Physico-chemical and biological properties of slag from blast furnaces after iron-nickel ore smelting

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Abstract:

The slag from examined waste dumps contains small amounts of macroelements, relatively high quantities of available iron, nickel and chromium, exhibits an alkaline reaction and low water capacity. Biological analyses demonstrated that symbiotic and asymbiotic nitrogen-fixing bacteria, as well as some papilionaceous species (*Pisum sativum* L., *Lupinus luteus* L., *Sarothamnus scoparius* L.) and some grasses (*Bromus sterilis* L., nad *Bromus inermis* Leyss.), find favorable conditions for development on this slag. The experiments indicate that the main factors delimiting plants growth and development on the slag are: lack of available nitrogen, excess of iron, nickel and chromium, and the dry dust layer forming on the slag surface.

INTRODUCTION

The problem of recultivation of waste dump and industrial dumping grounds is at present one of the main tasks of science and practical management, since its aim is to attenuate the consequences of the noxious influence of industry on the environment. Not all industrial wastes are suitable for secondary exploitation but sometimes the dumped wastes can be brought under cultivation by introducing plants onto them.

The development of a vegetal cover on industrial wastes has been studied by a number of authors. These elaborations concern wastes and industrial dumping grounds of various kind (Gussone 1969), waste tips and areas of open pit brown coal mining (Barthel 1965, Brüning 1965; Brüning et al. 1965; Dunger 1968), waste tips and dump heaps of mineral coal mines (Górski and Nazarewicz 1956; Zubikowska 1956), dump heaps and waste material from iron and zinc mills and from galena and calamine dumps (Mazaraki 1956; Mazaraki et al. 1956; Mazaraki 1957), earth overlay heaps and waste material after open pit mining of iron and nickel ore (Sulej et al. 1970). The above enumerated studies as well as a number of other ones concerned, beside certain practical solutions, above

all basic investigations since each type of dumps represents an individual set of environmental factors requiring detailed biological studies in order to establish the possibility and lines of recultivation.

The present study was undertaken in order to establish certain biological and physico-chemical properties of the material from a dump formed of slag after iron-nickel ore smelting. The investigations consisted in measurement of acidity, determination of the content of mineral components available to plants and of certain biological properties chosen on the basis of microbiological tests. As supplement to the studies short glasshouse tests with indicator plants in pots were performed.

These laboratory investigations may be an aid in the eventual elaboration of dump recultivation.

MATERIAL AND METHODS

The material was taken from the slope of a waste heap on which slag had no more been dumped for 7 years. The surface area from which the samples were taken was about 10 000 m². In May 1971 about 100 samples were taken from two levels: from the surface (0–15 cm) and from deeper layers (75–90 cm). The samples from both levels were air dried separately and were mixed thoroughly.

The mechanical composition of the slag was determined by screening. Hydrolitic acidity was determined by Kappen's method, pH (H₂O) and pH(KCl) by the potentiometric method in 5 replications, with preservation of the slag-to-solution ratio 1 : 5. The sorption properties were determined after Kappen.

The content of available mineral elements was determined with the use of Morgan's universal solution (Nowosielski 1968). The particular elements from Morgan's solution were determined by the methods described in the preceding paper (Sulej et al. 1970). The results of analysis of the particular available mineral components are given as means of 5 replications. Total iron, nickel and chromium contents were determined in 10 per cent HCl extract. Iron was determined by the 2,2'-dipyridyl method, nickel by the dimethylglyoxime method and chromium by the diphenylcarbazide method (Marczenko 1968).

Seed germination tests were run as follows: a weighed air dried amount of dry slag was placed on a Petri dish, moistened with water and 100 seeds were sown on it. As control served compost soil. The dishes were covered and kept in a dark thermostat (25°C). After two days the number of germinated seeds was counted and the results were given as per cent of the control. The experiments were repeated twice.

For pot cultures slag was used in the amount of 6 kg per pot. As control served pots filled with compost. The following test plants were sown or set in the pots: *Pisum sativum* L., variety Alaska, *Lupinus luteus* L., *Sarothamnus scoparius* L., *Trifolium repens* L., *Lycopersicum esculentum* Mill. cv. Karzelek puławski, *Raphanus sativus* L., *Bromus inermis* Leyss. For each plant species 5 replications were made in the glasshouse experiments.

