

Phosphate immobilization from aqueous solution by fly ashes in relation to their composition

Jiangang Chen, Hainan Kong*, Deyi Wu, Xuechu Chen, Dalei Zhang, Zhenhua Sun

School of Environmental Science and Engineering, Shanghai JiaoTong University, Shanghai 200240, China

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Abstract

Phosphate sorption capacities of 15 Chinese fly ashes were determined and related to their composition. The data of P sorption were best fitted to Langmuir equation, and the calculated sorption maxima of phosphate (Q_m) ranged from 5.51 to 42.55 mg/g. The Q_m value showed a significantly positive correlation with total Ca content ($r=0.9836^{**}$) and total Fe content ($r=0.8049^{**}$), but negative correlation with total Si and total Al content. Correlation coefficients of CaO ($r=0.9647^{**}$) and CaSO₄ ($r=0.9399^{**}$) were much greater than that of CaCO₃ ($r=0.6361^*$). Correlation coefficients of Q_m with Fe₂O_{3d} and Al₂O_{3d} were much higher than those of total Fe and total Al contents, respectively. Fractionation of P sorbed by fly ash revealed that loosely bound P fraction and/or Ca + Mg-P fraction were the dominant form of immobilized phosphate. Ca content was strongly correlated with the Ca + Mg-P fraction instead of Mg content, whereas Fe content was highly correlated with Fe–Al-P fraction compared with Al content. The loosely bound P was correlated well with both Ca and Fe content. The greatest removal of phosphate occurred at alkaline conditions for high calcium fly ash, at neutral pH levels for medium calcium fly ash, while low calcium fly ash immobilized little phosphate at all pH values. This behavior was explained by the reaction of phosphate with Ca and Fe related components. It was concluded that P immobilization by fly ash was governed by Ca ingredient (especially CaO and CaSO₄) and Fe ingredient (especially Fe₂O_{3d}).

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1. Introduction

Fly ash is a waste product of coal-fired power plants. Approximately 160 million tonnes of fly ash is produced annually in China, and only about 40% of this material is productively reused, principally in construction-related applications due to the pozzolanic characteristics of fly ash. Phosphate in the effluents from municipal and industrial plants can cause eutrophication in relatively stagnant water bodies. Therefore, the treatment of effluents for the removal of phosphate before discharge is required. Coal fly ash has been given great attention as a potential material for phosphate removal in recent years since it is easily available and cost-effective [1–9].

Ugurlu and Salman [2] found that a Turkish fly ash is an efficient adsorbent in phosphate removal due to the high concen-

tration of calcite present (33.83%). Tsitouridou and Georgiou [5] compared three fly ashes with different calcium contents and indicated that phosphate removal involved an adsorption and/or precipitation process. Vordonis and Koutsoukos [6] determined that the uptake of orthophosphate by four calcium-rich (10–32%) Greek fly ashes exceeded the amount predicted by monolayer coverage, suggesting either multiplayer adsorption or precipitation. Cheung and Venkitachalam [7] investigated the removal of phosphate by two fly ashes with high and low calcium contents, and concluded that P-removal was primarily due to precipitation of phosphate with Ca²⁺ ions in solution. Oguz [8] suggested that the removal of phosphate by a medium calcium fly ash (with CaO content of 11.57%) predominantly took place by precipitation mechanism, ion exchange and weak physical interactions between the surface of sorbent and the metallic salts of phosphate. Experimental data and constant capacitance model approach (CCM) for a low calcium (~1 wt.% as CaO), acidic (pH ~4.5) Type F fly ash by Grubb et al. [9] revealed that the immobilization of phosphate was attributed chiefly to the formation of insoluble aluminum and iron phosphates.

* Corresponding author at: School of Environmental Science and Engineering, Shanghai JiaoTong University, No. 800, Dongchuan Road, Minhang District, Shanghai 200240, China. Tel.: +86 21 5474 5704; fax: +86 21 5474 0825.

E-mail address: hnkong@sjtu.edu.cn (H. Kong).

