Clays and Clay Minerals, Vol. 52, No. 5, 650–656, 2004.

EFFECTS OF γ RADIATION ON CHROMATE IMMOBILIZATION BY CALCINED HYDROTALCITES

SONIA MARTINEZ-GALLEGOS[1,2] AND SILVIA BULBULIAN[1,*]

[1] Instituto Nacional de Investigaciones Nucleares, A.P.18-1027, Col. Escandón, Delegación Miguel Hidalgo, C.P. 11801, México D.F.

[2] Facultad de Ciencias, Universidad Autónoma del Estado de México, Instituto Literario no. 100 Col. Centro, Toluca, Edo. de México, C.P. 50000

Abstract—The ability of hydrotalcites to retain anionic wastes was studied. In particular, Cr(VI)-adsorbed hydrotalcites were heated to immobilize Cr(VI) in the solid sample. When the heating temperature increased up to 500ºC, the lamellar structure of hydrotalcite was lost. At high temperatures (1200ºC), the solids were recrystallized in the form of a spinel. Lixiviation with 1 N and 5 N NaCl solutions were utilized to simulate the effect of sea water and of concentrated NaCl solutions in salt mines on the immobilization of Cr. Radiation damage on the solid containing the immobilized Cr was studied by γ-irradiating with a ^{60}Co source at 1000 and 6000 kGy. The Cr-containing samples heated at 1200ºC, whether irradiated or not, safely immobilized Cr in the hydrotalcite mainly in the form of $MgCr_2O_4$ spinel. Irradiation of hydrotalcites revealed two different effects: (1) samples heated up to 1200ºC evolved as a solid in which chromium was retained more firmly than in the non-irradiated material, irradiation enhancing the spinel formation; (2) the structure of samples heated at 1200ºC developed a preferential crystallite orientation rather than a purely random one or new location of chromium ions, this effect did not affect Cr immobilization in the solid. Chromium lixiviation with 5 N NaCl solution was always less than the corresponding value with 1 N NaCl solution, probably due to the poor mobility of Cl^- ions in the highly concentrated NaCl solution.

Key Words—Chromium Immobilization, Gamma Irradiation Effects, Hydrotalcite, Mg-Cr Spinel.

INTRODUCTION

The production of nuclear fuel and subsequent generation of electricity result in the formation of a substantial amount of radioactive waste, the safe treatment and disposal of which are complex problems. Radioactive wastes were originally immobilized and sealed in barrels and then deposited in sea water. Some are actually stored in salt mines (Yui *et al*., 2003). As has been discussed in previous papers, zeolites may retain radioactive cations from aqueous solutions (Bosch *et al*., 1995), the use of vitrification in order to immobilize these cations in solids has also been widely reported (Thamzil, 1997). Immobilization of radioactive cations in vitrified material was studied through lixiviation by using NaCl solutions (Földeslová *et al*., 1996; Bulbulian and Bosch, 2000); however, there are not as many research projects dealing with the immobilization of anions in solids. Although organic resins have been applied to remove anionic species from radioactive wastewaters, they are not recommended for practical application because of their radiolytic decomposition (O'Dwyer *et al*., 1995). As an alternative, Mg-Al layered double hydroxides, also referred to in this paper as hydrotalcite or HT-Al, have been proposed. They consist of a brucite-like network in which the divalent cations are partially substituted by trivalent ones. In the brucite-like sheets, each cation is octahedrally surrounded by hydroxyl radicals, the octahedra sharing edges to form two-dimensional sheets which carry an excess of positive charge due to the presence of M^{3+}; this is balanced, however, by interlayer anions and water molecules which bind the sheets together (Labajos and Rives, 1996; Châtelet *et al*., 1996; Hibino and Tsunashima, 1998; Ulibarri *et al*., 2001).

In the literature there are extensive discussions about the properties of hydrotalcites, which are known to decompose to Mg-Al oxide solid-solution upon heating at 500–800ºC, Al^{3+} in the structure remaining inside the MgO formed (Miyata, 1980). The resulting oxides readily rehydrate and adsorb anions to reconstruct the original hydrotalcite structure. Therefore, both hydrotalcite and Mg-Al oxide solid-solution are expected to find application in the uptake of anions from aqueous solutions (Hibino *et al*., 1999; Sato *et al*., 1988). Hydrotalcite decomposes above 1000ºC to Mg-Al oxide solid-solution and $MgAl_2O_4$ (spinel) which shows no capacity to take up anions. The general formula of spinels, AB_2O_4, embraces a wide variety of A and B atoms. The valences of A and B may be 2 and 3 as in $MgAl_2O_4$ (Rao and Gopalakrishnan, 1997).

