

論文の内容の要旨

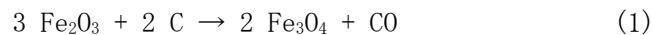
論文題目 Recovery of Phosphorus from Sewage Sludge Ash and Synthesis of Phosphate compounds
(下水汚泥灰からのリン回収とリン酸塩化合物の合成に関する研究)

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The purpose of this research work is to develop novel processing methods designed for the recovery of phosphorus from Sewage Sludge Ash (SSA) in order to obtain phosphates for useful applications. The first two methods are intended to obtain phosphates suitable for fertilizer formulations, which require the presence of soil-soluble phosphates; while the third method is aimed at obtaining hydroxyapatite, which is a phosphate suitable for applications in biomaterials.

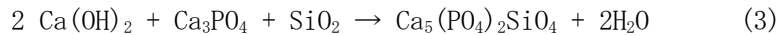
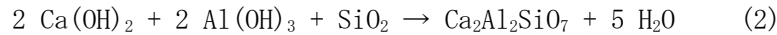
The first two methods developed use physical processing techniques that have not been studied as alternatives for the recovery of phosphorus from SSA yet. For instance, using High Gradient Magnetic Separation (HGMS) to remove the iron oxides commonly found on SSA to increase the percentage of phosphorus. Similarly, using the surface properties of phosphates, to promote their concentration in a particular phase using physical methods like liquid-liquid separation and flotation. On the other hand, the third method refers to the development of a novel technique for the synthesis of hydroxyapatite (HAP), carried out entirely in the highly alkaline region, while including the potential usage of SSA as a source of recycled phosphorus.

The first method highlighted that the SSA sample has a phosphorus content of 18.5% P₂O₅ and it was difficult to achieve phosphate enrichment subjecting SSA to magnetic separation directly. Then, heating SSA samples under an inert atmosphere using carbon was shown to enhance SSA magnetization, as shown in reaction (1).



Also, performing this heating step using a mixture of SSA+carbon+Fe₂O₃ was shown to improve the soil-solubility of the phosphate phase obtained as the formation of calcium iron phosphate was observed. HGMS separation at 0.1 T of the aforementioned sample, followed by the flotation of the “nonmagnetic-fraction” at pH 10, yielded a further relative difference of 19% in phosphorus content in the froth, indicating that Method #1 constitutes an alternative approach for the recovery of phosphorus from SSA, as evidence was found in this study indicating that using a heating step under reducing conditions and N₂ atmosphere, followed by HGMS and flotation, can promote an overall phosphorus recovery from SSA of about 30%; indicating this method could be easily implemented as a pre-treatment option for SSA samples containing large amounts of iron oxides.

The second method pointed out the feasibility of obtaining *silicocarnotite* (Ca₅(PO₄)₂SiO₄) and *gehlenite* (Ca₂Al₂SiO₇) simultaneously at temperatures in the range 1200 - 1400 ° C, as evidenced on thermogravimetric and X-ray diffraction results, when reactions (2) and (3) were carried out at temperatures in that range:



In addition, to study SSA as a potential precursor for reactions (2) and (3), a SSA sample with a phosphate content of 18.5% wt. was mixed with a controlled amount of Ca(OH)₂ to promote the simultaneous formation of silicocarnotite and gehlenite. This sample was labeled “*H-Ash*” (heated ash), and its structure was validated using XRF and XRD, confirming the presence of the phases silicocarnotite and gehlenite.

Zeta potential measurements were used as an approximation for the surface charge of all the products. Hence, aqueous mixtures of silicocarnotite and gehlenite were prepared separately and evaluated using a zeta potential analyzer for pH values ranging from pH 2.5 to pH 11, indicating that silicocarnotite is positive below pH 5.5 and gehlenite is negative throughout the whole pH range studied.

For the separation experiments, 25 mL samples containing 10% wt. of solid material were prepared and mixed with different doses of sodium dodecyl sulfate (SDS). It is proposed that an anionic surfactant like SDS will interact with the positively charged surface of silicocarnotite and form reverse micelles, which can then be captured by an organic solvent. The final steps were the incorporation of kerosene to the aforementioned mixtures in a 2:5 ratio, and the thorough mixing of the resultant blends. After 30 minutes of settling time, both fractions dried, and analyzed using XRF to assess the P205 content on each fraction.

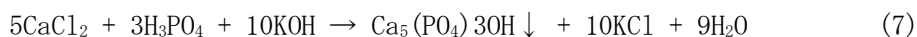
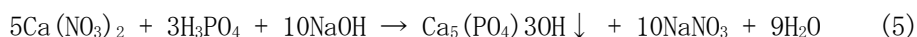
The separation procedure was carried out at two different pH values. The first value

(pH = 5.5), was selected based on the result of the zeta potential analysis, specifically, the point of zero charge of silicocarnotite. The second value (pH = 4.0) was selected based on the solubility of silicocarnotite below this pH.

