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

Gheorghe DOBRA[1], Laurentiu FILIPESCU[2], Nicolae ANGHELOVICI[1], Vicol ALISTARH[1], Sorin ILIEV[1]

[1] VIMETCO ALUM, 82 Isaccei street, Tulcea, Romania
[2] University, Politehnica Bucharest, Romania

dobra@alro.ro, laurentiu_filipescu@yahoo.co.uk, nanghelovici@alum.ro, valistarh@alum.ro, siliev@alum.ro

Abstract

Vimetco Alum SA alumina refinery in Romania has made improved bauxite residue disposal technology, which now complies with the EU and national environmental regulation: large and safe dams, dry stacking bauxite residue disposal, pluvial water collecting channel and treatments units, bauxite residue continuous surface moistening, etc.[1] This paper discusses an experimental investigation for converting the weathered local dry land-filled bauxite residue into nutritive composite support for plant growth. The paper includes agrochemical characterisation of bauxite residue and preliminary plant growth tests at the laboratory scale. The experimental data showed that macro- and micro-element content in the tailored soils can be tuned to the normal content domain recommended for plant nutrition.

Introduction

The alumina refinery is located on the outskirts of Tulcea town (Romania) and the red mud disposal site is 5 km from away from the site. After the 2009 landfill site retrofit and further improvements involving the switch from red mud lagoo impoundment to deep thickening and dry disposal, the disposal site complies with most of the EU directives regarding environmental protection. Large and safe dams, full fencing and complete surveillance, site partial closure facing the highest dam, dry land-filling, pluvial water collecting and treatment units, and detouring channel for preventing site over-flooding were carefully designed and built up due to the close proximity of natural protected areas in the Danube delta. Also, a water-sprinkling service is in use to keep the dry material surface moistened.[1] Some experts from Hatch Ltd., Technical University of Civil Engineering Bucharest and SC IPROLAM SA Bucharest developed the best local concept for switching to red mud dry stacking. Also, the refinery received professional assistance for design and construction of the red mud slurry pumping system, thickening equipment and thickened material spreading over the older layers of already carbonated and dried red mud. Environmental risk has been considerably reduced compared to previous technology for red mud disposal. Some new technologies for red mud slurry pH control and reduction are still under investigation, and a new water management program for stockpiled red mud surface moistening will be soon implemented. Monitoring conducted in recent years by prestigious research institutes in Romania, by research and laboratory tests, has concluded that the red mud disposal site environmental impact on surrounding agricultural area is not significant.

Chemical and Agrochemical Properties of the Red Mud

Investigations about red mud variable composition started in 2011, when Vimetco Alum SA accumulated a good experience in processing Sierra Leone bauxite and started some projects to find technologies for converting the red mud into a commercial product. The studies were made in cooperation with INCDPAPM-ICPA Bucharest. These studies mainly concern the use of raw or processed red mud as alkaline adjuvant for acidic soils or as a major component in artificial soils used for remediation and landscape architecture. Collected data concerning the chemical composition and heavy metal content, already published[1,2], were technically used for formulation of suitable nutritive red mud composite materials. According to these data, the red mud elemental composition, as compared with common soils composition, is largely disequilibrated, and particularly from the point of view of macro and mezzo nutrient contents. But, the heavy metals content lays close to the acceptable standards values, even for the leachable chromium.[3,4] Red mud agrochemical properties were described in the paper.[1] According to the published data, only phosphorus (200 mg/kg) and potassium (300 mg/kg) mobility seems to be appropriate as values for sustaining plant growth, as happens in common soils. The real problem with red mud conversion into fertile soils is the high level of Na [1+] (5300 mg/kg) and Ca [2+] (2800 mg/kg) ionic mobility. An advanced technology for the sodium removal from red mud is a problem of efficiency and production costs. In any future plans, this technology could be reconsidered as feasible by alumina refineries, not only as a problem of materials balance optimisation, but also as a way to improve red mud quality for its further processing to secondary products.

Mineralogical Phases in Sierra Leone Bauxite and in its Processing Red Mud

This study was highly required due to some difficulties that occurred in processing this type of raw material in Bayer technology, mainly those connected to the high silica content, low digestion rate, as well as to low thickening rate of the red mud. On the other hand, the mineralogy of bauxite and red mud is a key indicator for the best choice of main processing parameters in Bayer technology. The DRXP data acquisition was made on a BRUKER D8 ADVANCE diffractometer, using DIFFRAC^{plus} XRD Commender (Bruker AXS) program. The major phases identified in both materials are gibbsite ($Al_2O_3 \cdot 3H_2O$), alumino-goethite ($(Fe_{0.7768 \pm 0.0021} Al_{0.2232 \pm 0.0021})O(OH)$), aluminated hematite ($(Fe_{0.9294 \pm 0.0031} Al_{0.0706 \pm 0.0031})_2O_3$). Silica ($SiO_2$) is incorporated in the minor phases Kaolinite ($Al_4(OH)_8(Si_4O_{10})$), Quartz (SiO_2) and Zircon ($ZrSiO_4$) in bauxite, and as Katoite ($Ca_3Al_2(SiO_4)(OH)_8$), Sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$), Quartz and Zircon in red mud. TiO_2 is incorporated in the minor phases Ilmenite ($FeTiO_3$), Anatase (TiO_2) in bauxite, and as Ilmenite, Anatase and Rutile (TiO_2) in red mud.

