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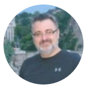

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Use of Red Mud for Toxic Metals Removal: The Case of Nickel

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Abstract: The presence of red mud was found to remove effectively nickel ions from dilute aqueous solutions (50 mg dm^{-3}). Red mud, being an industrial solid by-product/waste from alumina production during bauxite processing, was found to act simultaneously as an alkalinity regulator, causing precipitation of nickel as the insoluble hydroxide, as an adsorbent of the formed nickel hydroxide and as a flocculant of the resultant fine particulate matter. Sedimentation was subsequently considered as a possible solid/liquid separation technique. Various parameters, such as dispersion pH, red mud and nickel concentrations and ζ-potential, were examined and promising results were obtained.

Key words: red mud, nickel, removal, dilute solutions.

INTRODUCTION

As the problem of solid wastes disposal has now attained complex dimensions, it becomes essential either to find suitable ways for the safe disposal of these wastes or to suggest novel uses, considering them as by-products. Otherwise, these will remain an accumulated waste, contributing highly to environmental pollution.[1] Utilization techniques for each industrial waste vary widely according to the specific physico-chemical characteristics, collection and processing techniques adopted, intrinsic value of the retrievable material from the by-products, and techno-economic feasibility of manufacturing materials of economic and competitive value, as well as the availability, marketability and public acceptance of the finished product.[2]

Bauxite refining is a typical case of chemical processing, which yields red mud, a solid waste by-product with concomitant problems and costs in handling, storage and a search for further uses. Red mud is produced during digestion of pulverized bauxite with sodium hydroxide at elevated temperatures and pressures, according to the Bayer method. It will generally issue from the washing thickeners as a highly alkaline (pH 10–12·5) slurry at approximately 15–30% solids, and be pumped to a disposal lake. Iron impurities impart the brick red colour of the mud.

Red mud is composed mainly of non-toxic fine particles of silica, aluminium, iron, calcium and titanium oxides along with some other minor components.[3] Therefore, it has a complex chemical make-up, dependent upon its parent bauxite ore, aluminium extraction conditions, and impurity control. Due to its relatively high lime and sodium hydroxide content (originating from the Bayer process), red mud is relatively toxic and always poses a serious pollution hazard; it also has significant alkaline properties. Depending upon the number of mud washing stages, the water associated with the mud may contain 3–10 g dm^{-3} alkalinity (expressed as Na_2CO_3).

In addition, the amount produced is significant. Around 1–2 tons of residue is generated per ton of alumina produced. It is estimated that in Greece around 10000 metric tonnes of red mud are produced annually.[4] The fineness of solid particles and the large quantity of residue make further disposal or utilization very difficult. The most common solution to the red mud waste problem is total impoundment. The slurries are stored in ponds where the solids settle and the supernatant liquor becomes available for recirculation through the process. The difficulty of reclaiming residue disposal areas stems from the high alkalinity, salinity and sodicity of the

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residue.[5] The main problem of reclamation of the red mud residue areas is associated with dewatering and the associated caustic removal. A number of industries produce wastes that have an acidic nature (e.g. gypsum). If these wastes can be integrated with the caustic waste disposal from alumina production then the total problems can be decreased.[6] In the absence of uses for the waste there are added costs for building and maintaining the ponds. Finding a profitable use for this waste could further benefit the economics of the industry.

The potential uses of red mud have been classified into:[7] (a) recovery of major constituents, (b) recovery of by-products, (c) direct uses, and (d) incorporation into products. It is apparent from the great number of publications that there has been no lack of effort given to the utilization of these wastes, but that no consistent use has been maintained on a scale sufficiently large to consume current output and diminish the stockpiles.

Red mud, due to high aluminium, iron, and calcium content has been suggested as a cheap adsorbent for phosphates[8,9] or toxic metals removal (e.g. As, Cr, Pb, Cd),[10-13] as well as for water or wastewater treatment.[14,15] The basic advantage of red mud is its versatility, since it is comprised of a mixture of useful adsorbents and flocculants, all of which can be used for treatment of several effluents. It is worth noting also that for the majority of red mud applications only limited information is available, as the obtained results have usually been patented.

Nickel is a common toxic metal present in wastewaters from metal plating operations, silver refining, acid mine drainage, steel and printing works, motor vehicle and aircraft industries, in concentrations ranging from 900 mg dm^{-3} in used plating baths, down to 3·4 mg dm^{-3} in acid mine drainage.[16] The main methods applied for the removal of nickel from wastewaters include precipitation/flocculation[17] or adsorption on activated carbon,[18] clay minerals,[19] oxide adsorbents,[20,21] manganese oxide,[22] fly ash[23] and natural organic matter,[24] but the cost of these methods is relatively high. More economical nickel removal could be performed in a system which uses one plant's waste to treat another's effluent.

