STUDY ON RESTORATION OF TOPSOIL ON THE WASTE DUMPS IN JIU'S VALLEY

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This paper presents a descriptive study on vegetal soil restoration on waste dumps from Jiu's Valley. The introduction refers to the activation of nitrogen. The article content presents nitrogen fixation and amonia formation. There are also presented considerations on anthropogenic soils and a comparative study between waste dumps from Ukraine and Jiu's Valley. The paper ends with conclusions regarding anthropogenic soils, enzymatic activities and the existance of bacteria in soils.

Keywords: anthropogenic soil, enzymological analysis, waste dump

Introduction

Altough nitrogen forms many compounds, the nitrogen molecule, N_2, is very little reactive.

Very low rate of all reactions of nitrogen is influenced on the one hand, by the strength of $N \equiv N$ connections and therefore a higher activation energy is necesary to break this bond, and on the other hand low polarized action of N_2, which prevents the formation of high polarity transition states, states which usually occur in replacement reaction of electrophilicity and nucleophiles agents.

In this sense, a way to fix nitrogen, which must be taken into account in the future, is based on the observation that bacteria can convert atmospheric N_2, at room temperature, into a series of compounds. The main underlying process of fixing nitrogen in the soil is catalytic conversion of dinitrogen in NH_4^+ in the presence of an enzyme called nitrogenase, located in the root nodules of legumes. Nitrogenase contains in active site Fe and Mo ions. These discoveries have led to the conclusion that catalysts can be obtained in which the metal ions can be coordinated to N_2, resulting in its reduction.

In this way many N_2 complexes were prepared. In some cases, preparation is very simple, consisting of N_2 bubbling through an aqueous solution of a complex:

$$[Ru(NH_3)_5(OH)]^{+2}_{(aq)} + N_{2\,(g)} \rightarrow [Ru(NH_3)_5(N_2)]^{+2}_{(aq)} + H_2O_{(l)}$$

N_2 molecule can function as linking, beeing linked to the metal as the isoelectronic molecule of CO. In the Ru(II) complex, the $N \equiv N$ connection is very little modified. However, when N_2 is coordinated to a metal center with strongly reducing character, the nitrogen-nitrogen connection considerably lengthens by retrodonation of orbital π electrons of N_2. Although no catalysts were obtained for N_2 reduction, there is hope in this regard because it is possible that the N_2 bounded in some of these complexes may be transformed in NH_4^+:

$$cis - [W(N_2)_2\{P(CH_3)_2(C_6H_5)\}_4] \xrightarrow{H_2SO_4} N_2 + NH_4^+ + W(IV)\text{ compounds}$$

The nitrogen fixation

Nature uses a way of obtaining NH_3 completely different from the industrial way, but much more complicated. The reducing agent used by nature is ATP and the reaction can be represented as:

$$N_2 + 16MgATP + 8e^- + 8H^+ \rightarrow 2NH_3 + 16MgADP + 16P_i + H_2,$$

where Pi is inorganic phosphate. This process is probably much less effective than the Haber process, because the energy consumption required for reduction of hydrogen, as well as for protectection against atmospheric oxygen of the biological system with a high reducing potential.

The special characteristic, attractive, of such a process is that it occurs at room temperature and pressure in Rhizobium organisms living in the roots of vegetables (alfalfa, beans, clover, peas etc.), as well as in some bacteria or blue-green algae. Nitrogenase enzyme catalyzes the reaction under anaerobic conditions, being able to destroy the high inertia of the $N \equiv N$ molecule.

The mechanical details of N_2 fixation are still unclear, but it id known that nitrogenase uses for this purpose an iron-sulfur protein and a molybdenum-sulfur protein.

