BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE

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BAUXITE RESIDUE SAFETY DISPOSAL AND FRIENDLY ENVIRONMENTAL PROCESSING PERMANENT CARE AT VIMETCO ALUM SA TULCEA

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This paper concerns an experimental investigation on the conversion of weathered bauxite residue into a nutritive composite support for plant growth.

The study is previewed by a presentation of the bauxite residue site disposal, after 2009 full retrofit, followed by some successive improvements for complaining with the EU directives recommendation regarding environmental protection.

The paper includes:

VIMETCO ALUM SA TULCEA bauxite residue site disposal description

Alumina refinery is located on the outskirts of Tulcea town (Romania) and the red mud disposal site is located at 5 km distance from refinery.
The red mud storage technology was changed starting 2009 and this includes the switching from red mud sludge lagoon impoundment to paste thickening and dry stacking.

The main improvements brought in by the new implemented technology for red mud disposal concern the following changes:

- ✓ paste thickener
- ✓ dry stacking
- ✓ consolidation of the dams
- ✓ full fencing and complete surveillance
- ✓ site partial closure facing the main dam and planting of 30,000 trees
- ✓ pluvial water collecting and detouring channel for preventing site over-flooding
- ✓ water-sprinkling systems to keep the dry material surface moistened
- ✓ pumping systems for the red mud adduction and for returning the clarified liquor to refinery in order to be used into the technological process
- ✓ a waste water monitoring system consisting in drilling boreholes and piezometric landmarks.

All the changes were done in cooperation with specialists from Hatch Ltd Australia, Technical University of Civil Engineering Bucharest and Iprolam SA Bucharest.

VIMETCO ALUM SA TULCEA bauxite residue site disposal description cont'

The entire work complies to the EU directives recommendation regarding the environmental protection.

The environmental risk has been considerably reduced compared to previous technology for red mud disposal.

During the recent years there were performed several monitoring services conducted by some prestigious research institutes in Romania, respectively ICIM Bucharest (Research Institute of the Ministry of Environment), ECOIND Bucharest, IMNR Bucharest, IPROCHIM SA Bucharest and others, through researches and laboratory tests.

Also, the environmental authorities are performing periodical inspections on site in order to verify the complying to the environmental regulations.

All these supplementary activities lead to the conclusion that the environmental impact of the red mud disposal site over surrounding agricultural area is not significant.

VIMETCO ALUM SA TULCEA bauxite residue site disposal description cont’

The above mentioned changings are illustrated by the following pictures

P1. Frontal dam, illuminated fencing and pumping station

VIMETCO ALUM SA TULCEA bauxite residue site disposal description cont'

P2. Dyke and pluvial water detouring channel

VIMETCO ALUM SA TULCEA bauxite residue site disposal description cont'

P3. Rehabilitated area ~ 5 hectares

VIMETCO ALUM SA TULCEA bauxite residue site disposal description cont'

P4. Paste thickener & red mud moistening sprinklers

Chemical and agrochemical properties of the red mud considering Sierra Leone bauxite as raw material

Investigations about red mud variable composition started in 2011, when Alum Tulcea accumulated a good experience in processing Sierra Leone bauxite and started some projects to find technologies for conversion the red mud into a commercial product.

Some of these studies mainly concern the use of raw or processed red mud as alkaline adjuvant for acidic soils or as a major component in artificial soils used for remediation and landscape architecture.

All the studies were made in cooperation with ICPA Bucharest (Soil Science Institute).

Table 1. Chemical composition of the red mud from Alum Tulcea

Al_2O_3	CaO	MgO	K_2O	Na_2O	SiO_2	Fe_2O_3	MnO	TiO_2	Total oxides	PC	Total
18.16	**3.66**	**0.16**	**0.15**	**6.87**	**7.50**	**44.6**	**0.03**	**3.16**	**84.40**	**15.2**	**99.8**

Table 2. Macronutrients and microelements content in red mud

Macro-elements	mass %	Micro-elements	ppm
Fe	28.8	Cd	**0.369**
Al	9.3	Co	**0.870**
Na	5,3	Cr	**604.0**
Ca	2.80	Cu	**71.00**
K	0.094	Mn	**260.0**
Mg	0.056	Pb	**1.100**
P	0.92	Zn	**56.00**
N	0.06		
$C_{organic}$	0.340		
$C_{anorganic}$	**0.886**		

Chemical and agrochemical properties of the red mud considering Sierra Leone bauxite as raw material cont'

Table 3. Red Mud agrochemical properties

Ionic mobility	mg/Kg	Ion exchange capacity	meq./100g red mud	Total ion exchange capacity	meq./100g red mud
P_{AL}	196+-	Na at pH 7	128.63	T_{Na}	**62.58**
K_{AL}	287	Na in water	26.45	T_{NH4}	**29.48**
		Na exchangeable	**100.15**	**-**	**-**

According to above data, the red mud elemental composition, as compared with common soils composition, is largely non-equilibrated, mainly from the point of view of macro and mezzo nutrient contents.

