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Selective recovery of phosphorus as AlPO4 from silicon-free CFB-derived fly ash leachate

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1. Introduction

Phosphorus (P) is an irreplaceable essential element for crop growth and food production. Modern agricultural practice requires a steady supply of chemical fertilizer containing phosphorus. Apatite mineral is the main raw material used in manufacturing P-fertilizer, this is depleting and about 100 years of economical mining is estimated to remain [1, 2]. As a sustainable supply of affordable phosphorus is at risk, immediate measures are required to reduce our use of non-renewable phosphate rock by being more efficient in the use of phosphorus and recycling of P-rich wastes [3, 4]. Inorganic ash residues from the combustion of various fuels are being considered as resources for phosphorus recycling. P recovery using chemical extraction from sewage sludge ash [5, 6, 7, 8, 9, 10, 11], municipal solid-waste incineration fly ash [12], chicken manure incineration ash [13], and fractionation from biomass fly ash [14] show great potential towards mitigating the threat of a phosphorus-supply crisis.

In recent years, recovery methods for phosphorus from solid ash materials have been extensively studied. Some methods involve release of P to liquid phase by various means, such as supercritical water oxidation [15] and acid extraction followed by precipitation [5, 12, 13], liquid-liquid/solvent extraction [6, 8] and adsorption [7] based recovery, while other methods include P-recovery via thermo-chemical [9], electro-kinetic [10], and bio-leaching and accumulation [11]. Feasibility of the extraction procedures and the purity of P-products greatly depend on concentration of phosphorus and other major elements, such as iron (Fe), aluminum (Al), calcium (Ca), and silicon (Si) in the leachate solution [12, 16]. Previous precipitation-based attempts of P recovery from fly ash leachate solutions were focused on precipitation of phosphorus with calcium due to the higher solubility of Ca-P solids in water than that of Al/Fe-P solids, and their potential usability as chemical fertilizers. In addition, these studies demonstrated a two step precipitation method involving removal of Fe impurities at pH 3, and recovery of P at pH 4; and a loss of phosphorus of up to 27% has been reported [5, 12, 13]. The fraction of P in the precipitate is highly affected by the pH and stoichiometric concentrations of Fe, Al, Ca, and Si, because phosphorus could potentially precipitate as $FePO_4$ at pH 1-3 [17], $AlPO_4$ at pH 3-5 [18], and $Ca_5(PO_4)_3OH$ at pH > 4 [13]. Due to lack of commercial value as a raw material for the phosphate industry and its low solubility, iron phosphate is less favoured for P recovery from secondary resources [15]. Besides precipitation based removal of iron from the solution at lower pH; which is associated with a

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significant loss of P, Fe can be retained in the solution above pH 3 by adding certain chelating agents which react with Fe to form stable iron chelates [19], thus allowing precipitation of P with either Al or Ca.

This paper describes the procedure and results of P recovery in single precipitation step by retaining Fe in solution via EDTA chelation from the Si-free leachate solution obtained in our previous study [20]. pH values for precipitation and EDTA concentration have been optimized, and the obtained phosphorus products have been characterized and their usability is discussed.

2. Experimental

2.1. Materials

A fly ash (FA) sample originated from wood based biomass as fuel for combustion process was provided by Alholmens Kraft Oy. A RETSCH sieve shaker (AS200 basic) was employed for dry sieving with sieve size of 125 μm for 30 minutes. 100 g of FA was taken for screening. Then the fractionated FA (FFA) of particle size lower than 125 μm was used for acid leaching, while the other fraction was discarded. 0.25 g of each solid ash sample was dissolved in 3mL of aqua regia with 3-4 drops of hydrofluoric acid. The digestion was further assisted by ultrasound for 18 minutes at 60^{o}C . Elmasonic P (70 H) from Elma Schmidbauer GmbH was employed as ultrasonic source. The samples were shaken in between to release the evolved gas. This acid-digested solution was further diluted to 100 ml for element composition determination. Hydrochloric acid (≥37% HCl) from Honeywell-Fluka, nitric acid (≥65% HNO_3) and disodium ethylenediaminetetraacetic acid (EDTA) from Sigma-Aldrich, and sodium hydroxide (NaOH) from VWR chemicals, all of analytical grade, were used in the experiments.

2.2. Preparation of Si-free leachate solution

20 g of FFA was leached in 240 ml (LS ratio of 12) of 8 M hydrochloric acid solution. The leaching experiment was assisted with mechanical stirring and ultrasonic digestion for 20 min. The leachate solution was transferred to centrifuge tube and centrifuged (at 3500 rpm) for 15 minutes to separate the solid residue. Then the leachate solution was left for 5 hours to precipitate the silicon as silica-gel which was removed from the leachate solution by centrifugation. Details of Si-gel formation mechanism and kinetics are presented in our previous study [20].

