Georgia Tech Sponsored Research

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<td>Title</td>
<td>Evaluating Re-use Options for Iron-Rich Sludge for Du Pont Edgemoor Plant</td>
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5 August, 2000

Mr. Leonard J. Fasullo
DuPont White Pigment & Mineral Products
DuPont Edgemoor Plant
104 Hay Road
Edgemoor, DE 19809

RE: Evaluating Re-use Options for Iron-Rich™ Sludge from Du Pont Edgemoor Plant
Final report: Georgia Tech Project E20-E20

Dear Mr. Fasullo,

This letter report serves as the second and final annual report for our research project entitled Evaluating Re-use Options for Iron-Rich™ Sludge from Du Pont Edgemoor Plant. I appreciate your support over the last two years and no further sponsorship is requested as I am leaving Georgia Tech to pursue other opportunities. The Year 2 accomplishments are detailed below. Following the guidelines for the Year 1 annual report, this report is brief and less than 10 pages.

The attached research results illustrate a very high ability for the IR sludge to immobilize phosphate from aqueous solutions. Given the limitations of the analytical equipment and modeling approaches, it was not possible to determine if the mechanism of phosphate removal was precipitation or sorption, though it is believed that the latter is the predominant mechanism based on a literature review of iron- and alumina-rich porous media. The interactions between phosphate and iron- and alumina-rich porous media are detailed in the attached gallery proof of an invited paper recently accepted to a special issue of the Journal of Hazardous Materials. This paper is currently in press. Even though this paper focuses on fly ash applications, the amorphous and iron-rich nature of the IR sludge means that many of the same issues apply or are analogous.

Given the fact that we had many problems with the workability of the iron (IR) sludge in terms of generating a range of particle gradations in a manner similar to those grain size distributions attained with the original IR sludge samples upon which the original proposal was based, it may be worthwhile to explore two other applications. The phosphate concentrations used in the experimentation were quite high, reflective of industrial type effluents. Considering the phosphate loading to surface and groundwaters from phosphate fertilizers, chicken, pig and dairy farms, the IR sludge (by virtue of its non-hazardous classification) appears to be ideally suited for land application near or at such activities if the proper balance between the IR sludge application rate and soil or aqueous pH can be attained for the desired phosphate removal efficiency. Soil scientists are in a much better position than I to make a full assessment of this issue in the field. Land application may be explored on a per acre basis, or spot applications in a manner similar to oil adsorbents.

Secondly, it may be interesting to explore using the IR sludge in a manner similar to powder activated carbon (PAC) in industrial or municipal wastewater treatment plants. PAC is delivered into flash mixing units to removal dissolved hydrocarbons. It may be possible to use IR sludge in a similar manner to remove phosphate and to provide pH buffering, since the phosphate uptake of the IR sludge occurs very rapidly. The IR sludge would ultimately be removed from...
the wastewater in settling ponds or would be incorporated into the sludge. Both applications are likely to require regulatory approval but the enclosed data should provide compelling evidence of the IR sludge's ability to eliminate phosphate from aqueous streams.

If you have questions please do not hesitate to phone, fax or e-mail me. It has been a pleasure working with you on this project.

Sincerely,

Dennis G. Grubb, Ph.D.

cc: Mr. Jody R. Bacher, VFL Technologies

Attachments
Phosphate Immobilization Experiments with Iron Rich™

We had many problems with the workability of the iron (IR) sludge in terms of generating a range of particle gradations in a manner similar to those grain size distributions generated using the original IR sludge samples which were the basis of the proposal. Numerous approaches were taken in an attempt to make the IR sludge self binding including the addition of lime, fly ash and so on.

In discussions with you (Mr. Len Fasullo) this work was abandoned, and we began focusing on the geochemistry issues associated with the IR sludge and its ability to immobilize phosphate. The main motivation for working with phosphate is that it is usually the limiting bionutrient in ecosystems and excess quantities of phosphate create problems such as algal blooms and *Pfiesteria*. Accordingly, a series of phosphate (batch and column) immobilization experiments were conducted.

1.0 Time dependent batch equilibration experiments

The Iron Rich Sludge (IR sludge) was taken from 20-liter sealed buckets at its natural moisture content which was determined to be in the order of 101 to 117 %. The IR sludge was grated into chips or shreds, and was subsequently air-dried for approximately 48 hours. Once dried the IR sludge was pulverized with a mortar and pestle, to pass a #200 sieve (0.074 mm). The pulverized IR sludge was then used in the equilibration experiments.

Glass equilibration vials were presoaked in a 3% nitric acid bath for no less than 24 hours and were sequentially rinsed with a 3% nitric acid solution and B*Pure water prior to use. B*Pure water purified by organics and metals removal cartridges having a specific resistance of 17.8 megaohm-cm was used to prepare the stock solutions. Phosphorous was added as diabasic anhydrous sodium phosphate (Na₂HPO₄, 99.6% purity) to B*Pure (Deionized) water, pH=6.9-7.1, to produce the phosphate stock solutions. For all batch phosphate immobilization experiments, the stock solutions were added to glass vials containing pre-measured quantities of pulverized iron rich material to achieve the desired liquid:solids ratios.

To determine whether phosphate immobilization was instantaneous or time dependent, deionized water (0 mg P/L) and phosphorous stock solutions were blended with IR sludge at a ratio of 100:1 (wt basis). The liquid:solids ratio was selected on the basis of our observations that the IR sludge could remove high aqueous concentrations of phosphorus and many non-detects were measured at liquid:solids ratios less than 100:1 when the phosphate was present at concentrations on the order of 100 mg P/L. Phosphate stock solutions containing 150, 250 and 350 mg P/L were exposed to the IR sludge for contact times ranging from 0 (10 min.), 3, 6, 12, 48 and 96 hours. Triplicate samples were equilibrated on an orbital shaker (100 RPM) and the solution pH, and phosphate, sulfate and chloride concentrations were determined for each exposure interval.

Leachate samples were collected from the equilibration vials using latex free syringes fitted with styrene based strong acid resin syringe filters (OnGuard-H). Aqueous phosphate, sulfate and chloride concentrations were analyzed using a Dionex DX-500 high performance ion chromatograph (IC) fitted with an ED 40 electrochemical detector having a background conductivity between 2 and 3.5 μS. Ion separation was accomplished using a 25 μL sample injection loop on an Ionpac AS 16-4 mm column using a 35 mM NaOH eluent at a flow rate of 1.5 mL/min. A detection limit of 1 mg P/L was established for these concentrated systems.

1.1 Results

Figure 1 shows the equilibrated aqueous phosphorous concentrations in solution as a function of the initial phosphorous concentration and time for the 100:1 batch mixtures. The results at 10 minutes suggest that large concentrations of phosphorus can be removed very rapidly, on the order of 65 to 75%. Thereafter, the phosphorous concentrations tend to decrease asymptotically with time such that after 48 hours the phosphorus removal was on the order of 85 to 95% of the initial concentration. Figure 2 illustrates that although the phosphate stock solutions are alkaline in nature, the IR sludge stabilizes the pH of the stock solutions at a neutral condition while removing the phosphorus.
Figures 3 and 4 show the equilibrated aqueous sulfur and chloride concentrations in solution as a function of the initial phosphorous concentration and time for the 100:1 batch mixtures. As would be expected from the ore source and manufacturing process, essentially no sulfur is released from the IR sludge material, unlike other industrial byproducts (namely fly ash). Since the equilibrated chloride concentration is remains constant with the initial phosphate concentration, it appears from Figure 4 that the chlorides released from the IR sludge are essentially independent of the phosphorus uptake of the IR sludge.

