U.P.B. Sci. Bull., Series B, Vol. 72, Iss. 3, 2010 ISSN 1454-2331

REMOVAL CHROMIUM POLLUTION FROM LEATHER INDUSTRIES WASTES

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Nămolul şi apele uzate încărcate cu compuşi ai cromului reprezintă o povară pentru mediu, atât pentru industria de prelucrare a pielii, precum şi pentru multe alte ramuri de extracție şi producție care implică utilizarea de compuşi chimici ai cromului. Această lucrare adordează eliminarea cromului din apele reziduale şi din nămoluri prin două căi proiectate pentru a obține un material chimic stabil, care încorporează cromul rezidual, pentru depozitarea ca deşeu nepericulos. Prima cale implică reacția chimică şi sorbția în nămolul roşu tratat, ceea ce conduce la separarea hidroxidului de crom şi legarea în compuşi inerți. A doua cale se referă la precipitarea in situ a fosfatului de aluminiu şi magneziu ca absorbanți ai hidroxidului de crom în rețeaua lor cristalină.

Sludge and waste waters carrying chromium compounds are embarrassing environmental burdens for the both tanning and leather processing industries, as well as for many other manufacture branches involving extraction and use of the chromium chemicals. This paper approaches the chromium removal from waste waters and sludge by two pathways designed to produce a chemical stable material incorporating the waste chromium for landfilling as non-hazardous waste. First pathway involves the chemical reaction and sorbtion on treated red mud, which results in the separation of chromium hydroxide bound in inert compounds. Second pathway concerns in situ precipitation of aluminum and magnesium phosphate as adsorbents of chromium hydroxide in their crystalline lattice.

Keywords: chrome leather, red mud, chromium, adsorption, levigability

1. Introduction

Sludge and waste waters carrying chromium compounds are embarrassing environmental burdens for the both tanning and leather processing industries, as well as for many other manufacture branches involving extraction and use of the chromium chemicals.

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Most common ways to remove ionic chromium from these waste waters are the chemical precipitation and the adsorption on different materials, whose physical and chemical properties were particularly adjusted to yield high rates in chromium adsorption and easy recovery at rewarding output [1-20]. Numerous available technologies are relying on: precipitation of chromium and heavy metals as hydroxides [1-3], carbonates [4], and phosphates [5,6], co-precipitation [17,18] or precipitation coupled with coagulation [19,20], adsorption on coal and activated charcoals [9,10], clay [11] and activated clays as bentonite [12], clinoptilolite [13] and vermiculite [14] in order to improve thickening/dewatering rates of the particulate sludge [7,8], ionic exchange [15,16, 21], liquid-liquid extraction [22], electrochemical oxidation and reduction [23,24], ultra-filtration [1] and nano-filtration [25,26], bio-precipitation and bio-sorption [1], vitrification and encapsulation [27-30]. Most of these technologies are quite satisfactory in terms of chromium removal yields, but less convenient in terms of engineering requirements and cost.

This paper approaches the chromium removal from waste waters by two pathways designed to produce chemical stable materials incorporating waste chromium for landfilling as non-hazardous waste. First pathway comprises the preparation of new adsorbents able to catch chromium and bind it into their structure through ion exchange physical and chemical precipitation and co-precipitation. As a raw material for chromium binding and removal, red mud, the byproduct of alumina refineries, was considered as a valuable neutralizing material whose properties can be adjusted in to order accomplish the above task, by retaining on its surface the precipitated and co-precipitated of low solubility chromium compounds. Second pathway consists in once through chemical precipitation of the adsorbents right in the contaminated waters and sludge, followed by chromium adsorption, co-precipitation or bound in stable low solubility chemical compounds. There were considered as precipitated adsorbents the following classes of compounds: aluminum, magnesium and calcium phosphates and double hydrate oxides MO/Al_2O_3. Also, the co-precipitated and solid solutions of the above compounds may accommodate the chromium ion in their lattice structure, as far as pH handling may raise precipitation yield and rate of chromium removal.

