

PLANNING LOW COST TECHNOLOGIES TO ENHANCE THE AGRONOMIC EFFECTIVENESS AND USE OF LOW GRADE DOROWA PHOSPHATE ROCK

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Introduction

Availability and affordability of high analysis phosphate fertilisers is a major challenge in most African communal farming areas. While poorly-soluble, phosphate rock (PR) reserves are usually abundant and in close proximity, sulfur resources and low cost fertilizer technologies to produce plant available phosphorus fertilisers are lacking (Sagoe et al. 1998a). Where sulphur is available, its extraction has been largely pollutive. For example in Zimbabwe, several studies report pyrite mining activities led to acidification and heavy metal contamination of rivers impacting negatively on populations and diversity of aquatic organisms (Ravengai et al. 2005; Nyamadzawo et al. 2011). The direct application of locally occurring phosphate rocks is an economic way to supply P needs for growing crops (Msolla et al. 2005). However, when igneous phosphate rocks are directly applied in farmer's fields, there is seldom any meaningful yield improvement because the rocks are sparingly soluble and un-reactive (Nandwa and Bekunda 1998; Jansa et al. 2011; Nandwa et al. 2011).

This is true for Dorowa Phosphate Rock (DPR), which is an igneous PR that cannot be used directly by communal farmers due to its inability to provide phyto-available phosphorus (P). Several studies have reported its ineffectiveness, to improve maize, pasture and grain legume yields when un-acidulated (Govere et al. 2003; Nezomba et al. 2007). Alternative low cost and environmentally friendly processes to enable the use of local PR reserves are needed to drive crop production. Methods such as weak acid leaching and sintering with silicate minerals have not been tested for DPR. These have potential to reduce costs if agro-wastes are used to produce weak organic acids for DPR dissolution and recycled glass is used as a sintering additive.

The biological extraction of P from phosphate rock is a less expensive, low energy intensive, and environment friendly technology compared with conventional processes (Gaiind 2017). Agricultural wastes can be used to produce organic acids via pyrolysis and or fermentation. Such techniques have not been tested using Dorowa phosphate rock and dissolution rates of DPR in organic acids are largely unknown. The dissolution rate of a particular PR indicates its potential use in agriculture and depends on the PR's mineralogical composition, type of acid and pH of the extracting solution (Rafael et al. 2017). Organic acids are able to dissolve PRs through protonation and/or chelation reactions (Sagoe et al. 1998b). The effectiveness of organic acids to dissolve PRs depends on the nature of the phosphates in the rock, the number of acidic protons biochemically generated, and the pKa values of the acids (Ivanova et al. 2006). Sagoe et al., (1998a) reported at least 80% of the dissolved P from PR was as a result

of tartaric acid chelation effects which achieved comparable amounts of P to sulphuric acid and used ten times less the amount of protons that sulphuric acid used.

Another avenue not yet explored for DPR is the use of thermal energy and silicate minerals to improve DPRs agronomic value. The crystal structure of PRs can be collapsed by thermal energy driving off hydration water, fluoride and breaking down carbonates to result in greater citric acid soluble phosphorus (Francisco et al. 2007; Watti et al. 2016). When PRs are mixed with silicates, heating can result in isomorphous substitution of PO_4^{3-} by SiO_4^{4-} where the SiO_4^{2-} and SiO_4^{4-} enter the apatite structure in the vacant orthophosphate positions where carbonates have been driven off (Knubovets et al. 1997). Soluble phosphate compounds known as fused magnesium phosphate (FMP) with alkaline characteristics suitable for acidic soils can be produced (Da Silva and Kulay 2005).

This paper presents part of the results of an on-going project that seeks to come up with low cost technologies to improve the agronomic efficiency of Dorowa phosphate rock. Part of the specific objectives are to evaluate the potential of weak acid leaching on P solubilisation from DPR and to assess the effect of sintering DPR with silicate minerals on citric soluble P.

Materials and Methods

Samples

Dorowa PR was obtained from Dorowa mine in Buhera as a composite sample extracted from at least ten positions from the pile awaiting transportation for acidulation in June 2016. In order to compare P reactivity indices, other rock phosphates were included in P analysis and P extractability assessments. These were obtained from the Massey University fertilizer store and were Sechura, Arad and Jordan that were originally obtained from Peru, Israel and Jordan respectively. Sub-samples were obtained from the original samples using stainless steel sample splitters until a required amount was obtained. The rocks were finely ground to less than 150 μm using a RockLabs® ring mill.

