

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

I. Red Mud Chemical and Agrochemical Characterization

RADU LACATUSU^{1*}, ANATOLI KISELEV², NINETA RIZEA¹, MIHAELA LUNGU¹, RODICA LAZAR¹, MIHAELA MONICA STANCIU-BURILEANU¹, NICOLETA VRINCEANU¹, VENERA MIHAELA STROE¹, ROXANA GABRIELA POPA³, LAURENTIU FILIPESCU²

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

²SC Alum SA, Tulcea, 82 Isacsei Str., 820228, Romania

³University "Constantin Brancusi" Tg.Jiu, 30 Calea Eroilor, 210135, Tg. Jiu, Romania

In the last years, significant progresses were made in finding useful red mud applications as raw material for several products, even if the production costs are still unattractive. Some of the reported successful applications are concerning researches on: a) revegetation of the disposal area and b) polluted soils remediation. The purpose of this study concerns the properties investigation of Romanian red mud accumulated in the Tulcea alumina refinery disposal site and its conversion into a fertile composite material. According to experimental data, this by-product elemental composition is fully, but remediable disequibrated. Macro and mezzo nutrients content is below minimal suitability for plant growth. But, its loamy clayey-sandy texture sustains additional materials for properties change and improvement. Some corrections by mixing with selected waste or natural materials have to be stringently followed to overpass the low organic and nitrogen low concentrations.

Keywords: red mud, nutrients content, ionic mobility, salinity, agrochemical properties

Red mud, as a by-product from bauxite refineries, is a poly-dispersed particulate material with variable chemical and phase composition, according to its provenance in terms of raw bauxites mixing and processing, factory operational parameters and technical management, equipment renewal and optimization. Red mud chemical and phase composition is largely variable, but this does not significantly affect most of its physical properties, particularly those concerning the neutralization and safe landfilling. Most of the researches focusing red mud environmental issues were dedicated to systematic characterization of the raw, weathered and neutralized material [1-10], as well as to the safely neutral product impoundment and industrial uses exploratory attempts [11-26]. Some other subjects in red mud investigations are related to the red mud disposal site revegetation and red mud treatment and use as soil conditioner [27-40].

Our researches concern a comprehensive investigation for conversion of the weathered Romanian dry landfilled red mud into nutritive composite support for plant growth. First part of the researches were converging toward the chemical and agrochemical characterization of red mud already weathered over a short time at the actual disposal site located in Tulcea, Romania. Second part is related to the composite support formula optimization, according to the red mud chemical and agrochemical properties investigations and preliminary plant growth tests at the laboratory scale. Extended formulation and acid soils conditioning, as well as plant growth tests in the vegetation house are the subjects of the third part of our study. This paper is referring to the first part of the above mentioned topics.

Alumina refinery is situated on the outskirts of Tulcea town and the disposal site at 5 km distance from refinery in a natural protected area. According to the recent landfill

site retrofit in 2009, and switching from suspended red mud impoundment to deep thickening and red mud disposal in dry state, the disposal site comply with most of the EU directives recommendation regarding environmental protection: large and safe dams, full fencing and complete surveillance, partial closure of the area facing the highest dam, dry landfilling, pluvial water collecting and treatments, water-sprinkling service to keep the dry material surface moistened, detouring channel for preventing site over-flooding, etc.

Even if the weathering removes some of the red mud alkalinity, the large mass/volume of stored material, as well its exquisite rheological properties and particularly fine structure still come as a major environment embarrassment for this industry. Some compelling steps were made in finding useful application for the red mud as raw material for several products [11-14], but the production costs are still unattractive. Most of reported successful applications are framed to the revegetation of disposal area and polluted soils remediation. But, exceeding salinity, pH ranging from 11 to 12 and inadequate texture place the red mud far away from offering normal conditions for plant growth. Thus, for developing a composite material fulfilling at least the minimum plant growth requirements out of a material totally lacking microscopic and macroscopic life support properties, some complex and thoroughly researches are undeniable needed for any particularly red mud deposit. Actually, this is the purpose of our investigations.

Experimental part

Samples of the red mud for these experiments were taken randomly from a particularly located site of the disposal site, where the red mud was less deposited in the last 3 years. Hence, the collected material contains

* Tel: (+40) 0213184459

doubtlessly a large portion weathered red mud for at least for 3 years.

