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POTASSIUM RELEASE CHARACTERISTICS OF COAL MINES SPOILS*

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Potassium release characteristics of four coal mine spoils and one unmined soil from the western part of North Dakota (U.S.A.), was studied in a growth chamber (25^{o} day and 15^{o} night temperature, 12 hr of flourescent light daily with 50% relative humidity) by exhaustive cropping with barley. Five successive generations were grown. The exchangeable K was determined by leaching with neutral ammonium acetate and total K by boiling with 1*N* HNO_3.

The spoil materials contained a large reservoir of exchangeable (313 – 679 kg/ha) and total (1205 – 1763 kg/ha) K, with the exception of spoil from Centre. The release of K from nonexchangeable sources varied from 745 to 1478 kg/ha. Mobilization of nonexchangeable K was closely related to the amounts of K extracted by barley. Nonexchangeable K accounted for 58% of total K utilized by plants. The results suggest that most of the spoils appear to be well buffered against K depletion.

It is concluded from this study that the total K in the HNO_3 extract and K released from non-exchangeable forms by HNO_3 appeared to serve as better indexes than the initial exchangeable K or Woodruff's energy exchange to K release and removal by intensive cropping with barley.

INTRODUCTION

The spoils from surface coal mines in North Dakota are highly calcareous and sodic in character. The materials are finely textured and low in organic matter. A previous study has shown that plant-available phosphorus is extremely low, and without modest application of P, revegetation of spoils is not possible. [16]. Some other investigations have demonstrated that nitrogen application coupled with P addition greatly enhanced plant growth on spoils [18]. Wali and Freeman [23] reported that spoils from North Dakota contain sufficient amounts of plant available microelements necessary for plant growth.

Little information is available on the K status of the spoils, although there is evidence that the application of K did not appreciably increase plant growth on spoil when adequately supplied with P and N [17].

It is known that K in equilibrium solution can give first-hand information to predict K supplying power of soils. Some investigators have reported that exchangeable K is not a reliable index to its removal by cropping [4, 11]. Nuttall, *et al.* [10] using an isotopic dilution technique for K with oat plants, and using a single rate of K application, suggested that both exchangeable and non-exchangeable K should be used together to assess plant-available K. There is considerable evidence that not only water-soluble, exchangeable and nonexchangeable K but also the lattice K may be released and utilized by growing plants [3]. Ayres, *et al.* [2] have demonstrated that elephant grass *(Pennisetum perpureum)* removed 3,500 lb. of K per acre from unfertilized Hawaiian soil during a 4½ year period. Reports have shown that the amount of K released from nonexchangeable sources by boiling in 1*N* HNO_3 was highly correlated with K removal by greenhouse cropping [11, 15, 19]. The plant root is so efficient at mobilizing nutrients that during short-term intensive cropping, plants will release more K from soils than can be released by continuous extraction with various dilute acids [7].

The purpose of work reported here is to evaluate the K status (exchangeable and non exchangeable) of some spoil materials from surface coal mining in North Dakota, using barley (*Hordeum vulgare*) as an indicator plant under growth chamber conditions.

MATERIALS AND METHODS

Spoils from four coal mine sites in the western part of North Dakota were collected for this study. One surface soil (unmined) was also included in the investigation. The materials are high in carbonates and extremely low in available-P (except unmined soil). The samples were air dried,

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passed through a 2-mm sieve and stored in plastic containers for various determinations and for the growth chamber experiment. Some important characteristics are presented in Table 1.

Laboratory. The energy of exchange for replacement of calcium and magnesium by K was determined by using a modified Woodruff formula. Originally Woodruff [24] used following expression to calculate the free energy of exchange:

$$\Delta F = RT \ln \frac{a_K}{\sqrt{a_{Ca}}}$$

Later this relationship was modified by Schofield and Taylor [20] and Taylor [22] by assuming that magnesium also behaves like calcium in dilute solutions. The expression then becomes:

$$\Delta F = RT \ln \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}}$$

$$\text{or } \Delta F = 1364 \log \frac{a_K}{\sqrt{a_{Ca} + a_{Mg}}} \quad \text{where}$$

a_K, a_{Ca} and a_{Mg} are the activities of the ions in moles/l. in the saturated extract.

