



Removal of fluoride from the acid digestion liquor in production process of nitrophosphate fertilizer



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ARTICLE INFO

Article history:

Received 3 July 2015

Received in revised form 11 September 2015

Accepted 12 September 2015

Available online 15 September 2015

Keywords:

Fluoride removal

Defluorination

Fluorine recovery

Potassium hexafluorosilicate

Precipitation

Nitrophosphate

ABSTRACT

Fluorine is a major pollutant in the conversion of phosphate rock to nitrophosphate fertilizer. In this paper, removal of fluoride in the nitrophosphate process was investigated. Fluoride ion-selective electrode and acid–base titration method were employed to determine the fluoride content and species in the actual acid digestion liquor. It was found that fluoride was present in two forms of H_2SiF_6 (0.78 wt% F^-) and HF (0.10 wt% F^-). Precipitation tests were performed both in pure fluoride solution ($\text{H}_2\text{SiF}_6 + \text{HF} + \text{H}_2\text{O}$) and actual acid digestion liquor using KNO_3 as precipitant. Influences of reaction time, temperature and KNO_3 addition were studied. The precipitates obtained were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF). Precipitation experiments revealed that the addition of KNO_3 would remove the fluoride effectively, and the obtained precipitates were the high-purity K_2SiF_6 . The maximum fluoride removal efficiency could reach 88.52% at 25 °C when 400% excess of KNO_3 was added in the pure fluoride solution after 1 h. However, the fluoride removal efficiency reached only 70.22% in actual acid digestion liquor under the same experimental conditions. These obtained results are important and meaningful for the sustainable development of nitrophosphate fertilizer.

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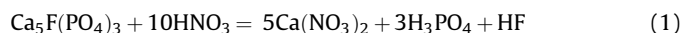
1. Introduction

Nitrophosphate is the general name of nitrogenous and phosphorus compound fertilizer by nitric acid decomposing phosphate rock. The nitric acid is used both for digestion of phosphate rock and for the addition of nitrate nutrient to the fertilizer product. Current worldwide production of nitrophosphate is over 30,000 kt/a. Tianji Brand nitrophosphate of China is a typical nitrogen and phosphorus fertilizer, total nutrient is 42%, and the ratio of N/ P_2O_5 is about 2:1 [1]. The main steps of producing nitrophosphate based on the Odda process are as follows [2–4]:

- Rock phosphate storage and handling
- Digestion of phosphate rock with nitric acid
- Cooling of the digestion liquor, crystallization and separation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
- Mother liquor neutralization with ammonia gas

- Evaporation of slurry, granulation, drying and the post-processing of the product

In the digestion process, nitric acid decomposing phosphate rock occurs according to the simplified reaction (1) [3,5,6]:



The exothermic digestion reaction makes the temperature of digesting acidic mixture raise to about 65 °C. Hydrogen fluoride, evolved during the acid digestion of phosphate rock, reacts with active silica coming into acid digestion liquor with the phosphate rock, to produce silicon tetrafluoride (SiF_4) and hydrofluosilicic acid (H_2SiF_6) according to the following reactions (2) and (3) [5,7]:



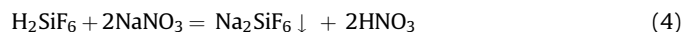
Phosphate rocks contain about 4% fluorine. Minor parts of the fluorine as SiF_4 will be released into gaseous phase and then be absorbed in the tower, while the majority of the fluorine as H_2SiF_6 and HF will exist in the acid digestion liquor and eventually enter into fertilizer [3,7]. As a consequence, the acid digestion liquor

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contains phosphoric acid, nitric acid, calcium nitrate, fluosilicic acid and other nitrates impurities such as magnesium nitrate, aluminum nitrate and iron (III) nitrate. The presence of fluorine in the acid digestion liquor will cause a series of problems for the subsequent process steps, for example, the difficult separation of solid and liquor, the increased viscosity of the neutralized slurry and even the degeneration of dissolved phosphorus in the product [5,7,8]. Moreover, the use of the fluorine-containing fertilizer could cause the pollution to ecosystems. With the grade declining of phosphate rock in recent years, manufacturing enterprise will have to utilize mid-grade and low-grade phosphate rock in production process of nitrophosphate [9]. In this case, the system is inevitably introduced too much fluorine and other impurities. Taking into account of all the above, the fluorine must be removed from the nitrophosphate process and be reclaimed as useful resources.