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2.3. Identification of P recovery parameters

The composition of fly ash is important in the development of phosphorus extraction. The wet chemical extraction of P-products is based on the solubility of its salts as a function of pH [21]. Hence, only pH and the ratio of EDTA concentration to iron and aluminum concentration (ER =[EDTA]/[Fe+Al]) are selected as important parameters for P recovery in this study. The precipitation-based recovery of P was conducted at room temperature.

2.4. Experimental method

Response surface method (RSM), a combination of mathematical and statistical techniques [22], was used to study the effects of pH and ER. Orthogonal central composite design (CCD) consisting of total 12 runs including 4 repeats on the center points was created and analyzed using RcmdrPlugin.DoE plug-in (version 0.12-3) [23, 24] in an R software environment [25]. 10 ml of Si-free leachate solution was taken and the required weight of EDTA was added to maintain the ER value with an accuracy of ±0.01. These solutions were titrated with freshly prepared 3M NaOH to achieve the targeted pH with an accuracy of ±0.1. The analyte concentration was determined only from the supernatant.Table S1 shows the operating parameters for the experimental runs. Using least-square regression from the software, optimum conditions for total recovery of phosphorus were then identified.

2.5. Recovery experiment

An additional study was conducted to analyze the effect of pH on the purity of precipitated P-products at optimal ER values. For this study, 20 ml of Si-free leachate solution was titrated with 3M NaOH to adjust the pH between 3 and 5; three replicates were used in the experiment. The titrated solutions were left to stand for several hours. The solution was then filtered with Whatman No. 41 filter paper) and washed 5 times with ultrapure water. The precipitant was oven dried at $60^{o}C$ and samples were recovered directly from filter paper for characterization.

2.6. Analysis of leachate solution

Speciation of the solution phase was done with the Medusa & Hydra program [26]. The components considered were aluminum, iron, calcium, phosphorus as $H_nPO^{(3-n)-}_4$, EDTA and chlorine. Concentrations of analytes similar to the leachate solution were used in the equilibrium calculation; the dilution effect due to NaOH addition during titration was also considered. The ionic

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strength of the solution is set at 1, unless otherwise stated. All the soluble and solid complexes available in the database were allowed.

2.7. Analytical methods

The concentration of analytes in the solution were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES PerkinElmer Optima 8300). Titration of acid leachate solution with 3M NaOH was conducted with TitroLine easy unit (SCHOTT Instruments GmbH). Bruker Quantax400 EDS coupled with Zeiss EVO-50XVP and Bruker Alpha Platinum-ATR were employed respectively for elemental and infrared analysis of precipitant obtained at pH 3-4.6. 250 mg of final P-product (precipitant obtained at optimal pH and ER value) was dissolved in 3 mL of aqua regia and diluted to 50 mL for determination of trace elements by ICP-OES. The aliquot was further diluted by a factor of 10 for determination of P and other elements. An X–ray powder diffraction analysis of final P-product was done with a PANalytical X'Pert Pro alpha 1 diffractometer using Johansson monochromatized Cu $K_{\alpha 1}$ radiation (λ = 1.5406 ; tube settings: 45 kV, 40 mA). The data were recorded from a spinning sample by X'Celerator detector in the 2θ-range of 6–80^o with a step size of 0.017^o and counting times of 120 s per step. The diffraction data were handled by X'Pert HighScore Plus v. 4.5 program.

3. Results and discussion

3.1. Fly ash and acid leachate characterization

The elemental composition of the pristine fly ash (FA), recovered fly ash with particle size lower than 125μm (FFA) and discarded fraction containing particles greater than 125μm are listed in Table 1. In this study, FFA is used in the context of phosphorus recovery. Most of undesired elements, including Si, Ca, Fe, Al, etc. can be removed by sieving fractionation of fly ash [14]. Properties of fly ash and acid leachate solutions are briefly presented and discussed in our earlier study [20], which summarizes that P concentration increases by a factor of 1.38 and Si decreases by a factor of 3.8 during the fly ash fractionation at sieve size of 125 μm. In addition, leaching of fly ash with 8M HCl acid removes of 98% of silica as silica gel in 5 h. The obtained Si-free leachate solution is used in this study for phosphorus recovery.

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Table 1: Elemental composition and heavy metal content of FA (pristine fly ash), FFA (recovered fly ash with particle size lower than 125µm) and DFA (discarded fraction of FA containing particles greater than 125µm) measured by ICP-OES after extracting with aqua regia and 3-4 drops of HF.

