

The efficiency of dolomitic limestone, basic slag and peat ash as liming agents, and as calcium and magnesium sources for turnip rape

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Abstract. Incubation and pot experiments were carried out on muddy fine sand and fine sand soils to determine the efficiency of dolomitic limestone and of industrial by-products, basic slag and peat ash, as liming agents. Calcitic limestone was used as reference material. In the incubation experiment 0, 0.6, 1.2 and 2.4 g calcitic limestone were applied to 390 g (muddy fine sand) or 360 g (fine sand) of air-dry soil. The amount of other liming agents added was 2.4 g. In the pot experiment the weights of soil were 3.9 kg (muddy fine sand) and 3.6 kg (fine sand) and 24 g of liming agent was applied. The turnip rape (*Brassica campestris* v. *oleifera* f. *annua* cv. Candle) was grown in two growing seasons and the crops were cut at the flowering stage. In both experiments the soils were sampled for analysis after four and sixteen months.

The acidity of the soils was neutralized with the liming agents to the same extent in the pot and the incubation experiments. The increases in $\text{pH}(\text{CaCl}_2)$ obtained in the incubation experiment with 2.4 g liming agents were on the muddy fine sand and fine sand for calcitic limestone 2.0 and 1.4, for dolomitic limestone 1.5 and 1.1, for peat ash 0.3 and 0.2, for basic slag 0.8 and 0.6, respectively. At the end of the incubation 2.4 g of dolomitic limestone, peat ash and basic slag had increased the $\text{pH}(\text{CaCl}_2)$ of the soils to the same extent as 1.7 g, 0.4 g or 0.8 g of calcitic limestone, respectively.

The proportion of non-exchangeable Ca at pH 7 of the amount added in 2.4 g liming agents was for calcitic limestone 14 and 23 %, for dolomitic limestone 42 and 52 %, for peat ash 27 and 51 %, and for basic slag 59 and 64 %, in the muddy fine sand and fine sand soils, respectively. Of the Mg added in dolomitic limestone, about 45 % was non-exchangeable, and in basic slag about 65 %.

In the pot experiment about 13 % (average of the two soils) of the Ca applied in calcitic limestone was not found in turnip rape or as neutral 1 M ammonium acetate extractable from the soil. The corresponding value for dolomitic limestone was 41 %, for peat ash 45 % and for basic slag 65 %. The Mg applied in the liming agents but not found in turnip rape or in the soil amounted to 42 % for dolomitic limestone, 74 % for peat ash and 67 % for basic slag.

The efficiency of basic slag as a liming agent will be overestimated if it is measured by the amount of acid neutralized or by the content of Ca and Mg ($\text{Ca} + 1.65 \times \text{Mg}$) soluble in 1 M HCl. The amount of Ca soluble in 1 M HCl, alone, may provide a better, though not good, measure of the neutralizing ability of basic slag.

Introduction

Calcitic and dolomitic limestones are the most widely used liming agents in Finnish agriculture. Basic slags, by-products of the iron and steel industry,

have a local use. In future peat will be used as a fuel in power plants and the supply of peat ash to agriculture can be expected to increase.

The original Bessemer process gave basic slag with a high content of phosphorus (Thomas slag) and its main use in agriculture was as a phosphorus fertilizer. Recent developments in the process are designed to produce slags of low phosphorus content (BROWN and THATCHER 1969) and the basic slags are now principally only liming agents.

The efficiency of basic slag and peat ash as liming agents has been little studied. NORRMAN (1978) supposed silicatic liming agents (slags) to be able to neutralize the acidity of soil equivalently to carbonatic agents (limestones) if the total content of Ca in the slag was over 30 %. The results of BUCHER (1951) revealed that in acid soil the neutralizing capacity of slag was weaker than that of calcitic limestone when both were ground to the same fineness.

The purpose of the present investigation was to study the effects of fine ground basic slag and peat ash on the pH(CaCl₂), on the effective cation exchange capacity and on neutral 1 M ammonium acetate extractable Ca, Mg and K contents of two acid soils in incubation and pot experiments, and to compare the effects with those of calcitic and dolomitic limestones. The availability of Ca, Mg and K of these liming agents for turnip rape (*Brassica campestris* v. *oleifera* f. *annua*) was studied in the pot experiment.

Materials and methods

Two topsoils (volume 500 l) were taken from the cultivated area of the Viikki Experimental Farm (University of Helsinki) for the experiments. Both soils were acidic, the main difference being the higher content of organic carbon in the fine sand (Table 1). The muddy fine sand was a post glacial deposit (Littorina Sea) near the Gulf of Finland.

Calcitic and dolomitic limestones (here referred to as lime and dolomite, resp.) were commercial Finnish products. Basic slag (slag) was process slag from the iron industry, cooled with water and ground. Peat ash (ash) from a peat power plant was a grate ash, containing 63 % sand. The properties of the liming agents are presented in Table 2.

The pot experiment was performed in Mitscherlich-pots in the years 1980 and 1981. The pots were kept out of doors in a netwalled hall provided with a polycarbonate roof. Between the two growing seasons the pots were covered.

