Alkaly Earth Metal Salts as Neutralizers of Red Mud from Alumina Refining

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Red mud disposal embodies the most critical issue in any alumina refinery. Reasons like caustic nature, huge discardable quantities and unusual rheological properties are demanding neutralization of the red mud with simple and non-expensive available chemicals to allow its future reuse or at least for its safe disposal. This paper purpose was to investigate the neutralization of the red mud alkalinity with concentrated neutralizers in order to increase the rates of stabilized solid crystallization on the red mud particles surface, as well as to promote the crystallization of hydroxide and hydrotalcite phases, which are mainly responsible for heavy metals entrapment in their crystalline structure. It was found that the end down limit of neutralization with sulphuric acid in order to prepare adsorbent materials or simply to prepare red mud for disposal as non-hazardous material is the pH 8.5 - 9.0, when the entire sodicity is removed from red mud and aluminium silicate ion exchanging phases are insignificantly altered, preserving their both ion exchange and acid neutralizing capacities. Alkali metal earth salt as neutralizers act similarly with sea water, releasing the sodicity into liquid phase and conveying the entire alkalinity into the mixture of new born solid phases like hydrocalumite, hydrotalcite carbonate and hydrotalcite sulphate. Adequate neutralization process parameters (aluminate content, reactant concentrations, neutralization rates, temperature, etc.) improve the performances of neutralized red mud as adsorbent and frame its properties to some quality reproducible standards. Also, it was found the fresh red mud rich sodium aluminate is highly recomended to be selected and processed for working out good adsoption properties; if the neutralization process is practiced to yield a non hazardous material to be safely disposed, then the wheathered red mud is recomended to be selected for convenient neutralization process.

Keywords: red mud disposal, hydrocalumite, hydrotalcite, heavy metals entrapping

Bayer process for the refining bauxite to alumina bears the economical and environmental burden of red mud as its ancillary byproduct. This residual matter is characterized by the significant alkalinity coming from sodium aluminate, equally distributed on the quite inert crystalline surface of the major constituents: hematite (Fe_2O_3), titanium dioxide (TiO_2) polymorphs anatase and rutile, boehmite (gama-AlOOH), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$), gypsum ($CaSO_4 \cdot 2H_2O$) and others. Red mud coming from various sources may exhibit large differences in composition depending on the origin of bauxite, technology operational parameters and yield of alumina extraction in each production unit [1]. Typical values for bulk chemical constituent concentrations in red mud would account for: 30-60wt% Fe_2O_3, 10-20wt% Al_2O_3, 3-5wt% SiO_2, 2-10wt% Na_2O, 2-8wt% CaO, 4-8wt% TiO_2 and 3-8wt% other trace constituents [2]. Actually, the inorganic red mud phases which are new born during bauxite refining can be divided into three groups: a) “NAS” phases: $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot Na_2X$ (X= CO_2^{2-}, $2OH^-$, $SO4^{2-}$, $2Cl^-$) and particularly sodalite $\{Na_6[Al_6Si_6]_{24}(CO_3)_2 \cdot 2H_2O\}$, cancrinite $(NaAlSiO_4)_6 \cdot CaCO_3$, hydroxycancrinite $[(NaAlSiO_4)_6 \cdot NaOH \cdot H_2O]$, tricalciumaluminatehydrates ($xCaO \cdot yAl_2O_3 \cdot zH_2O$), chantalite ($CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 2H_2O$), hydrogarnet $[Ca_3Al_2(SiO_4)_n(OH)_{12-4n}]$ and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$); b) “CAS-CFS” phases: $3CaO(Fe_2O_3)_x (Al_2O_3)_{1-x} \cdot k\ SiO_2 \cdot (6-2k)\ H_2O$ and c) “NT-CT” phases: $Na_2Ti_3O_7 \cdot 3H_2O$ (kassite, perovskite, portlandite) [3,4]. The raw material is characterized by a high pH (12-12.5), high BET surface area (13-22 m^2/g), high total alkalinity (5-6 g/L), high electrical conductivity (60-350 dS/m), high ion exchangeable sodium percentage (≈100%), and poor water holding capacity [2]. Red mud remarkable acid neutralizing capacity (ANC) subsists even after apparent neutralization up to pH 9.0-9.5. It is originating not only from the total free alkalinity boarded onto the large surface of porous particles, but also from all new born solid phases mentioned above, which can release calcium and sodium ions like zeolitic compounds. Lin [5] notice the ANC of stacking dry stored red mud is higher than that of the wet impoundment red mud, because the dried material well crystallized zeolitic phases accumulate more exchangeable sodium and calcium ions.

The environmental impacts of the red mud disposal are properly summarized [6, 7], but it is important to note that several of these impacts are concerning the non neutralized red mud. Red mud disposal embodies the most critical issue in any alumina refinery, not only for the huge discardable quantity, but also for its caustic nature and unusual rheological properties. Neutralization of red mud by a simple and non-expensive treatment to allow its future reuse seems to be a realistically convenient step for its safe disposal. A lot of work was devoted to red mud neutralization, as well as to available resources of neutralizing agents [8-11]. Most of the published papers encompass some very active areas in environmental

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research field concerning: heavy metal trapping from residual acid waters as a benefit of ANC of red mud [12-14], heavy metal fixation in soils [15-16], soil neutralizing and conditioning [17-18], etc. There are several works on red mud reuse [19-21]. Many other papers reported the unusual red mud capacity to capture and bind heavy metals from solution onto the very finely grained particles of Fe_2O_3, Al_2O_3 and TiO_2 as well as onto the new born phases during alumina refining process or particularly during certain steps of neutralization process [5, 22]. Ability to adsorb trace metals comes from high ratios surface/volume and high charge/mass ratios developed by raw material when pH is brought down to less than 8 by any neutralizer [23-26]. Merely, high adsorption affinity of heavy metals on red mud is assigned to the chemisorption reactions at the surface of the particulate components, but it was shown that red mud with high levels of cancrinite grown on hematite particles surface may incorporate heavy metal in the cages and channels of its structure [23]. Other mechanisms of heavy metal trap in red mud concern co-precipitation of their insoluble metal hydroxides, intermediates $\{[Fe_2(OH)_4]^{2+}$, $[Fe_3(OH)_4]^{5+}$, $[Al_4(OH)_8]^{2+}$ and $[Al_8(OH)_{20}]^{4+}\}$ formation at the adsorbent surface, uncharged hydroxides condensation onto hydroxyl groups exposed on the red mud particle surface, zeolitic structure re-crystallization by weathering and ionic exchange [21]. When sea water is used as neutralizer, magnesium and calcium ions accelerate the building of new born phases at particles surface in red mud and by this induce a chemical stabilization of the deposited silicate phases. Also, it is possible that heavy metals ions to be substituted in silicate phase crystalline structure and in this case the chemical stabilization originates from the new oxide bond. This paper purpose is to investigate the neutralization of the red mud alkalinity with concentrated neutralizers in order to increase the rates of stabilized solid phases crystallization on the red mud particles surface, as well as to promote the crystallization of hydroxide and hydrotalcite phases, which are mainly responsible for heavy metals entrapment in their crystalline structure. For the sake of finding inexpensive neutralizers, there were chosen $MgCl_2$, $CaCl_2$, $MgSO_4$ and their mixtures as convenient reactants. The study included analysis of the liquid phase in equilibrium with neutralized red mud at variable *p*H from 8 to 13. Also, the researches were extended over the neutralization process with H_2SO_4 up to the limits of the equilibrium *p*H in red mud. Most of the experiments were focused on crystallized and amorphous phases born in neutralized red mud and their behavior as further adsorbents or simply as stability builders for safety red mud disposal as a non-hazardous material.