The following determinations were made for the chemical and physical characterizations of the red mud, using standard methods and procedures [41]:

- pH potentiometric measurements, using a combined glass – calomel electrode coupled to a Mettler Delta 340 potentiometer;

- organic carbon, by volumetric analysis, using the Walkley-Black modified by Gogoasă method [42];

- total nitrogen, by the Kjeldahl method, using the Gerhardt Tecator automatic equipment, and the Schott automatic equipment for digestion, distillation, respectively titration;

- the mobile contents of phosphorus, potassium, calcium, and magnesium, soluble in the ammonium acetate-lactate solution at pH 3.7 (AL), were determined by spectrophotometry (phosphorus), flame photometry (potassium, calcium), and by atomic absorption spectrometry (magnesium); an UV-VIS Cecil 204 spectrophotometer, a Flapho 4 flame photometer, and a Solar AA atomic absorption spectrometer were used;

- the total soluble salts content was determined conductometrically, using a MC 226 Mettler conductometer; Additionally, some ions from the natural material samples were determined volumetrically (CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-}), or by flame photometry (Ca^{2+} , K^+ , Na^+) and by atomic absorption spectrometry (Mg^{2+});

- red mud samples were mineralized with perchloric (HClO_4) and nitric (HNO_3) acids mixture and, finally, the residuum was dissolved in hydrochloric solution; the measurements encompassed both total heavy metals content (cadmium, cobalt, chromium, iron, manganese, nickel, lead, zinc) and total contents of phosphorus, potassium, calcium, and magnesium; the heavy metals and magnesium contents were measured by atomic absorption spectrometry using air-acetylene flame atomization method; the phosphorus was measured spectrophotometrically, and the calcium and potassium by flame photometry; also, the above mentioned equipment, UV-VIS Cecil 204 spectrophotometer, a Flapho 4 flame photometer, and a Solar AA atomic absorption spectrometer, were used;

- the overall chemical analysis was carried out by inductively coupled plasma atomic emission (ICP-OES), on a GBC device, Integra XL model;

- particle-size distribution was determined for the physical characterizations, by the Kacinski method [43].

Results and discussions

Full chemical analysis

The red mud is a mixture of many mineralogical phases incorporated into a solution containing mostly sodium salts

(aluminate, hydroxide and carbonate) and all the impurities collected by alkaline lye over the production line. The overall composition of the red mud analyzed in this report is presented in the table 1. Additionally, some older data are attached, pointing to material technological variability and weathering extent [6]. Actually the analyzed samples are similar as the 2011 ones and certainly different from the 2006 samples. Some ways this difference comes from changes in the bauxite composition used in the last years and certainly from the switching from red mud suspension impoundment to dry disposal.

The prevalence of iron (Fe) and aluminum (Al) oxides in red mud composition is obvious. Iron oxide accounts for 52.9% of all the dried red mud's major chemical constituents and the aluminum oxide as much as 21.2%. In a descending series, silicon (Si), sodium (Na), calcium (Ca) and titanium (Ti) oxides come after these two main constituents. Their contribution rose to 8.9, 8.2, 4.3 and respectively, 3.7%. Among the other constituents, inorganic carbon makes up to 1.88%, organic carbon 0.35%, and potassium (K), magnesium (Mg), phosphorus (P) oxides and nitrogen (N) all together up to 0.4%. A suggestive distribution of red mud chemical constituents is given the figure 1.

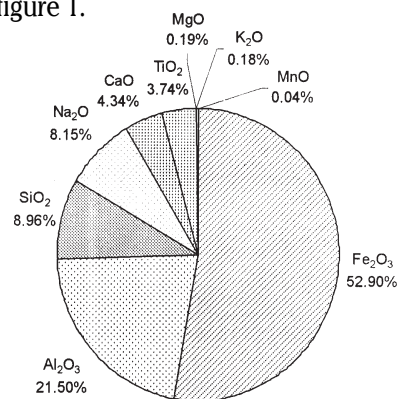


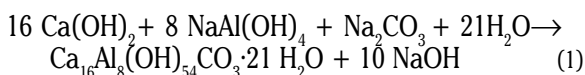
Fig. 1. Chemical constituents and their mass distribution in red mud

The calcination loss (IL) means the total water retained on particle surface as humidity and some of water released from the poor crystallized hydrates. Only calcination to high temperature (2011 sample) may relieve the entire hydration water and eventually the water turning out from reactions between certain compounds from the red mud composition. This surface humidity, which is proportional with specific surface area of the particulate material, may be lost or gained on simple exposure to air. As much water is held on particle surface, as much alkalinity is subsumed. On the other hand, as much water is held on particle surface, as much are enforced the interactions of red mud with the presumptive materials used for removing alkalinity and building up the nutritive composite supports for plant growth.