Each pot was filled with 4.5 kg of moist soil (in air-dry state the weight of muddy fine sand 3.9 kg and fine sand 3.6 kg), and the soil treated with 24 g of liming agent and the following amounts of nutrients: 1000 mg N as NH₄NO₃, 400 mg P and 1000 mg K as K₂HPO₄, 10 mg B as H₃BO₃, 15 mg Cu as CuSO₄·5H₂O, 10 mg Mn as MnSO₄·4H₂O, 10 mg Zn as ZnSO₄·7H₂O and 5 mg Mo as Na₂MoO₄·2H₂O. The nutrient treatment in the second spring was the same as in the first. Liming treatments were made in the first spring only. In addition to the limed soils the experiment included control soils without added liming agents. All treatments were repeated four times.

Turnip rape (cult. Candle) was sown at a density of 20 seeds per pot two days after liming and fertilization. Twenty days after germination the plants were thinned to nine. The crops were cut in the first year at the end of flowering and in the second year at the beginning of flowering.

The incubation experiment was performed in ½ l plastic pots, into each of which 450 g of soil (in air-dry state 390 g of muddy fine sand and 360 g of fine sand) was weighed. The following liming treatments were made: no liming, 0.6 g, 1.2 g or 2.4 g of lime, 2.4 g of dolomite, 2.4 g of ash and 2.4 g of slag. The soils were supplemented with nutrients N, P, K, B, Cu, Mn, Zn and Mo in amounts 1/10 of those applied in the pot experiment. The soil moisture was regulated with de-ionized water to 25 % of the air-dry soil and maintained near this level with monthly waterings. The incubation was continued for 16 months. For four months (May-August 1980) the pots were outdoors in the nethall, for the next eight months (September

Table 1. The properties of the soils

	Muddy fine sand	Fine sand
Particle size distribution, %		
<2 μm	22	23
2-20 μm	19	12
20-200 μm	57	58
>200 μm	2	7
Org. C, %	3.0	6.4
pH(CaCl ₂)	4.8	4.8
Exchangeable (pH 7) cations, me/kg soil		
Ca ²⁺	56	95
Mg ²⁺	13	9
K ⁺	6	9
Na ⁺	3	2
Effective cation exchange capacity, me/kg soil	76	102
1 M KCl extractable (Al+H), me/kg soil	9	7

Table 2. Liming materials

	Calcitic limestone (lime)	Dolomitic limestone (dolomite)	Peat ash (ash)	Basic slag (slag)
Acid neutralized equivalent to Ca, %	39.4	37.2	9.6	31.1
1 M HCl soluble				
Ca, %	37.0	18.6	5.5	20.6
Mg, %	1.1	10.8	0.5	5.6
K, %	0.04	0.12	0.24	0.47
Neutralizing ability				
Ca+1.65×Mg, %	38.8	36.4	6.3	29.8
Sieve analyses, %				
<0.125 mm				5.4
0.125-0.250 mm				50.9
0.250-0.500 mm				13.8
0.500-1.000 mm				28.6
>1.000 mm				1.3

1980-April 1981) inside at constant temperature +5 °C, and during the final four months (May-August 1981) again outdoors. Each pot was covered with perforated plastic film and all the pots together with black plastic film, as a shelter against the light.

Analyses: The liming agents were analyzed for 1 M HCl soluble Ca, Mg and K, and the "neutralizing ability" Ca + 1.65×Mg was calculated in per cent. The amount (me) of 1 M HCl neutralized with the liming agents was also determined and calculated as Ca %. The slag was sieved and the sand content of the peat ash was weighed.

After harvesting, the plant material was kept at 60 °C until dry and then heated at 105 °C two hours. For the analyses the plant material was ground with a Willey-mill. Wet combustion procedure with the acid mixture HClO₄ : H₂SO₄ : HNO₃ (1:2.5:10) was performed (SCHARRER and MUNK 1956). The total contents of Ca and Mg were determined by atomic absorption spectrophotometry (Varian 1000) with interference element La and total content of K was determined by flame photometry (Lange, model 6).

The soils of the pot experiment were sampled shortly after the two harvestings and those of the incubation experiment at equivalent times (after 4 and 16 months incubation). The neutral 1 M ammonium acetate extractable (exchangeable in pH 7) Ca, Mg and K contents (method described by JOKINEN 1981), the effective cation exchange capacity (ECEC) and 1 M KCl extractable (Al+H) content (KAILA 1971), and the pH(CaCl₂) were determined from air-dry soils.

Statistics: The significant differences between the liming treatments were estimated by Duncan's new multiple range test (STEEL and TORRIE 1960). In the tables the results of individual soils signified with a common letter do not deviate significantly (P=0.05).

Results

Incubation experiment

The increases in pH(CaCl₂) obtained with the three levels of lime seemed to be a little lower in fine sand soil than in muddy fine sand (Table 3). This was probably because of the higher organic carbon content of the fine sand.

On the basis of the pH(CaCl₂) values obtained without liming and with three levels of lime, a "neutralizing line" was drawn. The equivalent amounts of lime giving the same pH(CaCl₂) as 2.4 g other liming agents were then

Table 3. The pH(CaCl₂), the ECEC (me/kg soil), the 1 M KCl extractable Al+H (me/kg soil) and exchangeable (pH 7) Ca and Mg (mg/kg soil) in the soils without liming and with four liming agents after four and sixteen months incubation.

