Plant Growth Suitable Nutritive Red Mud Composite Materials from the Romanian Dry Landfilled Red Mud

II. Formulation nutritive composite materials and plant growth tests at laboratory and glasshouse scale

RADU LACATUSU[1]*, ANATOLI KISELEV[2], VENERA MIHAELA STROE[1], NINETA RIZEA[1], MIHAELA LUNGU[1], RODICA LAZAR[1], MIHAELA MONICA STANCIU-BURILEANU[1], ILIE CALCIU[1], ROXANA GABRIELA POPA[3], LAURENTIU FILIPESCU[2]

[1]National Research and Development Institute for Soil Science, Agrochemistry, and Environment - RISSA Bucharest, 61 Marasesti Blv., 011464, Bucharest, Romania

[2] SC Alum SA, Tulcea, 82 Isaccei Str., 820228, Tulcea, Romania

[3] "C. Brancusi" University of Tg. Jiu, 30 Calea Eroilor, 210135, Tg. Jiu, Romania

According the red mud chemical and agrochemical properties evaluated in the previous paper, there were set up two experiments concerning individual types of nutritive red mud composite formulations. Adjuvant materials selected for deep changes in the basic red mud agrochemical properties were: phosphogypsum (PG), sludge from urban biological waste water treatment factories (SWBT), sludge from water softening stage in chemical plants (SWCT), organic compost (OC), marine algae debris (MA), wood sawdust (WS), acidic peat (AP) and acidic soil (AaS) from Albota region, Romania. Agrochemical analysis of the adjuvant materials and the first type of nutritive red mud composite materials has shown that adjuvant materials themselves and all formulated composites are conveying a large dowry of mineral salts with neutral (PG, OC and MA), and alkaline (SWBT and SWCT) reaction, containing macro, mezzo and micronutrients at variable concentrations. Satisfactory concentrations of organic carbon have been carried in by SWBT (17%), OC (9.2%) and MA (1-8 %) and most all the adjuvant materials and more than that, enough buffering capacity and nutritive ionic species to sustain the crops growth. In the first type of red mud composite material, theoretical expected changes might accomplish a real conversion of the red mud into a nutritive composite material. But, soluble salts contents ranging from 1.874 to 2.888 mg/100g composite mixture, with dominant molecular species sodium carbonate did lead to rather infertile composite formulations. The second type of red mud composite materials SWBT and MA were replaced by the rich carbon and high power buffering materials as WS, AP and AaS and the ratios adjuvant materials/RM were increased to 700/1000 - 900/1000. Study of Triticum durum response to this new type of red mud composite has shown a real emerging fertility in these materials and sustainability in plants crop growth. This was an encouraging step toward better balanced formulations.

Keywords: red mud, composite materials, agrochemical properties, plant growth, Triticum durum

Researches concerning the red mud uses in agriculture could be arrayed under some common titles frequently found in literature: a) changing red mud composition for eventual capping and revegetation, and b) heavy metal immobilization and acid soils remediation. Environmental constrictions forced all the alumina producers to do some preliminary treatments before stockpiling the red mud in dumps. Accordingly, the types of red mud available for the above uses are variable in both composition and physical properties [1]. Some pretreated varieties like carbonated red mud (CRM), bitterns concentrate treated red mud (BRM) or aged red mud/gypsum) (ARMG) mixtures can be delivered by some companies [2-4].

Changing red mud composition, capping and revegetation

Direct revegetation of the stockpiled red mud surface is not possible due to high *p*H, sodicity and salinity, as well as due to the poor nutrients content. Common strategies for red mud surface revegetation are including: a) the constructing of a soil cap over the protected areas, b) amending the red mud with sand, clay or other materials, c) revegetating the sandy surrounds, and d) further covering the cap with materials sustaining plant growth. Beside the limitations due to salinity, sodicity, alkalinity, aluminum toxicity and drawbacks due to macro- and micronutrients deficit, the red mud physical properties are also problematic, since material has a very low water holding capacity and dries to form a dusty embarrassing source. An integrated approach includes gypsum amendments for reducing pH and improving porosity, organic amendments and inorganic fertilizers supply for providing essential nutrients, and for ameliorating C/N ratio and physical properties. Overall, saline tolerant plant species are recommended for capping and revegetation [5]. Some papers give details about the real capping processes. Gypsum, sewage sludge and calcium oxy-phosphate, at various proportions, were selected as organic or inorganic ameliorants for red mud in a laboratory and field tests concerning an extended trial over three plant species (*Tamarix sp.*, *Pistacia lentiscus* and *Juniperus macrocarpa)* and six grass species (*Festuca rubra, Medicago lupulina, Medicago sativa, Trifolium subterreneum, Sanguisorba minor* and *Lolium rigidum*) Gypsum, calcium oxy-phosphate and sewage sludge added at rates 7.5, 2 and 5 or 10 g per 100 g dried red mud led to the pH decrease to values lower than 8 and to the immobilization of soluble aluminum coming from red mud. Sewage sludge brought in the mixture significant quantities of organic matter and improved the structure of gypsum amended nutritive

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* *Tel.: 0723451925*

substrate. The *Tamarix sp.* and *Pistacia lentiscus* proved to be the most promising species for red mud stockpile capping and revegetation [6, 7]. A two year study over a long-term nutrient management in rehabilitated area, by incorporating phosphogypsum and sewage sludge in red mud, was made targeting the nutrient composition in the aerial portions of the two grass plants *Lolium perenne* and *Holcus lanatus.* as main objective. After one year, the herbage calcium levels were found at normal values, but the nitrogen, manganese, potassium and magnesium were below critical levels. Sodium levels declined each year without signs of capillary fluids rising from the red mud source. Further decreases in the nitrogen, calcium, manganese, magnesium, phosphorous and potassium content in the second year suggests a severe nutrient shortage in the fertile substrate. Consequently, for long-term success of revegetation of red mud amended with phosphogypsum and sewage sludge, the nutrients deficiency in the substrate has to be overcome by adequate fertilization [8]. Other studies identified some alkalinity tolerant woody species of plants which can easily accommodate the superficial treated red mud media*: Casuarina obesa, Melaleuca lanceolata, M. armillaris., M. nesophila, Eucalyptus loxophleba, E. halophila, E. platypus, Tamarix aphylla* and its particular clones of *E. camaldulensis, E. spathulata, E. tetragona, E. preissiana, E. gomphocephala, E. diptera and E. occidentalis* [9]. The mechanical structure of capping soils covering red mud deposits is highly required to prevent poor drainage during the wet season, as well as the salt capillary rise and salts surface accumulation during the dry season. Availability of water in soil capping is determinant for long term survival of the composite material vegetative fertility. On the other hand, the vegetation cover prevents deterioration of the soil substrate surface and minimizes the capillary rise of sodicity and alkalinity from the disposed red mud [10].