There are two peculiarities in both materials mass composition, namely:

a) almost entire iron quantity is incorporated in two solid solutions (considered as compounds) (alumino-goethite and aluminated hematite), which are very stable from chemical point of view, and naturally will pass unconverted into red mud, carrying with them important amounts of irrecuperable Al_2O_3;

b) both materials contain unusual large concentrations of amorphous unidentified compounds (Table 1).

Table 1: Red mud composition. Comparison between DRXP and XRF data

MP/ CC	Bauxite, DRXP, from which the MP, %	Bauxite, XRF, from which the total CC, %	RM, DRXP, from which the CC in CF, %	RM, XRF, from which the total CC, %
Al2O3	32.50 (gibbsite)	48.07	8.81	19.35
Fe_2O_3	18.50	20.30	27.88	45.95
Na_2O	-	-	0.56	3.38
SiO_2	2.15	3.36	1.63	9.30
CaO	0.01	0.01	1.61	4.91
TiO_2	0.34	1.53	1.66	2.25
Al_2O_3 (amorphous)	15.50	-	10.54	-
Difference	31.00	26.73	47.31	14.31
MP - mineralogical phases ; CC – chemical constituents; CF – crystalline phases;				

The differences between the XRF analysis data and DRXP analysis data converted in the terms of chemical constituents are accounted as amorphous phases and recorded as total difference in last line of the Table 1. Mass balance of the chemical constituents in DRXP data and respectively, in XRF data show that all the main chemical constituents coexist in both materials as crystalline and amorphous phases. Because the available alumina in the Sierra Leone sample was found to be 37.0 % and the gibbsite crystalline phase in bauxite accounts for 32.5 %, it is reasonable to conclude the difference 37.0 - 32.5 = 4.5 % come from the amorphous phases containing Al_2O_3. So far, it could be roughly accepted that the amorphous phases contain the same chemical constituents as the crystalline phases. This is an important bauxite property, because the crystalline gibbsite may react with Bayer liquors with different rates than the amorphous phases containing Al_2O_3. From the bauxite and red mud mineralogy, it can be concluded that Sierra Leone bauxite processing implies significant changes in the applied Bayer technology, namely: improving bauxite preparation process at source, changing process parameters in desilication and digestion steps and maybe hastening the investments in red mud filtration.

Red Mud Treatments Before and After Stockpiling

Environmental constrictions forced most of the alumina producers to do some preliminary treatments before stockpiling the red mud. Accordingly, the types of red mud available for any use are variable in both composition and physical properties[5,7]. So far, any plan to trade the red mud implies the preliminary treatments and characterisation. For this purpose Vimetco Alum SA investigated the red mud chemistry, toxicity, safe disposal and its environmental hazards. Namely, the red mud content in heavy metals was investigated at CCSACBRNE Bucharest, INCDECOIND Bucharest and INCDPAPM-ICPA Bucharest, the red mud composition and alkalinity at National Institute for Research & Development in Chemistry and Petrochemistry Bucharest, INCD-ECOIND Bucharest and INCDPAPM-ICPA Bucharest, the red mud radioactivity at Horia Hulubei INCD Nuclear Engineering Bucharest, and the red mud corrosivity at Medico-Military Research Center Bucharest.

Recently INCD-ECOIND Bucharest has finished a report on red mud alkalinity decay during natural weathering. All the reports on heavy metals confirmed the stability of their compounds in red mud during conservation in dry state at Vimetco Alum SA as a non-hazardous material.

As Horia Hulubei INCD Nuclear Engineering Bucharest report says the concentration of gamma radiation radio-nuclides in red mud are below the minimum detectable activity - AMD according the ISO 11920/2010. Also, the total radioactivity measured on red mud samples is below the soil natural radioactivity, which is about 40/Bq/kG.

The Medico-Military Research Centre Bucharest corrosivity test were carried out on the red mud samples with pH 11.2, 11.6 and 12.2 prepared from raw weathered samples, collected from older layers at Vimetco Alum SA red mud disposal site. The test of dermal corrosivity showed that all the samples are non-corrosive. Further investigations are needed in order to have a better understanding of the bauxite residue characteristics.

Red Mud as Adjuvant for Acid Soils Remediation

A series of experiments were carried out in 2011 and 2012, including some stages for studying the accommodation of different species from spontaneous flora or common cultivated species to different formulations containing red mud. The results were partially published.[1,2] The most promising results were obtained with maize plants, cultivated on types of soil related to acid soils remediation strategy. In this paper there are reported the data of a full experiment ran at glasshouse scale.