Element	Major elements (%)						Trace elements (mg/kg)						
	P	Al	Fe	Si	Mg	Ca	Zn	Cu	Cr	Pb	Ni	As	Cd
FA	1.21	3.38	2.01	17.3	2.16	15.4	1704	89.6	45.1	26.3	24.6	6.7	8.6
FFA (<125µm)	1.67	3.11	2.03	4.54	2.83	21.7	2595	99.7	50.4	35.2	33.7	11.7	11.5
DFA (>125µm)	0.47	4.16	2.15	30.3	1.03	5.4	475	82.5	44.8	12.8	12.4	<LOQ	<LOQ

3.2. Phosphorus chemistry in leachate solution

Solid-ash residue may consist of phosphorus as P-oxide and phosphate of Ca, Al, Fe, and Mg metals [27, 28, 29]. $H_nPO_4^{(3-n)-}$ derivates of phosphate are generally assumed to predominate in the solution phase when metal phosphates and P-oxides react with acid or base [30]. Furthermore, the fraction of $H_nPO^{(3-n)-}_4$ derivates is a function of pH and various salts of such phosphate derivatives may precipitate at different pH [12, 13, 21]. Analysis of various phosphate species in acidic media with Medusa/Hydra program reveals predominance of $FePO_4$ below pH 2.5, $AlPO_4$ between pH 3-5, and $Fe_3(PO_4)_2$ and $Ca_5(PO_4)_3OH$ above pH 5 (Fig. 1). This strongly implies the possibility of P-recovery as $FePO_4$, $AlPO_4$ and $Ca_5(PO_4)_3OH$ at pH's where they predominate.

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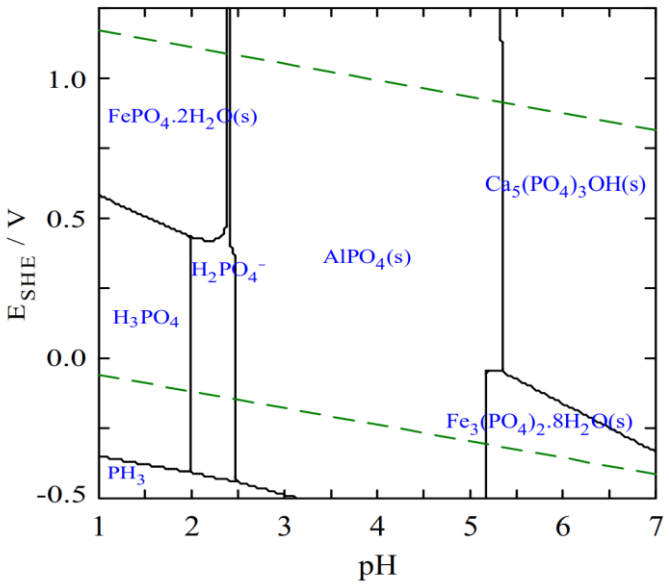

Figure 1: Eh-pH diagram representing predominant phosphorus species in solution phase. Equilibrium calculations with 24 mM of [PO_4] and PO_4:Fe:Al:Ca = 1:1:1:10 (molar fraction) were made using the Medusa/Hydra program. Area between the dashed green line (- - -) represents the stability region of water.

Stoichiometric concentrations of Fe, Al, and Ca and the reduction potential of the solution also play an important role in the efficient recovery of phosphorus. $Fe/P_{(mol)} \geq 1$ ($Fe/P_{(mass)} \geq 1.8$) and solutions with high reduction potential i.e., strong oxidizing conditions, are required for $FePO_4$ precipitation. However, recovery of phosphorus with iron is challenging because of akaganéite ($Fe(OH)_{1-x}Cl_x$) co-precipitation, this is a predominant species in chloride media and its solubility equilibria allows its precipitation at pH less than 2 [31, 32]. Fe speciation with Medusa/Hydra program in 2M Cl^- solution also indicates the precipitation of akaganéite alongside $FePO_4$, which is shown in Fig. S1 (cf. supporting information). Furthermore, chloride concentration and reduction potential of the solution seem to have an adverse effect on $FePO_4$ formation as seen in Fig. S2. In the context of phosphorus recovery, $Fe/P_{(mol)}$ of 115 in first precipitant at pH 3 was observed by Kaikake et. al., which indicates that iron phosphate was a minor component in the precipitate [13]. Due to lack of commercial value of iron phosphate, lower value of Fe/P molar ratio (0.42 in the leachate solution) and tendency of akaganéite co-precipitation, phosphorus recovery with iron is not explored in this study. Instead, the prevention of the precipitation of iron from the solution with Fe-EDTA chelation and recovery of phosphorus with either aluminum or calcium is studied. Use

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of such a masking reagent is beneficial and economical in comparison to a two-step precipitation, since the earlier method avoids the use of a separate reactor during the recovery process.