Goswamee *et al*. (1998) investigated the adsorption of Cr(VI) by various uncalcined and calcined layered double hydroxides to examine the effect of calcination

* E-mail address of corresponding author: sb@nuclear.inin.mx

DOI: 10.1346/CCMN.2004.0520511

for 30 min on Cr release from the Cr(VI)-adsorbed Mg-Al layered double hydroxides. Chromium adsorption (2.26 meq/g) was achieved by rehydrating calcined hydrotalcites in 0.03 N $K_2Cr_2O_7$ aqueous solution. Chromium release was determined with aqueous solutions containing CO_3^{2-} and Cl^- . Goswamee *et al.* (1998) found that $Cr_2O_7^{2-}$-adsorbed Mg-Al-layered double hydroxide, calcined up to 1250ºC, resulted in the formation of MgO and $MgAl_2O_4$ as the predominant phases along with some other unidentified minor phases, and that this process did not immobilize the Cr in the solid-state structure. Labajos and Rives (1996), having prepared hydrotalcite-like compounds containing Mg(II) and Cr(III) or Ni(II) and Cr(III) by the coprecipitacion method, found that calcination at high temperatures leads to the formation of $MgCr_2O_4$ spinel. Châtelet *et al.* (1996) studied the competition between monovalent anions such as Cl^- and divalent anions such as CrO_4^{2-} for calcined and uncalcined hydrotalcites. They found, for divalent anions, the presence of two kinds of anion retention sites in hydrotalcite: sites within the interlayer region corresponding to the structured anion exchange capacity of the material and adsorption onto external surfaces; in the particular case of CrO_4^{2-} they found that adsorption <2.1 meq/g indicates an exchange mechanism in the interlayer region, and adsorption >2.1 meq/g corresponds to anions retained on external surface sites.

Based on the research indicated in the literature (Châtelet *et al.*, 1996; Labajos and Rives, 1996; Goswamee *et al.*, 1998), Cr(VI)-adsorbed hydrotalcites were chosen to perform this study. Samples were heated at various temperatures to examine the immobilization of Cr. The irradiation effect of radioactive wastes was simulated through irradiation with ^{60}Co γ. Lixiviation with 1 N and 5 N NaCl solutions was utilized to simulate the effect of sea water and of concentrated NaCl solutions in salt mines on the immobilization of Cr in the studied samples.

MATERIALS AND METHODS

Commercial, analytical-grade reagents were used without further purification. Hydrotalcite synthetic powder, with the general formula $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ was prepared, with a Mg:Al = 3 ratio, as described previously by Sato *et al.* (1988): 1000 mL of 0.25 mol/L $AlCl_3$ and 0.75 mol/L $MgCl_2{\cdot}6H_2O$ aqueous solutions were added dropwise to 1000 mL of 0.5 mol/L Na_2CO_3 and 2.5 mol/L NaOH under vigorous stirring. Both solutions were previously heated and maintained at 60ºC during the stirring. Once produced, hydrotalcite was separated by filtration and then washed by dialysis with deionized water until no chloride was detected. The hydrotalcite was dried at room temperature in an open dish for 5 days and then again at 80ºC in air for 3 h and crushed in an agate mortar. This product was destroyed by heating at 500ºC producing a calcined HT-Al. In the present case, 15.5 g of this calcined hydrotalcite were recrystallized as HT by the addition of 400 mL of 0.17 N ammonium chromate solution at room temperature. The mixtures were shaken for 24 h and the solids were separated by centrifugation. They were then washed with deionized water.

Chromium(VI)-adsorbed hydrotalcite is also referred to in this paper as HT-Cr. Heated and γ-irradiated samples were characterized and tested for Cr(VI) desorption when shaken with 1 N and 5 N NaCl solution for 2 h. Solids and liquids were separated by centrifugation and the Cr present in the NaCl solution was analyzed by neutron activation by irradiating the samples in a TRIGA MARK III nuclear reactor for 30 min, with an approximate neutron flux of 10^{12}n/cm^{2}s. The 320 keV photopeak from ^{51}Cr produced by the nuclear reaction $^{50}Cr(n,\gamma)^{51}Cr$ was measured with a Ge/hyperpure solid-state detector coupled to a computerized 4096 channel pulse height analyzer.

The HT-Cr samples were heated for 3 h at 500, 600, 800, 1000 and 1200ºC. They are referred to, in this paper, according to their heating temperature, *e.g.* sample HT-Al-1200, refers to the HT-Al sample heated at 1200ºC. Some samples were γ irradiated in an Industrial Irradiator JS6500 of ^{60}Co γ-beam at 1000 or 6000 kGy; these doses were chosen, based on previous experiences with Co-zeolite vitrification (Bulbulian and Bosch, 2000).