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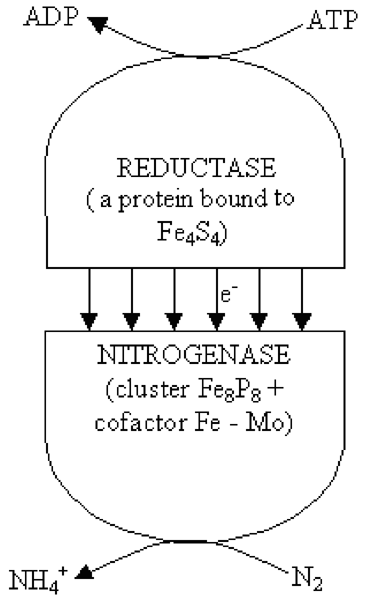

Figure 1 *Coupling made between dephosphorylation of ATP to ADP and reduction of molecular nitrogen (N_2) to NH_4^+*

The structure of complexes containing molecular nitrogen is well known in inorganic chemistry, but this one is completely different from the proposed structure of biological compounds. In the presence of a strong acid, N_2 in some inorganic complexes undergo a reduction proces, induced by protons, to ammonium ion:

$$[Mo(PR_3)(N_2)_2] + 8H^+ \leftrightarrow 2NH_4^+ + N_2 + Mo(VI) + ...$$

The idea that multiple binding sites containing metals may facilitate the reduction of N_2 echoed in organometallic chemistry, where it was shown that metal clusters facilitate proton-induced reduction of the CO molecule - isoelectronic molecule with N_2.

Anthropogenic soils

Anthropogenic soils are soils formed from mining-technical biological recultivation of overburden materials, waste dumps and other residues of the open pit and underground mining and other industrial activities. Also, all these residues constitute a dangerous source of environmental pollution.

By definition, the evolution of anthropogenic soils is the transformation of all these residues in agricultural or forest soils or land used for other purposes (parks, playgrounds etc.). Simultaneously, this process is accompanied by the reduction or elimination of the polluting effects of waste on the environment. The practical importance of this process is growing because of the development of mining and other industries leading to increasing quantities of waste and, therefore, recultivation of degraded land is becoming a major economic necessity. It is estimated that by 1980 on the surface of the earth there have been accumulated about 1,600 billion m^3 of waste dumps and the volume has increased annually by about 40 billion m^3. As a comparison we remember that water erosion affects a smaller volume of soil, that does not exceed 13 billion m^3 per year. According to some estimates, in order to extract a million tonnes of coal about 40 to 50 hectares of farmland are put out of the normal circuit.

The evolution of anthropogenic soils presents a theoretical importance, related to a deeper knowledge of landscape development looked upon as a whole.

The evolution of anthropogenic soils, which reflects recultivation efficiency, is studied by various methods including a series of physical, chemical and biological methods. Enzymological methods, have also been applied and found that the enzyme activity is a good indicator for anthropogenic soils evolution.

Chemical methods who include the determination of humus, base exchange capacitie and hydrogen exchange capacitie, nutrients such as N, P, K, B does not lead to results that can be directly correlated with fertility and implicitly crop production made on those soils .

For a better assessment of the ability of land to be vegetated some analysis are needed to be performed to reflect the enzymatic activity of bacteria existing in soil.

Of interest for enzyme activity, is catalase, urease, invertase etc.

Catalase can be measured by the ability to cleave hydrogen peroxide by the soil. It was found that the ability to cleave H_2O_2, in particular its termolabile component, always give higher values in well-developed plots with plants than in plots where plant growth was inhibited. Recultivated waste dumps properties to make possible for forest species to grow can be assessed by measuring the catalytic activity.

Urease is the proces of decomposition of urea by soil enzymes. Urease is measured by the amount of ammonium formed in 100 g soil in 40 hours.

Invertase is a process of hydrolysis of sugar with the formation of fructose and glucose. Invertase is measured by the amount of inverted sugar by a gram of soil in 40 hours.

Studies of the mine waste dumps recultivate at Iurkov in Ukraine determined invertase, urease and catalase activities in the soils of plots planted with lupine and black alder compared with fallow plots. The results in table 1 show that the enzyme activities decreased with depth in all plots from which samples were collected. Under the action of recultivation, enzymatic activities were clearly increased, sometimes several times, compared with activities recorded in control plots. Perennial lupine effect was stronger than that of black alder. Because lupine the humus content and total nitrogen content also increased, from 2.94 - 2.87 times, respectively 2.94 - 3.30 times. In alder plots, the humus content and total nitrogen content increased 1.95 times, respectively 1.81 times.

The results show that the recultivation with black alder and in particular with the green fertilizer plant (perennial lupine) makes it possible to increase the fertility levels of anthropogenic soils in a relatively short period of time.