3.3. Effect of pH and EDTA on phosphorus recovery

The interference of unwanted metals in the solution can be masked by ethylenediaminetetraacetic acid (EDTA). EDTA as a chelating agent in recovery processes has been used in struvite precipitation by Ca-masking [33] and Ni recovery by Fe-masking [34]. Thus, excessive contamination of the recovered P-products is prevented by a careful control of EDTA concentration and pH of the solution. The dependence of phosphorus recovery on pH and efficacy of Fe chelation with EDTA were tested using response surface methodology. A central composite design consisting of 12 runs was created and the experiments were run on the sequential order as provided by the program (RcmdrPlugin.DoE plug-in in R environment). The operational value and experimental recovery values of P, Al, Fe, and Ca are presented in Table S2. A pH domain between 3.8 and 5.2 was evaluated to identify the optimum range for efficient phosphorus recovery. Meanwhile, the ratio of EDTA and sum of Fe and Al concentrations (ER =[EDTA]/[Fe+Al]) was varied between 0.29 and 1.71 to test the feasibility of phosphorus precipitation with aluminum or calcium. The concentration of EDTA is equal to that of Fe (i.e. [EDTA]=[Fe]) at an ER value of 0.29. Therefore, ER value of 0.29 is selected as minimum operating value for this study where complete chelation of Fe by EDTA is assumed, based on stoichiometric equilibria. An [EDTA]/[Fe] value of 1 was also used in the recovery of Ni by chelation of Fe with EDTA [34]. Higher ER values were also investigated in order to explore the feasibility of phosphorus precipitation with calcium because there is stoichiometric equilibrium between EDTA and the sum of Fe and Al concentration at an ER value of 1, which suggests chelation of both Fe and Al.

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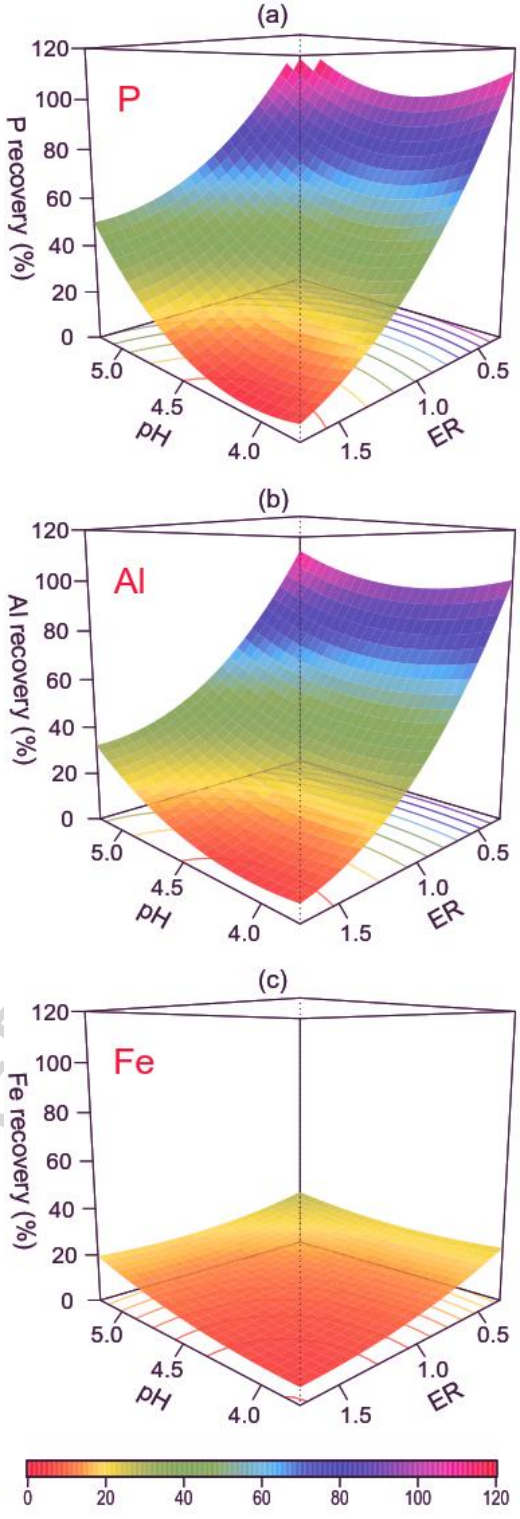

Figure 2: Response surface for the recovery of phosphorus (a), aluminum (b), and iron (c) as a function of pH and ER (=[EDTA]/[Fe+Al]) on based on central composite design (CCD). ER of 0.29 indicates stoichiometric equilibrium between EDTA and Fe i.e. [EDTA]/[Fe]=1