Experimental part

Raw materials, reagents and additives

Red mud was collected as a bulk sample of 20-25 L from the surface of an open storage pond run up by an alumina refinery operated under variable bauxite quality and technological parameters. Beside its heterogeneous provenance, the sample was carrying a random mixture of fresh and weathered material, because it was picked up at the drainage end of pond, opposite to the hydraulic transport line discharging point. After preliminary thickening, the slurry with approximate 400-500 g solid phase per liter was stocked as experimental material. Chemical and mineralogical composition of some other small samples collected over a 6 month period from hydraulic transport line and other points of the pond was in good agreement with the analysis of stocked red mud selected as experimental material. Sulphuric acid 96 %, p.a., hydrochloric acid 32%, p.a., as well calcium and magnesium salts p.a. used as neutralization agents of red mud were products of SC Chimopar SA Romania.

Neutralization protocols

Red mud neutralization was carefully carried out at room temperature by adding regularly very small quantities of sulphuric acid 20% solution into well mixed slurry under continuous *p*H monitoring. For achieving slurry right homogenization and the slow end up to the desired pH final value without involving the irreversible chemical reactions workable at lower *p*H values, long time lag periods were left after each share of added acid [28]. For the research end goals, the neutralization was ceased at *p*H 10.0, 9.0 and respectively 8.0, and whole samples were stored for further analysis and experiments. Expected reactions taking place during neutralizations are:

$$NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O \qquad (1)$$
$$2NaAlO_2 + H_2SO_4 + 2H_2O \rightarrow Na_2SO_4 + 2Al(OH)_3 \qquad (2)$$
$$2Al(OH)_3 + H_2SO_4 \rightarrow [Al(OH)_2]_2SO_4 + H_2O \qquad (3)$$
$$Al(OH)_3 + H_2SO_4 \rightarrow Al(OH)SO_4 + 2H_2O \qquad (4)$$

Other reactions concern silicates and aluminum silicates partial decomposition with or without washing out of the reaction products beside sodium sulphate [27, 28].

Calcium and magnesium salts react with red mud components on different ways, mainly due to the precipitation of some amorphous or crystalline classes of CaO $(MgO)/Al_2O_3/SiO_2/Na_2O$ compounds and limited available silica for attaining normal ratios Al_2O_3/SiO_2 in common stoichiometric aluminum silicates. As was shown before [8, 19, 21, 22] the calcium ions may be bound more as calcium aluminium silicate $(Ca_2Al_2(SiO_4)(OH)_8)$ and less as cancrinite $Ca_2Na_6[Al_6Si_6O_{24}](CO3)_2 \cdot 2H_2O$, as far as Mg^{2+} ions are immobilized in red mud as magnesium aluminum silicate $(Mg_{6-x}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8 \cdot Mg(OH)_2)$ or layered dihydroxides with general formula $[M_{1-x}^{2+} M_x^{3+}(OH)_2]^{x+} X_{x/m}^{m-} \cdot nH_2O$, where M^{2+} = Mg or Fe, M^{3+} = Al or Fe and X^{m-} = OH-, Cl-, CO_3^{2-} or SO_4^{2-}. Formation of such compounds require much longer time to attain solid-liquid chemical equilibrium and consequently, small shares as 0.5 – 5ml of solutions 1M containing $CaCl_2$, $MgCl_2$, $MgSO_4$ or their mixtures were added from 24 to 24 h and stirred with the red mud slurry, monitoring *p*H up to the values 10.0, 9.0 and respectively 8.0. After the neutralization, the samples containing both liquid and solid phases were stored for further analysis and experiments. According to the literature [19], all the compounds born during neutralization process are carrying higher ion exchange capacities than silicate phases in the raw red mud. Supplementary, for better identification of the precipitated phases, samples of clear liquid removed by filtration of the raw red mud were neutralized with the same reactants up to the *p*H 10.0, 9.0 and respectively 8.0, over the similar time intervals.

Methods of analysis

The *p*H was measured with Consort C833 ionometer without any preliminary dilution. Calcium and magnesium were analyzed by EDTA titration. Mineralogical phases were identified by XRD using Dron 2 spectrometer along with their semi-quantitative elemental analysis by Philips PW2400 X-ray fluorescence spectrometer. Specific areas of the raw and neutralized red mud samples were measured on an ASAP 2020 System using nitrogen as adsorbing gas.

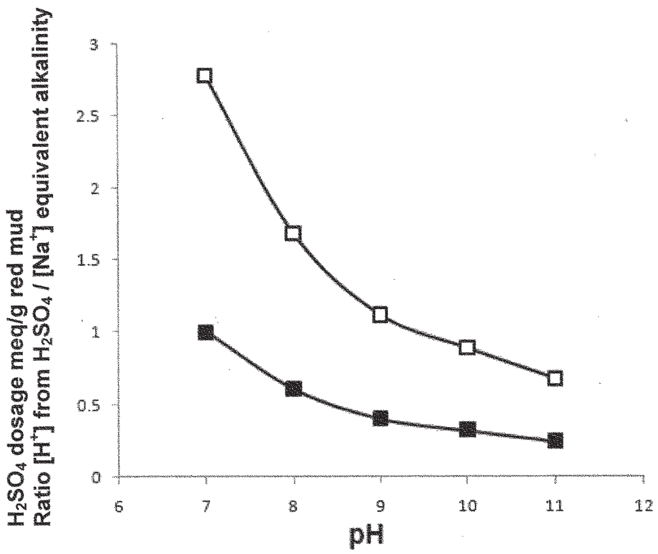

Fig. 1. Added H_2SO_4 for neutralization in meq/g and ratio $[H^+]/[OH^{=}]$ total alkalinity; ■H_2SO_4 dosage meq/g red mud; □ Ratio $[H^+]$ from H_2SO_4 / $[Na^+]$ equivalent alkalinity

Results and discussions

Neutralization with sulphuric acid

Red mud neutralization with strong acids was studied extensively by many authors for samples of red mud variable in term of provenance and compositions [28-30]. Initial rapid consumption of acid and leaching of alkaline solids from the red mud was commonly observed, but the extent of individual samples neutralization rather depends on the red mud composition and less on the amount or rate of acid added.

