# CHAPTER 4

# EXPERIMENTAL

## 4.1. Materials

Samples of fly ash (Matla fly ash, M432), slag (slagment, M223) and ordinary Portland cement (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). All the chemicals used were of analytical grade. De-ionised water from a Modulab system was used for preparing solutions for all the experiments.

## 4.2. Apparatus

A temperature-regulated Labcon platform shaker (Labotech, Johannesburg) was used for solution agitation. Absorbance measurements were made using a Shimadzu UV-150 digital double-beam spectrophotometer (SA Scientific, Johannesburg). A Siemens D5000 spectrometer (Bruker-AXS Pty (Ltd), Bryanston) was used for XRD analyses, and a Siemens SRS 3300 XRF spectrometer (Bruker-AXS Pty (Ltd), Bryanston) was used for chemical analysis. Particle size analysis was performed with a Malvern Mastersizer instrument

(Micron Scientific, Farramere). Particle fractionation was done using a sieving system from Labquip (SA Scientific, Johannesburg).

### 4.3. Procedures

#### 4.3.1. Characterisation of the sorbents

The chemical oxide composition of the fly ash, slag and OPC samples was determined by XRF spectrometry after being prepared as fused disks according to standard procedures. XRD scans were performed using Cu $K_\alpha$ radiation ($\lambda$= 0.154 nm) at a speed of 0.2 degrees 2 theta/min. For particle size analysis, 1 g of material was suspended in water with sodium metaphosphate as dispersing agent and pumped past a laser beam. Laser Fraunhofer diffractometry principles were used and an algorithm software was applied to the data collected by computer to calculate parameters of interest such as specific surface area, mean particle diameter and density.

#### 4.3.2. Composition of the cement blends

The percentage fly ash and percentage slag in the respective cement blends were calculated from values of CaO content of the fly ash, slag and each of the cement blends. These were determined experimentally as follows: An intimate mixture of 0.2 g sample and 0.8 g oven dried anhydrous lithium tetra-borate ($Li_2B_4O_7$) was

made and placed in a platinum crucible and then fused at 850°C in a muffle furnace for 15 minutes. The glassy product was dissolved by boiling in 100 ml of 10 % $HNO_3$, transferred quantitatively to a 500-ml volumetric flask and made up to the mark with de-ionised water. 25-ml aliquots were titrated with 0.01 M standardised EDTA solution using HHSNNA (2-hydroxy-1-[2-hydroxy-4-sulpho-1-naphthylazo]-3-naphthoic acid) indicator. 8 M KOH solution was used to precipitate $Mg^{2+}$ and triethanolamine to mask $Fe^{3+}$, $Al^{3+}$ and $Ti^{4+}$.

### 4.3.3. Phosphate ion calibration curve

The procedure used was based on the yellow ($\lambda$= 470 nm) vanadomolybdo-phosphoric acid UV/VIS spectrophotometric method described by Arnold (1985).

*Preparation of $PO_4^{3-}$ stock solution and calibration standards*

Anhydrous potassium di-hydrogen phosphate, $KH_2PO_4$, was oven dried overnight at 110°C and 2.1950 g was then dissolved and diluted to 1000 ml to obtain a 500 mg/l $PO_4^{3-}$(as P) solution. 1.0, 2.5, 5.0, 10, 20, 40, 50 and 60 mg/l $PO_4^{3-}$(as P) calibration standards were then prepared in 50-ml volumetric flasks by appropriate dilution of the stock solution.

*Preparation of vanadate-molybdate reagent*

25 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was dissolved in 300 ml de-ionised water to obtain Solution A. 1.25 g ammonium metavanadate, $NH_4VO_3$, was dissolved in 300 ml boiling de-ionised water, cooled, and 330 ml concentrated HCl added to obtain Solution B. Solution B was then cooled to room temperature. Solution A was poured into Solution B, mixed well, and then diluted to 1000 ml.

*Preparation of calibration curve*

35 ml of each calibration standard was placed in a 50-ml volumetric flask. 10 ml vanadate-molybdate reagent was added and diluted to the mark with de-ionised water. A blank was prepared in which 35 ml de-ionised water was substituted for the calibration standard. After the yellow colour had developed for at least 10 minutes, the absorbance of each calibration standard was measured in a 10-mm glass cuvette versus the blank at a wavelength of 470 nm. A plot of absorbance versus concentration was then constructed to obtain a least-squares calibration curve.

### 4.3.4. Kinetics of phosphate ion removal

2-g samples of sorbent were weighed accurately and placed in several 250-ml 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 then closed with rubber stoppers and continuously shaken on a mechanical platform shaker at a speed of 120 cycles per minute. The concentration of $PO_4^{3-}$ was determined for the contents of one flask at a time at pre-determined time intervals.

