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The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends

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Abstract

Phosphate ions have been removed from aqueous solution by fly ash, slag, ordinary Portland cement (OPC) and related cement blends. The rate and efficiency of PO_4^{3-} removal were found to increase in the order: fly ash, slag, OPC, apparently mimicking the order of increasing percent CaO in the adsorbents. Blending OPC with fly ash or slag evidently results in diminished PO_4^{3-} removal efficiency. Better removal was obtained at higher solute concentration, acidic pH and higher temperature. The effect of particle size and the speed of mixing were found not to be significant. A first-order kinetic model was used to obtain values for overall sorption rate constants and intraparticle diffusion constants. The Frumkin isotherm was found to be the appropriate equation for modelling isotherms from the experimental adsorption data, and values have been obtained for the isotherm constants. A 400-mg/l PO_4^{3-} (as P) solution was fed at a steady velocity of 2.0 cm/min through a 2.0-cm fixed-bed column (at pH 9.0 and 25 °C), and breakthrough curves were constructed to obtain estimated adsorption capacity values of 32, 60, 75, 78 and 83 mg PO_4^{3-}/g adsorbent for fly ash, slag, OPC + fly ash, OPC + slag and OPC, respectively.

Keywords: Fly ash; Slag; OPC; Adsorption; Phosphate ions; Frumkin isotherm

1. Introduction

The addition of the by-product phosphogypsum to cement has been reported to significantly extend the setting time of the concrete [1], relative to the addition of natural gypsum. Erdogan et al. [2] found that for ordinary Portland cement (OPC), the effect was minimised if the phosphogypsum was pretreated by washing with lime milk, whereas for trass (a pozzolanic ash of volcanic origin that is chemically similar to fly ash) cement, this pretreatment was not required. This study was undertaken to investigate whether this phenomenon could perhaps be related to the adsorption of phosphate from aqueous solution by mineral admixtures such as fly ash and slag. Secondly, environmental and economic concerns have led to an ongoing search to find effective ways to utilise the huge amount of fly ash that is land-filled or stockpiled. In the year 2000, only 18 out of the over 56 million metric tons of fly ash generated in the US were utilised [3]; for South Africa, the fractional utilisation was even lower at 1.2 of 25 million metric tons production [4].

Due to the high percentages of alumina and silica, fly ash is a good candidate for use as an economic adsorbent for large-scale use. It has been found to remove F^- [5,6], Cr^{3+} [7], Cu^{2+}, Pb^{2+} and Cd^{2+} [8] ions as well as phenolic compounds [9,10] from aqueous solution. Johansson and Gustafsson [11] studied the use of slags and opaka as sorbing filter materials for on-site wastewater treatment, and suggested the possible use of PO_4^{3-} saturated slag as fertiliser if the P is retained in the hydroxyapatite form, in which the P is available for plant nutrition. This study was, therefore, also used to investigate the feasibility of using these cementitious adsorbents, especially fly ash (a by-product of coal combustion for electric power generation) and slag (a by-product of the manufacture of pig iron in a blast furnace), to remove phosphate ions from aqueous solution, as a possible technique for wastewater treatment.

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An earlier study [12] on the removal of phosphate ion from aqueous solution by fly ash and slag established that the Frumkin isotherm (Eq. (1)) [13] is the appropriate equation for modelling the experimental adsorption data:

$$\nu = \log(\beta/55.55) + 2\alpha\Phi/2.303 \qquad (1)$$

where $\nu = \log[\Phi/(1-\Phi)c]$, c = concentration of the solute that is in equilibrium with the adsorbent, $\Phi = M/M_{\mathrm{ads}}$, M = mass of solute adsorbed at equilibrium, M_{ads} = the maximum mass of solute adsorbed at equilibrium, α = the lateral interaction coefficient and β = a constant that describes the adsorption equilibrium ($\beta = \exp(-\Delta G^0_{\mathrm{ads}}/RT)$, where $\Delta G^0_{\mathrm{ads}}$ represents the standard free energy of adsorption. This equation is a useful isotherm for fitting nonideal adsorption systems, and can be arrived at theoretically in terms of surface heterogeneity and in terms of repulsive forces between adsorbed molecules [14].

