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Communication

An investigation of phosphate ion adsorption from aqueous solution by fly ash and slag

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Abstract

The removal of phosphate ions from aqueous solution by fly ash and slag has been investigated. The chemical composition of each adsorbent has been determined by XRF and XRD, as well as some important physical characteristics such as BET surface area and mean particle size. The effect of contact time on the rate of PO_4^{3-} removal has been studied, and slag was found to remove the solute faster than fly ash. The Frumkin isotherm was found to be the most appropriate equation for constructing adsorption isotherms from the experimental adsorption data. The values of the isotherm constants have been obtained. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fly ash; Slag; Adsorption; Frumkin isotherm

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1. Introduction

When phosphogypsum is added to cement as a set-retarder, setting times are significantly extended [1]. This phenomenon is ascribed to the action of the phosphate ions present in the gypsum in various forms. It is quite conceivable that the phosphate ions going into solution upon water addition to the phosphogypsum containing cement interferes in some way with the hydration process and this is the basis for the delayed setting times observed. However, it has been found that cement containing fly ash is less sensitive to this phenomenon than ordinary Portland cement [2]. This immediately raises the question if there is not, perhaps, some type of interaction between the fly ash and the phosphate ions, e.g. adsorption or “binding”, responsible for this. It is known in the case of chloride ions causing corrosion of reinforcement in concrete, that cement replacement materials like fly ash and blast furnace slag can “bind” the chloride ions to their hydration products and therefore limit their mobility and ultimate influence on the rebar in concrete [3].

Fly ash has been found to readily remove F^- [4] and Cr^{3+} [5] ions as well as phenolic compounds [6] from aqueous solution. It was therefore decided that an investigation be made on the adsorption of phosphate ions on mineral admixtures such as fly ash and slag. Appropriate adsorption isotherms may be constructed by fitting the experimentally obtained data to the Langmuir (1), Freundlich (2) and Frumkin (3) [7] isotherm Eqs. (1–3):

$$(1/x) = (1/[x_m K])(1/c) + (1/x_m) \tag{1}$$

$$\log x = \log K + (1/n)\log c \tag{2}$$

where x is the mass of solute (PO_4^{3-}) adsorbed per mass of adsorbent, x_m is the limiting mass of solute that can be taken up per mass of adsorbent, K and n are constants, and c is the concentration of the solute in the solution that is in equilibrium with the adsorbent.

$$\upsilon = \log(\beta/55.55) + 2\alpha\Phi/2.303 \tag{3}$$

where $\upsilon = \log(\Phi/(1-\Phi)c)$, c has the same meaning as in (1) and (2), $\Phi = M/M_{ads}$, M is the mass of solute adsorbed at equilibrium, M_{ads} is the maximum mass of solute adsorbed at equilibrium, α is the lateral interaction coefficient, and β is a constant that describes the adsorption

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

	Fly ash (%)	Slag (%)
SiO_2	52.4	33.4
Al_2O_3	33.7	11.0
Fe_2O_3	3.6	0.7
Mn_2O_3	<0.1	0.4
TiO_2	1.7	0.6
CaO	4.1	33.3
MgO	1.1	18.0
P_2O_5	0.3	0.0
SO_3	0.2	0.6
Cl	<0.1	<0.1
K_2O	0.6	0.3
Na_2O	0.5	0.2
LOI @ 1000°C	0.8	1.7
Total	99.0	100.2
BET surface area (m^2/g)	0.66	1.11
Mean particle size (μm)	25.7	31.4
Density (g/cm^3)	2.21	2.82

Table 2
Experimental adsorption data

	Fly ash		Slag	
Mass of adsorbent (g)	Mass of PO_4^{3-} adsorbed (mg)	$[PO_4^{3-}]$ after adsorption (mg/l)	Mass of PO_4^{3-} adsorbed (mg)	$[PO_4^{3-}]$ after adsorption (mg/l)
0.5	5.44	72.8	5.98	70.1
2	5.62	71.9	11.2	43.8
3	5.72	71.4	15.1	24.5
3.5	6.43	70.2	17.0	1.79
4	7.00	65.0	19.8	1.01
5	8.26	58.7	20.0	0.16
pH of slurries/ solutions	9.8		10.0	