In order to determine eventual nickel and chromium accumulation in the plants tests experiments were carried out with *Bromus sterilis* L. An equal number of seeds was sown into the pots with slag from the two soil levels as well as on compost soil (control) in six replications. After germination the pots were placed in the greenhouse and watered with distilled water. After 45 days the grass was cut just above the slag surface and the leaf dry mass was determined for the particular pots, and the nickel and chromium content was analysed.

The total number of bacteria was determined by inoculating slag samples on a medium with soil extract. The nutritional requirements of the most frequent bacteria in the slag were determined on the basis of their intensity of growth (changes in optical density) in liquid media (Lochhead and Chase 1943). Available nitrogen was determined by the *Aspergillus niger* method (Nowosielski 1968). Nitrogen (N-NO₃) content "mobilized" by 21-day incubation and the amount of nitrogen bound owing to this incubation were determined by the method described by Fedorov (1951). The results of nitrogen analysis are given as means of 3 replications. Moreover, each experiment for nitrogen determination was repeated twice.

RESULTS

The slag examined was taken from a still used dump estimated to be 40—50 years old. This dump consists of drift ash and finegrained slag from iron-nickel ore smelting. The slag samples were taken from a slope of the dump heap which for about 7 years had not been covered with fresh slag layers. The deeper layers of the dump from a rather compact layer which holds moisture rather well. On the surface, however, the dump dries up quickly and when rainfall is lacking has a readily drifting dust cover.

The dump on its entire surface is deprived of vegetation. Only at the bases of the dumping ground, where it comes into contact with the neighbouring fields, sporadically growing willows (*Salix viminalis* L.), *Calamagrostis epigeios* L. and *Bromus inermis* Leyss, may be found, and exceptionally *Poa pratensis* L.

Mechanical analysis (Table 1) demonstrates that both on the surface and in the deeper layers the percentual composition of the particular fractions of the slag is similar. Particles of diameter between 1.0 and 0.1 mm constitute the main mass of the dump components (55—60%). Particles with dimensions larger than 1 mm

Table 1
Mechanical composition of blastfurnace slag

Sampling depth cm	Percentual content of mechanical fractions diameter in mm							
	>1,0	1.0—0.5	0.5—0.25	0.25—0.1	0.1—0.075	<0,075	1.0—0.1	0.1—0.075
0—15	23.0	25.2	19.1	15.5	8.2	9.0	59.8	17.2
75—90	25.4	25.4	16.0	13.9	9.3	10.0	55.3	19.3

form about 25%. About 18 per cent consists of dust. It should be mentioned that particles with a diameter larger than 2 mm constitute only a small percent of the slag.

The above described structure of the components of the dump does not ensure good water balance conditions. This is confirmed by the results of tests of the water capacity of the slag (Table 2). The data in this table indicate a low hygroscopic water content and low capillary capacity. The total water capacity which only slightly exceeds capillary capacity indicates a very restricted possibility of water holding capacity in the slag. Investigations performed directly on the dump demonstrated, however, a relatively high moisture content in its deeper layers. The surface layers, on the other hand, readily dry up when there is no rainfall for a few days, forming a several centimetre thick dust layer.

The slag independently of the depth of the layer sampled gives an alkaline reaction (Table 2) showing a tendency to pH rise with increasing depth. The pH (KCl) value does not differ much from pH (H_2O), whereas hydrolytic activity is very low. This is understandable in view of the alkaline reaction of the slag. It was also found that the slag shows a relatively high exchangeable sorption capacity (T), almost equal to the sum of the exchangeable bases (S). In connection with this the degree of saturation of the slag with exchangeable cations is very high, of the order of 99 per cent.

The content of mineral components available to plants in the slag from different layers of the dump is shown in table 3. It may be seen from the data that the slag contains relatively large quantities of available potassium and calcium. The amounts of these elements do not differ much between the two layers. The amount of magnesium is very low as compared to that of calcium. Moreover, a washing out of available magnesium from the surface layers into the deeper ones is observed.

The contents of available phosphorus and sulphur are relatively high, but the content of available nitrogen in the form of nitrates and ammonium ions is very low. Comparison of total nitrogen content determined by Kjeldahl's method in air-day slag (Table 6) with the content of nitrogen ($N-NH_4$) dissolved in the extraction solution (Table 3) indicates indeed negligible amount of this component in the slag investigated.