Table 1
RED MUD OVERALL COMPOSITION (%)

Constituents	2012 - Chemical	2011 - XRF	2006 - XRF
Fe_2O_3	44.60 ± 1.65	58.9	69.5
Al_2O_3	18.16 ± 0.66	20.0	17.0
SiO_2	7.55 ± 0.27	9.3	7.1
Na_2O	6.87 ± 0.27	-	-
CaO	3.66 ± 0.09	4.9	3.6
TiO_2	3.16 ± 0.42	3.4	9.4
MgO	0.16 ± 0.04	-	-
K_2O	0.15 ± 0.02	1.0	-
MnO	0.03 ± 0.00	0.12	0.17
Total oxides	84.3 ± 1.61	97.6	
Calcination loss (PC)	15.2 ± 1.31	59.5 at 650°C	17.5
Total amount	99.5 ± 1.46	-	-

Red mud alkalinity is not related only to liquid phase ionic species as: Na^{1+} , K^{1+} , AlO_2^{-1} , Al^{3+} , Ca^{2+} , Mg^{2+} and other. Most of the alkalinity is associated with mineralogical phases. The red mud mineralogy is not the subject of this paper, but it is relevant to have an accurate view about the contribution of the mineralogy in the context of red mud interactions with soils mineralogy. Actually, the red mud contains residual solid phases from non-reacted bauxites. These phases are mostly chemically inert. Only the new born mineralogical phases during bauxite digestion are chemically reactive. These phases have general formula: $3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot \text{Na}_2\text{X}$, where X is CO_3^{2-} , 2OH^- , SO_4^{2-} or 2Cl^- , and the typical representatives are: sodalite - $\text{Na}_4[\text{Al}_6\text{Si}_6]_{24}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, cancrinite - $(\text{NaAlSiO}_4)_6 \cdot \text{CaCO}_3$, hydroxycancrinite - $\text{NaAlSiO}_4 \cdot \text{NaOH} \cdot \text{H}_2\text{O}$, tricalcium-aluminate hydrates - $x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{H}_2\text{O}$, chantalite - $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$, hydrogarnet - $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_{12-4n}$ and kaolinite - $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Also, the high content of calcium in red mud can decompose the sodium aluminate or even the sodalite during red mud wash. An amorphous phase might first be formed and then the hydroxicalumite crystallizes slowly at the expense of amorphous, all over where the drying and air carbonation of the stockpiled red mud takes place [44]:



Since most of the oxides from the table 1 are certainly bonded into all low solubility crystalline or amorphous compounds born during bauxite digestion, less of the ionic species can apparently interfere with soil conditioning byproducts or with the soil itself. Nevertheless, if additional materials brought in the red mud for its conversion in a nutritive support are carrying enough acidity to drop red mud pH, some new ionic or hydrated molecular species are release in the soil. Most of them are alkaline ions and silica compounds occurring from sodalite and cancrinite decomposition processes. The extent of these reactions depends on available gibbsite in the wearing red mud, pair ions substitution in the crystalline lattice of basic compounds, silica reactivity and silica concurrent reactions. A convenient turn of these reactions is the release of plant available silica species, which proved to be a valuable growth assistance resource [45-47].

Red mud elemental composition is chiefly disequilibrated, when it is compared with common soils averaged compositions. So far, red mud contains, on an average, 12.5 times more iron, 1.8 times more aluminium, 7 times more sodium, 2.1 times more calcium, but 16.7 times less magnesium, 13.3 times less potassium and less than 21 times nitrogen [48]. Therefore, from the macronutrients contents point of view, the red mud constitutes a totally unsuitable environment for plant growth. The only exception is the phosphorus, whose total average content is practically equal to that of 0.092% [49].

However, as happened in the case any kind of fertile soil, not all the elements are exhibiting any contribution to fertility. Major parts of the elements are bound in inert compounds and their service is limited just for sustaining texture and porosity. The same structure resides also in red mud, but with some other inappropriate components, as can be seen in the figure 2. Practically, the main constituents are built-in a particulate non-reactive material. Only small parts of the chemical compounds are passing into soil solution and interact with other classes of products added for inducing fertility and nutritive status. From this

point of view the red mud under diverse mixed states of neutralization has to be taken as any other unfertile soil ready to be processed and ameliorated (fig. 2). In this material, the minor components, organic carbon and nitrogen concentration and ratio (fig.3) has to be totally changed, appealing both to some other carbon-rich natural or residual resources and organic or inorganic nitrogen fertilizers. Actually, this is what our work is intended to be carried through.

