CHAPTER 5

PHOSPHORUS AVAILABILITY FROM SLAGS

INTRODUCTION

Phosphorus is found in soils under normal pH conditions mainly in the $H_2PO_4^-$ form and is subject to reactions with sesquioxide mineral surfaces at acidic pH (Mengel & Kirkby, 1987). This is one of the main reasons for the widespread deficiency of P in South African soils. From a plant nutrition perspective three main soil P fractions are important namely:

- P in the soil solution
- P in the labile pool
- P in the non-labile pool

The reaction of P with sesquioxide mineral surfaces leads to the situation where the P concentration in the soil solution is very low yet in equilibrium with the P held on particle surfaces. The non-labile pool is the largest and contains the insoluble P that can only be released very slowly into the labile pool. In soils with an above neutral pH the P reacts mainly with Ca to form insoluble minerals such as apetite (Mengel & Kirkby, 1987).

In the case where soils with a low pH and a high P-fixing capacity undergo a change in pH (increase) as in the case of lime addition the P becomes more available due to a change in the charge properties of the soil (Hingston. *et al.*, 1967).

Silica in the form of H_4SiO_4 is also found in the soil solution and its concentration is determined by the soil solution pH and through equilibrium with several Si minerals present in the soil (Elgawhary & Lindsay, 1972). Both P and Si are found in the soil solution in the form of anions and tend to undergo similar reactions with soil minerals (Hingston, *et al.*, 1967). Although P is more strongly bonded to sesquioxides than Si both of these compete for the same adsorption sites on minerals. The soil minerals and their affinity for P and also the P and Si anion concentration in solution, therefore, determine equilibrium. The adsorption of P is much stronger than Si at acidic pH but this situation changes at neutral and alkaline pH when Si is more strongly adsorbed (Hingston, *et al.*, 1967).

A further factor influencing the P equilibrium in the soil solution is the Si concentration and changes therein. If the Si concentration increases and the pH of the soil rises to neutral or alkaline the Si begins to replace P on the soil particles. The result of this effect is an increase in the labile P-pool and a subsequent increased uptake by plants grown on this soil (Reifenberg & Buckwold, 1954; Raupach & Piper, 1959; Datta, Shinde, & Kamath, 1962; Scheffer & Henze, 1962). In pure nutrient solutions there is an antagonistic effect between P and Si in terms of plant uptake but in soils on the other hand the "antagonism" leads to higher P levels in plants (Gaussmann, 1962).

Slags in many cases contain appreciable amounts of either P or Si or both (Table 5.1). In the USA basic slag was used until 1975 as a source of P, but the P-content has since decreased from 50-100g P kg^{-1} to around 10g P kg^{-1} (Barber, 1984). Most of the phosphates in the slag are complex and not soluble in water, but it is released in soil and is therefore more available to the plant, especially when the slags are very fine (Cooke, 1982).

The effect of Si in slags has already been thoroughly documented (Neergaard, 1962; Scheffer & Henze, 1962; Hunter, 1965; Roy, Ali, & Fox, 1971) and is regularly used to motivate the use of slags as agricultural limes. The amount of P applied to the soil during the use of slags could, if available to the plant, reduce the farmer's need for fertiliser P from other sources

TABLE 5.1. Average P and Si content of two slags before refining into agricultural lime (Source: Columbus Steel and Highveld Steel).

Chemical Compound	Columbus Steel %	Highveld Steel %
P	-	0.4
SiO_2	30.6	17.9

The Si seems to have a pronounced effect on the mobilisation of soil-P in soils with a high P fixing capacity as well as the plant uptake of fertiliser-P in soils with lower P fixing capacities (Datta, *et al.*, 1962).

The pH where the above-mentioned competition between Si and P becomes significant is above 6.5, which would imply that the user would have to lime to levels higher than these to benefit from it. This would be impractical and could cause other nutritional problems.

Very little work has been done on the interaction of Si and P from slags in recent years except for a few recent studies in Eastern Europe (Ivanov, 1992) as well as studies on the ability of slags to immobilise excessive P in solution in Western Europe (Vanacker, 1999). Most of the work done on P availability from slags took place in the 1950s and '60s.

The aim of this study was to determine the amount of P available to the plant from the applied slags and make deductions concerning the influence Si has on soil P and P applied.

