Processing of Phosphorus Slag with Recovery of Rare Earth Metals and Obtaining Silicon Containing Cake

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Abstract. The present research is devoted to the processing of slag generating during the yellow phosphorus production. In this paper are presented studies on leaching of phosphorus production slag by nitric acid with recovery of rare earth metals (REMs) into solution. REMs recovery into the solution achieved 98 % during the leaching process with using 7.5 mol/L of HNO_3, liquid-to-solid ratio is 2.6 :1, temperature is 60°C, process duration is 1 hour and stirrer speed is 500 rpm. Behaviour during the leaching of associated components such as calcium, aluminium, and iron was studied. After the leaching cake contains ~75-85 % of SiO_2 and it might be useful for obtaining of precipitated silicon dioxide. With the purpose of separation from the impurities, recovery and concentrating of REMs, the obtained solution after leaching was subjected to extraction processing methods. The influence of ratio of organic and aqueous phases (O : A) on the extraction of rare earth metals by tributyl phosphate (TBP) with concentrations from 20 up to 100 % was studied. The REMs extraction with increasing TBP concentration under changes O:A ratio from 1:20 down to 1:1 into the organic phase from the solutions after nitric acid leaching increased from 22.2 up to 99.3%. The duration effect of REMs extraction process was studied by tributyl phosphate. It is revealed that with increasing of duration of the extraction process from 10 to 30 minutes REMs recovery into the organic phase almost did not changed. The behaviour of iron in the extraction process by TBP was studied. It was found that such accompanying components as calcium and aluminium by tributyl phosphate didn't extracted. To construct isotherm of REMs extraction of by tributyl phosphate was used variable volume method. It was calculated three-step extraction is needed for REMs recovery from the solutions after nitric acid leaching of phosphorus production slag. The process of the three-steps counter current extraction of rare earth metals was modelled from the solutions after slag leaching with using 50 % of TBP in kerosene at the ratios O:A = 1:6 and 1:20. So, REMs recovery into the extract achieved 97.0 and 76.5 %, respectively. It was offered flowsheet of processing of phosphorus slag production with extraction of rare earth metals and obtaining silicon containing cake.

1. Introduction

Phosphorus slag is one of the largest-tonnage waste of yellow phosphorus production, which is being piled up for many decades at slag disposal areas contaminating environment and causing ecological

problems in Southern regions of Kazakhstan. Phosphorous slag is generally used in the manufacture of construction materials and products made of the construction materials [1, 2]. Despite the existing slag utilization activities, the most part of slag remains at the slag disposal areas [3]. One of the reasons for the low slag utilization level is a low price of the manufactured products.

Phosphorus production slag which is 90-92% represented by pseudo-wollastonite glass (90-92%) [4], may serve as a source for production of precipitated silicon dioxide ("white soot") – a high value added product being high in demand in Kazakhstan. There are data from conducted research in processing phosphorus slag with production of precipitated silicon dioxide [5, 6]. As is known, phosphorus-bearing raw materials are used as a source for production of REMs, and phosphorus production slag as a waste from electrothermal phosphorite processing is no exception. The total concentration of rare-earth metals in slag may achieve 500-600 ppm [7]. Therefore, phosphorus slag may become a source for production of not only "white soot", but also REMs, production of which is relevant today. There are data from phosphorus-bearing source material processing research, in particular, apatite concentrate [8, 9], as well as semi-finished products and waste from processing there of [10, 11] with extraction of rare-earth metals. Phosphogypsum (phosphodihydrate, phosphohemihydrate) – apatite raw material processing waste – is leached by sulfuric or nitric acid solutions. Selection of a reagent for phosphorus slag decomposition considered a potential for extraction of both rare-earth metals and precipitated silicon dioxide. Considering the task statement, a decision was made to use nitric acid as a reagent for leaching phosphorus slag [12]. Moreover, along with recovery of rare-earth metals into the solution, cake with high concentration of silicon was produced which may be suitable for production of precipitated silicon dioxide. The nitric-acid solution resulted from leaching and containing rare-earth metals, also contains calcium, aluminium, and iron impurities. Solvent extraction is one of the effective methods for seperation from major impurities and concentrating for the extractable component. Tributyl phosphate is widely used as solvent for extraction of REMs from nitric-acid solutions [13]. In the works [14, 15] TBP was used in extraction of REMs from the solutions resulted from leaching of apatite concentrate and apatite concentrate processing waste by nitric acid. However, the solutions resulted from phosphorus slag leaching by nitric acid may differ considerably in the concentration of REMs and in the impurity profile. Therefore, studies of phosphorus slag leaching by nitric acid and extracting REMs from solution for separation from the major part of the impurities and concentrating for the extractable components is of interest.