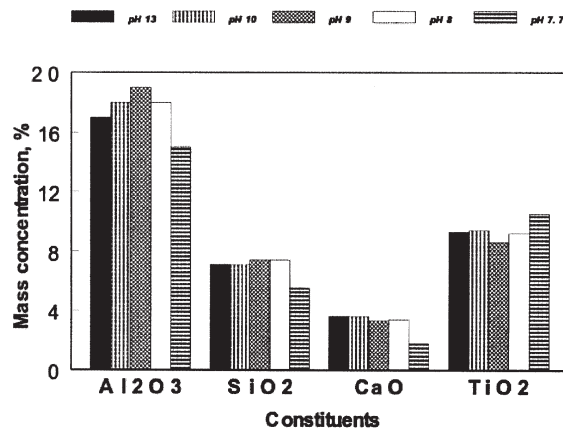


Fig. 2. Constituents distribution in raw and neutralized red mud

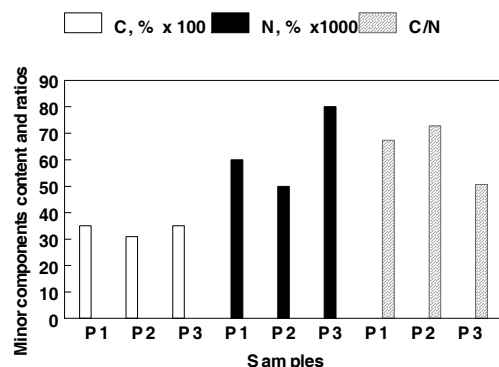


Fig. 3. Minor components content and ratios in red mud

Total heavy metals (including micronutrients) content

From all the analyzed heavy metals (table 2), only chromium (Cr) in the red mud exceeds the common acknowledged values in soils (almost 25 times the soil normal content and 6 times the maximum allowable limit value ($100 \text{ mg} \cdot \text{kg}^{-1}$) [48]. The red mud high chromium concentrations are inherited from bauxite (table 2). Most of the bauxite's total chromium content could not be

Table 2
THE HEAVY METALS AND MICROELEMENTS ($\text{mg} \cdot \text{kg}^{-1}$) THE BAUXITE AND RED MUD STOCKPILED BY SC ALUM SA TULCEA

Chemical element	Red mud		Bauxite	
	$\bar{x} \pm \sigma$	$\bar{x} \pm \sigma$	$\bar{x} \pm \sigma$	$\bar{x} \pm \sigma$
Cd	0.37	0.17	0.03	0.02
Co	8.70	1.90	8.60	0.30
Cr	604.00	62.00	346.00	19.10
Cu	71.00	4.00	31.00	1.00
Mn	260.00	12.00	322.50	12.00
Pb	1.10	0.20	15.40	0.70
Zn	56.00	8.00	19.30	0.60

removed by bauxite alkaline processing and expectedly accumulates in the red mud. Accordingly, almost the entire chromium dowry is built-in insoluble compounds, which already passed through an overloaded process of digestion under pressure at a temperature at least as high as 140°C. Our previous investigations did show the leachable parts of these compounds are lying under the regular levels and the concentrations of leached chromium are decreasing as the pH drops toward usual values in soils [5, 6, 17, 18].

The other heavy metals concentration in the red mud composition seems to be close to the normal values found in soils. Nevertheless, following the technological process, a slight increase in these metals concentrations was noticed, but within the normal limits, especially for cadmium, copper, manganese and zinc (chemical elements with nutritive role) contents. Also, a fourteen fold decrease in lead content was assessed, as far as cobalt content remained practically at the same level.

The above data are in good agreement with the same measurements done for other refineries red mud, namely: cadmium (Cd, 27), chromium (Cr, 538), copper (Cu, 78), lead (Pb, 57), nickel (Ni, 985), mercury (Hg, 67), arsenic (As, 267), comparable to those above mentioned [5-9]. It turns out that only chromium, out of the heavy metals, could have a negative effect on plant growth in a possible nutritive support containing red mud, but only in remediable limits.

Cation exchange propertie

Red mud total ion exchange capacity is atypically measured by two different experimental methods, considering: a) soil saturation with sodium with T_{Na} value and b) soil saturation with ammonium with T_{NH_4} value (table 3). The first determination (T_{Na}) is accompanied by errors due to the high sodium content in the red mud. The second determination of cationic exchange capacity (T_{NH_4}) is closer to real value, because ammonium ion is missing from red mud composition.

In any case, the 20.48 meq/100 g red mud value seems to be satisfactory for a medium in which both dissolution and cationic exchange processes are taking place simultaneously. Most of these data are impaired by very high sodium quantities coming from the saline system. Thus, the 126.63 meq/100 g red mud of the sodium soluble in the ammonium acetate (CH_3COONH_4) solution at pH 7.0 is certainly very high, but it stands for subsuming both the water soluble sodium (26.45 meq/100 g red mud) and exchangeable sodium (100.18 meq/100 g red mud). The last value is, on an average, 50 times higher than the values of exchangeable sodium in non-halomorphic soils [48]. Accordingly, under such conditions, toxicity levels of sodium in red mud are and could be very high, not only in the liquid accompanying phase, but even in the colloidal fractions of wetted material. This problem has to be apprehended with much more caution. Technically, advanced sodium removal from red mud is a problem of efficiency and production costs, which could be acknowledged in any future plant plan. Beside, dry landfill, weathering and mixing with appropriate materials may alleviate factually the sodium toxicity, mainly when pH is brought to less than 7.0.