MATERIALS AND METHODS

The testing of P availability from slags was carried out in two trials. Trial 1 has already been discussed in detail in Chapter 2. Amongst others the spinach was tested for P by H_2SO_4/H_2O_2 digestion solution (ALASA, 1998) and the P determined by Auto Analyser (AA).

For Trial 2 a soil with a low pH and P content (Table 3.1) was chosen to minimise the effect of Si on soil-P. Four slags and a laboratory reagent $CaCO_3$ were added to this soil in 4 kg pots at three pH targets (5.5, 6.0, and 6.5) and the amounts of lime were calculated as described in Chapter 3. The slags were selected from the original liming materials in Trial 1. Each slag was digested with $HClO_4$:$2HNO_3$ (ALASA, 1998) and the amount of P determined by Auto Analyser. This digestion procedure was chosen due to the influence of Sulphur on the AA, even though the above reagent was prescribed for plant material and an H_2SO_4 digestion prescribed for limes.

The citric acid soluble P of each slag was determined in a 2% aqueous citric acid solution by adding 5g of the liming material to 500ml of the solution (ALASA, 1998). The solution was stirred for 30 minutes and the P determined by AA again.

Wheat was simultaneously grown in the same pots for three months, harvested, weighed and P determined on the plant material as for the spinach in Trial 1.

RESULTS AND DISCUSSION

The total and citric acid soluble P content of the slags are given in Table 5.2. The levels for Limes 3 and 6 are lower than expected when the values of Table 5.1 are taken into account. A factor that could play a role here is the addition of other liming materials (dolomitic limes) to the slags in its preparation to comply with the regulations for dolomitic lime, therefore diluting the slag in terms of P content. Furthermore, the values given in Table 5.1 are long-term average values obtained from the industry and the possibility exists that the P-content varied and was lower than average at the time of sampling. The citric acid soluble P seems in most cases to be two thirds of the total value.

TABLE 5.2. Total and citric acid soluble P in four slags.

Lime	Source	Total P (%)	Citric Acid Soluble P (%)
2	Columbus	0.006	0.004
3	Highveld	0.126	0.095
6	Highveld	0.126	0.089
11	ISCOR Vereniging	0.019	0.015

The P levels in the plants for Trial 1 are tabulated in Table 5.3 and presented graphically in Figures 5.1 and 5.2. In most cases the P-uptake increased moderately with increasing pH. All the limes performed more or less the same with regard to P uptake by the spinach except for Lime 2 (and to a lesser extent Lime 11 at neutral pH values), which had a higher P-uptake above pH 6.5. Lime 2 has a very low P-content (Table 5.2) but high Si content (Table 5.1) and the soil had a relatively high P-content (Table 3.1). It is difficult to conclude whether the increase in P-content can be attributed to the higher availability soil P at higher pH, or due to the presence of Si from the slag. Limes 3 and 6 contain higher amounts of P than Lime 2 and both indicated a slight increase in P-uptake at pH values above 7.5. The P-content of the slags is probably too low to make any significant contribution to the plant available P.

TABLE 5.3. P-content of spinach leaves for twelve liming materials (Trial 1).

Lime	Application rate	Spinach P content (%)	pH of soil
1	1	0.19	6.35
	2	0.21	6.91
	3	0.21	7.29
2	1	0.25	6.05
	2	0.35	7.27
	3	0.42	7.88
3	1	0.26	6.33
	2	0.27	7.42
	3	0.32	7.61
4	1	0.26	6.05
	2	0.21	6.55
	3	0.25	7.34
5	1	0.20	6.15
	2	0.29	7.11
	3	0.30	7.54
6	1	0.23	6.22
	2	0.26	7.18
	3	0.32	7.60
7	1	0.20	6.19
	2	0.26	7.02
	3	0.30	7.86
8	1	0.18	6.58
	2	0.22	7.18
	3	0.24	7.53
9	1	0.23	6.37
	2	0.24	6.95
	3	0.24	7.43
10	1	0.18	6.25
	2	0.23	6.79
	3	0.20	7.21
11	1	0.19	5.91
	2	0.28	6.78
	3	0.28	7.27
12	1	0.18	6.12
	2	0.21	6.78
	3	0.28	7.60

The soil chosen for Trial 2 had a much lower P-content to reduce the effect of Si on soil P and to limit the plant P-content mainly to the P available from the slag. The P content of the wheat grown in this trial is indicated in Table 5.4 and Figure 5.3.