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The predicted response surfaces for the recovery of phosphorus, aluminum and iron are presented in Fig.2, while the predicted coefficients values for the quadratic model are summarized in Table S3. Multiple R^2 values of 0.966, 0.981, and 0.866 were obtained respectively for P, Al, and Fe response models and the fit based on the summary of least-square regression is depicted in Table S4. In addition, Fig. S3 also suggest lack of outliers within the experiment domain. Therefore, the reliability of predicted response surface within the experiment domain is validated with the help of regression parameters and the error in model prediction increases in the order of Al < P < Fe model. A lower ER value of 0.3 and pH range of 4-5 yield the highest phosphorus recovery, the patterns of P and Al recoveries were similar which is expected due to $AlPO_4$ precipitation. When pH is increased from 3.8 to 5.2, more iron is precipitated from the solution; the amount decreases when the ER value is increased due to the formation of stable Fe-EDTA complexes. The progression of P, Al, and Fe precipitation from the solution is also supported with equilibrium model made in Medusa/ Hydra program as portrayed in Fig. 3, which shows that the selectivity of EDTA in the experiment domain decreases in the order of Fe > Al > Ca. This indicates that higher EDTA concentrations also form stable EDTA chelates with Al and Ca, thus reducing the phosphorus precipitation, as seen in Fig. 2a. These calculations also point to the predominance of $AlPO_4$ solid in precipitation, which is highest near pH 4 and decreases with increasing EDTA concentration. Therefore, the effect of pH on the purity of recovered $AlPO_4$ product was further studied at an [EDTA]/[Fe] value of 1.

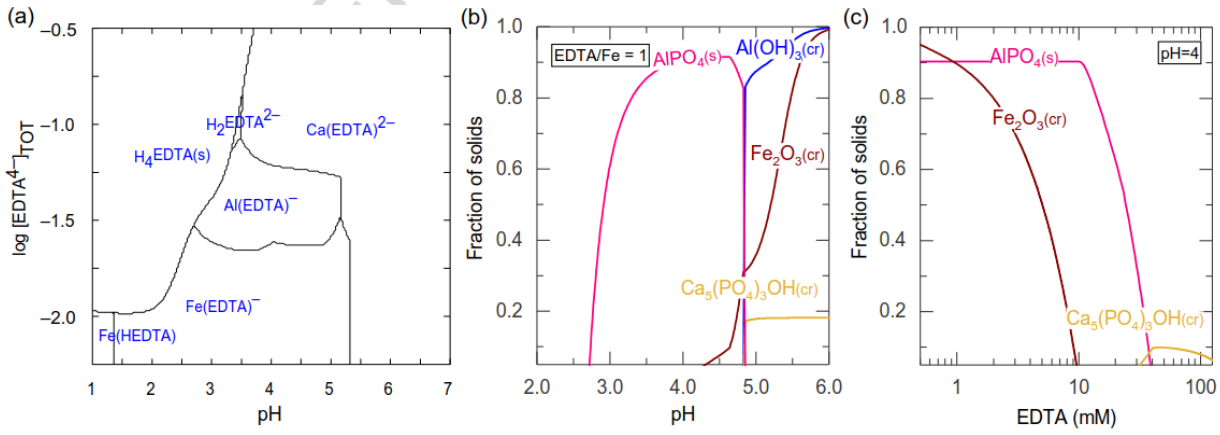

Figure 3: Speciation of EDTA complexes as a function of pH and EDTA concentration (a), and solid species as a function of pH (b) and EDTA concentration (c) in the leachate solution using Medusa and Hydra program.

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3.4. The purity of phosphorus product

The concentrations of selective analytes, P, Al, Fe and Ca, were measured at various pH's and the fractions remaining in the solution are shown in Fig. 4a. This shows that phosphorus and aluminum recoveries are near 100% at pH 4, while the efficiency of Fe chelation by EDTA is 70-75% which are similar to the results obtained with the RSM model. The elemental composition of dry precipitated products reveals that solids with higher P content (>20%) are obtained between pH 3.5 and 4, as shown in Fig. 4b. The maximum theoretical phosphorus fraction in pure dry $AlPO_4$ is 25.4%. Infrared spectra of these precipitants were compared with those of synthetic $AlPO_4$ precipitated by the titration of solution containing 0.1 M of $Al(NO_3)_3$ and H_3PO_4 with 1M NaOH at pH 4 (Fig. 4c). The recovered products exhibit characteristic P-O stretching peaks at 1050 cm^{-1} compared to those of synthetic $AlPO_4$ at 1065 cm^{-1}. As the pH increases, shifts of the ν(P-O) bands to lower energy, in terms of cm^{-1}, are also observed, which is due to a significant decrease in the force constant for the P-O and P-OH bands with decreasing protonation [35, 36]. The difference between ν(P-O) bands of precipitated and synthetic $AlPO_4$ obtained at pH 4 is due to impurities in the precipitate which weaken the P-O bonds. Based on these observations, pH value of 4 and [EDTA]/[Fe] ratio of 1 are identified as the optimal conditions for the recovery of P-products with low level of impurities.