The heavy metals concentration in the red mud composition is very close to the normal values found in soils, excepting total chromium content. Chromium concentration should be carefully regarded, because our previous data have shown the leachable parts of chromium are decreasing under the acceptable standards, as far as the pH drops toward usual values in soils.

Total soluble salt content found in the red mud composition was 1836 mg per 100 g dry material, very high when it is compared with accepted values for soil salinity. Also there were recorded high levels of Na [1+] (5300 mg/kg) and Ca[2+] (2800 mg/kg, ionic mobility).

All these properties of the row or weathered by-product, make it to a totally unsuitable support for plant growth.

Mineralogical phases in Sierra Leone bauxite and in the red mud coming from technological process

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Sierra Leone bauxite and the red mud coming from this type of bauxite processing were thoroughly investigated by XRD and XRF analysis for full characteriztion as chemical and mineralogical composition.

Table 4. Red mud composition (Quantitative). Comparison between the obtained data with the two analysis methods: DRXP and XRF

Mineralogical phase / Chemical constituents	RM, DRXP, Mineral constituents %	RM, DRXP, Chemical constituents, %	RM, XRF, Chemical constituents, %
Gibbsite	1.25	-	-
Goethite	35.31	-	-
Hematite	12.46	-	-
Al_2O_3	-	8.81	19.35
Fe_2O_3	-	27.88	45.95
Sodalite	2.31	-	-
Na_2O	-	0.56	3.38
Quartz	0.39	-	-
Katoite	2.51	-	-
SiO_2	-	1.63	9.30
Calcite	1.01	-	-
CaO	-	1.61	4.91
Rutile	0.76	-	-
Anatase	0.5	-	-
Ilmenite	3.15	-	-
TiO_2	-		2.25
Al_2O_3(amorphous)	10.5	-	-
Difference	29.8 as amorphous	Difference: 59,51 as amorphous	Difference:14.31 % others as both amorphous and crystalline

The entire mass of Fe_2O_3 is in solid solutions: alumino-goethite and aluminuous hematite. These compounds incorporates some quantities of unusable Al_2O_3.

Mineralogical phases in Sierra Leone bauxite and in the red mud coming from technological process cont'

All the chemical constituents of Sierra Leone bauxite are laying in both in crystalline and amorphous state.

A significat mass of amorphous phases is accompanying the well defined mineralogical phases in both bauxite and red mud. Amorphuos state originates from the excesive wearing of the crystalline phases, during bauxite mineralogical history.

From the bauxite and red mud mineralogy, it can be concluded that Sierra Leone bauxite processing implies significant changes in the applied Bayer technology, namely:

- ✓ improving bauxite preparation process at source,
- ✓ changing process parameters in milling, desilication and digestion stages, as well as in thickening steps,
- ✓ and maybe hastening the investments in red mud filtration.

The red mud composition is unusual for this type of products, because more than 50 (mass) % of the raw bauxite is not reacting in Bayer process.

Filtration of the red mud will improve at large extent the quality of red mud supposed to be converted to fertile unconventional soils.

Red mud environmental properties investigation

Red mud toxicity is related to its alkalinity, radioactivity and heavy metals content.

The red mud chemistry, toxicity, safe disposal and its environmental hazards was investigated at several institutes: ECOIND SA Bucharest, ICPA Bucharest ICECHIM SA Bucharest and Defence and Ecology Research Centre Bucharest

All the reports on heavy metals confirmed the stability of their compounds in red mud during conservation in dry state as a non hazardous material.

Recently, ECOIND Bucharest has finished a report on red mud alkalinity decay during natural carbonation and eventually heavy metals stabilization.

Red mud radioactivity was investigated at Institute of Nuclear Engineering Bucharest.

The report conclusion, on Minimum Detectable Activity (MDA) according the ISO 11920/2010 is: Total radioactivity measured on red mud samples is below the mean soil natural radioactivity, which is about 40/Bq/kg.

Red mud environmental properties investigation cont'

The Medico-Military Research Centre Bucharest has carried out several corrosivity tests on the red mud samples having the following pH values: 11.2, 11.6 and 12.2, prepared from row weathered samples, collected from surface layers at the red mud disposal site.

After tests validation the sample 3 (pH 12.2) has been classified as irritating to rabbit eyes, sample 1 (pH 11.2) as non-irritating and sample 2 (pH 11.6) as minimum irritating.

