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ORIGINAL SCIENTIFIC PAPER

Changes of the main parameters of soil fertility as influenced by metallurgical slag application

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Abstract

The aim of this research was to investigate the effect of Ca - containing metallurgical slag, taken from different deposition sites of Steel factory – Smederevo, Serbia, on the changes of basic chemical characteristics and granulometric composition of Pseudogley, a type of soil with very acid reaction. The obtained results imposed that metallurgical slag showed positive effects on the main chemical properties of the study soil comparing to non-fertilized one, which could not be said for the soil granulometric composition, possibly due to a short time period before analyses. Generaly, it was concluded that the studied metallurgical slag of the standardized chemical composition can be added to the acid soils toward amelioration the fertility without adverse effects.

Key words: metallurgical slag, liming, chemical properties, granulometric composition, Pseudogley

Introduction

The majority of Serbian soils is characterized by high soil acidity and application of only organic and mineral fertilizer is not enough to sustain their productivity. Thus, on these soils it is necessary to apply Ca-containing fertilizers – calcifiers, for improving their physico-chemical and biological properties. The application of traditional alkaline liming materials for the amelioration of soil acidity consequently improving crop production and it's a common practice (Foth and Ellis, 1997). However, the alkaline nature and the need for sustainable and environmentally acceptable disposal options for metallurgical slag (Lopez et al., 1995) have prompted its use as a liming material on acid agricultural soils. The slag consists primarily of calcium silicate minerals, and has nearly the same ability to neutralize soil acidity as agricultural limestone. Therefore, it is particularly important to develop new technologies to utilize metallurgical slag as resource materials in order to decrease the land used for disposal of slag and reducing environmental pollution.

Along with other lime materials (ground slag stone, saturated slag etc.) present in Serbia, metallurgical slag from Steel factory - Smederevo (Serbia) can be of great importance. Thus, these investigations were aimed to define the main parameters for possible wider usage of this secondary raw materials for amelioration and fertilization of acid soils in Serbia.

Material and methods

The study was carried out in pot experiments, under semi-controlled condition in the greenhouse of the Institute of Soil Science, Belgrade, from April to July, during 2009. In the experiments the comparisons of the effect of metallurgical slag with other lime materials (ground limestone and hydrated lime) in combination without and with standard fertilizers (organic and mineral) were studied. The experiment was undertaken with Pseudogley, a type of soil from central Serbia region that has very low pH. The designed experiments were in three replications: 1. Control – no fertilizer (**T1**); 2. NPK mineral fertilizer [composite NPK (15:15:15)] + manure – standard fertilization (**T2**); 3. $CaCO_3$, no standard fertilization (**T3**); 4. $Ca(OH)_2$, no standard fertilization

(**T4**); 5. Metallurgical slag, no standard fertilization (**T5**); 6. NPK mineral fertilizer [composite NPK (15:15:15)] + manure + $CaCO_3$ (**T6**); 7. NPK mineral fertilizer [composite NPK (15:15:15)] + manure + $Ca(OH)_2$ (**T7**); 8. NPK mineral fertilizer [composite NPK (15:15:15)] + manure + metallurgical slag (**T8**). The experiment was performed in plastic pots with 4 kg of homogenized soils. Spring barley was chosen as an experimental crop due to its good response to neutralization of soil acidity. Before planting the barley, the amount of fertilizers and slag was measured according to the experiment design and mixed with soil (calculated as for 1 ha): NPK – 15:15:15 = 500 kg ha^{-1}; Manure = 30 t ha^{-1}; $CaCO_3$ = 4 t ha^{-1}; $Ca(OH)_2$ = 2,8 t ha^{-1}; Metallurgical slag = 4 t ha^{-1} (same as the amount of $CaCO_3$, in spite of lower amount of slag). All three lime materials with granulation of 0.2 mm were applied in the experiment.

Before industrial homogenizing and standard grinding the chemical composition of five composite samples of metallurgical slag used from different deposition sites was analyzed. Soils from all the fertilization treatments were analyzed for their basic chemical properties and granulometric composition at the beginning of experiment and at the end of vegetation period.

Chemical properties of the study soil were determined using the following chemical analyses: pH in water and 1M KCl was analyzed potentiometrically with glass electrode (SRPS ISO, 2007); total N was analyzed on elemental CNS analyzer Vario EL III (Nelson and Sommers, 1996); available P_2O_5 and K_2O were analyzed by Al-method according to Egner-Riehm (Riehm, 1958)], where K was determined by flame emission photometry and P by spectrophotometer after color development with ammonium molybdate and $SnCl_2$; Ca and Mg were extracted by ammonium acetate followed by determination on atomic adsorption analyzer SensAA Dual (GBC Scientific Equipment Pty Ltd, Victoria, Australia) (Wright and Stuczynski, 1996); microelements (Fe, Mn, Zn, Cu) were determined with an ICAP 6300 ICP optical emission spectrometer, after the samples were digested with concentrated HNO_3 for extraction of total forms, and by DTPA for extraction of soluble forms of the elements (Soltanpour et al., 1996); the total content of $CaCO_3$ in slag studied was determined using the "rapid titration method" by Piper (van Reeuwijk, 2002).