equilibrium ($\beta = \exp(-\Delta G^{\circ}_{ads}/RT)$, where ΔG°_{ads} represents the standard free energy of adsorption). The basis for the Langmuir isotherm is that all sites on the surface are the same, and that there are no interactions between adsorbed molecules. This is referred to as ideal adsorption. Non-ideal systems are fitted to an empirical adsorption isotherm, the Freundlich isotherm, where the amount adsorbed keeps increasing as the concentration of the solute increases. Another useful adsorption isotherm is suggested by the Russian physical chemists, A. Slygin and A. Frumkin (3). Both these last two isotherms can be arrived at theoretically in terms of surface heterogeneity and in terms of repulsive forces between adsorbed molecules [8].

2. Experimental

2.1. Materials and apparatus

Samples of fly ash (Matla fly ash, M432) and slag (slagment, M223) were obtained from PPC Technical Services (Germiston), where they were also analysed by XRF and XRD. Surface area determination was done using a BET instrument. A temperature-regulated Labcon platform shaker was used for solution agitation. Absorbance measurements were made using a Unicam UV–Vis spectro-

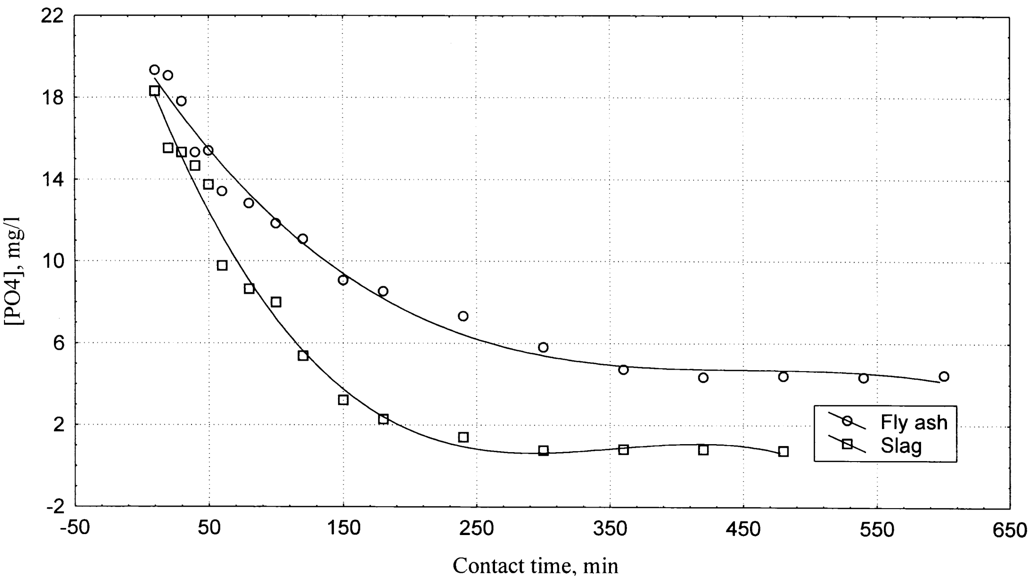

Fig. 1. Rate of phosphate removal from 20 mg/l solution at 25°C by 2 g adsorbent.

Table 3
Isotherm linear correlation coefficients and Frumkin constants

	Langmuir	Freundlich	Frumkin		
	R	*R*	*R*	α	β
Fly ash	0.6158	0.5285	0.9958	3.061	0.0254
Slag	0.6306	0.7137	0.9299	6.712	0.0019

photometer. All chemicals used were of analytical grade. High purity water was used for preparing solutions.

2.2. Procedures

The determination of phosphate was done using the yellow vanadomolybdophosphoric acid method described in most works on water analysis [9].

