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THE USE OF METALLURGICAL SLAG AS A BY-PRODUCT OF THE STEEL INDUSTRY IN CHEMICAL MELIORATION OF ACID SOILS

Aleksandra Stanojković-Sebić*, Srboljub Maksimović, Dragana Jošić, Radmila Pivić

Institute of Soil Science, Teodora Drajzera 7, Belgrade, Serbia

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Abstract

The effect of metallurgical slag application on chemical properties of the soils with limited productive ability (Stagnosol), as well as on chemical composition of cultivated vegetables (spinach and cabbage) as experimental crops, through the vegetative experiments performed in semi-controlled conditions, was studied. The long-term investigations were aimed to define the main parameters for possible wider usage of this secondary raw material (by-product of the steel industry, respectively) for chemical melioration and fertilization of acid soils in Serbia, as well as to indicate the justification of its application in agricultural practice. Generally, 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.
Keywords: Metallurgical slag, raw industrial material, chemical melioration, Stagnosol

Introduction

In ferrous metallurgy, slags are usually by-products. They are secondary raw materials for the production of building materials (such as slag sitalls) and lime and phosphorus fertilizers; they are also used as a recycle in metallurgy.

In the iron and steel making process, a very large amount of metallurgical slag is generated. 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, reducing environmental pollution, and also promoting the continuous and highly efficient development of metallurgical industry not only in the World, but also in Serbia.

Although metallurgical slag has the largest quantitative share in the overall metallurgical waste [1], its physicochemical property offers a high potential for its utilization in agriculture. In addition, metallurgical slag contains CaO, SiO_2 and several complex minerals. There are also some trace elements such as zinc and copper. All of

* Corresponding author: Aleksandra Stanojković-Sebić, astanojkovic@yahoo.com

these components could promote the growth of crops [2]. Some slags may contain elevated concentrations of trace metals such as iron, cadmium, chromium, copper, lead, molybdenum, nickel and zinc. All of these metals occur naturally in soil, and many of them are essential plant nutrients. Although metallurgical slags contain varying concentrations of trace elements, the bioavailability of these metals is very low [3].

The alkaline nature and the need for sustainable and environmentally acceptable disposal options for metallurgical slag have also prompted its use as a liming material on acid agricultural soils [4]. Certain authors reported on field trials in Pennsylvania that crop yields of corn, wheat, oats, buckwheat and soybeans with metallurgical slag application were as good or better than an equivalent amount of limestone [5].

For normal soils maintaining and increasing of its productive ability is possible via optimal application of organic and mineral fertilizer. However, for the majority of Serbian soils, characterized by high soil acidity, application of only these fertilizers is not enough to sustain soil productivity. On these soils, along with regular fertilization, it is necessary to apply calcium containing fertilizers - calcifiers, for improving their physico-chemical and biological properties.

The use of traditional alkaline liming materials such as limestone, dolomite and burnt lime to acid soils for the amelioration of acidity consequently improving crop production is a common practice [6, 7]. Along with these materials present in Serbia, metallurgical slag from Steel factory - Smederevo (Serbia) can be of great importance.

Regarding the preceding comments, the main purpose of this research was to investigate the effect of calcium containing metallurgical slag, a by-product from Steel factory from Smederevo, Republic of Serbia, comparing to the effects of selected commercial lime materials and fertilizers, on chemical properties of the soils with limited productive ability (high acidity), as well as on chemical composition of the cultivated vegetables (spinach and cabbage) as experimental crops.

Experimental Procedure

The study was carried out in pot experiments, under semi-controlled condition in the greenhouse of the Institute of Soil Science, Belgrade, from the third decade of February to the beginning of June, during 2011. In the experiments the comparisons of the effect of metallurgical slag with other lime materials (ground limestone and hydrated lime) in combination with and without standard fertilizers (organic and mineral) were studied. The ground limestone (calcium carbonate or calcite, $CaCO_3$) contains 60% of carbonate. Hydrated lime (slaked lime, $Ca(OH)_2$) reacts very rapidly and has a TNV (Total Neutralizing Value) of 135, thus 740 kg of hydrated lime is equivalent to one ton of ground limestone i.e. the TNV = 135 [8].