The sorption of solute from liquid phase to solid phase may be considered as a reversible reaction with equilibrium being established between two phases. If this can be described with a first-order reversible kinetic model, then the overall rate constant for the process, k', and the intraparticle diffusion coefficient, D_i, can be determined, respectively, from the relations [15]:

$$\ln[1 - U(t)] = -k't \qquad (2)$$

$$t_{1/2} = 0.030r^2/D_i \qquad (3)$$

where the fractional attainment of equilibrium, $U(t) = X/X_e$, X = fraction of adsorbate sorbed at time t, X_e = fraction of adsorbate sorbed at equilibrium, $t_{1/2}$ = time at which $X/X_e = 0.5$ [given by $(\ln 2)/k'$] and r = mean radius of adsorbent particles (assuming spherical geometry for the adsorbent).

For a fixed-bed unit operating at a steady liquor flow rate, and for which a symmetrical breakthrough S curve has been obtained experimentally, the height of the mass transfer zone, h_Z, and the specific dynamic adsorption capacity, C_T, are given, respectively, by the relations [16]:

$$h_Z = h_T[V_Z/(V_T - 0.5V_Z)] \qquad (4)$$

$$C_T = \int_0^{V_T} (X_0 - X)\mathrm{d}V/m \qquad (5)$$

where h_T = bed height, V_T = volume of effluent collected upon exhaustion of the bed, V_E = volume of effluent collected up to breakthrough, $V_Z = V_T - V_E$, X_0 = influent concentration, X = effluent concentration, V = effluent volume and m = mass of adsorbent.

2. Experimental

2.1. Materials and apparatus

Samples of fly ash (Matla fly ash, M432), slag (slagment, M223), OPC (Hercules OPC, CEM I 42,5) and two cement blends, Hercules OPC + fly ash and De Hoek OPC + slag, were obtained from PPC Technical Services (Germiston, South Africa). The samples were analysed by X-ray fluorescence (XRF) and X-ray diffraction (XRD) using a Siemens SRS 3300 and a Siemens D 5000 spectrometers (Siemens, Bryanston, S.A.) respectively. Particle sizes were also measured with a Malvern Mastersizer instrument. A temperature-regulated Labcon (Johannesburg, S.A.) platform shaker was used for solution agitation. A sieving system from Labquip (Johannesburg, S.A.) was used for particle fractionation. Absorbance measurements were made using a Unicam (S.A. scientific, Johannesburg, S.A.) UV–visible spectrophotometer. All chemicals used were of analytical grade. Deionised water was used for preparing solutions.

2.2. Procedures

The chemical oxide compositions of the fly ash, slag and OPC samples were determined by XRF spectrometry after being prepared as fused disks according to standard procedures. XRD scans were performed using Cu K_α radiation at a speed of 0.2° 2θ/min. For particle size analysis, 1 g of material was suspended in water with sodium metaphos-

Table 1
Chemical composition and physical characteristics of fly ash, slag and OPC

	Fly ash (%)	Slag (%)	OPC (%)
SiO_2	52.4	33.4	22.5
Al_2O_3	33.7	11.0	4.5
Fe_2O_3	3.6	0.7	1.4
Mn_2O_3	< 0.1	0.4	0.9
TiO_2	1.7	0.6	0.2
CaO	4.1	33.3	63.2
MgO	1.1	18.0	3.6
P_2O_5	0.3	0.0	0.2
SO_3	0.2	0.6	2.4
Cl	< 0.1	< 0.1	< 0.1
K_2O	0.6	0.3	0.8
Na_2O	0.5	0.2	0.1
LOI at 1000 °C	0.8	1.7	1.0
Total	99.0	100.2	100.8
CaO/SiO_2	0.08	1.00	2.81
Potential compound composition[a]			
C_3S tricalcium silicate			54.0
C_2S dicalcium silicate			23.8
C_3A tricalcium aluminate			9.6
C_4AF tetracalcium alumino ferrite			4.3
Specific surface area (m^2/g)	1.42	1.29	1.38
Mean particle diameter (μm)	25.7	31.4	20.8
Density (g/cm^3)	2.21	2.82	3.02

[a] Calculated using the Bogue equations [19].