This study aims to evaluate Greek red mud in the treatment of toxic metal cations-bearing wastewaters, examining nickel as a typical case. The role of red mud in nickel removal was found to be rather complex, since it appears to act as a precipitant of nickel, forming the insoluble hydroxide (sweep flocculation), as a conventional adsorbent and as a flocculant of the hydrolytic products.

EXPERIMENTAL

The red mud samples used in this work came from an alumina production plant located in central Greece which processed the bauxites of this area. Although the original fully hydrated red mud slurry was expected to be more active, for reasons of experimental comparisons the samples were prepared by repeated washing using tap and deionized water, followed by drying in air, i.e. red mud was used in its natural form without any other pretreatment. Other workers have suggested pretreatment could increase the red mud effectiveness.[8,9]

The chemical composition of the resultant solid material (major components), as analysed by XRF, is shown in Table 1. The composition of red mud depends on the origin and related composition of the source materials and variations of the order ±10% from the average value are possible. The variation in the composition of bauxite residue slurry makes each type of residue unique in its physico-chemical properties—even for plants processing bauxite of relatively uniform characteristics. The composition of red mud minerals is claylike, but the actual minerals depend upon the ore as well as the conditions in the Bayer process. As a result of this composition red mud may act both as a flocculant and adsorbent for wastewaters.

The liquid phase consists mainly of water which contains sodium hydroxide and has pH values in the range of 11·7 to 12·5. It was proved that repeated water washing of mud slurry gives an initial slight fall in pH value, but this remains generally above 10 as washing is continued. Analysis of the liquors showed that Na, Ca, Al and Si were being leached during further washing, suggesting that zeolitic-type calcium aluminate minerals precipitated during desilication are causing this buffering.[3]

The particle size distribution was obtained by means of an Elzone size analyser and is shown in Fig. 1 (differential and cumulative distributions). A rather uniform size distribution was observed; around 50% of the particles were found to have diameters below 40 μm (fines), while the other 50% were in the range between 40 and 160 μm. The finest mud fractions also contain most of the alkaline capacity of the mud.[3] The particle size distribution differs significantly among various samples, depending on the origin of the ore, and strongly influences the ease with which residue settles in water or compacts on land. Due to this size distribution, the specific surface area of red mud, determined by BET, was found to be 17 m^2 g^{-1}, i.e. rather low. The electrokinetic measurements of red mud dispersions were carried out

TABLE 1
Chemical Composition of the Red Mud Samples

Major constituent	*Content* (%)
Al_2O_3	16·94
Fe_2O_3	39·34
CaO	13·2
SiO_2	6·95
TiO_2	4·79

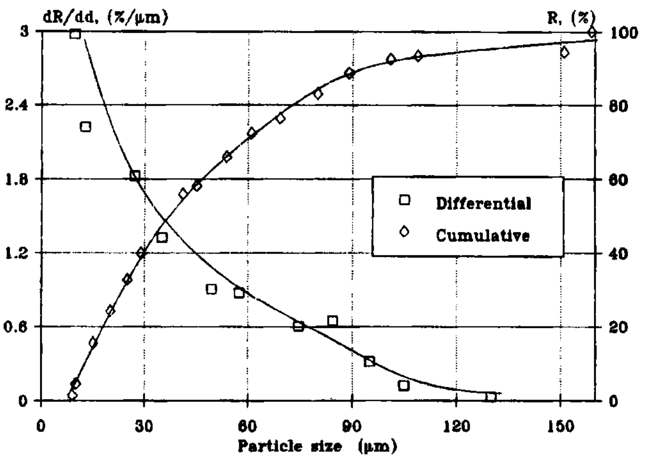

Fig. 1. Particle size distribution of the used red mud samples.

by means of a micro-electrophoretic apparatus (Rank Brothers, Mark II), using a flat cell.

The nickel removal capability of the red mud was assessed by using standard jar testing procedures. Stock solutions of nickel were prepared using $NiSO_4$ (Fluka, purum p.a.) using deionized water. One dm^3 of nickel solution, containing 50 mg dm^{-3} Ni(II)—unless otherwise stated, having an original pH around 5—was added to a beaker containing preweighed amounts of red mud. The dispersion was then stirred at 300 rpm in ambient temperatures (20–25°C), using a mechanical agitator and the pH was adjusted (if necessary) to the desired values by additions of sulphuric acid or sodium hydroxide solutions and it was continuously controlled. This stirring rate was found to be sufficient to thoroughly mix the contents of the beaker. During preliminary experiments a contact time of 600 s was found to be enough either for pH equilibration or for achieving the maximum nickel removal. The dispersion was then filtered by means of a G_4 Gooch glass crucible (with a mean pore diameter of 10–16 μm) and the resultant clear solution was assayed by standard AAS procedures in order to determine the remaining nickel concentration. The percentage removal (Re%) was calculated in the usual way.