The shaking was interrupted momentarily at the pre-determined time intervals for a flask to be removed. 50 ml of the supernatant solution was decanted, filtered (Whatman No. 42), and 35 ml of the filtrate transferred to a 50-ml volumetric flask. 10 ml of vanadate-molybdate reagent was then added and the solution made up to the mark with de-ionised water. After the yellow colour had developed for 10 minutes, the absorbance was measured at 470 nm. The phosphate monitoring was carried out at 10-minute intervals for the first 1 hour, then at longer intervals thereafter until the absorbance values levelled off. A graph of $[PO_4^{3-}]$ versus time was then constructed.

### 4.3.5. Factors influencing phosphate removal kinetics and efficiency

#### 4.3.5.1. 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 of concentration on the kinetics of phosphate removal

by 2 g sorbent at pH 9.0 and 25°C following the procedure described in Section 2.3.4.

#### 4.3.5.2. Effect of particle size

400 g of sorbent was shaken mechanically for 20 minutes in a stack of sieves of various apertures to obtain fractions of different particle sizes. 2 g of 45-75, 75-90, 90-150, 150-300, and >300-$\mu$m fractions were 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. The flasks were then shaken continuously for 16 hours to attain equilibrium. The residual phosphate concentration in the supernatant solutions was determined.

#### 4.3.5.3. Effect of temperature

2 g of sorbent were 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 hours to attain equilibrium, with the flasks 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.

#### 4.3.5.4. Effect of pH

2 g of sorbent were 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 hours to attain equilibrium, after which the residual concentration of phosphate in the supernatant solutions was determined.

### 4.3.6. Adsorption isotherms

Various masses (0.5, 2, 3, 4 and 5 g) of sorbent 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 hours to attain equilibrium, after which the residual concentration of phosphate in the supernatant solutions was determined.

### 4.3.7. Breakthrough curves for the estimation of adsorption capacity

The set-up used for the breakthrough experiments is shown in Figure 4.1. 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 sorbent and 8 g inert sand (to improve porosity) and another layer of glass wool was placed at the 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). Figure 4.1 (not drawn to scale) illustrates the experimental set-up used.

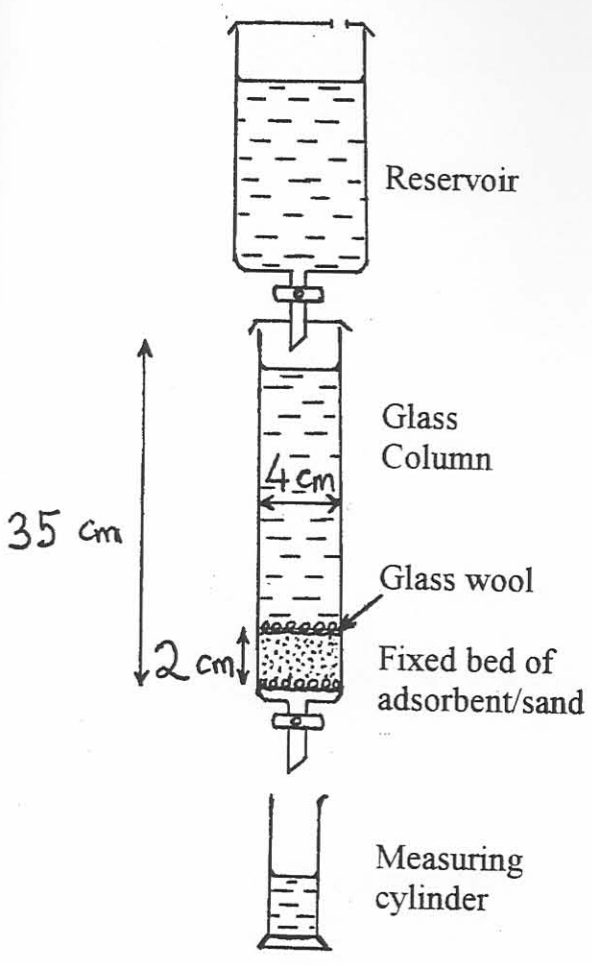


**Figure 4.1. Schematic of the set-up used for the breakthrough experiments.**

The concentration of phosphate in the effluent was monitored at half-minute intervals by collecting 5 $cm^3$ of it for analysis until the effluent concentration approached that of the influent. For practical purposes the breakthrough and

exhaustion times (see Section 1.4) were taken to be the times at which the effluent concentration reached 5 and 95 %, respectively, of the influent concentration.