Table 1
Chemical composition of fly ashes used in this study (wt.%)

Material	T-SiO ₂	T-Fe ₂ O ₃	T-Al ₂ O ₃	T-CaO	T-MgO	Fe ₂ O _{3d}	Al ₂ O _{3d}	CaCO ₃	CaSO ₄
Xiamen	46.44	5.55	35.27	5.80	0.83	1.14	0.11	1.23	1.59
Minhang	49.30	4.84	33.01	2.98	0.95	0.77	0.06	0.59	1.02
Shenzhen	47.16	5.78	22.31	3.81	1.43	0.99	0.09	0.88	1.31
Shidongyichang C ^a	49.44	4.96	30.22	3.48	1.01	0.57	0.05	0.24	0.74
Shidongyichang F ^b	52.06	7.08	28.34	3.81	0.77	0.64	0.06	0.17	0.93
Wujin C	47.00	9.91	19.9	13.84	1.25	2.40	0.09	0.74	2.86
Wujin F	42.16	10.62	17.34	16.08	1.49	3.70	0.20	0.80	5.11
Waigaoqiao	45.88	9.91	22.91	10.94	1.43	2.24	0.12	0.57	3.19
Shidongerchang C	52.56	9.23	23.42	6.31	1.25	1.53	0.17	0.24	1.74
Shidongerchang F	51.36	9.70	22.13	6.90	1.61	1.50	0.17	0.19	2.01
Yangpu C	49.8	3.79	38.53	2.16	0.36	0.57	0.03	0.11	0.71
Yangpu F	65.36	4.38	20.24	2.58	1.61	0.64	0.08	0.13	0.31
Datong	50.92	7.81	32.63	2.08	0.66	0.65	0.01	0.07	0.86
Baoshan	51.11	9.41	15.66	8.32	0.98	1.57	0.03	2.73	1.83
Nanshi	34.36	10.4	17.91	20.37	1.52	4.04	0.28	5.57	3.96

^a C refers to coarse fly ash.

^b F refers to fine fly ash.

Although it is generally accepted that the immobilization of phosphate by fly ash involves sorption and/or precipitation mechanism and calcium, iron and aluminum are the key factors affecting P sorption, the studies concerning the removal of phosphate by fly ash have been performed by using only one or several fly ashes. Therefore, it is difficult to explore the relative importance of different components of fly ash in P sorption by relating the P-removal properties of the fly ashes to their chemical composition. It is also deemed that the selection of a fly ash with a high P sorption capacity is of utmost importance to obtain a sustained P-removal in the long term in practice.

In the present study, the P-removal capacities of 15 fly ashes having different composition were investigated by batch experiments, and the fractionation of phosphate sorbed was also conducted. The experimental data were related to the chemical composition of these fly ashes. The results obtained provided useful information for both the sorption mechanism and the selection of fly ash as an effective material for phosphate removal.

2. Materials and methods

2.1. Materials

Fly ashes used in the experiments were collected from power plants which burn raw coals originated from different coal mines in China. For chemical analysis except silicon, the fly ashes were digested with hydrogen fluoride in conjunction with perchloric acid and dissolved later by hydrochloric acid. While for the analysis of silicon, the fly ashes were melted with sodium hydroxide. The elements in solution were then analyzed using an inductively coupled plasma emission analysis equipment (IRIS advantage 1000). The total amount of Si, Al, Fe, Ca, and Mg was presented in the form of stable oxides in Table 1.

Free iron oxide (Fe₂O_{3d}) and free aluminum oxide (Al₂O_{3d}) were analyzed by a dithionite–citrate–bicarbonate (DCB) extraction method [10]. DCB extracts both crystalline and poorly crystalline Fe and Al oxides. CaCO₃ was analyzed by a modified Van Slyke manometric method [11]. CaSO₄ was determined

by dissolution in hydrochloric acid of total sulphates followed by precipitation with barium chloride [12]. The obtained results were also summarized in Table 1.

