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Precipitation treatment of effluent acidic wastewater from phosphate-containing fertilizer industry: Characterization of solid and liquid products

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ABSTRACT

The effluent ponds from phosphoric acid and fertilizer industries are a worldwide problem. Wastewater in these ponds contains high concentration of acids and heavy metals that seriously contaminates the environment and underground water. On the other hand, it contains valuable components such as phosphoric acid, fluorine and flousilicic acid. In this work, wastewater samples from effluent pond of the Indo Jordan Chemicals (IJC) plant were collected. These samples were characterized for their pH, and chemical composition. The pH of pond water was found to be about 0.8 due to its high content of HF, H_2SiF_6 and H_3PO_4. Potentiometric titration, chloride and fluoride ion selective electrodes and other acid base titration methods were employed to determine the content of the above acids. AAS was also used to determine the content of heavy metals in this waste water. Potentiometric titration curves were produced to determine the optimum neutralization conditions for several synthetic mixtures made from the above acids, and for real effluent wastewater. XRD, XRF and SEM analyses were employed for analysis of the products of calcium hydroxide neutralizations. It was found that fluorine is present in effluent pond water in two forms: HF and H_2SiF_6. Precipitation experiments revealed that the reaction of H_2SiF_6 with $Ca(OH)_2$ yielded only CaF_2 with no $CaSiF_6$. Furthermore, it was found that it is possible to separate sulfate in an initial precipitation stage. Additionally, it is possible to remove almost all fluoride in the form of CaF_2 leaving at least 60% of H_3PO_4 in water. Amorphous silica could be removed by aging the solution after fluoride removal.

1. Introduction

Phosphate rock is an essential raw material in the manufacture of various chemical fertilizers. The main component of phosphate fertilizers is phosphoric acid (PA). PA is the second-largest mineral acid produced worldwide, considering its volume and value. Its production is performed via two different processing routes: wet and thermal methods. The thermal route involves electric-furnace smelting of the phosphate-containing minerals, using coke and silica to produce elemental phosphorous, which is then converted to PA by first burning (oxidizing) the phosphorus to P_2O_5 and then absorbing the obtained P_2O_5 in water. The wet method process is based on sulfuric acid lixiviation of apatite rock ($Ca_{10}P_6O_{24}F_2$- fluoroapatite or $Ca_{10}P_6O_{24}(OH)_2$- hydroxyapatite) [1].

In this process H_2SiF_6 is generated as by-product.

The major part is sent to effluent pond if not used for production of AlF_3. In addition, effluent pond receives part of the washing water from the filtration unit of phosphogypsum, as well as effluent water from deionization unit (sulfuric acid production requires deionized water), which contains high concentration of ions including Ca^{2+}, Na^+, K^+, Mg^+, F^-, Cl^-, and SO_4^{2-}. The effluent pond receives also wastewater from spillages collected from various places of the plant.

Therefore, effluent pond contains very complex mixture of acids including HF, H_2SiF_6, H_3PO_4 and small quantities of sulfuric acid. effluent ponds, in PA producing plants, forms real challenge to the fertilizer industry [2] from several points of view including water losses, phosphate losses, fluoride losses, and most importantly the possible environmental damage that such water would cause if reaches the ground water. Thus, before this water can be released to the environment, it must be treated or purified to remove the phosphoric acid and other impurities. However, currently the general practise employed, to deal with effluent ponds, in most phosphoric acid plants is leaving the pond for evaporation where huge amount of water and valuable compounds are lost.

Therefore, many research works have been directed toward the treatment of such industrial acidic wastewater [2–6]. Most

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research work focused on fluoride removal from various effluent streams by electrochemical means [7], using quick lime [5], solvent extraction [4], adsorption processes [8–10] and other means. Shen et al. [7] investigated the removal of fluoride ions (15 mg/l) using a combined electrocoagulation and electrofotation process. Both Fe^{3+} and Mg^{2+} were used as a coagulant solution at low concentration of 50 mg/l. The results showed that the combined process reduced the fluoride concentration down to 2 mg/l at pH 6, charge loading is at 4.97 F/m^3 water, and the residence time is 20 min. On the other hand, Islam and Patel [5] used activated and ordinary quick lime for removing fluoride from a synthetic aqueous solution. The results showed that the removal percentage of fluoride was 80.6% with an effluent concentration of 9.7 mg/L. The author did not recommend this technique to be employed to treat wastewater for domestic purpose, since it cannot bring fluoride within permissible limit (1.5 mg/L) and also increases the pH of treated water.

Another technique was used for removing fluoride ion from an aqueous solution [11]. This removal process was achieved by adsorption of fluoride using the original and activated red mud forms in a batch equilibration technique. It was found that the maximum removal of fluoride ion was obtained at pH 5.5 and the sufficient time for adsorption equilibrium of fluoride ions is 2 h. Recently, synthesized anion clay (called meixnerite) and its calcinations product was conducted to remove the fluoride ion [12]. The investigated clay consists of MgO and $Al(OH)_3$ at a ratio of 3:1. Batch sorption experiments were performed to investigate the effects of contact time and initial fluoride concentration on fluoride uptake by uncalcined and calcined meixnerite. This is due to greater availability of fluoride to its interlayer sites, since the interlayers were generated during reaction of the F-containing solution with the calcined material and some F^- did not have to diffuse from the solution into the interlayers to replace existing OH^- ions as it did for the uncalcined meixnerite.