	Incubation time, months												
	4		16		4		16		4		16		
	pH(CaCl ₂)		ECEC me/kg soil		Al+H me/kg soil		Ca mg/kg soil		Mg mg/kg soil		K mg/kg soil		
<i>Muddy fine sand</i>													
No liming		4.3 ^a	4.4 ^a	82 ^a	80 ^a	15.0 ^f	15.4 ^g	1113 ^a	1166 ^a	166 ^a	166 ^a	486 ^c	449 ^d
Lime 0.6 g		5.1 ^c	5.0 ^c	96 ^c	97 ^c	5.1 ^d	4.9 ^e	1600 ^d	1720 ^b	176 ^a	177 ^b	439 ^{ab}	428 ^{bc}
Lime 1.2 g		5.7 ^d	5.6 ^c	117 ^d	120 ^d	3.0 ^c	2.8 ^c	2063 ^e	2281 ^c	180 ^a	182 ^b	447 ^b	415 ^{ab}
Lime 2.4 g		6.5 ^f	6.4 ^g	143 ^e	150 ^f	1.2 ^a	1.6 ^a	2758 ^d	3132 ^d	175 ^a	177 ^b	413 ^a	409 ^a
Dolomite 2.4 g		5.9 ^e	5.9 ^f	118 ^d	125 ^e	2.2 ^b	2.3 ^b	1627 ^d	1826 ^b	449 ^c	527 ^d	442 ^{ab}	424 ^{abc}
Ash 2.4 g		4.6 ^b	4.7 ^b	87 ^b	87 ^b	9.9 ^e	9.2 ^f	1253 ^b	1413 ^a	171 ^a	182 ^b	477 ^c	456 ^c
Slag 2.4 g		5.1 ^c	5.2 ^d	97 ^c	101 ^c	5.1 ^d	3.8 ^d	1494 ^c	1685 ^b	271 ^b	288 ^c	462 ^{bc}	439 ^{cd}
<i>Fine sand</i>													
No liming		4.4 ^a	4.5 ^a	117 ^a	119 ^a	12.0 ^e	11.4 ^f	1731 ^a	2043 ^a	120 ^a	141 ^a	631 ^b	567 ^a
Lime 0.6 g		5.0 ^c	4.9 ^b	139 ^c	136 ^c	5.2 ^c	5.2 ^d	2256 ^c	2556 ^c	126 ^a	139 ^a	584 ^a	566 ^a
Lime 1.2 g		5.4 ^d	5.3 ^d	161 ^d	160 ^e	4.2 ^{bc}	3.7 ^b	2779 ^d	3101 ^d	132 ^a	144 ^{ab}	606 ^{ab}	563 ^a
Lime 2.4 g		5.9 ^f	5.9 ^f	197 ^e	190 ^e	2.6 ^a	2.7 ^a	3747 ^e	3935 ^e	140 ^a	147 ^b	612 ^{ab}	570 ^a
Dolomite 2.4 g		5.5 ^e	5.6 ^e	157 ^d	167 ^d	3.4 ^{ab}	3.3 ^b	2324 ^c	2642 ^c	411 ^c	520 ^d	587 ^a	564 ^a
Ash 2.4 g		4.6 ^b	4.8 ^b	125 ^b	124 ^b	10.0 ^d	8.1 ^e	2006 ^b	2223 ^b	131 ^a	147 ^b	632 ^b	577 ^a
Slag 2.4 g		5.0 ^c	5.1 ^c	138 ^c	145 ^d	5.6 ^c	4.5 ^c	2163 ^c	2538 ^c	217 ^b	265 ^c	605 ^{ab}	574 ^a

read from the line. After 16 months incubation the following increases in $\text{pH}(\text{CaCl}_2)$ and lime equivalents were found:

	Muddy fine sand		Fine sand	
	Increase in $\text{pH}(\text{CaCl}_2)$	Equivalent lime g	Increase in $\text{pH}(\text{CaCl}_2)$	Equivalent lime g
Dolomite	1.5	1.6	1.1	1.8
Ash	0.3	0.3	0.2	0.4
Slag	0.8	0.8	0.6	0.8

For equal increases in $\text{pH}(\text{CaCl}_2)$ on both soils the amount of dolomite needed was about 40 % higher than the amount of lime, the amount of ash about sevenfold the amount of lime and the amount of slag about threefold the amount of lime.

When the amount of acid neutralized by lime (as Ca, %), the neutralizing ability ($\text{Ca} + 1.65 \times \text{Mg}$, %) and the 1 M HCl soluble Ca content (Ca, %) of the lime are each indicated by 100, the respective properties of the other liming agents obtained are the values given below. The increases in $\text{pH}(\text{CaCl}_2)$ obtained with 2.4 g of liming agents are shown in columns 4 and 5.