The slag contains relatively large quantities of available microelements such as iron, nickel and chromium (Table 3). The total content of the enumerated microelements in the slag determined from HCl is, as seen from table 4, very high. These elements, therefore, may be unfavorable to the development on the dump of a number of plant species and microorganisms.

The rather large amount of exchangeable ions occurring in the slag are not dangerous in the general salinity of the slag, since both levels of dump showed a zero salinity when measured in terms of resistance to sodium chloride.

The slag did not prove toxic to the germinating seeds. As seen from table 5, germination on the slag did not differ much from that of the control seeds. Only clover seeds, and in a smaller extent radish seeds, showed a poorer germination on the slag from deeper layers.

Table 2
Water capacity, acidity and sorption properties of slag

Sampling depth cm	Water capacity in weight %			Acidity			Sorption		
	hygroscopic	capillary	total	pH (H ₂ O)	pH (KCl)	H ^h	me/100g		
0-15	0.25-0.27	23.31-25.00	25.31-26.51	8.6-8.8	8.2-8.4	0.34-0.37	69.8	70.7	99.8
75-90	0.26-0.27	24.08-25.25	25.97-27.50	8.6-8.8	8.5-8.6	0.48-0.52	67.4	67.9	99.3

Table 3
Content of available mineral elements in mg/100 g of air-dry slag

Sampling depth cm	K	Ca	Mg	N-NO ₃	N-NH ₄	P	S-SO ₄	Fe	Ni	Cr
0-15	125.0-130.0	207.5-226.6	8.0-16.3	0.47-0.59	3.10-3.93	8.40-9.20	23.8-24.41	154.0-208.0	18.3-20.8	0.4-0.70
75-90	123.5-125.0	222.5-241.5	26.4-43.7	0.36-0.39	2.87-3.59	7.10-7.80	25.6-27.1	127.0-132.0	16.3-20.3	0.3-0.45

Table 4

Total content of micronutrients in mg/100 g of air-dry slag

Sampling depth cm	Fe	Ni	Cr
0—15	1733.0—2320.0	175.0—200.0	2.0—2.5
75—90	1892 —2240.0	182.0—220.0	3.5—4.3

In the surface layers the dump the number of bacteria varied within the limits, of $13\text{--}56 \times 10^4$ per 1 g of slag, and in the deeper layer it was $8\text{--}15 \times 10^4$. The number of *Actinomycetales* was on the average about $1\text{--}7 \times 10^1$ per 1 g of slag, in both investigated levels. The values obtained are very low as compared with the number of bacteria in soil, but it should be borne in mind that the slag from the dump hardly contains any organic matter and that the concentration of nickel and chromium is relatively high and these elements may be toxic for many microorganisms.

Table 5

Average seed germination

Sampling depth cm	Seeds germinate in per cent of control			
	white clover	charlock	radish	tomato
0—15	93	96	94	100
75—90	78	94	82	100

The attempt at physiological characterization of the isolated bacteria demonstrated an interesting phenomenon. The bacteria (*Coccidia*) which constituted the majority among the microorganisms isolated proved rather demanding as regards nutrient substance. Their development was optimal on a medium containing amino acids, as nitrogen source. On a simple medium containing glucose and potassium nitrate as nitrogen source, their growth was rather poor. These results seem to prove that the bacteria occurring on the dump are adapted to the utilization of organic remains (amino acids), the source of which may be other bacteria or fungi introduced into the dump with rainfall.

Available nitrogen was determined as a sum of mineral nitrogen in water-soluble organic compounds such as amino acids and amides, by the *Aspergillus niger* method. The latter allows estimation at high approximation of the nitrogen amount which the plants can take up from the soil. This is particularly important in the case of mining dumps which are to be recultivated, since it indicates the possibility of utilization of all nitrogen sources both of nitrogen which is available and that mobilized in the slag during culture of mycelium for some dozen days or so. Chemical methods only show the current nitrogen content, regardless of the possibility of mobilizing certain forms of available nitrogen. The dry mycelial mass values plotted on the standard curve indicate that in the slag from the dump surface the amount of available nitrogen varies within the limits of 18—22 mg/100 g slag, and 10—12 mg in the deeper

layers (Table 6). These values are much higher than those obtained by chemical analyses (Table 6) and indicate that the slag has some reserves of various forms of nitrogen available to plants.