Soluble salts content and ionic mobility

A relative very high total soluble salt in red mud composition is clearly presented in the table 4. The value of 1836 mg per 100 g dry red mud is 18 times higher than the concentration limit of 100 mg soluble salts from which

Table 3
CATION EXCHANGE PROPERTIES OF THE RED MUD

Properties	meq/100 g dry mud
T_{Na}	62.58
T_{NH_4}	20.48
Exchangeable Na	100.18 ± 1.32
Na soluble in CH_3COONH_4 at pH = 7.0	126.63 ± 1.64
Water soluble Na at pH 7.0	26.45 ± 0.32

Table 4
AVERAGED RED MUD IONIC AND MOLECULAR SALTS CONCENTRATION

Ionic concentration, mg/100 g dried red mud	$\bar{x} \pm \sigma$	Formal molecular share in salt content, %
CO_3^{2-}	784±3	-
HCO_3^{-}	64±29	-
SO_4^{2-}	19±0	-
Cl^{-}	32±1.7	-
Ca^{2+}	1±0	-
Mg^{2+}	0±0	-
Na^{+}	609±7	-
K^{+}	6±0	-
Total	1836	-
Na_2CO_3	-	91.9
$NaHCO_3$	-	3.4
$Ca(HCO_3)_2$	-	0.2
Na_2SO_4	-	1.4
$NaCl$	-	2.5
KCl	-	0.6
Total	-	100

soil salinity begins to be harmful the plant growth. Expected prevalence of CO_3^{2-} and Na^{+} ions was demonstrated experimentally. This gives specificity to the total soluble salts parameter.

According to the visualized data in the table 4, no less than 91.9% of the Na_2CO_3 is formally present in bulk salt composition. Other components (sodium bicarbonate, sodium chloride, sodium sulphate, potassium chloride, and calcium bicarbonate account for no significant concentrations in common limits. Factually, the salt composition from the table 4 is a proof of the red mud weathering. However, the data from this table should be cautiously evaluated. Significant parts of sodium and carbonate ions are confined in poor or insoluble aluminates and aluminosilicates, as it has been shown above. The same view is valid for the Ca^{2+} , Mg^{2+} and SO_4^{2-} ions. Only parts of the total ionic concentration of these ions are involved in the red mud real alkalinity. Their share is slowly diminishing as the red mud is weathering under CO_2 continuous absorption, and calcium ions or acid entities brought in by rains waters. Thus, the alkalinity effect as an impairing factor on plant growth is better expressed by the ionic species mobility than by ionic species concentrations in red mud or in red mud accompanying liquid phase.

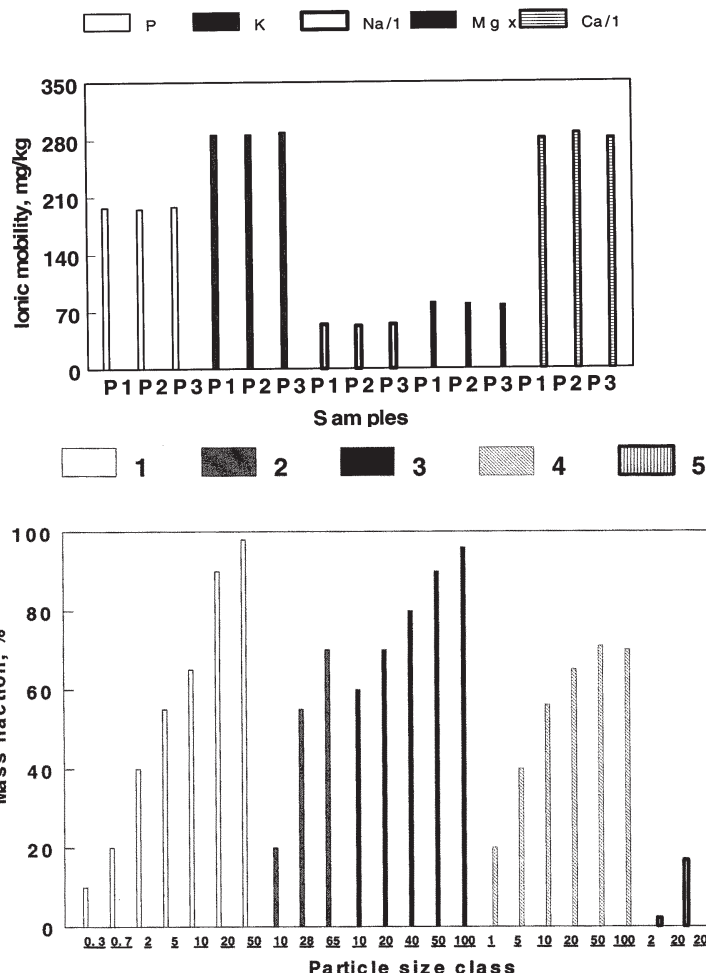


Fig. 4. Ionic mobility in weathered red mud mediated over 10 measurements in different samples