Actually, chemical neutralization occurs in some more steps and might be controlled by the rate of adding sulphuric acid. If the acid dosage is slowed down to some minimal levels, firstly, the free residual sodium hydroxide and sodium aluminate are reacting carrying into solution the entire sodium content, otherwise evenly distributed over red mud particles and strongly adsorbed on the surface of inert solid phases. Reactions (1-4) describe this side of the process, graphically represented in the figure 1 by the straight line dosage and respectively ratio $[H^+]/[OH^-]$ total alkalinity versus red mud pH from initial value down to *p*H 9. In the above mentioned figure 1, the sulphuric acid doses were calculated from the total alkalinity of lye impregnating solid phases in the red mud. In case of these particularly studied samples, the diluted lye made up approximate 50%wt of the wet red mud and has a saline content of 13.6 g/L. With the saline composition given in the table 1, the $[OH^-]$ total alkalinity calculated with formula:

$$[OH^-] = [Na^+] + 3*2[Al_2O_3] \qquad (5)$$

was found 0.36 meq/g red mud. Additionally, some colloidal $Al(OH)_3$ [31] might be dissolved as far as it survived in diluted soda lye or at least it has given birth to some reactive layer of gibbsite onto the inert particle surface. Other way, at higher rate of acid feeding, before liquid phase total alkalinity depletion, the acid outsets the dissolution of alkaline solid phases (carbonate phases mainly) and may release by ionic exchange some new ions into solution or may alter the chemical or even mineralogical composition of some alkaline phases. When the $[OH^-]$ total alkalinity is balanced by the added sulphuric acid, i.g. ratio $[H^+]/[OH^-]$ total alkalinity equals1.0, the second stage of neutralization process begins with removal of alkali metals and other ions bonded by electrical charges, and may end up with total dissolution of the silicate phases. From the figure 1 it can be seen that around *p*H 8.0-8.5 the first stage of neutralization is consummated and the free alkalinity of the liquid phase was depleted. Up to this point, the entire quantities of sodium and sulphate ions involved in the reactions (1-4) were removed from particulate solid phases and washed out by the liquid phase. In the next stage of neutralization beyond *p*H 8, reactions of sulphuric acid with alkaline solid phases occur, from where comes larger acid consumption and asymptotic raise of both curves in the figure 1. On the other hand, from the table 1 it could be seen the major participation of any component in red mud composition remains unchanged when the *p*H is dropped from initial values to 8.0. A significant decrease in gibbsite concentration comes off evidently at *p*H 7.7, and may be at lower *p*H values the entire quantity of labile gibbsite originating from aluminate hydrolysis is washed out from red mud leaving back just the Al_2O_3 as bohemite. When excessive hydrochloric acid 10%wt was used as neutralizer up to *p*H 7, one third of total Al_2O_3 in red mud has already reacted and was conveyed to liquid phase. According to table 1 the other constituent concentrations in solid phase are significantly diminished (SiO_2, SO_3, CaO etc.) toward lower pH values, due to the partial dissolution of silicate phases as sodalites ($3[Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot (2+k)H2O] \cdot Na_2X$) and hydroxycancrinites $[4Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot (OH)_2 \cdot 2H_2O]$ or their substituted compounds containing CO_3^{2-}, SO_4^{2-}, Cl^{1-}, Mg^{2-}, K^{1+}, etc. This process is more explicitly presented in

Table 1

RAW AND NEUTRALIZED RED MUD COMPOSITION

Components, %	Red mud neutralization pH					Neutralized exceedingly treated with diluted HCl	Liquid phase (saline phase)
	Initial (13.3)	10	9	8	7.7		
Al_2O_3	17.0	18.0	19.0	18.0	15.0	12.0	33.2
SiO_2	7.1	7.1	7.4	7.4	5.5	1.2	2.4
P_2O_5	0.6	0.5	0.7	0.6	0.59	0.8	2.5
SO_3	0.73	0.8	1.0	1.5	0.42	0.5	12.3
Cl	1.2	0.9	1.1	1.2	1.0	1.6	18.6
CaO	3.56	3.6	3.3	3.4	1.78	0.7	0.31
TiO_2	9.31	9.4	8.6	9.2	10.5	11.4	-
V_2O_5	0.25	0.3	0.2	0.2	0.24	0.3	0.58
Cr_2O_3	0.35	0.3	0.3	0.3	0.33	0.4	0.23
MnO	0.17	0.2	0.1	0.2	0.21	0.2	-
Fe_2O_3	59.5	59.0	50.9	57.8	64.2	71.0	0.14
PbO	0.5	0.2	0.1	0.1	0.06	0.1	-
Na_2O	-	-	-	-	-	-	28

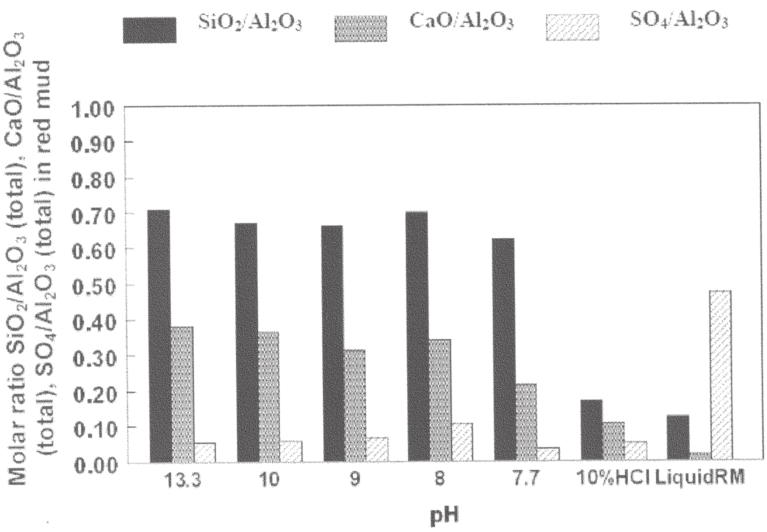

Fig. 2. Molar ratio SiO_2/Al_2O_3 (total), CaO/ Al_2O_3 (total), SO_4/ Al_2O_3 (total) in sulphuric acid neutralized red mud