The experiment was undertaken with Stagnosol [9], a type of soil from central Serbia region that has very low pH and poor physical and biological properties. The following designed experiments were in three replications: Control – no fertilizer (T1); NPK mineral fertilizer [composite NPK (15:15:15)] + manure – standard fertilization (T2); $CaCO_{3,}$ no standard fertilization (T3); $Ca(OH)_2$, no standard fertilization (T4); Metallurgical slag, no standard fertilization (T5); NPK mineral fertilizer [composite NPK (15:15:15)] + manure + $CaCO_3$ (T6); NPK mineral fertilizer [composite NPK (15:15:15)] + manure + $Ca(OH)_2$ (T7); 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.

Common spinach, *Spinacea oleracea*, and cabbage, *Brassica oleracea* var. *capitata*, were chosen as experimental crops. The spinach was grown from the third decade of February to the beginning of April, and the cabbage - from April to the beginning of June, both vegetables during 2011. Before planting the crops, 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. The analyses of the study soil were done before the experiment was established and after the crops biomass was taken.

The following chemical analyses were done: pH in water and 1M KCl was analyzed potentiometrically with glass electrode [10]; total N was analyzed on elemental CNS analyzer Vario EL III [11]; available P_2O_5 and K_2O were analyzed by Al-method according to Egner-Riehm [12], where K was determined by flame emission photometry and P by spectrophotometer; Ca and Mg were extracted by ammonium acetate followed by determination on atomic adsorption analyzer SensAA Dual, GBC Scientific Equipment Pty Ltd, Victoria, Australia [13]; determination of effective cation exchange capacity (CEC) and base saturation level was done by the standardized method using barium chloride solution [14]; trace elements were determined with an inductively coupled plasma optical emission spectrometer ICAP 6300 (ICP-OES), after the samples were digested with concentrated HNO_3 for extraction of total forms, and by DTPA (Diethylene Triamine Penta Acetic Acid) solution for extraction of soluble forms of the elements [15]; the total content of $CaCO_3$ in slag studied was determined using the “rapid titration method” by Piper [16].

The aboveground biomass of spinach and cabbage plants was taken and after drying at 105°C the plant biomass was weighed.

For all the plant samples from all the treatments the chemical composition of the aboveground biomass was analyzed. The contents of N, P and K were determined by so called “wet” combustion, i.e. they were heated to boiling with the mixture of concentrated acids: H_2SO_4 and $HClO_4$. In the obtained solution, N was determined by the method of alkaline distillation and titration, P - by spectrophotometer with molybdate, and K – by flame emission photometry [17]. In the determination of Ca, Mg, investigated trace biogenic elements (Fe, Zn, Cu) and Cd as the toxic heavy metal, plant material was converted to a solution by the so-called "dry" combustion, i.e., first by heating at 550ºC (for several hours) and then by treating the obtained ash with hydrochloric acid. These elements were determined by Atomic Absorption Spectrometry (AAS) [18].

Statistical analyses were performed using SPSS/SYSTAT - 16 software. The effects of treatments on all the variables were tested using ANOVA method.

Results and discussion

Properties and composition of metallurgical slag from Steel factory – Smederevo are shown inTable 1.

Results of laboratory investigations showed that this material has very alkaline reaction (pH =12.50), with the content of Ca in oxide forms (CaO) from 33 to 45 %, of which about 50 % is easily soluble (in 1 M ammonium acetate). Content of total Mg is about 0.40 %, which was mainly in forms of MgO (0.70 %). Total P contained in the material is about 0.60 %, where nearly all the amount was in forms available for plants. Content of total Fe is expectedly high (about 15 %), while the amount of its soluble forms is only 0.30%. The third element (along with Ca and Fe) is Mn, with total amount of about 1.8 %, but with low (insignificant) amounts of its soluble forms. The studied metallurgical slag contains lower amounts (10-20 mg kg^{-1}) of Zn and a little higher amount of Cu (about 200 mg kg^{-1}).