Exchangeable K was determined by leaching 10 g air-dried samples with 100 ml neutral 1*N* NH_4OAc. The exchangeable K included water soluble K. The HNO_3 extraction of K was made by using the method followed by Partt and Morse [13], in which 2.5 g of air-dried samples were placed in 125-ml flasks, 25 ml 1*N* HNO_3 was added, and the flasks were placed on a hot plate at a constant temperature of 120° for 25 min. After cooling, the extract was filtrated into 100-ml volumetric flasks, samples washed with 0.1*N* HNO_3 to volume and K determined. Non-exchangeable K released was determined by sub tracting exchangeable K from the total K in the HNO_3 extract.

Growth Chamber. In order to assess the release of K to the plants, 200 g of the air-dry material were weighed into 16 oz of round-waxed cartons. Three replicates were used. A bianket application of N and P at the rate of 50 ppm each was made. In addition, minor elements in the amounts used by Martini and Suarez [9] were also added in the solution. Fifty pregerminated seeds of barley were planted in each carton, and distilled water was applied to approximate field capacity. The cartons were without drainage to prevent the K loss through leaching. The plants were grown in growth chamber at 25° day and 15° night temperatures, 12 hr of flourescent light daily and 50% relative humidity.

Harvesting was done after three weeks of growth by cutting plants at the soil surface. Plants were dried at 70°, weighed, ground in Wiley mill, digested in 5:1 nitric–perchloric acid mixture and analyzed for K by use of an atomic absorption spectrophotometer.

After each harvest, the spoils were air-dried, pulverized and repotted without removing the roots. A total of five successive crops was obtained. After the third crop, another application of N and P at the above rate was made. At the termination of the experiment, the contents of the cartons were air-dried, ground and passed through a sieve to remove the roots, and the spoil materials were analyzed for exchangeable K after cropping.

A check treatment was similarly grown in vermiculite using a modified Hoagland solution (less K) to make corrections for K derived from the seed source. The total amount of K taken up by the five crops of barley was taken as a measure of available K.

RESULTS AND DISCUSSION

Energy of Exchange. The energy of exchange of Ca and Mg with K and the total dry matter yield are presented

Table 1. Characteristics of materials used.

Spoils	pH saturation paste	CEC (me/100 g)	$CaCO_3$ (%)	O.M. (%)	Saturation extract analysis (me/1) K	Ca	Mg	Na	Silt (%)	Sand (%)	Clay (%)
North Beulah	8.52	30.6	12.0	1.1	0.59	1.29	1.63	27.8	34	32	34
South Beulah	8.08	28.8	11.3	1.4	2.31	27.5	28.08	55.4	46	15	39
Centre	8.30	33.1	9.2	0.6	0.005	1.05	1.02	4.35	33	35	32
Glenharold Spoil	8.32	37.1	10.2	1.8	1.46	1.66	1.44	2.76	37	27	37
Glenharold (unmined soil)	8.08	25.6	2.5	3.5	0.44	6.25	2.08	0.41	23	63	14

in Table 2. Woodruff [24] reported that the energies of exchange for replacement of calcium with potassium ranging from −3,500 to −4,000 cal. were associated with K deficiency. A range from −2,500 to −3,000 cal represented a suitable balance between Ca and K. Energies of exchange more than −2,000 cal. were associated with excessive K supply. On the basis of this test, the Centre spoil is potentially K-deficient, the Glenharold spoil has an excessive supply of K and rest of the spoils and the unmined soil are classified as having an adequate supply of K.

The energies of exchange showed no relationship with total crop yield (Table 2) or total K uptake by the plants (Table 3). However, the Centre spoil, which is classified as K-deficient, developed symptoms of K-deficiency after the first crop. The Glenharold unmined soil, which had an adequate amount of K according to Woodruff's concept, also exhibited severe K-deficiency symptoms by the third crop. The barley on the other spoils grew vigorously and did not exhibit K-deficiency symptoms. In the unmined soil all the plant available-K was probably exhausted by the first two crops. In rest of the spoils K from nonexchangeable sources probably continued to be released by successive crops.

Table 2. Energies of exchange, Δ F, for different spoils, potassium adsorption ratio (KAR), and yield of 5 barley crops.