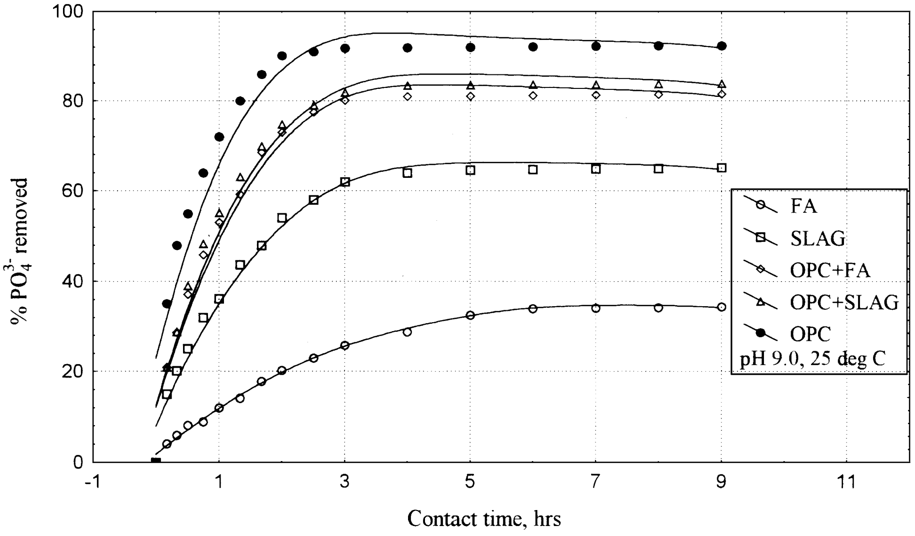

Fig. 1. Kinetics of PO_4^{3-} removal from 80 mg/l solution by 2 g of adsorbent.

phate as dispersing agent and pumped past a laser beam. Laser diffractometry principles were used and the Fraunhofer algorithm was applied to the data collected by the computer to calculate the parameters of interest.

The determination of phosphate (as phosphorous) was done spectrophotometrically using the yellow ($\lambda = 470$ nm) vanadomolybdo-phosphoric acid method [17]. The method is widely used to determine dissolved phosphorous in natural waters and wastewaters. The calibration curve obtained was linear up to ca. 55 mg/l P, with a detection limit (3σ) of 0.2 mg/l P.

2.2.1. Kinetics of phosphate removal

Two-gram samples of adsorbent were weighed and placed in several 250-cm^3 Erlenmeyer flasks, each containing 200 ml of 80 mg/l PO_4^{3-} (as P) solution at pH 9.0 and 25 °C [anhydrous KH_2PO_4 was used to prepare a 500 mg/l PO_4^{3-} (as P) stock solution]. The flasks were stoppered and continuously shaken at a speed of 120 cycles/min. The shaking was interrupted momentarily at predetermined time intervals for a flask to be removed and the concentration of phosphate in the decanted and filtered (Whatman no. 42) (Watman, Merck, Johannesburg, S.A.) supernatant solution to be determined. The phosphate monitoring was carried out at 10-min intervals for the first 1 h, then at longer intervals thereafter until the absorbance values levelled off.

2.2.2. Effect of concentration

Solutions of different initial concentrations—20, 40, 60, 80 mg/l PO_4^{3-} (as P)—were used to investigate the effect

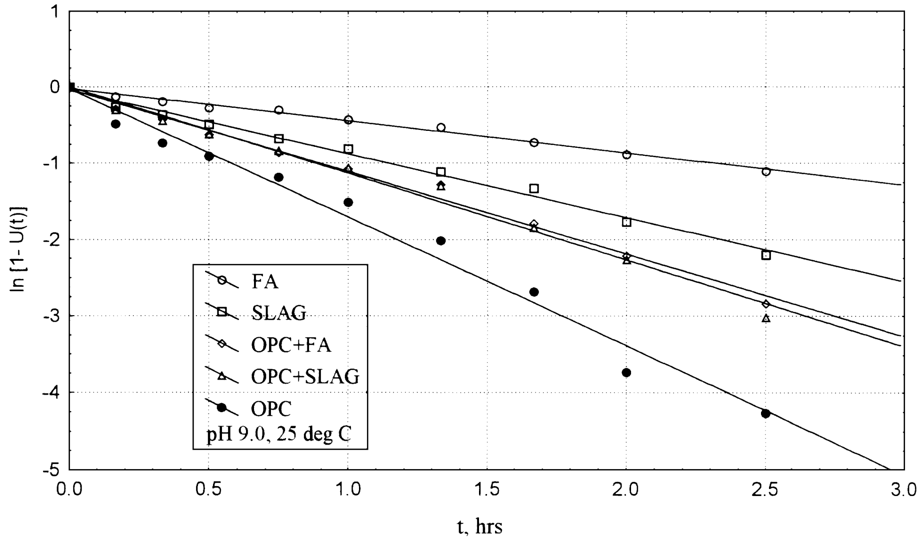

Fig. 2. Application of first-order kinetics to the experimental adsorption data.