2. Experimental

2.1 Materials

The raw material used for experimental purposes is long-storage phosphorus production slag from slag disposal areas of KazPhosphate LLP, Zhambyl Branch, (NDPhP), collected since 1990 till 1995 with the following composition, wt. %: 36.9 SiO_2; 43.2 CaO; 5.2 Al_2O_3; 2.0 P_2O_5; 1.63 Fe_2O_3; 0.58 Na_2O; 2.4 MgO; 0.14 TiO_2; $\sum$REMs – 536.48 ppm. The leaching reagent solution was prepared with the use of 65% nitric acid. Rare-earth metals were extracted with the use of TBP. Kerosene was used as a diluent.

2.2 Methods

The experiments were conducted in a temperature-controlled airproof cell. The pulp was mixed using a variable-speed OST basic stirrer. The constant temperature was stabilized using TL-TC-01 thermostat. Slag was pre-ground in a centrifugal mill and was sieved to obtain a powder of 0.05 mm size. Extraction experiments were carried out in separating funnel 20 ± 5^0C and in predetermined proportions of the organic and aqueous phases. The phases were mixed mechanically. The phases were separated by sedimentation. The resultant solutions were analyzed to determine the content of calcium, aluminium, iron, and $\sum$REMs. The quantitative content of major elements and compounds was determined by chemical methods of analysis. An Optima 8300DV ICP atomic emission spectrometer was used to determine the quantitative content of rare-earth metals.

3. Results and Discussions

3.1 Phosphorus slag leaching by nitric acid

Leaching was carried out under the following conditions: nitric acid concentration = 7.5 mol/L; liquid-to-solid ratio = 2.6:1; temperature = 60 ºC; process time = 1 h; mixer rotation speed = 500 rpm. The resulted solution had the following composition, g/L: 0.198 $\sum$REMs; 177 CaO; 17.3 Al_2O_3; 1.7 Fe_2O_3. The recovery of REMs, calcium, aluminium, and iron into solution was 98, 99.1, 99 and 18.8 %, respectively. After leaching, the cake had the following composition, % (wt): 82-86 SiO_2; 0.11 CaO; 0.11 Al_2O_3; 2.7 Fe_2O_3. Silicon-containing cake may be suitable for production of precipitated silicon dioxide. For separation from major impurities and concentration, REMs-containing solution was studied with the use of solvent extraction method.

3.2 The effect of organic and aqueous phases ratio on the extraction of REMs

In the studies the phases contacted for 5 minutes within the range of O:A ratios from 1:1 to 1:20 are presented in Table 1.

Table 1. The influence of organic and aqueous phases ratio on the extraction of REMs and iron at various TBP concentrations