Table 6

Content of various nitrogen fractions in mg/100 g of air-dry slag, determined by chemical and biological methods

Sampling depth cm	Chemical methods		Method of Aspergillus niger
	colorimetric	Kjeldahl	
0—15	3.56—4.48	3.42—4.06	18.3—22.0
75—90	3.02—3.96	3.15—3.64	9.7—12.0

Investigation on the activity of nitrifying bacteria in the slag (Table 7) point to the presence in it of a bacterial microflora. The very low nitrate increments, however, obtained as the results of 21-day incubation of slag samples in laboratory conditions are evidence of a low nitrifying activity in the slag. There exist, on the other hand favorable conditions in the slag for development of bacteria binding molecular nitrogen. Experiments with incubation of slag samples from two levels of the dump (Table 7) under conditions optimal for the growth of nitrogen binding

Table 7

Mean N-NO_3 and N-NH_4 content in mg/100 g of air-dry slag

Sampling depth cm	N-NO_3			N-NH_4		
	before incubation	after incubation	increment	before incubation	after incubation	increment
0—15	0.47—0.59	2.30—2.60	1.97—2.01	4.06—4.20	51.38—66.78	47.32—62.58
75—90	0.36—0.39	2.00—2.20	1.64—1.91	3.64—3.80	43.24—55.98	39.60—52.18

bacteria demonstrated that there exist in the slag both from surface and deeper layers favorable conditions for the development of bacteria fixing nitrogen from the atmosphere. The high bound nitrogen increment values (within the limits of 39—62 mg/100 g slag) show, besides, that there is a possibility of natural enrichment of the dump in nitrogen.

Owing to the relatively high nickel content in the slag, the danger of its accumulation in the plants arises. Experiments were performed in glasshouse conditions on *Bromus inermis* Leyss. which is not demanding as far as soil conditions are concerned. The data in table 8 and photo 3B indicate that the grass yield was much lower on slag from the deeper dump layers than on those from the surface although, as compared with the yield of the control plants, a diminution of the yield in the surface layers is also observed. Chemical analyses demonstrated a relatively high accumulation of nickel in the grass blades, independently of the level from which the slag samples were taken. On the other hand, no accumulation of chromium in the blades was noted.

Fig. 1. A — *Pisum sativum*; B — *Lupinus luteus*; C — *Sarothamnus scoparius*
 1 — Control; 2 — Slag (0-15 cm depth); 3 — Slag (75-90 cm depth)

Fig. 2. A — Grains of *Pisum sativum*; B — Nodule formation on roots of *Lupinus luteus*

Explanation as for Fig. 1.

From among the species of indicator plants cultivated in pots with slag m s l y papilionaceous plants such as pea, lupin or broom grew normally without major differences in their development as compared with the control plants (Fig. 1 — photos A, B and C). Neither did the harvest of pea seeds per seedling differ much from that on the control plants. Profuse nodulation was observed on the roots of the above named plants (Fig. 2B). White clover however, grew poorly (Fig. 3A) in spite of the abundance of nodules.

Young tomato seedlings transplanted to the pots with slag took root, but their growth was completely inhibited. The plants showed symptoms typical of nitrogen deficit manifested in the product' on of anthocyanins. After several days culture these seedlings died. Radish reacted in a similar way; several days after germination severe chlorosis was noted in the young seedlings. The grasses (*Bromus inermis* and *B. sterilis*) proved more resistant (Table 8), and under glasshouse conditions during culture for several ten-day periods gave a certain increment of mass.

DISCUSSION

The above described experiments indicate that in slag from blast furnaces poured out in dump heaps there exist conditions favorable to the development of life of various soil microorganisms and conditions suitable for the development of

Fig. 3. A — *Trifolium repens*; B — *Bromus sterilis*

Explanation as for Fig. 1.

at least some species of higher plants. This is manifested among other things by a high activity of microorganisms binding atmospheric nitrogen, a somewhat less intensive activity of nitrifying bacteria and the presence of symbiotic bacteria. This is associated with good growth of papilionaceous plants such as peas, lupin and broom on the slag and the possibility of growth of certain grasses resistant to drought.