2.2.1. Rate of PO_4^{3-} removal

Two-gram samples of adsorbent were weighed and placed in several 250-ml Erlenmeyer flasks, each containing 200 ml of 20 mg/l PO_4^{3-} solution (anhydrous KH_2PO_4 was used to prepare a 500 mg/l PO_4^{3-} stock solution). The flasks were stoppered and continuously shaken at 25°C at a speed of 120 cycles per minute. The concentration of PO_4^{3-} was determined for the contents of one flask at pre-determined time intervals. The shaking was interrupted momentarily for a flask to be removed. A 50-ml supernatant solution were decanted, filtered (Whatman No. 42), and 35 ml of the filtrate transferred to a 50-ml volumetric flask. A 10-ml vanadate–molybdate reagent were then added, made up to the mark with distilled water, and the absorbance measured at 470 nm after the yellow colour had developed for 10 min. The PO_4^{3-} monitoring was carried out at 10-min intervals for the first 1 h, and at longer intervals thereafter until the absorbance values levelled off.

2.2.2. Adsorption isotherms

Various masses (0.5, 2, 3, 3.5, 4 and 5 g) of adsorbent were shaken with 200 ml of 100 mg/l PO_4^{3-} solution at 25°C for 16 h to attain equilibrium; the residual PO_4^{3-} concentration was then measured after shaking was stopped.

3. Results and discussion

The chemical composition and some important physical characteristics 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 rate of PO_4^{3-} removal from aqueous solution by the adsorbents. It can be seen that slag removed PO_4^{3-} at a faster rate than fly ash. The uptake of PO_4^{3-} by slag virtually ceased after a contact time of about 5 h, compared to about 7 h for fly ash.

Table 2 shows the experimentally obtained adsorption data as well as the pH values measured for the slurries/solutions. At these high pH values (ca. 10), the predominant form of phosphate ions in solution is expected to be the unprotonated orthophosphate species, PO_4^{3-}. The results of attempts to fit these data to the Langmuir, Freundlich, and Frumkin isotherm equations are shown in Table 3. It is quite evident from these values that both the Langmuir and Freundlich isotherms provide poor fits. The fit for the Frumkin isotherm, on the other hand, is good, especially that obtained for fly ash. The constants for the Frumkin isotherm have been calculated and reported in Table 3. Fig. 2 gives the graphical representation of the Frumkin isotherm for the adsorption of phosphate ions on fly ash and slag.

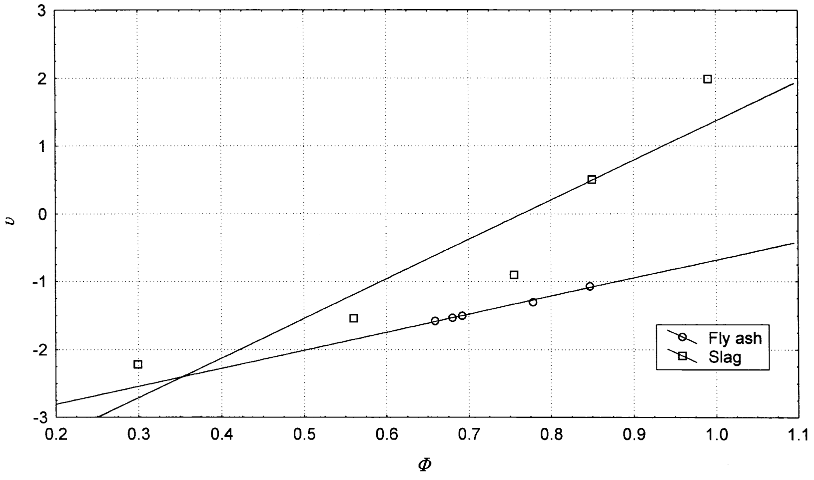

Fig. 2. Application of the Frumkin equation to experimental adsorption data.

4. Conclusions

It is assumed in the Langmuir model that while the adsorbed molecules occupy sites, they do not interact with each other. The high α values obtained in this study seem to be indicative of such interaction occurring to a significant degree. The Frumkin isotherm is evidently a good model for describing the adsorption of PO_4^{3-} from the aqueous solution by fly ash and slag.

The study is currently being extended to investigate the influence of factors such as pH, concentration, adsorbent particle size and temperature on the kinetics and efficiency of PO_4^{3-} removal, to estimate adsorption capacities by constructing breakthrough curves, and to use simultaneous TG-DSC analysis to study the effect of PO_4^{3-} adsorption on the thermal decomposition patterns of the adsorbents as well as to determine any changes in enthalpies of adsorption.

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