Soil granulimetric composition was analyzed by determination of particle size distribution in mineral soil material, using the standardized method by sieving and sedimentation (ISO, 2009).

Statistical analyses were performed using SPSS/SYSTAT - 16 software. The effects of treatments on all the variables were tested using ANOVA method. In certain tables below (3, 4 and 5), NSD indicates no significant difference at the P=0.05 level of significance whereas *, ** and *** indicates statistical significant differences at the P<0.05, P<0.01 and P<0.001 levels, respectively. LSD indicates least significant differences.

Results and discussion

The results of the laboratory investigations of properties and composition of metallurgical slag studied (Table 1) showed that this material has very alkaline reaction (pH = 12.50), with the content of Ca in oxide forms (CaO) from 33-45 %, of which about 50 % is easily soluble (in 1 M ammonium acetate). Content of total magnesium is about 0.40 % that was mainly in forms of MgO (0.70 %). Total phosphorous contained in the material is about 0.60 % where nearly all the amount was in plant available forms. Content of total iron is expectedly high enough (about 150 000 mg kg^{-1}), while the amount of readily available forms is only 3.38 mg kg^{-1}. The third element (along with Ca and Fe) is Mn, with total amount about 18 000 mg kg^{-1}, but with low (insignificant) amounts of soluble forms. The studied metallurgical slag contains lower amounts of zinc and a little higher amount of Cu (about 2 000 000 mg kg^{-1}).

According to previous studies (Yusiharni et al., 2007), metallurgical slag stone (ground steel slag) contains 22-38 % CaO and 3,5-6,5 % MgO. Oxides of calcium and magnesium are partially free, and partially bound to carbonates and silicate that are easily hydrolyzed. Upon the neutralization rate this slag stone material is classified between burned (oxide) slag and ground slag stone (calcium carbonate). Together with Ca and Mg the major part of Si (7-15 % as SiO_2), especially free Si acids, can have influence on increasing of SiO_2:R_2O_3 ratio (sesquioxide of Al and Fe) in soil, what reduces the phytotoxic effects of soluble Al and Fe on crops. Besides above mentioned positive effects of Ca, Mg and Si, content of citrate-soluble phosphorus that varies between 0.5-2 % P_2O_5 and other biogenic and microelements in smaller amounts improves its fertilization benefits compared to the other slag materials that are applied for soil neutralization.

Table 1. Properties and composition of metallurgical slag (means ± standard deviation)

Property	Value	Property	Value
pH in H_2O	12.48±0.04	Total P_2O_5 (%)	0.61±0.10
Total Ca (%)	26.20±3.48	Total Fe (mg kg^{-1})	153400±7900
Total CaO (%)	36.60±4.83	Available Fe (in DTPA, mg kg^{-1})	3.38±0.96
Total $CaCO_3$ (%)	65.80±8.64	Total Mn (mg kg^{-1})	18000±1500
Available Ca (%)	17.18±1.98	Available Mn (in DTPA, mg kg^{-1})	3.12±1.04
Total Mg (%)	0.41±0.04	Total Zn (mg kg^{-1})	146000±55900
Available Mg (%)	0.07±0.02	Total Cu (mg kg^{-1})	2288000±154000

All above mentioned benefits of metallurgical slag confirm the fact that for the past years the production and application of this material in agricultural areas has increased in many developed countries. In several researches an increase of pH, exchangeable Ca and Mg and decrease of mobile Al in acid soils by using different doses of metallurgical slag was reported (Rodriguez et al., 1994).

In Table 2 the results of soil physical and chemical properties before the experiment was established are given.

Table 2. Physical and chemical properties of Pseudogley before the experiment was established

Granulometric composition	Value (means ± standard deviation)
Bulky sand, 2-0.2 mm	5.0±0.59
Miniature sand, 0.2-0.02 mm	25.9±1.33
Dust, 0.02-0.002 mm	45.1±1.22
Clay, < 0.002 mm	24.0±0.21
Total sand, > 0.02 mm	30.9±1.05
Dust + clay, < 0.02 mm	69.1±1.05
Chemical properties and elementary composition	**Value (means ± standard deviation)**
pH in H_2O	5.48±0.01
pH in 1M KCl	4.45±0.01
Total N (%)	0.24±0.01
Available P_2O_5 (mg $100g^{-1}$)	3.73±0.28
Available K_2O (mg $100g^{-1}$)	19.8±1.54
Available Ca (mg $100g^{-1}$)	240±19
Available Mg (mg $100g^{-1}$)	35±3.89

The results shows that the study soil is medium heavy by mechanical properties, with total technical clay fraction about 69% and colloidal clay fraction of 24%.