The high activity of the bacteria fixing atmospheric nitrogen reflected in an increment of fixed N_2 of the order of 39–62 mg/100 g of slag indicates that the dumped wastes from blast furnaces after iron–nickel ore smelting exhibit properties which

Table 8

Yield and content of nickel in dry weight of 45 days old *Bromus sterilis*

Sampling depth cm	Dry weight g	Nickel $\mu\text{g/g d.wt.}$
0–15	0.710–0.780	14.9–16.5
75–90	0.435–0.480	15.3–16.5
control	0.910–0.960	trace

make possible the formation of a plant cover on them in natural conditions. This conclusion finds support in vegetation experiments with such papilionaceous plants as pea, yellow lupin, broom and clover, which grew almost normally on the slag with profuse nodulation on the roots. Physical and chemical analyses of the slag composition also revealed almost optimal conditions for the development of bacteria fixing atmospheric nitrogen, namely, an alkaline reaction and a relatively high calcium content. The conditions much less favourable for the development of nitrifying bacteria may be explained by the excessive amounts of available microelements such as iron, nickel and chromium. This fact, however, does not seem to be a major obstacle to the mobilization or improvement of nitrogen reserves, since experiments on the growth of the fungus *Aspergillus* demonstrated an intensive growth of its mycelium. The content of available nitrogen forms determined by this method is much higher than that determined chemically. This would seem to indicate that the dump is relatively rich in various forms of available nitrogen. As shown by the present investigations the content of available nitrogen forms is continuously improved by the activity of the bacterial microflora present in the slag. Thus, the certain nitrogen deficit revealed by chemical methods is not the main factor which makes recultivation of dumps difficult.

On the basis of the analyses performed it would seem that the main factors inhibiting plant growth on the dump are the too highly alkaline pH, the excess of microelements and the moisture conditions. The alkaline pH of the slag necessitates the selection of appropriate plants. As regards the excess of microelements mainly iron, nickel and chromium, this may restrict the development not only of bacteria flora, but also number of species of higher plants. It is not excluded that the unsuccessful tomato and radish cultures in pots were due to the excess of nickel and chromium, beside the deficit of mineral components and mainly nitrogen.

The present studies demonstrated, however, that at least some papilionaceous plants grow normally on the dump. Remains the problem of the usefulness of these plants for consumption or fodder on account of accumulation in them of certain amounts of nickel and chromium. Brome grass was found to accumulate rather large quantities of nickel. It is possible that other plants also may accumulate certain amounts of these compounds. Although the development of grasses (*Bromus sterilis* L. and *B. inermis* Leyss.) was less intensive as compared with the control, the fact that these grasses took root and grew on the slag indicates their usefulness for producing a ground cover on the dump.

The main factor restricting plant growth on the dump in natural condition are, doubtlessly, beside the nitrogen deficit the water conditions. The low capillary capacity hardly differing from the total capacity shows a limited possibility of water accumulation. Actually the water content in the dump in natural conditions seems sufficient, since the slag forming the dump has a high capillary capacity. The rising water does not evaporate from dump, because the surface is covered with a layer of dust which prevents evaporation. Nevertheless this dry dust makes germination of seeds impossible in natural conditions and causes rapid drying up of plants with a shallow or horizontally spreading root system. These facts indicate that,

beside papilionaceous plants, only those with a deep root system will be able to develop on slag dumps if the deficient basic mineral components are supplemented.

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Fizyko-chemiczne i biologiczne właściwości żużli z pieca hutniczego po wytopie rudy żelazowo-niklowej

Streszczenie

Badano niektóre właściwości fizyko-chemiczne i biologiczne żużli pobranych z hałdy wytworzonej ze składowania odpadów po wytopie rudy żelazowo-niklowej.

Stwierdzono, iż żużle wykazują niekorzystne dla rozwoju roślin właściwości wodne. Odczyn żużli jest słabo alkaliczny. Żużle hałdy zawierają dość duże ilości dostępnego potasu i wapnia oraz

siarki, natomiast ilość magnezu jest niewielka i jest on wymywany do warstw głębszych. Mikroelementy (Fe, Ni, Cr) występują w żużlach w bardzo dużych ilościach oraz są akumulowane przez rośliny. Ilości azotu oznaczonego metodami chemicznymi są bardzo niskie, niewystarczające dla rozwoju szeregu roślin.

Intensywność procesów nitryfikacyjnych w badanych żużlach jest bardzo niska. Stwierdzono natomiast wysoką aktywność wolnożyjących bakterii wiążących azot atmosferyczny. W żużlach występują także bakterie brodawkowe, czego dowodem jest dobry wzrost roślin motylkowych na żużlach w warunkach szklarniowych i obfita nodulacja na korzeniach.