Heavy metal immobilization and acid soils remediation

Accumulation of heavy metals and metalloids in soils is taking place continuously in the expanding industrial areas through: a) disposal of high metal wastes, b) coal combustion residues and mine tailings, c) high doses of fertilizers and pesticides land application; d) wastewater irrigation, sewage sludge and animal manures disposal, e) spillage of leaded petrochemicals and paints, etc. Unlike organic contaminants which are oxidized to safe compounds, the metals are withstanding as toxic contaminants, even if their speciation and bioavailability may change under the action of environmental factors. Heavy metals chemical in situ immobilizations, alongside with the soil excavation followed by dumping it into landfills, washing and phytoremediation are the most frequently applied technique for remediation the heavy metal-contaminated sites [11, 12]. Beside preventing both the contamination of underlying groundwater and food chain (through plant uptake and animal transfer) and reduction in crop yield, the reasons of heavy metal immobilization in contaminated sites are standing in their large impacts on the microbial activity and biodegradation of organic pollutants [13, 14]. In situ chemical immobilization concerns the addition of several types of chemical additive to contaminated soil, to change the speciation, mobility and bioavailability of heavy metals by chemical reactions, precipitation or co-precipitation, absorption and complexing, ion exchange and other particular mechanisms, thereby decreasing metal solubility. The purpose of the immobilization process is not the metal contaminants removal from soils, but their binding in some secured unleachable compounds [15]. Suitable additives have to be selected according to characteristics of the contaminated soil. Minerals and industrial by-products of low cost, different vegetal and manure composts, as well as their mixtures, have been applied for immobilization of lead, chrome, mercury, cadmium, arsenic, copper and zinc in contaminated soils, including the red mud from dumps as rehabilitating soil [5, 16-18]. There is about a large number of different amendments, by which the following are the most promising: gypsum, phosphogypsum, red gypsum and lime [19-21], clays, carbonates, phosphates [22, 23], apatite and hydroxyl-apatite [24, 25], silicon calcium fertilizers [26], zeolites or their synthetic substitutes [27-28], metallurgical slag, coal fly ash, coal bottom ash, water treatment sludge and red mud [29], sugar foam and ashes from the combustion of biomass [30], organic matter (bio-solids) [31] and several composts [32]. Some studies have shown that red mud or modified red mud are increasing the acid soils pH and effectively reduce the mobility and bioavailability of heavy metals, including lead, cadmium, chrome, copper and zinc, limiting crops damage in yields and quality. [4, 33-37]. Specifically, the use of ball milling for the remediation of heavy metals contaminated soils, with or without the use of additives, prove to be able to reduce the leachable fraction of metals to levels lower than the regulatory thresholds [38]. Many studies, have shown that red mud applied to soils can be very effective in reducing phosphorous leaching [39], improving pasture growth [40], ameliorating soil acidity [41-43], increasing metal sorption and decreasing soluble metal concentrations, and by all these means reducing the metals availability [44, 45]. Also, red mud application leads to a reduction in heavy metal uptake by plants [19, 46-48]. Nevertheless, the soil remediation with red mud is not just a simple problem of mixing and dispersing. The simple addition of red mud to soils involves increases in *p*H, total dissolved solids (TDS), dissolved organic compounds (DOC), as well as, the concentrations of oxy-anion-forming heavy metals in the soil solutions. The extent of these changes depends highly on the final mixture pH and buffering soil capacity. The pH values above 8.5-9.0 are promoting relative larger increases in concentration of aluminum, vanadium and arsenic. Soils with low organic carbon and clay content have a low buffering capacity and are promoting more risks for heavy metal mobilization from both red mud and soil itself. This is why the red mud should be associated with other materials rich in organic carbon when it is used for poor acid soils remediation [49].

This paper purpose is related to an extended investigation over deep changes in red mud chemical composition and properties, in order to convert it into a nutritive composite material by mixing with adequate, cheap and easy available by-products, and natural materials. The study includes trial runs for finding the best nutritive red mud composite materials, and trial runs in laboratory and glasshouse for selecting alkalinity tolerant plant species and varieties, which can accommodate the amended nutritive red mud materials for long term survival.

Experimental part

Materials and methods

Conversion of the red mud into a nutritive medium requires additional materials able to promote major decreases in the basic red mud alkalinity and salt content, as well as raising in the organic matter and nutritive elements concentrations from its composition. The following byproducts from other technologies were considered as reasonable suited for proper application as diluents and alkalinity buffers: a) phosphogypsum from the phosphate fertilizers industry; b) sludge from urban biological waste water treatment factories; c) sludge from water softening stage in chemical plants; d) organic compost. Additional sea algae debris collected from the Romanian Black Sea shore, as well as sawdust, acidic peat and acidic soil from Albota region, Romania were used to improve the red mud physical and chemical properties. These auxiliary materials and the reasons they were selected are described below.

Phosphogypsum

Addition of the gypsum and phosphogypsum to red mud produces three types of interactions: a) neutralization; b) heavy metals immobilization c) increase in salinity (TDS) and organic compounds concentrations (DOC) and d) changes in soil structure. At lower water concentrations in both materials, all these changes are very slow and incomplete in a reasonable time of mixing. When water is excessive, all the changes take place during far lower time, especially neutralization process. As neutralizing agent, the gypsum and phosphogypsum act through Ca^{2+} ion release in aqueous phase [50]:

$$2OH^{1-} + CaSO_4 \bullet 2H_2O + 2CO_2 \rightarrow CaCO_3 + SO_4^{2-} + 2H_2O + H_2CO_3 \tag{1}$$

$$NaOH + H_2CO_3 \rightarrow NaHCO_3 + H_2O \tag{2}$$

In diluted systems, the Ca^{2+} ions brought in by gypsum and phosphogypsum may substitute Na+ from exchange complexes, and also mobilize available alumina from red mud with expected precipitatation of the poorly soluble calcium aluminates [36]. These changes associated with red mud *p*H diminishing could explain the vegetation salt stress abatement when gypsum and phosphorgypsum are replacing lime for acid soils remediation or for red mud dumps rehabilitation [8, 51-55]. The fate of heavy metals depends largely on *p*H, on the pore-water formation, as well as on the rate of *p*H stabilization after all interactions red mud- phosphogypsum are ceasing. About 86% aluminum and 81% arsenic are removed from solution during calcite precipitation (reaction 1) as non-exchangeable ions, aluminum as neo-formed Al oxy-hydroxides and arsenic as scavenged oxide in the precipitated calcite [50]. Molybdate ion sorption on the soil minerals is low and hence, molybdenum concentrations in phosphogypsum amended red mud remained unchanged at the *p*H variation [49]. In the acidic soils, phosphogypsum, red gypsum and dolomitic residues are boosting the heavy metal sorption capacity. The lead retention was attributed to the anglesite precipitation and to the binding on edge charges in the kaolinite minerals. Cadmium and copper were immobilized as hydroxyl-chlorides. Also, it was found the lead, cadmium and copper are associated with organic mater in treated soils [56]. As it was noticed above, addition of alkaline red mud to the acidic soils results in variable increases of TDS and DOC, as well as in aluminum, arsenic, vanadium and molybdenum with a risky threshold placed above pH 8.5-9.0. Supplementary gypsum alleviates the intensity of these processes, but the phosphogypsum effect is limited to less than 10% contribution to the total mixture with soil. This is valid for both diluted and concentrate systems. Accordingly, either red mud or phosphogypsum could not participate in the nutritive fertile composite material with a fraction greater than a critical value tolerated by the soil or gross fertile nutritive material composition [36,49]. Also, the pattern of increasing DOC concentrations due to large fraction of red mud and phosphogypsum is effectively related to the organic matter present in the fertile material composition. Alkalinity of the red mud - phosphogypsum mixtures all together with clay mineral dissolution and sorption reactions produces an unintended alkaline extraction, liberating organic matter to solution. Under critical conditions on short terms, this may become one of the main unwanted buffering mechanism in soil remediation or fertile composite material formulation [57-59]. Phosphogypsum addition to the acidic soils can improve certainly the soil structure through increasing hydraulic conductivity [60]. But, the increased salinity, which can damage the plant crops and soil microbial life, is the major drawback in long term over-loadings the amending soils with these adjuvant materials [61]. Hence, the gypsum and phosphogypsum addition has to be carefully adjusted to the purpose of soils amending. Eventually, long terms trials of plant germination and heavy metals plant uptake are recommended as an extension research, before the assessment of any soil remediation technology or fertile plant growth composite material formulation.