Table 2
The values of first-order reaction rate constants and intraparticle diffusion coefficients

Adsorbent	% CaO[a]	k' (/h)	D_i (cm^2/s)
Fly ash	4.5	0.423	8.40×10^{-12}
Slag	34.1	0.837	2.51×10^{-11}
OPC + fly ash	57.3	1.082	ND
OPC + slag	58.2	1.136	ND
OPC	63.8	1.682	8.72×10^{-11}

ND, not determined.

[a] Determined by EDTA titrimetry after 1:4 fluxing with anhydrous $Li_2B_4O_7$. These values were used to calculate the composition of the blends: OPC + 11% fly ash and OPC + 19% slag.

of concentration on the kinetics of phosphate removal by 2 g of adsorbent at pH 9.0 and 25 °C following the procedure described in Section 2.2.1.

2.2.3. *Effect of particle size*

Four hundred grams of adsorbent was shaken mechanically for 20 min in a stack of sieves of various apertures to obtain fractions of different particle size. Two grams of 45-, 75-, 90-, 150- and 300-μm fractions was placed in Erlenmeyer flasks, each containing 200 ml of 80 mg/l PO_4^{3-} (as P) solution at pH 9.0 and 25 °C, and shaken continuously for 16 h to attain equilibrium, after which the residual concentration of phosphate in the supernatant solutions was determined.

2.2.4. *Effect of temperature*

Two grams of adsorbent was placed in Erlenmeyer flasks, each containing 200 ml of 80 mg/l PO_4^{3-} (as P) solution at pH 9.0. The flasks were shaken continuously for 16 h to attain equilibrium, surrounded by water set at various temperatures (25, 40, 50 and 60 °C), after which the residual concentration of phosphate in the supernatant solutions was determined.

2.2.5. *Effect of pH*

Two grams of adsorbent was placed in Erlenmeyer flasks, each containing 200 ml of 80 mg/l PO_4^{3-} (as P) solution at 25 °C and at initial pH values of 3.0, 5.0, 7.0, 9.0 and 11.0 (adjusted to the required pH value using 0.1 M HCl and 0.1 M NaOH). The flasks were shaken continuously for 16 h to attain equilibrium, after which the residual concentration of phosphate in the supernatant solutions was determined.

2.2.6. *Adsorption isotherms*

Various masses (0.5, 2, 3, 4 and 5 g) of adsorbent were shaken continuously with 200 ml of 100 mg/l PO_4^{3-} (as P) solution at pH 9.0 and 25 °C for 16 h to attain equilibrium, after which the residual concentration of phosphate in the supernatant solutions was determined.

2.2.7. *Breakthrough curves*

A glass column (4 cm ID, 35 cm high) with a tap at one end was clamped vertically and a 10-mm layer of glass wool inserted near the bottom. The space above the plug was packed with a bed made by intricately mixing 5 g of adsorbent and 8 g of inert sand (to improve porosity) and another layer of glass wool was placed on top of the bed. The space above the bed was filled with a 400-mg/l PO_4^{3-} (as P) solution (at pH 9.0, 25 °C), which was then allowed to flow continuously through the bed at a steady velocity of 2.0 cm/min (volumetric flow rate of 25 cm^3/min). The concentration of phosphate in the effluent was monitored at half-minute intervals by collecting 5 cm^3 for analysis

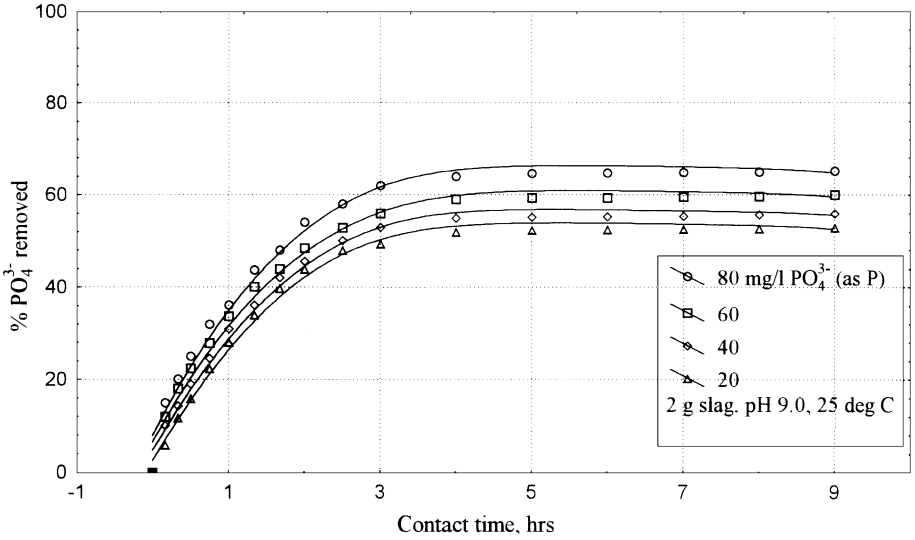

Fig. 3. Effect of concentration on the kinetics of PO_4^{3-} removal.

