

Jean B. Diatta*, Ewa Chudzińska**

**CHEMICAL REMEDIATION OF ZINC CONTAMINATED SOILS BY
APPLYING A CEMENT-BROWN COAL-BASED COMPONENT
(CEMBRO)**

**CHEMICZNA REMEDIACJA GLEB ZANIECZYSZCZONYCH CYNKIEM
PRZEZ ZASTOSOWANIE PREPARATU CEMENT-WĘGIEL BRUNATNY
(CEMBRO)**

Słowa kluczowe: chemiczna stabilizacja, cynk, cement, węgiel brunatny, CEMBRO, pojemność buforowa, zdolność generowania protonów, zdolność retencyjna.

Key words: chemical stabilization, zinc, cement, brown coal, CEMBRO, buffering capacity, proton generation capacity, retention capacity.

Badania przeprowadzono w celu oceny efektywności cementu (CEM), węgla brunatnego (BC) oraz preparatu „CEMBRO” w procesie stabilizacji/remediacji gleb zanieczyszczonych cynkiem. Testowany preparat „CEMBRO” przygotowano w oparciu o cement i węgiel brunatny przy różnych stosunkach masowych. Do badań użyto gleby silnie skażonej cynkiem przez działalność huty cynku i ołowiu w Miasteczku Śląskim. Cement, węgiel brunatny i „CEMBRO” zastosowano w trzech dawkach 0; 0,5; 1,5 i 3,0% po czym obiekty inkubowano przez trzy miesiące. Efektywność stabilizacji/chemicznej remediacji oszacowano na podstawie:

- ilości ekstrahowanych biodostępnych ($0,10 \text{ mola NaNO}_3 \text{ dm}^{-3} = \text{Bio}_{\text{Zn}}$) i wymiennych ($1 \text{ mola CH}_3\text{COONH}_4 \text{ dm}^{-3} = \text{Ex}_{\text{Zn}}$) form Zn,
 - oceny zmian w kompleksie sorpcyjnym
- oraz
- właściwości buforowych gleb.

Wyniki ujawniły, że na obiektach, gdzie zastosowano 100% CEM oraz preparat „CEMBRO” z większym udziałem CEM, odczyn miał decydujący wpływ na stabilizację Zn. W razie zasto-

* **Prof. nadzw. dr hab. Jean B. Diatta – Katedra Chemii Rolnej, Uniwersytet Przyrodniczy w Poznaniu, ul. Wojska Polskiego 71F, 60-625 Poznań; tel.: 61 848 77 83; e-mail: Jeandiatta63@yahoo.com;**

** **Dr Ewa Chudzińska – Zakład Genetyki, Uniwersytet im. Adama Mickiewicza w Poznaniu, ul. Umultowska 89, 61-614, Poznań; tel.: 61 829 58 62; e-mail: evpell@amu.edu.pl**

sowania „CEMBRO” z większym udziałem BC i 100% BC, pH odegrało natomiast drugorzędną rolę w procesie chemicznej remediacji. Geochemiczne reakcje cynku (Zn) i jego potencjalna labilność oszacowane na podstawie zdolności generowania protonów (α) przez adsorbowane jony Zn oraz zdolność retencyjną (β) badanych obiektów ujawniły, że dawka 1,5% powinna być rekomendowana dla składów „CEMBRO” od 30/70 do 20/80, czyli odpowiednio CEM/BC.

1. INTRODUCTION

Soil functions to cycle and supply nutrients as well as water for the production of biomass. Its quality levels is a multifunctional phenomenon, which serves as one of the most important biogeochemical regulators of the flow of substances into, through and out of the ecosystem [Snakin et al. 1996]. Hence the anthropogenic disturbance of soils can lead to critical changes in the biosphere, which, in the end, may threaten the very existence of human beings [Logan 1990]. The time-scale as well as the magnitude of chemical degradation of soils were decidedly formulated by Lal and Stewart [1990], that „...despite its widespread severity and global impact, soil degradation remains an emotional rhetoric rather than a precise and quantifiable scientific entity”.