2. Experimental

Neutralization protocols. Red mud neutralization was carried out at room temperature with sulphuric acid 20% solution, by adding small quantities of this into well mixed slurry under continuous pH monitoring. For the research end goals, the suitable timing of acid shares addition was carefully considered in order to avoid the reactions:

$$2Al(OH)_3+H_2SO_4 \rightarrow [Al(OH)_2]_2SO_4+2H_2O \qquad (1)$$

$$Al(OH)_3+H_2SO_4 \rightarrow Al(OH)SO_4+2H_2O \qquad (2)$$

and further silicates and aluminum silicates partial decomposition [27, 28]. Neutralization was deliberated ceased when pH reached the value 8.0. As was shown by other authors [8,19,22,23] the 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 $M^{2+} = Mg^{2+}$ or Fe^{2+}, $M^{3+} = Al^{3+}$ or Fe^{3+} and $X^{m-} = OH^-$, Cl^-, CO_3^{2-} or SO_4^{2-}. Because there are no significant amounts of magnesium compounds in red mud, such compounds have to be precipitated in the liquid phase accompanying the entire mass of red mud in any circumstances. According to Smith and his team the following reactions are possible [31]:

$$4MgCl_2+2NaAl(OH)_4+4NaOH+Na_2CO_3 \rightarrow Mg_4Al_2(CO_3)(OH)_{12} \cdot xH_2O+8NaCl \qquad (3)$$

$$8MgCl_2+2NaAl(OH)_4+12NaOH+1/2Na_2CO_3 \rightarrow Mg_8Al_2Cl(CO_3)_{0.5}(OH)_{20} \cdot xH_2O+15NaCl \qquad (4)$$

The yields and compound ratios in the new born solid phases depend on: available gibbsite and red mud wearing, (CaO +MgO)/ gibbsite ratios; particle surface availability and reactivity; silica concurrent reactions; concurrent reaction products; pair ions substitution in the crystalline lattice of basic compounds; reaction condition as temperature, pH, rate of neutralization, etc. Red nud neutralization with $CaCl_2$ solution take another route. Actually, calcium ions are bound in red mud mostly as hydroxicancrinite $Ca_2Na_6[Al_6Si_6O_{24}](CO_3)_2 \cdot 2H_2O$, and therefore, the liquid phase is merely in equilibrium with this compound. Additional calcium ions brought in by neutralizing solution interacts with destabilized sodium aluminate and creates some supersaturation which is quickly discharged as an amorphous phase onto the surface of hydroxicancrinite and sodalites. Parts or the entire amorphous phase crystallizes out slowly as hydrocalumite $[Ca_{16}Al_8(OH)_{54}CO_3 \bullet 21H_2O]$ [32] under some excess of calcium ions [31]:

$$16CaCl_2+8NaAl(OH)_4+22NaOH+Na_2CO_3+21H_2O \rightarrow Ca_{16}Al_8(OH)_{54}CO_3 \bullet 21H_2O+32NaCl \qquad (5)$$

Because conversion of the hydroxicancrinite into hydrocalumite does not bring about penetration of the Cr^{3+} ion into adsorbent crystal lattice, it seems the calcium ion is not essential in preparing the red mud as long lasting adsorbent for chromium compounds. Any way, formation of layered dihydroxides, with or without parallel hydrocalumite precipitation, requires longer time to attain solid-liquid chemical equilibrium. Consequently, small shares as 0.5 – 5 ml of solutions 1 M containing $MgCl_2$, $MgSO_4$ and their mixtures with $CaCl_2$ were added from 24 to 24 hours and stirred with the red mud slurry, monitoring pH, up to value 9.0. According to the literature [19], all the compounds resulted during neutralization process are carrying higher ion exchange capacities than silicate phases in the raw red mud.

Samples analysis. Zero charge point (ZCP) of each sample provides information on the neutralization level reached by the red mud. This parameter can be computed from potentiometric titration of the red mud samples suspensions in 0.01 M, 0.1 M and 0.5 M NaCl electrolyte solutions. Thus, the surface charge σ computed with formula:

$$\sigma = \frac{\Delta\upsilon \times N \times F \times 100}{S \times A \times V} \tag{1}$$

where:

$\Delta\upsilon$ = volume of HCl solution used in the red mud sample titration – volume of HCl or NaOH solution used in blank (electrolyte) titration at the same pH value;
N = normality of the titrating solution (0.1 N);
F = 96500 C;
S = specific area of the red mud;
A = amount of red mud weighed on the analytical balance;
V = the electrolyte volume being used (100 ml)

can be plotted against pH. Figure 1 illustrates the way to assess the zero charge point (ZCP) from the σ = f (pH) plot. Also, from the same figure it can be read the pH value at ZCP for each sample of red mud.