The sedimentation experiments were carried out using 1 dm^3 of nickel/red mud dispersions, which were allowed to settle for appropriate time intervals. Ten cm^3 aliquots were then sucked from the liquid surface for the subsequent determination of the remaining nickel.

In the desorption investigations, 10 g of red mud were initially added to 1 dm^3 of a 1000 mg dm^{-3} nickel solution. The dispersion was then stirred (pH above 10), filtered and the resultant liquid was assayed for its nickel content. The obtained red mud, loaded with determined amounts of abstracted nickel, was subsequently dried. Appropriate amounts of the obtained material, were then redispersed in distilled water, pH was adjusted to the desired value and the dispersion was stirred similarly with the aforementioned conditions, before the determination of the released nickel.

RESULTS AND DISCUSSION

Nickel precipitation

Most toxic metals are usually removed via coprecipitation. Red mud has a high free-base content which can increase the pH of wastewater to a level where toxic metal hydroxides are easily precipitated, initially in the form of a fine colloidal dispersion. The process is induced by the formation of hydroxyl gels, due mainly to strongly hydrolysable species of dissolved aluminium or ferric ions, which display stronger tendencies for ionic adsorption. The particles then aggregate to form hydroxide flocs which enmesh the originally existing colloids. The entire process is usually referred to as 'sweep flocculation'.

The equilibrium pH values of the dispersions achieved in the presence of different red mud additions, are shown in Fig. 2. It becomes apparent that the addition of around 5 g dm^{-3} of red mud (or more) leads to the shift of pH towards the alkaline range (pH above 8), where nickel ion is precipitated as insoluble hydroxide. In the same figure the adsorbed concentration of nickel is also given. Almost total adsorption of the initial nickel concentration was reached, hence total nickel removal was obtained, for red mud additions higher than 7 g dm^{-3}. Additional pH measurements were carried out in the presence of increased nickel and red mud concentrations and are shown in Fig. 3. By the appropriate control of red mud addition, the pH value of the resultant dispersion could be maintained sufficiently alkaline, despite the relatively low initial concentrations of nickel.

Red mud, disposed in semi-solid form, entrains moisture with an alkalinity of 10–20 g dm^{-3} (expressed as

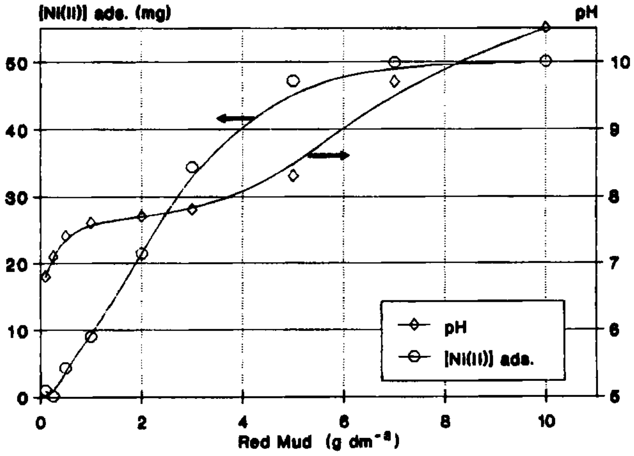

Fig. 2. Influence of red mud concentration on adsorbed nickel and the respective pH values of the dispersion.

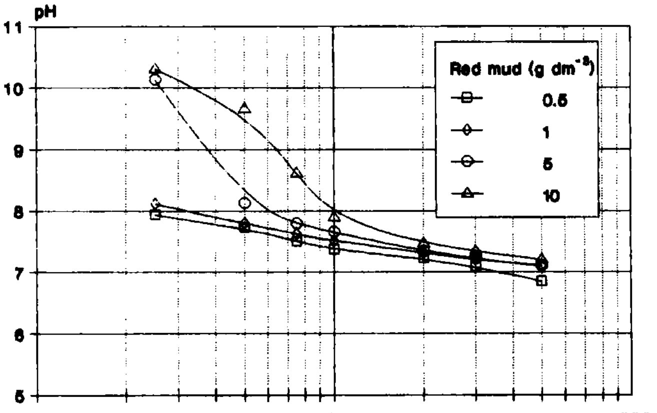

Fig. 3. Influence of nickel concentration on the resulting pH values of the red mud dispersion.