2.2. Batch phosphate sorption experiments

Phosphate solutions with P concentration ranging from 25 to 1000 mgP/L were prepared from the stock solution of 5000 mgP/L of anhydrous KH₂PO₄ and were adjusted for pH to 5.0 (the unadjusted pH range of P solutions was 4.6–5.1 due to the addition of different amounts of KH₂PO₄). Forty millilitres of the phosphate solutions were added to centrifuge tubes containing 0.4 g dw of fly ash. The tubes were then agitated in an orbital shaker at 200 rpm for 24 h (reaction time of 24 h was found to be enough for phosphate to achieve equilibrium in pre-experiments) at room temperature. The suspensions were subsequently centrifuged and the supernatants were determined for phosphate by the molybdenum–blue ascorbic acid method [13] with a Unico spectrophotometer (model UV-2102PCS). The amount of phosphate sorbed was calculated from the difference between the initial and final P concentration in solution. Analyses were performed in duplicate and the data were expressed as the average value.

2.3. Fractionation of sorbed phosphate

Forty millilitre of phosphate solution with a concentration of 1000 mgP/L were put into a pre-weighed centrifuge tube (W1) containing about 0.4 g dw of fly ash (W2). After shaking for 24 h at room temperature, the suspension was centrifuged, and the tube with residue was weighed again (W3). The supernatant was analyzed for phosphate concentration (C). The amount of remained phosphate that was not adsorbed by fly ash (W4) was calculated by the equation:

$$\frac{W3 - W2 - W1 \text{ (g)}}{1000} \times C \text{ (mg/L)} \text{ (assuming the density of the residual solution as 1 g/mL).}$$

A sequential extraction scheme was performed following a protocol modified from Hieltjes and Lijklema [14]. The fractionation scheme comprises: (1) two consecutive extractions in 1 mol/L NH₄Cl at pH 7 (denoted loosely bound-P, calculated by subtracting W4 from the amount of extracted P); (2) two consecutive extractions in 0.1 mol/L NaOH followed by extraction in 1 mol/L NaCl (denoted Fe + Al bound-P); (3) two consecutive extraction in 0.5 mol/L HCl (denoted Ca + Mg bound-P); (4) analysis of the remaining P in fly ash after ignition at 550 °C and extraction in boiling 1 mol/L HCl (denoted residual-P). Analyses were performed in duplicate for each fly ash and the mean data were reported.

2.4. Effect of pH on phosphate immobilization

Three representative fly ashes with high, medium and low calcium contents were chosen to evaluate the effect of pH on phosphate immobilization. Approximately 0.4 g of each sample was put into centrifuge tubes, and 40 ml of solution containing 200 mgP/L were added. The suspensions were adjusted to desired pH levels by using 0.01 or 0.1 mol/L HCl or NaOH solution. The tubes were then agitated for 24 h at room temperature. The suspensions were subsequently centrifuged and the supernatants were determined for phosphate and pH. The amount of P sorbed was calculated from the difference between the initial and final P concentration in solution (the volume of NaOH or HCl solution added was considered in the calculation).

The experiment using deionized water instead of P solution was also conducted following the same procedure and the supernatants were used to analyze Ca²⁺ and Fe³⁺ ion concentrations. The concentration of Ca²⁺ ion was determined by EDTA titrimetric method [10], and Fe³⁺ concentration was analyzed by joint colorimetric method using ferron as indicator [10].

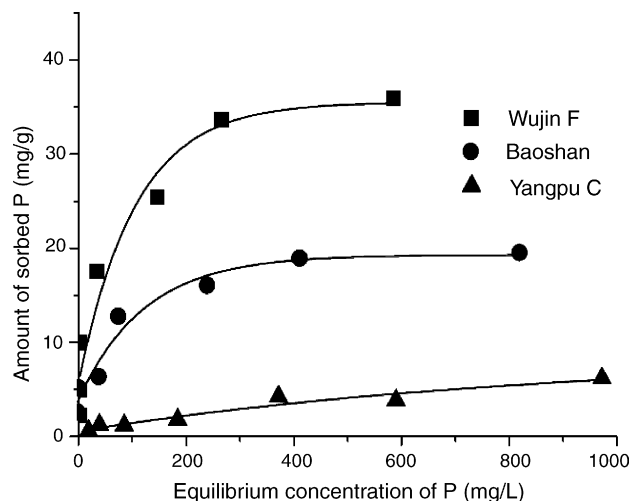


Fig. 1. P sorption isotherms of three representative fly ashes.

