

Sorption extraction of REE and other cationic impurities from phosphoric acid solution

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Abstract

Topicality of the research

Thermal phosphoric acid is a product of high purity, but its manufacturing cost is quite expensive, and it also has a negative impact on the environment due to the emissions of toxic gases. The extracted phosphoric acid, obtained by processing of phosphate ores with sulfuric acid contains between 15 and 42% by the weight of P_2O_5 , in addition the observed concentrations of accompanying impurities may reach up to 15% by weight and depend on the composition of the material and the conditions of decomposition, such as the type of used acid and its concentration. In recent years there has been an increase in the production of pure extracted phosphoric acid, the quality of the finished acid is controlled to meet the consumer needs and thus suitable purification methods are applied. A large amount of extracted phosphoric acid is used for the production of sodium tripolyphosphate in detergents industry. In order to obtain the detergent compound from extracted phosphoric acid, it is necessary to remove iron, aluminium and calcium cations from the used acid, because they are the main impurities in the solution of acid.

Besides these cationic impurities, the extracted phosphoric acid contains 0.1 to 1.0 g/l of rare earth elements, which are used as materials for high-tech industries, such as the semiconductor industry, aerospace, nuclear power, etc. In the processing of phosphate raw materials, the complex task is to recover valuable rare earth elements and remove cationic impurities from phosphoric acid solution. Ion exchange adsorption in the presence of a suitable adsorbent can become an effective method for achieving this goal, as it is applicable to dilute solutions, suspension solutions or in the sludge. As such, the development of ion exchange

technology in the purification of phosphoric acid and simultaneous recovery of rare earth elements is an urgent task.

Purposes and tasks of the work: development of technological solutions for the process of extracting rare earth metals and other cationic impurities from a phosphoric acid solution using sorption method.

To achieve the goals of the thesis, the following tasks are set out and solved:

- analyse new and updated resources of literatures in the study area, identify research subjects;
- research on the absorption of lanthanum, calcium, iron and aluminium ions from phosphoric acid solution under static conditions using ion exchange resins, calculate the quantitative properties of the process, analyse the selectivity of the sorbent, and select suitable ion exchange resins for the recovery of REE;
- study kinetic of the adsorption of lanthanum and aluminium ions from phosphoric acid solution on macro-porous cation exchange resin containing sulfonic groups;
- research on the selective adsorption of REE and calcium from phosphoric acid under dynamic conditions using cation exchange resins containing sulfonic groups, eluting and separating lanthanum from aluminium-containing eluate;
- research on the adsorption process of iron and aluminium ions from phosphoric acid solution by phosphorus-containing sorbents;
- propose a technological process to recover REE and remove cationic impurities from phosphoric acid solution using adsorption method.

Scientific novelty of the work

New data have been obtained on the sorption extraction of lanthanide, iron, aluminium and calcium ions from a phosphoric acid solution by ion-exchange resins, depending on the porous structure and functional group of the sorbent, the selectivity of the ion exchange resins for the studied ions has been established:

- macro-porous sulfonic cation exchanger MTS1600 is the most selective to REE ions, regardless of the ionic form of resin in terms of sorption selectivity, trivalent cations are arranged in the series $\text{La}^{3+} > \text{Fe}^{3+} > \text{Al}^{3+}$;
- calcium is the main competing ion in the sorption of REE by the MTS1600 resin, the distribution coefficients of Ca^{2+} and La^{3+} are 79.8 and 40.6, respectively;
- the selectivity of adsorption of cations from a phosphoric acid solution is due to the formation of phosphate complexes with various shapes and durability;
- phosphorus -containing resins selectively extract iron and aluminium ions.

The kinetics of cation adsorption by macroporous sulfonic cation exchange resins is described by a pseudo-second order model. The adsorption of lanthanum is determined by the rate of interaction between ions and the functional group of cation exchangers ($E_a = 35,69 \text{ kJ/mol}$) and the adsorption of aluminium ions is mainly limited by the diffusion process ($E_a = 10,77 \text{ kJ/mol}$).

Practical significance of the work

Technological solutions of purification of phosphoric acid from cationic impurities by the sorption method with the associated extraction of rare earth elements and desorption of cations from the sorbent phase have been developed:

- it is recommended to extract REE and calcium ions from phosphoric acid solution using macroporous sulfonic cation exchanger under dynamic conditions with following elution of ions from sorbent phase by ammonium nitrate solution and separation of REE from calcium by precipitation;
- adsorption of iron and aluminium ions should be carried out under static conditions using phosphorus-containing sorbents, desorption of aluminium is recommended to be carried out with sodium hydroxide, desorption of iron - by solution of hydrochloric acid.