Since heavy metals are by essence non-biodegradable, therefore action should be taken to mitigate their direct bioavailability and transfer to the food chain [Panayotova and Velikov 2002]. The potential risk to the environment may originate from soluble fractions of heavy metals, basically. The mitigation of their negative effects is undertaken throughout remediation practices, of which stabilization is currently widely suggested.

Several materials (additives or stabilizers) have been used for the stabilization of heavy metals, Cu and Zn among others, in contaminated soils [Gupta et al. 2000; Basta and McGowen 2004]. One of the specific challenges still remains the choice of readily available, efficient, environmentally friendly and inexpensive heavy metal stabilizers, especially for Zn whose amounts in non-arable soils are the mostly used criterion for their toxicity classification.

Remediation techniques available for sites contaminated by heavy metals and zinc among others are numerous, but usually based either on extraction or stabilization of contaminants. Many of these techniques are expensive and also imply degradation of soil structure, which made them impractical for remediation of large area. Chemical stabilization [Mench et al. 1998; Vangronsveld and Cunningham 1998; Carlon et al. 2000] is an alternative method by applying materials, which lower the mobility of zinc as only its soluble fractions create potential risk to environment [Al-Turki and Helal 2004; Düring et al. 2003].

Bioavailability, mobility and toxicity of Zn strongly depends on its chemical speciation and soil properties such as pH and cation exchange capacity. By increasing pH or soil binding capacity Zn is immobilized in soil but the total content is still the same [Buczowski et al. 2002]. Chemical immobilization based on interaction between soil and amendments, which lead to acceleration of sorption, precipitation and complexation reactions reducing mobility of heavy metals [Madejón et al. 2006]. Therefore investigation with interacting organic matter com-

pounds and zinc in soils should pertinently evaluate some Zn threshold values, which may be indicative of a possible negative or positive reaction of soil microorganisms to Zn in the soil solution. Therefore the transfer of zinc from the soils into plant may be related to its dynamics as affected by the types and amounts of organic sorbents [Bolan et al. 2004].

The aim of the work was to evaluate the efficiency of a cement-brown coal based component (CEMBRO) for zinc stabilization in a soil contaminated by a Zn-Pb smelter activity. The specific purpose was to exhibit the impact of chemical changes as well as those dealing with soils buffering capacities on Zn chemical stabilization and the resulting significance for site revitalization.

2. MATERIALS AND METHODS

2.1. Location of the soil sampling

The sampling area lies within the impact zone of the Miasteczko Slaskie Zinc Smelter, (N 51°41'03" and E 15°57'12", Poland) whose activity started since 1966. This zone is surrounded in the north, west and east by a large Lubliniec Forest complex, and in the south-east by the localities of Zyglin and Zygliniec, quarters of the Miasteczko Slaskie. A population of pine as part of artificial restoration, mainly of mixed forest, sporadically mixed wood grows in the impact zone.

2.2. Physical and chemical analysis

Ten soil samples were collected randomly at the depth 0–30 cm and mixed thoroughly to form the representative soil sample used for the current study. Prior to physical and chemical analysis the soil was air-dried and sieved through a 2.0 mm polyethylene sieve. Granulometric composition was determined by the areometric method, whereas organic carbon ($C_{org.}$) by the Tiurin method as reported by Mocek et al. [2001]. Soil pH at soil/solution ratio of 1:5 (0.010 mole $CaCl_2$) was determined potentiometrically using a pH-meter [Polish Standard, 1994], and the electrical conductivity (EC) was assayed in water extracts according to Rhoades [1996]. The effective cation exchange capacity (CEC_e) was obtained by summation of 1 mole $KCl \cdot dm^{-3}$ extractable acidity (EA) and exchangeable alkaline cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) extracted by 1 mole $CH_3COONH_4 \cdot dm^{-3}$ (pH 7.0) as described by Thomas [1982]. Acid soluble forms of Zn were extracted by using 1 mole $HCl \cdot dm^{-3}$ [Kashem et al., 2007], whereas bioavailable forms were assayed by 0.10 mole $NaNO_3 \cdot dm^{-3}$ [Gupta, Hani 1989]. The choice of the 1 mole $HCl \cdot dm^{-3}$ was attributed to the fact, that soils within the investigated area are basically sandy. Therefore amounts of metal determined by this chemical test are suggested to be designated as pseudo-total. All performed chemical tests were run in du-

plication and metals as well as other elements were determined by the FAAS method (Flame Atomic Absorption Spectrophotometry, Varian 250 plus).