X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using CuKα radiation. Crystalline compounds were identified conventionally using JCPDS files. Spinel ($MgAl_2O_4$, $MgCr_2O_4$) and MgO diffraction peaks were marked with s or o respectively.

Infrared (IR) spectra of samples in KBr pellets were recorded in the range 400–4000 cm^{-1} using a Nicolet Magna-IR spectrometer.

RESULTS AND DISCUSSION

Cr content

The neutron activation analysis of Cr showed that under the present experimental conditions, Cr(VI) adsorption in the calcined HT sample was 3.2 meq/g. After calcination, the color of HT-Cr samples changed permanently from yellow to green when heated at 500–800ºC and to red when heated at 1000–1200ºC.

X-ray diffraction

The XRD patterns of HT-Al, HT-Cr and γ-irradiated HT-Cr samples unheated, and heated at 500 and 600ºC are similar to those reported in the literature (Hibino *et al.*, 1999), thus showing that HT-Al and HT-Cr decompose with increasing temperature, forming a Mg-Al and/or Cr oxide solid-solution which is proven by the change of color of the sample from yellow to green.

When heated at 800°C, the γ-irradiated HT-Al sample (Figure 1) forms both an oxide solid-solution (JCPDS file 45-0946) and a small amount of Mg-Al spinel. In Figure 1 the intensities of the s(311) reflections of the HT-Al sample at 37.105°2θ and 35.805°2θ possibly indicate $MgAl_2O_4$ spinels described by JCPDS files 21-1152 and 21-0540. The HT-Cr-800 sample displays only one s(311) diffraction peak at 36.38°2θ.

At 1200°C (Figure 2), HT-Al forms MgO (JCPDS 45-0946) and $MgAl_2O_4$ spinel (JCPDS 21-1152). However, the Cr(VI)-adsorbed hydrotalcite (HT-Cr) resulted in the formation of MgO and $MgCr_2O_4$ (JCPDS 10-0351) as the predominant phases along with a minor amount of $MgAl_2O_4$. The disagreement between the results obtained by Goswamee *et al.* (1998) who suggested that Cr(VI)-adsorbed Mg-Al-layered double hydroxide, calcined up to 1250°C resulted in the formation of MgO and $MgAl_2O_4$ and those obtained in the present paper may be due to the following: (1) different Mg:Al content in the hydrotalcites: 2.2 and 3 respectively; (2) different Cr(VI) aqueous solution to rehydrate calcined hydrotalcite, 0.03 N $K_2Cr_2O_7$ and 0.17 N $(NH_4)_2CrO_4$ solutions; (3) distribution of Cr(VI) in different sites, mainly within the interlayer region in samples prepared by Goswamee *et al.* (1998) and in samples prepared in the present paper, within sites in the interlayer region and on the external surface of hydrotalcite (Châtelet *et al.*, 1996); and (4) different heating periods for the HT-Cr samples of 0.5 and 3 h, respectively.

As a consequence of the different materials obtained, Goswamee *et al.* (1998) reported Cr adsorption of 2.26 meq/g which for $Cr_2O_7^{2-}$ is 2.26 mmol of Cr/g. In the current paper, Cr(VI) adsorption was found to be 3.2 meq/g which for CrO_4^{2-} is 1.6 mmol/g. Therefore, a significantly larger amount of Cr was absorbed in the material prepared by Goswamee *et al.* (1998). On the other hand Cr(VI) was distributed differently in hydrotalcites, within interlayer sites and in the external surface sites. The results of both papers show that the heating of hydrotalcites which contain more Cr does not necessarily induce $MgCr_2O_4$ spinel formation. It is probably formed due to the long heating periods (3 h) at high temperatures and/or to Cr(VI) adsorbed in the external surface sites of hydrotalcites.

The relative content of the spinel structure and MgO was estimated from the areas under the diffraction peaks. Since no internal standard was introduced, the X-ray absorption for each compound was assumed to be the