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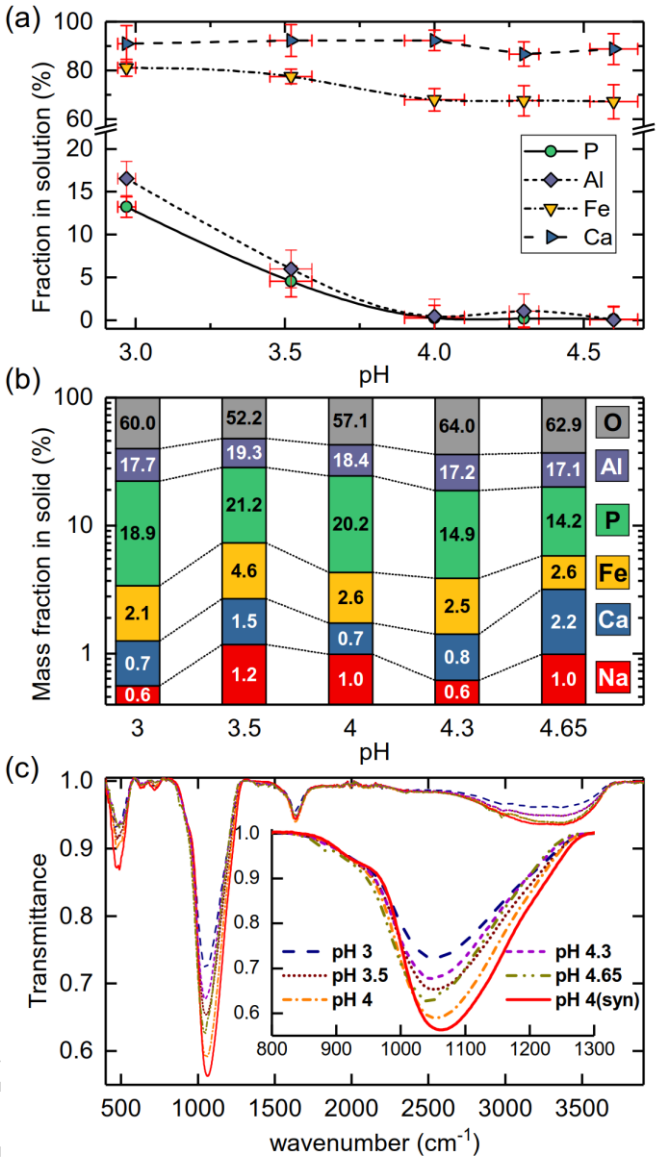

Figure 4: Effect of pH on (a) recovery of phosphorus and other major analytes from solution, (b) fraction of P in solid precipitant, and (c) positioning of *ν*(P-O) bands of solids as compared to the synthetic $AlPO_4$ in IR spectrum.

3.5. Efficacy of proposed phosphorus recovery method

The concentration of major (P, Al, Fe, Si, & Ca) and trace (Zn, Cu, Cr, Pb, Ni, As, & Cd) elements at each step during the recovery method is summarized in Table 2. Leaching efficiency of over 100% is accounted for some analytes, which is attributed to inhomogeneity of the fly ash and errors in analytical precision. This method includes the following steps; a) fractionation of fly ash with sieve size of 125 μm, b) 8 M HCl acid leaching, c) silica removal by aging of silica gel

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until precipitation, and d) phosphorus recovery with aluminum by masking Fe with EDTA. This method allows efficient removal of Si as gel prior to selective precipitation of phosphorus with aluminum by masking of iron with EDTA. Fig. S4 shows the advantage of Si removal on the composition of final product, where precipitation of the leachate obtained with 2M HCl at pH 3.5 yields a phosphorus product containing 7.9, 9.1, 6.9, and 13.1 $\%_{(wt.)}$ of P, Al, Fe, and Si, respectively. This signifies the importance of Si removal prior to the phosphorus recovery via precipitation.

Table 2: Concentration of major and trace elements during fractionation of fly ash (FFA), acid leaching, silicon removal by Si-gel precipitation, and recovery of phosphorus via precipitation at pH 4.

Element	FFA	8M HCl leaching (LS=12)		Ageing of Si-gel (5hr)		P-precipitation (pH=4, [EDTA]/[Fe]=1)		
	(<125 µm)	Leachate	Dissolved	Supernatant	Retained in Si-gel	Filtrate		Recovery
	(mg/kg)	(mg/L)	(%)[+]	(mg/L)	(%)*	(mg(L)	SD	(%)
P	16737	1452	104.1	1491	10.7	3.91	0.52	99.92
Al	31002	1319	51.1	1337	11.8	6.07	0.66	98.52
Fe	20365	1095	64.5	1106	12.1	230.5	11.4	31.93
Si	45359	1950	32.3	20.95	98.5	-	-	-
Mg	28314	2151	91.2	2176	12.0	574.7	21.9	13.71
Ca	217524	17720	97.8	17370	14.7	4358	204	18.03
Zn	2595.47	226.62	104.8	225.50	13.4	50.59	0.88	26.72
Cu	99.73	7.57	91.1	7.36	15.4	1.95	0.03	13.48
Cr	50.36	3.37	80.2	3.34	13.8	0.27	0.02	73.32
Pb	35.21	3.07	104.8	3.15	10.9	0.37	0.03	61.88
Ni	33.66	2.43	86.5	2.34	16.0	0.52	0.01	27.64
As	11.71	1.06	108.7	0.74	39.1	0.17	0.03	23.98
Cd	11.54	0.99	103.1	0.98	13.6	0.25	0.01	18.00