The test of acute toxicity/irritation and dermal corrosivity showed that all the samples are non-corrosive.

Repeated tests showed that acute conjunctive irritation occurs at pH 11.8.

According to these tests the corrosivity threshold in red mud is located at pH 11.8.

Red mud as adjuvant for acid soils remediation

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Objectives

The main objective of this study was the checking of a plant response, in terms of growth parameters, to a non conventional soil formulated from red mud and additives able to change the red mud chemical and agrochemical properties till the level of a medium fertility natural soil.

The interest was to find a valid solution for a quick closure of a small area in red mud disposal site or for rehabilitation of a damaged acid soil.

<u>The damaged acid soil considered for this test was Albota albic luvisol (Arges) Romania</u>

Many studies, underlined that red mud application to any soil is very effective for reducing phosphorous leaching, improving pasture growth ameliorating soil acidity, increasing metal sorption and decreasing soluble metal concentrations, and above all, the red mud reduces the heavy metals availability.

But, the mixing of red mud with additives and others damaged soils is not a simple problem of mixing and dispersing. There are some common strategies for sustaining deep changes in properties of the unconventional soils containing red mud.

Some of these strategies were used by Alum in cooperation with ICPA Bucharest for tailoring some suitable red mud composite soils.

Red mud as adjuvant for acid soils remediation cont'

Experimental

Albota albic luvisol is a tipical acid soil with moderate pH, *medium hydrolitic acidity* (A_h), and low trophic level due to its poor content in *exchangeble bases (SB), humus*, *total nitrogen (N_t), nitric nitrogen ($N\text{-}NO_3$), mobile phosphorus (P_{AL})* and *mobile potassium (K_{AL}).* Its low *bases saturation degree (V)* is specific for oligo-mezo-basic soils.

Table 5. The agro-chemical properties of the upper horizons (0-20 cm) from Albota albic luvisol (Arges county)

Depth	pH $_{H2O}$	SB	Ah	V	Nt	$N\text{-}NO_3$	Humus	P_t	P_{AL}	K_{AL}
cm		meq/100 g		%		mg/kg	%		mg/kg	
0-20	5.10	10.06	5.86	63.2	0.100	0.9	1.98	0.047	14.3	92
20-40	5.31	10.94	5.11	68.2	0.094	0.75	1.86	0.045	13.0	100

SB- Exchangeable Bases; Ah – Hydrolitic acidity; V-Bases saturation degree

Red mud as adjuvant for acid soils remediation cont'

Fertilization

For organic fertilization was used natural organic compost (table 6). The mineral fertilization comprises a mixture of ammonium nitrate and potassium hydrogen phosphate with quantitative formula N_{120} $P_{60}K_{40}$ (i.e. 120, 60 and 40 kg/ha). Total added minerals nutrients is 200 kg/ha.

Table 6. The agro-chemical properties of organic compost used in unconventional soils formulation are given in the table below

Identification	pH (H_{2O})	$C_{organic}$	M.O.	N_t	C/N	N-NO_3*	P (H_2O)*	K (H_2O)*
		%				mg/Kg		
Organic compost	7.35	25.6	68.0	1.34	22.3	65.0	12.8	470

M.O. – organic mass; Nt – total nitrogen; C/N – ratio carbon /nitrogen; N-NO3 – nitrate nitrogen; P(H2O) - soluble phosphorus; K(H2O) - soluble potassium

Careful formulation of the unconventional soils had as a target a favorable domain to control the chemical and agrochemical properties, avoiding excesive contents of soluble salts and heavy metals.

Red mud as adjuvant for acid soils remediation

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Experimental set up and unconventional soils presentation

An experiment with 6 variants was set up at 16 July 2012. The plant used for test was maize. The experiment comprises 3 repetitions for each variant using vegetation pots with a capacity of 8 kg soil.

Table 7. Experimental variants

Experimental variants	***Composition***
1	Control 1; Non-ammended; Non-fertilized
2	Control 2; Non-ammended; Organic fertilization - 40 t/ha
3	Control 3; Non-ammended; Organic fertilization - 80 t/ha
4	Red mud ammended - 15 t/ha; Organic fertilization - 40 t/ha; Mineral fertilization – $N_{120}P_{60}K_{40}$ (120 kg N/ha + 60 kg P_2O_5/ha + 40kg/ha K_2O) total inorganic nutrients 200 kg / ha
5	Red mud ammended - 30 t/ha; Organic fertilization - 40 t/ha; Mineral fertilization - $N_{120}P_{60}K_{40}$ (120 kg N/ha + 60 kg P_2O_5/ha + 40kg/ha K_2O) total inorganic nutrients 200 kg / ha
6	Red mud ammended - 75 t/ha; Organic fertilization - 40 t/ha Mineral fertilization - $N_{120}P_{60}K_{40}$ (120 kg N/ha + 60 kg P_2O_5/ha + 40kg /ha K_2O) total inorganic nutrients 200 kg / ha

Red mud as adjuvant for acid soils remediation cont'

The experimental program followed the basic procedures of INCDPAPM-ICPA Bucharest shortly described in our previous papers.

