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Blast furnace slags as sorbents of phosphate from water solutions

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Abstract

The paper is focused on the sorption of phosphorus from aqueous solutions by crystalline and amorphous blast furnace slags. Slag sorption kinetics were measured, adsorption tests were carried out and the effect of acidification on the sorption properties of slags was studied. The kinetic measurements confirmed that the sorption of phosphorus on crystalline as well as amorphous slags can be described by a model involving pseudo-second-order reactions. For all slag types, phosphorus sorption follows the Langmuir adsorption isotherm. The acid neutralizing capacities of crystalline and amorphous slags were determined. In the case of the crystalline slags, buffering intervals were found to exist during which the slag minerals dissolve in the sequence bredigite–gehlenite–diaspor. There is a high correlation ($R^2 = 0.9989$) between $\mathrm{ANC}_{3.8}$ and the saturation capacities of crystalline and amorphous slags.

Keywords: Phosphate sorption; Blast furnace slag; Sorption kinetics; Acid neutralizing capacity

1. Introduction

Anthropogenic activity is responsible for a paradoxical situation: phosphate resources are becoming depleted and, at the same time, their contents in waste waters keep growing, causing eutrophication. In turn, waste water treatment is conducive to the generation of vast quantities of sewage sludge. The commonly used two-stage municipal sewage treatment tends to concentrate the phosphate ions in the recirculated sludge water. Chemical precipitation of phosphorus yields products which, owing to their composition, do not lend themselves easily to a direct utilization in agriculture. This ought to give an impetus to the development of alternative technologies aimed at products better suited for phosphorus recycling.

During the last 20 yr, alternative methods of phosphorus removal in wastewater treatment have been attracting increasing attention. The use of inorganic sorbents (including activated alumina, fly ash, blast furnace slag (BFS), zeolite, various soils containing metal oxides, goethite, pumice, titanium oxide) appears to be a promising alternative (Özacar, 2003).

BFSs appear to have considerable potential as low-cost sorbents of phosphorus from aqueous solutions. Batch and column experiments as well as field research have demonstrated a high P sorption capacity of BFS (Johansson and Gustafsson, 2000).

However, the application of slags in the sorption of phosphorus from aqueous solutions faces a number of problems, too. BFS is a complex CaO–MgO–Al_2O_3–SiO_2 system which also incorporates a number of minor components that can concentrate on the slag surface

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during crystallization or during transition to the glassy state, and can affect the sorption of phosphates. The reaction of these oxides with water may be alkaline (CaO), acidic (SiO_2) or amphoteric (MgO, Al_2O_3). In commonly encountered BFS compositions, MgO tends to behave as an alkaline oxide and Al_2O_3 as an acidic oxide. The hydration equilibria, which may take several days to establish, can be interpreted using the protolytic theory.

Phosphorus sorption experiments tend to yield discrepant results even with slags of very similar chemical compositions. The sorption capacity varies from 0.65 to 44.2 g (P) kg^{-1} and the sorption mechanisms follow the Freundlich (Lee et al., 1996), Langmuir (Sakadevan and Bavor, 1998), Frumkin (Agyei et al., 2000) or Temkin and Dubinin (Özacar, 2003) isotherms. Latest studies have even indicated (Oguz, 2005) that all three models (Freundlich, Langmuir and Dubinin-Radushkevich) provide adequate descriptions of phosphate adsorption on slags. Apparently, the large scatter of results of phosphorus sorption on BFSs relates to the fact that these substances are not fully and unambiguously defined by their chemical, mineralogical and phase compositions. The problem has now been studied for nearly 20 years (Yamada, 1986) and still it is evident that more detailed research is needed to elucidate the sorption of phosphates. First of all, a simple way of characterizing the hydration equilibrium in the BFS–phosphate system has to be found.

This paper reports on a study into the mechanisms of phosphorus retention by BFS from aqueous solutions. The study of heterogeneous acid–base equilibria can make a significant contribution toward explaining these mechanisms. Therefore, the results of adsorption experiments on BFSs are compared with the results of acid–base measurements carried out in systems involving slags and aqueous solutions of phosphates.

Table 1
Specific surface of BFSs

Sample	Grain size (mm)	S^{BET} ($m^2 g^{-1}$)
CS	0–0.1	0.65
FAS-I	0–0.063	0.90
AS-I	0–0.1	0.50
CAS-I	0.1–0.18	<0.1
AS-II	0–0.1	0.45

2. Materials and methods

A sample of crystalline BFS (designated as CS) and samples of amorphous BFSs (designated as AS-I and AS-II) were studied. All samples were provided by ISPAT-NH Ostrava. The slags were ground to less than 0.1 mm grain size. Two more samples of different granularity were prepared from the AS-I (amorphous) slag. The specific surface areas S^{BET} of the samples were determined by the thermal desorption method using a 'Chrom 4' gas chromatograph fed with nitrogen as adsorbate. The results are given in Table 1.

The chemical compositions of the slag samples were determined using the XRFS (EDS SPECTRO X-LAB) apparatus and are shown in Table 2 (in wt%).

The concentrations of Ca(II), Mg(II) and Al(III) in the slag leachates were determined using a JOBIN YVON model 24 atomic emission spectrometer. The phosphorus concentrations in sorption measurements were determined in the leachates as molybdenum blue using a spectrophotometric method according to Murphy and Riley (1962). KH_2PO_4 was used to prepare standard phosphorus solutions for the sorption measurements. All chemicals used were of analytic grade.

2.1. Measurements of phosphorus sorption kinetics

To establish the time dependence of phosphorus sorption on BFSs, a series of suspensions in 250 ml plastic bottles was prepared, each containing 1 g of sample and 100 cm^3 of phosphate solution having a concentration of 200 mg (PO_4) dm^{-3}. These suspensions were agitated in a horizontal shaking apparatus that vibrated at the rate of 200 min^{-1}, and were filtered repeatedly. Residual phosphorus contents of the filtrates were determined photometrically. The results thus obtained were analysed by applying the pseudo-second-order kinetic equation and the intra-particle diffusion model (Özacar, 2003; Ruixia et al., 2002).

Table 2
Chemical composition of slags (%)

Sorbent	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	K_2O	Na_2O
CS	38.02	13.71	38.63	6.55	—	0.23	0.58	0.48	0.47
AS-I	32.1	15.6	40.4	7.2	0.24	—	0.68	0.48	1.5
AS-II	33.6	15.1	40.2	6.2	0.72	—	0.61	0.57	1.7