Some research works have focused on neutralization of pond water using several neutralization agents. For example, Mooney et al. [13] have employed double liming technique to treat acid water. This method consists of adding a calcium compound (such as $CaCO_3$, $Ca(OH)_2$, and CaO) to the acid water, in two stages, such that the phosphate and other impurities form solids precipitates that settle and are separated from the thus purified water. In another work, different steps were conducted to treat the acid water which depended on the adjustment of pH of the solution [14]. The process started with adding strong base (such as NaOH, or KOH) to the acid water until the pH reaches the value in the range of 6–8. This step will cause a formation of solid precipitation which could be separated either by settling, centrifuging, or filtration processes. The amount of calcium and fluorine is now reduced. The clear liquid is now allowed to age (16 h – 16 days) in order to allow silicic acid to decompose into hydrated silicon dioxide which is again removed by settling, centrifuging, or filtration processes. Finally, strong acid is added to the solution (with pH of 2–4) in order to permit the removal of pure water from the liquid without causing precipitation of salts. The liquid solution could be removed by reverse osmosis or evaporation without the formation of solid precipitation [14].

However, there was very limited work that has been carried on systems containing HF, H_2SiF_6 and P_2O_5 [2,3,6]. Grzmil and Wronkowski [6] studied the removal of phosphates and fluorides from industrial wastewater. They used both synthetic and real wastewater. The later wastewater produced from wet phosphoric acid process. The separation of phosphates and fluorides was achieved by two steps; the first one was precipitation of phosphates and fluorides ions by calcium and iron in the presence of aluminum as the complexing agent of the fluoride ions. At pH of 3, 12–13% of fluorides and 85–91% of phosphates were transferred to the solid phase, while at pH of 8, the formed precipitate was 82.5% of fluorides and 3.5% of phosphates. In the second step where the remaining solution containing only a small amount of the aluminum and iron ions, in two-stage precipitation by calcium in the first stage (pH 3) 85–88% of fluorides and up to 17% of phosphates are obtained, whereas in the second stage (pH 8) phosphates are 63–73% and fluorides are 1–4%. The phosphate precipitate could be utilized in the fertilizer industry.

Grzmil and Wronkowski [15] studied the recovery of phosphate from a model solution and effluents of the wet process phosphoric acid production in the form of struvite $NH_4MgPO_4{\cdot}6H_2O$. The main factors influencing the precipitation of struvite were, pH, the molar ratio $Mg^{2+} : NH^{4+} : PO_4^{3-}$ as well as the presence of fluorides. The concluded that struvite precipitation should be carried out at pH 10.5–11 and at molar ratio of $Mg^{2+} : NH^{4+} : PO_4^{3-}$ equal to 1.8:1.1:1.0 respectively [15,16]. Fluorides were found also to precipitate in the form of CaF_2.

In another process, the phosphoric ion was separated by the addition of iron and aluminum salts [17]. This process will precipitate deposits of $FePO_4{\cdot}2H_2O$ (strengite) and $AlPO_4{\cdot}2H_2O$ (variscite). The formation of deposit flocks is dependent on the pH value as well as on the solubility of metal phosphate. In this work, good results were obtained at pH 5–6 in which the phosphates of iron and aluminum possess the lowest solubility. Although, the phosphate precipitation by the metal salts leads to the formation of large quantities of sludge, they have some potential fertilizing value.

With the current shortage of water in Jordan and the increased demands on fresh water, it is very important to treat wastewater collected in an effluent pond for reuse. Additionally, wastewater from phosphoric acid plants contains P_2O_5 and fluorides which could be utilized to produce by-products. Therefore, this paper discusses a chemical precipitation method using hydrated lime $Ca(OH)_2$) whereby calcium fluoride compounds are selectively precipitated. In addition precipitation of phosphate has been evaluated. This was based on the build-up of potentiometric titration curves of both real and synthetic samples containing H_3PO_4, HF and H_2SiF_6. The synthetic mixtures of acids were prepared so that they were similar in acids content found in real wastewater samples. Selective precipitation was relied on pH and temperatures at which various compound were precipitated. Chemical and physical properties of the precipitates were characterized to evaluate their suitability for metallurgical and agricultural uses.

2. Experimental work

2.1. Materials and chemicals

All chemicals used in the current work were of chemical grade (HF, H_2SiF_6, H_3PO_4, NaOH). NaOH solution (1.93 M) was prepared from pellets and standardized using potassium-hydrogen phthalate and phenol phthalene indicator. This solution was used for potentiometric titration of synthetic acid mixtures. Calcium hydroxide powder (Merck®) was used for precipitation experiments. Dionized water was used for the preparation of all solutions and washing up the labware used in the current study.

2.2. Effluent water samples

Wastewater samples were collected from effluent pond at IJC plant. The locations and samples designations are shown in Fig. 1. Seven samples were collected from evaporation pond (samples 5–11). Sample 5 was collected directly from the pipe which delivers water to the pond. Fig. 1 also shows the contribution of each source to the stream sent to effluent pond. It is *important to point* out that the right side of the evaporation pond (new pond)