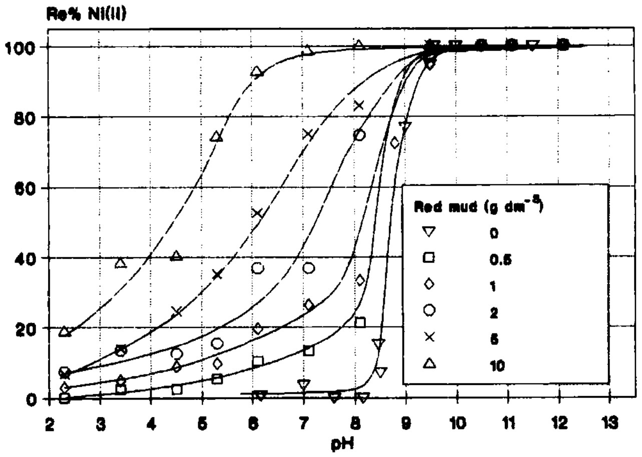

Fig. 4. pH influence on nickel removal, using different initial red mud concentrations.

Na$_2$CO$_3$). This is however not the only source of alkalinity as evidenced by repeated washings of the mud, which although it decreases the salinity of the mud does not greatly influence its high pH value. Red mud has a high cation exchange capacity and exchange sites are occupied by sodium, due to the use of sodium hydroxide in the bauxite refining process.[3] The presence of calcium carbonate in the mud, although very insoluble, provides some calcium cations, which are preferentially exchanged. This results in the formation of sodium carbonate in solution, giving a high pH value. Further calcium carbonate will dissolve and sodium carbonate will be formed until an equilibrium is reached, but the final pH is almost always above 9·5 when the red mud concentration in the dispersion is higher than 5% (w/v).

Effect of red mud as an adsorbent of the nickel hydroxide

Sometimes composite adsorbents prepared from solid wastes may be beneficial over a relatively wide pH range due to the diversity of the constituents, whereas pure coagulant chemicals can only function within a limited pH range. Natural waste adsorbents, like red mud, have physical and semi-chemical adsorption as their primary mode of action.[3] As well as metals removal through precipitation as hydroxides, these may also condense as uncharged hydroxides on the surfaces of oxide group adsorbents. The nickel removal in the presence of red mud in the whole pH range, is shown in Fig. 4. It can be observed that by increasing the concentration of the solid phase, the effective nickel removal is possible at progressively lower pH values than those required for precipitation of nickel ion in the absence of a solid phase.

In order to obtain more information about the interactions between red mud and nickel, ζ-potential measurements were performed. A characteristic reversal of the red mud ζ-potential sign, was observed in the presence of nickel ions in a pH range between 7 and 9 (Fig. 5). This reversal can be attributed to the specific adsorption of cationic nickel hydroxo-complexes, taking into consideration that the formation of these species is thermodynamically favourable in this pH range—see also Fig. 6, where a literature-based ionic equilibrium diagram of nickel species is presented.[25] It seems in this case, that red mud constitutes an adsorbent of the soluble cationic nickel hydroxo-complexes, following a well-defined mechanism characterized as 'surface precipitation'.[26,27] The point of ζ-potential reversal (pzr) observed in the absence of nickel, occurs at pH 6·7 (Fig. 5) and constitutes also the point of zero charge (pzc) of the red mud. In the presence of nickel ions an outer layer of adsorbed nickel hydroxo-species is formed, which leads to the change of the electrokinetic features of the underlying oxide surface.[28] The latter, therefore, behaves as nickel hydroxide; indeed, the pzc of precipitated nickel hydroxide was reported to be in the pH range between 9·2 and 10[29]—see also Fig. 5. Similar interactions were also detected in the case of copper ion adsorption onto pyrite surface.[30]

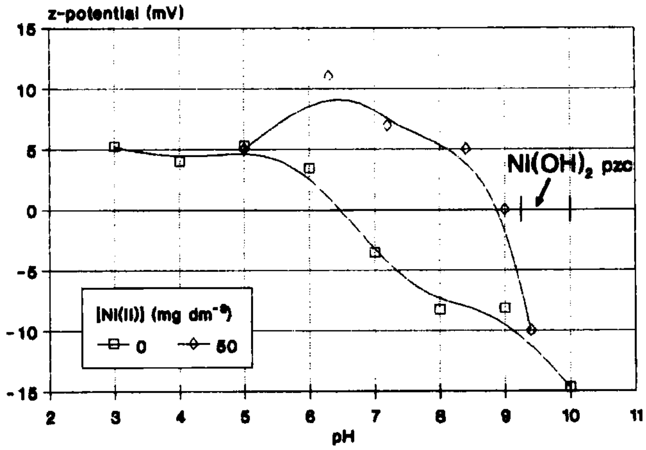

Fig. 5. ζ-potential of red mud (0·5 g dm^{-3}) as a function of the dispersion pH in the presence (50 mg dm^{-3}) and absence of nickel ions.