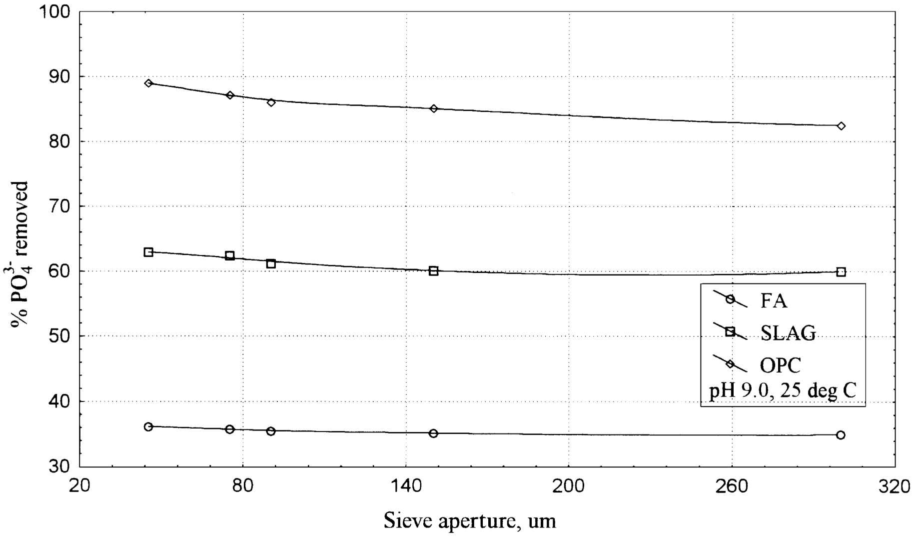

Fig. 4. Effect of particle size on the efficiency of PO_4^{3-} removal.

until the effluent concentration approached that of the influent.

3. Results and discussion

The chemical composition and particle dimensions of the adsorbents are shown in Table 1. XRD analysis showed that the main mineral phase of the fly ash is quartz with smaller amounts of mullite and sillimanite, while the major crystalline phase of the slag is tricalcium silicate. Fig. 1 illustrates the variation of percent removal of PO_4^{3-} with time for the different adsorbents. It can be seen that OPC removed PO_4^{3-} at the fastest rate and fly ash the slowest. The uptake of PO_4^{3-} by OPC virtually ceased after a contact time of about 3 h, compared to about 6 h for fly ash, with 84% and 34% PO_4^{3-} removal at equilibrium, respectively. The blending of OPC with fly ash or slag was observed to lead to a decrease in the rate and efficiency of phosphate removal. Although slag removes PO_4^{3-} better than fly ash, 19% replacement of OPC with slag evidently results in a blend with lower PO_4^{3-} removal efficiency than 11% replacement with fly ash.

Plots according to Eq. (2) are presented in Fig. 2. The good straight line fit observed indicates that the sorption reaction may be approximated by first-order reversible kinetics; the calculated rate constants are given in Table 2. It was found that the adsorption rate was not significantly affected by the rate of mixing, providing evidence that intraparticle diffusion is the controlling resistance rather

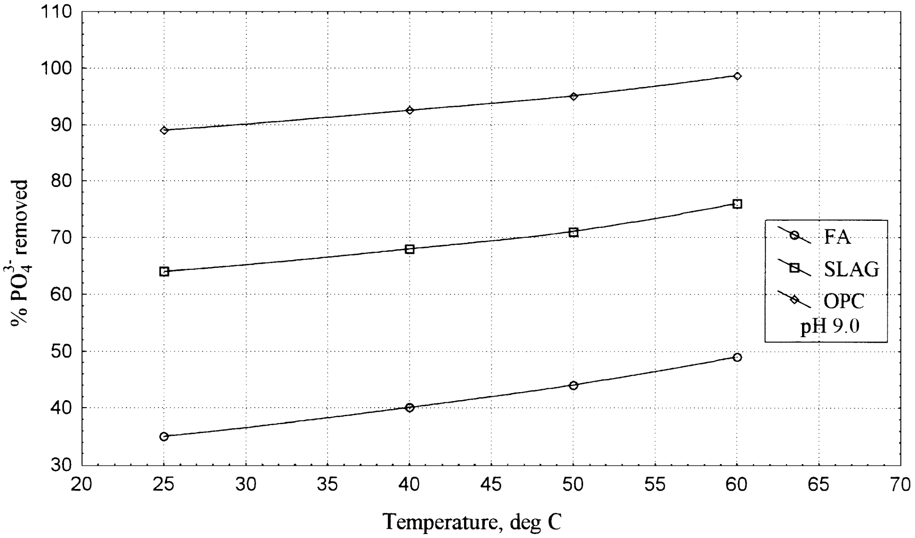

Fig. 5. Effect of temperature on the efficiency of PO_4^{3-} removal.