Experiment description: Materials. Acid soil was a representative one from Albota (Arges) Romania, known as Albota albitic. This soil is a typical acid soil with moderate pH, medium hydrolitic acidity (A_h), and low trophic level due to its poor content in exchangeable bases (SB), humus, total nitrogen (N_t), nitric nitrogen ($N\text{-}NO_3$), mobile phosphorus (P_{AL} -14.3 mg·kg^{-1}) and mobile potassium (K_{AL} – 92 mg·kg^{-1}). Red mud was from the older layers of factory deposit (the same source as the above characterised samples).

Fertilisation: For organic fertilisation a natural organic compost was used. The mineral fertilisation comprises a mixture of ammonium nitrate and potassium hydrogen phosphate with formula N_{120} $P_{60}K_{40}$ (i.e. 120, 60 and 40 Kg/ha).

Experimental set up: An experiment with 6 variants was set up at 16 July 2012. The experiment comprises 3 repetitions for each variant using vegetation pots with a capacity of 8 kg soil. The experimental program followed the basic procedures of INCDPAPM-ICPA Bucharest shortly described in the paper.[2,9]

Results: Amending the luvosol albic from Albota soil with red mud doses of 15, 30 and 75 t/ha, organic compost 40 t/ha and mineral fertilisers 40 t/ha, the new composite soil pH increases up to 1.5 – 2.2 units. Hence, from a moderately acidic reaction of initial soil, by amending, there were reached the slightly alkaline domains in the experimental soils. Amending the luvosol albic from Albota soil with the above organic compost doses and mineral fertilisers, the initial soil acquired significant increases in organic C, total N, and mobile phosphorus and potassium content. Amending the luvosol albic from Albota soil with the above doses organic compost and mineral fertilisers, there were improved both cation exchange and exchangeable bases properties, without significant increase in a soil soluble salt content. The above amendments contributed to rises in the plants waist, green mass and dried mass and significant gains in vegetal mass, as well as in cobs and grains yield. The above amendments contributed to significant rises N and Na content in maize leaves at maturity stage, without reaching toxic levels. Accumulated P and K gains were recorded only in the case of low organic compost amendments. Even if some significant fluctuations were noticed in values of heavy metals in leaves, no toxic levels were recorded. Large fluctuations of metal macro- and micro-nutrients in cobs and grain were recorded, but no value exceeded the normal figures. All the details about this subject will be soon published.[10]

References

1. R. Lacatusu, A. Kiselev, N. Rizea, M. Lungu, R. Lazar, M. M. Stanciu-Burileanu, N. Vranceanu, V. M. Stroe, R. G. Popa and L. Filipescu, ”Plant Growth Suitable Nutritive Red Mud Composite Materials from The Romanian Dry Landfilled Red Mud. I. Red Mud Chemical and Agrochemical Characterisation” *Rev. Chim*, **65** (9) 1008-1014 (2014).
2. R. Lacatusu, A. Kiselev, V. M. Stroe, N. Rizea, M. Lungu, R. Lazar, M.M. Stanciu-Burileanu, I. Calciu, R. G. Popa and L. Filipescu, ”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” *Rev. Chim*, **65** (11) 1294-1305 (2014).
3. M. Niculescu, A.D. Ionita and L. Filipescu, “Chromium Adsorption on Neutralized Red Mud”, *Rev. Chim* **61** (2) 200-205 (2010).
4. M. Niculescu, A.D. Ionita, D. Simion, M. Crudu and L. Filipescu, “Red Mud – New Material for Tannery Residual Chromium Binding”, *UPB Sci.Bull.Series Chemistry,* **72** (3) 99-114 (2010).
5. K. Snars and R. J. Gilkes, “Evaluation of Bauxite Residues (Red Muds) of Different Origins for Environmental Applications”, *Appl. Clay Sci.*, **46** 13-20 (2009).
6. L. M. Despland, “Study of Bauxsol Pellets' Efficiency in Wastewater Treatment and their Biocompatibility with Microbial Communities”, *PhD Thesis*, Southern Cross University, Lismore, NSW, Australia, 2013.
7. S. Rai, L. Wasewar, D. H. Lataye, J. Mukhopadhyay and C. K. Yoo, “Feasibility of Red Mud Neutralisation with Sea Water Using Taguchi’s Methodology”, *Arch. Environ. Sci.,* **6** 13-33 (2012).
8. J. H. Draize, G. Woodward and H. O. Calvery, “Methods for the Study of Irritation and Toxicity of Substances Applied Topically to the Skin and Mucous Membranes”, *J. Pharmacol. Exp. Ther.,* **82** 377-390 (1944).
9. Kabat-Pendias, H. Pendias, *Trace Elements in Soils. 3rd Ed.,* Boca Raton, London, New York, 2001.
10. G. Dobra, L. Filipescu, N. Anghelovici, V. Alistarh, S. Iliev and R. Lacatusu, ”Plant Growth Suitable Nutritive Red Mud Composite Materials from the Romanian Dry Landfilled Red Mud. III, *Acid Soils Remediation*” (in press).