[+] Recovery (%) = $(C^{leachate}_{mg/L} / C^{FFA}_{mg/kg}) \times LS \times 100$; where C = analytes concentration

* Retained in Si-gel (%) = $(1- v_f(C/C_0)) \times 100$; where $v_f = 0.87$ (volume fraction recovered after Si-gel removal) C_0,C are concentration before and after Si removal

3.6. Characterization and usage of phosphorus product

Table 3 contains the element composition of the final P-product obtained at pH of 4 and [EDTA]/[Fe] ratio of 1. The pure precipitate consists of 16.31 and 18.08 % of aluminum and phosphorus, giving an Al/P ratio of 0.90, which is close to the theoretical ratio of 0.87 in synthetic $AlPO_4$. The diffuse peaks near 28-29^o 2θ in the XRD pattern (Fig. 5) indicate the formation of

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amorphous aluminum phosphates. Similar XRD patterns were observed for the aluminum phosphate precipitated from aluminum sludge [18] and aqueous solution of 50-100 ˚C [37]. In addition, the infrared spectra of precipitated compounds resemble to that of synthetic aluminum phosphate (Fig. 4c). The recovered $AlPO_4$ also contains some EDTA fraction in the solid as shown by CHN values in Table 3. The major impurity in the recovered product is Fe at 2.18%, while that of other elements is less than 1%. The trace metal concentrations were also determined with ICP-OES; their concentrations are lower than the maximum limit values for use as fertilizer [38]. Despite the low solubility of aluminum phosphate in water, these P-products can be used as slow P-releasing fertilizers. However, aluminum toxicity in plants may prohibit its use as fertilizer, especially in acidic soils [39]. The industrial use of aluminum phosphate recovered from ash material is very limited. Therefore, either new uses of recycled aluminum phosphate and/or conversion of aluminum phosphate to more usable phosphorous compounds such as calcium and/or sodium phosphate need to be developed [40].

Table 3: Concentration of major and trace elements in the precipitate obtained at pH=4 and [EDTA]/[Fe] = 1.

Major element	P	Al	Fe	Ca	Mg	C	H	N
(wt%)	18.08	16.31	2.18	0.63	0.12	1.26	3.13	0.15
Trace element	Zn	Cu	Cr	Pb	Ni	As	Cd	
(mg/kg)	1323	19.4	258	104	8.14	37.9	1.19	
	(4500)	(700)	(300)	(150)	(150)	(40)	(25)	

* Values in ( ) are limit values for fertilizer use [38]

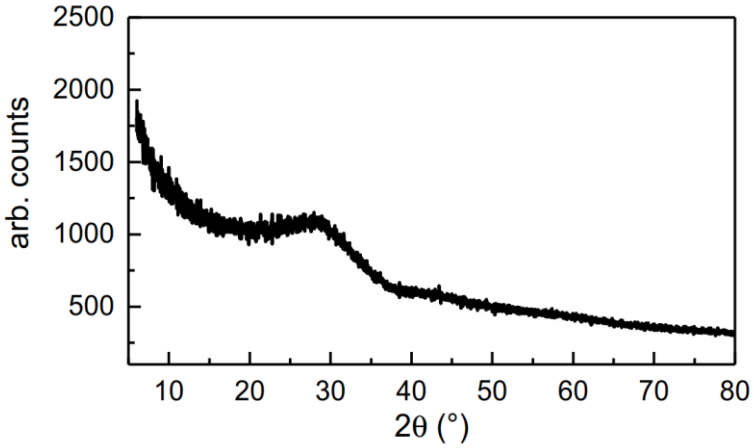

Figure 5: X-ray diffraction pattern showing the amorphous nature of the P-product obtained at pH 4.

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4. Conclusion

The recovery of P from highly siliceous fly ash originating from CFB-boilers with acid leaching followed by removal of Si by gelation was investigated in this study. The fly ash was treated with higher molar (8M) concentration of hydrochloric acid to obtain a phosphorus-rich solution, despite the possibility of economical leaching with lower molar (2M) HCl. Our previous study revealed that fly ash leaching with higher acid concentration facilitates the formation of Si-gel in a shorter time, thus allowing the removal of 98% of silica in only 5 h. The removal of silica from the solution is critical for the purity of the recovered P-product, as Si not only co-precipitates with phosphorus but also promotes co-precipitation of other metals. After removing Si from the solution, iron co-precipitation was prevented by EDTA chelation, which further increased the purity of recovered P-products. A pH value of 4 and [EDTA]/[Fe] ratio of 1 were identified as optimal conditions for phosphorus precipitation with aluminum. Besides 16.31% of Al and 18.08% of P, the recovered P-product contains of only 2.18% of Fe and 0.63% of Ca. In addition, the trace elements with hazardous character are present at low levels of concentration. The prevention of iron inclusion into the P-product by use of Fe-masking EDTA is recommended, instead of Fe removal via a two-step precipitation, since the earlier method significantly lowers the cost of recovery by eliminating the need of additional reactor and utilities.