Specific areas of the raw and neutralized red mud samples were measured on an ASAP (Accelerated Surface Area and Porosimetry) 2020 System with nitrogen as analysis adsorbent. For the trials of chromium retention on the neutralized red mud some solutions of basic chromium sulphate of variable concentrations within the common range found in the tannery effluents were prepared. Adsorption tests were accompanied with pair standard tests of leachability. The pH was measured with Consort C833 ionmeter. Calcium and magnesium were analyzed by EDTA titration. Chromium in liquid phases was analyzed with Varian AA240FS fast sequential AAS spectrometer. Mineralogical phases were identified by XRD using Dron 2 spectrometer along with their semi-quantitative elemental analysis by Philips PW2400 X-ray fluorescence spectrometer.

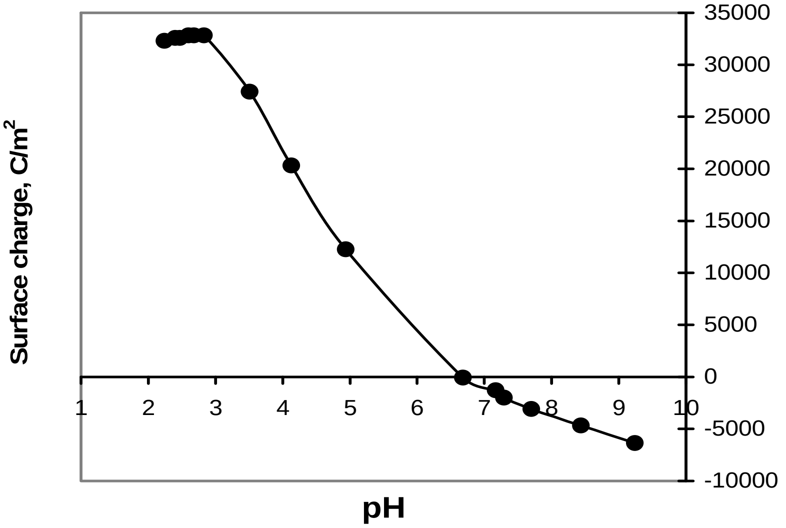

Fig. 1. ZCP identification in dry red mud suspended in 0.5 M NaCl electrolyte solution

3. Results and discussions

Pathway I. Red mud preparation as chromium adsorbent for retention and landfilling

Raw red mud 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 sodium ion exchangeable percentage (≈100%), and poor water holding capacity.

Composition and composition related properties were described in another paper [33]. Mainly, high pH values comes from AlO_2^{1-} ions present in liquid phase and high total alkalinity from the crystalline gibbsite ($Al_2O_3 \cdot 3H_2O$) in the solid phase. High ion exchanging capacity originates from large particles specific surface area, as well as from silicate and aluminium silicate solid phases born during the Bayer process alumina refining as: sodalite $Na_6[Al_6Si_6]_{24}(CO_3)_2 \cdot 2H_2O$, cancrinite $(NaAlSiO_4)_6 \cdot CaCO_3$, hydroxycancrinite $(NaAlSiO_4)_6 \cdot NaOH \cdot H_2O$, tricalcium aluminatehydrates ($xCaO \cdot yAl_2O_3 \cdot zH_2O$), kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Accordingly, any change in composition and properties made for better chromium sequestration must preserve specific surface area and respectively silicate and aluminium silicate solid phases.

In good agreement with the previous researches concerning the solid phases precipitated or crystallized during the red mud neutralization, the best suited treatments for the red mud, able to improve its quality as adsorbent and promote chromium sequestration into the crystal lattice of the new crystallized dihydroxide compounds are:

- Neutralization with mineral acid for the removal of excessive alkalinity and soluble and poor crystallized solid phases without major changes in the specific surface area and silicate and aluminium silicate solid phases;
- Neutralization with alkali earth metal salts to improve the crystallinity of the silicate and aluminium silicate solid phases and, above all, to promote the crystallization of the low solubility compounds which might include chromium in their lattice.

Step by step, slowly neutralization of the raw red mud at low temperature with diluted acid preserves silicate and aluminium silicate solid phases and furthermore specific surface and ion exchange capacity. Figure 2 illustrates the preservation of silicate and aluminium silicate solid phases by small changes observed in (CaO + MgO)/Al_2O_3 ratios in solid phases. Factually, this ratio drops only from 0.32 to 0.30, less then 7%, which could not change significantly the surface properties of the neutralized material.