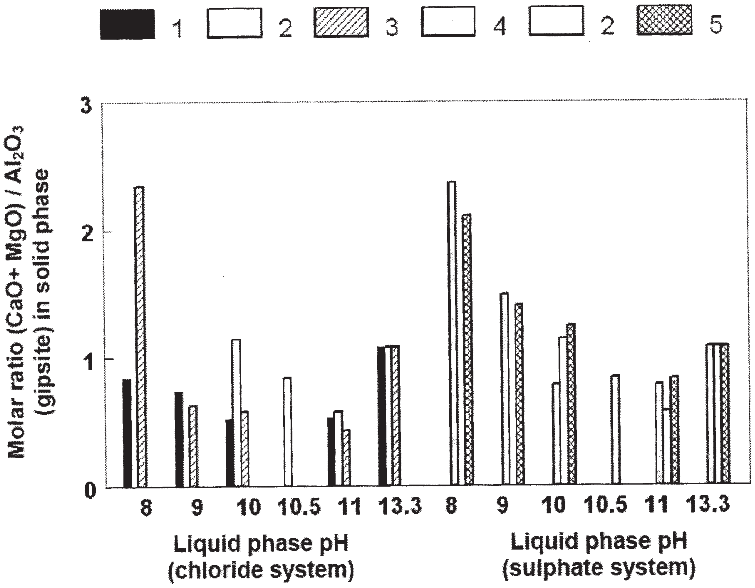

Fig. 3. Molar ratio (CaO + MgO) / Al_2O_3 (available gibbsite) in solid phase versus liquid phase pH; 1- $MgCl_2$; 2 – $CaCl_2$; 3 – $MgCl_2$ + $CaCl_2$; 4 – $MgSO_4$; 5 - $MgSO_4$+ $CaCl_2$

figure 2, where the variation of molar ratios SiO_2/Al_2O_3 (total), CaO/ Al_2O_3 (total), SO_4/ Al_2O_3 (total) during neutralization consequentially shows the alkaline solid phases dissolution was certainly taking place at *p*H as lower as 7.0. As far as *p*H remains close to 8.0, no component containing calcium and silica in red mud (calcium aluminates, calcium silicates, calcium aluminum silicate, etc.) is decomposed or changed in its molar ratios against any other component (table 1). Even if the sulphate ion concentration rises in solid phase as the neutralization advances, this is only due to the sulphate inclusions in aluminum silicates formula and not due to calcium sulphate crystallization. Thus, because the ion exchange phases remain unchanged, superficial neutralization does not affect ion exchange capacity. On the contrary, it was shown the surface area of red mud after acid neutralization was extended from 18.9 and 25.2m^2/g, due to some specific dissolution of the cancrinite layer overgrown on red mud particle surface during washing stages before disposal [22]. Also, it has been noted that the removal of free alkalinity from ion exchange solid phases definitely results in total surface extension and moreover in a kind of polishing and chemical activation of the cleaned surfaces [30]. Our data are in good agreement with *p*H value of 8.3 considered as neutralization equilibrium point [32], as well as with the pH 8.5 recommended [28] as end down limit of neutralization in order to prepare adsorbent materials or simply to prepare red mud for disposal as non-hazardous material.

Neutralization with alkali earth metal salts

Common salts of calcium and magnesium used as neutralizers for red mud act similarly with sea waters, due to their capacity to remove alumina, silica and other constituents from chemically labile solid phases and diluted aluminate solutions, bonding them as insoluble aluminates and aluminate silicate compounds with or without sodium ions capture. These compounds crop up high specificity for heavy metal adsorption and preserve the high initial acid neutralizing capacity (ANC) by incorporating the entire sodium alkalinity in new crystalline and amorphous calcium and magnesium aluminate silicate solid phases. As was reported in the case of sea water neutralization, the unequivocal composition and number of the precipitated phases are mainly dependent on the neutralization process restrictions and limitations [33]. Some other differences in the case of this study may come from the raise in reactants concentration and from variation in ratios magnesium/calcium in any particular neutralizing system. Five series of experiments were set up to investigate the ways $CaCl_2$, $MgCl_2$, $MgSO_4$ and their mixtures may alter the composition and properties of the neutralized red mud. First 3 series concern the neutralization with $CaCl_2$ 1M, $MgCl_2$ 1M, respectively with $MgSO_4$ 1M solutions, and the next two, the neutralization with the binary mixtures 1:1 volume of the three neutralizing solutions ($CaCl_2$ 1M + $MgCl_2$ 1M and $CaCl_2$ 1M + $MgSO_4$ 1M). Planed experiments were initially intended to find out which the interaction

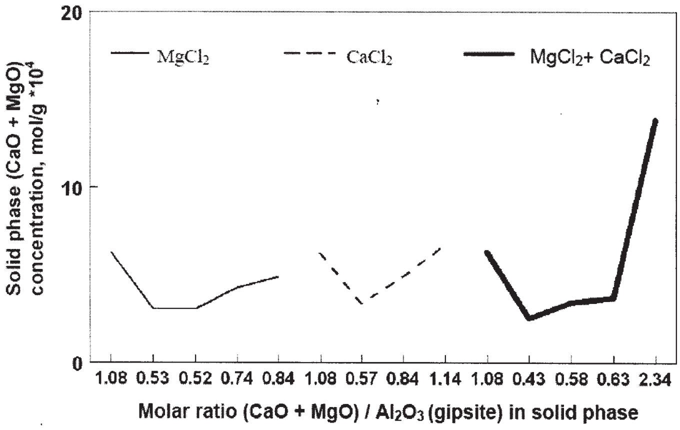

Fig. 4. Variation of (CaO + MgO) concentration in solid phase versus molar ratio (CaO + MgO) / Al_2O_3 (gipsite) in solid phase for red mud neutralized with $MgCl_2$-$CaCl_2$ system

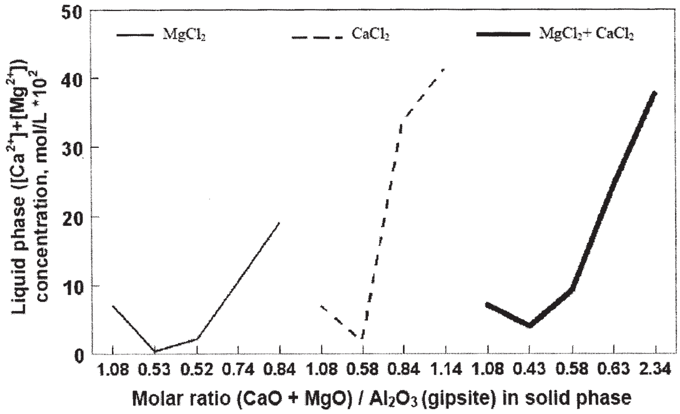

Fig. 5. Variation of ($[Ca^{2+}]$ + $[Mg^{2+}]$) concentration in liquid phase versus molar ratio (CaO + MgO) / Al_2O_3 (gipsite) in solid phase for red mud neutralized with $MgCl_2$-$CaCl_2$ system.