The effect of increased initial nickel concentration on nickel adsorption per unit of adsorbate, investigated at

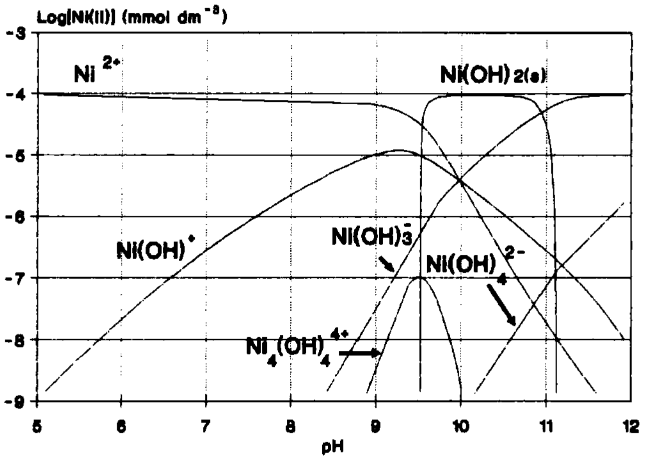

Fig. 6. Ionic species distribution diagram for the initial nickel concentration 50 mg dm^{-3}.

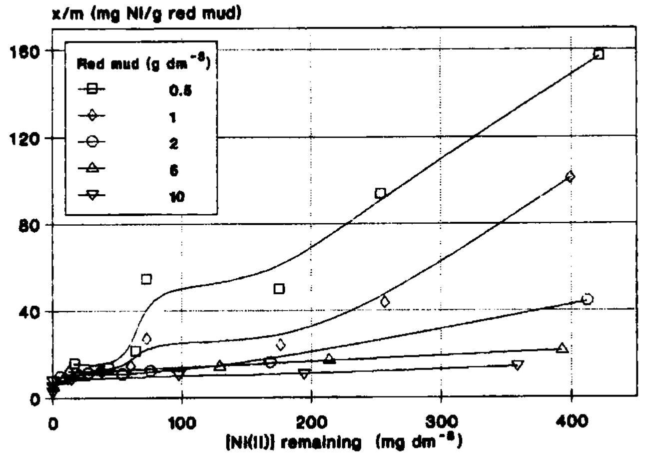

Fig. 7. Influence of initial nickel concentration on nickel adsorption per unit of adsorbate, using different red mud concentrations at the equilibrium pH of the dispersion—see Fig. 3.

the equilibrium pH of the system (see Fig. 3), i.e. without further pH regulation, against the remaining nickel concentration after 600 s contact time is shown in Fig. 7. It again becomes apparent that the appropriate addition of red mud leads to the effective removal of nickel ion, provided that the dispersion is sufficiently alkaline (pH above 8). Similar results were observed in Fig. 8, where the influence of initial red mud concentration at several pH values (constant for each experimental series), is presented. In Table 2 a comparison between the removal efficiencies of several toxic metals (Ni, Pb, Cu, Cd) using red mud is given.

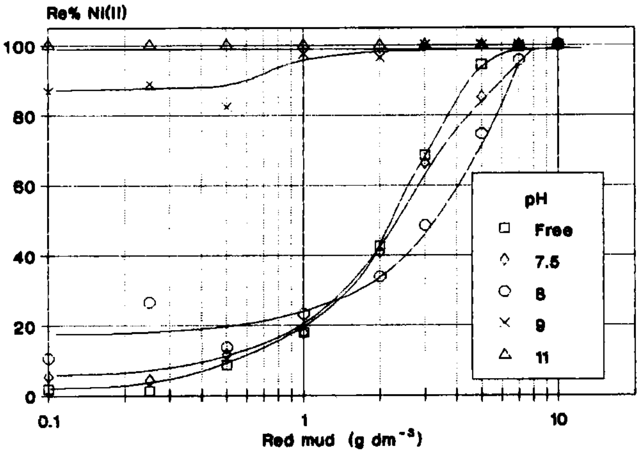

Fig. 8. Influence of red mud concentration on nickel removal, at different dispersion pH values (constant for each experimental series).

Effect of red mud as a flocculant

Besides sweep flocculation, hydrolysable aluminium and ferric ions can cause flocculation by specific adsorption of hydrolytic products. In spite of their decreased charge, hydrolysed metal ions may be more effective flocculants. The multi-nuclear hydrolysis products, formed as kinetic intermediates, such as $Fe_2(OH)_4^{2+}$, $Fe_3(OH)_4^{5+}$, $Al_4(OH)_8^{4+}$ and $Al_8(OH)_{20}^{4+}$, are even more effective flocculants than their parent ions, due to their higher charge and strong specific adsorptivities. However, higher sludge volumes are produced when red mud is used, in comparison with other (more conventional) flocculants, like alum.