Spoil	Δ F Cal/M	K availability status	KAR	Yield (g/pot)
North Beulah	−2474	Adequate	0.488	7.4
South Beulah	−2542	"	0.438	8.6
Centre	−3830	Deficient	0.005	6.7
Glenharold	−1958	Excessive	1.123	8.0
Glenharold (unmined)	−2964	Adequate	0.216	7.0

The appearance of K deficiency symptoms was associated with a plant K content of 1.6 and 1.7% for the Centre spoil and the Glenharold unmined soil respectively, in the harvest following the appearance of symptoms. By the time of the fifth harvest, the barley was making very little growth in the unmined soil and removing very little additional K. Almost all of K taken up by plants at the end of the experiment came from the seed source.

The results suggest that the Woodruff's energy of exchange is not a reliable index for plant available K. Woodruff [24] has neither studied the relationship between the energies of exchange and the crop yield, nor has he compared this concept with conventional soil tests. Laws [8] reportedly did not find any relationship with energy of exchange and crop responses and/or plant uptake of K. In the other studies, however, good agreement between Woodruff's energy concept and crop yield and plant K uptake has been reported [21].

Potassium Release by Cropping. The cumulative uptake of K by continuous cropping, presented in Fig. 1, shows a linear relationship up to the fourth crop for the North and South Beulah, and Glenharold spoils. By the fifth crop, a sharp decrease in K uptake was observed indicating that most of the available K has been exhausted. For the Centre spoil, K uptake decreased with each successive cropping. The rate of K uptake was the lowest for the unmined soil. The K release to the crops was in the order: South Beulah > North Beulah ⩾ Glenharold > Centre > unmined. The total amounts of K release to five crops by the above spoils were 1955, 1660 1535, 996, and 656 kg/ha, respectively. (Fig. 1).

Reitmeier, *et al.* [14] under intensive cropping found that by the fifth or sixth harvest the rapidly exchangeable

Table 3. Change in exchangeable K during cropping and K released from nonexchangeable from by cropping and by extraction with HNO_3 (kg/ha).

Spoil	Exch. K before cropping	Exch. K after cropping	Total K taken up by plants	K released by cropping*	Non-exch. K taken up by plants †	HNO_3	Non-exch. K released by HNO_3
North Beulah	679	101	1660	1082	880	1508	829
South Beulah	567	90	1955	1478	1298	1763	1196
Centre	313	62	996	745	621	1205	891
Glenharold	459	106	1535	1182	970	1625	1166
Glenharold (unmined)	431	56	656	281	169	1479	1048

*Total K taken up by plants + (Exch. K after cropping−Exch. K before cropping).

†Total K taken up by plants−(Exch. K before cropping + Exch. K after cropping).

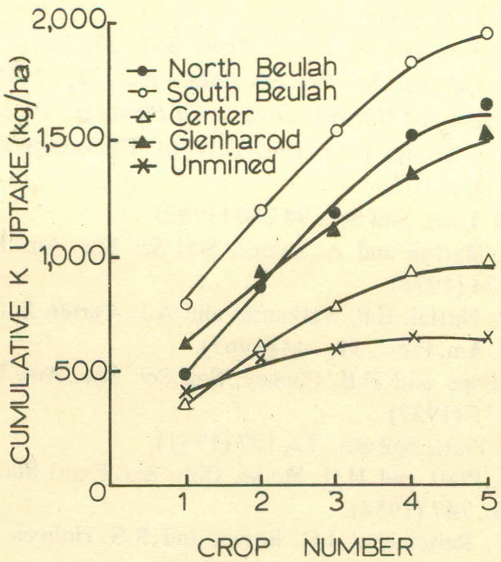

Fig. 1. Removal of K by five successive cropping with barley.

K contents of most of the soils approach their lowest values. After this stage the K source is mainly from the nonexchangeable phase. Most of the spoils used in this investigation showed a definite drop in K uptake by the fifth harvest. Similar results have been reported with some of the soils used by Ahenkorah [1].

The rate of K release by the Glenharold unmined soil was much slower as compared with the Glenharold spoil. This could be related to differences in the degree of weathering [12]. The spoils are not exposed to weathering conditions for a sufficient period of time and are poorly drained. Because of the fine texture of the spoils and insufficient precipitation in the western part of North Dakota, one might expect this as the usual result of normal weathering process by impeded drainage. Garman [6] has also suggested that the poorly drained soils have a somewhat higher K release rates than the well drained soils.