In conclusion, the phosphorus content was significantly increased from 1.21% in pristine fly ash to 18.08% in the final product. The proposed recovery method may contribute to meet future phosphorus demand and sustain a continuous supply of phosphorus.

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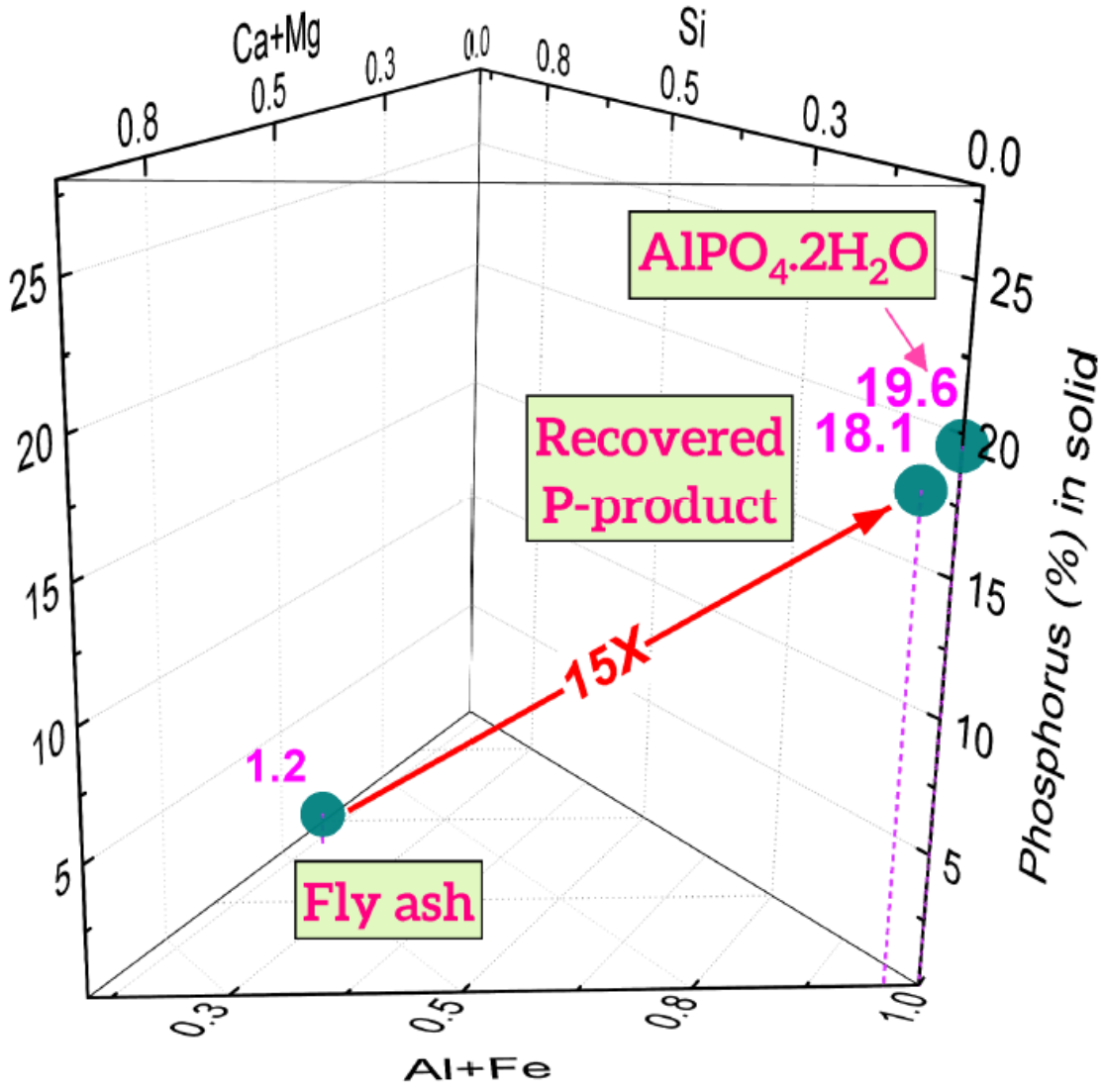
Graphical abstract



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Highlights

- Phosphorus (P) is precipitated with aluminum at pH 4 with 98% recovery efficiency.
- EDTA is used for masking of iron (Fe), and ~70% of Fe is prevented from precipitation.
- The recovered P-product contains 18% and 16.3% of P and Al respectively as major elements and 2.2% of Fe as impurity.

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