As is shown in Fig. 9(a), red mud may act as an effective flocculant of the hydrolysed nickel species, formed at pH 8. Addition of red mud in the order of 5 g dm^{-3} was found sufficient for high nickel removal (over 90%) and rapid sedimentation of the nickel hydroxide, within a retention time as low as 0·6 ks.

TABLE 2
Use of Red Mud for Toxic Metals Removal—Comparison with Literature Data[10]

Conditions	*Removal efficiency*
Red mud: 0·5–2 g dm^{-3}, contact time: 10 min	
Ni(II): 25–50 mg dm^{-3}	10–15mg g^{-1} red mud
Red mud: 10 g dm^{-3}, contact time: 5 h	
Pb(II): 25–45 mg dm^{-3}	10–14 mg g^{-1} red mud
Cu(II): 5–25 mg dm^{-3}	Higher than 7 mg g^{-1} red mud
Cd(II): 5–25 mg dm^{-3}	Higher than 5 mg g^{-1} red mud

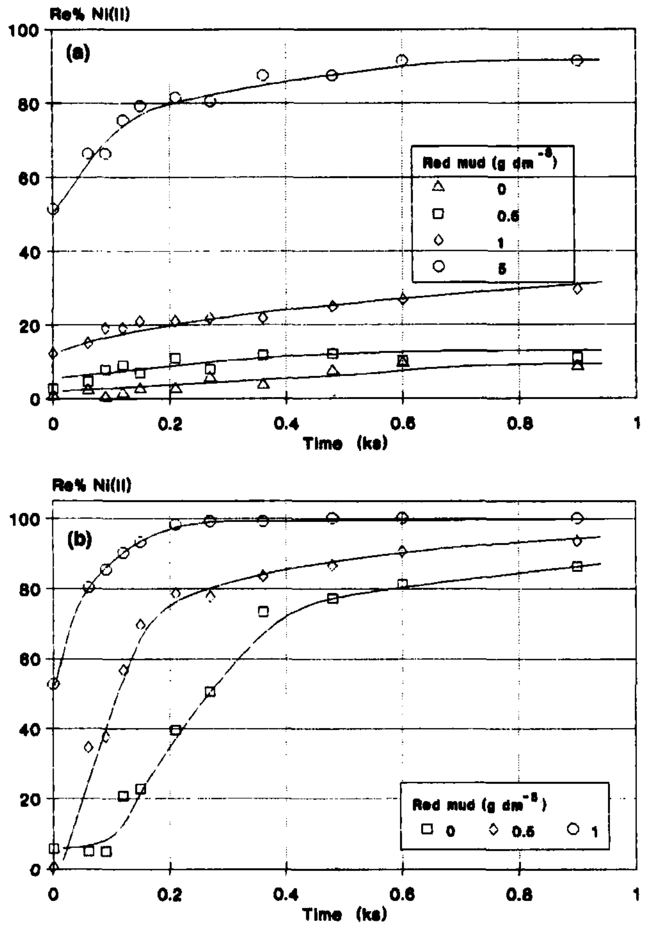

Fig. 9. Influence of sedimentation time on nickel removal, using different red mud concentrations, at pH values (constant) of (a) 8 and (b) 11.

Lower red mud concentrations (1 g dm^{-3}) aids substantially nickel hydroxide sedimentation, but at higher pH values (11—Fig. 9(b)). These results are considered to be very promising, since similar effective removals were reported to be obtained when lime precipitation (pH 11·5) was used, followed by sedimentation and additional filtration, but retention times of the order of 6 h were required for this purpose.[17] Red mud produced a good settling floc, leaving a relatively clear supernatant. This indicates that it was capable of enhancing suspended solids removal, as has also been demonstrated in the literature.[31-33]

Desorption studies

After the adsorption and sedimentation step, the resulting nickel-bearing sludge should be safely deposited. The stability of this sludge, from the point of view of nickel resolubilization, was studied and the results are shown in Fig. 10. It is apparent that partial desorption of nickel is possible only in acidic media (pH lower than 5). When the pH was maintained above 5, as is the usual case of an environment rich in red mud, desorption of nickel was not observed. Leaching tests following addition of acidic gypsum to red mud (up to 11% w/w of the red mud), showed that it was not possible for the pH of the mixture to be reduced below 8·3, which is the usual pH of calcareous soils or the pH of $CaCO_3$ in equilibrium with atmospheric CO_2, while at the same time the leaching of Al, Fe, and Cd from the red mud/gypsum mixture was negligible.[34]

