most prospective REE source in Russia (Binnemans et al., 2013). There are two methods of treating apatite concentrate used in Russian phosphoric fertilizers production. The lesser part of apatite (approximately 1 million tons per year) is treated by the nitric acid method; whereas, the greater part (approx. 4 million tons per year) is treated using the sulfuric acid method resulting in formation of phosphogypsum as an industrial waste. Despite a relatively low REE content (~ 0.45%), phosphogypsum may be considered as an anthropogenic source of REE. The main advantage of this REE source is absence of costs for mining and disintegration of a natural raw material. Another advantage of phosphogypsum is absence of natural radionuclides; therefore, deactivation of REE and deposition of radioactive waste are not necessary. According to various assessments, there are 250 to 500 million tons of phosphogypsum in Russia (Lokshin and Tareeva, 2015).

Formation of phosphogypsum as a waste at the Sredneuralsky Copper Smelting Plant (Sverdlovsk region, Russia) was conditioned by a widespread interbranch cooperation of non-ferrous metallurgy and chemical industry at 1960s in USSR. Use of sulfide ores of non-ferrous metals resulted in an intensive release of sulfur oxides. Therefore, many non-ferrous metallurgical plants (e.g., Mednogorsk Copper and Sulfur Complex) produced sulfur and sulfuric acid besides target metals. A great quantity of cheap sulfuric acid made it profitable to produce phosphoric fertilizers using imported raw materials such as apatite or phosphorite (Ptacek, 2016).

Approximately 11 million tons of phosphogypsum was accumulated for more than 30 years of double superphosphate production at the Sredneuralsky Copper Smelting Plant. It was found that the average content REE oxides in this phosphogypsum is 0.43 – 0.52%. Therefore, total amount of REE in the phosphogypsum is estimated to be approximately 50,000 tons.

Despite a significant quantity of works focusing on development of technologies for phosphogypsum treatment, today there is no commercially acceptable technology for reprocessing this type of waste (Binnemans et al., 2015). Existing technologies either only are lab-scale rather than commercial scale (whereas, one big plant may produce annually up to two million tons of phosphogypsum) or do not provide for REE recovery from phosphogypsum (Canovas et al., 2017).

There are several technologies developed for a partial phosphogypsum treatment with REE recovery (Binnemans et al., 2015). One of them is based on thermal decomposition of phosphogypsum resulting in formation of phospholime (calcium oxide contaminated by phosphates) and sulfur dioxide. After this, REE are separated from phospholime resulting in formation of phosphochalk (calcium carbonate contaminated by phosphates). Sulfur dioxide may be trapped and used for sulfuric acid production (Bu et al., 2011). Another method includes leaching phosphogypsum by sulfuric acid resulting in transfer of phosphorus and lanthanides to the solution and formation of gypsum precipitate. After leaching, the gypsum precipitate is filtered and then REE concentrate is precipitated from