2.0 Batch equilibration experiments at different liquid:solids ratios

In an effort to potentially optimize on IR sludge usage as a function of the quantity of phosphorus to be removed from an aqueous solution, a series of experiments was completed in which both the liquid:solids ratio and initial phosphorous concentration were varied. The same procedures outlined in Section 1.0 were adopted. However, since a majority of the phosphate uptake occurred almost instantaneously, the exposure time was limited to 3 hours based on the time intensive nature of the analytical work and the fact that unit operations in wastewater treatment attempt to target short residence times. Also, longer exposure times result in greater removal, and our main purpose was to illustrate the general capabilities of phosphorus removal from aqueous solutions.

The batch equilibration experiments were completed using phosphate stock solutions containing 150, 250 and 350 mg P/L. IR sludge was added to these solutions using the following liquid:solids ratios: 10:1, 20:1, 50:1, 75:1, 100:1 and 200:1. The initial pHs of the stock solutions were 8.40, 8.42 and 8.34 for 150, 250 and 350 mg P/L solutions, respectively. The equilibrated pH of the equilibrated IR sludge:DI water mixtures ranged between 6.4 to 6.8 for the various liquid:solids ratios.

2.1 Results

Figure 5 shows equilibrated phosphorous concentrations as a function of the initial phosphorous concentration and the liquid:solids ratio, where the solids content was set to unity (1). For liquid:solids ratio less than 20:1, no phosphorous was detected in solution (1 mg P/L detection limit) regardless of the initial phosphorous concentration. For the initial concentrations tested, the removal of phosphorous from solution for the 50:1, 100:1 and 200:1 mixture ratios varied between 95-97%, 65-91%, and 3-51%, respectively.

Figure 6 shows the equilibrated pHs of the leachate solutions were measured between 6.8 and 7.8. A slight increasing trend is observed as the IR sludge becomes increasingly dilute (up to 200:1), although the IR sludge is still effective in lowering the pH of the phosphate solutions. The corresponding equilibrated sulfur and chloride concentrations are shown in Figures 7 and 8. Again the sulfur concentrations are low but Figure 7 shows an increase in the sulfur concentration which peaks at a liquid:solids ratio of 20:1—the exact reason for this is not known.

As with Figure 4, Figure 8 illustrates that the equilibrated chloride concentration is essentially independent of the initial phosphorous concentration and the effect of dilution is clearly observed as the IR sludge becomes increasingly dilute in the mixtures (up to 200:1). Comparison of the chloride concentrations for the 50:1, 100:1 and 200:1 mixtures suggests a linear dilution effect. The peak chloride concentration measured (10:1) was on the order of 6,250 mg Cl/L.

3.0 Batch equilibration experiments at different liquid:solids ratios using washed IR Sludge

Since the released concentrations of chloride were high in the previous experiments, concern may arise regarding impacts to fresh water quality. Accordingly, the experiments described in Section 2.0 were repeated using IR sludge that was pre-leached of chlorides. IR sludge was pre-equilibrated for 24 hours with DI water at liquid:solids ratio of 35:1. The drained liquid was subsequently analyzed to establish a baseline chloride concentration of approximately 2,100 mg Cl/L. The washed IR sludge was then allowed to air-dry for 48 hours prior to batch testing with the phosphate stock solutions. The influence of the
liquid:solids ratio on the measured pH and sulfur and chloride concentrations for IR sludge soaked in DI water for 24 hours was also determined.

3.1 Results

The washing of the IR sludge with DI water had a decisive impact on the solution pH and the equilibrated concentrations of phosphate, sulfur and chloride. Figure 9 illustrates diminished phosphorus removal of the washed IR sludge at low liquid:solids ratios. Instead of the curves being concave up, as in the case of the natural (unwashed) IR sludge, the curves are concave down. In almost every case, the natural IR sludge removes more phosphorus from the aqueous solution than the washed IR sludge (200:1, 350 mg P/L test excepted).

Figure 10 shows the equilibrated pH for the natural and washed IR sludge mixtures as a function of liquid:solids ratio and initial phosphorus concentration. IR sludge exposed to DI water produced equilibrated pHs on the order of 5.9 to 6.7, indicating that the IR sludge is slightly acidic in nature. The washing of the IR consequently results in the inability of the IR to buffer the phosphate stock solutions. At liquid:solids ratios above 50:1, no buffering is provided by the washed IR sludge, i.e., the pH of the equilibrated stock solutions is very close to or greater than their initial values.

The trends observed in Figures 9 and 10 partially relate to the speciation of phosphorus as a function of pH in the presence of iron rich media, especially if IR washing removes soluble iron and changes the nature of the iron species at the particle surface and its pH buffering capacity. In calcium deficient systems, phosphorus precipitates with soluble iron and binds strongly to iron oxide surfaces under acidic pH conditions. If soluble iron and buffering capacity of IR sludge are removed or diminished, the solution pH and equilibrated phosphorus concentration (as HPO$_4^{2-}$, and H$_2$PO$_4^-$) are likely increase, as observed in Figures 9 and 10.

Figure 11 indicates that the IR sludge exposed to DI water produces very low sulfur concentrations. However, washing of the IR sludge with subsequent exposure to phosphate at low liquid:solids ratios (<50:1) suggest that phosphorus may expel sulfur from the particle surfaces of the IR sludge. It is known that phosphate binds more strongly with iron oxides than sulfate, and this may be a partial explanation for the observed trends before the effects of aqueous dilution of IR take effect (>50:1).

Figure 12 shows that the washing of the IR sludge dramatically reduces the equilibrated chloride concentrations from 6,700 mg Cl/L to approximately 600 mg Cl/L in the case of 10:1 liquid to solids ratio, i.e., a reduction of approximately two orders of magnitude. The effects of aqueous dilution are observed thereafter at higher liquid:solids ratios.

4.0 Column experiments

Four IR sludge packed geochemical column tests were completed in an upflow mode, using the geochemical columns described in “Appendix B” of the first Annual Report dated, November 22, 1999. For your convenience, a schematic of the bank of geochemical columns and a detail of an individual column are reproduced in Figures 13 and 14, respectively. The IR sludge used to pack the columns consisted of grated chips air dried for no less than 48 hours. The chips were then sieved through #4 (4.75 mm) and #10 (2 mm) sieves. The material retained on the #10 sieve was used in the experiments. The packing of the IR sludge chips in the columns resulted in particle breakage and the creation of fines. Some migration of fine IR sludge particles in the columns was observed.

The columns were designated Columns 1 to 4 (C1 though C4, respectively). Columns C1 and C2 were packed in such a way that the central third of the 30 cm long column was filled with loosely tamped IR sludge chips. The chips were deposited in the flow column under a column of DI water to increase the degree of saturation. The top and bottom thirds of the column were packed with graded Ottawa sand, as shown in Figure 14. The volume of IR sludge chips corresponds to approximately 280 cm$^3$ assuming a porosity of 0.3. In columns C3 and C4, the lower two thirds of the columns (~19 cm) were packed with IR
sludge chips corresponding to a volume of approximately 520 cm³ based on a porosity of 0.3. After the columns were packed, they were flushed with DI water for 2 weeks.

A multi-channel peristaltic pump (Ismatec IPC-8) was used to deliver a flow rate of 1.65 cm³/min, which corresponds to a Darcy velocity of approximately 0.62 m/day. For columns C1 and C2 this flow rate corresponded to flushing 5 pore volumes of IR sludge every 6 hours. For columns C3 and C4 a pore volume was flushed every 12 hours. After the column saturation with DI water, this liquid was substituted by phosphorous stock solution (200 mg P/L). This involved draining the bottom reservoir of the column to avoid dilution of the initial phosphate concentration prior to injection into the Ottawa sand. The experiments were terminated at 85 pore volumes. Leachate samples collected from the columns were collected using latex free syringes fitted with styrene based strong acid resin syringe filters (OnGuard-H). Aqueous phosphate, sulfate and chloride concentrations were analyzed similar to the procedure described in section 1.