2.3. Cement (CEM) and Brown Coal (BC) chemical composition and CEMBRO characteristics

Portland cement is a popular material used in for building. Its consists of grinded clinker (50–65% $3\text{CaO}\cdot\text{SiO}_2$; 20% $2\text{CaO}\cdot\text{SiO}_2$; 10% $4\text{Ca}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$; 10% $3\text{CaO}\cdot\text{Al}_2\text{O}_3$), [Neville 1977] and gypsum. Due to the high content of calcium oxides, once introduced into the soil, it raises soil pH which acts as heavy metals immobilizing factor. Furthermore the aluminum, iron and silicon compounds enhances the potential capacity for metals sorbing. Brown coal used in this study came from Konin brown coal basin (Poland). The chemical compositions of both materials used as stabilizers are listed in Tables 1 and 2.

Table 1. Chemical composition of Portland cement

Tabela 1. Chemiczne właściwości cementu typu Portland

Cement (CEM)	pH (H ₂ O)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Zn
		%				mg·kg ⁻¹
	13.10	64.50	21.97	4.75	2.20	18.66

Table 2. Chemical properties of brown coal

Tabela 2. Chemiczne właściwości węgla brunatnego

Brown coal (BC)	pH (H ₂ O)	C _{org}	N _{tot}	C : N	Zn mg·kg ⁻¹
		g·kg ⁻¹			
	6.28	448	3.7	121:1	0.15

The cement-brown coal based component namely CEMBRO was obtained by properly mixing cement and brown coal at different ratios as shown below (Tab. 3):

Table 3. CEMBRO component at different cement (CEM) to brown coal (BC) ratios

Tabela 3. Preparat CEMBRO przy różnych stosunkach cementu (CEM) do węgla brunatnego (BC)

Cement CEM (%)	CEMBRO component		Brown coal BC (%)
100	A	–	0
90	B	90 / 10	10
80	C	80 / 20	20
60	D	60 / 40	40
50	E	50 / 50	50
40	F	40 / 60	60
30	G	30 / 70	70
20	H	20 / 80	80
10	I	10 / 90	90
0	J	–	100

2.4. Experimental design and incubation process

CEMBRO was added to 1.0 kg of Zn contaminated soil at the rates 0, 0.5, 1.5 and 3.0% (dry weight basis). The same applied for cement alone (CEM) as well as brown coal (BC), which were also incorporated at rates as reported above. All treatments were three times replicated, kept moist at 75% FWHC (Field water holding capacity) and incubated for 14 weeks at $18 \pm 2^\circ\text{C}$. Soil samples collected at the end of the incubation period were chemically analysed as described in the sub-section „*Physical and chemical analysis*”.

Computations and statistical evaluations were made by using the Statgraphics® software and Excel® sheet facilities.

3. RESULTS AND DISCUSSION

3.1. CEMBRO-induced pH and organic carbon changes

The investigated soil is typically sandy and characterized by a low content of organic carbon ($7.3 \text{ g} \cdot \text{kg}^{-1}$) as reported in Table 4. These properties along with soil pH were the core for exhibiting significantly low both exchangeable calcium as well as cation exchange capacity (CEC). Moreover the acidic nature of the soil environment may have been one of the limiting factors affecting grasses and shrubs growth.