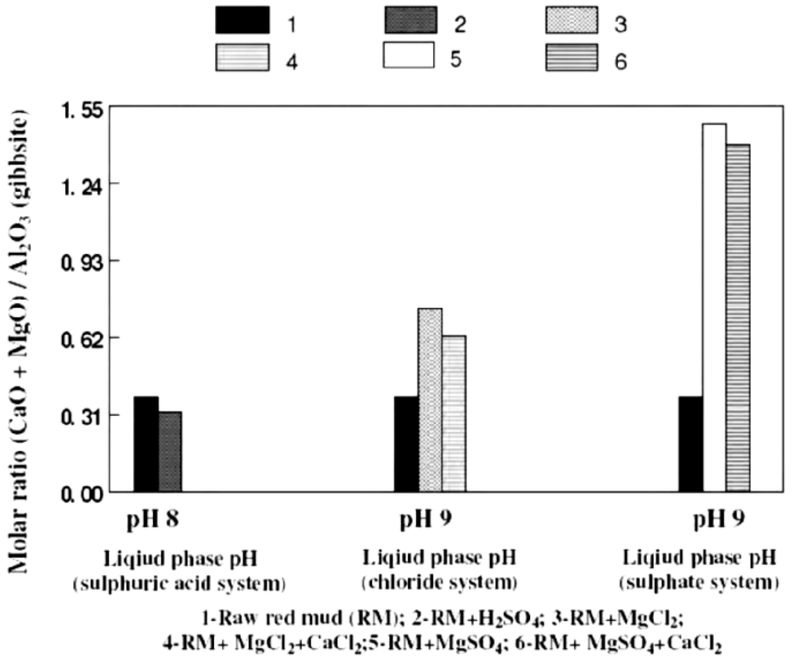

Fig. 2. Molar ratio (CaO+MgO)/ Al_2O_3 in sulphuric acid and magnesium salts neutralized red mud

From chemical point of view, common salts of calcium and magnesium used as neutralizers for red mud act similarly as sea waters. This last process was intensely studied by McConchie and his team [34]. Through the $MgCl_2$ 1M solution and $MgCl_2$ + $CaCl_2$ 1M or $MgSO_4$ + $CaCl_2$ 1M solution mixture neutralization of raw red mud, the solid phase composition was change due to conversion of the aluminate gibbsite into hydrotalcite carbonate. This very low soluble compound bind the chromium not only by ionic exchange, but also by lattice intercalation, which results in full chromium immobilization and the inertness of the entire mass of red mud. These new born compounds: crop up high specificity for heavy metal (including chromium) 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. First observation concerning the precipitation and crystallization of new compounds is illustrated in the figure 2 (right side), where the ratios (CaO + MgO)/Al_2O_3 show significant increases after neutralization. Increases of this ratio by 105-130% for chloride systems and by 335-360% in sulphate systems are suggesting the full incorporating of magnesium and calcium new compounds in the neutralized red mud. In spite of larger raises of the ratios (CaO + MgO)/Al_2O_3 in sulphate systems, the capacity of hydrocalumite to bind chromium into its crystal lattice is very poor and conclusively the neutralization with magnesium salts remains the best way to follow for a lasting sequestration of Cr^{3+} ions from waste waters. Another observation on neutralizing with magnesium salts, shows an increase of specific surface of red mud particles [35], suggesting an improvement of sorption properties of the material. Even if, at the end of precipitation process the rections 3 and 4 are incomplete and the precipitated phase is not completely crystalized, therefore, chromium sorption capacty is not by far affected, but chromium leachablility has to be carefully investigated in order to estimate the the eventual chromium release during amorphous phases slow crystallization. For an all over evaluation, the zero charge points of the magnesium salts neutralized red mud has to be considered as a references to the ending pH of neutralization process.

Figure 3 display the measured ZPC for dry and wet red mud samples. The results are definitely poor, primarily due to the high concentrations of residual chromium in depleted solutions (figure 4), even in the experiments carried out with diluted inward solutions requiring sorption capacities bellow the measured mean capacity of red mud used samples.