Contrary to the spinach, the P content of the wheat decreased with an increasing pH. The values though are influenced by the increase in growth of the plants with the higher application rates of the lime. Figure 5.4 indicates the wheat growth per pot. With the low amount of available P the concentration in the plant decreased as the plant mass increased. This is to a very large extent confirmed by the amounts of P taken from the soil (Table 5.4) although it appears that some of the slags performed marginally better than others. From the P contents of the plants it would seem that the slags contributed very little P. When the amount of P that was added to the soil in the different slags (Table 5.5) is calculated, it is clear that these values are very low and it would therefore be difficult to distinguish between P from the slags or the soil. If all the lime reacted in the soil and most of the P was in the available form these values would still be low but there might have been a difference between the limes with low levels and those with high levels in terms of P-uptake.

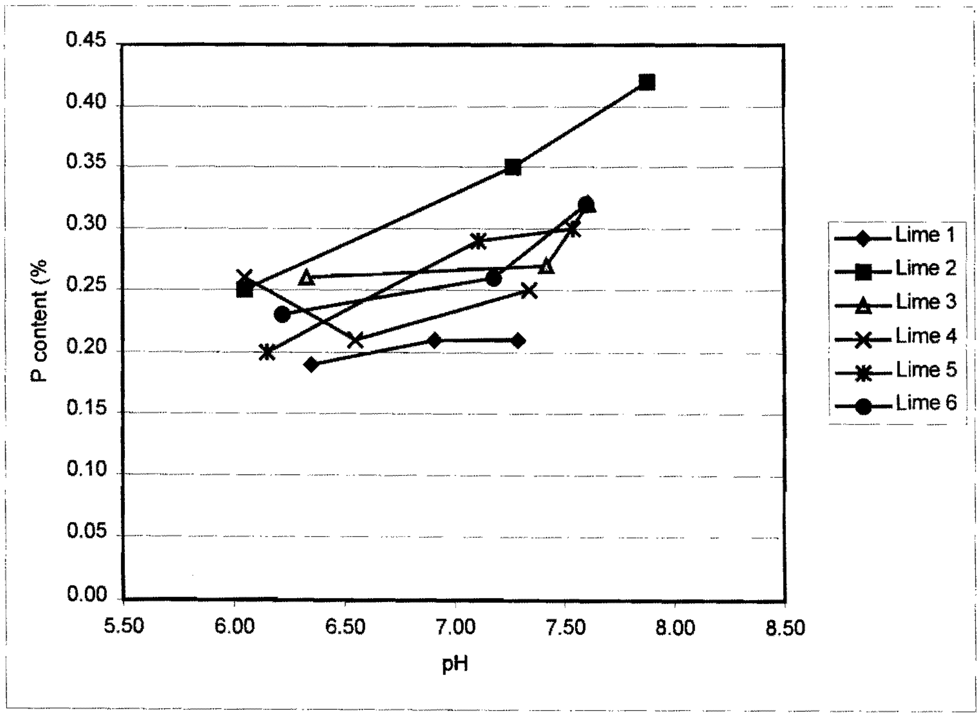

Figure 5.1. P content of spinach grown on soil ameliorated with Limes 1 to 6.