Municipal and industrial bio and inorganic sludge

Composts selection in the formulation of the genuine nutritive composite materials or improving the soil quality parameters encounters two conflicting environmental aspects: a) increasing ratios of composted wastes or byproducts in the mapped out mixtures and b) preserving soil quality parameters by preventing contamination [62]. Heavy metals monitoring in any of the composted constituents is a reasonable basis for achieving a sustainable balance between the mixing materials. All kinds of municipal and industrial solid wastes contain heavy metals in higher concentrations than those usually assessed values for soil background. Consequently, an increase in heavy metals availability for transfer into crop plants is expected, when composts are used for amending soils or preparing nutritive composite materials. The heavy metals toxicity depends mainly on bio-available and leachable fraction rather than their total concentrations in the compost or amended soil. Pore water and water fraction in soil have the highest potential of contamination surface water and ground waters, and further the food chain. Parts of these metals are customarily bound by complexation to the compost matrix with additional green waste or by aerobic composting [62]. Introducing neutralized red mud and well adjusted *p*H control during mixing, the heavy metals bioavailability can be effectively diminished below the risk-based thresholds that protect human health over a large interval of contaminant concentrations [15]. Lime, natural zeolites and clays, plants charcoals and other carbonaceous materials addition during composting process are diminishing water solubility of heavy metals and their leachablility, mainly through some substantial increases in *p*H brought in by adjuvant. Less information is available on bioavailability and leachability of Hg, As, Ba, Se and Ag in the composts [63]. However, there is good experimental evidence demonstrating that the monitoring of both heavy metals bioavailability and crop uptake of metals from composted bio-solids mixtures should be systematically evaluated for further applications. Rich in organic and inorganic plant nutrients, the sewage sludge adds more fertilizing potential in the poor carbon and nutrients soils. This may be a substitute for fertilizers, but availability of potential toxic metals often restricts its uses. Besides, sustained sludge amendments significantly modify soil chemical, physical and biological properties, and adequate corrections have to be made frequently [64]. Examples of common assessment of bioavailability and leachability in composts are provided in paper [63]. Recently, there was demonstrated that heavy metals brought in soils with agricultural composts have only positive effects on the soil microbial status and fertility [62]. Municipal sewage sludge is used as agent for Pb, Zn, and Cd immobilization in many kind of contaminated soils [65], but only when the heavy metal translocation in plants is out of any risks [66, 67].

Wood Sawdust

The saw dust is a common bulking agent in soil remediation process and procedures for changing soils properties, structure and fertility [68]. There are four reasons to use sawdust in formulation any compost employed either for soil remediation or for soil fertilization: a) improves compost fertilizing qualities and serve for balancing the optimal C/N ratio in compost; b) brings about lowering or increasing *p*H and decreases in EC (electrical conductivity) values, which finally led to lower available heavy metals content in the final compost formula; c) increases water-holding capacity of soils in the arid areas; d) causes the lowering of moisture loss from the composting piles [69]. Due to its low content in heavy metals, the sawdust serves always as a ready available material for amending agricultural and industrial sludge rich in heavy metals [11,70]. Also, sawdust found many applications as sorbent and bio-sorbent for heavy metals and other contaminants from the polluted soils [71, 72]. From red mud composition change and soil remediation point of view, sawdust capacity to reduce bioavalability of chromium seems to be promising [73, 74].

Acidic Peat

Acidic peat is a common soil amendment applied in mixture with other materials used for soil properties control (especially compactness and good aeration). Acidic peat contains some nutrients, but due to its high cation exchange capacity helps the soil to hold nutrients out of the pluvial washings. Also, acidic peat serves for the soil carbon content and pH control, as well as for weeds repeling and heavy metals immobilization [75, 76].

Materials for experiments

Red mud and sludge from water chemical softening were provided by SC Alum SA Tulcea, Romania. Chemical and physical characterization of the red mud was fully given in our previous paper [77]. Phosphogypsum came from Donau Chem SA Turnu Magurele, Romania and the sludge from urban waste water biological treatment by S.C. RAJA S.A. Constanta, Romania. Acidic peat from Estonia resources was peovided by SC Alonet Turba SRL Dorohoi, Romania and sawdust from O-MacForest Cernter SRL, Campulung, Romania. Stable manure and straw compost was picked up from common agricultural aids stores. Samples of acidic soil were collected from SCDA Albota-Pitesti. All the chemical and agrochemical parameters of the selected adjuvants for formulation of the red mud genuine nutritive composite materials are presented in the tables 1-5, using both experimental and literature data [75-82].

Analysis methods

Different formulations between the raw red mud and the additional materials chosen as conditioners for the nutritive properties control were well mixed and tapped, and further naturally dried up till a reasonable humidity. Both raw materials and composite mixtures were analyzed mostly by recommended STAS and ISO methods described in our previous paper [77]. Other specific methods of analysis demanded by the experimental plan will be described together with the experimental data.

Experimental plans

There were set up two experiments concerning two individual types of nutritive red mud composite formulations using the above mentioned adjuvant in different combinations and ratios. Each experiment was carried out according to the following steps: a) formulation the mixtures composition with particular contribution of every adjuvant to some supposed nutritive blends in terms of macronutrient concentrations and carbon/nitrogen (C/N) ratios; b) designing variants and replications; c) preparation the composite nutritive blends and maintaining them at 80% of their molecular water capacity for 20 days; c) chemical analysis for evaluation the macronutrient status, *p*H, C/N ratios, mobile potassium and phosphorus capacity, ionic soluble salts composition and salts content; d) sowing the plants; e) monitoring the plant growth parameters and crop performances; f) chemical analysis of the dry plant green mass and g) data statistical analysis. The details of each plan will be presented in the section results and discussions. All the experiments were carried out during 2011-2012 vegetative seasons.

Statistical analysis

Analytical data concerning both soils chemical composition, as well as, the plant growth performances and yields during the laboratory and green house experiments have been processed according to the statistical variance analysis adapted for agricultural and biological experiments [83] Statistical analysis was made by using Statis V1.5 programe [84]. Statistical differences between experimental variants were denoted by letters „a”. „b” and „c” for all type of comparisons, according to Tukey method described by [85] and [86]. The same letter stands for values with non significant differences from mean value and the different letters stand for values at particular significance levels.

Results and discussions

Characterization of adjuvant materials used for the nutritive red mud composite materials formulation

Macronutrients

Analytical data concerning *p*H and macro-nutrients content in all the adjuvant materials used for red mud composite materials preparation are presented in table 1 and 2.

These tables highlight the neutral reaction of phosphogypsum and compost and the slight alcalinity reaction of the sludge from S.C. RAJA S.A. Constanta waste water biological treatment unit (SWBT). Also, the sludge from natural water chemical treatment (SWCT) brings in any formulation significant alkaline compounds. Conversely, the wood sawdust and acidic peat strongly acid reaction may be simply used to induce high rates in red mud neutralization. Phosphogypsum capacity to neutralize red mud alkalinity is well known from other reports [8, 53, 67, 87] and mainly depends on wearing state of the collected samples (actually picked up from a closed disposal site) and ratios used in preparation the red mud composite material. Beside its buffering role, the phosphogypsum contains significant phosphorus and calcium quantities. High organic carbon concentration was found in wood sawdust (46-50 %) and acidic peat (20-45

No.	Conditioning materials	pH	C_{org}	N	P	K	Ca	Mg
1	Red mud (common values) (RM)	12.08	0.626	0.02	0.092	0.12	2.61	0.09
2	Phosphogypsum (PG)	7.06	-	-	2.15	0.07	11.0	0.40
3	Sludge from municipal water biological treatment (SWBT)	7.83	17.0	3.45	1.54	0.52	3.0	1.15
4	Sludge from natural water chemical treatment (SWCT)	9.40	0.383	0.31	-	0.46	2.03	0.78
5	Organic compost (OC)	7.13	9.2	1.16	0.60	1.14	3.0	1.20
6	Marine algae (MA)	7.1-7.2 [78]	1-8 [79]	1.94	0.10	3.42	21.0	0.86
7	Wood sawdust (WS)	5.62	46-50 [80]	0.13	0.087	0.06	0.21	0.10
8	Acidic peat (AP)	4.28	20-45 [75]	0.63	0.076	0.03	0.73	0.08
9	Albota acid soil (AaS)	5.29	1.92	0.18	0.05	0.45	0.67	1.02