| O:A | 20 % TBP | | | | 30 % TBP | | | |
| | Concentration in raffinate | | Recovery in extract, % | | Concentration in raffinate | | Recovery in extract, % | |
	$\sum$REMs, mg/L	Fe_2O_3, g/L	$\sum$REMs	Fe_2O_3	$\sum$REMs, mg/L	Fe_2O_3, g/L	$\sum$REMs	Fe_2O_3
1:1	10.1	0.2	94.7	87.8	6.5	0.1	96.7	93.7
1:2	27.2	0.5	85.7	69.8	13.2	0.3	93.3	83.8
1:4	62.6	1.4	67.2	19.8	29.8	0.7	85.0	60.7
1:6	80.2	1.7	58.0	0	44.6	1.3	77.5	26.6
1:8	100.9	1.7	47.6	0	57.5	1.5	71.0	13.3
1:10	114.2	1.7	40.1	0	71.9	1.7	63.7	0
1:20	148.5	1.7	22.2	0	74.3	1.7	62.5	0
O:A	40 % TBP				50 % TBP			
	Concentration in raffinate		Recovery in extract, %		Concentration in raffinate		Recovery in extract, %	
	$\sum$REMs, mg/L	Fe_2O_3, g/L	$\sum$REMs	Fe_2O_3	$\sum$REMs, mg/L	Fe_2O_3, g/L	$\sum$REMs	Fe_2O_3
1:1	5.1	0.1	97.3	94.2	4.9	0.1	97.5	96.8
1:2	7.9	0.2	95.9	88.4	7.7	0.1	96.1	93.1
1:4	16.2	0.5	91.5	70.3	17.6	0.4	91.1	75.7
1:6	33.1	0.9	82.6	46.5	26.6	0.7	86.6	60.1
1:8	39.6	1.2	79.2	30.8	37.8	1.1	80.9	37.0
1:10	45.8	1.3	76.0	22.7	38.8	1.2	80.4	28.3
1:20	83.8	1.7	56.1	0	85.9	1.7	56.7	0
O:A	60 % TBP				100 % TBP			
	Concentration in raffinate		Recovery in extract, %		Concentration in raffinate		Recovery in extract, %	
	$\sum$REMs, mg/L	Fe_2O_3, g/L	$\sum$REMs	Fe_2O_3	$\sum$REMs, mg/L	Fe_2O_3, g/L	$\sum$REMs	Fe_2O_3
1:1	4.8	0.1	97.6	95.2	1.4	0.1	99.3	95.3
1:2	6.3	0.1	96.8	91.9	1.6	0.1	99.2	94.6
1:4	13.7	0.4	93.1	79.2	2.0	0.2	99.0	90.8
1:6	22.3	0.6	88.7	66.5	3.1	0.3	98.4	80.6
1:8	33.0	0.9	83.3	49.7	4.1	0.4	97.9	74.6
1:10	39.6	1.3	80.0	26.6	4.7	0.6	97.6	67.9
1:20	66.8	1.7	66.3	0	9.1	1.2	95.4	28.9

At any TBP concentration with aqueous phase increasing from 1 to 20 parts, extraction of REMs and iron from the solutions decreases. With increasing concentration of the extracting agent, the recovery of REMs into the extract increases, and this is more significant at high O:A ratios. The rate of REMs extraction at 100 % TBP across the studied range of the O:A ratio was more than 95%. At low TBP concentrations and at the O:A ratios from 1:6 and higher, iron extraction into the organic phase was lower or was not extracted in some cases. As the experiments showed, aluminium has practically not extracted into the organic phase, calcium was not extracted, too, except for O:A ratio =1:1, at 60 % TBP concentration the extraction rate was 0.6% and O:A ratio =1:1 and 1:2 at 100 % TBP concentration, the extraction rate was from ~4 to~16 %, respectively.

3.3 The effect of the process time on the extraction of rare-earth metals
The test was carried out at 100% TBP concentration, O:A ratio = 1:4 and phase contact time = 10, 15, 20 and 30 minutes (Table 2).The phase contact time does not have a significant effect on the extraction of REMs and iron. However, low quantity of calcium passes into the extract at the phase contact time ≥15 minutes. No extraction of aluminium was observed.

Table 2. The effect of the time of contact between the organic and aqueous phases on the extraction of rare-earth metals, iron and calcium

Phase contact time, min.	Concentration in raffinate			Recovery in extract, %		
	$\sum$REMs, mg/L	Fe_2O_3, g/L	CaO, g/L	$\sum$REMs	Fe_2O_3	CaO
10	6.0	0.1	177.0	97.0	91,9	0
15	6.6	0.1	175.7	96.7	91.9	0.6
20	7.6	0.2	173.0	96.2	90.8	2.1
30	6.4	0.1	173.0	96.7	91.9	2.1

Multistage counter-current extraction process is the most effective method for recovery of value metals from solutions with high results and separation of components. The number of extraction steps may be determined using extraction isotherm.

