

Sorption of aqueous phosphorus onto bituminous and lignitous coal ashes

Jinying Yan^a, Donald W. Kirk^a, Charles Q. Jia^{a,*}, Xinan Liu^b

^a Department of Chemical Engineering and Applied Chemistry, University of Toronto,
200 College Street, Toronto, Ontario, Canada M5S 3E5

^b College of Chemical Engineering, Chongqing University, Chongqing, China

Received 15 October 2006; received in revised form 21 February 2007; accepted 22 February 2007

Available online 1 March 2007

Abstract

Aiming at the development of a phosphorus removal technology for waste water, phosphate (PO_4^{3-}) retention behavior of bituminous and lignitous coal ashes was investigated using a batch reactor. Ash samples, including fresh and weathered fly and bottom ashes, were studied for their sorption isotherms and reversibility. Fly ashes had a much higher phosphate retention capacity (4000–30,000 mg P/kg) than bottom ashes (15–600 mg P/kg). Lignitous coal ashes were more capable of retaining phosphate than bituminous coal ashes. The retention process was largely irreversible, and the irreversibility increased with the increase in the retention capacity. Weathering enlarged the retention capacity of the bituminous bottom ash, but substantially lowered that of the fly ash, likely due to the difference in the weather-induced changes between the fly and bottom ashes. Sorption isotherms of fly ashes were found to be adequately represented by the Langmuir model while those of bottom ashes fitted better to the Freundlich model. Concentrations of Ca^{2+} and PO_4^{3-} in the aqueous phase were measured at the end of sorption and desorption experiments, and were compared with solubilities of three calcium phosphate minerals. The aqueous solutions were saturated or super-saturated with respect to tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), and slightly under-saturated with respect to amorphous calcium phosphate. It is concluded that precipitation of calcium phosphate is the predominant mechanism for phosphate retention by coal ash under the conditions studied. There is a strong and positive correlation between alkalinity and phosphate sorption capacity. Consequently, acid neutralization capacity (ANC) can be used as an indicator of phosphate sorption capacity of coal ashes.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Bituminous and lignitous coal ashes; Phosphorus removal; Sorption capacity and mechanism; Speciation; Acid neutralization capacity

1. Introduction

Worldwide, approximately 500 million tonnes of coal ashes are produced annually, while most of the ashes are disposed of in landfills and surface impoundments. In Canada, for example, in 1998 only 25% of fly ash and 10% of bottom ash were utilized for cement/concrete productions, mining applications and road-base construction [1]. Driven mainly by environmental regulations, there is a growing interest in coal ash utilization, particularly in the area of waste management, where coal ashes are often used as a sorbent for various pollutants especially in water. It has been shown that coal ashes have significant retention capacity for various contaminants, ranging from

anions [2–4] and cations [5–7] to dissolved organic compounds [8–12].

As a critical nutrient for aquatic plant species, phosphorus (P) often controls the productivity of phytoplankton in fresh water ecosystems; its oversupply can result in eutrophication [13]. In the past, large point sources (primarily industrial) were the focus of P pollution prevention. Because of the progress in controlling P discharge from industrial operations, the contribution of non-point sources, such as agricultural soils, to surface water phosphorus is becoming more significant [14–16]. In North America and Europe, the concern over P levels in fresh water has led to the development of new guidelines and legislation for P management.

Many alkaline materials, such as calcite [17], have been studied for use as filter units in constructed wetland systems to remove phosphorus. Shiltona et al. [18] documented the long-term field data for steelmaking slag-based filters used for P

* Corresponding author. Tel.: +1 416 946 3097; fax: +1 416 978 8605.
E-mail address: cqjia@chem-eng.toronto.edu (C.Q. Jia).

Table 1
A summary of ash samples

Sample ID	Coal types	Ash types	Sampling status	Surface area (m ² /kg)	MPD (mm)
LB-f	Lignite	Bottom	Fresh/wet	7.1	1.98
LF-f	Lignite	Fly	Fresh/wet	27.7	1.05
BB-f	Bituminous	Bottom	Fresh/wet	10.5	1.92
BB-w ^a	Bituminous	Bottom	Weathered/wet	117	0.07
BF-f	Bituminous	Fly	Fresh/dry	96.9	0.11
BF-w ^b	Bituminous	Fly	Weathered/wet	78.7	0.15

L: Lignite; B: bituminous; F: fly; B: bottom; f: fresh; w: weathered.

^a The “BB-w” ash had been in the landfill for about 1–2 years, and was sampled from the top of the landfill.

^b The “BF-w” ash had been in the soil-covered landfill for 4–5 years and was sampled from the top of the landfill but underneath the soil layer.

removal. Although coal ashes have been examined previously as a potential P retention material in various settings, most of the previous studies [2–4], however, focused on the use of ash as an additive to soil for increasing P retention capacity. There is a significant knowledge gap as to how the dissolved P interacts with coal ashes and what determines P retention capacity. Objectives of this study were to evaluate P retention capacity of typical coal ashes, to analyze physical/chemical properties of ashes and to relate them to the P retention behavior of ashes. It is hoped that this study will lead to a better understanding of mechanisms of P retention and lay a foundation for the development of coal ash-based systems for controlling P discharge to aquatic systems.