Fig. 5. Particle size distribution in calcined, dried and wet red mud. 1.Pocos Caldos Brazil; 2.Alcan Canada; 3.Nalco India; 4.Alum Romania

Previously, it was shown the total phosphorus found in red mud is 0.092%. Expectedly, the mobile phosphorus, determined as soluble phosphorus in the acetate-lactate solution at pH 3.7, is also high, standing for a good supply of this macronutrient (fig. 4). More alike, the total potassium content is as high as 0.094% and consequently a comparable mobile fraction, as in the case of phosphorus, did outcome (fig. 4).

The levels of these ions mobility, close to 200 mg/kg for phosphorus and close to 300 mg/kg for potassium, are enough to sustain the plant growth as happens in common soils. Magnesium ion mobility is far behind the phosphorus and potassium mobility (20 times less than phosphorus and 35 times less than potassium). This is due to poor solubility and low ion exchange capacity of the magnesium compounds in red mud. May be most of the magnesium is bound by replacing calcium in calcium aluminates and aluminosilicates. But, this shortcoming may be over-passed easily by careful selection of the additional improving materials in red mud conditioning. The real problem of red mud conversion into fertile soil is the high level of Na^{1+} (5300 mg/kg) and (2800 mg/kg) ionic mobility. Above all, some corrections are also required due to organic and nitrogen low concentrations in red mud. Parts of mobile Na^{1+} and Ca^{2+} ions could be removed by air carbonation of the selected fractions of raw material, and over-weathering it under pluvial waters washing and natural temperature variation over long periods. Adequate selected waste or natural materials able to carry organic carbon and enough acidity to lessen pH level may be used for mixing in order to outweigh the deficiencies in red mud composition.

Texture

The red mud texture mainly depends on its chemical and mineralogical composition, with significant contribution of very fine fraction of the iron oxides. It was reported that the red mud's texture varies between clayey-sandy loam and clay, in which 2-20 μm particles are prevalent in dried and over-dried (semi-calcined) red mud [51, 52].

In the normal dry stored (PC around 15%) by SC Alum SA Tulcea in its own disposal site, the coarse sandy 2.000-200 μm fraction raises up to 58.6%, followed, in a decreasing series, by fine sandy fraction (200-20 μm) with a 24.4% share. The fine dusty like particles fraction 20-2 μm imparted a 14.8% share, while the very fine colloidal particles (smaller than 2 μm) accounts only for 2.2%. A comparison with other dried and semi-calcined samples is given in figure 5 [53-56]. This mineral particle size distribution bears a coarse loamy sandy type texture, coarser than other well described types of red mud from Australia [51,52]. This particular texture might be helpful in mixing and processing the red mud to some fertile composite materials.

Conclusions

Red mud elemental composition, as compared with common soils composition, is largely disequibrated, and particularly from the point of view of macro and mezzo nutrient contents. Thus, red mud contains, on an average, 12.5 times more iron, 1.8 times more aluminum, 7 times more sodium, 2.1 times more calcium, but 16.7 times less magnesium, 13.3 times less potassium and less than 21 times nitrogen. Therefore, raw or weathered byproduct is a totally unsuitable support for plant growth.

The heavy metals concentration in the red mud composition is very close to the normal values found in soils, excepting total chromium content. The measured concentrations are in good agreement with other refineries data cadmium (Cd, 27), chromium (Cr, 538), copper (Cu, 78), lead (Pb, 57), nickel (Ni, 985), mercury (Hg, 67), arsenic (As, 267). Chromium concentration should be cautiously ascertained, because our previous data have shown the leachable parts of chromium are decreasing beyond the mg/kg) and potassium (300 mg/kg) mobility seems to be appropriate values for sustaining the plant growth as happens in common soils.

An advanced technology for the sodium removal from red mud is a problem of efficiency and production costs. In any future plan this technology could be reconsidered as feasible by alumina refineries not only as a problem of materials consumption optimization, but also as a way to improve red mud quality for its further processing to secondary products.

Beside dry landfill and weathering, parts of mobile and ions could be removed by air carbonation of the isolating the raw material, and over-weathering it under pluvial waters washing and natural temperature variation over long periods.

Adequate selected waste or natural materials able to carry organic carbon and enough acidity to lessen pH level may be used for mixing in order to outweigh the all shortcomings from red mud disequilibrium composition. Also, the mixing with appropriate materials may alleviate factually the sodium toxicity, mainly when pH is brought as low as 7.5-8.5.