3. Results and discussion

3.1. The sorption isotherm of phosphate on fly ashes

Sorption isotherms of three representative fly ashes, which had low, medium, and high calcium content, were shown in Fig. 1. All other isotherms had similar shape. Sorption data were fitted to the Langmuir and Freundlich models:

- Langmuir equation: $C/q = C/Q_m + 1/bQ_m$,
- Freundlich equation: $q = kC^n$,

where q is the amount of P sorbed per unit of sorbent (mg/g), C the concentration of P in solution at equilibrium (mg/L), Q_m the Langmuir sorption maximum (mg/g), b a constant related to the binding strength of P, k and n in the Freundlich model are constants specific to each sorbent. In general, k showed a good

Table 2
Langmuir and Freundlich isotherm parameters of fly ashes

Material	Langmuir equation			Freundlich equation		
	b (L/mg)	Q_m (mg/g)	r	k (L/g)	n	r
Xiamen	0.029	16.23	0.992	4.29	0.193	0.985
Minhang	0.008	6.00	0.985	0.43	0.380	0.942
Shenzhen	0.011	7.47	0.988	0.38	0.464	0.881
Shidongyichang C ^a	0.007	5.51	0.965	0.42	0.361	0.954
Shidongyichang F ^b	0.015	5.88	0.973	0.70	0.328	0.807
Wujin C	0.060	31.85	0.994	8.35	0.200	0.725
Wujin F	0.052	36.5	0.995	7.13	0.254	0.861
Waigaoqiao	0.044	29.24	0.996	6.50	0.227	0.875
Shidongerchang C	0.020	16.26	0.990	2.80	0.256	0.969
Shidongerchang F	0.020	16.84	0.989	2.82	0.262	0.981
Yangpu C	0.003	7.71	0.896	0.11	0.571	0.971
Yangpu F	0.006	7.51	0.922	0.35	0.443	0.913
Datong	0.005	6.35	0.960	0.17	0.518	0.963
Baoshan	0.026	20.16	0.995	3.49	0.264	0.958
Nanshi	0.029	42.55	0.975	8.31	0.229	0.863

^a C refers to coarse fly ash.

^b F refers to fine fly ash.

correlation with the Langmuir sorption maximum, Q_m [15,16]. Similarly, the obtained correlation coefficient between k and Q_m was 0.9718** in this study. However, it should be noted that k and Q_m do not actually reflect the same characteristics. The Freundlich k represents the amount of P sorbed when the solution concentration is unity. Q_m , on the other hand, represents the saturation level of sorbed P at high solution concentrations. A high value of n implies a relative large change in sorbed P when the solution concentration deviates from unity [7].

The sorption parameters and correlation coefficients were listed in Table 2. Although both equations were suitable for the description of P sorption isotherm by fly ash, the Langmuir equation gave a better fit than the Freundlich equation according to their correlation coefficients (r). The P sorption maximum (Q_m) of the fly ashes studied varied widely and ranged from 5.51 mg/g for Shidongyichang C to 42.55 mg/g for Nanshi.

The Langmuir and Freundlich parameters could be compared with other sorbents based on metal oxides/hydroxides from literatures. Zeng et al. [17] reported that the values of Q_m , b , k and n for the P sorption on iron oxide tailing were 8.21 mg/g, 0.444, 3.59 L/g and 0.190, respectively. Borggaard et al. [18] investigated P sorption on synthesized aluminum oxide, ferrihydrite and goethite with the same initial pH as this study and obtained Q_m values of 35.03, 42.78 and 6.42 mg/g, and the b values of 4.548, 3.903 and 9.935, respectively. Cheung and Venkitachalam [7] found that sorption data of phosphate by two fly ashes fitted well with both Langmuir and Freundlich equations, and the values of Q_m , b , k and n reported were 13.77 mg/g, 0.280, 12.3 L/g and 0.010 for the high calcium fly ash, 3.08 mg/g, 0.015, 0.113 L/g and 0.580 for the low calcium fly ash, respectively.