2. Materials and experimental methods

2.1. Materials

Three factors were considered during coal ash sampling: the type of coal, the type of coal ash, and the potential changes in physicochemical properties due to weathering. Six samples were chosen to represent the major coal ashes produced by power plants burning bituminous and lignite coal in Canada. For each coal, two types of ashes, fly ash and bottom ash were collected. Since there has been a large quantity of coal ash deposited in landfills for long time, two weathered samples of bituminous coal ashes (fly ash and bottom ash) were also collected. Table 1 summarizes the conditions of the six samples.

Mineral compositions of the ashes were determined using X-ray powder diffraction technique. With over 50% of amorphous phases, major crystalline phases identified in the ashes were aluminum silicates containing alkaline and alkaline earth metals such as albite, anorthite and gehlenite. This is consistent with the relatively weak effects of weathering on chemical

composition of ashes, which will be discussed later. Interestingly, the specific silicate minerals found in the bituminous ashes differ from those in the lignitous ashes. Two major minerals shared by the two coal groups were hematite and quartz. Particle size distribution and chemical composition of six samples were also measured. Particle size was determined via mechanical sieving following ASTM standard procedure (D6913-04e1). Table 1 shows the results of particle size analyses after removing large particles (mainly unburned coal) and the geometric surface area calculated. MPD stands for the mean particle diameter defined by ASTM standard method D2862-97. Geometric surface area is calculated based on the particle size distribution of ash sample under the assumption of spherical particles. Weathering significantly lowered the MPD of bottom ash, but had a smaller effect on fly ashes. The decrease in particle size of bottom ash is attributed to the freeze–thaw cycles of pore water in ash particles during weathering. As expected, fly ashes are much finer particles than bottom ashes.

Ash compositions were determined with borate fusion XRF combined with liquid chromatography by the Analytical Services at Lakefield Research Inc. The results are given in Table 2. In general, they are aluminum-rich silicate-based materials containing small amounts of sulfate and carbonate. Interestingly, the fly and bottom ashes from the same coal have a very similar chemical composition of major elements, suggesting that it is their difference in physical properties such as particle size separating them in the combustion/collection process. On the other hand, there is a significant difference between lignite ashes and bituminous ashes, particularly in their Ca, Mg and Si contents. Consequently, they are very different in alkalinity. Weathering did not result in any substantial change in chemical composition, even in Na and K, suggesting chemical stability of ash matrices in the natural environment. According to the ASTM classification scheme C618-98, the bituminous coal ashes belong to

Table 2
Chemical compositions of major elements in coal ashes

Sample ID	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	SO ₄	CO ₃
BB-f	55.4	23.0	6.7	1.3	5.9	1.5	0.7	1.6	0.4	0.7
BB-w	51.8	22.3	7.4	1.1	5.0	1.0	0.6	1.3	0.4	1.5
LB-f	39.1	17.9	7.1	0.9	16.5	3.5	5.8	0.5	0.4	0.3
BF-f	47.6	21.7	5.1	1.2	6.4	1.5	0.9	1.5	1.3	2.1
BF-w	46.0	21.1	11.0	1.1	5.1	1.0	0.7	1.1	0.4	2.5
LF-f	37.9	18.7	5.3	0.9	16.3	3.4	7.7	0.7	3.5	0.1

the Class F ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$), and the lignite coal ashes are the Class C ($50\% < \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 < 70\%$).

2.2. Experimental methods

Sorption/desorption experiments were carried out in a batch reactor following the ASTM standard procedure (D4646-87). The batch reactor was equipped with a Mistral multi-stirrer. All experiments were carried out at room temperatures (22–25 °C) and duplicated. All data reported was an average of two values. Their relative differences were all less than 10%, in most of the cases less than 5%.

In the sorption experiment, samples were dried, weighted, and added to the solution of set phosphate concentration. The solid/liquid ratio was controlled at 1/20 g/mL (12.5 g/250 mL). To determine the sorption isotherms, the initial concentration of phosphate was varied. For bottom ashes, the concentration range was 5–40 mg HPO_4^{2-} /L, while for fly ashes it was 200–1500 mg/L. The ionic strength of the solution was kept constant (0.01 M) by adjusting with NaNO_3 . Based on our previous study on kinetics, all sorption experiments were performed for 72 h to ensure equilibrium. Liquid samples were withdrawn using a 0.22 μm syringe filter unit and analyzed for pH, PO_4^{3-} , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} . At the end of a sorption experiment, the solid and liquid were separated using a vacuum filter with a water aspirator. The solid was then dried and subsequently used in desorption experiments.