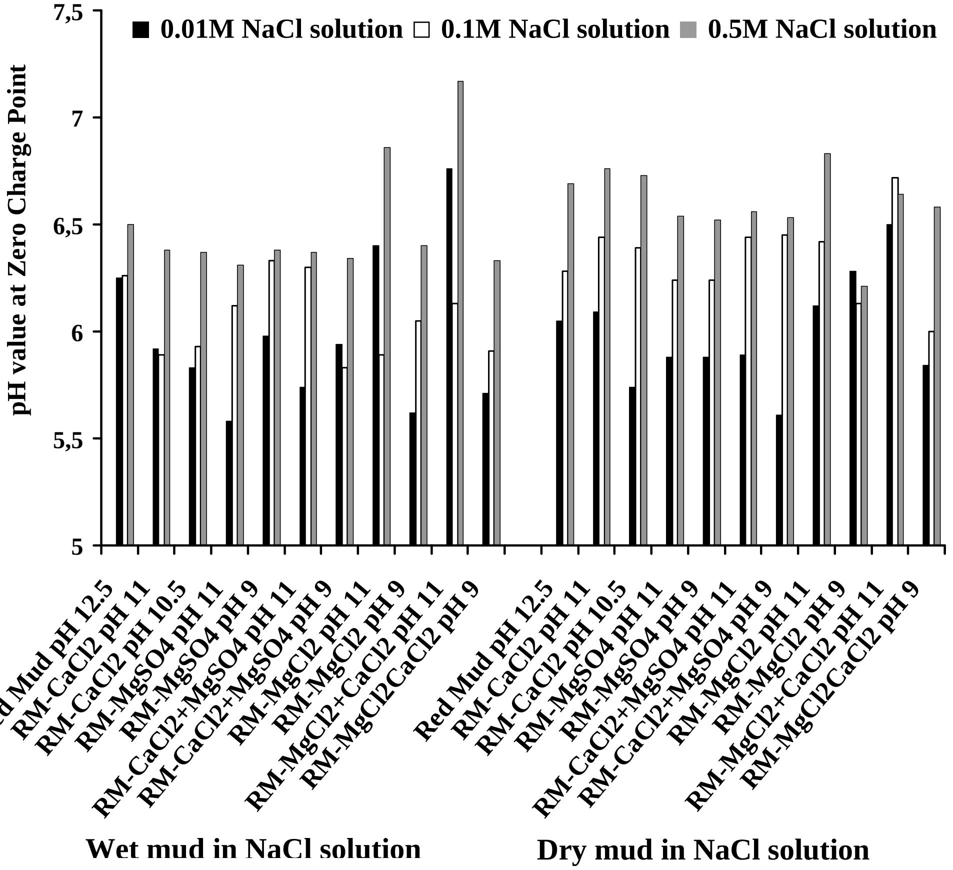

Fig. 3. Zero charge points of the dried and wet neutralized red mud.

When ZPC is reached, the red mud reactivity passes through a minimum value. From figure 3, the samples neutralized with magnesium salts at pH 9 still hold enough surface charge to sustain the chromium sorption process in terms of yields and rates.

Figures 4 and 5 illustrate the status of chromium adsorption on neutralized red mud with sulphuric acid and magnesium salts, respectively. Both figures are referring to equilibrium data between solutions with variable concentrations in chromium and neutralized red mud at constant ratio liquid/solid, 10/1 wt.

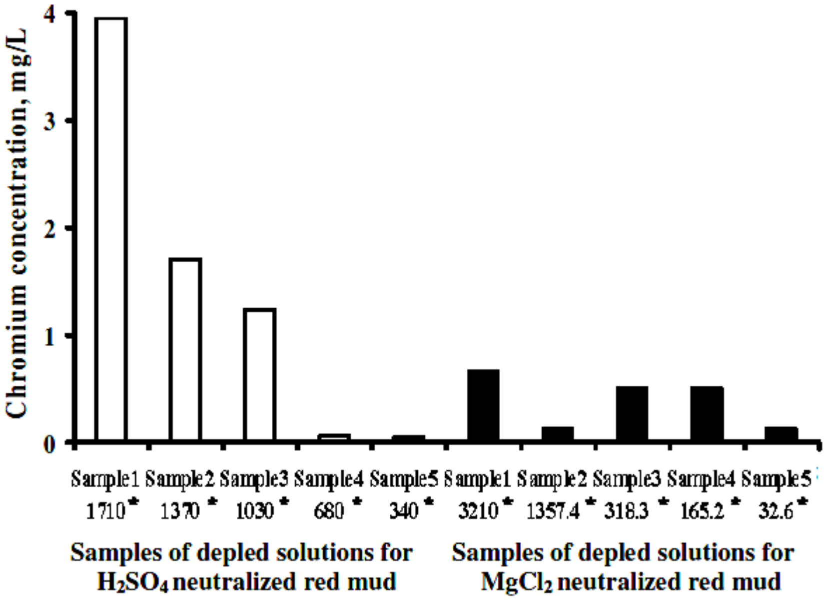

Fig. 4. Chromium concentration in depleted solutions from neutralized red mud;
* chromium concentration in initial solutions, mg/L