Table 1
MACRO AND MEZZO-NUTRIENTS CONTENT (%) AND *p*H OF THE ADJUVANT MATERIALS (MEAN DATA)

Table 2
MAIN CHARACTERISTICS OF THE ALBOTA LUVISOL

Material	Depth	pH	SB meq/100 g	Ah, meq/100 g	V_{Ah}, %	Nt, %	N-NO_3, mg/kg	Humus, %	Pt, %	P_{AL}, mg/kg	K_{AL}, mg/kg
Albota luvisol	0-20	5.10	10.06	5.86	63.2	0.100	9.0	1.98	0.047	14.3	92
	20-40	5.31	10.94	5.11	68.2	0.094	7.5	1.86	0.045	13.0	100

SB – Total exchangebele bases; Ah – Hydrolitic acidity; V_{Ah} – Cationic saturation degree; N_t – Total content of nitrogen; N-NO_3 - Content of nitric nitrogen; P_t - Total content of phosphorus; P_{AL} – Content of mobile phosphorus; K_{AL} - Content of mobile potassium.

%), as well as, in the SWBT (17%), organic compost (9.2%) and marine algae (1-8 %), Total amounts of main macronutrients (nitrogen, phosphorus, potassium) and secondary macronutrients (calcium, magnesium) totalizes 9.66% in SWBT, 7.6% in compost and 27.1% (but 21.0 only as calcium) in the marine algae. The other adjuvant materials contribution in nutrients is noteworthy, but rather modest. According to the above data, all the adjuvant materials presume enough buffering capacity and nutritive ionic species to sustain the crops growth.

Micronutrients and heavy metals

The status of microelements and heavy metal content in all the adjuvant materials used for red mud composite material formulations are presented in table 3.

Table 3 outlines the contents of micronutrients, which are highly required for any crop for growth, as cobalt copper, iron, manganese (Mn), and zinc, as well as, the heavy metals as cadmium, chromium, nickel, and lead with potential risk and toxicity, when their concentration passed over a specific threshold. Out of these elements, only cadmium in phosphogypsum has a higher content (2.56 mg•kg^{-1}), close to the soils maximum accepted limits (3.00 mg•kg^{-1}) [88]. Some varieties of sawdust and acidic peat may contain disputable concentrations in cadmium. The content of the other heavy metals with toxic effect is out of any risk. On the other hand, the content of the micronutrients lies in the worthwhile ranges for sludge, compost and sea algae. The latter have the highest content of manganese, too. Beside the other micronutrients, the SWBT, organic compost, wood sawdust and acidic peat

Table 3
MICRONUTRIENTS AND HEAVY METALS (mg/KG) IN THE ADJUVANT MATERIALS

No.	Adjuvant	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	RM	-	9.8	380	68.7	27681	206	15.1	49	24
2	PG	2.56	1.6	-	16,3	766	10,1	6,4	7,0	39
3	SWBT	0.84	3,5	36.9	119	7697	285	50,0	48	570
4	SWCT	0.263	5.87	0.26	6.5	10273	131	11.4	41.3	26.8
5	OC	0,36	4.1	17.2	31	12843	437	22	22	116
6	MA	0,38	3.7	-	7,8	1150	553	6,9	-	31
7	WS	0.05–5 82]	-	0.2–0[82]	0.5-200[82]	119.5 [82]	9 – 84 [81]	0.1–80[81]	10.1[82]	5-290[81]
8	AP [75]	0.43-8.9	-	0.5-110	1.2-37	20-2500	2.0-2300	0.3-32	1,7-53	2.9-4.6

Parameter	RM	SWBT	SWCT	OC	WS	AP [75]
Dry residue	1525	972	172	540.00	10.8	24.6
Conductometric residue	1836	1111.80	176	992.00	-	-
NO_3^-	-	10.30	-	179.00	1200-160[81]	-
CO_3^{2-}	794	-	27	-	-	-
HCO_3^-	64.30	737	70	85.00	-	-
SO_4^{2-}	19	43	17	38.00	148 [81]	-
Cl^-	32	34.60	15	37.60	10-30 [81]	-
Ca^{2+}	1	14.60	2	52.00	46.2 [82]	60-5300
Mg^{2+}	0	9.60	28	34.60	31.4 [82]	12-370
Na^+	609	40.60	6	28.60	1-5 [81]	2.3-20
K^+	6	92.70	7	264.00	40.8 [82]	2.8-100

Table 4
DRY RESIDUE AND TOTAL SOLUBLE IONIC SALTS (mg/100G) IN THE ADJUVANT MATERIALS

Parameter	RM	SWBT	SWCT	OC
Na_2CO_3	91.9	-	9.5	-
$NaHCO_3$	3.4	31,1	-	2.7
$Ca(HCO_3)_2$	0.2	12.9	3.5	19.2
$MgCO_3$,	-	-	22.4	-
$Mg(HCO_3)_2$,	-	14	37.5	21.1
$MgSO_4$,	-	-	12.4	-
$MgCl_2$,	-	-	8.9	-
Na_2SO_4,	1.4	-	-	6.5
NaCl,	2.5	-	-	-
KCl,	0.6	7	6	33
K_2SO_4,	-	6.4	-	18
$KHCO_3$,	-	28.6	-	
Total,	100	100	100	100

Table 5
FORMAL MOLECULAR SHARE IN SALT CONTENT 9% OF THE ADJUVANT MATERIALS

also contains large amount of zinc, a really important element for plant nutrition. All over, the available secondary resources of any adjuvant for converting the red mud into fertile composite materials are carrying in much of the desired micronutrient at satisfactory concentrations.

Total ionic species and soluble salts content in the adjuvant materials

Waste water biological treatment sludge and organic compost have the high total soluble salts content, namely 0.972 g/100 g in SWBT and respectively, 0.540 g /100 g in OC. Less soluble salts were found in SWCT (0.172 g/100 g) and minimum quantities in WS and AP (table 4).

Among the anions, the bicarbonate ion (HCO_3^-) outbalances the other species in the SWBT and the nitrate ion (NO_3^-), sulphate ion (SO_4^{2-}) and in (Cl^-) the OC. Among the cations, potassium (K^+), (Na^+) and (Ca^+) outbalances the other species in both SWBT and OC adjuvant materials (table 5). Hence, the probable distribution of soluble salts percentage in the above materials is that which is presented in the table 5. According to the experimental data, the adjuvant materials are conveying a large dowry of mineral salts with neutral (PG, OC and MA) and acid (WS and AP) reaction, containing macro, mezzo and micronutrients at high concentrations. Particularly, the dominant molecular formal species in red mud salts charge is the sodium carbonate, accounting for 91.1% from total salts content (table 5).

First experiment. Testing the first type of red mud composite materials fertility

Purpose of the experiment

The main purpose of this experiment is the preparation and fertility testing of some fertile composite materials using as adjuvant materials for red mud properties control PG, SWBT, OC, MA and additional nitrogen as ammonium nitrate. SWCT was dropped due to its very high concentrations in calcium and magnesium, which causes unwanted changes in the total soluble salt composition. Composition of the nutritive red mud composite materials were compared with some reported data over some well known fertile soils composition [89].

Variants

With the above mentioned adjuvant materials, five groups of four variants totalizing twenty experimental variants were made up for testing the composite materials fertility. In each variant, the red mud quantity was the same (1,000 g), and the adjuvant materials participation was variable in progressive doses and ratios, equivalent to 50-300 t/ha, if the nutritive red mud composite materials are applied in the field at reasonable dosages (table 6).