Desorption was carried out in a two-step process with solid samples produced from the sorption experiments. Each step took 24 h. The solid/liquid ratio was kept at 1/10. Liquid samples were withdrawn using a 0.22 μm syringe filter unit and analyzed for pH, PO_4^{3-} , Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} . The concentration of phosphate was determined with APHA vanadomolybdophosphoric acid colorimetry method (4500-P-C). Cation concentrations were analyzed with an inductively coupled plasma (ICP) and an atomic absorption spectrometry (AAS) following the ASTM standard procedure (C1109-93) Acid neutralization capacity (ANC) of ashes was determined in a batch reactor using a series of titrations of a mixture of ash/water (S/L = 20) with HCl for 24 h. A plot of acid consumption against the pH of solution gives the values of ANC over a pH range. The ANC reported is the amount of HCl neutralized (in mM) by 1 g of the ash at pH 7.0. For more details about ANC measurement, one is referred to Yan [19].

Sorption isotherms determined experimentally were evaluated using the Langmuir model and the Freundlich model, which are widely used to describe P retention isotherms for natural materials [20]. The Langmuir model can be expressed as

$$q = \frac{q_m b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (1)$$

where q stands for a solute sorbed by the solid phase (mg/kg), q_m is maximum sorption capacity corresponding to complete sorption at all sites (mg/kg), b is a sorption coefficient related to bonding energy (L/mg), C_{eq} is the solute concentration in aqueous phase at equilibrium (mg/L).

The Freundlich equation is the most widely used nonlinear sorption model. This semi-empirical model can be expressed as

$$q = K_F C_{\text{eq}}^n \quad (2)$$

where K_F is sorption coefficient related to sorption capacity and n is an empirical constant.

The physical meaning of n is not entirely clear, but has values less than 1 and is related to sorption intensity, i.e. the characteristics of the sorbent [21].

3. Results and discussion

3.1. Sorption/desorption behavior

As shown in Table 3, the fly ashes followed the Langmuir model well, while the bottom ashes fitted the Freundlich equation better. Also included in Table 3 are the measured amounts of P sorbed by ashes and the initial P concentrations. The values of K_F and q_m (both are a measure of sorption capacity) suggest that for the same ash type, lignite ashes have a greater capacity than bituminous coal ashes. According to the observed amounts of P sorbed, for the same coal, fly ashes had much larger P retention capacity compared to the bottom ashes.

The Langmuir parameter, q_m , represents a maximum sorption capacity. For all three fly ashes, the highest amount of P sorbed was very close to the q_m , suggesting that equilibrium was reached after 72 h. It was also observed that the fly ash with a higher value of b resulted in a lower P concentration in solution. This is expected since the b is a measure of bonding force of P to the sorbent. Weathering lowered b from greater than 1.33 to about 0.11, and reduced P sorption capacity substantially. The lignite fly ash had a much greater b , likely due to its much higher

Table 3
Sorption isotherms, acid neutralization capacity and initial pH of slurry

Ashes	Models	Initial P (mg/L)	R^2	K_F (L/kg)	N	P sorbed (mg/kg)	ANC (mMH/g)	Initial pH
BB-f	Freundlich	5–40	0.999	5.0	0.77	14–81	0.012	9.5
BB-w	Freundlich	5–40	0.969	6.8	0.74	18–101	0.022	9.5
LB-f	Freundlich	5–40	0.924	503	1.38	90–787	0.174	9.7
Ashes	Models	Initial P (mg/L)	R^2	q_m (mg/kg)	b (L/g)	P sorbed (mg/kg)	ANC (mMH/g)	Initial pH
BF-f	Langmuir	450–700	0.999	12500	1.33	910–12500	0.336	11.3
BF-w	Langmuir	200–600	0.994	10600	0.11	3900–10000	0.205	9.7
LF-f	Langmuir	950–1500	0.994	28600	7.45	19400–29500	1.097	11.6

Table 4
Desorption behavior of P sorbed by ashes

Samples	% P lost in desorption	Desorption pH	Sorption pH
BB-f	43.5–50.8	8.7–9.2	7.9–9.3
BB-w	48.7–67.1	8.9–9.2	8.0–8.8
LB-f	5.7–7.0	9.6–9.7	9.5–9.8
BF-f	0.2–1.2	9.4–10.0	9.0–9.8
BF-w	3.5–6.8	8.6–9.2	8.3–9.0
LF-f	0.1–0.2	10.3–10.5	10.4–10.7

content of Ca. Although Freundlich parameters, K_F and n , do not directly give the maximum sorption capacity, they may be used to evaluate P sorption in a similar way as Langmuir parameters. As shown in Table 3, the fresh lignite bottom ash had the largest K_F and the highest amount of sorbed P measured, while the fresh bituminous ash was at the opposite extreme. Overall, the retention capacity seems to correlate positively to K_F .

Weathering lowered the capacity of fly ash, but not that of bottom ash. Indeed, there seemed an increase in K_F as well as the observed amount of P sorbed after weathering. Weathering can potentially affect the P sorption capacity by facilitating physical and chemical changes of ashes. As shown in Table 2, the weathered bottom ash had smaller particle size and greater surface area than the fresh one. Table 2 also shows an increase in carbonate content and decrease in alkaline and alkaline earth metals content in fly and bottom ash after weathering. Bottom ashes are known to contain less water-soluble species than fly ashes and therefore are less susceptible to chemical changes. On the other hand, the decrease in particle size of bottom ash was much more significant than that of the fly ash. If one factors in the increase in surface area after weathering and evaluates P sorption on a surface area basis (mg P/m^2), the weathered bottom ash becomes less sorptive. It is believed that the weather-induced chemical changes will lower the activity of an ash as a P sorbent while physical changes may enlarge the surface area available for sorption and hence increase the retention capacity.