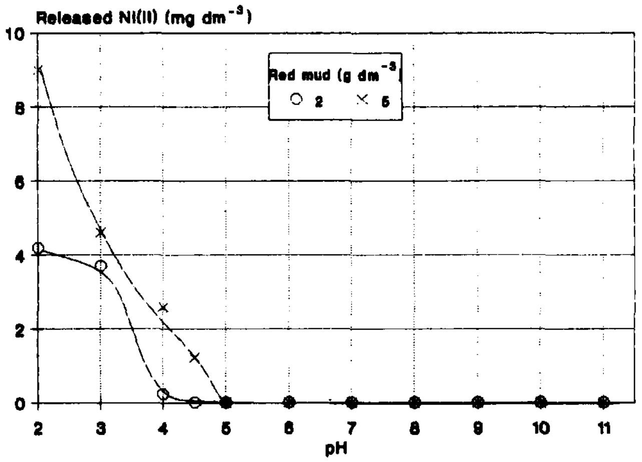

Fig. 10. pH influence on the release of nickel from nickel-bearing red mud, using two different initial red mud concentrations.

CONCLUSIONS

In the present work a simple, fast and promising method for the treatment of toxic metal cations-bearing wastewaters is suggested. The appropriate addition of red mud was found to lead to the almost complete removal of nickel ions and it was found to be an effective scavenger for these ions, causing the precipitation of nickel as insoluble hydroxide, adsorbing nickel hydroxo-complexes and aiding the flocculation/sedimentation of the aforementioned species. For 50 mg dm^{-3} initial nickel concentration, red mud dosage levels required to achieve a remaining nickel concentration lower than 1 mg dm^{-3}, at the equilibrium pH of the red mud dispersion, are of the order of 7 g dm^{-3}. The stability of the obtained sludge was found to be high, permitting its safe co-disposal in red mud stabilization ponds.