The results of the experiments carried out for the liquid-liquid separation process using kerosene and sodium dodecyl sulfate (SDS) indicated that the anionic nature of SDS promotes the clustering of silicocarnotite in the organic fraction, but it does not affect the gehlenite in an appreciable manner. When this separation process was carried out for samples containing synthetic silicocarnotite and gehlenite simultaneously, the P₂O₅ concentration (21.12%) in the organic fraction was approximately 2 times higher than the P₂O₅ concentration found in the aqueous fraction (10.13%), indicating that silicocarnotite was enriched from “*H-Ash*” by the separation technique proposed. In addition, the method presented benefits from the simplicity of the physical process of liquid-liquid separation, implying that it is possible to scale up the process (e. g. using a sequence of liquid-liquid separation vessels) in order to improve the yield of phosphorus recovery.

Lastly, the third method highlighted that the formation of HAP via chemical precipitation is thermodynamically more favored under highly alkaline conditions (pH >11), as long as the supply of Ca²⁺, (PO₄)³⁻ and (OH)⁻ is guaranteed, which is the basis for the novel HAP synthesis technique proposed in this work.

This novel synthesis refers to the wet chemical route for HAP, carried out entirely in the highly alkaline region (pH ≥ 11), as the system Ca²⁺ and (PO₄)³⁻ ions develop in solution is more thermodynamically favored at high pH values. For this purpose, the program HSC Chemistry version 5.1, the computational package MEDUSA and the HYDRA database were used to study the favorability of HAP synthesis for chemical systems in solution. Then, several reactions usually employed in the synthesis of HAP via chemical precipitation were selected and the thermodynamic parameters involved in the formation of 1 mol HAP at 25 ° C and 1 bar of pressure were calculated. Using the results of the assessment, reactions 4-7 were proposed as study cases for the synthesis of HAP under highly alkaline conditions:



where HAP is predicted to precipitate as Ca₅(PO₄)OH.

Consequently, to study the synthesis proposed, the experimental synthesis of HAP was carried out for the reactions described in reactions (4)-(7), and the obtained

solids were characterized using XRD analysis and SEM imaging. To evaluate the composition and Ca/P ratio, the final HAP powders obtained were analyzed using ICP-MS.

Modeling predicted that the concentration of $(\text{HPO}_4)^-$ ions decays rapidly and allows for the formation of the $(\text{PO}_4)^{3-}$ anion at pH higher than 11, indicating the direct interaction of $(\text{PO}_4)^{3-}$ and Ca^{2+} to form HAP in this pH region. On the other hand, when the synthesis was carried out experimentally, ICP-MS analysis for the powders throughout all the reactions tested highlighted that the molar ratio between Ca and P in HAP varies in the range: $\text{Ca/P} = 1.40$ to $\text{Ca/P} = 1.94$. Likewise, XRD analysis on the powders pointed out that HAP structures are readily formed at this pH, in accordance with the prediction made by the computer software.

In terms of SSA, leaching using different acids (HCl , H_2SO_4 , HNO_3 ; concentration 1M) was performed to assess their effect on phosphate retrieval. Hence, samples of 5% SSA in acid solution were prepared and leached. After separation, the solid was dried and analyzed using XRF, while the leachate was analyzed using ICP-OES. Lastly, the leachate was used for subsequent experiments to test its use as a recycled source of phosphate via the same technique used for reactions (4)-(7).

When SSA acts as a source of recycled phosphorus, our results showed that mineral acids are effective at phosphorus leaching, with H_2SO_4 having the largest leaching potential. When this leachate is used to synthesize HAP, the product attains a Ca/P molar ratio of 1.95 and an XRD resembling synthetic HAP. These results are extremely promising since they indicate there is no difference between using recycled sources of phosphate for HAP synthesis via the novel method presented in this thesis. Nonetheless, more conclusive results for the purification step of SSA leachate are needed to have a detailed view of the process.

In summary, this research work presented 3 original alternative methods designed to achieve the recovery of phosphorus from SSA and the formation of phosphates useful for agriculture in the case of methods #1 and #2, and phosphates useful for biomaterials in the case of method #3. The first two methods are suggested to recover phosphorus from SSA by means of physical techniques, and at the same time produce soil-soluble phosphate phases which are suitable for fertilizers. Likewise, the third method introduced a completely novel synthesis process for HAP formation at high pH values and showed the feasibility of using leachate from SSA as a low-cost source of recycled phosphate. Therefore, this method is an entirely original approach and might have an advantage over traditional techniques that require pure phosphate reactants for the synthesis of HAP.