4.1 Results

Figures 15 to 18 show the phosphorus breakthrough curves for the IR sludge packed columns leached with a 200 mg P/L stock solution. Phosphorus broke through columns C1 and C2 (at SP-4) between approximately 20 and 25 pore volumes for a pore volume residence time of 6 hours. Similar performance was attained with columns C3 and C4 which suggests that the phosphate immobilization occurring in the IR sludge was sufficiently rapid that the selected flow rate did not result in premature breakthrough of phosphate. The difference in the breakthrough curves at SP-2 between the two sets of experiments (C1,2 vs. C3,4) resulted from the SP-2 being nested in the IR sludge in the latter set of experiments.

Figures 19 to 22 show the leached sulfur concentrations from the four respective columns. Since the columns were leached with DI water for two weeks prior to phosphorus injection, the influent concentrations of sulfur are very low. Comparison of Figures 15 to 18 with Figures 19 to 22 provide very strong suggestive evidence that the immobilization of phosphate results from sorption of phosphate on the IR sludge chip surfaces. The leaching of sulfur from the columns appears to be coincident with the leading edge of the phosphate front as it migrated through the IR sludge, suggesting that sulfur was being displaced from the IR sludge chip surfaces by the phosphorus. Unfortunately, it was not possible to measure the internal pH of the columns. Nevertheless, the phosphorus and sulfur curves are very suggestive of the propagation of a pH front through the columns.

Figures 23 to 26 show the leached sulfur concentration from the four respective columns. These chloride concentrations are significantly lower than the batch experiments suggesting more extensive washing (leaching) of the IR sludge may have occurred.

The column experiments illustrate the ability of IR sludge to immobilize large concentrations of phosphorus in a flow through mode. The immobilization of phosphorus is not as efficient as the batch experiments for a variety of reasons: the batch experiments involved a finer grained material with more surface area for sorption and precipitation reactions to occur; the leaching of IR sludge was more extensive in the columns that the pre-washed IR batch experiments; and differences in mixing processes (stirred versus flow through). Greater control over the gradation of the IR sludge which would allow for the creation of sand sized particles would improve the phosphate immobilization of the IR sludge in a packed column configuration.
Figure 1: Equilibrated phosphorous concentrations for iron rich sludge (100:1) batch mixtures versus time and initial phosphorous concentration.
Figure 2: Equilibrated pH for iron rich sludge (100:1) batch mixtures versus time and initial phosphorous concentration.

- IR : pH = 6.4 - 6.8
- pHo = 8.40 for 150 mg P/L solution
- pHo = 8.42 for 250 mg P/L solution
- pHo = 8.34 for 350 mg P/L solution
Figure 3: Equilibrated sulfur concentrations for iron rich sludge (100:1) batch mixtures versus time and initial phosphorous concentration.
Figure 4: Equilibrated chloride concentrations for iron rich sludge (100:1) batch mixtures versus time and initial phosphorous concentration.
Figure 5: Equilibrated phosphorous concentrations for iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.
Figure 6: Equilibrated pH for iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.

- 150 mg P/L
- 250 mg P/L
- 350 mg P/L

IR in DI water: pH = 6.4 - 6.8

pH = 8.40 for 150 mg P/L solution
pH = 8.42 for 250 mg P/L solution
pH = 8.34 for 350 mg P/L solution
Figure 7: Equilibrated sulfur concentrations for iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.
Figure 8: Equilibrated chloride concentrations for iron rich sludge batch mixtures versus liquid : solids ratio and initial phosphorous concentration.
Figure 9: Equilibrated phosphorous concentrations for natural and washed iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.
Figure 10: Equilibrated pH for natural and washed iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.

- IR (washed) pH = 6.8 - 7.4
- IR pH = 6.4 - 6.8
- pHo = 8.40 for 150 mg P/L solution
- pHo = 8.42 for 250 mg P/L solution
- pHo = 8.34 for 350 mg P/L solution

Legend:
- 150 mg P/L
- 250 mg P/L
- 350 mg P/L
- 150 mg P/L (washed)
- 250 mg P/L (washed)
- 350 mg P/L (washed)
- 0 mg P/L (washed)
Figure 11: Equilibrated sulfur concentrations for natural and washed iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.
Figure 12: Equilibrated chloride concentrations for natural and washed iron rich sludge batch mixtures versus liquid:solids ratio and initial phosphorous concentration.
Figure 13. Schematic of geochemical testing columns to monitor leachate attenuation using Iron Rich™ media (upflow mode).
Figure 14. Detail of geochemical testing column in upflow mode.
Figure 15: Phosphorous breakthrough curves for an iron rich sludge packed column (#1) leached with a 200 mg P/L solution.
Figure 16: Phosphorous breakthrough curves for an iron rich sludge packed column (#2) leached with a 200 mg P/L solution.
Figure 17: Phosphorous breakthrough curves for an iron rich sludge packed column (#3) leached with a 200 mg P/L solution.
Figure 18: Phosphorous breakthrough curves for an iron rich sludge packed column (#4) leached with a 200 mg P/L solution.
Figure 19: Sulfur breakthrough curves for an iron rich sludge packed column (#1) leached with a 200 mg P/L solution.
Figure 20: Sulfur breakthrough curves for an iron rich sludge packed column (#2) leached with a 200 mg P/L solution.
Figure 21: Sulfur breakthrough curves for an iron rich sludge packed column (#3) leached with a 200 mg P/L solution.
Figure 22: Sulfur breakthrough curves for an iron rich sludge packed column (#4) leached with a 200 mg P/L solution.
Figure 23: Chloride breakthrough curves for an iron rich packed column (#1) leached with a 200 mg P/L solution.
Figure 24: Chloride breakthrough curves for an iron rich sludge packed column (#2) leached with a 200 mg P/L solution.
Figure 25: Chloride breakthrough curves for an iron rich sludge packed column (#3) leached with a 200 mg P/L solution.
Figure 26: Chloride breakthrough curves for an iron rich sludge packed column (#4) leached with a 200 mg P/L solution.
Phosphate immobilization using an acidic type F fly ash

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Received 11 December 1999; received in revised form 24 February 2000; accepted 25 February 2000

Abstract

Batch equilibration experiments using a low calcium (~ 1 wt.% as CaO), acidic (pH ~ 4.5) Type F fly ash demonstrated phosphate immobilization on the order of 100% to 75% for 50 and 100 mg P/l solutions, respectively. A loosely compacted column of fly ash similarly removed 10 mg P/l for over 85 pore volumes. While the interactions between phosphate- and calcium-rich (Type C) ashes are relatively well understood, insight into the mechanisms of phosphate immobilization in Type F ash necessitated a review of the phosphate chemistry and interactions with acidic geomedia. Phosphate adsorption was subsequently modeled using a constant capacitance model approach (CCM) excluding precipitation reactions. Our CCM predictions of total phosphate immobilization (20%) were substantially less than the results of the batch equilibration experiments and phosphate adsorption predicted by other researchers examining near pure natural and synthetic geomedia due to the compositional heterogeneity of the fly ash. Nevertheless, for the amorphous and crystalline phases studied, the immobilization of phosphate in the Type F fly ash is attributed to the formation of insoluble aluminum and iron phosphates at low to medium values of pH. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fly ash; Phosphate; Sorption; Precipitation; Acid conditions

1. Introduction

According to the American Coal Ash Association [1], sixty million tons of fly ash are produced annually in the United States, and only 25% to 30% of this material is productively re-used, principally in construction-related applications due to the poz­ zolanic characteristics of fly ash. The remaining 45 million tons are impounded or
landfilled. In seeking alternatives for productive reuse, coal burning and fly ash management activities are recognized to frequently occur in northern regions that also suffer from environmental problems due from phosphorous loading to surface and groundwater from concentrated agricultural activities including soil fertilization, feed lots, diaries, and pig and poultry farms. The National Water Quality Inventory 1994 Report to Congress cited nutrients (nitrogen and phosphorus) as one of the leading causes of water quality problems in rivers, lakes, and estuaries resulting in eutrophication, increased fish mortality and outbreaks of microbes such as *Pfiesteria piscicida*. Because fly ash is enriched with the oxides of aluminum, iron, calcium, and silica, fly ash emerges as candidate material to treat phosphate-laden effluents since aluminum, iron and calcium are known to strongly adsorb or precipitate phosphates in many agricultural, industrial and environmental applications [2,3]. To illustrate the general capabilities of fly ash to immobilize phosphate [4-11], we consider four studies.