Table 4 shows the percent loss of sorbed P in the desorption measurements. For fly ashes, desorption varied from 0.1 to 6.8%, suggesting that P retention by fly ash is largely irreversible. Weathering increased desorption by 3.3 to 5.6% for the bituminous fly ash. The desorption of P from lignite bottom ashes was also very low. Bituminous bottom ashes however lost 43–67% of the sorbed P. There was a striking difference in release rate between bituminous and lignite bottom ashes. Weathering increased desorption by 5.2–16.3% for bituminous bottom ash. Overall, the highest sorption is associated with the most irreversible sorption, suggesting that high retention capacity is not the result of physical adsorption which is largely reversible. Chemical processes, including chemical adsorption, must play much greater roles in the P retention for fly ashes as well as the more alkaline lignite bottom ash. The irreversibility of P sorption by coal ashes is similar to that observed for soil-like materials where the sorbed P is considered as inner-sphere complex species [22], meaning chemical sorption.

Table 4 also gives the final solution pH recorded for desorption as well as sorption. Their ranges were quite similar, implying

that the change in the composition of bulk ash during sorption experiments was insignificant. In some cases, the desorption pH was slightly higher than the sorption pH, likely due to the smaller buffering capacity of the solution with less dissolved phosphate. From the data, the higher the desorption pH, the lower the percent loss of P. It will be demonstrated later that there is a strong and positive correlation between alkalinity and the P sorption capacity.

3.2. Solution chemistry and phosphate precipitates

Total dissolved PO_4^{3-} , Ca^{2+} , Mg^{2+} , Fe^{3+} and Al^{3+} in aqueous solutions were analyzed at the end of all sorption and desorption experiments. Using PHREEQC, a geochemistry package [23] along with measured concentrations of major cations, phosphate and pH, chemical speciation calculations were performed to identify major aqueous species and potential precipitates. The existing database of PHREEQC was augmented with additional thermodynamic data [24,25] for the precipitation reactions of common phosphate minerals. The major ionic species identified include Ca^{2+} , Mg^{2+} , HPO_4^{2-} , MgOH^+ and CaPO_4^- . The potential precipitates of phosphate found were all calcium-based, including hydroxyapatite (HAP, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), tricalcium phosphate (TCP, $\beta\text{-Ca}_3(\text{PO}_4)_2$), octacalcium phosphate (OCP, $\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$), and amorphous calcium phosphate (ACP2). Among the four calcium phosphate precipitates, ACP2 is the most soluble, while HAP is the least soluble.

To determine the degree of saturation of the aqueous solution with respect to various calcium phosphate minerals, the pH-dependence of the solubility of three phosphate precipitates (HAP, TCP and ACP2) are presented in Figs. 1 and 2, using a double-function-parameter approach [24]. Also shown in these figures are Ca^{2+} and HPO_4^{2-} measured at a specific pH at the end of sorption and desorption experiments. As shown in Figs. 1 and 2, the aqueous phase in all four cases would be supersaturated with respect to hydroxyapatite, the least soluble solid phase, suggesting the possibility of precipitation of HAP. X-ray diffraction analysis (not included for conciseness) indicated that HAP was the only crystalline calcium phosphate phase in the ashes studied. It is well known that solubility of calcium phosphate precipitates is a function of pH. With the double-function parameters used in Figs. 1 and 2, the slope of lines represents the dependence of solubility on pH. Experimental data have a similar slope in all cases. This similarity implies that precipitation/dissolution of calcium phosphate played a very important role in determining the amount of phosphate dissolved in the aqueous phase. Therefore, the amount of phosphate removed or retained by ashes should largely depend on the calcium available from the ashes for the precipitation reaction.

Sorption experiments started with a high concentration of phosphate; calcium for a precipitation reaction would have to be supplied by the ash. Upon reaching a super-saturation, crystalline phases of calcium phosphate, such as TCP and HAP, could grow at the surface of ash particles following heterogeneous nucleation. Figs. 1 and 2 show that all solutions were under-saturated with respect to amorphous calcium phosphate,

