

Short Communication

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THE DISSOLUTION KINETICS OF SINGLE SUPERPHOSPHATE FERTILIZER

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Perhaps the major impediment to increasing food production in both the humid and dry tropics is that many soils are infertile (Sanchez 1976; Sale and Mokwunye 1993). One of the fertility constraints in tropical soils is the low level of available phosphorus (P) resulting from P deficiency in many soils and from the high capacity of other soils to immobilize P. It is well established that P is one of the major nutrients limiting crop production in the tropics (Naidu *et al* 1993). At present, the major phosphatic fertilizer used in correcting P deficiency in most tropical soils is single superphosphate (SSP), which is manufactured by acidulating phosphate rock (PR) with sulphuric acid.

Single superphosphate consists of two major components: soluble monocalcium phosphate (MCP) and water insoluble residues (WIR), consisting mainly of residual PR with minor secondary components. The agronomic effectiveness of SSP, just like other phosphatic fertilizers, depends on the amount of water soluble P, and on the amount of water insoluble residual P that may be released slowly during the period of plant growth (Condron *et al* 1994). The amount of water soluble P in SSP is influenced by the mineralogical composition of the PR used in production, and by the reaction conditions. The amount of plant available P, that may be released slowly from the WIR components, depends on the reactivity of the residue in addition to soil factors (Khasawneh and Doll 1978; Stephen and Condron 1986).

When SSP is applied to soil, the water soluble MCP component in it is hydrolysed to phosphoric acid which then reacts with the previously unreacted PR of the WIR component, as shown in eqs. (1) and (2) (McLean and Wheeler 1964).



Both reactions above represent the congruent dissolution of SSP in soils. Although the literature dealing with the dissolution of SSP in soils is considerable, there has generally been little empirical evidence to explain the rate and nature of SSP dissolution in soils. Indeed the confirmation and understanding of the operating reaction mechanisms are essential in

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explaining the solubility and consequent agronomic potential of fertilizers. The purpose of this work was to elucidate the kinetics and mechanism of dissolution of SSP in aqueous solutions under important physicochemical conditions. The present study was carried out in continuation of previous kinetic studies on acidulation of PR (Olanipekun 1999a; 1999b).

Finely pulverized (100% < 0.16 mm) PR from Gbokoto, Ogun State (Nigeria) was acidulated with H₂SO₄ (65%) in plastic beaker, using an acid:rock ratio of 0.63 (w/w), the manufacturing procedure has been described elsewhere (Olanipekun 1994). The fertilizer thus prepared was finely ground (80% < 88µm), and analysis gave the major elements (in %) as Ca(24.3), P(9.86) S(9.25), Al(0.52), and Fe(0.43). The mineral assemblage of the SSP and reaction residues was determined using the procedure of Klug and Alexander (1974) and a Philips X-ray powder diffractometer with Co-Kα radiation (50 kV, 40 mA). The major phosphate mineral present in the PR was fluorapatite.

The kinetic experiments were conducted in a 250 ml Pyrex reaction flask immersed in a thermostated water bath, and equipped with a thermometer and a stirring rod. For each run, 2 g of SSP was suspended in 200 ml aqueous solution of pre-determined pH and temperature. The contents were well agitated at various speeds. Thereafter, solution samples of 2 ml were withdrawn at appropriate times during a run, diluted with distilled water and analyzed for phosphate by complexing with a mixed "vanadomolybdate" reagent and the optical density measured at 420 nm (Welcher 1963).

The fraction of phosphate dissolved against time plots for different stirring speeds ranging from 100 to 500 rpm, under the following experimental conditions :pH, 3.5 and temperature, 26°C, are given in Fig 1. The result shows the dependence of rate on the stirring speed. In all cases, the dissolution rate increased with increasing speed of agitation. Plots of the initial values of observed rate against $w^{1/2}$ (w is the stirring speed in rad s^{-1}), as in Fig 2, gave a straight line. This indicates that the initial dissolution rate is overall transport controlled (Burkin 1966).