Control 1 is the damaged soil control sample. Control 2 and 3 are simple damaged soil fertilized samples. Variants 4-6 are really unconventional soil samples.

During the vegetation stages, in addition to maintaining steady growth factors there have been made observations regarding the *emergence* (percentage of emerged plants in dynamics), *plant height* (in dynamics), and *morphological aspects* (emergence of various phenomena such as chlorosis, stagnation in growth, leaf necrosis).

During vegetation stages there were made measurements on plants waist till the cropping day, and two plant thinnings on 30 July and 20 August.

At the end of the growing season, there were harvested plant samples for measuring the green and dry mass of aerial parts and root parts. Also, there were made typical chemical analysis for plants and grain.

At the end of the growing season were taken plant organs samples and soil samples.

The samples were measured and analyzed, according to the ICPA Bucharest methodology taking into consideration the ISO European methods.

All analytical data were statistically calculated using statistical parameters and variance analysis.

Red mud as adjuvant for acid soils remediation cont'

Analytical data on the soil chemistry in the experimental variants are given in table 8.

Table 8. Agro-chemical properties of the Albota soil ammended with red mud and organic compost

Variants	pH	Humus	$C_{organic}$	N_t	C/N	$N\text{-}NO_3$	P_{Al}	K_{AL}
		%				mg/Kg		
V1	5.10	1.98	-	0.100	-	0.9	14.3	**92**
V2	6.64	15.28	8.9	0.246	41.9	1	41	**187**
V3	6.45	11.28	6.5	0.227	33.7	4	57	**278**
V4	6.79	11.20	6.5	0.224	33.8	37	45	**172**
V5	7.07	12.08	7.0	0.239	34.3	37	39	**320**
V6	7.29	15,12	8.8	0.218	46.9	37	37	**196**
DL 5%	**0.18**	**-**	**1**	**0.018**	**5.8**	**2.9**	**5**	**19**

The acid moderately soil Albota, non-amended and fertilized, has the pH(H_2O) = 5.1 . By amending this soil with regular doses of organic compost and mineral fertilizers, the soil pH is proportionally raising up till a low - acid –alkaline soil reaction.

Red mud as adjuvant for acid soils remediation cont'

By amending of Albota soil with regular doses of organic compost and mineral fertilizers, according the table presented below, a lot of changes took place in soil solution chemistry (table 9).

Thus, the total exchangeable bases (SB), degree of bases saturation (V%) and total capacity of cationic exchange are raising substantially and the hydrolitic acidity recorded a decisive decrease.

Table 9. Exchange cationic properties of the tailored soils

Variants	SB, meq/100 g	A_h, meq/100 g	Total ionic exchange, meq/100g	V(%)
1	11.37	6.02	17.39	**65.4**
2	11.89	5.29	17.18	**69.2**
3	14.63	4.35	18.97	**77.4**
4	14.50	5.53	20.02	**72.4**
5	15.02	4.33	19.35	**77.6**
6	**18.30**	**2.19**	**20.50**	**89.3**

Roughly, the amending of Albota soil with regular doses of organic compost and mineral fertilizers, leads to:

- pH raise to slightly alkaline and proper soil mineral properties,
- improves the content of organic C and total N and,
- raises the mobility of P and K at moderate doses of organic compost.

Red mud as adjuvant for acid soils remediation cont'd

After harvesting, the soil preserves some of the acquired changed properties due to the previous amendments. The agro-chemical properties of the depleted soil after harvesting are given in the table 10.

Tabelul 10. Agro-chemical properties of the Albota soil ammended with red mud after harvest

Variants	pH	$C_{organic}$	N_t	C/N	P_{Al}	K_{AL}
		%			mg/Kg	
V1	5.11	1.53	0.138	13.2	24	**89**
V2	5.29	1.90	0.144	15.4	33	**81**
V3	5.57	2.05	0.154	15.6	29	**75**
V4	5.66	1.80	0.141	14.9	130	**128**
V5	5.90	177	0.157	13,.2	180	**119**
V6	6.72	1.77	0.193	10,7	258	**172**
DL 5%	**0,17**	**0.20**	**0.05**	**0.16**	**15**	**18**

But some changes in C organic, total nitrogen, mobile phosphorus and mobile potassium are visible.