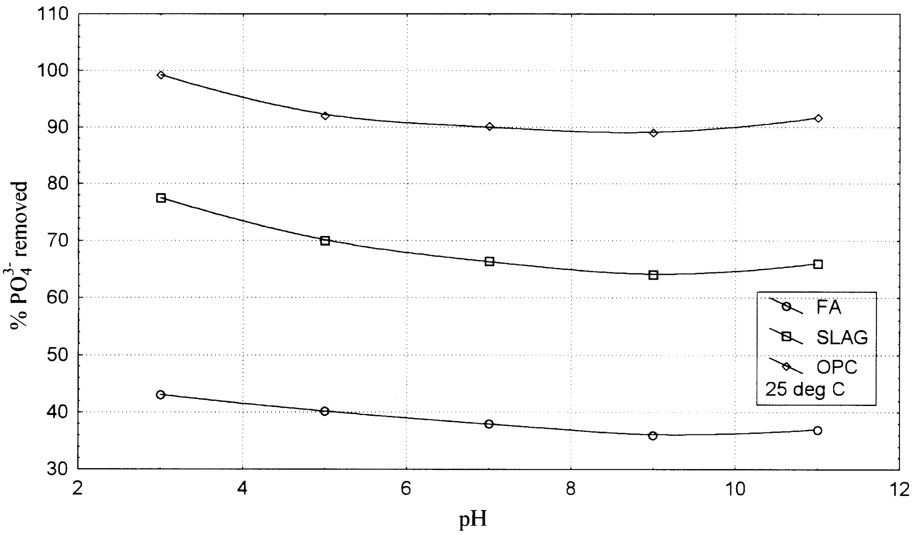

Fig. 6. Effect of pH on the efficiency of PO_4^{3-} removal.

than the external diffusion. The values of intraparticle diffusion constants calculated using Eq. (3) are also given in Table 2. The value obtained for OPC is an order of magnitude greater than that for fly ash.

Tabikh and Miller [18] postulated that acid phosphate from phosphogypsum deprotonates and then precipitates as calcium phosphate on the surface of the grain in the alkaline region in the immediate vicinity of a hydrating particle; this provides a protective barrier against attack by water, resulting in the delayed setting times observed. Hence, the affinity of phosphate (the adsorbate, from the acid phosphate KH_2PO_4) for CaO (in the adsorbent) observed in this study is hardly surprising. This would also explain why pretreatment of the phosphogypsum by washing with lime milk [2] was successful in minimising the effect on setting time extension.

In the light of the report by Erdogan et al. [2], the observation made in this study, namely, that OPC removes phosphate ions faster and more efficiently than the pozzolanic fly ash, was *not* expected. Since cement containing fly ash is reportedly not susceptible to the phenomenon of phosphate-induced setting time extension, it was thought reasonable to expect that perhaps the fly ash preferentially immobilised the offending phosphate ions via adsorption or some kind of "binding," which would require fly ash to remove phosphate much more efficiently than OPC itself. Evidently, this reported effect is probably due, rather, to the resultant decreased penetrability of the concrete, in the presence of fly ash, to the ingress of phosphate.

The rate and separation efficiency of PO_4^{3-} from aqueous solution were found to increase with the initial phosphate concentration over the concentration range studied. The data for slag are shown in Fig. 3. Although there was some increase in the percent PO_4^{3-} removed as the adsorbent (fly ash, slag and OPC) particle size decreased (Fig. 4), this increase was not proportionate to the increased surface area. This gives an indication that for these adsorbents, chemisorption is a more significant contributory phenomenon to the removal of PO_4^{3-} than physical adsorption. This observation is consistent with the findings of Johansson and Gustafsson [11], who suggested that Ca–P precipitation predominates surface adsorption as a mechanism for phosphate removal by slag. The effect of temperature on the efficiency of PO_4^{3-} removal by fly ash, slag and

Table 3
Experimental adsorption data

Mass of adsorbent (g)	Fly ash		Slag		OPC	
	P[a] after adsorption (mg/l)	P[a] adsorbed (mg)	P[a] after adsorption (mg/l)	P[a] adsorbed (mg)	P[a] after adsorption (mg/l)	P[a] adsorbed (mg)
0.5	72.8	5.44	48.5	10.3	34.4	13.1
2	71.9	5.62	46.7	10.6	32.2	13.6
3	71.4	5.72	45.8	10.8	31.1	13.8
3.5	70.2	6.43	43.5	11.3	28.2	14.4
4	65.0	7.00	33.7	13.3	15.6	16.9
5	58.7	8.26	21.7	15.7	0.4	19.9

[a] PO_4^{3-} (as P).