Acknowledgement: The authors are grateful for technical and financial support from SC VIMETCO ALUM SA Tulcea, Romania

References

- GRÁFE, M., TAPPERO, R., LANDERS, M., GAN, B., AUSTIN, P., TAYLOR, Z., KLAUBER, C., International seminar on bauxite residue (red mud) 2011, Goa, India, TRAVAUX 36 (40), 2011, p.15;
- WU, C.S., LIU, D.Y., Journal of Nanomaterials, 2011, ID 628592 (open access);
- KLAUBER, C., KLAUBER, C., CSIRO Document, DMR-3610, 2009;
- SNARS, K., GILKES, R.J., Applied Clay Science 46, 2009, p.13;
- NICULESCU, M., IONITA, A.D., RADOVICI, C., FILIPESCU, L., Premier Colloque Francophone sur La Matériaux, Le procedes et L'environnement, Volume des Papiers (Editors: Cornel Anton, Delia Arnaud – Cormos, Jean – Pierre Lecompte, Patrick Leprat, Alina Melinescu, Maria Preda), Editura Printech, Bucuresti, 2009, p. 89;
- NICULESCU, M., IONITA, A.D., FILIPESCU, L., Rev. Chim. (Bucharest) 60, no.11, 2009, p. 1189;
- ATASOY, A. J. Therm. Anal. Calorim. 81, 2005, p. 357;
- HANAHAN, C., Environ. Eng. Sci., 21, nr.2, 2004, p.125;
- TATHAVADKAR, V., ANTONY, M. P., JHA, A., Light Metals, 2002, p. 199;
- HIND, R., BHARGAVA, S. K., GROCCOTT, S. C., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 146, nr.1-3, 1999, p. 359;
- RAI, S.B., WASEWAR K.L., MISHRA R.S., MUKHOPADHYAY, P., CHADDHA, M.J., MUKHOPADHYAY, J., Desalination and Water Treatment, 51, nr.10-12, 2013, p. 2185;
- RAI, S.B., WASEWAR K.L., MUKHOPADHYAY, J. YOO, C.K., USLU, H., Arch. Environ. Sci. 6, 2012, p.13;
- PARLIKAR U.V., SAHA, P.K., KHADILKAR, S.A., International seminar on bauxite residue (red mud) 2011, Goa, India, TRAVAUX 36 (40), 2011, p. 208,
- KLAUBER, C., KLAUBER, C., International seminar on bauxite residue (red mud) 2011, Goa, India, TRAVAUX 36 (40), 2011, p. 188,
- PANOV, A., KLIMENTENOK, G., International seminar on bauxite residue (red mud) 2011, Goa, India, TRAVAUX 36 (40), 2011, p. 297,