Red mud as adjuvant for acid soils remediation cont'

Crop measurements and yields

There were measured the following parameters on the plants organs: plant waist, leaves mass, stems mass, roots mass, husks mass, and cobs and grains mass. Also, there were determined the content of macronutrients and micronutrients in maize leaves and maize grains.
The results presented in the following figures 1-6.

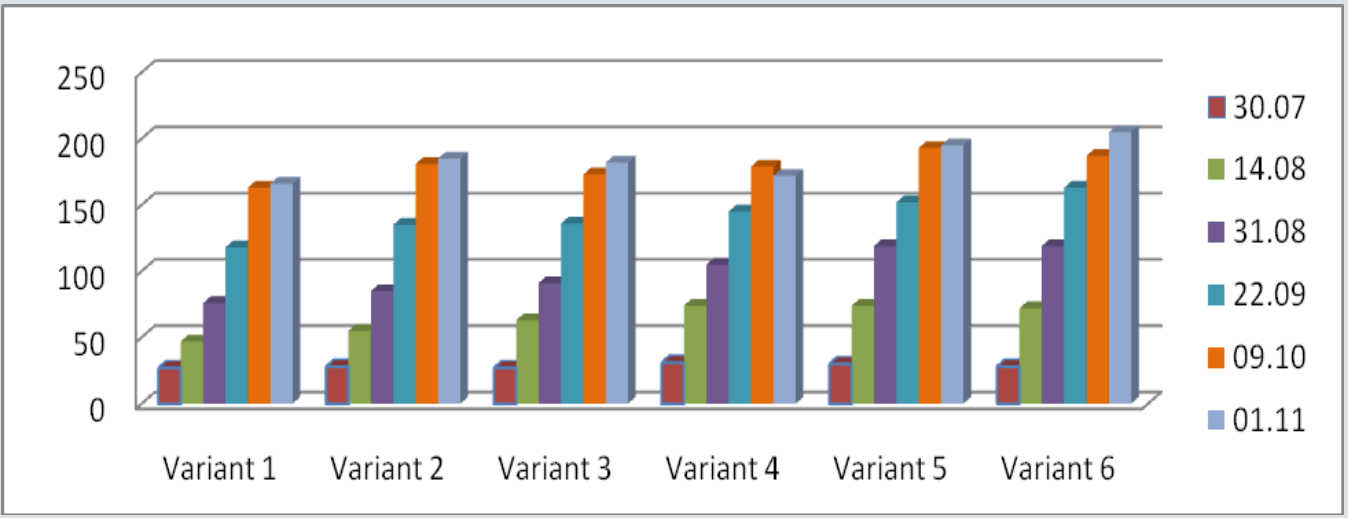

Figure 1.

Albota Albic luvosoil amendment and fertilization effect on the plants waist (cm) during the experimental period

The plants waist was constantly growing in all variants, and the amendment and fertilization effects are evident since early stages until the final harvesting. The control variants (V1 – V3) are far behind in growth against the amended ones in all the stages without exceptions.

Red mud as adjuvant for acid soils remediation cont'

