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

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Abstract

Vimetco Alum SA alumina refinery in Romania has made improvements on the 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 concerns an experimental investigation for conversion the weathered local dry land-filled bauxite residue into nutritive composite support for plant growth. The paper includes agrochemical characterization of bauxite residue and preliminary plant growth tests at the laboratory scale. The experimental data showed that the macro- and micro-elements content in the tailored soils can be tuned to the normal content domain recommended for plant nutrition.

Introduction

Alumina refinery is located on the outskirts of Tulcea town (Romania) and the red mud disposal site at 5 km distance from refinery. After the recent landfill site retrofit in 2009 and the further appropriate improvements concerning the switching from red mud sludge lagooning impoundment to deep thickening and disposal in dry state, the disposal site comply with most of the EU directives recommendation regarding environmental protection. Due to close natural protected areas in the Danube delta, 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. 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 had developed the best local concept for the switching to red mud dry stacking. Also, the refinery received professional assistance for design and construction of the red mud slurry pumping system, thickening equipments 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 conversion 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 agro-chemical properties were described in the 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 the 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 optimization, 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 by some difficulties in processing this type of raw material, 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 aquisition was made on a BRUKER D8 ADVANCE difractometer, 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 ($ZrSiO_4$) for bauxite, and as Katoite ($Ca_3Al_2(SiO_4)(OH)_8$), Sodalite ($Na_8(Al_6Si_6O_{24})Cl_2$), Quartz and Zircon for 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 matrials 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 naturaly 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 2).

Table 2: Red mud composition. Comparation 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, %
Al_2O_3	32.5 (gibbsite)	48.07	8.81	19.35
Al_2O_3.	18.5	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)	15.5	-	10.54	-
Difference	31.0	26.73	47.31	14.31
MP - minralogical phases ; CC – chemical constituents; CF – crystaline 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 2. Mass balance of the chemical constituents in DRXP data and respectively, in XRF data shows that all the main chemical constituents coexists in both materials as crystalline and amorphous phases. Because the available alumina in Sierra Leone sample was found 37.0 % and the gibbsite crystalline phase in bauxite accounts for 32.5 %, is reasonable to conclude the diffence 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 in dumps. Accordingly, the types of red mud available for any use are variable in both composition and physical properties. [5-7]. So far, any tentative 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, INCD-ECOIND 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 row weathered samples, collected from older layers at Vimetco Alum SA red mud disposal site. After test validation the sample 3 (pH 12.2) has been classified as irritating to rabbit eyes, sample 1 (pH 11.2) as non-irritating and sample 3 (pH 11.6) as minimum irritating [7]. The test of acute toxicity/irritation and dermal corrosivity showed that all the samples are non-corrosive. Repeated tests showed that acute conjunctive irritation occurs with certainty at pH 11.8 [8]. According to these tests the corrosivity threshold in red mud is certainly located at pH 11.8.

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 in the papers [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 tipical acid soil with moderate pH, medium hydrolitic acidity (A_h),) and low trophic level due to its poor content in exchangeble bases (SB), humus, total nitrogen (N_t), nitric nitogen ($N\text{-}NO_3$), 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 characterized samples.

Fertilization: For organic fertilization was used natural organic compost. The mineral fertilization 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 fertilizers 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 fertilizers, 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 fertilizers, there were improved both cation exchange and exchangeable bases properties, without significant increases in soil soluble salt content. The above amendments contributed to rises in the plants waist, green mass and dried mass and significant gains in vegetal mass, as well as in cobs and grains yield. The above amendments contributed to significant rises N and Na content in maize leaves at maturity stage, without reaching toxic levels. Accumulated P and K gains were recorded only in the case of low organic compost amendments. Even if some significant fluctuations were noticed in values of heavy metals in leaves, no toxic levels were recorded. 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].

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