	Acid neutral. as Ca, %	Soluble in 1 M HCl		Increases in $\text{pH}(\text{CaCl}_2)$	
		$\text{Ca} + 1.65 \times \text{Mg}$ %	Ca %	Muddy fine sand	Fine sand
Lime	100	100	100	2.0	1.4
Dolomite	94	94	50	1.5	1.1
Ash	24	16	15	0.3	0.2
Slag	79	77	56	0.8	0.6

In this comparison it was assumed that after 16 months incubation all the lime applied would be reacted in the soil. The difference between the values determined in the laboratory and measured in the experiment was largest for slag. Evidently the amount of Ca soluble in 1 M HCl is a better measure of the neutralizing ability of the slag than are the other properties analyzed. All three methods gave equivalent information for the ash. The differences for dolomite and lime are similar to those obtained in earlier studies (JAAKKOLA and JOKINEN 1980, JOKINEN 1982).

The ECEC was highest in soils treated with 2.4 g of lime (Table 3). After 16 months the increase in ECEC brought about by 2.4 g of dolomite was equivalent to 1.4 g of lime. The corresponding results for ash and slag were 0.3 and 0.75 g, respectively. These values are the means of the two soils, since there were no differences between them. In muddy fine sand there seemed to be a slight increase in ECEC between 4 and 16 months incubation when the soil was treated with dolomite or slag. This may point to a slower dissolution of these liming agents than of lime and ash.

At the end of the incubation the 1 M KCl extractable (Al+H) content of the soils treated with 2.4 g slag was equivalent to 0.9 g of lime, with dolomite equivalent to 1.6 g lime and with ash equivalent to 0.4 g lime. The proportion of Al to the (Al+H) was in unlimed muddy fine sand about 6 % and in unlimed fine sand about 5 %. In the limed soils the proportion of Al varied from 0.7 % (lime 2.4 g) to 5.2 % (ash 2.4 g).

The efficiency of dolomite, ash and slag as liming agents relative to lime, measured on the basis of ECEC and of 1 M KCl extractable (Al+H), corroborates the evaluation made on the basis of pH(CaCl₂).

In comparison with the original condition, the pH(CaCl₂) of unlimed soils was decreased and the content of (Al+H) increased during the incubation. Further the conductivity in incubated muddy fine sand was 5.5 μ S and in fine sand 6.5 μ S; in the original soils the conductivities were 0.8 μ S, and 0.5 μ S, respectively. All these changes in soil properties were attributable to the nutrient treatments.

The exchangeable Ca content of the soils when treated with 2.4 g of slag was the same as with 0.6 g lime (Table 3). On muddy fine sand the ash had no significant effect on the Ca content, and on fine sand the Ca content was a little higher than without liming. Dolomite gave the same exchangeable Ca contents as 0.6 g lime.

At the most, 14 % of the 1 M HCl soluble Ca added in lime to the muddy fine sand was non-exchangeable at the end of the experiment (Table 4). The corresponding result for the fine sand was 23 %. On both soils the proportion of the non-exchangeable Ca of that added in dolomite, ash and slag was

Table 4. The amounts of 1 M HCl soluble Ca and Mg (mg/kg soil) added with liming agents and the proportion (%) of the non-exchangeable (pH 7) cations in the soil out of the added at the end of the incubation experiment.

Limings		Calcium			Magnesium		
		Added mg/kg	Non-exchange- able (pH 7) mg/kg	%	Added mg/kg	Non-exchange- able (pH 7) mg/kg	%
<i>Muddy fine sand</i>							
Lime	0.6 g	569	15	3 ^a	17	6	35 ^a
Lime	1.2 g	1139	24	2 ^a	34	18	52 ^{bc}
Lime	2.4 g	2277	311	14 ^b	65	54	83 ^d
Dolomite	2.4 g	1145	485	42 ^d	662	301	45 ^{ab}
Ash	2.4 g	338	91	27 ^c	32	16	50 ^{ab}
Slag	2.4 g	1268	749	59 ^e	342	220	64 ^c
<i>Fine sand</i>							
Lime	0.6 g	617	104	17 ^a	18	20	111 ^d
Lime	1.2 g	1233	175	14 ^a	37	34	92 ^c
Lime	2.4 g	2467	575	23 ^a	73	67	92 ^c
Dolomite	2.4 g	1240	641	52 ^b	717	338	47 ^a
Ash	2.4 g	367	187	51 ^b	35	29	83 ^c
Slag	2.4 g	1373	878	64 ^b	370	246	67 ^b

significantly higher than in lime. Over 60 % of the 1 M HCl soluble Ca of slag was non-exchangeable after 16 months incubation.

Equal amounts of 1 M HCl soluble Mg were added in 2.4 g ash and 1.2 g lime. At the end of incubation the exchangeable magnesium content of these treatments did not deviate significantly (Table 3). The exchangeable magnesium content of soils limed with slag was lower than of soils limed with dolomite, since the amount of 1 M HCl soluble magnesium added was about 50 % of the magnesium added in dolomite.

The increasing amount of lime (containing 1.1 % Mg) had no significant effect on the exchangeable Mg content of the soils. The fixation of Mg to non-exchangeable form was not observed in this incubation experiment. The 0.01 M CaCl₂ extractable Mg decreased with increasing amounts of lime (results not presented).

After four months incubation about 58 % of the Mg applied in dolomite was non-exchangeable and after 16 months about 46 % (Table 4). The corresponding figures for slag were 71 and 65 %. In relative terms the release of Mg from slag was less than from dolomite. The release of Mg took place during the whole experimental period but was slower in the period between 4 and 16 months.