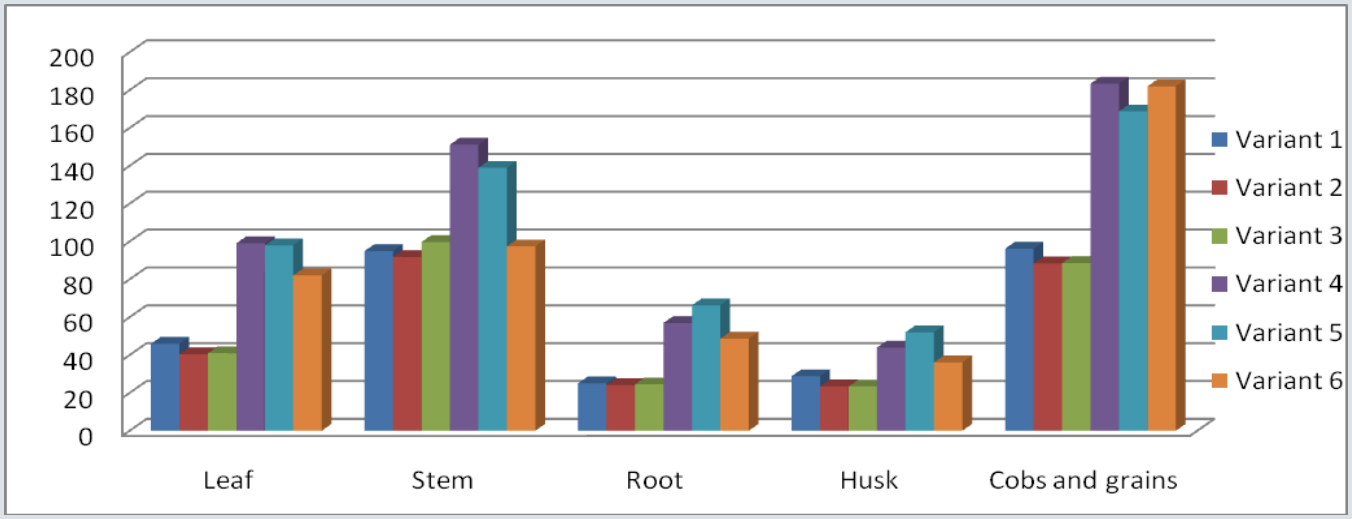

Figure 2.

Albota Albic luvosoil amendment and fertilization effect on the maize mass plant organs (g/plant) after harvesting

Amendment and fertilization effect on the maize mass plant organs is selective and some characteristically patterns may be seen for each plant part.

The strongest effect is visible on cobs and grains, where yields are almost double than in variants 1-3.

Red mud as adjuvant for acid soils remediation cont'

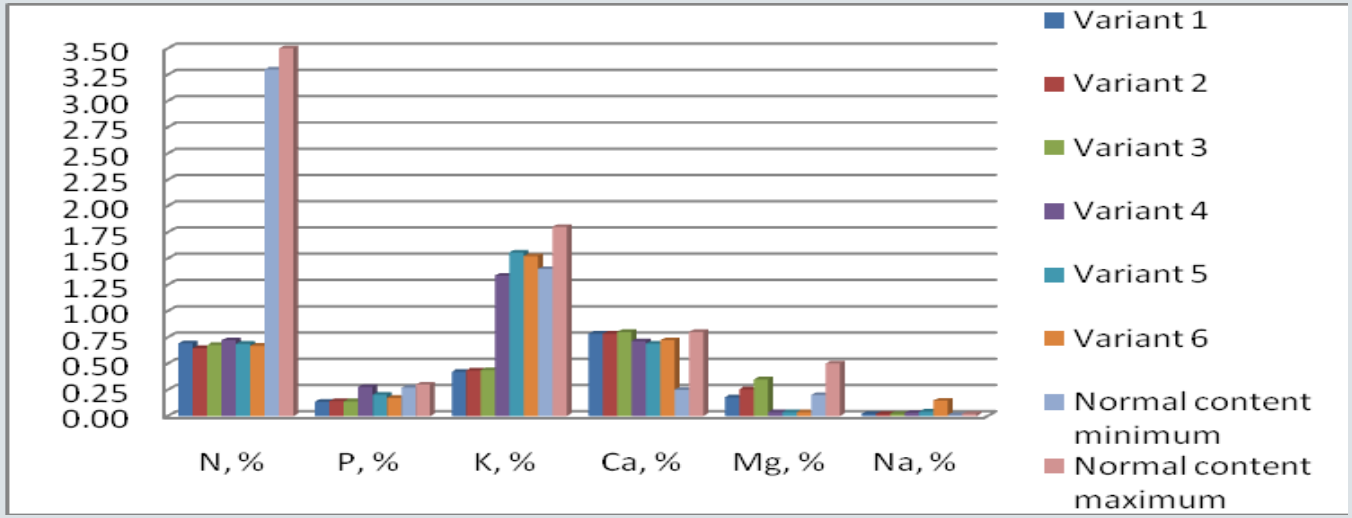

Figure 3.

Albota Albic luvosoil amendment and fertilization effect on the macronutrients in maize leaves

Phosphorus level in leaves is closer to the normal content, but its concentration drops evidently and significantly as the red mud concentration in soil increases from variant 4 (phosphorus content is equal with normal concentration in maize leaves) to variant 6.

Potassium (exceeding in concentration and mobility in soil) effect is visible, and in the variant 4-6 case, all its concentration raise to normal values for maize. The same conclusion is valid for calcium, due to its exceeding concentrations even in the control samples.

Magnesium has a different behaviour. At low levels of red mud in soil, magnesium is blocked as insoluble in red mud and it is missing from maize leaves.