3.2. Correlation between Q_m and chemical composition

Univariate linear regression analyses of each measured chemical composition of the fly ashes versus Q_m value were performed and the results were presented in Table 3. It was shown that the chemical composition best correlated with Q_m was total calcium content ($r=0.9836^{**}$) followed by total iron content ($r=0.8049^{**}$). Correlation coefficients of Q_m with silica and aluminum showed statistically significant negative relationship. However, it can be hardly considered that aluminum and silica

Table 3
Correlation coefficients between Q_m and chemical composition of fly ashes determined

Composition	r
T-CaO	0.9836**
T-Fe ₂ O ₃	0.8049**
T-SiO ₂	-0.6875**
T-Al ₂ O ₃	-0.6335
T-MgO	0.5112
f.CaO	0.9647**
CaCO ₃	0.6361*
CaSO ₄	0.9399**
Fe ₂ O _{3d}	0.9731**
Al ₂ O _{3d}	0.7545**

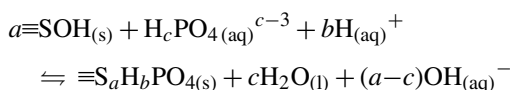
* and ** indicate statistically significant relation at the 95% significance level and the 99% significance level, respectively.

related components would hinder the sorption of phosphate. It was thought that, since fly ashes with high calcium and high iron contents generally had relatively low contents of silica and aluminum, and vice versa (Table 1), the negative correlation of Q_m with silica and aluminum content might just reflect the importance of calcium and iron in phosphate fixation. The low magnesium content in fly ash and low r value of T-MgO with Q_m indicated that phosphate immobilized by magnesium is negligible.

The amount of CaSO₄ in all fly ashes was higher than that of CaCO₃ except for Nanshi and Baoshan, and the average percentages of CaSO₄ and CaCO₃ in total Ca were 27.18% and 11.41%, respectively. The remaining calcium constituent accounted for 42.52–82.95% of the total Ca content and was thought to be mainly free calcium oxide (f.CaO) [19,20]. Correlation coefficients of Q_m with CaCO₃, CaSO₄, and free CaO were 0.6361*, 0.9399** and 0.9647**, respectively (Table 3). This suggested that free CaO and CaSO₄ contributed substantially to phosphate immobilization in total Ca, while CaCO₃ appeared to play only a minor role. The solubility products of Ca(OH)₂, CaSO₄, and CaCO₃ are 5.5×10^{-6} , 9.1×10^{-6} and 2.9×10^{-9} , respectively. The higher K_{sp} values of Ca(OH)₂ and CaSO₄ implied that Ca²⁺ ions can be more easily dissolved into the solution, resulting in higher P-removal efficiency compared with CaCO₃.

The percentage of Fe₂O_{3d} in total Fe ranged from 8.37% for Datong to 38.88% for Nanshi with an average value of 18.75%, whereas Al₂O_{3d} only accounted for 0.15–1.40% in total Al with a mean value of 0.77%. Correlation coefficients of Q_m with Fe₂O_{3d} and Al₂O_{3d} were higher than those of total Fe and total Al contents, respectively.

Based on the r values and the amount of each chemical composition in fly ash, it was believed that Ca ingredient (especially CaO and CaSO₄) and Fe ingredient (especially Fe₂O_{3d}) contributed primarily to P immobilization. It is known that high pH and high Ca²⁺ concentration are advantageous for calcium phosphate precipitation [21–23]. The contributing mechanism of calcium ingredients in phosphate immobilization of fly ash may be the formation of calcium phosphate precipitation by the reaction of dissolved Ca²⁺ with the phosphate in solution since the f.CaO and CaSO₄ with relatively high solubility accounted for a considerable part in total calcium of fly ash. The possible contributing mechanism of Fe₂O_{3d} and Al₂O_{3d} for the removal of phosphate can be explained by an adsorption process through the ligand exchange between phosphate and the hydroxide groups on the surface of the hydroxylated oxides. When the oxides' surface of Fe₂O_{3d} and Al₂O_{3d} is protonated and thus positively charged, it is suitable for anion adsorption [24,25]. The model describing phosphate adsorption was given by the following ligand exchange reactions:



The S refers to a metal atom in a hydroxylated oxide, OH refers to a reactive surface hydroxyl, a , b and c are stoichiometric coefficients and ($c \leq 3$) is the degree of protonation of the phosphate ion [26–28].