Higgins et al. [10] explored the potential to treat eutrophic water (pH ~ 9) from Lake Charles East (IN) with total (suspended plus soluble orthophosphate) phosphorus concentrations of 600 µg P/l in a series of 1-L-jar tests using combinations of fly ash, lime and gypsum. Treatments with gypsum (100 to 500 mg/l) and fly ash (20 g/l) were found to be relatively ineffective in reducing the total concentrations of phosphate to below 60%, which increased with increasing gypsum dosage and with orthophosphate typically accounting for approximately 50% of the total phosphorus. A 90% reduction in orthophosphate was achieved with 500 mg/l gypsum dose when the pH was increased to 10. Lime, a stronger alkali, was subsequently used in conjunction with fly ash since its calcium content obviated the need for gypsum. Since a lime application of 300 mg/l to lake water (600 µg P/l; pH ~ 8.41) reduced the orthophosphate concentrations to 17 µg P/l with a final pH of 10.2, it was deemed that a lower lime dosage of 200 mg/l was a sufficient dosage rate given both the soluble phosphorus removal rate and lower final pH (41 µg P/l; pH ~ 9.4). While the addition of 20 g/l of fly ash had a small effect on the soluble concentrations, the primary benefit realized was significant reductions in the suspended phosphate concentrations, presumably due to the advantageous settling characteristics of fly ash solids. Using total lime and fly ash application rates of 200 mg/l and 20 g/l, respectively, a optimization study of material dosing and sequencing rates on lake water (640 µg P/l; pH ~ 8.9) showed that two sequential half dosages (100 mg/l, 10 g/l) achieved essentially the same phosphorus removal as the sequenced full dosages, but simultaneous application of the full dosages produced the overall lowest total phosphorus concentrations (150 µg P/l) without a substantial change in pH (~ 9.1). Algae studies performed in parallel with the jar test indicated that a 10 g/l dosage of fly ash was more effective than 300 mg/l of lime in reducing bacterial counts though it was not known whether the improvement resulted from more effective binding of phosphate and sealing of sediments after settling, removal of other growth factors, or the release of an inhibitory substance. An 85-day pond study using in-situ caissons as treatment cells showed dramatic reductions (> 95%) in soluble and total phosphorus concentrations when 20 g/l of fly ash and lime (500 mg/l) were added on Days 1 and 7, respectively.

In batch adsorption studies conducted at pHs of 5.25 and 8.25, Vordonis et al. [5] determined that the uptake of orthophosphate by four calcium-rich (10-32%) Greek fly
ashes exceeded the amount predicted by monolayer coverage, which suggested either multilayer adsorption or precipitation (see Table 1). The fly ashes also contained magnesium at 2.2% to 6.3% and had specific surface areas (SSA) of 5.1 to 6.7 m²/g. To distinguish between these two mechanisms of immobilization, several additional properties were determined: the zero points of charge (ZPC) varied between 8.9 and 10.3 (pH) units, and the isoelectric points (IEPs) were on the order of 7.0 to 8 units. The oxide chemistry of the ashes (see Table 2) and their large positive surface charges (i.e., below their ZPCs) suggested that the electrostatic binding of anions would be the preferential mechanism of phosphate uptake. Ash samples prewashed with potassium nitrate (0.01 mol KNO₃/dm³) at pH 5.25 showed no difference in phosphate uptake except for a sample containing 31.9% calcium that underwent a large decrease in phosphate uptake. It was thought that calcium phosphate may have formed in the unwashed sample but no calcium phosphate was detected by X-ray fluorescence (XRF). Given the chemically heterogeneous nature of fly ash, the presence of magnesium also suggested that the formation of apatite precipitates would be inhibited [12]. In the ashes exposed to phosphate solutions, adsorbed phosphate bands (PO₄³⁻) were detected by IR spectroscopy, but the acidic phosphates (H₂PO₄⁻, HPO₄²⁻), which are mostly soluble in the pH range of 5 to 9 [13] were not detected. A shift in the IEPs of the ashes to a more acidic condition suggested that phosphate sorption occurred as opposed to the formation of apatite, which would have resulted in a more basic IEP.

Ugurlu and Salman [6] conducted batch and columns experiments with a calcium-rich (34%) fly ash with a LOI of 10% and an average particle size between 0.125 and 0.063 mm. Adsorption studies were conducted with 20, 50 and 100 mg P/l solutions at constant pH (not reported) at temperatures between 27°C and 50°C. Adsorbent doses of fly ash from 4 to 20 g/l produced over 95% removal of phosphate (20 mg P/l) for contact times as little as 5 min. When the phosphate concentrations were increased to 50 and 100 mg P/l at the lowest adsorbent dose (4 g/l), phosphate removal by fly ash was still greater than 93% and 60% for contact times greater than 10 min, respectively, with peak adsorption observed at 40°C. However, the role of pH (initial stock solution, or equilibrated solution) was not discussed. In a 5-cm diameter, 65-cm long column packed with fly ash permeated with the 100 mg P/l solution with a residence time on the order of 60 min, the phosphate removal efficiency and effluent pH respectively decreased from 95% to 80% and 11.29 to 8.83 pH units over a 72-h period. When the fly ash from the bottom (outlet) of the column was exhumed and analyzed by XRF, it was very similar to the unused ash except that a significant reduction in calcium content was

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PZC of selected minerals

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</table>

observed (8%), suggesting that calcium dissolution occurred within the entire column and that the mobilized calcium was purportedly available to precipitate the dissolved phosphate. Additional batch studies conducted at high pH (> 11.5) confirmed calcium dissolution from the fly ash. X-ray diffraction (XRD) analyses of the fly ash exhumed from the column confirmed the appearance of amorphous apatite at the inlet, which became more crystalline with time. Phosphate sorption was implied by the XRD response that showed decreased masking of calcite surfaces along the longitudinal axis of the column. It was therefore concluded that adsorption of phosphate to calcite surfaces was the dominant immobilization mechanism.

The Electrical Power Research Institute (EPRI) [9] describes the land application of 345.22 metric tons/ha of an acidic coal ash containing 1.75 kg/ha of phosphorous to existing soils. Land application is a frequent fly ash disposal option accounting for 7.5% of the total amount of fly ash reuse, where the predominant application is for mine reclamation [1]. After the land application the bio-available phosphorous content in the fly ash-soil mixture was measured to be 33.63 kg/ha, substantially less than the 56.04 kg/ha measured in the soil before the land application. While the fly ash initially contained phosphorus, it was still capable of immobilizing an additional 22.42 kg/ha.

The reviewed articles and their citations suggested that the literature dealing with phosphorus and fly ash is dominated by calcium-rich ashes (Type C) not Type F ashes. The mechanism of phosphate immobilization in Type C ash was linked mainly to the formation of calcium phosphate, namely hydroxyapatite, at elevated pH. However, these studies remain somewhat relevant to Type F ashes because calcium often leaches from ash and the pH drifts with continued leaching or chemical weathering in aggressive environments. It appears that phosphate immobilization in acidic Type F ashes has not been extensively researched and the mechanisms of phosphate immobilization are expected to be very different based on mineralogical differences. To illustrate these differences, we provide an overview of the relevant phosphate chemistry, fly ash mineralogy and phosphate interactions with calcium deficient porous media that is then integrated with the results of our batch experiments and numerical modeling efforts.