There are several methods for the fluoride removal in production process of nitrophosphate fertilizer. Firstly, thermal treatment of phosphate rocks could completely remove fluorine to obtain fluorine-free phosphate rocks [10,11]. However, in calcination plants some drawbacks such as high capital cost, high energy-consuming and even low reactivity products would appear [12]. Secondly, a process for the removal of fluorine during the production of fertilizer once was provided by precipitating the ion during the ammoniation step and recovering fluorine by pyrolysis [13]. But the process was rarely employed due to its complicated operation and the impure by-product. Thirdly, researchers designed to introduce sodium ion or potassium ion in solutions containing H_2SiF_6 , which could form the precipitation of hexafluorosilicates of alkaline metals like the following reactions (4) and (5) [5,14–16]:



Therefore, the fluoride was converted into precipitates and reclaimed due to the low solubility of Na_2SiF_6 and K_2SiF_6 [17,18]. To remove and reclaim the fluoride in the nitrophosphate process, it is more ideal to use potassium nitrate (KNO_3) as precipitant due to several advantages as follows: solubility values of K_2SiF_6 were always lower than those of Na_2SiF_6 in water and acidic solutions [17,18], and the introduced potassium (K) is one of the essential nutrition elements to crops. Hence, the addition of KNO_3 in acid digestion liquor can not only effectively remove the fluoride but also facilitate the production of nitrogen–phosphorus–potassium (NPK) compound fertilizer [19]. On the other hand, the precipitation of K_2SiF_6 obtained has higher value of economy and widely industrial application: as insecticides in agriculture [20], as electrolytes for solar silicon electrolysis in photovoltaic applications [21–23], as alkali silicate binders in the cement industry [24], as catalytic products in the frosted glass industry [25], and as raw materials to prepare synthetic fluorine mica [26].

However, up to now relevant literatures on the fluoride removal from the acid digestion liquor in production process of nitrophosphate fertilizer are very lacking, and the key influence factors on the fluoride removal are poorly understood. The environmental sustainability and the declining grade of phosphate rock have increased the necessity for the fertilizer industry to restrict its output of fluorine to the environment. Thus, there is a need to study some key operating parameters to understand their influence on the fluoride removal from the acid digestion liquor and govern their behavior for the engineering application.

In this paper, removal of fluoride in the nitrophosphate process was firstly investigated. The fluoride content and species in acid digestion liquor were determined. Before precipitation tests, solubility values of K_2SiF_6 were measured at different temperatures. In order to figure out the optimal precipitation

conditions, precipitation tests were initially performed in pure fluoride solution similar to the acid digestion liquor. The influences of reaction time, temperature and KNO_3 addition were studied both in pure fluoride solution and acid digestion liquor. In addition, the differences between the fluoride removal efficiency calculated by precipitation and F^- concentration were also discussed. The obtained results were meaningful and helpful for further understanding of key influence factors on the fluoride removal, and also provided basic data which can be utilized for the removal of fluoride in production process of nitrophosphate fertilizer.

2. Experimental

2.1. Materials and chemicals

Nitric acid (HNO_3 , 65%), fluosilicic acid (H_2SiF_6 , 30%), hydrofluoric acid (HF, 40%), potassium nitrate (KNO_3 , 99.0%), potassium hexafluorosilicate (K_2SiF_6 , 98.0%) and sodium hydroxide (NaOH, 96.0%) were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (Beijing, China). All the chemicals were of analytical grade and used as received without further purification. Phosphate rock was provided by Shenzhen Batian Ecological Engineering Co. Ltd. (Shenzhen, China). The rock was firstly crushed, ground to powder, homogenized, passed through a sieve ASTM equivalent of 30 mesh, and then kept in an oven at 105°C for 48 h to remove moisture if any. Distilled water was used in all the experimental runs. For all fluoride-containing solutions, only polypropylene (PP) vessels were used for sample preparation, storage and precipitation tests.

2.2. Preparation of the acid digestion liquor

Specific amount of phosphate rock was mixed with excess of 110% over the stoichiometric quantity of HNO_3 (50 wt%) in the digestion reactor. The particle size distribution of phosphate rock is shown in Fig. 1. Considering the exothermic acid digestion reaction, the mixture was kept at constant temperature of 65°C and stirred at 300 rpm with an agitator for 1 h time. Urea solution was also added in the digestion reactor to control NO_x in off-gases. After separating the acid-insoluble materials (A.I) by vacuum filtration, the acid digestion liquor was obtained and stored in polypropylene bucket for further analysis and precipitation tests.

2.3. Analytical methods

In the acid digestion liquor, the phosphate ion concentration was determined employing vanadium ammonium molybdate

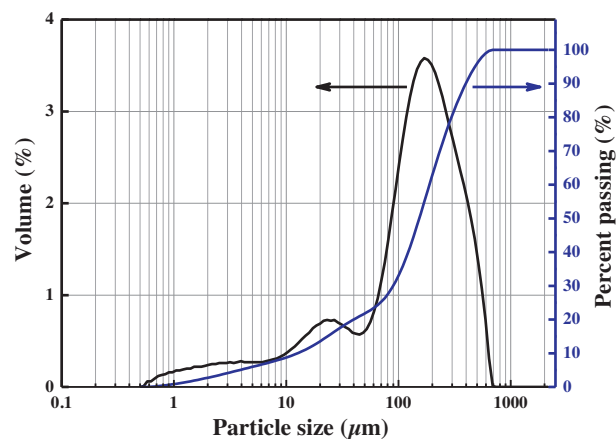


Fig. 1. Particle size distribution curves of phosphate rock ($d_{10} = 12.678 \mu\text{m}$, $d_{20} = 39.885 \mu\text{m}$, $d_{50} = 153.195 \mu\text{m}$, $d_{80} = 296.077 \mu\text{m}$, $d_{90} = 397.027 \mu\text{m}$).

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