products are separated when only a single neutralizing salt is added to red mud, and what happen when the new born phases nucleation and growth are overlapping each other or are overlapping the imminent calcium sulphate crystallization when neutralizing systems $MgCl_2$ + $CaCl_2$ and respectively $MgSO_4$ + $CaCl_2$ are applied. Because the neutralization process duration was extended to hundreds of hours till the target pH was reached, the new born phases are certainly in equilibrium with the liquid phase, and consequently the concentration of any constituent in liquid phase are corresponding to the equilibrium solubility of the new born phases mixture.

Available gibbsite quantities for reaction with calcium and magnesium make only 5% percents from total 17 percents of Al_2O_3 in red mud (according to the table 1, the total Al_2O_3 concentration in red mud is 17% and the total Al_2O_3 concentration in red mud neutralized with exceeding hydrochloric acid is 12%). The same amount of reactive Al_2O_3 resulted from differential thermal analysis data on red mud mineralogical composition. Some other small quantities of reactive Al_2O_3 come from destabilized aluminate in liquid phase on first adding of alkali earth metal salts. Albeit the available gibbsite is distributed on a large number of small particles, only a part of the entire particle surface could be reached by magnesium and calcium ions during neutralization. Reactions like those are also described [33]:

$$4MgCl_2+2NaAl(OH)_4+NaOH+Na_2CO_3\rightarrow$$
$$\rightarrow Mg_4Al_2(CO_3)(OH)_{12}\cdot xH_2O + 8NaCl \qquad (6)$$

$$8MgCl_2+2NaAl(OH)_4+12NaOH+1/2Na_2CO_3\rightarrow$$
$$\rightarrow Mg_8Al_2Cl(CO_3)_{0.5}(OH)_{20}\cdot xH_2O+15NaCl \qquad (7)$$

are theoretically possible, but their extent depends on many uncontrollable factors. Some of them are: coating the particle surface with a compact layer of reaction products, concurrent reactions and coating the particle surface with a compact layer of concurrent reaction products, available silica for concurrent reactions, and other ions substitution in the crystalline lattice of basic compounds. Thus, the neutralization process will never end up with total conversion of available gibbsite into new distinct solid phases. Solutions supersaturation, amorphous precipitates, mixture of unitary components, and the full or partial charge of ion exchange capacity carried out by new solid phases will work continuously for a long time as driving force for fulfilling both chemical reactions and crystallization process.

As it turns out from figure 3, for each neutralizer or neutralizing system there is a specific variation of the molar ratio (CaO + MgO) / Al_2O_3 (available gibbsite) in solid phase as pH slope down from initial value 13.3 to neutral 8.0 or less. The first drop in molar ratio (CaO + MgO)/ Al_2O_3 (available gibbsite) in solid phase up to pH 11.0 corresponds to the sodium aluminate destabilization with complete release of both $Ca(OH)_2$ and $Mg(OH)_2$ from free soluble ionic calcium and magnesium compounds, and rather less of $Al(OH)_3$ from destabilized aluminate, which partially conveys the red mud alkalinity into solid phase. But the magnitude of this fall is not explained only by preferential precipitation of $Ca(OH)_2$ and $Mg(OH)_2$. The data processing disregarded calcium and magnesium bond in raw red mud compounds, and accounted for the sum of the Ca^{2+} and Mg^{2+} concentrations merely the amount of these ions added as neutralizers. Therefore, the first points on the left ends of curves in the figure 4 and 6 are relegated to the real ratio (CaO + MgO) / Al_2O_3 (available gibbsite) in raw red mud and the rest of the points are regarding the ratio (CaO + MgO) / Al_2O_3 (available gibbsite) in the new solid phases substantiated during neutralization process. As it was shown before, when the sulphuric acid was the neutralizer, no one of the chemically labile solid phases residing in raw red mud interferes or reacts with the acid up to pH 8.0. Hence, the same chemical stability was assumed for the case of calcium and magnesium salts used as mild red mud neutralizers. Another evidence of $Ca(OH)_2$ and $Mg(OH)_2$ precipitation as the first step in the red mud neutralization process with alkali earth metal salts is clearly visualized in figure 5 and 7, where the first points on the left ends of curves stand for Ca^{2+} and Mg^{2+} concentrations in the liquid phase of red mud plotted against ratio (CaO + MgO) / Al_2O_3 (available gibbsite) in solid phase constituents from the red mud. Both these figures point out the severe decrease in Ca^{2+} and Mg^{2+} concentrations for all neutralizers and neutralizing systems not only in the first stage of neutralization, when $Ca(OH)_2$ and $Mg(OH)_2$ are truly precipitated, but also over the next stages, while new phases are crystallized out of the liquid phase. The same behavior consisting in electrostatic bridging calcium and magnesium cations as nuclei for the precipitation of magnesium and calcium hydroxides was observed when there was analyzing the chemistry of red mud neutralization by sea water [34, 35]. Hence, our data are conclusively in good agreement with the chemistry of the red mud neutralization by sea water, largely accepted in literature.

Further calcium and magnesium ions brought into solution by additional fed neutralizers cause the precipitation of hydroxycarbonates of aluminium, calcium, and magnesium, while the hydrotalcite-like compounds initially exhibiting colloidal behaviour at high *p*H lose stability and precipitate out of solution. Rates and yield of the reactions like (6) and (7) are different from one to another neutralizing salt, as well as the resulting compounds or mixture of compounds. Also, secondary reactions involving ions like HCO_3^-, CO_3^{2-}, SO_4^{2-}, SiO_3^{2-}, K^+ and other ionic impurities may change the unitary phases composition and their ionic solubility in the liquid phase out from which new compounds were born. All these interactions explain the differences and particularity of the molar ratio (CaO + MgO) / Al_2O_3 (available gibbsite) variation in solid phase versus liquid phase *p*H for each neutralizer or neutralizing system (fig. 3).