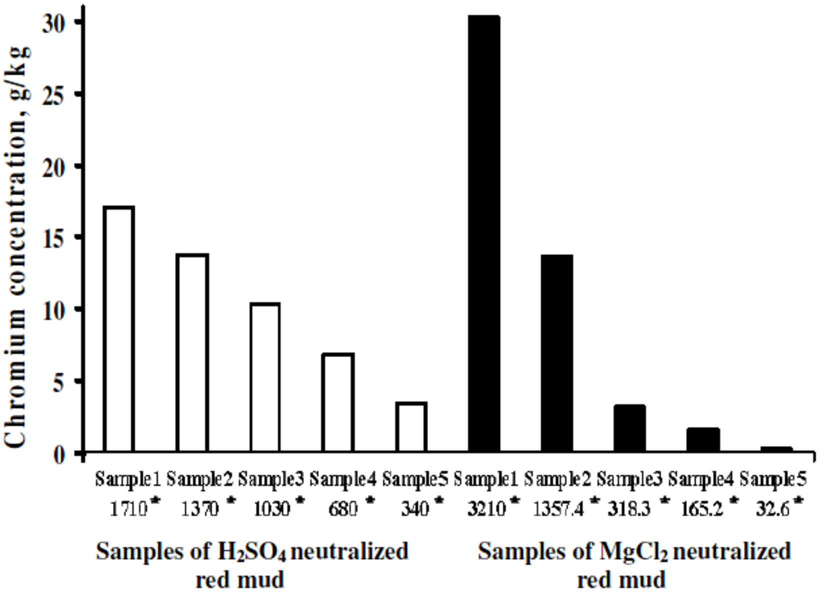

Fig. 5. Chromium retained in neutralized red mud;
* chromium concentration in initial solutions, mg/L

Data of chromium sorption on sulphuric acid neutralized red mud are definitely poor, primarily due to the high concentrations of residual chromium in depleted solutions (figure 4), even in the experiments carried out with diluted inward solutions requiring sorption capacities bellow the measured mean capacity of red mud used samples.

Figure 6 presents the standard leachability of chromium from equilibrium saturated samples.

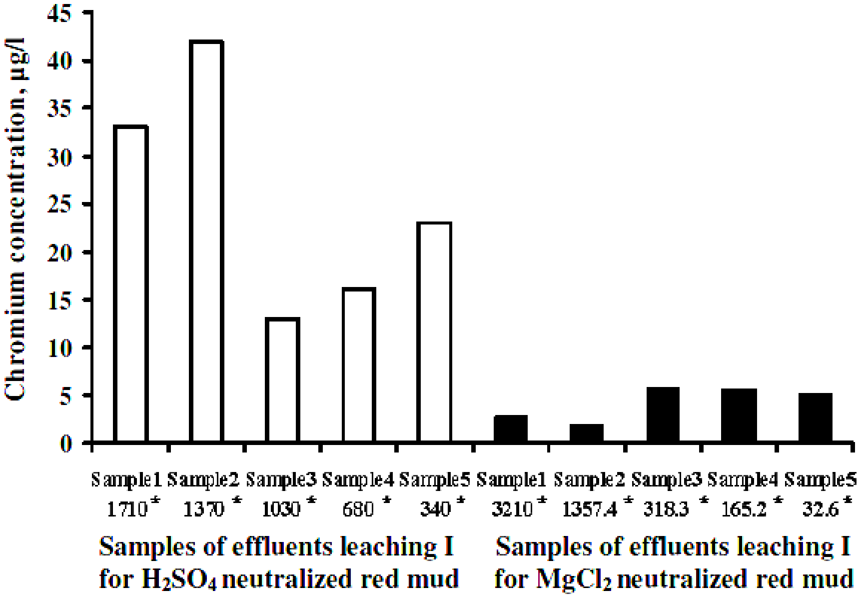

Fig. 6. Standard leachability of chromium sequestreted on the neutralized red mud;
* chromium concentration in initial solutions, mg/L