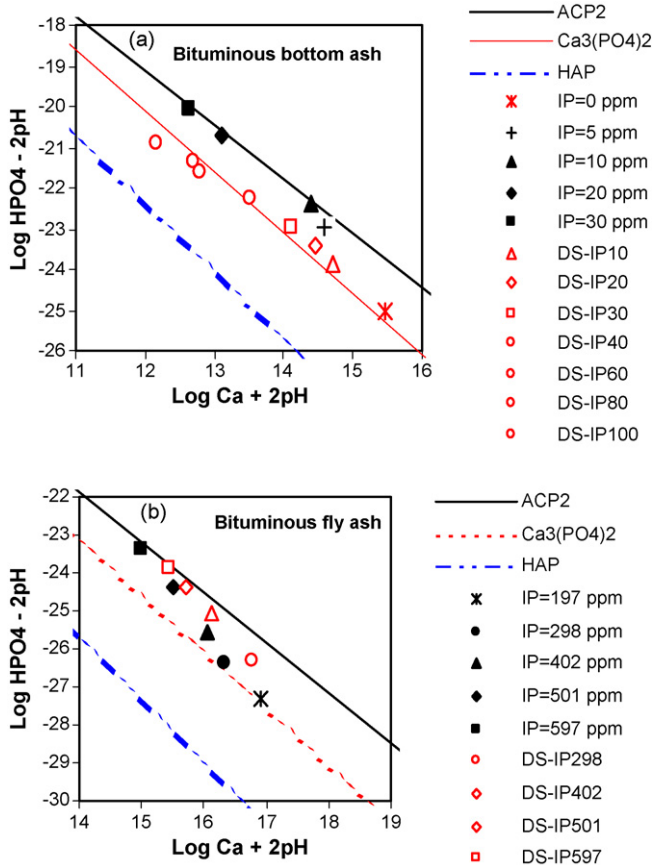


Fig. 1. Experimental dissolved Ca²⁺ and HPO₄²⁻ at various pHs with the bituminous bottom (a) and fly (b) ashes, as compared to theoretical solubilities of three calcium phosphate precipitates (Ca = activity of Ca²⁺; HPO₄ = activity of HPO₄²⁻; TCP = Ca₃(PO₄)₂; IP = initial P concentration; DS = desorption experiment).

except for one case of sorption on the bituminous bottom ash where the solution was essentially saturated. In soil systems, it has been proposed [26] that the calcium phosphate precipitated is initially meta-stable and gradually transforms into more stable, less soluble forms. A similar process could take place in the coal ash system during sorption. Initially, the meta-stable ACP could be formed from the over-saturated solution, and then gradually be transformed into TCP and finally HAP. The fact that most of the solutions were under-saturated with respect to ACP seems consistent with the argument of phase transformation of calcium phosphate precipitated. Indeed, the behavior of P sorption by coal ash somewhat resembles that in natural waters in which P concentration is controlled by solubilities of phosphate minerals [27]. This dependence on solubility was also found for phosphate removal by Ca-containing industrial slags [28]. Clearly, calcium phosphate precipitation is the predominant mechanism in P retention, especially when the pH of solution is relatively high. It is widely reported that surface adsorption of phosphate is unfavorable in an alkaline environment because of the competition for surface sites by hydroxide and phosphate ions [15,29,30]

In the case of desorption, the P-loaded ash separated after the sorption experiment would be the only source of Ca²⁺ and

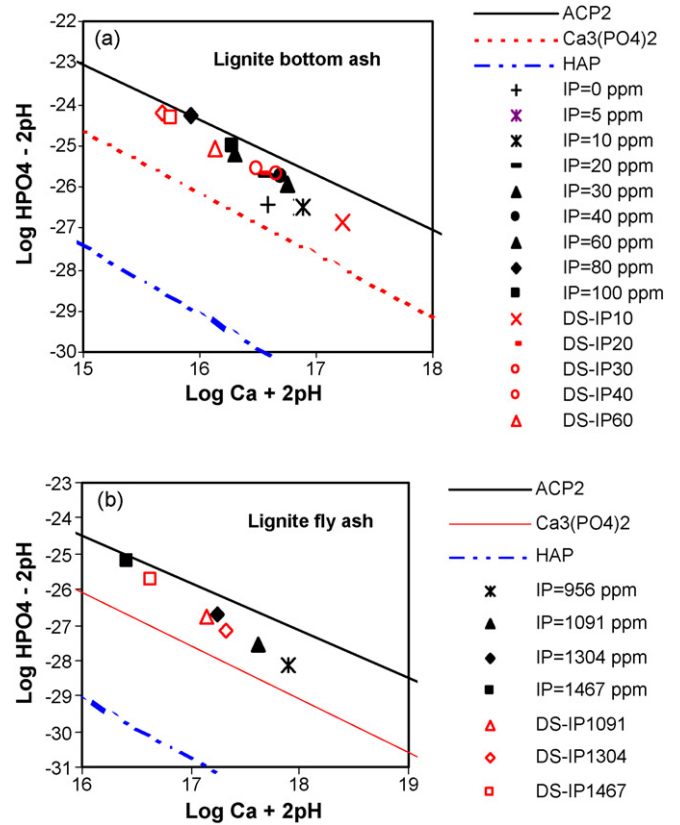


Fig. 2. Experimental dissolved Ca²⁺ and HPO₄²⁻ at various pHs with the lignite bottom (a) and fly (b) ashes, as compared to theoretical solubilities of three calcium phosphate precipitates (Ca = activity of Ca²⁺; HPO₄ = activity of HPO₄²⁻; Ca₃(PO₄)₂ = TCP; IP = initial P concentration; DS = desorption experiment).

