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Recovery of rare earth metals as critical raw materials from phosphorus slag of long-term storage

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A B S T R A C T

The present research is directed towards processing of slag originating during the yellow phosphorus production. The slag was investigated using physical and chemical treatment methods. The following group of rare earth elements were identified in phosphorus slag such as: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu. Thermodynamic calculation for reactions probability of phosphorous slag components with nitric acid was made. Nitric-acid leaching of slag generated during phosphorus production was investigated for extraction of rare earth metals (REMs). Silicon containing cake obtained after leaching was suitable for precipitated silicon dioxide production. Behaviour of associated components such as calcium, aluminium and iron was studied during the leaching process. The following optimum parameters were selected for leaching studies: nitric acid concentration was 7.5 mol/dm^3; solid-to-liquid ratio was 1:2.6–3; temperature was 50–80 °C; process duration was 1 h; pulp stirring rate was 500 rpm and the recovery of rare-earth metals, calcium, aluminum and iron into the solution were seen to be 85%, 98%, 80.7%, and 11.8%, respectively. Cake produced as a result of leaching contained ~80–85% of amorphous SiO_2. The solution obtained after phosphorus slag leaching was processed through solvent extraction methods to concentrate and separate it from basic macroimpurities. After precipitation of REMs oxalates from strip liquor and calcination of the precipitate a concentrate was obtained, which contained ~17% of ΣREMs oxides.

1. Introduction and background

At present, the processing of phosphorite ores is being carried out using high-temperature method and liquid processing technologies. Natural phosphoric ores are divided into two main types - apatite and phosphorite, in which phosphorus is found in the apatite group of minerals. A major quantity of processed phosphorus-containing raw materials is used to produce phosphoric acid, which, depending on the method of production, is called thermic or extraction. The most widely used method is the acid decomposition of phosphates. Sulfuric or nitric acids are more often used as acids for decomposition. The sulfuric acid decomposition method for the processing of apatite concentrate is based on the following decomposition reaction of the mineral:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 5nH_2O \rightarrow 2CaSO_4 \bullet nH_2O \downarrow + 3H_3PO_4 + HF \quad (1)$$

The nitric acid decomposition of the apatite proceeds according to the following reaction:

$$Ca_5(PO_4)_3F + 10HNO_3 \rightarrow 5Ca(NO_3)_2 + 3H_3PO_4 + HF \quad (2)$$

While choosing the method of processing, the quality of the phosphorite raw material plays an important role. Natural phosphates, which do not contain significant impurities of calcium or magnesium carbonates, magnesium silicates, iron and aluminum compounds are suitable for acidic decomposition. These impurities make it difficult to process phosphates and deteriorate the quality of the obtained products. The thermic method of processing allows the processing of low quality raw materials and helps in getting better quality of fertilizers. Initially, elemental phosphorus is obtained, for the production of which phosphorite, coke and quartzite are used. The method consists of reduction of phosphates by carbon in the presence of silica according to the following reaction:

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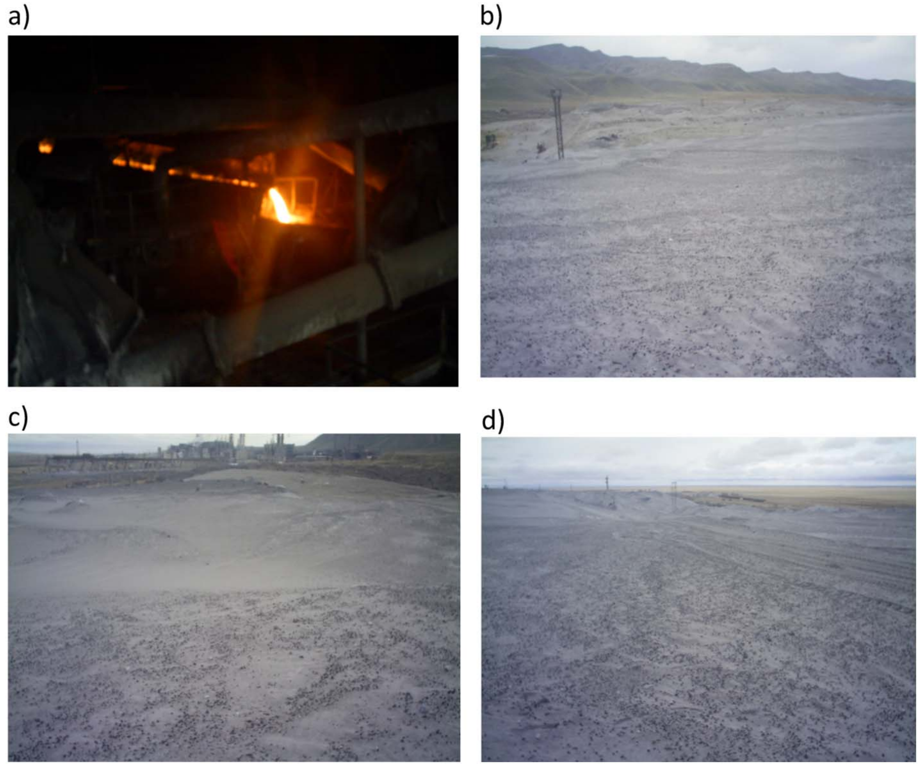

Fig. 1. Pictures of production of phosphorous slag (a) and slag disposal areas (b, c, d) of Kazphosphate LLP (NDPhP), Zhambyl Branch.