Sequential weak acid leaching experiments

A set of 5 phosphate rock/deionised (DI) water mixtures were obtained by mixing 0.5 g of Dorowa phosphate rock with 50 ml of DI water in 100 ml polyethylene screw top containers. The suspensions were shaken overnight and left to stand for a further 48 hours to ensure equilibration of the suspension. End point titrations were then performed using a TitraLab® 865 Autotitrator, with temperature set at $25^\circ\text{C} \pm 0.5$ and stirring at 600 rpm. The autotitrator was programmed such that 10 mins was allowed for equilibration to occur before initial pH was measured and titration only began when a stable pH reading had been reached. The burette speed was set at between 0.01 ml and 0.02 ml/min to improve accuracy of the end point. The proportional band was set at a pH of 0.01 with an end point delay of 30 mins to ensure equilibration at the final pH. Endpoints were set to 6, 5, 4 and 3 for the different samples and titrations were performed using 0.1 M citric acid. When pH endpoint equilibria were reached, samples were immediately taken out and filtered through a 0.45 μm Millipore® Nitrocellulose filter paper under suction. A fresh sample was used for each set pH point and after the PR was separated on the filter paper, it was washed in deionised water, recovered from the filter paper, resuspended in deionised water and the titration repeated on the same sample.

Sintering experiments

Dorowa PR, serpentine, dunite and soda lime glass were ground to pass through a 150 μ m sieve and dried in an oven overnight at 105°C. Dorowa PR was then weighed together with serpentine/dunite/soda lime glass into nickel crucibles to give ratios of 1:1, 1:2 and 2:1 (Dorowa PR:Silicate mineral). The total mass of product in each crucible was maintained at 3g and a Dorowa PR control was included that was not mixed with any silicate mineral. Other controls consisting of the silicate minerals were also included to check if the silicate minerals were contaminated with P. The samples were then transferred to a Carbolite® muffle furnace and the temperature was gradually raised to 1000 °C, which was maintained for 2 hours. The sintered product was removed from the furnace and left to air cool. After cooling the product was ground to less than 150 μ m and stored into plastic vials for analysis.

Chemical Analysis

Total P content, citric acid and formic acid extractable P were measured by UV-VIS spectrophotometry using a Jenway UV-VIS spectrophotometer (Hedley et al. 1988; Fertmark 2016). Metal element content in extracted solutions and HNO₃ digests was measured by atomic emission spectrophotometry using an Agilent^(R) MP-AES. For the principal cations, an ionisation suppressant solution of Cs/Sr was added to give a final concentration of 1000ppm (Kamala et al. 2014; Karlsson et al. 2015).

Results and Discussion

P content and P reactivity

Dorowa PR has a high total P (TP) content of 16.2% but only 11.7% and 9.3% of the TP is soluble in 2% citric and formic acid, respectively (Table 1). These values are very low compared to the other PRs analysed that had at least 31.5% and 46.4% P that was soluble in 2% citric acid and 2% formic acid, respectively. The low P solubility values of DPR in citric acid, formic acid and NAC show that it has very low potential for direct application without modification.

Table 1 Total P and its solubility in 2% citric acid, 2 % formic acid and neutral ammonium citrate (NAC) of Dorowa PR compared to other reactive rocks

Sample	Total P (% Dry weight)	Citric soluble P (%TP)	Formic soluble P (%TP)	NAC* Soluble P (%TP)
Dorowa	16.2 \pm 0.1	12.7 \pm 0.1	9.3 \pm 0.1	4.6 \pm 0.1
Sechura	12.8 \pm 0.0	46.3 \pm 0.1	60.2 \pm 0.7	41.7 \pm 0.3
Jordan	14.2 \pm 0.0	32.2 \pm 0.2	46.4 \pm 0.1	17.3 \pm 0.2
Arad	13.9 \pm 0.1	34.1 \pm 1.5	58.8 \pm 0.6	23.6 \pm 0.2

*product of two extractions. Soluble P expressed as % of total P in sample. Values after \pm are standard errors of means (SEM)

Effect of citric acid sequential extractions on P dissolution from DPR

The first citric acid extraction liberated more Fe and Ca in solution at every pH equilibrium point compared to the second and third extractions with the highest concentrations at pH 3 for all extractions (Figure 1). The amount of P in solution at pH 3 after the second extraction was comparable to the first extraction while there was a slight reduction at the third extraction. If the solution extracted at pH 3 were used to irrigate to 5mm depth the amount of nutrients applied per ha will be 9.33 kg P and 16.65 kg Ca. However, after 3 sequential extractions at pH 3, only 24.35 % of the total P in DPR was extracted. Further improvement in the P dissolution of DPR is needed.