Table 4. Physical and chemical characteristics of the investigated soil

Tabela 4. Fizyczne i chemiczne właściwości badanej gleby

Sand (2.0–0.02 mm)	Silt (0.02–0.002 mm)	Clay <0.002 mm	C _{org.}	pH		EC $\mu\text{S} \cdot \text{cm}^{-1}$	Ca _{ex}	CEC
				H ₂ O	CaCl ₂			
$\text{g} \cdot \text{kg}^{-1}$				$\text{cmol}_{(+)} \cdot \text{kg}^{-1}$				
790	120	90	7.3	6.4	5.3	38	0.91	1.54

Therefore it was assumed that the remediation of this ecosystem should be based on the raising of soil pH and *via* additions of calcium-bearing materials and incorporation of organic matter, whose reaction with calcium and sand fraction will significantly improve the structure. This is strategically important for a further revitalization of this site and similar ones, even. The CEMBRO conception as reported in Table 3 was elaborated to meet fully or partially expectations in this matter.

The gradual decrease of pH as illustrated on Figure 1 was strictly related to the greater share of brown coal (BC), i.e., an incorporation of more acidic functional groups. This coincides with a simultaneous decrease of the counteracting effect of calcium from with cement (CEM). The overall pH changes from CEM through CEMBRO to BC varied by 2.6, 2.1 and 1.9 pH unit, respectively for the rates 0.5, 1.5 and 3.0%. If we refer to the ratio 50/50, i.e., the CEMBRO

component consisting of 50% CEM and 50% BC, it comes out, that pH at the 60/40 as well as 40/60 ratios was kept quite unchanged and depended solely on the rates of applied CEMBRO. This finding is of crucial value in terms of economical planning in one hand and environmental remediation on the other hand, since it allows a flexible handling of cement and brown coal.

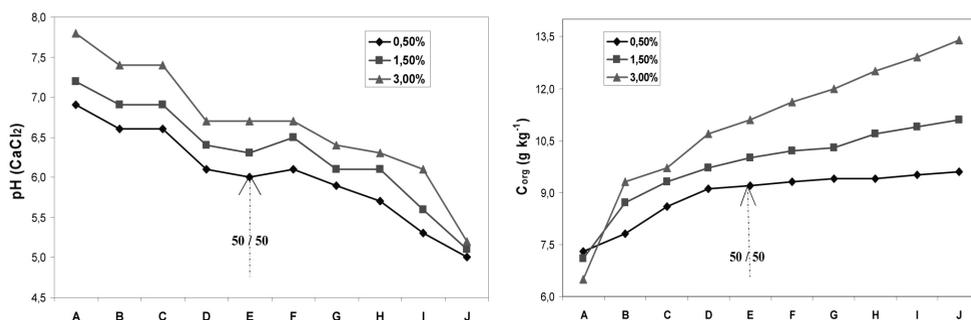


Fig. 1. Effect of CEMBRO application on pH and organic carbon status of soils (A, B.....J, see Tab. 3)

Rys. 2. Wpływ preparatu CEMBRO na pH i zawartość węgla organicznego w glebach (A, B.....J, patrz tab. 3)

The content of organic matter increased progressively along with CEMBRO rates, being higher in the case of 3.0%. It should be mentioned that chemically, brown coal is mostly inactive and its breakdown will proceed slowly due to the wide C:N ratio (121:1). Based on this sole characteristics, the formation of organic acid-sand conglomerates seems practically and hardly expectable. Therefore the addition of cement was intended to boost the emergence of functional groups *via* enhancing the dissolution of fulvic acids, which exhibit significant affinity for metal retention, Zn among others [Días-Barrientos et al. 2003]. In other words CEMBRO will provide the soil environment with appropriate amounts of Ca (64.50% CaO in CEM) to raise the extremely low Ca level, Si (21.97% SiO₂ in CEM) as a binding-stabilizing agents, and brown coal (44.8% C_{org} in BC) as whole „sticking” material as below. Such physical and chemical future of CEMBRO is not limited to the improvement of the soil structure (conglomerate formation), only, but also as Zn stabilizing tool, since its levels were very high to exhibit biological (bio) and (phyto)toxicity.

3.2. CEMBRO-aided Zn stabilization: Efficiency and perspectives

The susceptibility of the investigated soil ecosystem to degradation is limited not only to the exceptionally low levels of both organic matter and calcium, but to very high levels of acid-soluble (AS_{Zn}), exchangeable (Ex_{Zn}) and even bioavailable (Bio_{Zn}) Zn forms (Tab. 5). This is of great environmental, due to the fact that Ex_{Zn} and Bio_{Zn} fractions which generally exhibit direct impact on living organisms (i.e., microorganisms and plants), [Smolders 2005],

represent ca 49 and 10%, respectively as compared to AS_{Zn} . The sandy character of the degraded soil along with the substantially low organic matter content were fully responsible for the high lability of Zn as reported by Kabata-Pendias [1993].