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 \longrightarrow 2P\uparrow + 5CO\uparrow + 3CaSiO_3 \quad (3)$$

The P_2O_5 pentoxide, obtained after the combustion of phosphorus, forms phosphoric acid, when reacted with water. The advantage of the thermic method for obtaining phosphoric acid includes the possibility of producing acid of any concentration (up to 100% P_2O_5) and of high purity, while using any phosphates, even low-quality ones without preliminary enrichment.

The leading countries for yellow phosphorus producers are the USA, the Netherlands, China and Kazakhstan. According to Infomine Research Group (2016), at present the world production of phosphorus is ~20 million tons per year. During the processing of Karatau phosphate rocks (Kazakhstan) at Kazphosphate LLP (New Dzhambul Phosphorus Plant NDPhP), Zhambyl Branch, electro-thermic distillation of phosphorus resulted in the formation of large quantity of fiery-liquid melted slags (Fig. 1a). Since decades, the phosphorous slag is being stored in the slag disposal areas, thereby polluting the environment and creating ecological problems in the nearby regions. Dump fields of Kazakhstan contain over 17 million tons of phosphorous slag (Fig. 1b, c, d). Many studies have been conducted to find a way for phosphorus slag recycling. Research on this issue mainly focuses on recycling of phosphorus slag for the production of building materials and related items (Kennedy, 1987; Shi and Qian, 2000; Jiang et al., 2011; Qi and Peng, 2011; Qian et al., 2013; Sun et al., 2013; Falaleeva et al., 2014). In spite of all the measures designed to recycle phosphorus slag (Akhmetov et al., 1981), a major part of it remains in the slag disposal areas, thereby, deteriorating the environment in Southern regions of Kazakhstan. Phosphorus slag utilization is limited due to certain reasons such as the presence of harmful impurities and low cost of slag products.

To ensure better recycling of phosphorus slags, it is necessary to seek out methods to remove contaminating impurities in order to produce higher value marketable products. Precipitated silicon dioxide is one such value added products (In the international market the value of precipitated silicon dioxide varies from USD 650 to 2000 per ton depending on the grade).

Su et al. (2010) obtained precipitated silicon dioxide from slag derived through yellow phosphorus production by leaching with phosphoric acid. In the process, calcium was separated in the form of calcium phosphate monobasic. The content of iron in the precipitated silicon dioxide is seen to be higher than the established standards. Therefore nitric acid solution is used for its purification allowing up to ~0.02% decrease in iron concentration (Li et al., 2012).

In our previous works (Abisheva et al., 2005, 2006, 2008, 2013) on phosphorus slag processing for the production of precipitated silicon dioxide, the slag was leached with sodium carbonate solution for silicate solution production. The solution was subjected to purification in order to make it free from aluminum and the silicon dioxide having high specific surface area was then precipitated from the solution by carbonization.

Phosphorus slags which are mainly composed of calcium and silicon compounds also contain rare-earth metals (REMs), the production of which is currently one of the most prioritized goals. Phosphorous production slags contain REMs, which are in high demand in the modern high-technology industries and they include: yttrium, neodymium, europium, and lutetium. Nowadays, a strong demand for rare-earth metals has led to the development of knowledge-intensive industries such as radio electronics, information technology, nuclear power, aviation, rocket technologies, biomedicine, etc. Rare-earth metals are crucial for “green technologies”. They are used for the production of wind turbines, energy-saving bulbs and electric, as well as, hybrid vehicles.

Lately China, who is considered as the absolute world leader for producing rare earth metals announced a reduction of 72% in the export quotas of these metals, in order to stop depletion of its deposits (Smirnov, 2011). Severe reduction in rare-earth metal supplies to the external market (imposed by China) stimulated the importing countries to generate their own resource base. One of the definite problems is that the percentage of rare-earth metals, which are in great demand, is not very high in natural raw materials. “BRK – Leasing” Co. Ltd. Subsidiary of Joint Stock Company “Development Bank of Kazakhstan” (2007) noted that total production of REMs increased from 33 thousand tons to 75 thousand tons or by 2.3 times from 1990 to 1999, while the demand