Beside this main defficiency, the leacheates released from the solid adsorbent samples are richer in chromium than expected and moreover the chromium concentration in these leacheates (figure 6) barely depends on chromium charge in adsorbent phase (figure 5). Therefore, the red mud sulphuric acid neutralization produces poor quality adsorbents, which can be used only for chromium removal from chromium contaminated effluents. Further processing for the chromium reclamation as chromate is quite mandatory required. Thus, sulphuric acid neutralized red mud is not a quite reliable safe adsorbent for heavy metals and definitely could not be landfilled in storage sites as non hazardous material when it is charged with chromium. Adsorption test on magnesium salts neutralized red mud was initially set up to provide reliable data on chromium equilibrium concentration in solutions contacted with variable chromium charges in the adsorbing material (below its maximum preliminary evaluated sorption capacity, 60 g/kg). Chromium concentration in the depleted solutions equilibrated with magnesium chloride neutralized red mud at pH 9 is fairly under the reasonable admitted levels for industrial released effluents (figure 4). Also, these concentrations are certainly independent on adsorbent chromium charge. Furthermore, some improvements on this side of adsorption process may be accomplished by a better control of influent solutions pH before adsorption. Unexpectedly, equilibrium charges in chromium of the magnesium chloride treated red mud samples are very close to those of sulphuric neutralized red mud. If the new crystallized phases account for low sorption capacity, which is explained by small quantities of gibbsite available for hydrotalcite carbonate precipitation or crystallization, then the low sorption capacity itself is a reliable evidence that the new born hydrotalcite carbonate phases are really responsible for chromium sorption and eventual penetration into these new phases crystal lattice.

Pathway II. Once through chemical precipitation of the adsorbents in the contaminated water

Once through chemical precipitation of the adsorbents in the contaminated water involves chemical precipitation with adequate reactants (in row reactions stages, in row intermediaries mixtures, batch or continuous processing, etc.), chromium adsorption, chromium co-precipitation, chromium bound in stable low solubility chemical compounds, crystallization, separation, finishing. Intended adsorbents and predicted compounds as performing adsorbents, able to hook up chromium hydroxide or other chromium ionic species in their crystalline lattice considered for this investigation were: magnesium and calcium phosphates, hydrated double hydrate oxides ($MO/Al_2O_3/H_2O$) and their solid solutions incorporating chromium hydrated species. In situ precipitation of the adsorbing solid phases assumes the separation of chromium as a non-leachable and non hazardous material ready to be landfilled with or without preliminary treatment [36]. There are many reasons to sustain the opportunity of the approached research program: a) in situ adsorbents precipitation is concluded in a quite homogenous distribution of chromium moieties inside the entire volume or mass of adsorbent mixtures; b) in situ technique is fairly higher up to the physical or chemical adsorption, because produces a low volume disposable material, which in some circumstances can be vitrified for much safe long term storage; c) a quite homogenous mixture of chromium compounds in which alkali earth phosphates, hydrated double hydrate oxides ($MO/Al_2O_3/H_2O$) and their solid solutions incorporating some other oxide species than those of the chromium can find easily uses as pigments in cement, ceramics and glasses industry. Experimental development on the adsorbent precipitation in contaminated waters is given in the table 1. The precipitated adsorbent is magnesium/magnesium and calcium salts neutralized red mud with or without chromium phosphate co-precipitated along with hydrotalcite carbonate [33]. The contaminated water was a true residual solution collected from a tannery effluent. The chromium content in this solution was adjusted to 4.27 g/L and pH 7.0±0.2, so that, by mixing it with red mud at a ratio liquid solid 10/1 and assuming the full chromium entrapment in the precipitated adsorbent, the chromium concentration in the adsorbent will be 42.7 g/kg, which is equivalent to approximate 70.6% of the measured magnesium salts neutralized red mud capacity of chromium binding into hydrotalcite carbonate phases. Sample 1 and 3 bear just the products of the magnesium and respectively magnesium and calcium salts reactions. Samples 2 and 4 bear the products of magnesium and respectively magnesium and calcium salts reactions, as well as the co-precipitated phases containing magnesium, calcium and chromium ortho-phosphates. The amounts of magnesium/magnesium and calcium salts used for red mud neutralization are equal to amounts added for reaching pH 9 in the binary mixture red mud-salts.

Table 1

Data on one through adsorbent precipitation in contaminated waters

Sample number	Initial chromium concentration, g/L	Ratio liquid/solid (contaminated water/red mud)	Molar Ratio H_3PO_4/Cr^{3+}	Residual chromium concentration, μg /L	Chromium concentration in solid residual, g/kg
Sample 1	4,27	10/1	0	36	42.67
Sample 2	4,27	10/1	3/1	140	42.66
Sample 3	4,27	10/1	0	108	42.66
Sample 4	4,27	10/1	3/1	161	42.66

Experimental parameters of the batch precipitation were:

- reactants fed in row: chromium solution; red mud; ortho-phosphoric acid; alkali earth salts; neutralizers if needed.
- final pH 7.0 ± 0.2;
- temperature 25 °C.