HPO₄²⁻. Since similar solution compositions were found for both sorption and desorption, the experiments suggest that the form of the precipitates did not change significantly. In the case of bituminous bottom ash, there was a clear difference in solution chemistry between sorption and desorption (Fig. 1). This difference may be attributed to the limited amount of calcium phosphate in the P-loaded ash. The bituminous bottom ash had the least capacity for retaining phosphate, despite its similar chemical composition to the bituminous fly ash. Therefore, the rate of supply of Ca²⁺ from the bottom ash was too slow and that even after 72 h there was not yet a full utilization of Ca²⁺ in the bottom ash. Given the time required to determine P retention potential, there appears to be a need for a more effective analysis technique. Acid neutralization capacity is such a technique, which will be discussed next.

3.3. Acid neutralization capacity (ANC) and P sorption capacity

Table 3 gives the ANC values determined at pH 7.0 for all ashes along with the initial pH values of ash–water slurries at a L/S = 20 measured before adding phosphate. As expected, lignite ashes had a greater ANC and were more alkaline than bituminous ashes, while fly ashes had higher pH as well as much higher ANC than bottom ashes. Weathering substantially lowered the

initial pH and ANC of the bituminous fly ash. However, weathering did not change the initial pH of bituminous bottom ash slurries, but almost doubled its ANC. For MSWI bottom ashes Zevenbergen [31] reported that the transformation of soluble calcium-constituents to carbonates during weathering reduced the alkalinity of the ash. As shown in Table 2, there was a significant increase in carbonate content after weathering, despite the decline in almost all alkaline and alkaline earth metals. This difference in weathering effect is tentatively attributed to the difference in particle size and possibly in mineral compositions between the fly and bottom ashes. More work however is needed to determine the exact reason behind the increased ANC of bottom ash after weathering.

It has been demonstrated that precipitation of calcium phosphate is a very important mechanism in retaining phosphate. Ca is therefore a critical element in phosphate retention capacity. The total Ca content in an ash, however, provides little information about the behavior of Ca in the ash–water system [32]. Only the Ca that is accessible to the solution and the dissolved phosphate will likely contribute to the P retention. A study by Drizo et al. [33] provided evidence that P retention potential is linked to the alkaline mineral composition of the sorbent material. Although ANC is a measure of alkalinity of a material in an aqueous system, it was used previously as a measure of the amount of reactive alkaline earth metals such as Ca in various materials including coal ash [19,34]. If the major alkaline or alkaline earth element is Ca, ANC becomes a measure of the amount of Ca that is accessible to acid. Since HCl was used in ANC measurement, the value of ANC is about a half of the CaCl_2 formed (in mM) with 1 g of the ash. In Figs. 3 and 4, the measured maximum P retention capacities are plotted against the measured ANC for fly and bottom ashes, respectively. There is a strong positive correlation between ANC and P retention capacity, confirming the dependence of P retention capacity on the amount of calcium available to chemical reactions with the added phosphate. P retention capacity can be predicted based on the amount of “available” Ca calculated from the measured ANC and the Ca/PO_4 molar ratio for a given calcium phosphate mineral. In Figs. 3 and 4, the prediction was compared with measurements for fly and bottom ashes, respectively. As shown in Fig. 3, for fly ash the measured results were close to the predictions based on ACP ($\text{Ca}/\text{PO}_4 = 1.33$) and HAP ($\text{Ca}/\text{PO}_4 = 1.67$).

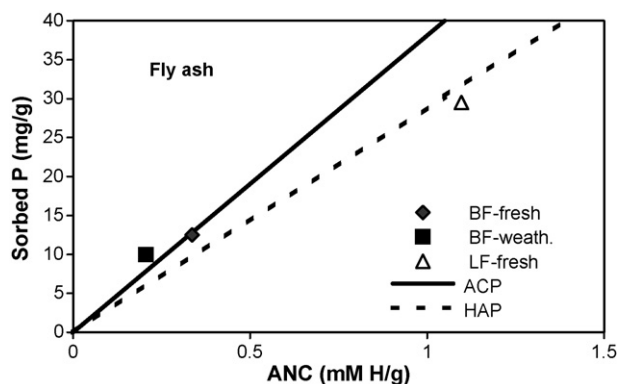


Fig. 3. Correlation between ANC and P retention capacities of fly ashes.

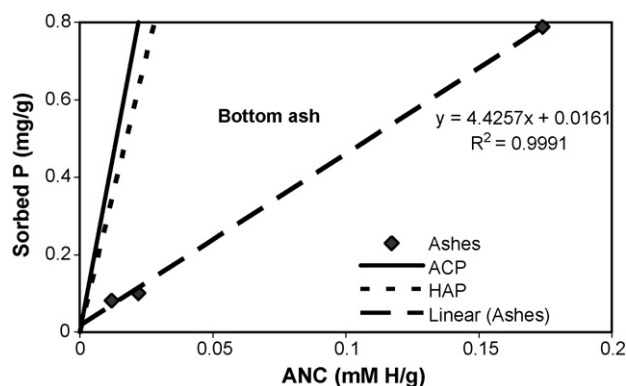


Fig. 4. Correlation between ANC and P retention capacities of bottom ashes.