These variants compositions in terms of adjuvant materials dosage and ratios cover all the theoretical expected changes in red mud composition and properties for its conversion into a nutritive composite material. The entire experiment was set up on four replications for each different composition entry, according to the testing plan. It was expected that after 20 days of continuing samples wetting for accomplishing 80% of the soils molecular water capacity, all the neutralization, double exchange and ion exchange reactions have reached the equilibrium and the composite materials, as well as their entrapped solution were fairly homogenized.

Macroelements status

Four representative mixtures, standing for the best equilibrated nutritive composite materials from macronutrients, *p*H and carbon/nitrogen ratios (C/N) point of view, were selected for a short agrochemical analysis. The samples 1-4 contains adjuvant materials (PG, OC and SWBT) in progressive increasing quantities added to 1000 g RM (mass ratio variation from 41.5/1000 to 364/1000) as shown in the table 7. Nitrogen as ammonium nitrate was added for significant change in C/N ratio and MA for increasing carbon and nitrogen content in nutritive composite materials. Under experimental conditions, small quantities of phosphogypsum added to the composite material (sample 1, table 7), along with other adjuvant materials, produces a large decrease in *p*H (1,96 unit comparing with RM from table 1). As far as more phosphogypsum is added, the rate of *p*H diminishing becomes smaller and smaller, but some satisfactory value for a fertile composite material, as 8.80, can be reached in the sample 4, when mass ratio RM/PG is 10/1. The other

Group I (V1–V4)	A. RM (1000g); B. PG (16.5 g; 33.0g; 66.0g; 99.0g); C. OC (12.5g; 25.0g; 50.0 g; 75.0g); and D. SWBT (12.5g; 25.0g; 50.0g; 75.0g).
Group II (V5-V8)	A. RM (1000g); B. PG (16.5g; 33.0g; 66.0g; 99.0g); C. OC (12.5g; 25.0g; 50.0g; 75.0g); D. SWBT(12.5g; 25.0g; 50.0g; 75.0g); and E. MA (10g).
Group III (V9–V12)	A. RM (1000g); B. PG (16.5g; 33.0 g; 66.0g; 99.0g); and C. OC (12.5g; 25.0g; 50.0g; 75.0g).
Group IV (V13–V16)	A. RM (1000g); B. PG (16.5g; 33.0g; 66.0g; 99.0g); and C. SWBT (12.5g; 25.0g; 50.0g; 75.0g).
Group V (V17–V20)	A. RM (1000g); B. PG (16.5 g; 33.0g; 66.0g; 99.0g); C. OC (12.5g; 25.0g; 50.0 g; 75.0g); D. SWBT (12.5g; 25.0g; 50.0g; 75.0g); and E. N as NH_4NO_3 (15g).

Table 6
VARIANTS OF THE FIRST EXPERIMENT (20 VARIANTS, 4 REPLICATIONS)

Table 7
MACRONUTRIENTS CONTENT (%) AND *p*H OF THE NUTRITIVE RED MUD COMPOSITE MATERIALS IN THE FIRST EXPERIMENT

No.	Composition (g)						pH_{H_2O}	$C_{org.}$	Nt	C/N Ratio	P_{AL}	K_{AL}
	RM	PG	OC	SWBT	MA	N		Concentratiation, %			NIM, $mg \cdot kg^{-1}$	
1	1000	16.5	12.5	12.5	-		10.12	0.46	0.027	27.2	262	582
2	1000	33.0	25.0	25.0	10,0		9.57a	0.59·	0.030	24.3	302a	658
3	1000	66.0	50.0	50.0	-		8.81b	0.87a	0.052a	20.2a	378b	830a
4	1000	99.0	75.0	75.0	-	15	8.80b	0.91b	0.072b	14.8b	417b	873b
NIM – Nutrients ionic mobility												
a, b, c (the same letter stands for values with non significant differences from mean value and the different letters stand for values at particular significance levels)												

Table 8
IONIC SALTS CONCENTRATION AND TOTAL SOLUBLE SALT (mg/100g) IN THE RED MUD NUTRITIVE SOILS IN THE FIRST EXPERIMENT

No.	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Total soluble salts
1	205	198	808	40	1.1	0.0	606	16.1	1.874
2	43 *a*	125*a*	1.324 *a*	33	5.1	0.0	747 *a*	20.5	2.297 *a*
3	17 *b*	46 *b*	1.658 *b*	29	77.2	0.6	767 *a*	27.3 *a*	2.623 *b*
4	4 *c*	49 *b*	1.890	25	110 *b*	0.6	781 *a*	29.6	2.888 *c*
a, b, c (the same letter stands for values with non significant differences from mean value and the different letters stand for values at particular significance levels)									

adjuvant materials fit in consequential quantities of organic carbon and nitrogen (SWBT and OC) and noteworthy quantities of phosphorus (PG and SWBT) and potassium (SWBT, OC and MA). At the highest level of additional adjuvant materials, the total organic carbon and total nitrogen contents account for 2.0, respectively 2.7 times the initial sample 1. Besides, these composition changes led to carbon-nitrogen ratios values down to a 14.8, close to this normal value in natural soils [89].

Mobile forms of phosphorus and potassium, soluble in the ammonium acetate-lactate solution (AL) at *p*H 3.7, have also recorded large edges over the starting material, 1.6 times higher as compared with the sample 1 for mobile phosphorus and 1.5 times higher for mobile potassium. Mainly, these particular values are not only equivalent to the very well supplied soils with these nutritive elements [89], but also exceed the common concentrations by 2.9 to 6.0 times. However, the accessibility of these elements for plants (especially the phosphorus) is not proportional with their ionic mobility [90]. Therefore, the most of the red mud composite materials proposed in the table 6 might be seen as suitable nutrient source sustaining the plant growth, as far as *p*H, organic carbon and total nitrogen are well balanced as in samples 3-5, and reasonable of mobile phosphorus and potassium concentrations are available.

Total soluble salts and water-soluble ions contents The most probable reactions between soluble constituents from all the adjuvant materials in the composite materials solution during the interval of 20 days, required for accumulation at lest 80% of the soil molecular water capacity are:

$$2\,NaOH + CO_2 \leftrightarrow Na_2CO_3 \qquad (3)$$

$$Na_2CO_3 + CO_2 + H_2O \leftrightarrow 2NaHCO_3 \qquad (4)$$

$$CaSO_4 + Na_2CO_3 \leftrightarrow Na_2SO_4 + CaCO_3 \qquad (5)$$

$$CaSO_4 + 2NaHCO_3 + Ca(HCO_3)_2 \qquad (6)$$

In the similar ways, act both the potassium and magnesium ions, too. Hence, the accumulation of large quantities of CO_3^{2-}, HCO_3, SO_4^{2-}, Cl^{--}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ in the red mud composite materials (table 8). Some of these ions are framed into insoluble compounds, but most of them remain in composite material solutions as inorganic compound of sodium, potassium and calcium soluble salts. The four above selected soils chemical analysis is given in the table 8.

As it was expected, the total soluble salts content in all the composite materials from table 8 are increasing proportionally and notably with the added adjuvant materials doses (from 1,874 to 2,888 mg/100g composite soil). In the soluble salt mixtures the dominant salt is sodium sulphate. Sodium ion was brought in by RM and sulphate ion by all the other adjuvant materials. Thus, sodium sulphate as dominant molecular species in total molar salt mixtures varies from 54.0 (sample 1) to 82.75 % (sample 4), replacing sodium carbonate (91.2%) from the red mud (table 5). Soils salinization begins at 100 mg soluble salts /100 g soil [91]. Accordingly, the above formulated red mud composite materials contain between 18 and 29 time more soluble salts. Taking into account the long time known high plant toxicity of sodium sulphate [91] and the red mud nutritive composite materials salt overloading, practically is not possible to grow plants on such a growth layers. Actually, not the missing of the nutrients and organic carbon is the cause of red mud composite materials infertility, but rather its high content in soluble salts (mainly in sodium sulphate).