The exchangeable (pH 7) K content of the soils decreased with increasing amounts of lime as a result of the fixation to non-exchangeable (Table 3). The K applied in slag and ash maintained the K content of the soils at that level of unlimed soils, or these liming agents did not promote the fixation of K into non-exchangeable form.

Pot experiment

The treatments with 24 g of lime, dolomite, ash or slag did not cause any significant differences in the yields of turnip rape harvested at the flowering stage (Table 5).

Relative to the unlimed control slag and ash had no effect on the Ca content of the turnip rape in either year (Table 5). Dolomite was as effective as lime in increasing the Ca content of yields, except in the fine sand in the second growing season.

The K applied in slag or ash did not cause any changes in the K content of turnip rape (results not presented).

The highest Mg content of turnip rape was obtained with dolomite and the lowest with lime in both growing seasons (Table 5). Relative to the unlimed control the Mg content of plants produced with slag was significantly higher; liming with ash had no effect on the Mg content of turnip rape.

On both soils the Ca uptake by turnip rape (total in two years) was almost the same with dolomite and slag (Table 6). All liming agents studied increased the Ca uptake by turnip rape but most of all lime. The apparent recovery of the Ca applied in dolomite and slag was lower than in lime and ash.

The total amount of Mg taken up by turnip rape was the same without

Table 5. The yields of turnip rape at the flowering stage (g/pot), and the total contents of Ca and Mg (mg/g dry matter) in plant material obtained without liming and with four liming agents in first and second growing seasons.

	Yield g/pot		Ca mg/g		Mg mg/g	
	1st	2nd	1st	2nd	1st	2nd
<i>Muddy fine sand</i>						
No liming	33.4 ^a	19.7 ^a	16.2 ^a	16.3 ^{ab}	2.2 ^{ab}	2.7 ^b
Lime	41.0 ^a	23.3 ^a	27.2 ^b	22.1 ^c	1.6 ^a	2.0 ^a
Dolomite	32.4 ^a	19.0 ^a	21.7 ^{ab}	20.1 ^{bc}	3.8 ^c	4.9 ^d
Ash	36.6 ^a	22.5 ^a	17.4 ^a	14.1 ^a	2.1 ^{ab}	2.2 ^a
Slag	36.0 ^a	24.8 ^a	17.9 ^a	15.5 ^a	2.5 ^b	3.1 ^c
<i>Fine sand</i>						
No liming	30.9 ^a	28.1 ^a	19.7 ^a	14.0 ^a	1.6 ^{ab}	1.6 ^a
Lime	35.6 ^a	31.0 ^a	28.8 ^b	18.5 ^b	1.3 ^a	1.4 ^a
Dolomite	34.0 ^a	30.7 ^a	22.3 ^{ab}	14.3 ^a	2.9 ^c	3.3 ^c
Ash	36.9 ^a	30.4 ^a	18.2 ^a	14.9 ^a	1.4 ^a	1.6 ^a
Slag	32.2 ^a	32.4 ^a	21.3 ^a	15.4 ^a	1.9 ^b	2.3 ^b

liming and with lime or ash (Table 6). Turnip rape was not able to utilize Mg applied in these liming agents. The apparent recovery of Mg from dolomite and slag amounted to 3–4 %. The increases in Mg uptake due to slag and dolomite were significant.

The exchangeable (pH 7) Ca content was highest in the soils treated with lime because of the great amount of Ca added in this material (Table 6). Though dolomite contained a lesser amount of 1 M HCl soluble Ca than slag, the exchangeable Ca content of the soils treated with dolomite was significantly higher.

Neither lime nor ash had any effect on the exchangeable Mg content of the soils (Table 6). The amount of 1 M HCl soluble Mg added to the soils in slag was about 50 % of the amount added in dolomite. The increase in exchangeable Mg content of the soil was with slag about 30 % of the increase obtained with dolomite.

In the pot experiment about 13 % of the Ca added in lime was not found in the yields or in exchangeable form in the soil (Table 6). The corresponding result for dolomite was about 40 %, for ash about 45 %, and for slag about 65 %. About 43 % of the Mg applied in dolomite, 67 % of that added with slag and 75 % of that added with ash were not in the yields or in exchangeable form in the soils.

At the termination of the pot experiment the pH(CaCl₂) of the soils was almost the same as in the incubation experiment. The greatest increase in pH(CaCl₂) was measured in the soils treated with lime and the increase diminished in the order dolomite > slag > ash (Table 7). The effect of liming agents on the pH(CaCl₂) was weaker on fine sand soil rich in organic carbon than in muddy fine sand.

The ECEC of muddy fine sand did not change upon application of peat ash (Table 7). With other liming agents the increases in ECEC were analogous to the increases in pH(CaCl₂) on both soils.

Table 6. The amounts of Ca and Mg (mg/kg soil) applied with liming agents, the total Ca or Mg uptake (mg/kg soil) by turnip rape, the exchangeable (pH 7) Ca and Mg contents (mg/kg soil) of the soils and the proportion (%) of added Ca or Mg not found in the yields or exchangeable in the soils (=non-exchangeable) at the end of the pot experiment.