Table 4
Fractionation of phosphorus sorbed on fly ash using an initial P concentration of 1000 mgP/L

Material	LB-P		Fe + Al-P		Ca + Mg-P		Res.-P	
	mg/g	%	mg/g	%	mg/g	%	mg/g	%
Xiamen	12.03	80.93	0.27	1.76	1.99	12.75	0.12	0.77
Minhang	2.93	79.2	0.14	3.64	0.42	11.05	0.13	3.41
Shenzhen	6.00	86.36	0.27	4.04	0.71	10.58	0.16	2.34
Shidongyichang C ^a	3.92	86.56	0.03	0.69	0.50	11.32	0.12	2.64
Shidongyichang F ^b	4.25	77.94	0.03	0.52	0.71	11.69	0.13	2.15
Wujin C	10.00	37.41	2.37	7.29	15.74	48.52	0.06	0.19
Wujin F	13.79	34.61	2.83	8.24	21.47	62.48	0.07	0.2
Waigaoqiao	16.36	69.3	0.42	1.49	5.01	17.89	0.12	0.43
Shidongerchang C	11.43	83.74	0.14	0.98	1.32	9.03	0.08	0.55
Shidongerchang F	11.85	83.99	0.18	1.25	1.86	12.98	0.08	0.54
Yangpu C	1.62	72.48	0.03	0.98	0.36	14.01	0.09	3.42
Yangpu F	3.56	78.61	0.27	5.22	0.26	5.07	0.12	2.27
Datong	1.63	77.58	0.23	12.02	0.23	12.02	0.12	6.03
Baoshan	17.39	69.62	1.43	5.77	6.20	24.99	0.01	0.06
Nanshi	16.48	37.72	3.04	7.47	23.38	57.41	0.06	0.16

^a C refers to coarse fly ash.

^b F refers to fine fly ash.

3.3. Fractionation of sorbed phosphate

The fractionation analysis of sorbed phosphate demonstrated that the loosely bound P fraction and/or the Ca + Mg-P fraction were the dominant forms of phosphorus immobilized by fly ash (Table 4). The fraction of P bound to Fe and Al and the residual P fraction constituted only small fractions (<13% and <7%, respectively) (Table 4).

According to the results of phosphorus fractionation, the fly ashes used in this study can be classified into three types. The first type was composed of Nanshi, Wujin C and Wujin F, which immobilized phosphate in the form of Ca + Mg-P and were characterized with high calcium contents and high Q_m values. The second type comprised Waigaoqiao and Baoshan, which immobilized phosphate mostly in the form of loosely bound P and Ca + Mg-P, and were characterized with medium calcium contents and medium Q_m values. The remained fly ashes can be categorized as the third type, which immobilized phosphate principally in the form of loosely bound P (>70%) and were characterized with low calcium content and low Q_m values.

The results of correlation analysis of main phosphorus fractions with the chemical compositions were given in Table 5. As seen from Table 5, Ca + Mg-P fraction showed a significant correlation ($r=0.9567^{**}$) with total Ca content, but weak correlation with total Mg content ($r=0.4245$). The Fe + Al-P fraction positively correlated with total Fe content ($r=0.6629^{**}$) but negatively with total Al content ($r=-0.6453^{**}$). Loosely bound P

fraction showed significant correlation with both the total Ca and total Fe content.

Similar to the case of Q_m , the r values for the correlation of free CaO, CaSO₄ and CaCO₃ with both Ca + Mg-P and LB-P indicated that phosphate immobilization was attributed to free CaO and CaSO₄ in the total Ca. It was also shown that both Fe + Al-P and LB-P were highly correlated with Fe₂O_{3d} and Al₂O_{3d} compared with total Fe and total Al contents, respectively. Therefore, the obtained results further suggested that calcium (especially free CaO and CaSO₄) and iron (especially Fe₂O_{3d}) were the main components involved in phosphate immobilization. It was thought that phosphate immobilization by calcium ingredients was achieved by calcium phosphate precipitation, resulting in the formation of Ca + Mg-P, while that by iron ingredients was fulfilled by adsorption through ligand exchange which gave rise to the formation of Fe + Al-P.