Red mud as adjuvant for acid soils remediation cont'

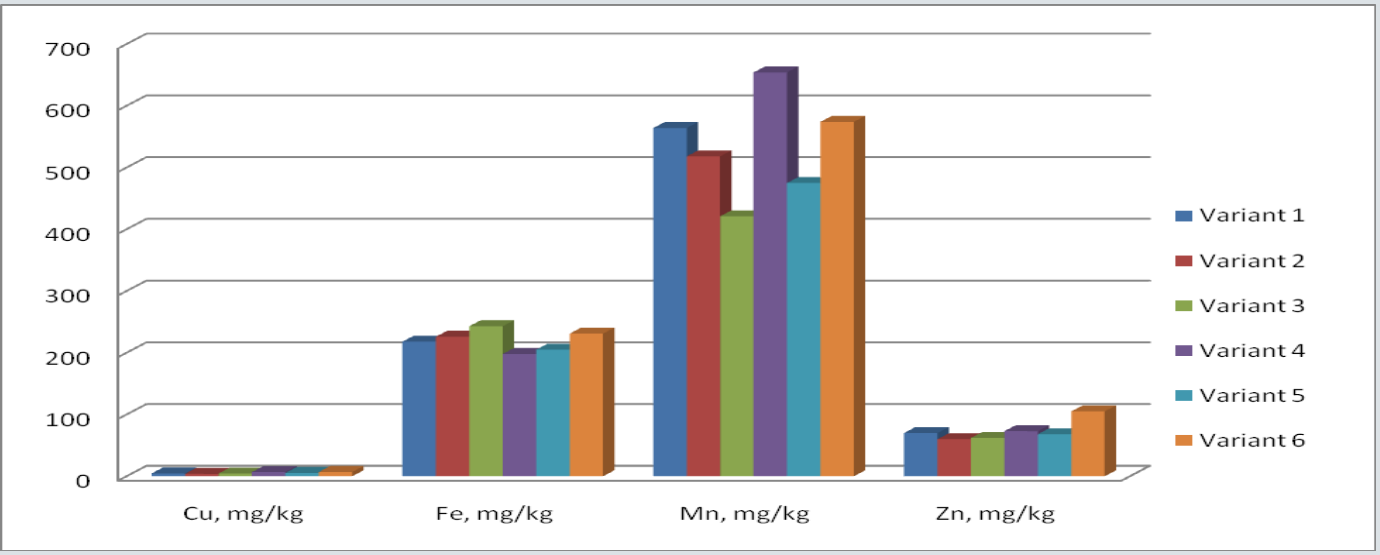

Figure 4.

Albota Albic luvosoil amendment and fertilization effect on the micro-nutrients in maize leaves

Roughly the use of red mud in acid soils rehabilitation programs, does not introduce critical problems concerning the heavy metals.

Red mud as adjuvant for acid soils remediation cont'

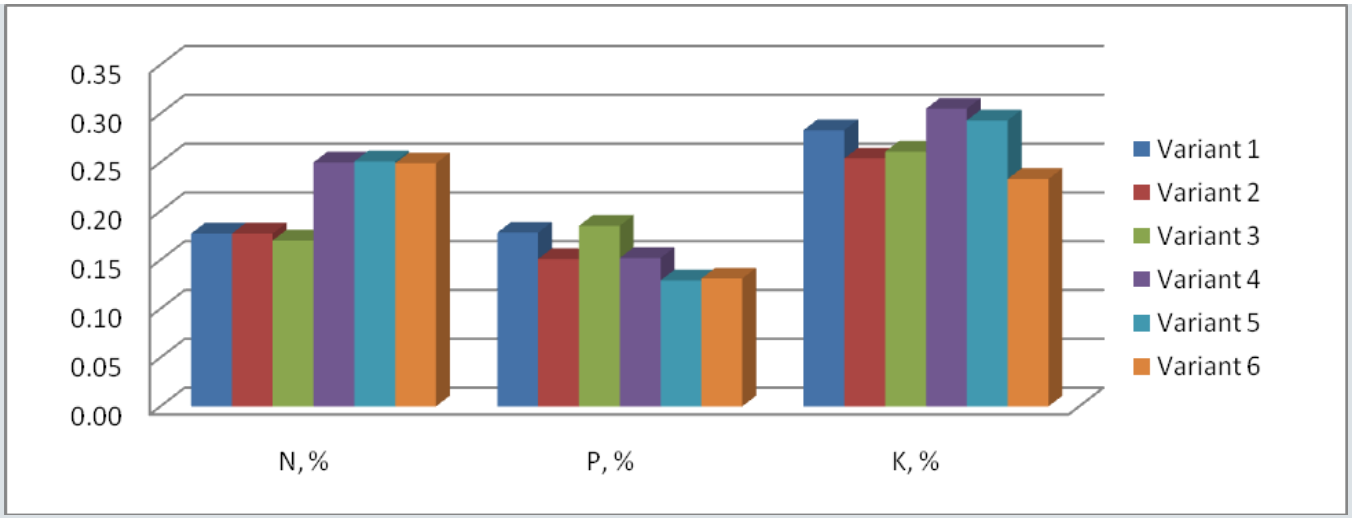

Figure 5.