	Calcium				Magnesium			
	Added in liming agents	Uptake by turnip rape	Ex- change- able (pH 7)	Non- ex- change- able	Added in liming agents	Uptake by turnip rape	Ex- change- able (pH 7)	Non- ex- change- able
	mg/kg soil			%	mg/kg soil			%
<i>Muddy fine sand</i>								
No liming		215 ^a	916 ^a			32 ^a	125 ^a	
Lime	2277	415 ^c	2661 ^c	15 ^a	65	28 ^a	133 ^a	95 ^c
Dolomite	1145	265 ^b	1542 ^d	41 ^b	662	54 ^c	478 ^c	43 ^a
Ash	338	241 ^{ab}	1073 ^b	46 ^b	32	31 ^a	135 ^a	71 ^b
Slag	1268	263 ^b	1295 ^c	66 ^c	342	43 ^b	226 ^b	67 ^b
<i>Fine sand</i>								
No liming		278 ^a	1705 ^a			26 ^a	98 ^a	
Lime	2467	432 ^c	3737 ^e	11 ^a	73	24 ^a	115 ^b	79 ^c
Dolomite	1240	321 ^b	2390 ^d	41 ^b	717	55 ^b	492 ^b	41 ^a
Ash	367	310 ^b	1880 ^b	43 ^b	35	27 ^a	106 ^{ab}	76 ^{bc}
Slag	1373	326 ^b	2152 ^c	64 ^c	370	37 ^{ab}	208 ^c	67 ^b

Table 7. The pH(CaCl₂), ECEC (me/kg soil) and 1 M KCl extractable (Al+H) content (me/kg soil) of the soils without liming and with four liming agents at the end of the pot experiment.

	Muddy fine sand			Fine sand		
	pH(CaCl ₂)	ECEC	(Al+H)	pH(CaCl ₂)	ECEC	(Al+H)
	me/kg soil			me/kg soil		
No liming	4.3 ^a	71 ^a	18.0 ^c	4.6 ^a	98 ^a	12.5 ^c
Lime	6.6 ^e	128 ^d	1.7 ^a	6.1 ^e	170 ^e	2.7 ^a
Dolomite	6.1 ^d	111 ^c	2.8 ^a	5.7 ^d	148 ^d	3.5 ^b
Ash	4.7 ^b	71 ^a	12.0 ^{bc}	4.8 ^b	103 ^b	8.8 ^d
Slag	5.3 ^c	88 ^b	5.0 ^{ab}	5.2 ^c	119 ^c	4.9 ^c

Discussion

In slag the Ca content, indicating the amount of acid neutralized, was about 79 % of the content in lime and about 84 % of the content in dolomite. In both the incubation and pot experiments the increases in pH(CaCl₂) obtained with slag were lower than expected on the basis of the laboratory analysis. The content of Ca + 1.65×Mg soluble in 1 M HCl did not give a better estimate for the neutralizing capacity of slag. The methods applied in Finland to carbonatic limestones, when applied to slag, would appear to lead

to an overestimation of its properties. The amount of Ca soluble in 1 M HCl may be a better indicator than the amount of Ca + 1.65×Mg or the amount of acid neutralized, though not a good one. Certainly the properties of slag as liming agent should be determined by other methods than are the properties of carbonatic limestones. TORSTENSON and ALVELID (1952) have proposed the use of 0.1 M or 0.05 M HCl.

After an experimental period of 16 months about 65 % of the 1 M HCl soluble Ca or Mg added in slag was neither in the yields nor in exchangeable form in the soils. The corresponding figure for lime was about 15 % and for dolomite about 35 %. The release of Ca and Mg from slag was very slow in both the pot and incubation experiments and it may be even slower in the field.

If we assume that the decomposition of slag will continue in the soil at the rate observed in the pot experiment, the whole amount of added slag (24 g/pot) may be decomposed after 40 months. However, NAUMANN (1939) found that in the soil a colloidal layer of silicic acid, amorphous oxides and hydroxides forms on the surface of the slag particles, causing the decomposition of slag to become slower and slower. Therefore the long-term effect of slag in the soil may fall short of expectation.

For this study the slag was ground to a fineness such that 98 % passed through 1-mm sieve, and the main fraction 0.125–0.250 mm comprised 51 %. In Finland the regulation is applied that 50 % of limestone should pass through 0.15-mm sieve and 98 % a 2-mm sieve. The fraction below 0.3 mm may comprise 70 % (JAAKKOLA and JOKINEN 1980). The slag of this study was ground near the same fineness than the two limestones. KAPPEN (1933), BUCHER (1951) and CHICHILO et al. (1954) studied slag and lime both ground to the same fineness. They observed slag to neutralize the soil acidity to a lesser degree than lime, when the amounts of agent added were such as to have equal neutralizing ability. JAAKKOLA (1979) in Finland obtained in field and pot experiments equivalent results to these. So far as the neutralizing ability of slag is concerned, our results are in good agreement as well.

The amount of slag recommended for agriculture should be at least threefold the amount of lime required, if equal increases in pH(CaCl₂) are to be obtained.