According to the previous studies [19], metallurgical slag stone (ground steel slag) contains 22-38 % CaO and 3.5-6.5 % MgO. Oxides of Ca and Mg are partially free, and partially bound to carbonates and silicates that are easily hydrolyzed. Upon the neutralization rate, this slag stone material is classified between burned (oxide) slag and ground slag stone (calcium carbonate). Other authors determined that an industrial slag contained high amounts of Na, Fe and carbon (as residual reducing substance), along with the considerable amounts of Pb, Si and Ca (CaO), and trace amounts of Cr, Cu, Zn and Ti [20].

The availability and alkaline nature of some industrial by-products qualify them as potential alternatives for lime in agriculture and they include metallurgical slag [21], although limited studies have been carried out on metallurgical steel slag and derivates [2]. In several studies [22, 23], an increase of pH, exchangeable Ca and Mg in acid soils under the influence of different doses of metallurgical slag was reported.

Table 1. Properties and composition of the studied 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 (%)	15.34±0.79
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 (%)	1.80±0.15
Available Ca (in 1M amonacetat, %)	17.18±1.98	Available Mn (in DTPA, mg kg^{-1})	3.12±1.04
Total Mg (%)	0.41±0.04	Total Zn (%)	14.60±5.59
Available Mg (in 1M amonacetat, %)	0.07±0.02	Total Cu (%)	228.8±15.4

In Table 2 the results of soil chemical characteristics and elemental composition of plowed layer of the studied Stagnosol before the experiment was established are given.

The optimum pH range for growth of most crops in soil is between 5.5 and 7.0, within which most plant nutritives is available [24]. In addition to the aforementioned growth limitations some trace elements may pose a toxicity threat if present at elevated levels as their availability and mobility increases under acidic conditions [25]. The studied Stagnosol had very acid soil reaction, with pH 4.45 in KCl. The soil possessed high potential acidity (Y) and significantly low saturation of CEC (Y =21.7: 11.5; V% =

46:74). Tested soil had low content of soluble P_2O_5 and was well supplied with available K_2O. Content of soluble Ca is low, while the contents of available Mg and trace elements are generally within the range of optimal supply.

Table 2. Chemical properties of the studied soil before the experiment was established (means ± standard deviation)

Property	Value	Property	Value
pH in H_2O	5.48±0.01	Available K_2O (mg $100g^{-1}$)	19.8±1.54
pH in 1M KCl	4.45±0.01	Available Ca (mg $100g^{-1}$)	240±19
The sum of bases - S (cmol kg^{-1})	11.98±0.95	Available Mg (mg $100g^{-1}$)	35±3.89
Potential acidity -Y´	21.66±1.81	Available Fe (mg $100g^{-1}$)	116±5.90
CEC (cmol kg^{-1})	26.06±0.9	Available Mn (mg $100g^{-1}$)	66±3.00
Base saturation - V (%)	45.97±2.0	Available Zn (mg $100g^{-1}$)	1.0±0.1
Total N (%)	0.24±0.01	Available Cu (mg $100g^{-1}$)	1.5±0.1
Available P_2O_5 (mg $100g^{-1}$)	3.73±0.28	Available Co (mg $100g^{-1}$)	0.21±0.01

The effect of metallurgical slag and selected lime materials on the changes of soil acidity and adsorptive complex is presented in Table 3. The results show significant decrease in soil acidity both comparing to the control and to the treatments with classical fertilization (NPK + manure). Similarly, slag fertilization influenced on the increase of basic cations in soil (S), decrease of potential acidity (Y) and increase of cation exchange capacity CEC and of base saturation (V%).