Second experiment. Testing the second type of red mud composite materials fertility

Purpose of the second experiment

The main objectives of this experiment were the removal of high salt content adjuvant materials (SWBT and MA) from red mud composite materials and replacing them with WS, AP and AaS. Also, the experiment encompassed the study of *Triticum durum* response to the new red mud composite materials, along with evaluation of the correlation between these materials composition, plant growth and green mass mineral composition.

Variants

There were formulated 3 soil variants with three replicates each of them. In all these variants, a constant RM quantity (1,000 g) was mixed with constant quantities of PG, OC and AaS from the 0-20 horizon (200 g of each), To these mixtures, additional AP were filled up in progressive increasing quantities from 50 to 150 g (as in table 9) for obtaining the second type of red mud composite materials. Samples were charged in vegetation pots (laboratory scale) and the new formulated red mud composite materials were withheld for 20 days at the constant humidity of 80% of each soil molecular water capacity.

Macronutrient status

The *p*H of the second type of red mud composite materials is moderately alkaline, with a slight, but

Table 9
VARIANTS OF THE SECOND EXPERIMENT (3 VARIANTS, 3 REPLICATIONS)

V1	a) RM(1,000 g); b) PG(200 g); c) OC(200 g); d) WS 50 g); e) AP(50 g); f) AaS(200 g)
V2	a) RM(1,000 g); b) PG (200 g); c) OC(200 g); d) WS(100 g); e)AP(100 g); f)AaS (200 g)
V3	a) RM(1,000 g); b) PG(200 g); c) OC 200 g); d) WS 150 g); e) AP(150 g); f) AaS 200 g)

Table 10
MACRONUTRIENTS CONTENT (%) AND *p*H OF THE RED MUD COMPOSITE MATERIALS IN THE SECOND EXPERIMENT (BEFORE SOWING)

Variants	pH_{H_2O}	$C_{organic}$	N_t	C/N	P_{AL}	P_{AL}*	K_{AL}
		Concentrations, %			Nutrient ionic mobility , $mg \cdot kg^{-1}$		
V1	8.53	3.52	0.195	21.2	200	45	1.052
V2	8.46 *a*	4.56 *a*	0.202	26.5 *a*	207	56	1.060
V3	8.42 *b*	5.61 *b*	0.196	33.4 *b*	200	58	1.112 *a*
*Corrected value depending on the material pH reaction							
a, b, c (the same letter stands for values with non significant differences from mean value and the different letters stand for values at particular significance levels)							

significant, decrease against the previous formulations. Lesser *p*H values were brought in more by the increasing doses of AP and WD and hardly by AaS. Actually, the first two adjuvant materials were contributing to the undoubted increase in organic carbon content, and consequently in the C/N ratio. The total nitrogen content is low, approximately equal in all variants, but higher and different from the first type of red mud composite materials. Much larger mobile phosphorus and potassium ions concentration than in the first type of red mud composite materials were recorded for all the variants (table10).

The similar analytical data obtained from red mud composite material after the harvesting *Triticum durum* crop are featuring some changes in the nutritive material composition, which are illustrated in the figures 1-3. According to these figures the changes are: a) little and non-significant changes in the *p*H of all variants fig. 1); b) large changes in organic carbon concentration in composite materials, proportionally with the total added AP and AaS (fig. 2), but these changes comes from mineralization process of the chemical compounds in added AP and AaS during vegetation stage and not from vegetal mass input by the plant roots; c) small but significant increases from variant 1 to variant 3 in total nitrogen concentrations, mainly due to the mineralization during vegetation stage (fig. 2); d) Significant increasing in C/N ratios, mainly due to the larger increases in carbon concentrations than nitrogen concentrations, proportionally with the total added AP and AaS (fig. 1); e) Moderate stationary increases in mobile phosphorus ion concentrations in all the variants (due to mineralization during vegetation stage), regardless to additional AP and AaS from V1 to V3 (fig. 3); f) Moderate stationary decreases in mobile potassium ion concentrations due to consumption during vegetation stage (fig. 3).

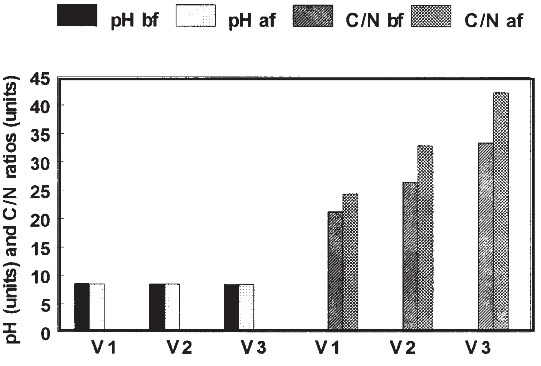

Fig. 1. Second experiment variants. *p*H and C/N ratio before sowing (bf) and after (af) harvesting

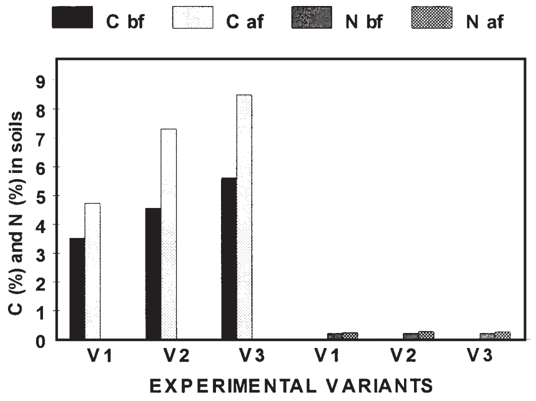

Fig. 2. Second experiment variants. Organic carbon (C) and total nitrogen (N) concentrations (%) before sowing (bf) and after harvesting (af)

Soluble salts status

The status of the ionic composition in composite material solutions before sowing and after harvesting is shown in the table 11. Total soluble salts content varies between 2240 to 2246 mg/100 g dry samples collected before sowing (variants V1 to V3) and between 2539 to 2979 mg/100 g dry samples collected after plant harvest (variants V1 to V3. Actually, these values are very high as compared to the 100 mg soluble salts per 100 g dry material, which is the starting concentration for set off soil salinization, and some plants are affected by different saline stresses. Also, all the above increases are particularly related to the sodium and sulphate ion concentrations. Analytical data concerning the composition of red mud composite materials after the harvesting *Triticum durum* crop are shown in the figure 4, correlated with data from table 11. Because all the ionic species concentrations are significantly increasing in the same proportions after harvesting, their ratios remain almost constant (fig. 4). Saline charge of the second type of red mud composite

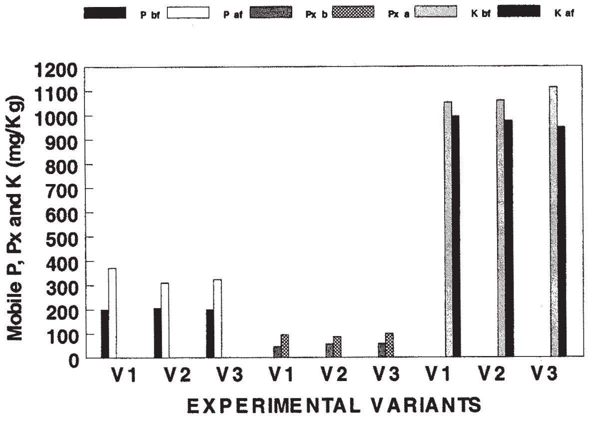

Fig. 3. Second experiment variants. Mobile phosphorus (P-total; P_x- at corrected *p*H) and potassium ions (K) before sowing (bf) and after (af) harvesting