Table 5. Acid soluble, exchangeable and bioavailable forms of Zn extracted from the soil

Tabela 5. Wymienne, biodostępne oraz rozpuszczalne w kwasie formy Zn ekstrahowane z badanej gleby

1 mole HCl Acid soluble (AS_{Zn})	1 mole CH_3COONH_4 Exchangeable (Ex_{Zn})	0.1 mole $NaNO_3$ Bioavailable (Bio_{Zn})
Zn ($mg \cdot kg^{-1}$)		
405.7	197.8	38.3

The specific aim of CEMBRO application was targeted for stabilizing Zn in order to create appropriate soil conditions for further vegetation establishment. The latter one may potentially take place under significantly reduced Zn solution concentrations. The overview of the efficiency course at particular CEMBRO rates is reported on the Figure 2.

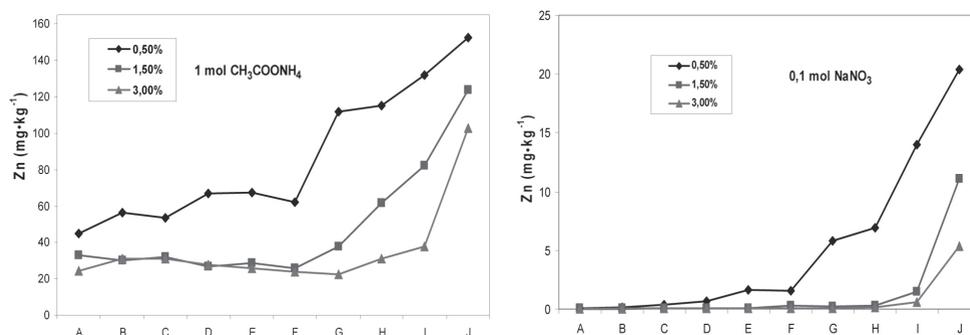


Fig. 2. Zinc stabilization efficiency estimated throughout Ex_{Zn} and Bio_{Zn} fractions at given CEMBRO rates (A, B,.....J, see Tab. 3)

Rys. 2. Skuteczność stabilizacji cynku oszacowana poprzez frakcje Ex_{Zn} i Bio_{Zn} dla wybranych dawek CEMBRO (A, B,.....J, patrz tab. 3)

Organic matter incorporated into soils contain organic compounds of different molecular weight and capacity for forming stable complexes with metallic cations (Zn among others) in solution. These compounds are characterized by one or more functional groups (carboxylic – COOH, phenolic – OH, and others), that exhibit negative charges, when fully dissociated [Sparks 1995]. This process may be strengthened by the raise of pH induced by the presence of cement which in turn increases the surface charge of organo-mineral colloids *via* deprotonation reactions [Davranche et al. 2003]. Such chemical reactions consequently lead to

a significant decrease of Zn in the ambient soil solution and favor its simultaneous mitigation [Dias et al. 2003]. The joint effect of CEMBRO components and the resulting Zn stabilization efficiency are listed in Table 6a and Table 6b for the most efficient ratio ranges only.

Table 6a. Zinc stabilization efficiency evaluated for exchangeable (Ex_{Zn}) Zn forms

Tabela 6a. Skuteczność stabilizacji cynku oceniona dla form Zn wymiennego (Ex_{Zn})

CEMBRO rates (%)	Ex_{Zn} (mean \pm SD)	Whole range (A.....J)	Stabilization Efficiency (%) [*]
		<i>Efficient ratio range (ERR)</i>	
0.5	58.7 \pm 8.7	A....F	70.3
1.5	30.7 \pm 4.1	A....G	84.5
3.0	27.2 \pm 3.5	A....H	86.3

$$* \frac{(Ex_{Zn} \text{ before stabilization} - Ex_{Zn} \text{ after stabilization}) \cdot 100}{Ex_{Zn} \text{ before stabilization}}$$