Albota Albic luvosoil amendment and fertilization effect on the macro-nutrients in maize grains

The macronutrients status in maize grains is quite normal.

Red mud as adjuvant for acid soils remediation cont'

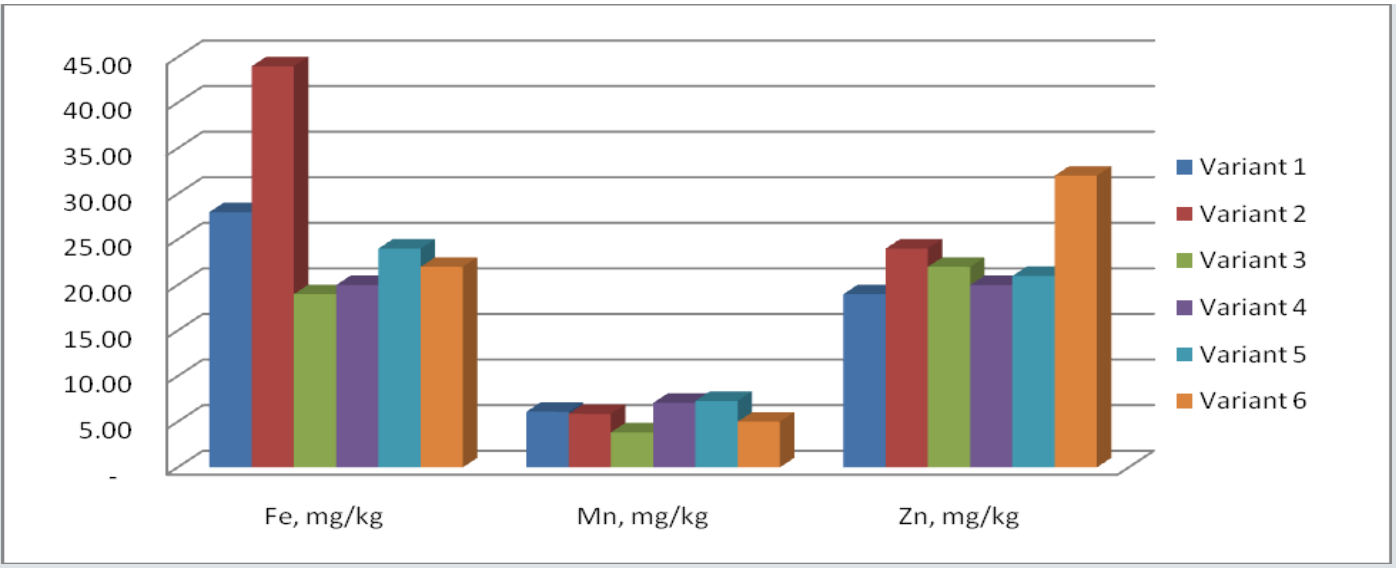

Figure 6.

Albota Albic luvosoil amendment and fertilization effect on the micro-nutrients in maize grains

Manganese and zinc concentrations in grains are normal. The other microelements, like cadmium, cobalt chromium, copper, nickel and lead, have insignificant values and their variation does change the conclusions of this report.

Conclusions

- ✓ Amending the luvosol albic from Albota soil with red mud doses of 15, 30 and 75 t / ha, organic compost 40 t / ha and mineral fertilisers 200 kg nutrients/ha, the new composite soils pH increases up to 1.5 – 2.2 units. Hence, the moderately acidic natural soil, by amending, was converted into slightly alkaline conventional soil.

- ✓ Amending the luvosol albic from Albota soil with the above organic compost doses and mineral fertilisers, the initial soil acquired significant increases in organic C, total N, and mobile phosphorus and potassium content.

- ✓ Amending the luvosol albic from Albota soil with the above doses organic compost and mineral fertilisers, there were improved both cation exchange and exchangeable bases properties, without significant increases in soil soluble salt content.

- ✓ The above amendments contributed to rises in the plants waist, green mass and dried mass and significant gains in vegetal mass, as well as in cobs and grains yield.

- ✓ The above amendments contributed to significant rises N and Na content in maize leaves at maturity stage, without reaching toxic levels. Accumulated P and K gains were recorded only in the case of low organic compost amendments.

- ✓ Even if some significant fluctuations were noticed in values of heavy metals in leaves, no toxic levels were recorded. The same conclusion is valid in case of macro- and micro-nutrients in cobs and grain.

Thank you !