16. BHATNAGAR, A., VILAR, V.J.P., BOTELHO C.M.S., BOAVENTURA R.A.R., Environmental Technology, 32, nr.3, 2011, p. 231;
17. NICULESCU, M., IONITA, A.D., FILIPESCU, L., Rev. Chim. (Bucharest), 61, no. 2, 2010, p. 200;
18. NICULESCU, M., IONITA, A.D., SIMION, D., CRUDU, M., FILIPESCU, L., UPB Sci.Bull.Series Chemistry, 72, nr.3, 2010, p. 99;
19. DIMITRIOS, D.D., GIANNOPOULOU, I.P., PANIAS, D., Mineral Processing and Extractive Metallurgy Review: An International Journal, 30, nr. 3), 2009, p. 211;
20. LIU, W., YANG, J., XIAO, B., Int. J. Miner. Process. 93, 2009, p. 220;
21. GHIGA, M., GAIDAU, C., RADOVICI, C., FILIPESCU, L., INCD ECOIND International Symposium "The Environment and Industry" – SIMI 2007 – Bucharest, October 2007, Academia Romana, Bucuresti, Romania, p. 62
22. GUO, Z.R., ZHANG, G., FANG, J., DOU, X., J. Clean. Prod., 14, 2006, p. 75
23. SANTONA, L., CASTALDI, P., MELIS, P., J. Hazard. Mater., 136, 2006, p. 324;
24. BRUNORI, C., CREMISINI, C., MASSANISSO, P., PINTO, V., TORRICELLI, L., J. Hazard. Mater., B117, 2005, p. 55
25. PARAMGURU, R. K., RATH, P.C., MISRA, V.N., Mineral Processing and Extractive Metallurgy Review: An International Journal, 26, nr. 1), 2004, p.1
26. McConchie D., Proceedings of the 6th International Alumina Quality Workshop, September, 2002, p. 327
27. COURTNEY R. G., KIRWAN L., Ecological Engineering, 42, 2012, p. 279
28. GREENBERG, J., KORANCHIE-BOAH, P., MERRICK, N.J., NICHOLS, R., GHOSH, R.,
29. SMITH, J.R., ISOVITSCH-PARKS, S.L., International seminar on bauxite residue (red mud) 2011, Goa, India, TRAVAUX 36 (40), 2011, p. 25
30. JONES B. E. H., HAYNES R. J., Critical Reviews in Environmental Science and Technology, 41, nr. 3, 2011, p.271;
31. COURTNEY R. G., TIMPSON J. P., Reclamation of fine fraction processing residue (red mud) amended with coarse fraction residue and gypsum, Water, Air and Soil Pollution, 164, nr. 1-4), 2005, p. 91;
32. MADDOCKS, G., REICHELTER-BRUSHETT, A., MCCONCHIE, D., VANGRONVELD, J., Environmental Toxicology and Chemistry, Vol. 24, nr. 3), 2005, p. 554;
33. SNARS, K., GILKES, R., HUGHES, J., Australian Journal of Soil Research 41, nr. 6), 2003, p.1229
34. EASTHAM, J., MORALD, T., Water Air and Soil Pollut. 171, 2006, p. 301
35. EASTHAM, J., MORALD, T., Water, Air, and Soil Pollution 3171, 2006, p. 315
36. GRAY, C.W., DUNHAM, S.J., DENNIS, P.G., ZHAO, F.J., McGrath, S.P., Environmental Pollution 142, 2006, p. 530
37. WEHR, J.B., FULTO, I., MENZIE, N.W., Environmental Management 37, nr. 93), 2006, p. 297
38. XENIDIS, A., HAROKOPOU, A.D., MYLONA, E., Brofas, G.m JOM, 2005, nr. 2), p. 42
39. COURTNEY, R.G., TIMPSON, J.P., Plant and Soil 266, 2004, p.187;
40. HAMDY, M.K., WILLIAMS, F.S., Journal of Industrial Microbiology & Biotechnology 27, 2001, p. 228
41. STOICA E., RĂUȚĂ C., FLOREA N., (Red.), Soil chemical analysis methods, Red. Prop. Teh. Agricolă, București, 1986, p. 481 (published in Romanian)
42. GOGOASA, T, D de S Comit Geol 42, 1959, p. 251 (in Romanian);
43. DUMITRU, E., CALCIU, I., CARABULEA, V., CANARACHE, A., Analysis methods used in the soil physics laboratory, Ed. Sitech, Craiova, 2009, p. 51 (Published in Romanian)
44. ZANG, M., PhD thesis, University of Waterloo, 2000
45. BOCHARNIKOVA, E.A., LOGINOV, S.V., MATYCHENKOV, V.V., STOROZHENKO, P.A., Russian Agricultural Sciences 36, nr. 6, 2010, p. 446
46. MA, J.F., TAKAHASHI, E., Soil, Fertilizer, and Plant Silicon Research in Japan, Amsterdam: Elsevier, 2002, p. 1

47. GASCHO, G.J., Silicon sources for agriculture. In: L.E. Datnoff, G.H. Snyder, G.H. Korndorfer, eds. *Silicon in Agriculture*. Amsterdam: Elsevier, 2001, p. 197
48. LACATUSU, R., *Agrochimie*, Ed. Helicon, Timisoara, 2000, p.250;
49. BORLAN Z., HERA CR., BUNESCU O., *Phosphorus Agrochemistry* Ed. Ceres, Bucharest, 1990, p.45 (published in Romanian)
50. M., GRÄFE, LANDERS, M., TAPPERO, R., KLAUBER, C., HUTOMO, G., GAN, B., GRABSCH, A., AUSTIN, P., DAVIES, I., *Proc. 19th World Congress of Soil Science, Soil Solutions for a Changing World*, 2010, Brisbane, Australia (published on DVD)
51. MCDONALD, R.C., ISBELL R.,F., SPEIGHT, J.G., WALKER, J., HOPKINS, M.S., *Australian Soil and Land Survey Field Handbook*, 2nd Edn., CSIRO, Australia, 1998, p. 49
52. THORNBUR M.R., HUGHES C.A., *Proceed. Intern. Conf. Bauxite Tailings*, Kingston, Jamaica, 1986, p. 1
53. RIBEIRO, D.V., LABRINCHA, J.A., MORELLI, M.R., *Use of Red Mud as Addition for Portland Cement Mortars*, *Journal of Materials Science and Engineering*, 4, nr. 8, 2010, p.1
54. ALLAIRE, C., *Light Metals*, 1992, p. 401
55. SAHU, R.C., PATEL, R., RAY, B. C., *Adsorption of Zn(II) on activated red mud: Neutralized by CO₂*, *Desalination* 266, 2011, p. 93
56. HAN, J., ZHANG, A., M., J. Han and D.A. Alzamora in: *Geotechnical Special Publication nr. 211, Geo-Frontiers 2011: Advances in Geotechnical Engineering*, ASCE, 2011, p1287

Manuscript received: 30.07.2013