The fact that the rate of release of K is initially linear may suggest that diffusion of K from the soil particles is the controlling mechanism of K uptake from the spoils. It is noted that curves for the North Beulah, South Beluah and Glenharold spoil showed steeper gradients than those for the Centre spoil and the unmined soil. Thus the release rates should reflect the relative capacity of the spoils to supply K. The linear relationship also implies that the size of K-pool did not change appreciably on cropping until most of the nonexchangeable K was utilized by plants.

Exchangeable, Nonexchangeable, and Plant Uptake of K. The exchangeable forms of K before and after cropping together with the data on the total uptake of K, release of nonexchangeable K by cropping and acid boiling are reported in Table 3. The contents of exchangeable K varied from 313 to 679 kg/ha. The spoil from the Centre contained the lowest amount of exchangeable K. During cropping, the exchangeable K decreased considerably (85%).

Since the nonexchangeable K is usually released only when the solution K concentration is brought to a low level either by intensive cropping or leaching, a procedure which will maintain low solution K should provide a means of estimating release of nonexchangeable K. Continuous and intensive cropping techniques have been used for this purpose [1, 6, 11] and in general have given good agreement with the plant uptake data. The intensive cropping used here decreased the exchangeable K to relatively low levels (Table 3) which permitted an evaluation of the plant mobilization of K from the nonexchangeable phase. The amount of K released by cropping was calculated by subtracting the decrease in exchangeable K during cropping from the total K removed by cropping. Barley removed amounts of K ranging from 656 to 1955 kg/ha for the different spoils (with 1360 kg as the average amount). The amount of K released by cropping ranged from 281 to 1478 kg of K/ha. Appreciable amount of nonexchangeable K was removed by barley from the spoils, varying from 621 to 1298 kg of K/ha, whereas little nonexchangeable K was released by the unmined soil. Assuming that the total K uptake less the decrease in exchangeable K during cropping is equal to the K from nonexchangeable sources, an average of 58% of the total K taken up was derived from the nonexchangeable phase. This estimate is in general in agreement with the results reported by Pope and Cheney [11] and Fox and Kacar (5).

Table 3 also shows that for the four spoils, HNO_3 extracted approximately as much K as was removed by five successive corpping by barley. For the Glenharold unmined soil, however, the amount of K released by cropping was much lower than that extracted by HNO_3.

The results further indicate that total K uptake and K released from nonexchangeable sources are not related to the initial exchangeable K. However, the total K removed by cropping, which considerably exceeded the exchangeable K, was highly correlated with K released by cropping (Fig. 2). This suggests that, to evaluate the K fertility status of soils, both the immediately available and moderately available forms of K should be evaluated. It is interesting to note that a chemical method (HNO_3) can remove a quality of K nearly equal to that removed by five barley crops, suggesting that this method can satisfactorily predict the K availability status of spoils. Pope and Cheney [11] has also reported similar conclusions, although their data

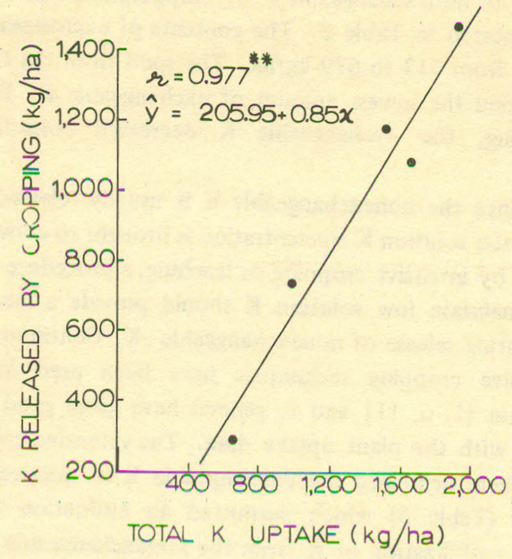

Fig. 2. Relationship between total K uptake and nonexchangeable K released by cropping.

indicated that the K removed by HNO_3 was over 2.5 times as much as removed by 10 successive cuttings of clover in the greenhouse (Fig. 2).

It is concluded from this study that with large reservoirs of exchangeable (313 – 679 kg/ha) and total (1205 – 1763 kg/ha) K, the spoils can support plant growth without K fertilization. Woodruff and McIntosh [25] have suggested that 125 lb K per acre are adequate for most of the crops. This quantity could vary, however, with the availability of soil moisture and whether annual or perennial crops are grown.

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