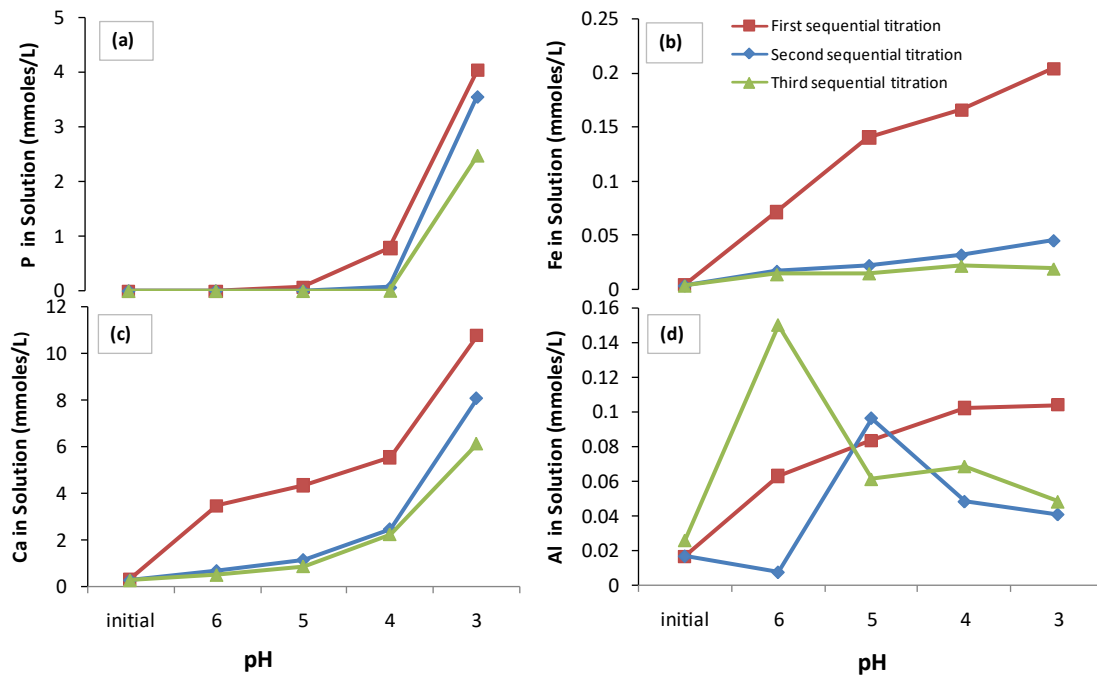


Figure 1. Dissolution of (a) P, (b) Fe, (c) Ca, and (d) Al from Dorowa PR after sequential titrations with 0.1 M citric acid

Effect of sintering/fusing with silicate minerals on citric acid soluble P

Products of sintering with serpentine at 1000 °C had citric solubility that was comparable to the un-sintered DPR products and therefore sintering with serpentine did not improve citric soluble P of DPR. This could be as a result of formation of insoluble crystals when slowly cooled in air. Sintering/fusion with soda glass was more consistent in improving DPR's citric soluble P at different mixing ratios. When the amount of DPR in soda glass/DPR mixture was 66.7% (Figure 2) the sintered product had 27.5 % of the total P soluble in citric acid. This will provide 29.7g of citric soluble P per kg of rock phosphate/soda glass mixture (2:1 ratio).

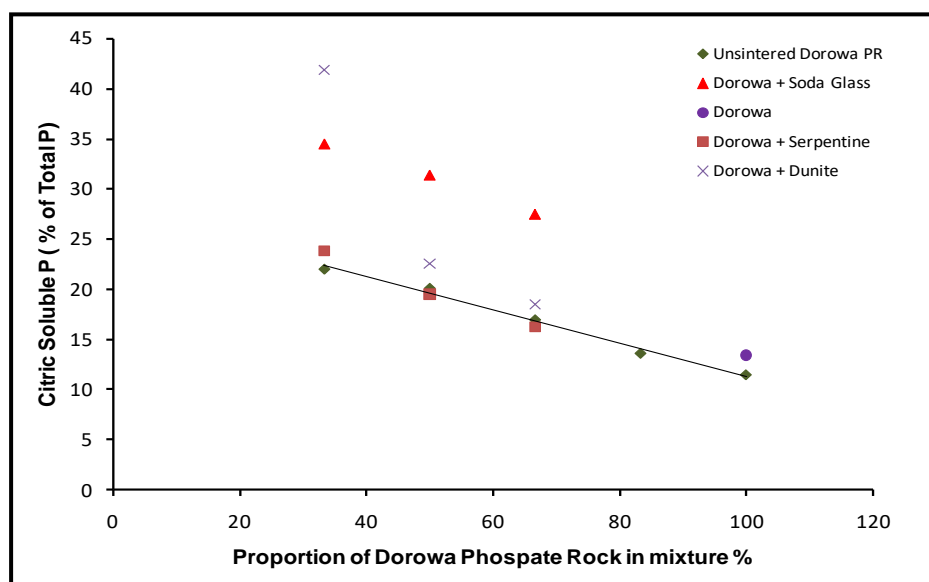


Figure 2. Effect of sintering/fusing with silicate minerals on citric acid soluble P

Conclusions

Sequential titration experiments revealed that the amount of P extracted with weak acids (such as citric acid) is low (up to 24.35 % with three sequential extractions). Further column leaching studies will be undertaken to improve the extractability of P from Dorowa phosphate rock. Based on citric solubility, the reactivity of DPR can be increased through sintering with soda glass with an ideal mixing ratio of 2:1 (DPR: Soda glass). Further studies should investigate more economical methods; for example, using DPR sintered/fused with recycled glass and adding chemical agents to lower the sintering/fusion temperatures. The effect of quenching the sintered product on solubility will also be explored. Validation of improved agronomic efficiency will be achieved through greenhouse experiments.

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