The loosely bound P, which constituted one of the main fractions of immobilized P and was determined by extraction with 1 M NH₄Cl at pH 7, consisted mainly of exchangeable P with Cl⁻ and easily soluble P released by dissolution of phosphate precipitate in aqueous solution of 1 M NH₄Cl. The calcium phosphate precipitate might be an amorphous form at the initial stage and evolved toward the thermodynamically more stable crystalline form of hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) [2]. Similarly, the P form immobilized by Fe₂O_{3d} was also believed to change with time [9,29]. These explained the significant correlation of the loosely bound P fraction with both the total

Table 5
Correlation coefficients between phosphorus fractions and relevant chemical composition of fly ash

P fraction	T-CaO	f.CaO	CaSO ₄	CaCO ₃	T-MgO	T-Fe ₂ O ₃	Fe ₂ O _{3d}	T-Al ₂ O ₃	Al ₂ O _{3d}
LB-P	0.7728**	0.7081**	0.7572**	0.5995*	0.5057	0.7866**	0.7586**	-0.6661**	0.6385*
Fe + Al-P	-	-	-	-	-	0.6629**	0.9051**	-0.6453**	0.5908*
Ca + Mg-P	0.9567**	0.9283**	0.895**	0.6583**	0.4245	-	-	-	-

* and ** indicate statistically significant relation at the 95% significance level and the 99% significance level, respectively.

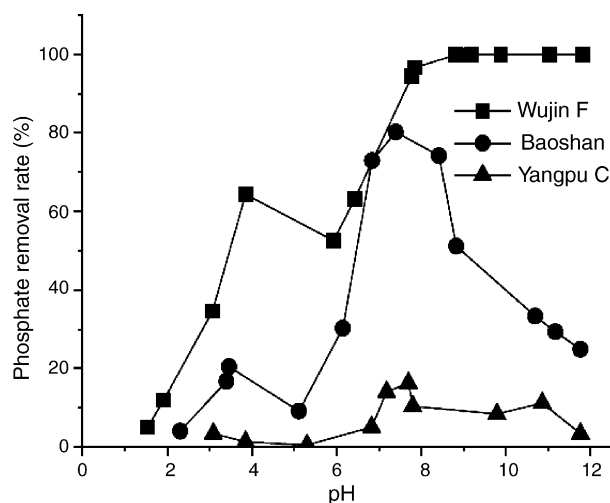


Fig. 2. Effect of pH on phosphate removal by high, medium and low calcium fly ashes.

Ca and total Fe content. The unstable phosphate forms could be easily dissolved by NH_4Cl solution to result in the loosely bound P fraction.

3.4. Effect of pH on phosphate immobilization

To investigate the effect of pH on phosphate immobilization, Wujin F, Baoshan and Yangpu C were selected as representatives of the above-mentioned three types of fly ash. They had high, medium and low calcium contents, respectively. The natural pH values of fly ash/water suspensions were 11.56, 8.74 and 6.41 for Wujin F, Baoshan and Yangpu C, respectively. It can be seen from Fig. 2 that, Wujin F showed the highest P-removal efficiency at alkaline conditions ($\text{pH} > 8.5$), Baoshan reached maximum phosphate immobilization at neutral pH values (6.5–8.5), while Yangpu C immobilized little phosphate at all pH levels. The concentration of Ca^{2+} in solution as a function of pH was shown in Table 6. Based on the value of solubility product (K_{sp}), it was presumed that calcium in solution originated mainly from the dissolution of CaO and CaSO_4 .

According to the equation:



It could be expected that the concentration of Ca^{2+} in solution decreased with the increase in pH value for each fly ash (Table 6). At all pH values, the concentration of Ca^{2+} in solution was in the order: Wujin F, Baoshan and Yangpu C which was in agreement with the calcium content in fly ash (Table 1). As shown in Table 6, although the concentration of Ca^{2+} was low at alkaline conditions for each fly ash, the Wujin F fly ash still had the concentration of 212 mg/L at pH 11.56, being much higher than Baoshan and Yangpu C fly ashes. It is known that both high pH and high Ca^{2+} concentration are crucial for calcium phosphate precipitation [21–23]. Thereby, low pH value with high calcium concentration (in the case of pH value less than about 6.5 for each fly ash), or high pH value with low calcium concentration (in the case of pH value higher than about 8.5 for Baoshan and Yangpu C) were not advantageous for phosphate immobilization (Fig. 2). As a result, the highest P-removal occurred at alkaline conditions for Wujin F ($\text{pH} > 8.5$), while there is a maximum phosphate removal at weakly alkaline conditions (within the pH range of about 6.5–8.5) for fly ashes with medium or low calcium content (Fig. 2).