Table 1

Plantation and its age	Depth	Invertase	Urease	Catalase
Perennial lupin(5 years)	0 - 2	39,48	136,9	209,8
	2 - 10	17,57	97,4	135,5
	10 - 20	6,45	61,5	84,7
Black alder (5 years)	0 - 2	30,82	125,6	168,2
	2 - 10	16,76	74,6	106,2
	10 - 20	3,68	42,7	74,3
Control (fallow)	0 - 2	6,56	70,5	124,0
	2 - 10	2,65	45,2	90,1
	10 - 20	1,56	15,2	59,4

Waste dumps from Iurkov recultivated with different species of trees and shrubs have become fertile soils in a relatively short time (9-14 years) already having a layer of humus and N content and a high enzymatic potential (table 2).

Table 2

Plantation and its age	Depth (cm)	Humus (%)	N (%)	N in humus (%)	Invertase	Urease
Sylva pine(14 years)	0 - 2	4,74	0,24	6,0	29,70	1,96
	2 - 5	2,33	0,12	5,1	10,00	0,56
	5 - 10	1,20	0,07	5,8	6,62	0,45
	10 - 20	0,41	0,02	5,0	4,42	0,34
	20 - 30	0,36	0,02	5,5	0,60	0,26
Acacia(9 years)	0 - 2	2,08	0,18	8,6	22,30	1,64
	2 - 5	1,02	0,09	9,0	8,03	0,62
	5 - 10	0,73	0,07	9,6	4,90	0,33
	10 - 20	0,16	0,01	6,2	1,12	0,28
	20 - 30	0,11	0,01	9,9	0,60	0,15
Sea buckthorn (9 years)	0 - 2	1,65	0,19	11,0	44,50	3,68
	2 - 5	0,75	0,06	8,0	11,20	0,72
	5 - 10	0,43	0,04	9,5	2,25	0,37
	10 - 20	0,26	0,02	8,0	1,71	0,16
	20 - 30	0,18	0,02	11,1	1,02	0,11
Black alder (9 years)	0 - 2	1,30	0,13	10,0	28,50	2,86
	2 - 5	1,03	0,12	11,6	13,50	0,84
	5 - 10	0,84	0,08	9,5	7,50	0,42
	10 - 20	0,17	0,03	17,6	4,70	0,32
	20 - 30	0,19	0,03	15,8	0,80	0,25
Control (fallow)	0 - 2	0,72	0,05	6,9	10,80	1,08
	2 - 5	0,43	0,02	4,6	5,20	0,71
	5 - 10	0,24	0,01	4,1	2,35	0,32
	10 - 20	0,23	0,01	4,3	0,10	0,20
	20 - 30	0,21	0,01	5,0	0	0

Waste dumps, consisting predominantly of loess from the brown coal open pit mining from Baidakov - Ukraine were also studied multilaterally. It was found, among others, that the invertase, urease and respiration activities (CO_2 production) are very low in the loess forming the quarry's walls and in the waste dumps of loess uncovered with vegetation. Enzymatic activities and respiration increased dramatically in parallel with the age of vegetation spontaneously installed on the loess consisting dumps. However, activity and respiration values were lower in waste dumps covered with 23 years old spontaneous vegetation, than the values measured in the soil area unaffected by mining (Table 3).

Table 3

Studied material	Invertase	Urease	Respiration
Material from the quarry walls	0.3	1.1	4.4
Material from the fallow waste dump	0.3	1.4	4.6
Material from the dump with spontaneous vegetation:			
1 year	1.2	1.5	5.1
2 years	2.2	2.0	-
4 years	4.1	2.3	28.7
23 years	7.0	4.5	35.3
Soil in the area (chernozem)	20.5	15.6	217.0

Also it was studied the enzyme activity and chemical composition of surface layer (0-50 cm) away from the ground and stored in heaps, before total overburdening and coal exploitation. Piles whose height was 1.5 - 4 m, were used after 3-5 years of storage to cover the leveled waste dumps for their recultivation. In the stored surface soil, catalase activity remained almost the same level as in the 0-50 cm layer of leached chernozem from the area unaffected by mining (native soil). However, urease activity decreased and proteinase activity increased somehow in the stored surface soil. The quantity and qualitative composition of humic substances I the stored soil had values close to those recorded in native soil.