Table 4
Frumkin isotherm constants and linear correlation coefficients

Adsorbent	R^2	α	β
Fly ash	.9918	3.061	0.0254
Slag	.9974	3.780	0.0149
OPC	.9945	4.976	0.0042

Table 5
Breakthrough data

Adsorbent	t_E[a] (min)	V_T (cm^3)	V_Z (cm^3)	h_Z (cm)	C_T (mg PO_4^{3-}/g)
Fly ash	2.8	187	116	1.742	32
Slag	7.0	312	138	1.133	60
OPC + fly ash	9.4	375	139	0.910	75
OPC + slag	9.9	388	140	0.881	78
OPC	10.8	412	142	0.833	83

[a] Breakthrough time.

OPC is illustrated in Fig. 5. The percent PO_4^{3-} removed was observed to increase with increasing temperature as expected, and it appears that some desorption may be occurring at higher temperatures. The decreasing slope of the temperature curve in the order fly ash, slag, OPC is indicative of decreasing activation energy for the PO_4^{3-} adsorption process.

Fig. 6 illustrates the variation of percent PO_4^{3-} removed with the initial pH of the aqueous solution for fly ash, slag and OPC. It can be seen from the figure that the efficiency of PO_4^{3-} removal increases steadily in acidic pH. There could be two reasons for this. Firstly, it may be due to the accumulation of positive charge on the adsorbent surface that increases its affinity for the negatively charged phosphate ions. Secondly, an increased proportion of phosphate ions will be converted to the acidic forms ($H_2PO_4^-$ and HPO_4^{2-}), which may be more readily removed from solution via deprotonation and subsequent precipitation as $Ca_3(PO_4)_2$, as suggested by Tabikh and Miller [18]. This would probably explain why the effect of lower pH on the efficiency of PO_4^{3-} removal was observed to be more significant for OPC and slag (higher percent CaO) than fly ash. The acidic pH would also release more Ca^{2+} ions from the cement, which decompose in acidic environments, to precipitate $Ca_3(PO_4)_2$. The observed slight increase in the efficiency of PO_4^{3-} removal beyond pH 9 could be due to the creation of favourable conditions for calcium phosphate precipitation at high pH, thus enhancing the removal of PO_4^{3-} by dissolved calcium, which is always present in the system.

Table 3 shows the experimentally obtained adsorption data for fly ash, slag and OPC. The fit of these data to the Frumkin isotherm is shown in Table 4, and the application of the Frumkin equation to the data is illustrated graphically in Fig. 7. Attempts to fit the data to the Langmuir and Freundlich isotherms yielded nonlinear plots with values of $R^2 < .4$. It is evident that the Frumkin isotherm is the appropriate one for fitting the data. The Frumkin constants were calculated and are shown in Table 4. The increasing value of the lateral interaction coefficient, α, in the order fly ash, slag and OPC reflects increasing phosphate-adsorbent strength of interaction. This appears to correspond to the order of increasing percent CaO in the adsorbents. It must be pointed out that magnesium, like calcium, will also dissolve to a certain extent and contribute to the observed PO_4^{3-} removal. However, this contribution appears to be relatively minor, considering the fact that slag contains nearly six times as much MgO as OPC (see Table 1).

The data obtained for the breakthrough experiments for the various adsorbents are shown in Table 5, and the corresponding breakthrough curves are represented in Fig.