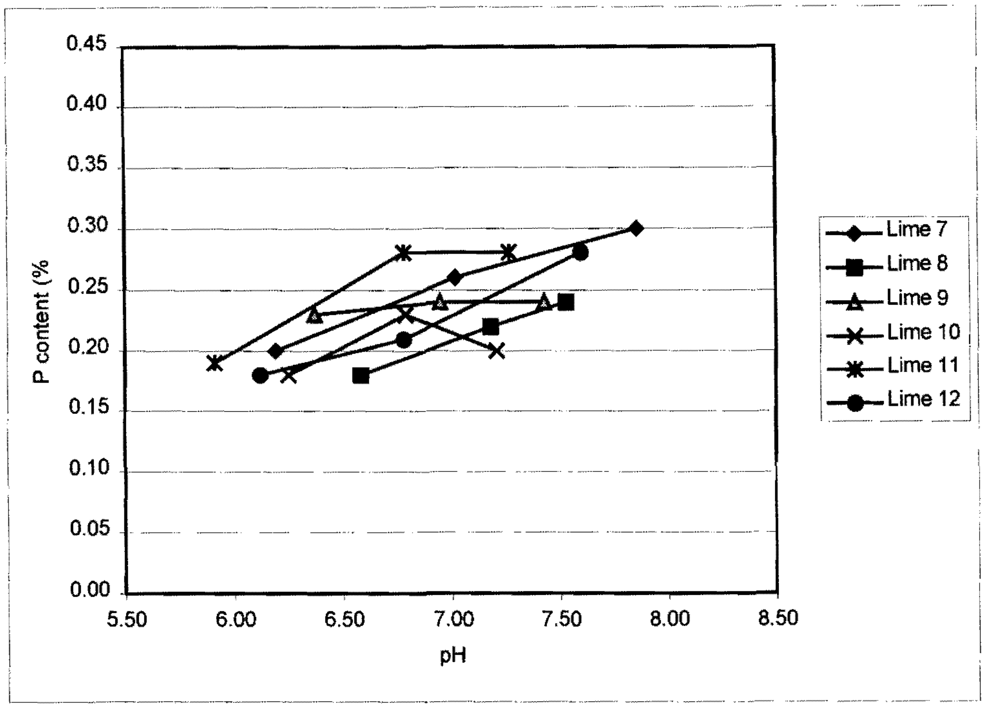

Figure 5.2. P content of spinach grown on soil ameliorated with Limes 7 to 12.

TABLE 5.4. Wheat yield and P content for four slags and a control treatment at three different application rates.

Lime	Application rate	Yield per pot (g)	Wheat P content (mg.kg^{-1})	P taken up (mg)	pH of soil
2	1	27.81	353.94	9.8	6.51
	2	32.25	232.03	7.5	6.87
	3	38.84	212.32	8.2	7.17
3	1	27.62	394.32	10.9	5.86
	2	30.93	352.89	10.9	6.09
	3	28.04	383.24	10.7	6.67
6	1	26.93	418.88	11.3	5.6
	2	25.09	372.77	9.4	5.95
	3	26.93	343.49	9.3	6.59
11	1	25.27	427.28	10.8	4.95
	2	27.48	497.77	13.7	5.04
	3	28.73	413.64	11.9	5.53
Lab	1	17.74	578.06	10.3	5.04
	2	17.72	622.59	11.0	5.43
	3	20.18	552.67	11.2	5.77

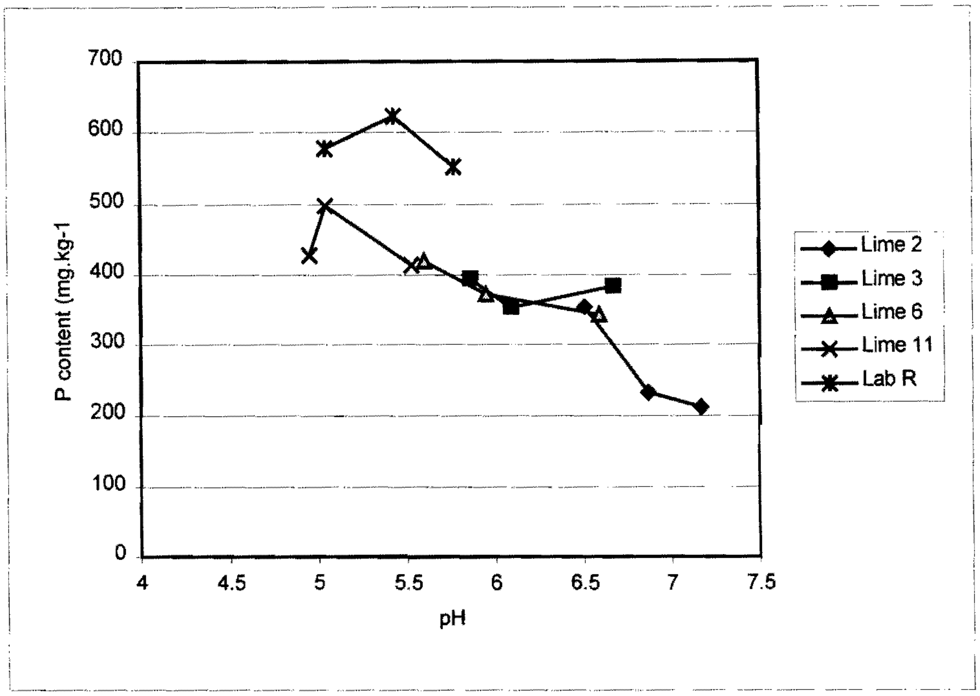

Figure 5.3. P content of wheat plants grown on soil ameliorated with four slags and a lime laboratory reagent at three application rates.