Experimental runs were also carried out at 500 rpm and 26°C for various pH over the range 3.0 to 5.0. The result in Fig 3 shows that the dissolution rate increases with decreasing pH, and follows the same pattern. This implies that the plant availability of P from the SSP is expected to increase with decreasing soil pH, provided it is used on soils with negligible amounts of pH dependent surface charge. In soils with significant amounts of pH dependent surface charge, as the pH decreases, phosphate adsorption capacity increases which immobilizes the P dissolved and may render it less available to plants (Barrow 1985).

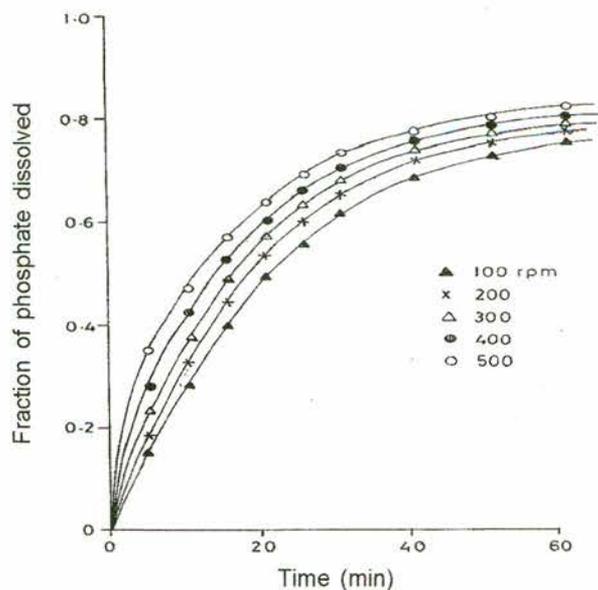


Fig 1. Plots of phosphate fraction dissolved vs. time at pH 3.5 and 26°C for various stirring speeds.

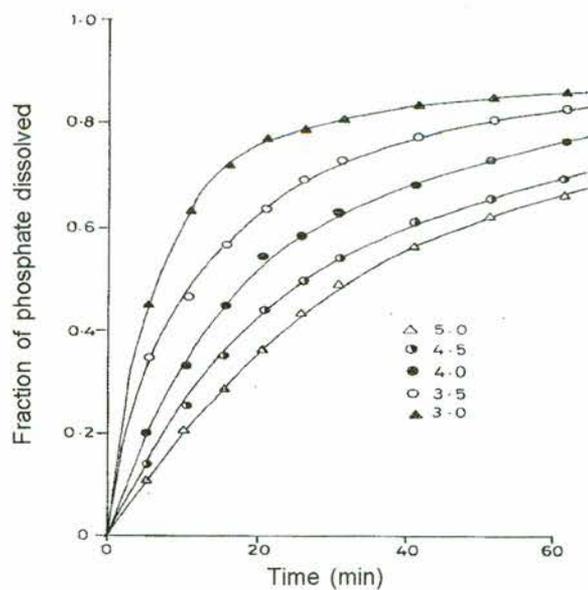


Fig 3. Plots of phosphate fraction dissolved vs. time for variation pH at 26°C and 500 rpm.