Experimental data concerning the distribution of calcium and magnesium ions in both liquid and solid phases for all neutralizing systems are recorded in the figures 4 – 7, where abscissa, molar ratio (CaO + MgO) / Al_2O_3 (gibbsite) in solid phase, always should be related to the pH variation as in the figure 3. Plateaux on the curves describing the variation of (CaO + MgO) concentration in solid phase (mmol/g) against molar ratio (CaO + MgO) / Al_2O_3 (gibbsite) in solid phase are accounting for a new precipitated compound in equilibrium with the matching solutions. These plateaux are certainly displayed in the case of neutralizers $MgCl_2$ and $MgSO_4$, as well as in the case of neutralizing system $MgCl_2$ + $CaCl_2$, and describe a specific separation from the liquid phase of a particular mixture MgO/Al_2O_3 in a well defined ratio, at constant rate, insofar the added magnesium ions mobilize more and more Al_2O_3 from solid phase and bind it into the new compounds (figures 4 and 6). Solid phases precipitated during the neutralization with $MgCl_2$ and $MgSO_4$ are hydrotalcite carbonate $[Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O]$ [36], and respectively hydrotalcitesulphate $[Mg_6Al_2(OH)_{16}(SO_4)\cdot 4H_2O]$ [37] like phases. Both compounds are poorly crystalized and mixed up with some other compounds born out of calcium, sodium and silica impurities. Another patern of red mud neutralization was observed in the case of calcium chloride as neutralizer. Because calcium is bound in red mud more as hydroxicancrinite $\{Ca_2Na_6[Al_6Si_6O_{24}](CO_3)_2\cdot 2H_2O\}$ and less as calcium aluminium silicate $[Ca_2Al_2(SiO_4)(OH)_8]$, the liquid phase is merely in equilibrium with these compounds. Additional calcium ions brought in by neutralizing solution interacts with destabilized sodium aluminate and may be also with sodalites $\{3[Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot(2+k)H2O]\cdot Na_2X\}$ resting as solid phases in red mud, and create some supersaturation which is quickly discharged as amorphous phase onto the surface in the above compounds. Parts of the amorphous phase crystallizes out slowly as hydrocalumite $[Ca_{16}Al_8(OH)_{54}CO_3\bullet 21H_2O]$ [38] under some excess of calcium ions:

$$16CaCl_2+8NaAl(OH)_4+22NaOH+Na_2CO_3+21H_2O\rightarrow$$
$$\rightarrow Ca_{16}Al_8(OH)_{54}CO_3\bullet 21H_2O+32\ NaCl \qquad (8)$$

The rest of amorphous is converted into calcite or calcium sulphate, if CO_3^{2-} and SO_4^{2-} ions are available. Final stage of the neutralization process is reached when amorphous phase leaves out of solution at about pH 10.0 - 10.5. At this point, some parts of the red mud alkalinity is transferred to solid phase and the neutralization process is practically terminated. In the figures 4 and 6 the first part of the proces until *p*H 11, precipitation of $Mg(OH)_2$ + $Ca(OH)_2$, corresponds to descending line. Raising line stands for precipitation of the amorphous hydroxycalunite structured phase, which concludes the neutralization

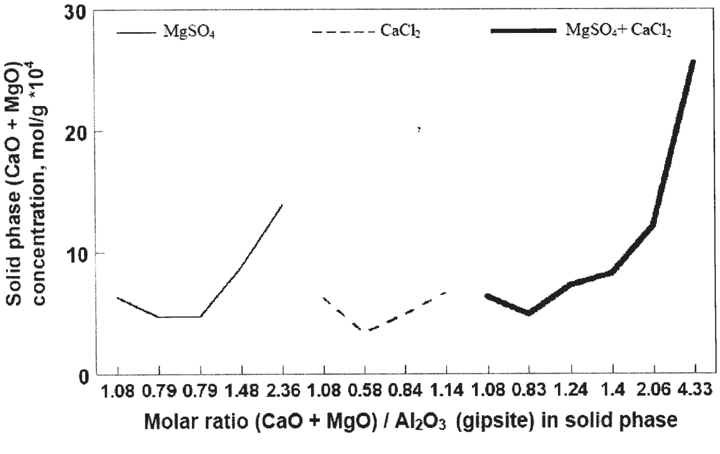

Fig. 6. Variation of (CaO + MgO) concentration in solid phase versus molar ratio (CaO + MgO) / Al_2O_3 (gipsite) in solid phase for red mud neutralized with $MgSO_4$-$CaCl_2$ system.

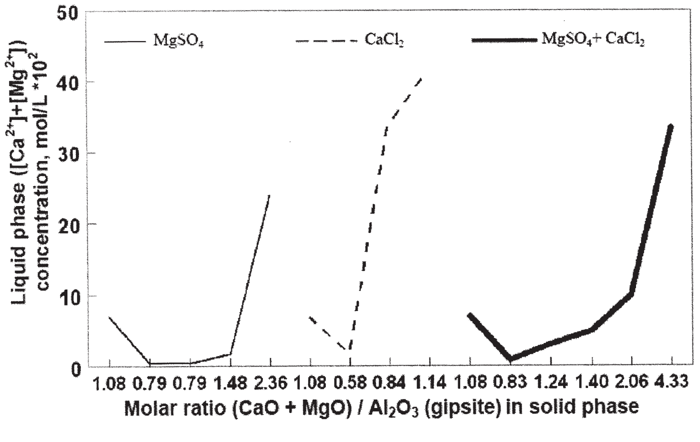

Fig. 7. Variation of ($[Ca^{2+}]$ + $[Mg^{2+}]$) concentration in liquid phase versus molar ratio (CaO + MgO) / Al_2O_3 (available gibbsite) in solid phase for red mud neutralized with $MgSO_4$-$CaCl_2$ system