Table 3. Effect of applied treatments on the changes of soil acidity and adsorptive complex (means ± standard deviation)

Treatment	pH		Adsorptive complex, in c mol kg^{-1}			
	H_2O	1M KCl	S	Y'	CEC	V%
T1	5.31±0.01	4.46±0.01	11.71±0.92	17.58±0.38	23.14±0.9	50.57±2.10
T2	5.35±0.03	4.67±0.03	11.98±0.69	16.42±0.14	22.66±0.74	52.86±1.32
T3	6.05±0.04	5.41±0.04	16.65±1.62	4.75±0.50	19.73±1.30	84.24±2.64
T4	5.96±0.06	5.35±0.14	16.11±2.31	7.08±3.13	20.72±3.88	78.40±7.30
T5	5.64±0.02	4.98±0.02	15.05±0.23	9.00±1.32	20.90±0.73	72.07±3.24
T6	5.81±0.02	5.35±0.11	17.05±1.67	5.33±1.46	20.51±0.72	82.98±5.31
T7	5.79±0.02	5.22±0.16	15.05±0.61	7.33±2.02	19.82±1.34	76.14±5.45
T8	5.67±0.01	4.93±0.02	15.58±0.40	8.17±0.58	20.8±0.20	74.59±1.78
P value	***	***	***	***	NSD	***
LSD (0.05)	0.05	0.15	2.18	1.51	2.81	7.18
LSD (0.01)	0.07	0.21	2.99	2.09	3.87	9.89

LSD - least significant differences; NSD - 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.

In Table 4 the contents of available forms of major elements (P, K, Ca, Mg) after fertilization by lime materials and their uptake by vegetables are presented. The results show that application of all the fertilizers and lime materials resulted in increased content of these elements. In addition, application of metallurgical slag resulted in increased amount of available P and Mg comparing to the classical lime materials. Regarding the contents of available trace metals in soil (Table 4), a small effect of the studied lime materials, along with metallurgical slag, on decrease of available forms of Fe and Mn was observed.

Table 4. Effect of applied treatments on the content of the soil available biogenic macroelements and trace metals (means ± standard deviation)

Treatment	Available macroelements (mg kg^{-1})				Available trace metals (mg kg^{-1})				
	P_2O_5	K_2O	Ca	Mg	Fe	Mn	Cu	Zn	Co
T1	2.63±0.33	11.82±1.64	214.67±18.90	35.03±3.92	113±5.9	57±2.9	1.8±0.10	1.6±0.06	0.17±0.01
T2	5.55±1.20	19.93±2.85	215.00±8.54	35.60±2.52	111±7.2	56±5.1	1.7±0.22	1.7±0.48	0.17±0.01
T3	3.23±0.67	13.85±0.62	290.67±20.55	33.80±3.44	100±2.7	37±2.1	1.5±0.15	1.2±0.06	0.13±0.01
T4	2.86±0.80	12.36±1.46	265.67±5.51	29.17±3.40	101±8.4	38±2.6	1.6±0.13	1.3±0.03	0.13±0.01
T5	4.08±1.30	11.82±2.08	267.67±11.59	34.23±3.79	107±10.4	44±3.0	1.7±0.14	1.4±0.01	0.15±0.01
T6	6.93±0.80	23.17±2.04	323.33±19.43	38.00±0.85	101±10.8	39±2.5	1.4±0.04	1.3±0.18	0.14±0.01
T7	6.78±0.03	22.23±1.69	272.00±12.53	31.70±3.16	94±5.1	35±6.0	1.5±0.14	1.3±0.11	0.13±0.02
T8	8.29±1.05	21.96±2.07	260.33±10.97	34.67±1.42	103±4.5	43±2.6	1.6±0.12	1.2±0.04	0.15±0.01
P value	***	***	***	NSD	NSD	***	NSD	NSD	***
LSD (0.05)	1.50	3.46	25.02	5.20	12.77	6.26	0.24	0.33	0.016
LSD (0.01)	2.07	4.76	34.48	7.17	17.60	8.63	0.33	0.45	0.023

LSD - least significant differences; NSD - 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.

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. 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 4-5 [26].