2. The chemistry of phosphate immobilization

The most frequently encountered species of phosphates in natural waters and effluents are orthophosphates (−PO₄), pyrophosphates (−P₂O₇) and tripolyphosphates (−P₃O₁₀) [13]. Orthophosphates are regulated by pH since phosphoric acid is triprotic
with acidity constants of $10^{-2.1}$, $10^{-7.2}$ and $10^{-12.3}$ for the successive deprotonation reactions, as shown in Fig. 1. Consequently, the acidic phosphates ($H_2PO_4^-$, $HPO_4^{2-}$) are the predominant aqueous species for the pH range of 5 to 9 [13]. Polyphosphates ($H_2P_3O_{10}^-$, $HP_3O_4^{2-}$, $HP_2O_4^{3-}$) may also be present in the same pH range but typically at concentrations less than the orthophosphates [14]. Phosphate immobilization has been extensively researched in two main fields, wastewater treatment [14–20] to prevent eutrophication of receiving (surface) waters, and soil science to understand the fate of the phosphate present in fertilizers [7,21–33].

In wastewater applications, the most common and successful methods to precipitate phosphate involve the dissolved cations $Al^{3+}$, $Ca^{2+}$, $Fe^{3+}$ and to a lesser extent $Fe^{2+}$ [14]. Iron and aluminum are typically administered as chloride (Fe) or sulfate salts (Fe, Al) whereas calcium is added as a lime (CaO). Solubility diagrams for metal phosphates in pure water show that when iron and aluminum are present, strengite ($FePO_4$) and variscite ($AlPO_4$) are the stable solid phases in the low pH range (<6.5). The minimum variscite solubility occurs at pH 6, i.e., 1 pH unit higher than strengite. At higher pHs (>6.5), the iron and aluminum chemistry becomes increasingly governed by the formation of oxides and hydroxides, and these conditions are more ideal for the precipitation of phosphate with calcium as apatites and hydroxyapatites even though the solubility of calcium is regulated by calcite ($CaCO_3$). In wastewater at neutral to mildly alkaline conditions, magnesium also promotes the formation of beta-tricalcium phosphates ($β-Ca_3(PO_4)_2$) and struvite ($MgNH_4PO_4$) if ammonia is also present, and calcium itself may be scavenged and incorporated into magnesium calcium carbonates if enough carbon is present [14].

Fig. 1. pC–pH diagram for a $3.22 \times 10^{-3}$ M $Na_2HPO_4$ solution.
Soil science research has focused on the optimal range of pH for phosphorus to remain in solution and thus bio-available. The fate of phosphorus appears to be more related to adsorption process on mineral or particle surfaces rather than precipitation, which is the chief approach of water treatment. For most crops, the optimum pH in terms of nutrients availability ranges between 6 and 6.8, which corresponds to phosphorus occurring as dissolved $\text{HPO}_4^{2-}$ and $\text{H}_2\text{PO}_4^-$. Phosphorus is generally considered insoluble at extreme pHs, i.e., below 5.5 and above 7.5. Phosphate adsorption onto mineral surfaces is most often regulated by the electrostatic attractions of the soluble phosphate ions and mineral surface. Phosphate ions are negatively charged, and are therefore attracted to the positively charged sites that are common to acidic soils. Phosphorous is strongly complexed with the constituents of acidic soils, namely iron and aluminum [24,34,35]. These soils are also typically deficient in calcium, as are type F ashes, and the relevance of iron and aluminum based interactions will be discussed later.

3. Fly ash mineralogy

Coals are composed of aluminosilicates (clays), carbonates, sulfides, chlorides and quartz that are oxidized at high temperatures (above 1500°C), which melts almost all of the inorganic components with the exception of quartz. The resulting fly ash typically has spheroid morphology with particle sizes ranging from less than a micron to several microns [36]. The ash particles evaluated by Dudas and Warren [36] were found to be predominately comprised of solid spheres, plerospheres (hollow spheres containing smaller spherical particles) and cenospheres (empty hollow spheres). They proposed a structural model for fly ash to aid in leaching experiments depending on the solid or hollow nature of the spheres. Solid particles were characterized by an exterior hull composed of aluminosilicate glass with embedded or accreted inorganic salts and oxides that are more reactive than the interior glass matrix. A thin shell of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) also may be located at or near the surface of the particle. However, mullite was found to be more closely associated with the surface of hollow spheres lacking a hull and featuring surface accretions of inorganic salts and oxides. Dudas and Warren [36] suggested that the exterior hull and the associated surface salts and oxides on the fly ash particles determine the sorption, leaching and weathering behavior of the ash.

Fast and slow rates of cooling result in the formation of amorphous and crystalline phases, respectively. The percentage of amorphous versus crystalline phases in fly ash varies considerably depending on the burning process. McCarthy et al. [37] surveyed 178 samples of fly ash from North America and observed that the crystalline portion of the fly ashes typically accounts for 20–40% of the ash. XRD patterns of fly ash indicate the presence of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), magnetite ($\text{Fe}_3\text{O}_4$), hematite ($\alpha$-$\text{Fe}_2\text{O}_3$), spinel ($\text{MgAl}_2\text{O}_4$) and quartz ($\text{SiO}_2$) [37,38]. The occurrence of these constituents depends on the cooling process. McCarthy [39] shows XRD patterns of different fractions of fly ash with a notorious increase in the amorphous phase in the smaller fractions. The amorphous phase is composed primarily of aluminosilicates and the oxides of aluminum, calcium, iron, magnesium, sodium and potassium. The amorphous phase appears in
Table 3
Chemical composition of various fly ashes in terms of the oxide contents
N/R: Not reported.

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Sample size</th>
<th>Composition (wt.%)</th>
<th>Reference</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>P$_2$O$_5$</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low calcium fly ash</td>
<td>USA</td>
<td>45</td>
<td>52.5</td>
<td>22.8</td>
<td>7.5</td>
<td>4.9</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
<td>N/R</td>
<td>N/R</td>
<td>McCarthy et al. [37]</td>
<td></td>
</tr>
<tr>
<td>( &lt; 10% CaO)</td>
<td>Pennsylvania</td>
<td>1</td>
<td>51.8</td>
<td>28.2</td>
<td>14.3</td>
<td>1.0</td>
<td>0.5</td>
<td>2.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.06</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td>Intermediate calcium fly ash</td>
<td>USA</td>
<td>36</td>
<td>48.5</td>
<td>19.6</td>
<td>6.2</td>
<td>15.2</td>
<td>3.2</td>
<td>0.8</td>
<td>1.5</td>
<td>N/R</td>
<td>N/R</td>
<td>McCarthy et al. [37]</td>
<td></td>
</tr>
<tr>
<td>(10–19.9% CaO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High calcium fly ash</td>
<td>USA</td>
<td>97</td>
<td>36.9</td>
<td>17.6</td>
<td>6.2</td>
<td>25.2</td>
<td>5.1</td>
<td>0.6</td>
<td>1.7</td>
<td>N/R</td>
<td>N/R</td>
<td>McCarthy et al. [37]</td>
<td></td>
</tr>
<tr>
<td>( &gt; 20% CaO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
XRD patterns as a broad halo centered approximately between 22° and 35° 2θ max, under the principal line of mullite [38]. The distribution of the minerals of the crystal phases depends on the type of coal burned. Mullite is found in bituminous and subbituminous ashes and it is usually absent from lignite ashes [36,38]. Hematite and spinel are found in considerable quantities in bituminous ashes, but are absent from low rank fly ashes; and quartz can be found in different proportions in all types of ashes.