3.4 Isotherm of extraction of rare-earth metals.
To build an isotherm of REMs extraction, variable volume method was used. The indicative number of counter-current extraction steps was graphically determined on the extraction isotherm. The extraction isotherm is shown in Figure 1.
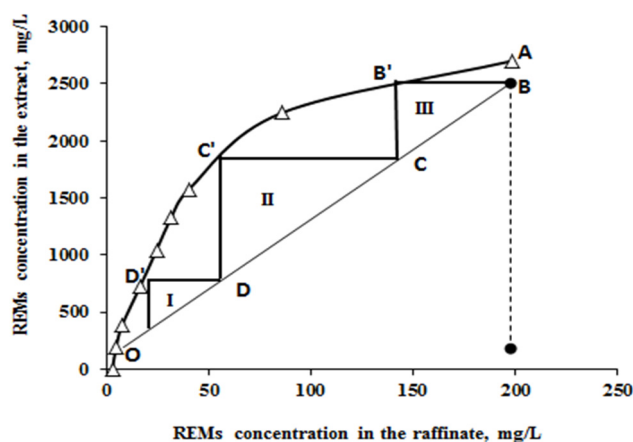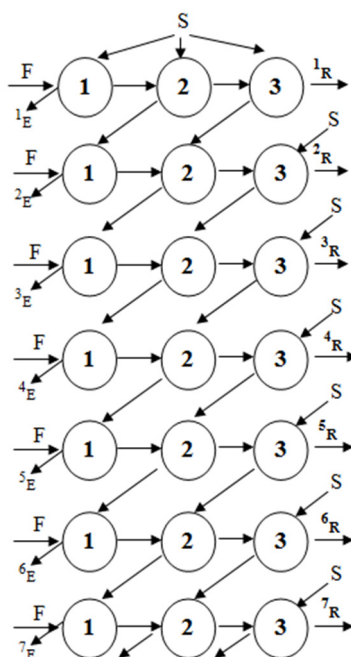

Figure 1. Rare-earth metals extraction isotherm, OD'C'B'A – extraction isotherm; BO – operating line; BB', CC', DD' – extraction steps

It was calculated on the basis of the extraction isotherm, that extraction of REMs from the examined solutions will require approximately three extraction steps. To confirm the correctness of the determined number of extraction steps, a three-step counter-current process of REMs extraction was modelled.

3.4 Modelling a three-step counter-current process of rare-earth metals extraction.
Multistage counter-current extraction was performed on a continuous mode. Fig. 2 shows a scheme of the process of REMs extraction from the examined solutions (F) using the extraction agent (S). Each cell with a number corresponds to one theoretical step (separating funnel). A set of stages 1-3 represents one cycle.

Figure 2. Scheme of a three-step counter-current extraction, F – the examined solutions; S – extraction agent; E – extract; R – raffinate

The shown scheme was used as a basis for extraction of rare-earth metals from the solution at the O:A ratios = 1:6 and 1:20. The higher O:A ratio (Table 3) increases the concentration of REMs in the raffinates (5.5 to 104.4 mg/L) and decreases the rate of extraction to the extract (97.0 to 42.9 %).

Table 3. Results of modelling of a three-stage counter-current extraction of rare-earth metals

| | O:A = 1: 6 | | | | O:A = 1: 20 | | |
| Cycle No. | REMs concentration, mg/L | | REMs extraction into extract, % | Cycle No. | REMs concentration, mg/L | | REMs extraction into extract, % |
	in raffinate	in extract			in raffinate	in extract	
1	5.5	1063.8	97.0	1	42.9	2798	76.5
2	9.1	1042.2	95.0	2	86.5	1926	52.7
3	13.4	1016.4	92.7	3	97.6	1704	46.6
4	17.8	990.0	90.3	4	100.7	1642	44.9
5	22.0	964.8	88.0	5	103.5	1586	43.4
6	23.5	955.8	87.1	6	103.9	1578	43.2
7	24.4	950.4	86.6	7	104.4	1568	42.9

At O:A = 1:6, the rate of extraction into the extract was 92.7 to 97 % from the first through the third cycle. At O:A = 1: 20 the REMs concentration in the extract was 2798 mg/L, but the extraction rate did not exceed 76.5%.