The deposited soil, after it was placed on the leveled dumps and its recultivation with perennial grasses, showed catalase and urease activities similar to activities of the seasonal average of the 0-50 cm layer of native soil, while proteinase activity was 3 times higher in the soil placed on the dumps than in native soil.

To verify the possibility of using these parameters for the waste dumps in from Jiu's Valley a series of tests were conducted on soil samples collected from waste dumps and their surrounding areas.

The obtained results are given in tables 4 and 5:

Table 4

Nr crt	Sample name	Invertase	Urease	Catalase
1	M.E. Petrila– control soil sample	37,213	3,383	6,089
2	M.E. Petrila–waste dump soil sample	14,536	1,264	2,300
3	M.E. Aninoasa – Tericon dump	9,200	0,800	1,472
4	M.E. Aninoasa – Tericon dump	8,291	0,721	1,326
5	Petrila processing plant– fertile soil	25,334	2,203	4,031
6	M.E. Livezeni – PA_3 dump	26,542	2,308	4,223
7	M.E. Aninoasa – Piscu dump	28,048	2,439	4,463
8	M.E. Aninoasa – Piscu dump	33,476	2,911	5,327
9	M.E. South Aninoasa – control sample	28,957	2,518	4,607
10	M.E. North Aninoasa – control sample	51,931	4,721	8,545

Table 5

Parameter	1	2	3	4	5	6	7	8	9	10
pH	5,4	6,1	7,6	5,8	5,4	7,6	7,2	5,8	5,4	6,1
Combustible parts	17,3	7,5	8,6	15,4	15,3	6,5	8,5	19,5	14,1	12,5
Coarse sand	54,39	56,69	66,67	14,48	42,64	42,64	62,64	46,51	59,89	18,23
Fine sand	32,48	21,58	20,28	39,59	29,25	29,25	21,80	27,47	17,24	35,46
Powder I	9,62	7,78	4,21	21,17	14,60	14,60	5,83	15,49	6,93	21,15
Powder II	2,36	1,63	0,63	12,38	4,73	4,73	1,75	4,00	1,59	10,69
Clay	1,15	12,32	8,21	12,38	8,78	8,78	7,98	6,53	14,35	14,47
Humidity	5,2	2,1	7,85	5,23	4,6	2,4	7,85	5,58	6,3	4,75
Humus	16,5	0	2,5	13,4	14,8	0,5	1,8	17,5	12,3	10,5
Exchange Bases	4,69	0	3,60	20,21	5,19	0	2,75	8,47	16,78	18,60
Hydrogen exchange	21,63	0	2,55	22,57	15,82	0,15	1,90	46,95	23,56	21,35
Total exchange capacity	26,32	0,00	6,15	42,78	21,01	0,15	4,65	55,42	40,34	39,95
Assimilable N	0,85	0	0,10	0,69	0,51	0,12	0,05	0,91	0,78	0,75
Assimilable P	16,2	0,6	0,15	12,12	14,7	0	0,25	13,6	15,60	16,30
Assimilable K	23,6	5,8	2,15	8,20	12,1	2,35	2,25	7,9	14,35	8,9

Conclusions

1. Anthropogenic soils are soils formed by recultivation of materials such as overburden, waste dumps and other residues of the open pit and underground mining and other industrial activities.
2. The evolution of anthropogenic soils, which reflects recultivation efficiency, is studied by various methods including a series of physical, chemical and biological methods.
3. Among the enzymatic activities, catalase, invertase, urease and nitrogenase are of interest
The pathway for nitrogen fixation, which should be considered in the future, is based on the observation that bacteria can produce at room temperature the convertion of atmospheric N_2 into a series of compounds.
4. The main process underlying the N_2 fixation in soil is catalytic conversion of dinitrogen in NH_4^+ in the presence of an enzyme called nitrogenase.
5. Although no catalysts were obtained for N_2 reduction, there is hope in this regard because it is possible that the N_2 bounded in some of these complexes may be transformed in NH_4^+
6. Determination of nutrient such as N, P, K and B does not lead to results that can be correlated with fertility and crop production performed on anthropogenic soils.
7. For a better assessment of the ability of land to be vegetated some analysis are needed to be performed to reflect the enzymatic activity of bacteria existing in soil.

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