The chemical composition of various fly ashes in terms of the oxide components is presented in Table 3. Fly ashes derived from lignite coal are more likely to have high calcium contents. De Groot et al. [40] surveyed 50 different coal fly ashes and found that the pH of solutions containing fly ash varied from 4 to 12.5 depending on the major element composition. This trend was also confirmed on the basis of five fly ashes by Theis and Wirth [8] who demonstrated that the maximum pH shift was attained with fly ash dosages as low as 1-2 mg/l. The pH shifts where found to be most closely correlated with the oxalate extractable iron (Fe$_{ox}$) and soluble calcium content at pH 3 (Ca$_{pH=3}$). Calcium deficient (Fe$_{ox}$/Ca$_{pH=3}$ > 3) fly ashes were associated with equilibrated pHs between 3 and 5 for the fly ash dosages of 200 g/l.

4. Montour ash characteristics

The subbituminous fly ash used in this study was obtained from electrostatic precipitator bins of the Pennsylvania Power & Light (PP&L) Montour facility located in Washingtonville, PA. A particle size analysis of the fly ash revealed that the ash is fairly uniform and composed of clay-sized particles with a mean diameter ($d_{50}$) of 0.02 mm according to ASTM-422. Fig. 1 shows a random sample of spherical fly ash particles with particle diameters ranging between 0.001 mm (1.7 μm) and 0.02 mm (20 μm), as determined using a scanning electron microscope (Hatachi S4100) with an integrated with a Noran light element energy dispersive X-ray spectrometer (SEM/EDX). Fig. 1 shows a typical feature of fly ashes that is plenospheres filled with smaller diameter spheres. The specific surface area of a random ash sample was determined to be 1.3 m$^2$/g based on a single point BET isotherm test completed by Micromeretics (Norcross, GA).

X-ray Fluorescence (XRF) was used to determine the chemical composition of the fly ash by Resource Materials Testing (Clermont, GA). The results of the XRF analyses suggest that the elemental chemistry is dominated by silica, aluminum and iron, as summarized in Table 3. The low calcium content (~ 1 wt.%) and the low carbon content (1.7 wt.%) determined by the loss on ignition (LOI) test suggests that precipitation and adsorption processes will be controlled by the interactions with reactive silica, aluminum and iron sites and not interactions involving calcium or magnesium oxides. XRD analyses of the Montour ash were completed using a Rigaku DMAX-B diffractometer (Cu radiation source) linked to powder diffraction database JCPDS that indicated that mullite, quartz and hematite were the key crystalline phases. One of the striking features of this ash is that while a Class F ash is defined as having no less than 70 wt.% SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ (combined) by ASTM C618, these oxides sum to 94% for the
Modified toxicity characteristic leaching procedure (TCLP) tests indicated that there are essentially no leachable heavy metals from the Montour ash (Fig. 2).

5. Phosphate immobilization experiments

Batch equilibration experiments were conducted using the Montour ash and phosphate stock solutions containing 50, 75 and 100 mg P/l. Glass equilibration vials were presoaked in a 3% nitric acid bath for no less than 24 h and were sequentially rinsed with a 3% nitric acid solution and B' Pure water prior to use. B' Pure water purified by organics and metals removal cartridges having a specific resistance of 17.8 MΩ cm was used to prepare the phosphorus stock solutions. Phosphorus was added as dibasic anhydrous sodium phosphate (Na$_2$HPO$_4$, 99.6% purity) to the B' Pure water (pH = 5.5) to produce the stock solutions. The initial pHs of the stock solutions were 8.60, 8.62 and 8.56, for the 50, 75, and 100 mg P/l solutions, respectively. The increase in the pH of the deionized water after addition of Na$_2$HPO$_4$ is attributed to the formation of H$_2$PO$_4^-$ ions, which scavenge protons (H$^+$) from the bulk solution thereby increasing pH, as suggested by Fig. 1 for a 100 mg P/l solution (3.22 × 10$^{-3}$ M Na$_2$HPO$_4$).

Deionized water blended with fly ash at a ratio of 10:1 (wt.%) produced an equilibrated leachate pH of approximately 4. An equilibrated leachate pH of 4.25 was obtained when fly ash was added to tap water (pH = 6.64) indicating that the equilibrated acidity of the leachate is relatively independent of the initial water source (deionized vs. tap water). For the batch phosphate immobilization experiments, the stock solutions were added to glass vials containing premeasured quantities of fly ash to achieve a liquids:solids ratio of 10:1. Triplicate samples were equilibrated on an orbital shaker (100 RPM) and the solution pH, and phosphate and sulfate concentrations were
determined at select intervals up to 96 h. Leachate samples were collected using latex free syringes fitted with styrene based strong acid resin syringe filters (OnGuard-H). Aqueous phosphate and sulfate concentrations were analyzed using a Dionex DX-500 high performance ion chromatograph (IC) fitted with an ED40 electrochemical detector having a background conductivity between 2 and 3.5 μS. Ion separation was accomplished using a 25 μl sample injection loop on an Ionpac AS16-4 mm column using a 35 mM NaOH eluent at a flow rate of 1.5 ml/min.

The equilibrated pH, and phosphorus and sulfate concentrations for 10:1 solution:fly ash mixtures versus initial phosphorus concentration and time are shown in Figs. 3-5, respectively. Fig. 3 illustrates that significant pH changes occur when the stock solution is added to the Montour ash, as indicated by the difference between the initial pH of stock solution (pH₀) and the equilibrated values (pH ~ 4–6). Fifty milligrams per liter of phosphorus had virtually no effect on the solution pH in the presence of fly ash. Fig. 4 demonstrates phosphate immobilization on the order of 100% to 75% for 50 and 100 mg P/l solutions, respectively. The removal of phosphate by the Type F ash used in our experiments is comparable or greater than that by the reviewed applications using Type C ash [5,6,10]. Fig. 5 shows that the fly ash released approximately 1230 mg SO₄²⁻/l into solution and that this concentration was essentially unaffected by the presence of phosphate in the deionized water.

A column experiment was also conducted using a 7-cm diameter, 14-cm long sample of pure Montour ash compacted to a loose condition by moist tamping. A 10 mg/l phosphate stock solution was prepared as described above. A reservoir of the stock

![Graph](image-url)

**Fig. 3.** Equilibrated pH for 10:1 solution:fly ash batch mixtures versus initial phosphorus concentration and time.
Fig. 4. Equilibrated phosphorus concentrations for 10:1 solution:fly ash batch mixtures versus initial phosphorus concentration and time.

Fig. 5. Equilibrated sulfate concentrations for 10:1 solution:fly ash batch mixtures versus initial phosphorus concentration and time.
solution had an initial pH of 8.5. Influent and effluent samples were collected at
locations immediately upgradient and downgradient of the column and it was deter­
mined that the column of pure Type F ash immobilized phosphate at dissolved
centinations of 10 mg P/l for over 85 pore volumes.

6. Interactions between phosphate and calcium-deficient media

In order to evaluate which mineral phases and interactions are responsible for
phosphate immobilization in the batch experiments, it is important to recall that the
metal oxide chemistry of the fly ash does not distinguish between the occurrence of the
elements in an amorphous or crystalline phase, or the actual mineral or compound. The
most dominant elements reported for Type F ashes are silicon, aluminum, and iron, as
suggested by Table 3. Even though the silica content of the Montour ash is high, and
quartz appears in most ashes, the low point of zero charge of quartz (PZC ~ 1.8–2.9)
[41,42] enables it to retain a net negative surface charge for the normal range of pH
encountered for most natural waters [43]. Therefore, quartz is not expected to adsorb
significant quantities of phosphorus. Consequently, in calcium and magnesium deficient
media, the principal reactions with phosphate are likely to involve iron and aluminum-
based minerals, depending on the pH of the system. The principal crystalline iron and
aluminum compounds in low calcium (< 10%) Type F ashes are hematite and spinel,
and mullite, respectively [39], but spinel was not detected by XRD for the Montour ash.
The principal form of amorphous aluminum is amorphous aluminosilicate. To provide
insight to the relevant interactions for the aluminum and iron compounds, it will be
helpful to consider soil science research since it has focused on phosphate interactions
with natural and synthetic iron- and aluminum-rich minerals, media and soils and has
demonstrated that phosphorus binds strongly with the iron and aluminum constituents in
acidic soils [22,24,27,31–35].