4. Conclusions

The study results showed that phosphorus slag leaching resulted in the solution containing ~0.2 g/L of REMs. The rare-earth metals may be separated from the related impurities of calcium, aluminium, and, partially, iron and concentrated by TBP extraction. It is more efficient to perform extraction at 50 % TBP counter-current in three steps at O:A = 1:6 or at 100 % TBP in one step at O:A = 1:20. Finally, it was offered flowsheet of phosphorus slag processing with REMs extraction and obtaining of silicon containing cake (Fig. 3).
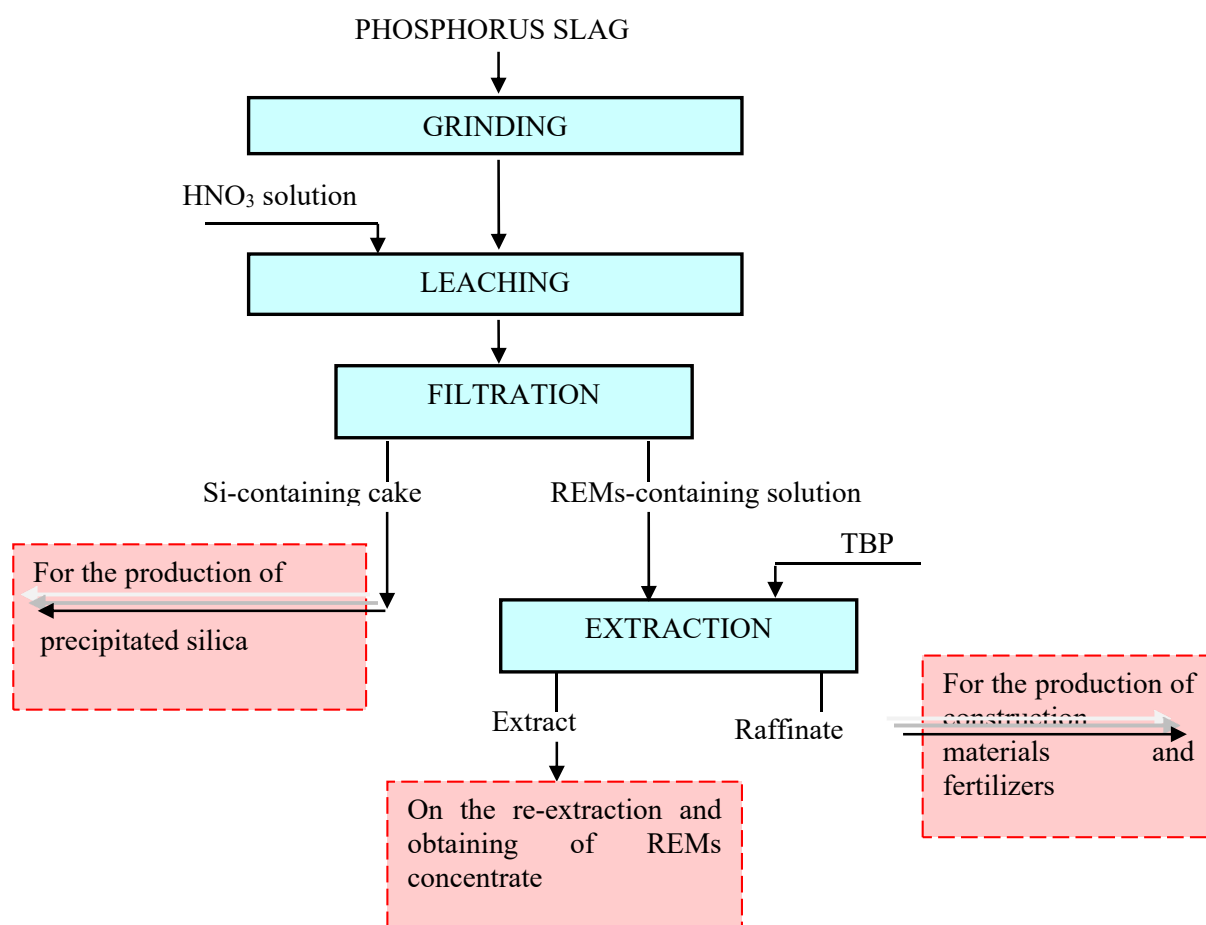
Figure 3. The flowsheet on the processing of phosphorus production slag

Acknowledgement(s)

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