At the natural pH levels of fly ash/water suspensions of 11.56, 8.74 and 6.41 for Wujin F, Baoshan and Yangpu C, the corresponding Ca^{2+} concentration were 212.5, 180 and 45 mg/L, respectively (Table 6). After the P sorption, the concentration of Ca^{2+} in solution of the three fly ashes decreased to 35, 15 and 12.5 mg/L with the final pH of 11.47, 8.69 and 6.52, respectively. This confirmed that reaction mechanism with calcium ingredients was through deposition as phosphate salts rather than trapped in Ca hydroxides floc.

It seemed that, when the pH value decreased to acidic conditions, it is not suitable for calcium phosphate precipitation though the concentration of Ca^{2+} increased remarkably [4,23]. That is, pH was the limiting factor for phosphate immobilization since relatively large amounts of Ca^{2+} ion was released. That is why the P-removal was low around pH 5. However, Fe-related components began to play an important role in phosphate immo-

Table 6
Effect of pH on Ca^{2+} and Fe^{3+} concentrations in deionized water equilibrated with fly ash

pH	Ca^{2+} (mg/L)			Fe^{3+} (mg/L)		
	Wujin F	Baoshan	Yangpu C	Wujin F	Baoshan	Yangpu C
12.19	192.5	32.5	7.5	N.D.	N.D.	N.D.
11.56	212.5	40	22.5	N.D.	N.D.	N.D.
10.35	297.5	100	27.5	N.D.	N.D.	N.D.
8.74	405	180	40	N.D.	N.D.	N.D.
7.2	415	207.5	40	N.D.	N.D.	N.D.
6.41	417.5	195	45	N.D.	N.D.	N.D.
4.86	437.5	260	55	N.D.	N.D.	N.D.
3.72	537.5	287.5	62.5	N.D.	N.D.	N.D.
2.67	577.5	280	70	N.D.	N.D.	N.D.
1.74	540	278	69	0.81	0.41	0.18

N.D.: not detectable.

bilization with the decrease of pH in solution [9,30,31]. Another maximum in removal of phosphate by fly ashes occurred around pH 3 since further decrease of pH to be less than 3 again abated the phosphate removal, due to the formation of non-ionic H_3PO_4 (Fig. 2). However, the concentration of Fe^{3+} in solution for fly ashes was only detectable at pH 1.74 (Table 6). The observation was in agreement with the results of Seidel [32] who concluded that the leachability of iron from coal fly ash occurred at $\text{pH} < 1.5$. Therefore, it was presumed that the immobilization by iron, as explained in more detail in Section 3.2, might be a ligand exchange process on the surface of Fe_2O_3 rather than the formation of sparingly soluble precipitate of FePO_4 in solution.

4. Conclusions

1. Sorption of phosphate by fly ash was best fitted to Langmuir equation. The sorption maxima ranged from 5.51 to 42.55 mg/g for the 15 fly ashes investigated.
2. Univariate linear regression analyses of each measured chemical composition of the fly ashes versus P sorption maxima indicated that P immobilization by fly ash was governed by Ca ingredient (especially CaO and CaSO_4) and Fe ingredient (especially Fe_2O_3).
3. The loosely bound P fraction and/or Ca + Mg-P fraction were the dominant fraction of phosphorus immobilized by fly ash. The Fe + Al-P and the residual P fractions constituted only small fractions (<13% and <7%, respectively). Ca was strongly correlated with the Ca+Mg-P fraction instead of Mg, whereas Fe was highly correlated with Fe–Al-P fraction compared with Al. The loosely bound P correlated well with both Ca and Fe content.
4. The greatest removal efficiency of phosphate occurred at alkaline conditions for high calcium fly ash, at neutral pH levels for medium calcium fly ash, while low calcium fly ash immobilized little phosphate at all pH values. The mechanism of P-removal by fly ash appears to be the formation of phosphate calcium precipitate and the sorption through ligand exchange with Fe related components.

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