process at a molar ratio (CaO + MgO) / Al_2O_3 (gibbsite) of about 1.1. Because the molar ratio is (CaO + MgO) / Al_2O_3 (gibbsite) in hydrocalunite is 4.0, the small ratio (CaO + MgO) / Al_2O_3 (gibbsite) found in neutralized red mud enlightens the poor capacity of calcium ions to mobilize gibbsite from solid phase and to convert it into neutral products (only a quarter of available reactive Al_2O_3 (gibbsite) is mobilized). Neutralization with $MgCl_2$ + $CaCl_2$ and $MgSO_4$ + $CaCl_2$ neutralizing systems by adding firstly the magnesium salts and then calcium salt does not introduce significant changes in neutralization parameters or in number and varieties of solid phases. Mainly hydrotalcite-like compounds are precipitated by magnesium ions in each system. Reactions generating hydrotalcite carbonate and hydrotalcite sulphate in both neutralizing systems are concurrent reactions for hydrocalunite crystallization from amorphous precipitates deposited on particulate phases containing calcium. This product is missing from red mud samples neutralized with both mixtures $MgCl_2$ + $CaCl_2$ and $MgSO_4$ + $CaCl_2$. Exceeding rates of neutralizing salts bring about the raise of ionic concentrations in liquid phase or, if the solubility products are reached, the double salts $CaMg_2Cl_6 \cdot 12\ H_2O$ in chloride-chloride system and $Na_{12}Mg_7\ (SO_4)_{13} \cdot 15\ H_2O$ in chloride – sulphate system are separated as distinct phases along with common salts already existing in raw red mud ($CaSO_4$, $CaCO_3$, NaCl, sodalite, cancrinite, etc.). Also, hydrated $CaSO_4$ is precipitated in chloride – sulphate system, but not at the expected rate, because double salt $Na_{12}Mg_7\ (SO_4)_{13} \cdot 15\ H_2O$ seems to have a smaller solubility product than $CaSO_4$ in liquid phase wetting neurtralized red mud (table 2). Unexpectedly the sodalites are removed from solid phase mixtures, most of the sodium beeing expeled into solution, while silica settled as amorphous phase. It seems the entire sodicity of red mud is removed and carried by liquid phase out of neutralized material. As the composition of liquid phase is depleting in aluminium and silica, as well in carbonates and sulphates, all the interactions with the neutralizing salts are ceassing and the added alkali metal salts will continuously raising their ions concentration in mother liquor (fig. 5, 7). The last change of slopes on each curve in the figures 5 and 7 are stamping the aproximate end of chemical reactions. Downward the end point on each curve in the figures 5 and 7 there are laying the liquid phase equilibrium concentration points. These points are expresing the sum ($[Ca^{2+}]$ and $[Mg^{2+}]$) concentration at any *p*H ending of the neutralization process. Actually, the variation of ($[Ca^{2+}] + [Mg^{2+}]$) concentration in liquid phase versus molar ratio (CaO + MgO) / Al_2O_3 (gipsite) in solid phase may be used to learn the real concentration of neutralizing ions added in red mud when (CaO + MgO) / Al_2O_3 (gipsite) in solid phase reaches the specified value at any given pH read from figure 3. According to the figures 5 and 7, the choice of neutralization end point and the final charge with calcium and magnesium ions of neutralized the red mud can be appraised independently of the initial sodicity or alkalinity of raw red mud. Any way the figure 3, and respectively figures 5 and 7 should be used together to find out both molar ratio (CaO + MgO) / Al_2O_3 (gipsite) in solid phase and ($[Ca^{2+}] + [Mg^{2+}]$) concentration in liquid phase from the demanded final *p*H in neutralized red mud.

Rather interlaced mixture of chemical compounds, crystaline and amorphous blends, separated during the raw red mud neutralization could be hardly characterized and the efforts to distinguish from XRD data the variety of chemical species like hydrotalcites, hydrocalunites, sodalites or cancrinites poorly crystallized beside the large number of hydrated and anhidrous simple or double salts of sodium, magnesium and calcium are mostly overwhelmingly boring and many times unsuccesfully consummated.

For refining the XRD data, new series of experiments were made separating the liquid phase from the raw red mud and neutralizing it with the same neutralizers and neutalizing systems. Slow decrese of pH down to 11 and 9 values was accompished by adding small amounts of neutralizars from 24 to 24 h and maintaining the samples under continuous mixing for some hundred hours for complete desuprasaturation of solutions and longer time lag for stable compounds crystallization out of liquid and amorphous phases, typically encountered for large molecular mass hydrated substances separating from aquoeous solutions. This time the support of the older weathered solid phases in red mud is completely removed. Therefore, all the reactions are taking place inside the diluted fluid conveying sodium aluminate and the accompanying ionic compositions released from red mud. In other words, all the crystalline and amorphous phases are forced to nucleate and grow in liquid phase without the subtantial contribution of the chemical labile compounds like gibbsite, sodalite, cancrinite etc. laying in red mud, as well as, in the absence of interactive surfaces provided by dormant solid phases making up the bulk of red mud. Main products of the neutralizing solutions interactions and the fluid phase in raw red mud are listed in table 2. New calcium aluminate phases nucleated and grown inside this fluid phase are the hydrotalcite carbonate, hydrotalcite sulphate and hydrocalumite. All of them are well crystallized and are undoubtedly corrresponding to the specified classes of alkali earth metal double hydroxides, namely hydrotalcite carbonate ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$; ratio MeO/Al_2O_3 6/1), hydrotalcite sulphate ($Mg_6Al_2(OH)_{16}(SO_4) \cdot 4H_2O$; ratio MeO/Al_2O_3 6/1) and hydrocalumite ($Ca_{16}Al_8(OH)_{54}CO_3 \bullet 21H_2O$ ratio MeO/Al_2O_3 4/1;). Ratio MeO/Al_2O_3 found in the separated solid phases are 2/1 in hydrotalcites and 1/1 in hydrocalumite. Probably, the pure mineralogical components are embeded in the amorphos mass rich in

Table 2

NEW BORN SOLID PHASES AT *p*H 9.0

Neutralizer	$MgCl_2$	$MgSO_4$	$CaCl_2$	$MgCl_2+CaCl_2$	$MgSO_4+CaCl_2$
Molar/ratio MgO/Al_2O_3 or CaO/Al_2O_3	1.78	2.09	1.1	2.72	2.46
Main mineralogical phase	Hydrotalcite carbonate	Hydrotalcite sulphate	Hydrocalunite	Hydrotalcite carbonate	Hydrotalcite sulphate
Aditional solid phases	NaCl, $CaCO_3$, $Mg(OH)_2$, $Al(OH)_3$.	Na_2SO_4, $CaSO_4$, $Mg(OH)_2$, $Al(OH)_3$, $Na_{12}Mg_7\ (SO_4)_{13} \cdot 15\ H_2O$.	NaCl, $CaCO_3$, $Ca(OH)_2$, $Al(OH)_3$, $CaCl_2 \cdot n\ H_2O$,	NaCl, $CaCO_3$, $Mg(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$, $CaMg_2Cl_6 \cdot 12\ H_2O$.	$CaSO_4$, $CaCO_3$, $Mg(OH)_2$, $Ca(OH)_2$, $Al(OH)_3$, $Na_{12}Mg_7\ (SO_4)_{13} \cdot 15\ H_2O$.