Table 11
IONIC COMPOSITION AND TOTAL SOLUBLE SALTS CONTENT (mg/100 g) OF THE SECOND TYPE OF RED MUD COMPOSITE MATERIALS BEFORE SOWING

Variant	HCO_3^-	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Mineral residue
V1	52	1.547	15	189	3	418	20	2.240
V2	51	1.163 *a*	17 *a*	176 *a*	4 *a*	525 *a*	23	2.460 *a*
V3	39 *a*	1.643 *b*	20 *b*	188	4 *a*	525 *a*	24 *a*	2.446 *a*
Values denoted by the same letter are not significantly different (probability < 0.001)								
a, b, c (the same letter stands for values with non significant differences from mean value and the different letters stand for values at particular significance levels)								

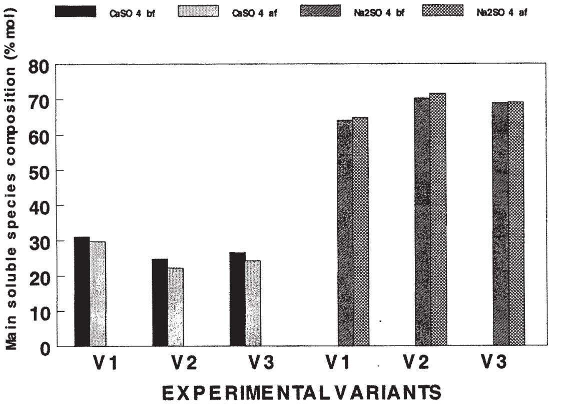

Fig. 4. Second experiment variants. Main molecular components concentration in the saline charge of soils with soluble salts before sowing (bf) and after (af) harvesting

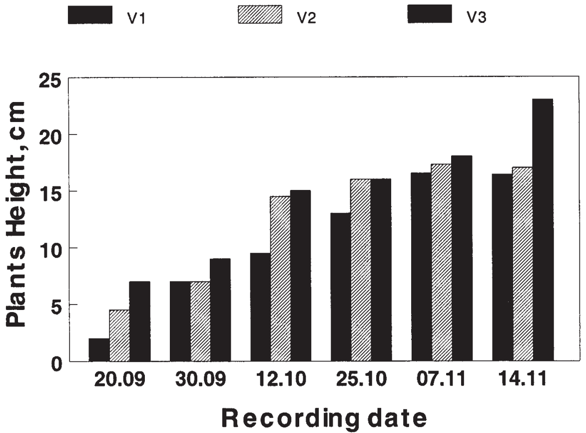

Fig. 5. Second experiment variants. *Triticum durum* plants hight during first vegetative stage (20.09.2011 – 14.11.2011)

materials is dominated by sodium, calcium and sulphate ions. The dominant salt is sodium sulphate, but at lower level than in table 8. As it is exhibited in the figure 4, calcium sulphate contribution is raising up to 30%, decreasing with adjuvant materials concentration in the composite materials (V1-V3) to lower values for composite materials after harvesting. Even if the sodium sulphate contribution after harvesting scored some little gains, the over all results are emphasizing the passing of the dominant component in saline material composition from sodium carbonate in red mud (91%) to the sodium sulphate and calcium suphate (sharing 64-71% and respectively, 24-31%). These changes come out from calcium and sulphate ions rich contribution of the adjuvant materials and certainly from the equilibrated formulations. Also, the chloride ion contribution in the second experiment soils is just half of this ion contribution in the first experiment soils (table 8 and Table 11), which is another gain in the formulation of the second type of composite materials.

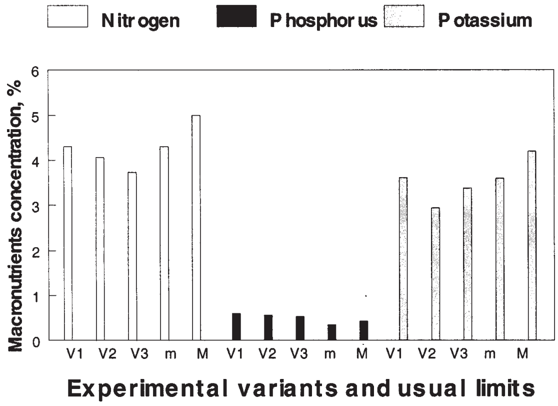

Fig. 6. Second experiment variants. Macronutrients contents in the dry green plants. m and M are minimum and maximum nutrients concentration in plants grown on normal soils

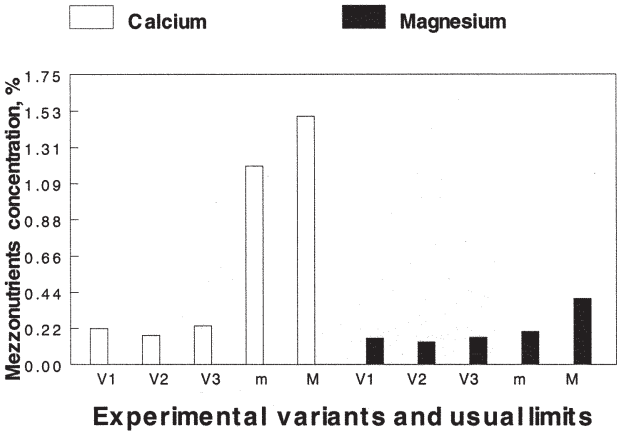

Fig. 7. Second experiment variants. Mezzo-nutrients content in the dry green plants; m and M are minimum and maximum nutrients concentration in plants grown on normal soils

Plant growth status

Triticum durum choice for this experiment was recommended by its low stress to salinity and poor conditions of growth. Five grams seeds were sowed in each pot, according to the experiment plan, on August 31st 2011. It was noted that the plants emerging was highly dependent on the sawdust and acidic peat concentration in the particular soil in the pots, Namely, on September 4th 2011, the plants sprang in the third variant pots, on September 6th 2011 in the second variant pots, and on September 7th 2011 in the first variant pots. The plants grew in satisfactory conditions, so that, a month and a half later they reached about 20 cm height. The rate of plants growth (fig. 5) was certainly explained by the same particular dependence on sawdust and peat concentration in the composite materials. Hence, the greater C/N ratio (fig. 1), C concentration greater at N constant concentration (fig. 2), and P and Px constant concentrations at greater K (figure 3) for variant 3 secured better growth rates in the variant V3, which was accommodating the highest doses of sawdust and acidic peat.

The analytical data regarding the macro (nitrogen, phosphorus, potassium) and mezzo nutrients (calcium, magnesium) contents show that the plants had enough supply of these elements, which is sustained by these elements content in the initial red mud composite

Table 12
NUTRIENT CONTENTS OF THE *TRITICUM DURUM* PLANTS GROWN ON THE SECOND TYPE OF RED MUD COMPOSITE MATERIALS AND ON THE NORMAL SOILS

Variant	N	P	K	Ca	Mg	Zn	Cu	Fe	Mn
	%					$mg\cdot kg^{-1}$			
V1	4.30	0.597	3.61	0.217	0.160	193	4.72	89	35.6
V2	4.06	0.564	2.94	0.176	0.138	65 a	5.29	81	33.3
V3	3.73 a	0.528 a	3.38 a	0.235	0.164	52 a	4.02	115	31.6 a
Normal contents [92]	4.3-5.0	0.35-0.43	3.6-4.2	1.2-1.5	0.2-0.4	29-40	2.6-9.8	21-200	55
a, b, c (the same letter stands for values with non significant differences from mean value and the different letters stand for values at particular significance levels)									

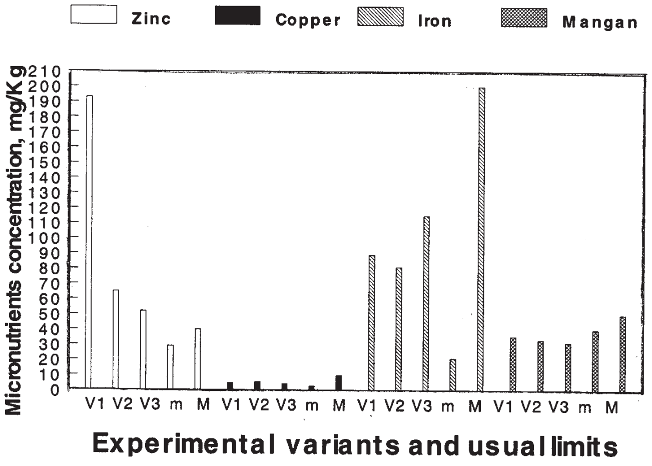

Fig. 8. Second experiment variants. Micronutrients content in the dry green plants; m and M are minimum and maximum nutrients concentration in plants grown on normal soil

materials before sowing (table 12) and in the soils analyzed after the plants harvest (figs. 1-3).