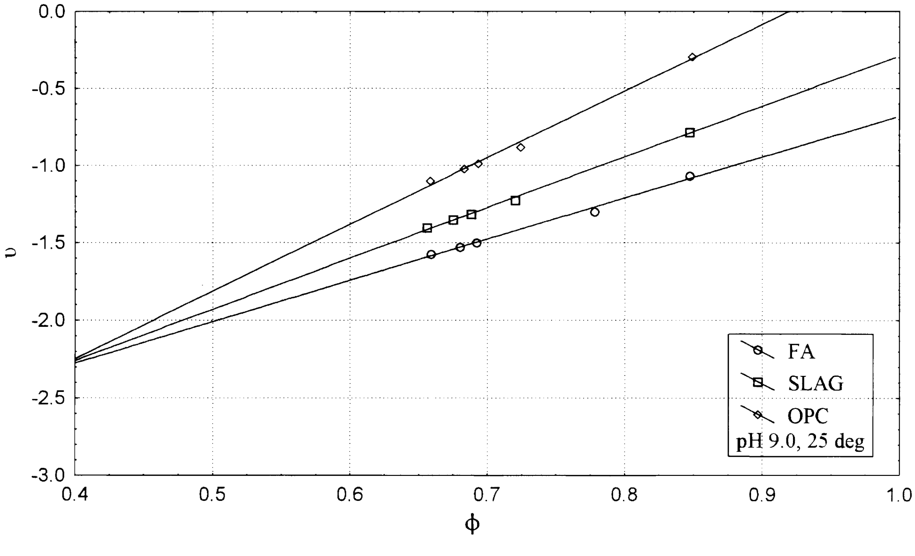

Fig. 7. Application of the Frumkin equation to experimental adsorption data.

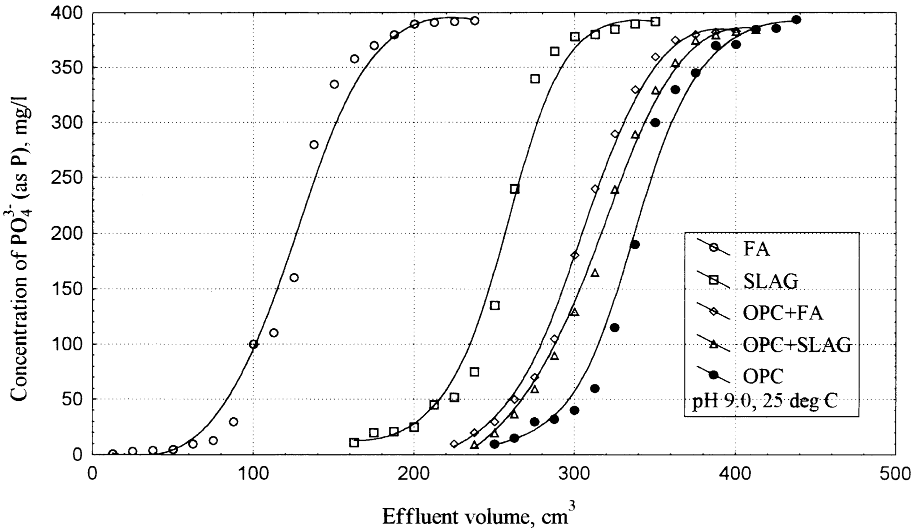

Fig. 8. Breakthrough curves for PO_4^{3-} adsorption.

8. The curves obtained were good approximations for characteristic symmetrical breakthrough *S* curves. For practical purposes, the breakthrough and exhaustion times were taken to be the times at which the effluent concentration reached 5% and 95%, respectively, of the influent concentration. The decreasing value of the height of the exchange zone, h_Z (see Eq. (4)), in the order fly ash, slag, OPC + fly ash, OPC + slag and OPC is a measure of increasing rate of ion exchange and/or phosphate removal, while the decreasing value of the breakthrough time, t_E, is indicative of increasing adsorption capacity. These experimentally obtained values can be extrapolated to calculate the capacity of a large-scale bed [15]. The capacity values, C_T, were obtained by graphical integration of Eq. (5). These values (Table 5) are quite substantial, and are of a similar order of magnitude as the 67 mg/g reported by Akgerman and Zardkoohi [9] for the adsorption of phenol on fly ash.

4. Conclusions

The by-products fly ash and slag have been used successfully for the removal of phosphate from aqueous solution. Potential economic utilisation of these materials might be either as a lining to slow down the seepage of nutrients such as phosphate from landfills, or as a fixed bed for treating agricultural and other waste waters. The phosphate-loaded solid waste may then be solidified by the addition of lime or Portland cement to a concrete mass that is stable and durable enough for safe disposal. The extent of phosphate removal by these adsorbents appears to be related to the percent CaO and/or Ca^{2+} ions released into solution via hydration and dissolution. The reported effect of fly ash on minimising undesirable setting time extension of phosphogypsum-containing concrete is probably due more to decreased penetrability that retards the ingress of phosphate ions than to preferential binding of free phosphate ions in the pore solution by the pozzolanic material itself.

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