Table 6b. Zinc stabilization efficiency evaluated for bioavailable (Bio_{Zn}) Zn forms

Tabela 6b. Skuteczność stabilizacji cynku oceniona dla form Zn biodostępnego (Bio_{Zn})

CEMBRO rates (%)	Bio_{Zn} (mean \pm SD)	Whole range (A.....J)	Stabilization Efficiency (%) [*]
		<i>Efficient ratio range (ERR)</i>	
0.5	0.75 \pm 0.67	A.....F	98.0
1.5	0.16 \pm 0.11	A.....H	99.6
3.0	0.13 \pm 0.17	A.....I	99.7

$$* \frac{(Bio_{Zn} \text{ before stabilization} - Bio_{Zn} \text{ after stabilization}) \cdot 100}{Bio_{Zn} \text{ before stabilization}}$$

The environmental friendly CEMBRO rate, which could be suggested as applicable and sufficiently efficient for Zn stabilization depended on the chemical test (Ex_{Zn} , or Bio_{Zn}) used for stabilization evaluation. Data reported on Fig. 2 and outcome to Tables 6a and 6b, clearly show, that all CEMBRO ratios were efficient up to 30/70 (namely G), mainly for the rates 1.5 and 3.0%. The lowest rate, i.e., 0.5% has proved relatively less efficient for the Ex_{Zn} assessment as compared to Bio_{Zn} forms. Therefore based on these efficiency levels the rate 1.5% should be recommended for the following CEMBRO ratios: 30/70 and 20/80 (Tab. 3). In perspectives the ratios from 1:2.5 up to 1:4 (i.e., CEM:BC) appeared to be ecologically efficient and safe for the investigated soil.

3.3. Geochemical reactions and Zn potential lability

Zinc stabilization as related to CEMBRO incorporation into the soils proceeded simultaneously throughout geochemical changes, among others the cation exchange capacity (CEC). The gradual decrease of soils capacity for Zn retention was reverse to brown coal

inputs. It means the higher the share of BC in CEMBRO, the relatively lowest the CEC of the soil (Fig. 3).

The analysis of data reported in the Fig. 3 implies, that zinc release to the ambient soil solution appeared to be closely related more to increasing BC rates than CEM. It has been reported [McBride 1989; McBride et al. 1997b], that metal reactions (zinc among others) with soil colloids proceeds through deprotonation reactions, which in turn tend to increase metal activity in the soil solution due to H^+ -based secondary acidification. These conditions are expected under current investigations since brown coal may decidedly favor such processes. The evaluation of this process was performed *via* proton generation capacity (α) of Zn adsorbed and the retention power (β) of the soils. These values were obtained from linear coefficients: $y = \alpha x \pm \beta$, where: $y = K_d$ (partition coefficient); $x = pH_{CaCl_2}$. Results are listed in Table 7.

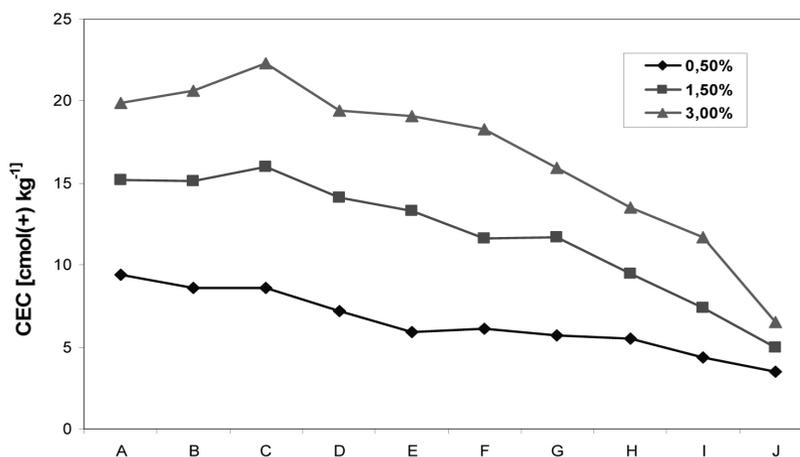


Fig. 3. Changes in the cation exchange capacity (CEC) of soils as induced by CEMBRO incorporation (A, B.....J, see Tab. 3).