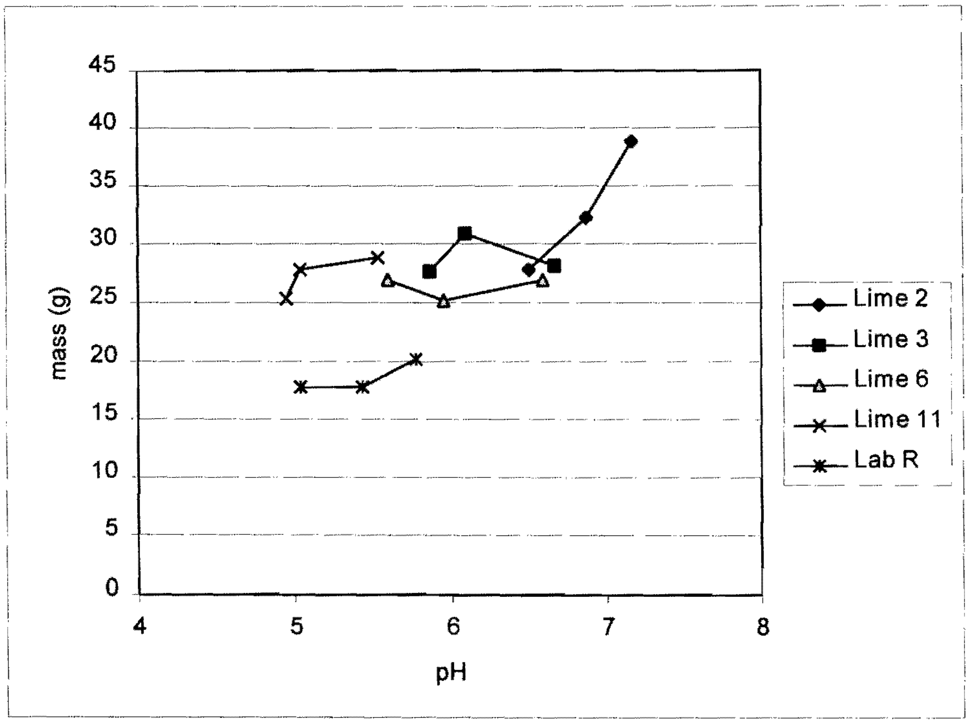

Figure 5.4. Average yield of wheat plants grown on soil ameliorated with five different liming materials at three application rates.

TABLE 5.5. Amounts of P applied to the soil in the different limes and application rates.

Lime	Rate	P-content (%)	Lime added (g pot^{-1})	P added (mg pot^{-1})	P added (kg ha^{-1})
2	1	0.006	10.28	0.62	0.70
	2		12.76	0.77	0.87
	3		15.24	0.91	1.02
3	1	0.126	8.08	10.18	11.45
	2		10.02	12.63	14.21
	3		11.97	15.08	16.97
6	1	0.126	8.82	11.11	12.50
	2		10.94	13.78	15.50
	3		13.07	16.47	18.53
11	1	0.019	5.53	1.05	1.18
	2		6.86	1.30	1.46
	3		8.19	1.56	1.76
Lab R	1	0	4.78	0	0
	2		5.93	0	0
	3		7.08	0	0

CONCLUSIONS

No clear indication exists concerning the amount of available P contributed by the slags and distinguishing it from the P supplied by the soil in the trials discussed above. Several problems exist namely:

- Low P-content of the slags,
- Small amounts of P in the slags that are immediately plant available due to the slow reaction of the liming materials in soil,
- The trials did not allow sufficient time for the P to be released,
- The trials did not allow for sufficient P to build up in the soil.

Although low, the contribution of P from the soil is relatively much higher than from the slags, therefore masking the slags' contribution. The trials therefore are very limited in their ability to predict P availability from the slags. The only indication concerning increased P uptake was in Trial 1 involving a lime with a very low P content but a high Si content.

In order to quantify the amount of P available from the slags, future trials would have to take into account the long-term application of slags and the simultaneous reacidification of the soil. In such a case the P applied in the slags would have had time to be released and consequently be adsorbed or fixed by the soil. It could be possible then to quantify the added P through P fractionations and/or long-term plant-uptake trials.