Hematite has a PZC on the order of 8.5 to 9.1 [41,44]. Below the PZC, hematite is
characterized by protonated surface hydroxyl (SOH⁺) groups that have the ability to
form inner sphere complexes with the phosphate ions that become so strongly attached
that sorption is essentially independent of the solution ionic strength [24,42,43]. Hematite,
however, has limited sorption capacity for anions compared to other iron bearing
minerals and oxides due to its crystallinity. For example, the reactive surface sites
present in the basal planes of hematite are not able to adsorb phosphate [20,30,31,33].
Baker et al. [20] researched phosphate removal by different iron and aluminum oxides.
They found that the rate of phosphate removal was much less using iron oxides than
using steel foundry oxides.

Aluminum is present in fly ash either as amorphous aluminosilicates or mullite.
Although mullite will not uptake as much phosphate as hematite, it must be included as
an important potential sorbent since it is generally present in relatively high amounts and
often covers fly ash particles with a thin shell [36]. Mullite has not been as extensively
researched as other aluminum bearing minerals because of its complexity. However,
some insight on mullite can be gained by considering the interaction of phosphate with
other aluminosilicates such as kaolinite [45]. van der Hoek et al. [45] indicated that both
minerals have AlO and SiO surface groups that are likely to behave similarly. The
difference in the structure and charge distribution between kaolinite and mullite will affect the sorption affinity, and thus, the results from kaolinite can only be qualitatively compared to mullite. The interaction between phosphate and either one of the amorphous phases of fly ash (amorphous iron and amorphous aluminosilicate) is expected to result in considerable phosphate immobilization. Higher adsorption is expected in these phases as compared to the crystalline phases, the main reason being that the disorganized internal structure of amorphous materials is associated with greater reactivity and site densities.

Phosphate adsorption by acidic soils and synthetic aluminosilicates was researched by Veith and Sposito [46], who observed that phosphate interactions with aluminosilicates were characterized by: (1) slow approach to equilibrium, (2) dissolution of silica from mineral structure, and (3) formation of Al–P compounds involving high quantities of P (almost 82% of P that was added to aluminum on an equimolar basis) though the nature of the formed phase is not accurately known. The influence of the silica/aluminum ratio on phosphate sorption was studied by Yuan [47] for three synthetic amorphous aluminosilicates and three soil samples. The sample with lowest Si/Al ratio, i.e., the highest aluminum content, retained the largest amount of phosphorous. Among aluminum bearing materials, noncrystalline hydrous aluminum oxides have higher bonding energy with phosphates than aluminum silicates and crystalline sesquioxides [46,47]. Additionally, the mechanism of phosphorous sorption on mineral surfaces is believed to be adsorption followed by precipitation [29,30]. This observation was supported by the appearance of crystalline phases after approximately 18 days of testing [30]. However, it was argued whether early precipitation could have been interpreted as sorption due to the lack of techniques able to identify the formation of very small crystals [30].

7. Modeling phosphate interactions with type F fly ash

The adsorption of phosphate by fly ash has been represented with empirical relationships such as Freundlich and Langmuir sorption isotherms (see Ref. [6] for detailed references). However, these isotherms are simply fitting curves and lack the sophistication to account for pH dependent behavior and the multiple valence states of dissolved phosphate species [25]. The batch experiments underwent large pH shifts, which changes the dominant phosphate species in the solution ($H_2PO_4^-$ or $HPO_4^{2-}$) as suggested by Fig. 1. It is therefore more appropriate to model such systems using approaches other than with Langmuir or Freundlich sorption isotherms.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Site density (sites/nm$^2$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>10</td>
<td>Davies and Kent [43]</td>
</tr>
<tr>
<td>Mullite</td>
<td>0.55</td>
<td>He et al. [51]</td>
</tr>
<tr>
<td>Amorphous iron</td>
<td>6.7</td>
<td>Goldberg and Sposito [24,25]</td>
</tr>
<tr>
<td>Amorphous aluminum</td>
<td>2.6</td>
<td>Goldberg and Sposito [24,25]</td>
</tr>
</tbody>
</table>
Table 5
Equations modeled by constant capacitance model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOH + H⁺ → FeOH⁺</td>
<td>( K^e )</td>
</tr>
<tr>
<td>FeOH - H⁺ → FeO⁻</td>
<td>( K^e )</td>
</tr>
<tr>
<td>AIOH + H⁺ → AIOH⁺</td>
<td>( K^f )</td>
</tr>
<tr>
<td>AIOH - H⁺ → AIO⁻</td>
<td>( K^f )</td>
</tr>
<tr>
<td>FeOH + PO₄⁻ + 3H⁺ → FeH₂PO₄ + H₂O</td>
<td>( K^e )</td>
</tr>
<tr>
<td>FeOH + PO₂⁻ + 2H⁺ → FeHPO₄⁻ + H₂O</td>
<td>( K^e )</td>
</tr>
<tr>
<td>FeOH + PO₂⁻ + H⁺ → FePO₄²⁻ + H₂O</td>
<td>( K^e )</td>
</tr>
<tr>
<td>AIOH + PO₄⁻ + 3H⁺ → AlH₂PO₄ + H₂O</td>
<td>( K^f )</td>
</tr>
<tr>
<td>AIOH + PO₂⁻ + 2H⁺ → AlHPO₄⁻ + H₂O</td>
<td>( K^f )</td>
</tr>
<tr>
<td>AIOH + PO₂⁻ + H⁺ → AlPO₄²⁻ + H₂O</td>
<td>( K^f )</td>
</tr>
</tbody>
</table>

Modeling the interactions of phosphate with the solid phase typically utilize surface complexation models (SCMs), which simulate the adsorption reactions occurring at the (crystal) mineral–water interface. For example, the computer program HYDRAQL evaluates chemical equilibria in aqueous batch systems and ion adsorption onto oxide minerals using SCMs [48]. Different SCM models are available that represent different mineral–water systems, i.e.: (i) constant capacitance model (CCM); (ii) diffuse layer model (DLM); (iii) triple-layer model (TLM); and (iv) four-layer model. The selection of the model to represent the mineral–water interface is governed by the binding mechanism between solute and solid and its dependence on the solution ionic strength. The CCM approach was selected because it assumes hydrogen, hydroxyl and inner sphere complexing ions (such as phosphate) are adsorbed in the same plane without ionic strength influencing the adsorption process. The CCM also requires less number of constants than other models. More importantly, phosphorous adsorption on hematite, corundum, and goethite has been successfully modeled using a CCM approach by Goldberg et al. [24-26,28]. Selenite and arsenate adsorption on the mullite phase in fly ash was also modeled with a CCM by van der Hoek et al. [45], who determined that selenite and arsenate form inner-sphere complexes with aluminum and iron, and that the reaction rate of selenite and arsenate is very rapid with the maximum arsenate sorption occurring within 2 h. The sorption of arsenate and selenite also has been successfully modeled on kaolinite by Goldberg and Glaubig [49,50]. Modeling phosphate–mullite interactions with CCM is therefore considered to be valid for phosphate based on the

Table 6
Representative surface complexation constants for minerals occurring in Type F ash
N/A = not available.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>log ( K_1 )</th>
<th>log ( K_2 )</th>
<th>log ( K_3 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>N/A</td>
<td>22.37</td>
<td>17.14</td>
<td>He et al. [51]</td>
</tr>
<tr>
<td>( \alpha-Fe_2O_3 )</td>
<td>7.43</td>
<td>2.06</td>
<td>-4.23</td>
<td>Breeuswama and Lyklema [44]</td>
</tr>
<tr>
<td>Amorphous iron</td>
<td>33.54</td>
<td>27.3</td>
<td>21.05</td>
<td>Anderson and Malotky (1979)</td>
</tr>
<tr>
<td>Amorphous aluminum</td>
<td>29.49</td>
<td>23.89</td>
<td>N/A</td>
<td>Rajan et al. (1974)</td>
</tr>
</tbody>
</table>
Tabic 7
Representative surface protonation constants for minerals occurring in Type F ash