The proportion of non-exchangeable Ca and Mg of that applied in slag was alike for both nutrients, revealing that there were no differences in the release of Ca and Mg from the fine ground slag.

The ability of ash to neutralize the soil was low. At the same time turnip rape was able to take up a greater percentage of the Ca applied in ash than of Ca applied in slag. The availability of Mg in ash for turnip rape was considered non-existent and the proportion of non-exchangeable Mg in the soil remained high.

In this study the exchangeable Mg content of the soils gave no evidence of the fixation of Mg to non-exchangeable form when lime was used. In earlier studies (e.g. KAILA 1974, JOKINEN 1981, JOKINEN 1982) such was observed. However, in comparison with the unlimed control the decreased Mg content and Mg uptake by turnip rape and 0.01 M CaCl₂ extractable Mg content of

the soils indicated that the available Mg resources in the soil for this plant were indeed reduced, even though the lime contained Mg.

Acknowledgements: The financial support received from the Foundation for Research of Kemira Oy is gratefully acknowledged. Rautaruukki Oy provided the basic slag and the City of Kuopio (Haapaniemi Power Plant) the peat ash for this study.

References

- BROWN, G. G. & THATCER, K. F. J. 1967. The production and properties of basic slag. *Proc. Fert. Soc.* 96: 1-47.
- BUCHER, R. 1951. Die Wirkung von grobem und feinem Hüttenkalk (Hochofenschlacke) auf Boden und Pflanzenertrag. *Z. Pflanzenern. Düng. Bodenk.* 53: 121-143.
- CHICHILO, P. P., ARMIGER, W. H., SPECHT, A. W. & WHITTAKER, C. W. 1954. Plant nutrients from slag. Furnace slag as a source of plant nutrients and its effectiveness relative to limestone. *J. Agric. Food Chem.* 2: 458-462.
- JAAKKOLA, A. 1979. Kalkkikivijauheen, dolomiittikalkin ja masuunikuonan vertailu. *MTTK, Maanviljelyskemian ja -fysiikan laitos Tiedote* 10: 1-17.
- & JOKINEN, R. 1980. Comparison of fine and coarse limestones in pot and field experiments. *Ann. Agric. Fenn.* 19: 108-124.
- JOKINEN, R. 1981. Soil magnesium and fertilizer magnesium uptake by ryegrass on nine mineral soils at two ammonium nitrate levels II. Magnesium content of soils. *Ann. Agric. Fenn.* 20: 244-252.
- 1981. Effect of liming on the magnesium status of some mineral soils and the fate of fertilizer magnesium. *J. Scient. Agric. Soc. Finl.* 53: 126-137.
- 1982. Effect of liming on the value of magnesium sulphate and two dolomitic limestones as magnesium sources for ryegrass. *J. Scient. Agric. Soc. Finl.* 54: 77-88.
- KAILA, A. 1971. Effective cation-exchange capacity in Finnish soils. *J. Scient. Agric. Soc. Finl.* 43: 178-186.
- 1974. Effect of liming on basic exchangeable cations of soil. *J. Scient. Agric. Soc. Finl.* 46: 167-174.
- KAPPEN, H. 1933. Die landwirtschaftliche Verwendbarkeit der Hochofenschlacken. *Arch. Pflanzenbau* 10: 87-128.
- NAUMANN, G. 1939. Über die Zersetzung von Eisenhochofenschlacken. *Bodenk. Pflanzenern.* 15: 74-126.
- NORRMAN, G. 1978. Slagger som kalkningsmedel. *Nord. Jordbr.forskn.* 60: 710-711.
- SCHARRER, K. & MUNK, H. 1956. Zur Methodik der nassen Veraschung in der agrilkulturchemischen Analyse. *Agrochimica* 1: 44-55.
- STEEL, R. G. D. & TORRIE, J. H. 1960. Principles and procedures of statistics. 481 p. New York.
- TORSTENSSON, G. & ALVELID, D. S. 1952. Om användning av masunslagg som kalkningsmedel i jordbruket. *Kung. Lantbr.akad. Tidsskrift* 91: 57-75.

Dolomiittikalkki, masuunikuona ja turpeen tuhka kalkitusaineina sekä kevätrypsin kalsiumin ja magnesiumin lähteinä

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Dolomiittikalkin, masuunikuonan ja turpeen tuhkan arvoa maan happamuutta neutraloivana aineena verrattiin kalkkikivijauheeseen sekä eri kalkitusaineiden vaikutusta maan vaihtuvan (pH 7) kalsiumin, magnesiumin ja kaliumin pitoisuuteen tutkittiin muhitus- ja astiakokeissa. Kevätrypsin (*Brassica campestris* v. *oleifera* f. *annua*; lajike Candle) kykyä käyttää hyväkseen eri kalkitusaineissa tulevaa kalsiumia ja magnesiumia selvitettiin astiakokeessa.