Close concentrations of the macronutrients and mezzo-nutrients in all variants are generally noticed in the analyzed dry green plant samples and non-significant differences were recorded between the experimental variants. (Table 12, figs. 6 and 7). The macro and mezzo-nutrients concentration in the dry green plants can be located the normal range of variation of each element in normal fertile soils (mC-minimum concentration and MC-maximum concentration). Namely, the nitrogen concentration is ranging between 3.51 and 4.32%, the phosphorus between 0.523 and 0.649%, the potassium between 2.86 and 3.76%, the calcium between 0.166 and 0.249%, and the magnesium between 0.125 and 0.164%. Slightly higher phosphorus concentrations, as well as, slightly lower calcium concentrations than the normal values in common soils seems to be in good agreement with the expected values at the fifth vegetation stage according with Feeks scale [93].

The analytical data regarding the micronutrients (zinc, copper, iron, manganese) showed that the plants had normal supply of these nutritive elements, except for the zinc content, which is a little higher especially in the dry green plants samples coming out from variant V1 (table 12 and fig. 8).

Conclusions

There were set up two experiments concerning two individual types of nutritive red mud composite formulations using the following adjuvant materials: phosphogypsum (PG), sludge from urban biological waste water treatment factories (SWBT), sludge from water softening stage in chemical plants (SWCT), organic compost (OC), marine algae debris (MA), wood sawdust (WS), acidic peat (AP) and acidic soil (AaS) from Albota region, Romania. Each experiment was carried out according the following steps: a) formulation particular fertile composite materials b) designing variants and replications; c) chemical analysis for evaluation the macronutrient status, *p*H, C/N ratios, potassium and phosphorus mobility, ionic soluble salts composition and salts content in formulated materials; e) monitoring composite materials after harvesting, the plant growth parameters and crop performances; f) chemical analysis of dry plant green mass and g) data statistical analysis.

Adjuvant materials chemical and agrochemical analysis has shown these materials themselves are conveying a large dowry of mineral salts with neutral (PG, OC and MA), acid (WS, AP and AaS) and alkaline (SWBT and SWCT) reaction, containing macro, mezzo and micronutrients at sustainable concentrations. Most of the saline constituents are adding to red mud much more salinity and are inducing numerous changes in molecular compounds distribution in the composite materials saline composition. Particularly, the dominant molecular formal species in red mud salts charge is the sodium carbonate, accounting for as much as 91.1% from total salts content, But the basic selection on adjuvant material was based on their capacity to improve red mud composition and properties. Thus, satisfactory concentrations of organic carbon are carried by WS (46-50 %), AP (20-45 %), SWBT (17%), OC (9.2%) and MA (1-8 %). Moreover, all the adjuvant materials presume enough buffering capacity and nutritive ionic species to sustain the crops growth.

First type of red mud composite material investigations was dedicated mainly to the study of correlations composition-agrochemical properties, and secondly, to the analysis of each constituent contribution to composite material fertility. Adjuvant materials for red mud properties control were PG, SWBT, OC, MA and N as NH_4NO_3. Their mass ratio adjuvant materials to RM in composite formulations was ranging from 41.5/1000 to 364/1000. All variants compositions in terms of adjuvant materials dosage and ratios cover all the theoretical expected changes in red mud composition and properties for its conversion into a nutritive composite material. Major and minor nutrients status, mobile forms of phosphorus and potassium, *p*H, well balanced organic carbon and total nitrogen content were equivalent to the very well supplied soils. The total soluble salts content in all formulated composite materials were increasing proportionally and notably with the added adjuvant materials doses from 1.874 to 2.888 mg/100g composite mixture. In the saline soluble mixtures the dominant salt is sodium sulphate (ranging from 54.0 to 82.75 %,) sodium ion being brought in by RM and sulphate ion by all the other adjuvant materials. It was concluded that through well balanced formulation, sodium sulphate as dominant molecular species was replacing sodium carbonate (91.2%) from the red. Since soils salinization begins at 100 mg soluble salts /100 g soil, it is expected that practically is not possible to grow plants on such a growth layers, chiefly due to salt composite material saline overloading. Actually, not the missing of the nutrients and organic carbon is the cause of red mud composite materials infertility, but rather its high content in soluble salts.

The second type of red mud composite material encompased the following constituents: RM, PG and OC at constant quantities and WS, AP and AaS (200 g) at progressive added quantities. So that, the high salt content adjuvant materials (SWBT and MA) were replaced by the rich carbon and high power buffering materials as WS, AP and AaS. Also, the experiment encompassed the study of *Triticum durum* response to the new red mud composite. The new adjuvant materials were contributing to the undoubted increase in organic carbon and nitrogen content, C/N ratio, as well as to some much larger mobile phosphorus and potassium ions concentrations red mud composite materials.

After the harvesting *Triticum durum* crop, significant changes in the nutritive material composition were taking place: a) large changes in organic carbon concentration coming from the composite materials mineralization process (proportionally with the total added WS, AP and AaS); b) small but significant increases in total nitrogen concentrations, mainly due to the mineralization process; c) significant increasing in C/N ratios; d) moderate stationary increases in mobile phosphorus ion concentrations in all the variants, due to mineralization during vegetation stage and regardless to additional WS, AP and e) moderate stationary decreases in mobile potassium ion concentrations due to consumption during vegetation stage. Accordingly, the soluble salts concentration before sowing and after harvesting varies between 2240-2246 mg/100 g dry samples collected before sowing and 2539- 2979 mg/100 g dry samples collected after plant harvest. These concentrations are very high as compared with minimum starting values for set off soil salinization, Nevertheless, the saline charge of the second type of red mud composite materials is not dominated by Na_2CO_3 as in the RM or Na_2SO_4 as in the first type of red mud composite materials. This time, the dominant salt position is shared by Na_2SO_4 and $CaSO_4$. This is an encouraging step toward better balanced formulations.

Triticum durum choice for this experiment was recommended by its low stress to salinity and poor conditions of growth. The analytical data regarding the macro (nitrogen, phosphorus, potassium) and mezzo nutrients (calcium, magnesium) contents in dry green plants show that the plants had enough supply of these elements (this conclusion is sustained by nutrients content in the initial red mud composite materials analysis before sowing and after the plants harvest. The macro and mezzonutrients concentration in the dry green plants can be located the normal range of variation of each element in normal fertile soils. Slightly lower calcium concentrations recorded in all variants seems to be in good agreement with the expected values at the fifth vegetation stage according with Feeks scale. The analytical data regarding the micronutrients (zinc, copper, iron, manganese) showed that the plants had normal supply of these nutritive elements, except for the zinc content, which is a little higher especially in the dry green plants samples coming out from variant V1.

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