Rys. 3. Zmiany w kationowej pojemności wymiennej (CEC) gleb pod wpływem CEMBRO (A, B.....J, patrz tab. 3)

The capacity of proton generation as induced by Zn adsorption decreases with increasing the share of BC in CEMBRO. This was attributed to the acidifying character of BC (Fig. 1), hence zinc ions were sufficiently active in the soil solution without a need for reacting with functional groups (deprotonation). Relationships between partition coefficients and soil pH yielded stronger coefficients of determination (R^2) at the lowest CEMBRO rates (i.e., 0.5%) as compared to the highest ones. This may be related to the emergence of great heterogeneity of Zn binding surfaces as a result of interacting high amounts of CEM with BC. On the other hand the power of soils for generating negative charges increased along with BC rates. Similar findings were reported by [Harter and Naidu 1995; Kumpiene 2003], who stated about the geochemical property of organic matter as a potential „reservoir” of func-

tional groups, i.e., negative charges. In fact the apparently high α values with simultaneously low β are indicative of weaker Zn retention properties of soils. Furthermore high solution concentrations of H^+ directly interferes with Zn ions and reduces their attraction by soil colloids. This is less probable at higher CEMBRO rates. These results support fully the view mentioned above on the rate 1.5% to be recommended for the following CEMBRO ratio ranges: from 30/70 to 20/80, i.e., namely CEM/BC, respectively.

Table 7. Proton generation capacity (α) and soil retention power (β) for Zn estimated for bioavailable (Bio_{Zn}) and exchangeable (Ex_{Zn}) forms

Tabela 7. Zdolność generowania protonów (α) oraz zdolność zatrzymywania (β) obliczone dla form Zn biodostępnego (Bio_{Zn}) i wymiennego (Ex_{Zn})

Chemical test	%	α	β	R^2
		mole protons / mole Zn sorbed	mole of negative charges / mole Zn sorbed	
^a K_d [$dm^3 \cdot kg^{-1}$] for Bio_{Zn}	0.5	1.23	-4.71	0.83
	1.5	1.18	-4.66	0.79
	3.0	0.96	-2.71	0.70
^b K_d [$dm^3 \cdot kg^{-1}$] for Ex_{Zn}	0.5	0.27	-0.01	0.85
	1.5	0.30	0.09	0.76
	3.0	0.19	0.77	0.53

^a $\frac{mg\ Zn\ kg^{-1}\ in\ 1\ mole\ HCl}{mg\ Zn\ dm^{-3}\ in\ 0.1\ mole\ NaNO_3}$; ^b $\frac{mg\ Zn\ kg^{-1}\ in\ 1\ mole\ HCl}{mg\ Zn\ dm^{-3}\ in\ 0.1\ mole\ CH_3COONH_4}$

4. CONCLUSIONS

1. The investigated soil is typically sandy and characterized by a low content of organic carbon. Moreover the acidic nature of the soil environment is one of the factors affecting grasses and plant growth.
2. The acid soluble Zn fraction amounted to $405.7\ mg \cdot kg^{-1}$ of which ca 49 and 10% were represented by exchangeable and bioavailable Zn forms, respectively. This is of great environmental concern due to the fact that these fractions will exert direct impact on living organisms.

3. The incorporation of cement alone to the sandy soil has led to a significant rise of the soil pH (up to 8), whereas the application of brown coal alone did not exert any marked influence on soil pH. The component „CEMBRO” has displayed a greater stabilization efficiency for Zn in treatments with a higher share of cement.
4. Geochemical reactions of Zn and its potential lability assessed on the basis of proton generation capacity (α) of sorbed Zn and the retention power (β) of soils revealed that the rate 1.5% should be recommended for the following „CEMBRO” ratio ranges: from 30/70 to 20/80, i.e., namely CEM/BC, respectively.

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