For the bottom ashes, however, the predictions based on both ACP and HAP gave much larger P-retention capacities than what were observed, suggesting the amount of Ca available to HCl was much greater than that to phosphate. Apparently, the release of Ca from bottom ashes during sorption experiments was much slower than that during ANC experiments. This difference may be attributed to the fact that CaCl_2 is much more water soluble than calcium phosphates. Calcium phosphates may precipitate on the surface of ash particles and hinder the release of phosphate from the inner part of the particles. The effect can be more significant for large particles. Particle size of bottom ashes was much greater than that of fly ashes. Despite this over estimation for the bottom ashes, the strong linear correlation between ANC and the measured P retention, we believe, justifies the use of ANC as a measure of phosphate retention capacity in an alkaline solution where the precipitation of calcium phosphates is the predominant retention mechanism.

4. Conclusions

- (1) Fly ashes had a much greater phosphate retention capacity (4–30 g P/kg) than bottom ashes (15–600 mg P/kg). Lignitinous coal ashes were more capable of retaining phosphate than bituminous coal ashes.
- (2) Sorption isotherms of fly ashes were found to be adequately represented by the Langmuir model while those of bottom ashes fitted better to the Freundlich model. The retention process was however largely irreversible. The irreversibility increased with the increase in the retention capacity, suggesting that chemical sorption/reactions played a major role in the retention process.
- (3) Weathering enlarged the retention capacity of the bituminous bottom ash, but substantially lowered that of the fly ash, which was attributed to the difference in the weather-induced changes between the fly and bottom ashes.
- (4) The aqueous solutions at the end of sorption/desorption experiments were saturated or super-saturated with respect to tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), and slightly under-saturated with respect to amorphous calcium phosphate. Precipitation of calcium phosphate is the predominant mechanism for phosphate retention by coal ash under the conditions studied.

- (5) The linear correlation between acid neutralization capacity (ANC) and phosphate sorption capacity led to the suggestion of using ANC as a simpler measure of phosphate sorption capacity of coal ashes.

Acknowledgments

The authors would like to thank Dr. A.L. Torrenueva of the Ontario Power Generation Inc. for helpful discussions and assistance in the sampling of ashes. We thank Falconbridge Limited for arranging some of the chemical analysis of ashes at Lakefield Research Inc. Perkin-Elmer's contribution through the ANALEST facility at the University of Toronto is also gratefully acknowledged. Financial support was provided by the Ontario Power Generation Inc., the Natural Science and Engineering Research Council of Canada (NSERC), and Natural Science Foundation of China (Project #20377054).