The results of the content of main and beneficial biogenic macroelements in aboveground biomass of spinach and cabbage show the noticeable differences between the treatments due to their dissolution in plants, especially for some elements (N, K), and due to higher accumulation of some elements and their mobilization from natural soil reserves primarily, as influenced by the additional lime materials (Table 5). Considering the main purpose of this study, the conclusion is that there is a tendency of a little increase of the contents of Ca and P in plants of spinach and cabbage in treatment with metallurgical slag (NPK+manure+metallurgical slag - T8).

Table 5. Effect of applied treatments on the content of biogenic macroelements and trace metals in tested vegetables (means ± standard deviation)

Treatment	Available macroelements (% of dry mass)					Trace metals (% of dry mass)			
	N	P	K	Ca	Mg	Fe	Zn	Cu	Cd
Spinach									
T1	6.26±0.06	1.53±0.02	3.06±0.07	1.27±0.02	0.45±0.03	12.62±0.25	20.97±0.07	0.13±0.01	0.07±0.007
T2	5.97±0.03	1.61±0.02	3.27±0.02	1.22±0.02	0.35±0.01	11.63±0.34	20.47±0.35	0.14±0.01	0.07±0.004
T3	5.67±0.03	1.60±0.02	2.86±0.02	1.25±0.03	0.37±0.01	11.25±0.17	20.02±0.03	0.12±0.01	0.06±0.003
T4	6.18±0.02	1.54±0.02	2.94±0.04	1.25±0.03	0.37±0.01	9.55±0.22	19.80±0.24	0.11±0.02	0.06±0.001
T5	5.64±0.02	1.55±0.03	2.83±0.02	1.24±0.02	0.33±0.04	12.57±0.10	20.55±0.09	0.13±0.01	0.06±0.002
T6	5.96±0.02	1.66±0.01	3.29±0.06	1.23±0.01	0.31±0.02	10.82±0.17	20.58±0.10	0.10±0.01	0.07±0.003
T7	6.07±0.03	1.57±0.02	3.08±0.02	1.23±0.02	0.28±0.01	10.26±0.14	18.93±0.07	0.08±0.01	0.06±0.002
T8	6.13±0.02	1.61±0.03	3.19±0.02	1.33±0.01	0.27±0.01	12.86±0.11	21.06±0.08	0.10±0.01	0.06±0.004
Cabbage									
T1	6.78±0.04	1.83±0.01	4.65±0.07	1.74±0.02	0.48±0.02	4.28±0.05	0.42±0.02	0.51±0.03	0.022±0.001
T2	6.47±0.03	1.93±0.02	4.97±0.06	1.67±0.03	0.37±0.02	3.94±0.03	0.41±0.01	0.55±0.03	0.021±0.002
T3	5.93±0.01	1.93±0.01	4.98±0.04	1.70±0.03	0.43±0.01	4.58±0.03	0.32±0.02	0.49±0.02	0.018±0.002
T4	6.33±0.03	1.81±0.03	4.13±0.05	1.63±0.03	0.39±0.03	4.81±0.04	0.37±0.01	0.45±0.01	0.021±0.003
T5	5.61±0.01	1.62±0.02	4.67±0.04	1.61±0.04	0.41±0.01	4.91±0.03	0.31±0.01	0.43±0.02	0.017±0.001
T6	6.45±0.02	1.99±0.01	4.99±0.05	1.69±0.02	0.33±0.01	3.67±0.02	0.41±0.02	0.39±0.02	0.022±0.003
T7	6.57±0.02	1.88±0.01	4.68±0.05	1.68±0.02	0.30±0.01	3.48±0.03	0.38±0.01	0.31±0.01	0.020±0.002
T8	6.63±0.01	1.92±0.03	4.84±0.06	1.82±0.04	0.29±0.02	4.36±0.05	0.42±0.02	0.40±0.02	0.020±0.003

Conclusion

The results of the paper indicate that the studied metallurgical slag showed positive effects on chemical properties of Stagnosol, a soil characterized by high acidity, comparing to non-fertilized one, as well as on chemical composition of experimental crops (spinach and cabbage). Generally, 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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