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REFERENCES

1. Goodman, G. T. & Chadwick, M. J., *Environmental Management of Mineral Wastes*. Sijthoff and Noordhoff, USA, 1978.

2. Zouboulis, A. I., Kydros, K. A. & Matis, K. A., Separation of metal ions by flotation: application of industrial solid wastes. Presented at the Inter. Symp., Particles Separation from Wastewaters, IAWQ, London (Sept. 10–12 1992). *Water Sci. & Tech.*, **27**(10) (1993) in press.
3. Wagh, A. R. & Desai, P. (eds), *Bauxite Tailings*, Proceedings of Inter. Conf. (Oct. 26–31 1986), The Jamaica Bauxite Inst., Kingston, 1988.
4. Spathis, P. K. & Zouboulis, A. I., Disposal of solid industrial wastes in Greece. In *Proceedings, 2nd Nat. Tech. Conf., Greek Mineral Wealth*, Tech. Chamber of Greece, Athens (Mar. 30–Apr. 4 1987), pp. 113–26 (in Greek).
5. Ho, G. E., Overcoming the salinity and sodicity of red mud for rehabilitation and reuse. *Proceedings, 43rd Purdue Industrial Waste Conf.*, Lewis, Chelsea, MI, 1989, pp. 641–9.
6. Glenister, D. J. & Thornber, M. M., Alkalinity of red mud and its application for the management of acid wastes. *Proceedings, 13th Austr. Chem. Eng. Conf.*, Aus. Inst. Chem. Eng., Australia, 1985, pp. 109–13.
7. Pincus, A. G., Wastes from processing of aluminium ores. *Proceedings, 1st Mineral Waste Utilization Symp.*, Bureau of Mines, USA (March 27–28 1968), pp. 40–9.
8. Shannon, E. E. & Verghese, K. I., Utilisation of aluminized red mud for phosphorus removal. *J. WPCF*, **48** (1976) 1948–54.
9. Siao, S. J. & Akashi, K., Phosphate removal from aqueous solutions by activated red mud. *J. WPCF*, **49** (1977) 280–5.
10. Arak, V. & Unseren, E., Treatment of wastewater and effluents with solid industrial wastes for the adsorptive removal of heavy metal contaminants. In *Flocculation in Biotechnology and Separation Systems*, ed. Y. A. Attia. Elsevier, Amsterdam, 1987, pp. 765–71.
11. Agency of Industrial Sciences and Technology, Arsenic adsorbent, Jpn. Kokai Tokkyo Koho, Patent No. 80 132633, 1980, 3 pp. (in Japanese) (*Chem. Abstr.*, **94**(10) (1981) 070821).
12. Shimizu, S. & Ishii, T., Treatment of chromium-containing waste. Jpn. Kokai Tokkyo Koho, Patent No. 79 62168, 1979, 2 pp. (in Japanese) (*Chem. Abstr.*, **91**(14) (1979) 112087).
13. Sanga, S., Removal of heavy metals from wastewater. Jpn. Kokai Tokkyo Koho, Patent No. 75 01560, 1975, 3 pp. (in Japanese) (*Chem. Abstr.*, **83**(02) (1975) 015292).
14. Couillard, D., Use of red mud, a residue of alumina production by the Bayer process, in water treatment. *Sci. Total Environ.*, **25** (1982) 181–91.
15. Ho, G. E., Gibbs, R. A. & Mathew, K., Bacteria and virus removal from secondary effluent in sand and red mud columns. *Water Sci. & Tech.*, **23** (1991) 261–70.
16. Sittig, M. (ed.), *Environmental Sources and Emissions Handbook*. Noyes Data Corp., N. Jersey, USA, 1975, pp. 97–104.
17. Patterson, J. W., *Industrial Wastewater Treatment Technology*. Butterworth, Boston, USA, 1985, pp. 217–31.
18. Bhattacharyya, D. & Cheng, C. Y. R., Activated carbon adsorption of heavy metal chelates from single and multicomponent systems. *Envir. Progress*, **6** (1987) 110–18.
19. Sharma, Y. C., Gupta, G. S., Prasad, G. & Rupainwar, D. C., Use of wollastonite in the removal of Ni(II) from aqueous solutions. *Water, Air, and Soil Pollution*, **49** (1990) 69–79.
20. Fuerstenau, D. W. & Osseo-Asare, K., Adsorption of copper, nickel and cobalt by oxide adsorbents from aqueous ammoniacal solutions. *J. Coll. & Interf. Sci.*, **118** (1987) 524–42.
21. Bowers, A. R. & Huang, C. P., Adsorption characteristics of metal–EDTA complexes onto hydrous oxides, *J. Coll. & Interf. Sci.*, **110** (1986) 575–90.
22. Laitinen, H. A. & Zhou, H., Characteristic adsorption of Ni(II) on MnO_2. *J. Coll. & Interf. Sci.*, **125** (1988) 45–50.
23. Zouboulis, A. I. & Mavros, P., Use of fly ash for the removal of nickel ions from waste waters. *Fresenius Envir. Bull.*, **1** (1992) 457–62.
24. Salim, R., Removal of nickel (II) from water using decaying leaves—effects of pH and type of leaves. *J. Environ. Sci. Health*, **A23** (1988) 183–97.
25. Baes, C. F. & Mesmer, R. E., *The Hydrolysis of Cations*, J. Wiley, New York, 1976, pp. 241–7.
26. Farley, K. J., Dzombak, D. A. & Morel, F. M., A surface precipitation model for the sorption of cations on metal oxides. *J. Coll. & Interf. Sci.*, **106** (1985) 226–42.
27. Theis, T. L. & Richter, R. O., Adsorption reactions of nickel species at oxide surfaces. In *Particulates in Water: Characterization, Fate, Effects and Removal*, eds. M. C. Kavanaugh & J. O. Leckie. Adv. in Chemistry Series Vol. 189, ACS, Washington, 1980, pp. 73–96.
28. Hunder, R. J., *Zeta Potential in Colloid Science—Principles and Applications*. Academic Press, New York, 1981, pp. 326–8.
29. Pravdic', V. & Bonacci, N., Electrokinetic studies on colloidal and precipitated nickel hydroxide. In *Colloid and Interface Science. Vol. IV: Hydrosols and Rheology*, ed. M. Kerker. Academic Press, New York, 1976, pp. 197–209.
30. Zouboulis, A. I., Kydros, K. A. & Matis, K. A., Adsorbing flotation of copper hydroxo-precipitates by pyrite fines. *Separ. Sci. & Tech.*, **27** (1992) 2143–55.
31. Ishikawa, H. & Yamakoshi, M., Flocculation treatment of wastewater from pulp manufacture. Jpn. Kokai Tokkyo Koho, Patent No. 76 56562, 1976, 4 pp. (in Japanese) (*Chem. Abstr.*, **85**(20) (1976) 148668).
32. Terui, A., Preparation of a flocculant from red mud. Jpn. Kokai Tokkyo Koho, Patent No. 75 73886, 1975, 3 pp. (in Japanese) (*Chem. Abstr.*, **83**(26) (1975) 209276).
33. Bayer, G. & Cherdron, E., Red mud flocculant for wastewater treatment. Ger. Offen., Patent No. 2242811, 1974, 9 pp. (in German) (*Chem. Abstr.*, **81**(02) (1974) 006109).
34. Ho, G. E., Mathew, K. & Newman, P. W. G., Leachate quality from gypsum neutralized red mud applied to sandy soils. *Water, Air and Soil Poll.*, **47** (1989) 1–18.