Kalkkikivijauhe ja dolomiittikalkki 2 olivat normaaleja kaupan olevia tuotteita. Turpeen tuhka saatiin Kuopion kaupungin Haapaniemen voimalasta. Tämän ns. arinatuhkan hiekkapitoisuus oli korkea. Rautaruukki Oy:stä saatu masuunikuona oli jäädytetty vedellä ja jauhettu niin, että 98 % läpäisi 1 mm seulan. Laboratoriossa määritettiin

- 1) kalkitusaineiden neutraloiman hapon määrä (milliekvivalentteina), joka kalsiumiksi muunnettuna ilmoittaa ekvivalenttisen kalsiumpitoisuuden (Ca, %)
- 2) 1 M HCl liukenevan kalsiumin määrä (Ca, %)
- 3) 1 M HCl liukenevan kalsiumin ja magnesiumin määrät, joiden perusteella laskettiin kaavan $Ca + 1,65xMg$ mukainen kalkitusaineiden neutraloiva kyky (%)

Kalkitusaineiden ominaisuudet on esitetty taulukossa 2.

Tutkimuksen kokeet toteutettiin kahdella happamalla maalla, liejuisella hienolla hiedalla ja karkealla hiedalla; kummankin pH(CaCl₂) 4,8. Muhituskokeessa 390 grammaan liejuista hienoa hietaa tai 360 g karkeaa hietaa lisättiin 0,6 g, 1,2 g tai 2,4 g kalkkikivijauhetta, 2,4 g dolomiittikalkkia, 2,4 g turpeen tuhkaa tai 2,4 g masuunikuonaa sekä 1/10 astiakokeeseen annettujen ravinteiden (N, P, K, B, Cu, Mn, Zn, Mo) määrästä. Kalkitsemattomiin verrannemaihin lisättiin vain ravinteet. Maiden kosteus pidettiin 25 % ilmakuivan maan painosta koko muhituksen ajan (16 kuukautta). Kasvukausien aikana astiat olivat ulkona, mutta valolta suojattuina ja talvella +5 °C vakiolämpötilassa.

Kaksi kasvukautta jatkunutta astiakoetta varten punnittiin Mitscherlich-astioihin 3,9 kg liejuista hienoa hietaa tai 3,6 kg karkeaa hietaa ja maihin sekoitettiin 24 g kalkkikivijauhetta, dolomiittikalkkia, turpeen tuhkaa tai masuunikuonaa. Kokeeseen kuului myös kalkitsemattomat verranne astiat kumpaakin maata. Välittömästi kalkituksen jälkeen maihin lisättiin ravinteita astiakokeisiin riittäviksi osoittautuneet määrät. Kevätrypsi kylvettiin aluksi tiheäksi kasvustoksi ja harvennettiin taimelle tulon jälkeen yhdeksäksi yksilöksi. Sato korjattiin kukintavaiheessa.

Kalkitusaineiden maan happamuutta neutraloivaa kykyä verrattiin pH(CaCl₂):n, efektiivisen kationinvaihtokapasiteetin ja 1 M KCl uuttuvan (Al+H) pitoisuuden perusteella. Muhituskokeessa 2,4 g dolomiittikalkkia, turpeen tuhkaa tai masuunikuonaa olivat saman arvoisia kuin vastaavasti 1,7 g, 0,4 g tai 0,8 g kalkkikivijauhetta. Samalla määrällä (2,4 g) eri kalkitusaineita saadut pH(CaCl₂)-luvun muutokset kalkitsemattomaan verrattuna olivat liejuisessa hienossa hiedassa ja karkeassa hiedassa seuraavat:

	Kalkki- kivijauhe	Dolomiitti- kalkki	Turpeen tuhka	Masuuni- kuona
IjHHT	2,0	1,5	0,3	0,8
KHt	1,4	1,1	0,2	0,6

Mikäli eri kalkitusaineilla halutaan saada yhtä suuri $\text{pH}(\text{CaCl}_2)$:n muutos, dolomiittikalkkia tulisi käyttää noin 1,4 kertaa, turpeen tuhkaa noin 7 kertaa ja masuunikuonaa noin 3 kertaa niin suuri määrä kuin kalkkikivijauhetta.

Astiakokeessa kevätrypsin sadot sisälsivät vain muutamia prosentteja kalkitusaineina lisätystä kalsiumista tai magnesiumista. Satojen ottaman ja maassa kokeen lopussa vaihtuvana (pH 7) olevan ravinnemäärän summa osoittaa näillä menetelmillä analysoitavissa olleita kalsiumin määriä. Kun kalkitusaineiden mukana maahan lisätystä ravinnemäärästä vähennetään analyyseissä löydettyt määrät, jäännös osoittaa uuttumattomaksi maahan jääneitä määriä. Kalkkikivijauheen sisältämästä kalsiumista oli uuttumattomana keskimäärin 13 %, dolomiittikalkin kalsiumista 41 %, turpeen tuhkan 45 % ja masuunikuonan 65 %. Lisätystä magnesiumista oli uuttumattomana 42 % dolomiittikalkilla, 74 % turpeen tuhalla ja 67 % masuunikuonalla käsitellyissä maissa.

Kalkkikivijauheiden ja dolomiittikalkkien neutraloivaa kykyä osoittavien menetelmien käyttö masuunikuonan ominaisuuksien analysoimiseen antaa masuunikuonasta liian edullisen kuvan. Sen vuoksi masuunikuonan arvo kalkitusaineena tulisi osoittaa jollakin muulla paremmin tarkoitukseen sopivalla menetelmällä.