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Evaluation of Phosphogypsum as a Secondary Resource: Effect of Commercial Acid Treatment on Purification Efficiency

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Abstract

Phosphoric acid is mainly produced via wet process method, based on the dissolution of phosphate ore in sulphuric acid. Phosphogypsum (PG) is a by-product of wet process, being generated 5 tons per 1 ton phosphoric acid. PG has an estimated 200-280 Mton of generation rate annually, only 15% being recycled and the rest 85% amount of untreated PG piles occupy large amounts of landfills. These PG piles attract attention in terms of environmental concerns, promoting searching of new alternative recycling processes. Valorization of PG as construction material offers a promising solution since it allows continuous consumption of PG stacks. Studies searching for a sustainable recycling of PG are generally conducted in cement industry. However, containing of a considerable amount of SO_4 groups makes PG unsuitable for re-use in cement industry, since excess SO_4 groups further react with C_3A (tricalcium aluminate phase) during hydratation of cement. This study focuses on the determination of optimum washing parameters of PG in terms of SO_4 removal. Washing experiments were conducted with H_2SO_4 pre- treatment, then water. It was concluded that SO_4 removal from PG can be effectively carried out with H_2SO_4 treatment, making PG a suitable material for use in cement industry.

Keywords: Phosphogypsum, Re-use, Sustainability, Purification

1. INTRODUCTION

Phosphoric acid is the main raw material in commercial phosphate-based fertilizer production. More than 90% of phosphoric acid is produced via wet process. Wet process phosphoric acid production can be explained as the dissolution of phosphate ore in sulphuric acid, generating 5 tons of phosphogypsum (PG) per 1 ton of phosphoric acid. Although wet process phosphoric acid is economically feasible, its main disadvantage is the generation of huge amounts of PG. Obtained PG is generally stored as stockpiles without any further treatment, occupying large amounts of landfills exposed to the environment, thus PG stockpiles are gaining attention in terms of environmental concern [1,2]. Recycling of PG is mostly conducted as construction material such as roadbed material, set retarder for cement, plaster board manufacturing etc [3]. Hovewer only 15% of PG is being recycled, rest 85% is stored without any further treatment due to its heterogenous structure. PG can basically be defined as ($CaSO_4.2H_2O$) similar the gypsum but depending on the origin of the phosphate ore utilized in phosphoric acid manufacturing process PG can also contain some impurities such as heavy metals, rare earth elements, fluorides, sulphates and trace elements [4,5]. Containing of considerable amount of SO_4

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groups makes PG unsuitable for re-use in cement industry, since excess SO_4 groups further react with C_3A (tricalcium aluminate phase) during hydratation of cement. In this study, PG samples were pre-treated with H_2SO_4, followed by washing with water. After filtration, cake samples were characterized with ICP-OES. According to results it is concluded that SO_4 removal from PG can be effectively carried out with H_2SO_4 treatment, making PG a suitable material for use in cement industry.

2. EXPERIMENTAL

PG sample was provided by a local fertilizer manufacturer. Sulfuric acid solution was prepared via a ready-to-use kit (Merck Titrisol 109981 Sulfuric acid). Ultrapure water (UPW) was prepared in Merck Millipore Direct-Q 8 UV Remote Water Purification System. SO_4 content of samples were measured with Agilent 5110 ICP-OES.

0.5 M sulfuric acid solution was prepared with Merck Titrisol ready to use kit. Prior to washing procedure, PG samples were pre-treated with 0.5 M H_2SO_4 solution in 1:10 and 1:20 solid:liquid ratios. After addition, experiment sets were stirred, sample taken and filtered. Acid treated PG was further washed with UPW in 1:10 and 1:20 solid:liquid ratios in both 500 and 1500 rpm mixing rates.

3. RESULTS & DISCUSSION

Untreated solid PG sample contains 15.4 wt % SO_4. According to results of dilute conditions (1:20 of solid:liquid ratio) and rapid stirring rate (1500 rpm) experiments, remaining SO_4 in PG sample is measured as 0.8 wt %. Maximum SO_4 removal from solid PG sample is calculated as 94.7%

4. CONCLUSIONS

In this study, PG sample is pre-treated with 0.5 M H_2SO_4 and then washed with water in order to observe the effect of commercial acid treatment on SO_4 removal efficiency. After acid treatment and washing, samples are filtered and SO_4 amounts in washed PG cakes were measured with ICP-OES. According to results, dilute conditions and increased stirring rate increases SO_4 removal efficiency.

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