The optimum pH range for growth of most crops in soil is between 5.5 and 7.0, within which most plant nutritives are available (Prasad and Power, 1997). The studied Pseudogley had very acid soil reaction, with pH in KCl 4.45, then, low content of readily available phosphorus and soluble calcium and is well supplied with available potassium. Content of available Mg is generally within the range of optimal supply.

Experiments in several European countries have demonstrated the ability of metallurgical slag to raise the pH of acid soils, increasing at the same time the Ca and Mg contents of the soils exchange complex (Adriano, 2001), and it has been shown that the slag modified the physical and chemical properties of the soil and lead to an increase in production of between 15 and 40% when 1.6 t ha^{-1} of metallurgical slag was applied to soils with pH values of 4-5.
The effect of the applied treatments on the changes of soil chemical properties is presented in Table 3.

Table 3. Effect of metallurgical slag and selected lime materials on the changes of soil acidity and content of available macroelements (means ± standard deviation)

Treatment	pH		Available biogenic macroelements (mg kg^{-1})			
	H_2O	1M KCl	P_2O_5	K_2O	Ca	Mg
T1	5.31±0.01	4.46±0.01	2.63±0.33	11.82±1.64	214.67±18.90	35.03±3.92
T2	5.35±0.03	4.67±0.03	5.55±1.20	19.93±2.85	215.00±8.54	35.60±2.52
T3	6.05±0.04	5.41±0.04	3.23±0.67	13.85±0.62	290.67±20.55	33.80±3.44
T4	5.96±0.06	5.35±0.14	2.86±0.80	12.36±1.46	265.67±5.51	29.17±3.40
T5	5.64±0.02	4.98±0.02	4.08±1.30	11.82±2.08	267.67±11.59	34.23±3.79
T6	5.81±0.02	5.35±0.11	6.93±0.80	23.17±2.04	323.33±19.43	38.00±0.85
T7	5.79±0.02	5.22±0.16	6.78±0.03	22.23±1.69	272.00±12.53	31.70±3.16
T8	5.67±0.01	4.93±0.02	8.29±1.05	21.96±2.07	260.33±10.97	34.67±1.42
P value	***	***	***	***	***	NSD
LSD (0.05)	0.05	0.15	1.50	3.46	25.02	5.20
LSD (0.01)	0.07	0.21	2.07	4.76	34.48	7.17

The results show *significant* decrease of soil acidity both comparing to the control and to the treatments with classical fertilization (NPK + manure). Regarding the content of the main available biogenic macroelements (P, K, Ca, Mg) after fertilization by lime materials, it could be noticed that all the fertilizers and lime materials resulted in increased availability of these elements. Application of slag materials, especially of metallurgical slag, resulted in increased amount of available phosphorous and magnesium comparing to the classical lime materials.

Table 4. Effect of metallurgical slag and selected lime materials on the changes of main soil physical properties (means ± standard deviation)

Treatment	Granulometric composition (mm)					
	Bulky sand 2-0.2	Miniature sand 0.2-0.02	Dust 0.02-0.002	Clay <0.002	Total sand >0.02	Dust+clay <0.02
T1	4.6±0.6	26.6±1.3	44.9±1.2	23.9±0.2	31.2±1.1	68.8±1.1
T2	4.9±0.7	25.7±0.8	45.1±0.5	24.3±1.8	30.7±1.4	69.3±1.4
T3	4.9±0.2	26.1±0.3	44.1±0.9	24.9±0.8	31.0±0.2	69.0±0.2
T4	4.8±0.7	26.9±1.4	45.2±0.2	23.8±0.8	31.1±0.9	68.9±0.9
T5	4.5±0.6	26.0±0.7	44.6±0.7	24.8±1.0	30.5±0.5	69.5±0.5
T6	4.9±0.5	25.8±0.8	44.5±0.7	24.8±1.0	30.7±0.3	69.3±0.3
T7	4.8±0.6	26.0±0.2	45.2±0.1	24.0±0.4	30.8±0.4	69.2±0.4
T8	4.9±0.7	26.6±1.3	44.3±1.1	24.2±1.1	31.5±0.7	68.5±0.7

The results of the granulometric composition of studied soil after the fertilization and application of lime materilas could not give an information about significant changes both of initial status and after application of lime materials (Table 4). Although the lime treated soils show generally a deep modification of the physical and mechanical properties (Russo et al., 2007), in this study the opposite effects are expected probably due to a short time period before analyses.

Conclusions

The results of the paper indicate that the studied metallurgical slag showed positive effects on basic chemical properties of pseudogley comparing to non-fertilized one, which could not be said for the soil granulometric composition, possibly due to a short time period before analyses. Generaly, it was estimated that the studied metallurgical slag of the standardized chemical composition can be added to the acid soils toward amelioration the fertility without adverse effects.

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