<table>
<thead>
<tr>
<th>Surface Group</th>
<th>$K_+^\text{FeOH}$</th>
<th>$K_+^\text{AlOH}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOH</td>
<td>8.05</td>
<td>-8.95</td>
<td>Breeuswama and Lyklema [44]</td>
</tr>
<tr>
<td>AlOH</td>
<td>7.89</td>
<td>-9.05</td>
<td>Huang and Stumm (1973)</td>
</tr>
</tbody>
</table>

Aforementioned considerations. Lastly, phosphate adsorption on $\gamma$-$\text{Al}_2\text{O}_3$ and kaolinite was modeled with a CCM to evaluate the competing mechanisms between phosphates and sulfates [51]. He et al. [51] showed a competing sorption mechanism between $\text{SO}_4^-$ and $\text{PO}_4^{3-}$ and suggested that $\text{SO}_4^-$ does not compete effectively with $\text{PO}_4^{3-}$ for adsorption sites, because $\text{SO}_4^-$ appears to form outer-sphere complexes. Phosphate adsorption on amorphous synthetic aluminum and iron phases also has been successfully modeled with CCM [24]. However, while phosphate and sulfate have been modeled and inner and outer sphere complexes, respectively [51]. Fig. 5 suggests that there may not be competitive adsorption effects between phosphate and sulfate, given the quantity of sulfate released by the fly ash. Since both anions desorb with increasing pH, the pH data for the 100 mg P/l curve at 96 h (1.5 pH units greater than for 0 and 50 mg P/l equilibrated solutions) may suggest that additional sulfate is being released by the fly ash rather than it being displaced from the fly ash surface by phosphate.

A capacitance constant of 1.06 F/m$^2$ was used and the ionic strength of the solution was chosen to be 0.1 M though it is not anticipated to influence the interactions between phosphate and iron and aluminum compounds [43]. It was assumed that each of the mineral phases acted independently. Sorption of phosphate was modeled on the basis of the crystalline minerals reported by XRD, i.e., hematite and mullite; and amorphous iron and aluminum. Due to the lack of quantitative data reported on XRD for the Montour ash, the percentage distribution of each phase was calculated based on average values given by McCarthy [39]: 3.9% hematite, 10.4% mullite, 17.81% amorphous aluminum, and 10.43% amorphous iron. The total surface area was that determined using the BET isotherm: 1.3 m$^2$/g. A surface site density of hematite 10 sites/nm$^2$ was assumed based on the acid-base titration method [25]. Due to the lack of phosphate binding constants for mullite, phosphate–mullite interactions were modeled on the basis of kaolinite following the approach of van der Hoek et al. [45]. The site density values adopted for the amorphous phases are presented in Table 4. The reactions presented in Table 5 were used to model sorption and the corresponding average surface complexation constants are summarized in Tables 6 and 7, which should be taken to qualitatively describe phosphate adsorption since even in synthetic oxides surfaces multiple types of surface sites are capable of adsorbing phosphates [43,51]. For illustrative purposes, the CCM simulation assumed an initial phosphorus concentration of 50 mg P/l, which was completely immobilized by fly ash, see Fig. 1.

8. Results and discussion

Fig. 6 presents the results of the SCM for pH ranging from 4 to 10 using the CCM approach for an initial phosphorus concentration of 50 mg P/l. The adsorption of
phosphate onto amorphous iron oxide increased with decreasing pH and essentially stabilized at 12% below pH 7. A somewhat similar trend was observed with amorphous aluminum in that the immobilized phosphate varies between 4% and 6% below pH 8. The adsorption of phosphate on hematite decreased from 4% with increasing pH due to the surface sites of hematite becoming more negatively charged toward its point of zero charge (8.5). Phosphate adsorption on kaolinite, although negligible compared to that of hematite, was consistent with the trends reported by He et al. [51], who studied phosphate adsorption on γ-Al$_2$O$_3$ and kaolinite. Kaolinite (surrogate for mullite) showed a maximum adsorption capacity at near neutral pH, decreasing at low pH most likely due to the known dissolution of kaolinite under acidic conditions that results in the formation of Al(OH)$_3$ [51]. Reduced or stabilized phosphate sorption at low pH is attributed to the aqueous speciation of phosphate as a function of pH. At low levels of pH (<2.1) the predominant dissolved phosphate species is H$_3$PO$_4$, which has less affinity for positively charged solids than H$_2$PO$_4^-$, HPO$_4^{2-}$ and PO$_4^{3-}$. Recall that H$_2$PO$_4^-$ and HPO$_4^{2-}$ are the predominant aqueous species for the pH range of 5 to 9 [13].

The total adsorption of phosphate in the fly ash surfaces at pH 4 was approximately 19%, much lower than the expected values based on the batch experiments. It is interesting; however, to notice that the adsorption of phosphate on kaolinite is negligible compared to hematite though some previous studies argued about the importance of mullite as an anion sorbing phase [45]. Our CCM predictions of phosphate immobilization are substantially less than the equilibration study and those results predicted by Goldberg et al. [24–26,28]. This is explained on the basis of the heterogeneity of the fly ash in comparison to the mineralogical purity of the natural and synthetic systems they studied and the fact that the constants determined for those media were far more representative of the total sample. While the approach of McCarthy et al. [39] was used, it is not known to what extent the adsorption parameters and site constants taken from pure geologic media are appropriate modeling acidic fly ash interactions with phosphate.
Nevertheless, for the amorphous and crystalline phases studied, the immobilization of phosphate in the Type F fly ash is attributed to the formation of insoluble aluminum and iron phosphates at low to medium values of pH. The crystalline phases played a minor role in phosphate immobilization. Therefore, it is concluded that the remaining 80% phosphate was immobilized by the amorphous phases of the type F fly ash and/or any precipitation reactions involving the amorphous phase such as those reported Veith and Sposito [46] between phosphate and allophanes (amorphous aluminosilicates), which are typically of volcanic origin and are characterized by a hollow spherules [52].

9. Conclusion

Batch equilibration experiments using a low calcium (~ 1 wt. % as CaO), acidic (pH ~ 4.5) Type F fly ash demonstrated phosphate immobilization on the order of 100% to 75% for 50 and 100 mg P/l solutions, respectively. A loosely compacted column of fly ash similarly removed 10 mg P/l for over 85 pore volumes. While the interactions between phosphate- and calcium-rich (Type C) ashes are relatively well understood, insight into the mechanisms of phosphate immobilization in Type F ash necessitated a review of the phosphate chemistry and interactions with acidic geomedia. Phosphate adsorption was subsequently modeled using a constant capacitance approach (CCM) excluding precipitation reactions. Our CCM predictions of total phosphate immobilization (20%) were substantially less than the results of the batch equilibration experiments and phosphate adsorption predicted by other researchers examining near pure natural and synthetic geomedia due to the compositional heterogeneity of the fly ash. Nevertheless, for the amorphous and crystalline phases studied, the immobilization of phosphate in the Type F fly ash is attributed to the formation of insoluble aluminum and iron phosphates at low to medium values of pH.

Given the high removal of the phosphate and the fact that the authors could not locate studies focusing on the phosphate interactions with the amorphous phases of low calcium fly ashes, these interactions should be more fully evaluated. If these interactions can be quantified and predicted in high quality Type F ashes (low toxic metals), some interesting beneficiation opportunities may emerge for the ashes.

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