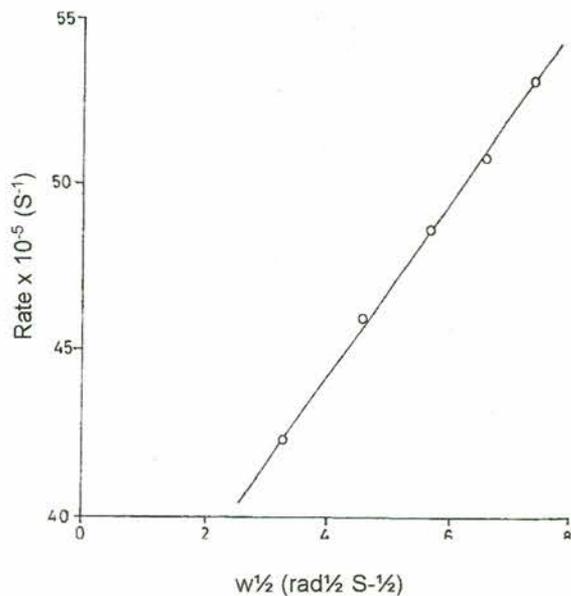


Fig 2. Variation of dissolution rate of phosphate fraction with stirring speed at pH 3.5 and 26°C.

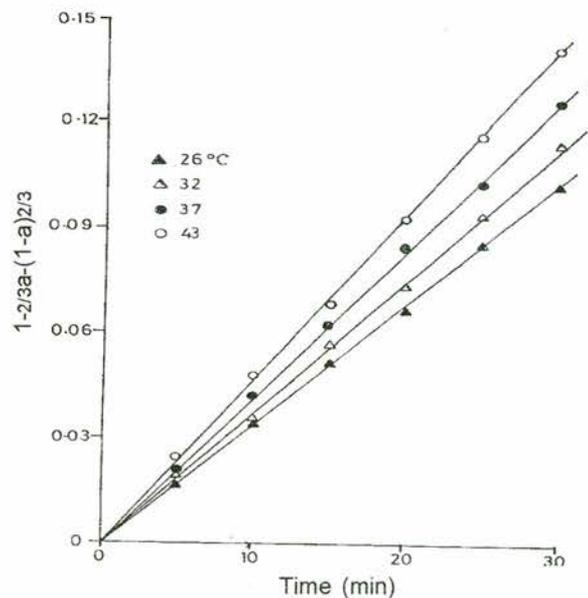


Fig 4. Plots of $1-2/3 a(1-a)^{2/3}$ vs. time for phosphate dissolution at 500 rpm and pH 3.5 for various temperatures.

The experimental data for the dissolution rate of phosphate were analyzed using two familiar kinetic models (Habashi 1979; Sohn and Wadsworth 1979), expressed by equs. (3) and (4),

$$1-(1-a)^{1/3} = k_1 t \dots\dots\dots (3)$$

$$1-2/3 a(1-a)^{2/3} = k_2 t \dots\dots\dots (4)$$

where a is the fraction of phosphate dissolved at time t , k_1 and k_2 are the overall rate constants. Equation 3 assumes that the

step controlling the dissolution rate is the chemical reaction taking place on the solid surface, and equ. 4 that the rate controlling step is the diffusion through a permeable product layer. Fitting of both kinetic equations with the appropriate experimental data indicated that only the diffusion kinetic model (equ. 4) gave linear plots Fig 4. The activation energy value of 14.3 kJ mol^{-1} , obtained from an Arrhenius plot is within the range normally associated with transport control in aqueous solutions (Glasstone *et al* 1941).

X-ray diffraction patterns were observed for some reaction residues. The analytical results showed a marked decrease in the intensity of the peaks associated with MCP and unreacted PR (fluorapatite). Also the diffraction peaks based on anhydrite, silica, and the complex aluminium and iron phosphate had become more obvious. Examination of the reaction residues under a low-powered microscope indicated pores or holes, randomly located, which were entirely absent in the original undissolved SSP. Thus, it may be concluded from this study that the dissolution rate of SSP is significantly influenced by both the pH and temperature of the dissolution medium. XRD analysis indicated that SSP dissolution proceeds by two mechanisms: hydrolysis of MCP to H_3PO_4 (equ. 1) and H_3PO_4 attack of the unreacted PR in the WIR (equ. 2). The initial process consists predominately of MCP dissolution, and is overall transport controlled with an associated activation energy of 14.3 kJ mol^{-1} .

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