Al_2O_3. Excessive quantities on alkali earth metal neutralizants added to red mud do not increase the content of these metal oxides in solid phase (figs. 5, 7), only because the the neutralizants are nor able to mobilize the available resurces of gibbsite from red mud. More than half of gibbsite content in red mud remain blocked inside the layers of freshly separated amorphous and crystallized calcium aluminates mixed with the other solid phases mentioned in the table 2. It should remembered that all the solid compounds mentioned in the table 2 are the outcome of nucleation and growth from aqueous phase. Even if compounds like hydrotalcite or hydrocalunite initially nucleate as amorpohous and in the aftermath sequence crystallize in regular shapes of some known cristalline lattices, their origin is liquid phase and their birth driving force is the supersaturation developed due to the chemical reactions between certain constituents of the liquid phase.

Identification of the same compounds in neutralized red mud leads to the assumption that all emerging new phases during neutralizing process are also confidently born in the liquid phase. Interference of the main red mud solid phases is not expected, because most of them are dormant phases. These phases have crossed all the low and high temperature stages in the alumina refining process, and have had enough time and opportunities to be converted into chemicaly stable cristalline phases. Consequently, their contributions to nucleation and growth has to be excluded. Labile phases like sodalites, cancrinites or calcium aluminum silicate do not seem to bring any contribution to the nucleation of new born phases, but may influence their crystal growth kinetics from amorphous, since any crystal growth from amorphous is mediated through aqueous phase. Also, the high specific surface of new born phases may adsorb or arrest selectively ionic constituents of the new phases and slow down the re-crystalization process. Conversely, labile phases might be disintegrated leaving constituents available for new born phases crystallization. This process has truly taken place, independent of the nature of neutralizant substance. Poor crystallinity of the compounds substantiated during red mud neutralizing process can be the result of such interference. The above mechanism may be exploited for impoving the quality of adsorbent products from netralized red mud. Good quality adsorbents presume the existence of sodalite, cancrinite, hydrocalunite and hydrotalcites phases in neutralized red mud. If these compounds pre-exist into red mud composition, the neutralization process should be carried on under convenient conditions to preserve their chemical stability and to stimulate the growth of the talcite like new phases. Adequate neutralization process parameters (aluminate content, reactant concentrations, neutralization rates, temperature,etc.) improve the adsorbent performances and frame their properties to some quality reproducible standards. Thus, if the neutral red mud adsorbent qualities are required, fresh red mud rich sodium aluminate is highly recomended to be selected and processed for this purpose. If the neutralization process is practiced to yield a non hazardous material to be safely disposed, then the wheathered red mud is recommended to be selected for convenient neutralization process.

Conclusions

The study of red mud neutralization was focused on the crystallized and amorphous phases born in during neutralization process as elements around which the adsorbent capacity and heavy metal entrapping ability might be developed or simply accounted for safety red mud disposal as a non-hazardous material. Neutralization with sulphuric acid occurs in some more steps and factually is controlled by the rate of adding sulphuric acid. When the acid dosage is slowed down to some minimal levels, firstly, the free residual sodium hydroxide and sodium aluminate are reacting, while the reaction products (mainly sodium sulphate) are conveyed into solution and washed out from the mixture of solid phases. By pH 8.5 - 9.0, the $[OH^-]$ total alkalinity is balanced by the added sulphuric acid the first stage of neutralization is consummated. Second stage of neutralization process involves the removal of alkali, alkali earth metals and other ions bonded by electrical charges, and further third stage end up with total dissolution of the silicate phases as the *p*H falls lower than 8.0. Because the ion exchange phases remain unchanged, superficial neutralization up to *p*H 8.0 does not affect ion exchange capacity. On the contrary, due to some specific dissolution of the cancrinite layer overgrown on red mud particle surface during washing stages before disposal, the removal of red mud sodicity obviously results in total surface extension and moreover in a kind of chemical activation of the cleaned surfaces. Otherwise, neutralization to *p*H less than 8.0, removes completely the chemically labile solid phases from red mud and leaves behind an inert material ready to be safe disposed.

Common salts of calcium and magnesium, mainly chloride and sulphate used as neutralizers for red mud act similarly with sea waters, due to their capacity to remove alumina, silica and other constituents from chemically labile solid phases and diluted aluminate solutions, bonding the entire red mud alkalinity into insoluble aluminates and aluminate silicate compounds with or without sodium ions capture. As it turns out, the first drop in molar ratio $(CaO + MgO)/ Al_2O_3$ (available gibbsite) in solid phase up to *p*H 11.0 corresponds to the sodium aluminate destabilization with complete release of both $Ca(OH)_2$ and $Mg(OH)_2$ from free soluble ionic calcium and magnesium compounds. Further calcium and magnesium ions brought into solution by additional fed neutralizers cause the precipitation of hydroxycarbonates of aluminium, calcium, and magnesium, while the colloidal hydrotalcite-like compounds lose stability and precipitate out of solution. Solid phases precipitated during the neutralization with $MgCl_2$ and $MgSO_4$ are hydrotalcite carbonate $(Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$, and respectively hydrotalcite-sulphate $(Mg_6Al_2(OH)_{16}(SO_4)\cdot 4H_2O)$ like phases. Both compounds are poorly crystalized and mixed up with some other compounds born out of calcium, sodium and silica impurities. Another patern of red mud neutralization was observed in the case of calcium chloride as neutralizer. In as much as calcium is bound in red mud more as hydroxicancrinite $(Ca_2Na_6[Al_6Si_6O_{24}](CO3)_2\cdot 2H_2O)$ and less as calcium aluminium silicate $(Ca_2Al_2(SiO_4)(OH)_8)$, the liquid phase is merely in equilibrium with these compounds. Additional calcium ions brought in by neutralizing solution interacts with destabilized sodium aluminate and may be also with sodalites $(3[Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot(2+k)H2O]\cdot Na_2X)$ resting as solid phases in red mud, and create some supersaturation which is quickly discharged as amorphous phase onto the surface in the above compounds. Parts of the amorphous phase crystallizes out slowly as hydrocalumite $(Ca_{16}Al_8(OH)_{54}CO_3\bullet 21H_2O)$, and the rest of amorphous is converted into calcite or calcium sulphate, if CO_3^{2-} and SO_4^{2-} ions are available. In this case, the final stage of the neutralization process is reached when amorphous is totaly consumed at about *p*H 10.0 - 10.5. Adequate neutralization process parameters (aluminate content, reactant concentrations, neutralization rates, temperature, etc.) improve the adsorbent performances and frame their properties to some quality reproducible standards. Fresh red mud rich in sodium aluminate is highly recomended to be selected and processed for the adsorbent qulities development in the neutralizd product. Reversely, the wheathered red mud is recomended to be selected for convenient neutralization process to yield a non hazardous material to be safely disposed.

Acknowledgment: This work was carried out with financial support of the CNCSIS, GRANT 97/2007

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Manuscript received: 20.02.2009