References

- [1] NRCAN, Coal combustion products—production and use, Mineral & Metals Sector, Natural Resources Canada, Ottawa, 1999.
- [2] C.A. Gray, A.P. Schwab, Phosphorus-fixing ability of high pH, high-calcium, coal-combustion, waste materials, *Water Air Soil Pollut.* 69 (1993) 309–320.
- [3] S.E. O'Reilly, J.T. Sims, Phosphorus adsorption and desorption in a sandy soil amended with high-rates of coal fly-ash, *Commun. Soil Sci. Plant Anal.* 26 (1995) 2983–2993.
- [4] W.L. Stout, A.N. Sharpley, H.B. Pionke, Reducing soil phosphorus solubility with coal combustion by-products, *J. Environ. Qual.* 27 (1998) 111–118.
- [5] L.J. Holcombe, B.P. Eynon, P. Switzer, Variability of elemental concentrations in power-plant ash, *Environ. Sci. Technol.* 19 (1985) 615–620.
- [6] C.B. Behr-Andres, G.K. Parish, N.J. Hutzler, Strategy for beneficial use of stoker-boiler coal ash, *J. Environ. Eng.* 120 (1992) 401–415.
- [7] R.K. Vempati, M.Y.A. Mollah, A.K. Chinthala, D.L. Cocke, J.H. Beeghly, Solidification/stabilization of toxic metal wastes using coke and coal combustion by-products, *Waste Manage.* 15 (1995) 433–440.
- [8] H.V. Mott, W.J. Weber Jr., Sorption of low-molecular-weight organic contaminants by fly-ash—considerations for the enhancement of cutoff barrier performance, *Environ. Sci. Technol.* 26 (1992) 1234–1242.
- [9] K. Banerjee, P.N. Cheremisinoff, S.L. Cheng, Adsorption kinetics of *o*-xylene by flyash, *Water Res.* 31 (1997) 249–261.
- [10] M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Removal of phenol by adsorption on coal fly ash and activated carbon, *Pollut. Res.* 16 (3) (1997) 170–175.
- [11] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1998) 2469–2479.
- [12] B. Sur, S.K. Chaudhuri, N.C. Pradhan, Removal of basic dyes from aqueous streams using a packed bed-containing low cost sorbent-catalyst: coal fly ash, *Int. J. Environ. Stud.* 54 (3/4) (1998) 175–176.
- [13] D.L. Correll, The role of phosphorus in the eutrophication of receiving waters: a review, *J. Environ. Qual.* 27 (1998) 261–266.
- [14] R. Parry, Agricultural phosphorus and water quality: a US Environmental Protection Agency perspective, *J. Environ. Qual.* 27 (1998) 258–261.
- [15] A.N. Sharpley, Global issues of phosphorus in terrestrial ecosystems, in: K.R. Reddy, G.A. O'Connor, C.L. Schelske (Eds.), *Phosphorus Biogeochemistry in Subtropical Ecosystems*, CRC Press LLC, 1999 (Chapter 1).
- [16] M.E. Bechmann, D. Berge, H.O. Eggestad, S.M. Vandsemb, Phosphorus transfer from agricultural areas and its impact on the eutrophication of lakes—two long-term integrated studies from Norway, *J. Hydrol.* 304 (1–4) (2005) 238–250.
- [17] C.A. Arias, H. Brix, N.H. Johansen, Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with a calcite filter, *Water Sci. Technol.* 48 (5) (2003) 51–58.
- [18] A.N. Shiltona, I. Elmetria, A. Drizob, S. Pratta, R.G. Haverkampa, S.C. Bilbyc, Phosphorus removal by an 'active' slag filter—a decade of full scale experience, *Water Res.* 40 (2006) 113–118.
- [19] J. Yan, Major leaching processes of combustion residues—characterisation, modelling and experimental investigation, Ph.D. thesis, ISBN 91-7170-325-X, Royal Institute of Technology, Stockholm, Sweden, October, 1998.
- [20] W.J. Weber Jr, P.M. McGinley, L.E. Katz, Sorption phenomena in sub-surface systems—concepts, models and effects on contaminant fate and transport, *Water Res.* 25 (1991) 499–552.
- [21] D.L. Sparks, *Kinetics of Soil Chemical Processes.*, Academic Press, Inc., San Diego, 1989.
- [22] W. Stumm, J.J. Morgan, *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, third ed., John Wiley & Sons, Inc., New York, 1996, p. 1022.
- [23] D.L. Parkhurst, User's guide to PHREEQC—a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations, *Water-Resources Investigations Report 95-4227*, U.S. Geological Survey, 1995.
- [24] W.L. Lindsay, *Chemical equilibria in soils*, John Wiley & Sons, New York, 1979.
- [25] M.R. Christoffersen, J. Christoffersen, W. Kibalczyk, Apparent solubilities of 2 amorphous calcium phosphates and of octacalcium phosphate in the temperature-range 30–42 °C, *J. Crystal Growth* 106 (1990) 349–354.
- [26] W.L. Lindsay, P.L.G. Vley, S.H. Chien, Phosphate minerals, in: J.B. Dixon, S.B. Weed (Eds.), *Minerals in Soil Environments*, second ed., Soil Science Society of America, 1989, pp. 1089–1130.
- [27] O.A. Diaz, K.R. Reddy, P.A. Moor Jr., Solubility of inorganic phosphorus in stream water as influenced by PH and calcium-concentration, *Water Res.* 8 (1994) 1755–1763.
- [28] L. Johansson, J.P. Gustafsson, Phosphate removal using blast furnace slags and opoka-mechanism, *Water Res.* 34 (2000) 259–265.
- [29] P.W. Schindler, G. Sposito, Surface complexation at (hydr)oxide surfaces, in: G.H. Bolt, et al. (Eds.), *Interactions at the Soil Colloid–Soil Solution Interface*, Edited by Kluwer Academic Publishers, Dordrecht, 1991, pp. 115–145.
- [30] C.J. Richardson, The role of wetlands in storage, release, and cycling of phosphorus on the landscape: a 25-year retrospective, in: K.R. Reddy, G.A. O'Connor, C.L. Schelske (Eds.), *Phosphorus Biogeochemistry in Subtropical Ecosystems*, CRC Press LLC, 1999 (Chapter 2).
- [31] C. Zevenbergen, Natural weathering of MSWI bottom ash: transformation of glassy constituents and implications for heavy metal leaching, Ph.D. thesis, Universiteit Utrecht, The Netherlands, 1994.
- [32] S.V. Mattigod, D. Rai, L.E. Eary, C.C. Ainsworth, Geochemical factors controlling the mobilization of inorganic constituents from fossil-fuel combustion residues. 1. Review of the major elements, *J. Environ. Qual.* 19 (1990) 188–201.
- [33] A. Drizo, Y. Comeau, C. Forget, R.P. Chapuis, Phosphorus saturation potential: a parameter for estimating the longevity of constructed wetland systems, *Environ. Sci. Technol.* 36 (21) (2002) 4642–4648.
- [34] C.A. Johnson, S. Brandenberger, P. Baccini, Acid neutralizing capacity of municipal waste incinerator bottom ash, *Environ. Sci. Technol.* 29 (1) (1995) 142–147.