Removal of Fluoride from Industrial Wastewater (Phosphate Production Plants) and its Conversion to Valuable Products

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ABSTRACT

In a lot of industrial processes, wastewaters are produced which contain fluoride ions. These ions are either separated from the wastewater or converted into other byproducts. The second way leads to an added value to these materials. Since the fluoride concentration in industrial wastewaters is much more than that of drinking water, methods specific for the industrial wastewater must be explored.

In this research work different ways for treatment of the fluoride- containing wastewaters of a variety of phosphate production units were studied. This study was concentrated on the parameters which affect the separation of fluoride and phosphate ions from the wastewater.
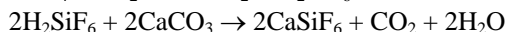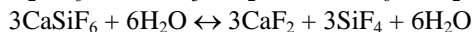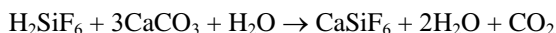
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INTRODUCTION

The fluoride and phosphate ions are present in from of fluosilicic acid and Phosphorous pentoxide, respectively. During the separation process, some calcium fluoride and silica is formed. Some new features of common production procedure of calcium fluoride and precipitated silica were declared. The first goal was to improve both the removal of fluoride and phosphate ions and the efficiency of production of valuable calcium fluoride and precipitated silica.

In order to reach the goals, all the common ways of F^- and P_2O_5 separation were studied and tested in laboratory scale. It was found that the most proper way to do this is the sequential mixing of the wastewater with calcium carbonate and calcium hydroxide. The most influencing factors, namely pH, mesh size of the reactants, concentration of the neutralizing dispersion, mixing intensity, sequence and rate of addition and the duration of the reaction were studied and optimized [1].

As no clear mechanism has yet been offered for the reaction and some unclear phenomena were occurring during the reaction, the mechanism of the reaction was studied in a more detailed manner. Having studied the results of a large number of research works on the reaction, we got to a new mechanism which had the ability to explain many features of this reaction. In this mechanism the occurrence of four serial intermediate reactions was proposed, in which some intermediate compounds are formed. This is the first explanation for this reaction, which can explain the formation of the observed products in the same order of the observations. Using this mechanism we were able to optimize reaction conditions in order to improve the removal process and the efficiency of calcium fluoride and precipitated silica.

$$H_2SiF_6 + 3CaCO_3 + H_2O \rightarrow CaSiF_6 + 2H_2O + CO_2$$
$$3CaSiF_6 + 6H_2O \leftrightarrow 3CaF_2 + 3SiF_4 + 6H_2O$$
$$3SiF_4 + 2H_2O \leftrightarrow SiO_2 + H_2SiF_6$$
$$2H_2SiF_6 + 2CaCO_3 \rightarrow 2CaSiF_6 + CO_2 + 2H_2O$$

The total reaction will be:
$$H_2SiF_6 + 3CaCO_3 \rightarrow 3CaF_2 + 3CO_2 + H_2O + SiO_2$$

RESULTS AND DISCUTION

In order to confirm the proposed mechanism, some experiments were performed. In these experiments we tried to separate and characterize the intermediate reaction products and compare their characteristics with that of predicted intermediates. Calcium fluoride is described in literature as a fine solid residue, having a

density of 2.25 gr/cm^3 and as insoluble in cold water and decomposable in warm water. To prove the formation of calcium fluoride as the intermediate reaction product the following experiment was performed:

About 155 grams of 10% calcium carbonate slurry was added dropwise to 50 ml of 22.5% fluosilicic acid at 5°C. These amounts correspond to a stoichiometric ratio of the reactants. The addition rate was 15.5 ml per minute. After 15 minutes the mixture was filtered and the pH of the filtrate was measured as to be 5. This directed us to the conclusion that no reaction has taken place in the mixture.

In a second stage, the temperature of the mixture was increased to 60°C. The measurement of the pH of the mixture revealed of value of 2. Adding 30 grams of calcium carbonate slurry cause pH to rise 4.5- 5.0 and a large amount of Co_2 to be liberated. Also calcium fluoride and silica precipitates were formed.

It has been suggested that, 95% of the total Co_2 is generated in that first 5 minutes immediately after the addition of calcium carbonate slurry to fluosilicic acid [2, 3, 4].

Therefore, at this stage only 30% of the fluoride ions have been converted to calcium fluoride. These observations may be explained by the proposed mechanism and offers that the rate- determining stage is the hydrolysis of SiF_6^{2-} ions. Thus it is possible to speed up the formation of calcium fluoride by rising the rate of the hydrolysis reaction of calcium fluosilicate. Adding alkali will lead to consumption of protons and then increases the rate of hydrolysis reaction. On the other hand it is possible to increases the hydrolysis rate by increasing the reaction temperature.

To determine the efficiency of the separation of fluoride ions form the wastewater the concentration of the fluoride ions should be measured during the reaction. Since the measurement procedure is complicated and time- consuming it was tried to find a relationship between the concentration of the fluoride ion and some other parameters which can be measurd more simply. It was found that there is a correlation between the fluoride concentration and the two parameters namely, the concentration of calcium ion and pH.

Having considered the theoretical pH values corresponding to precipitate formation of different compounds in the reaction vessel, the most proper pH of the reaction mixture was determined to obtain high purity calcium fluoride and silica [5, 6].

According to our calculations, the precipitation of calcium fluoride starts at a pH value of 2.48. At the same time also the phosphate impurities can react with calcium ions to from $CaHPO_4$ sediments. These sediments act like impurities in the calcium fluoride precipitates. Therefore the reaction conditions should be maintained so that the formation of these sediments is minimized. Hence we tried to calculate to pH at which the calcium hydrogen phosphate sediments are formed. According to our calculations, the calcium hydrogen phosphate precipitates are formed at a pH value of 3.3. Therefore during the separation of fluoride ions as calcium fluoride the pH value of the reaction mixture must be maintained at a value of 2.5- 3.0.

One of the most common problems of the reaction of calcium compounds and fluosilicic acid is "gel formation". Silica is present in solution as silicic acid, which can be later polymerize and form fine microgels. The formation of these microgels may lead to an increased viscosity of the mixture, which in turn decreases the reaction efficiency. The gelation time increases by increasing the pH of the solution and decreases by increasing the concentration of silicic acid. Increasing the temperature also may lead to a higher rate of gelation.

To prevent this problem, the free fluosilicic acid must be removed form the mixture. According to our calculations, the silica formation starts at a pH value of 7.4. Therefore it can be recommended to separate the silica precipitates at a pH value of 8.0 [7].

Conclusion

Applying the above- mentioned reaction conditions, it was possible to prepare calcium fluoride with a purity of 95- 99%. The prepared calcium fluoride was then used for the preparation of hydrogen fluoride.

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