Entire experiment was set up in order to measure solubility of the chromium and find distribution of the above metals between liquid and solid phases. The sorption data are given in the table 1 and figure 7.

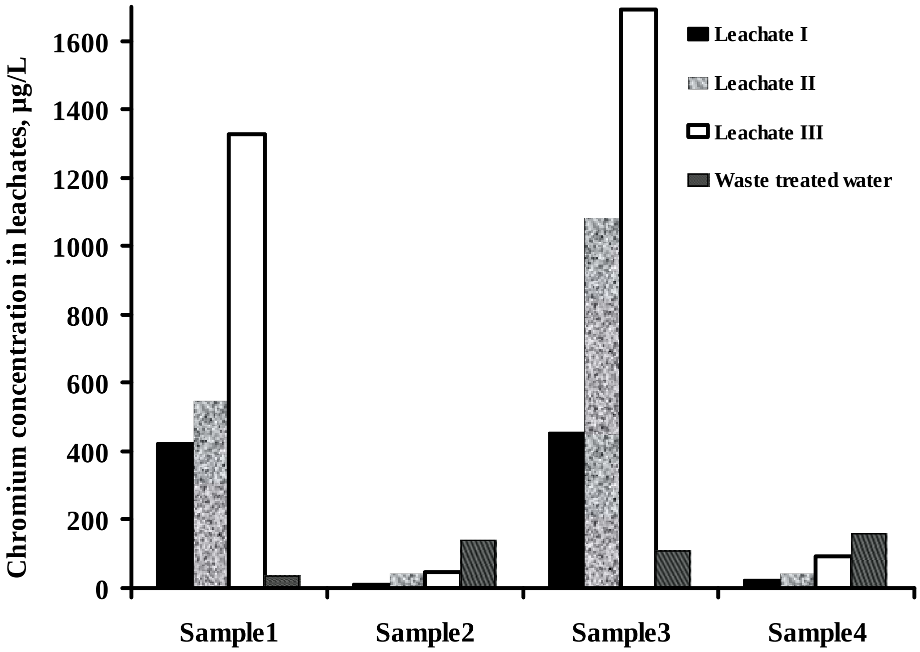

Fig. 7. Standard leachability of chromium sequestreted in one through precipitated absorbents

Very small chromium concentrations in the treated waters and high capacity of sorption in the in situ precipitated adsorbents can be seen for all four samples in table 1. Comparing these data with results of classical adsorption on the treated red mud from figures 4 and 5, the advantages of the new pathway designed for chromium removal and safe disposal of the solid wastes is evident in both terms of chemical precipitation yields and chromium concentrations in effluents. But the most important feature of this process is illustrated in figure 7 and concerns the issue of chromium leachability from charged adsorbents. Sample 1 and sample 3 exhibits large leachability indexes, comparable with chromium charged neutralized red mud (figure 6). But, when chromium is bound in phosphate adducts before chemical precipitation with alkali earth salts on the red mud particles surface, the leachability of chromium drops to as low as 20-100 µg/L. These values are far below the limits demanded for all waste waters classes.

6. Conclusions

Adequate red mud neutralization process parameters (aluminate content, reactant concentrations, neutralization rates, temperature,etc.) improve the adsorbent performances in chromium removal from contaminated waste waters and frame their properties to some quality reproducible standards. 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 porpose. 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.

The chemical chromium sequestration process involves the once through precipitation of adsorbing compounds from the low solubility classes of phosphates and hydroxides, accompanied by the total chromium adsorption and bonding into adsorbent crystal lattice. The approach subsumes the addition of phosphate ions as phosphoric acid into waste water to induce Cr^{3+} ion chelation, as well as the significant growth in chromium phosphate super saturation of liquid phase before mass precipitation of the adsorbents.

Chromium and aluminum are completely removed from chromate solutions completely and found integrally in the solid phase as moieties like $Cr(OH)_3$, $Cr(OH)_2Cl$, $Cr(OH)Cl_2$, $CrPO_4$, $AlPO_4$ and $Al(OH)_3$. The PO_4^{3-} ion is just partially precipitated as calcium, magnesium and aluminum insoluble phosphates. Thus, the lowest concentration of PO_4^{3-} ion in the mother liquors has to be considered as a criterion in appoint the best reactant combination and the appropriate reaction pH.

It was demonstrated the advanced chromium removal from tannery is possible and the resulted precipitated material could be easily converted to a safe disposable waste.

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