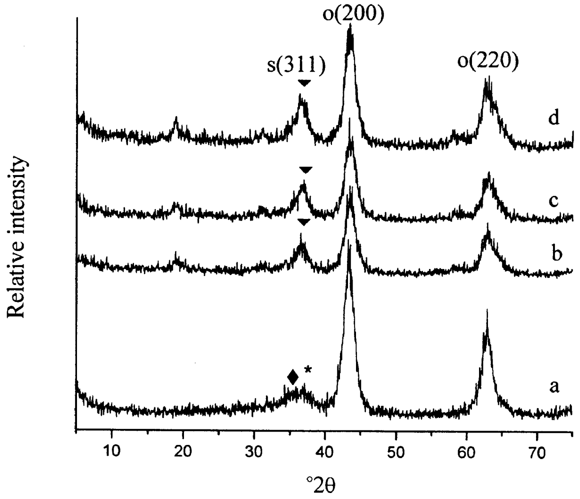

Figure 1. XRD patterns of samples: (a) HT-Al-800, (b) HT-Cr-800, (c) HT-Cr-800 γ-irradiated at 1000 kGy, and (d) HT-Cr-800 γ-irradiated at 6000 kGy; s = spinel, o = MgO, (*) $MgAl_2O_4$ spinel (JCPDS 21-1152), (◆) $MgAl_2O_4$ spinel (JCPDS 21-0540).

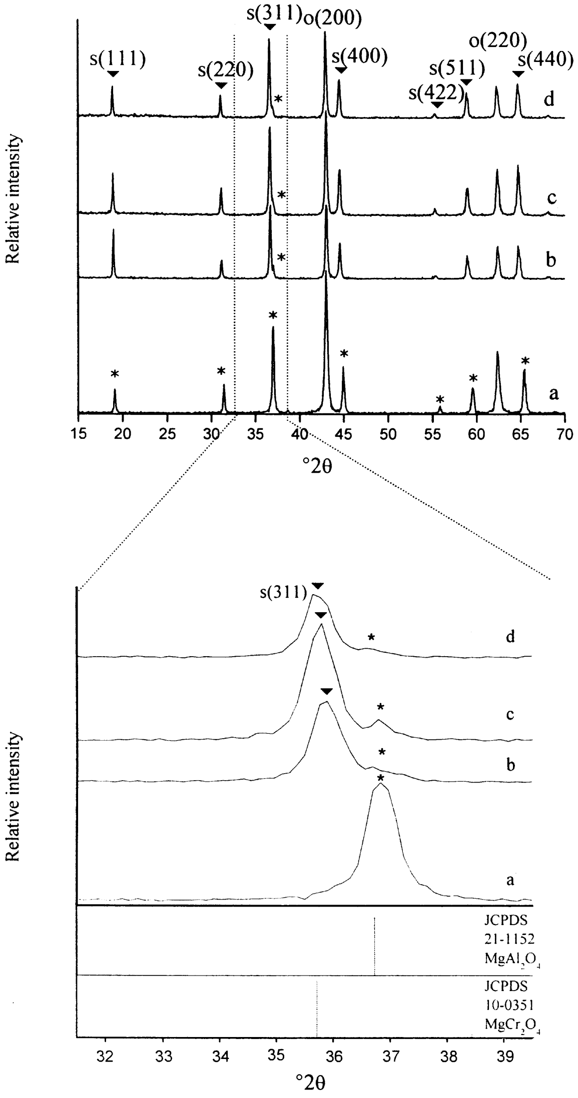

Figure 2. XRD patterns of samples: (a) HT-Al-1200, (b) HT-Cr-1200, (c) HT-Cr-1200 γ-irradiated at 1000 kGy, and (d) HT-Cr-1200 γ-irradiated at 6000 kGy; s = spinel, o = MgO; (*) $MgAl_2O_4$ spinel (JCPDS 21-1152), (▼) $MgCr_2O_4$ spinel (JCPDS 10-0351).

Table 1. Ratio of the integrated intensity s(311)/o(200) for samples heated at 800ºC, non-irradiated and γ-irradiated at 1000 or 6000 kGy.

Samples	HT-Al-800	HT-Cr-800	HT-Cr-800 1000 kGy	HT-Cr-800 6000 kGy
s(311)/o(200)	0.11	0.29	0.33	0.38

same. Only the most intense peaks of the spinel [s(311)] and magnesium oxide [(o(200)] were considered. The ratio of the integrated intensities of the s(311)/o(200) shows, in samples heated at 800ºC (Table 1), an increase from HT-Al (0.11) to HT-Cr (0.29) that can be explained by the greater electron density of Cr. Furthermore, a second and a third increase are also shown, first in the HT-Cr-800 sample irradiated at 1000 kGy (0.33) and then in the HT-Cr-800 sample irradiated at 6000 kGy (0.38).

Table 2 shows that the increase of the ratios of the integrated intensities s(311)/o(200) of HT-Cr-1200 as a consequence of γ-radiation is more moderate than those observed for samples heated at 800ºC. Once a large amount of $MgCr_2O_4$ has been formed during calcination at 1200ºC, γ-radiation slowly increases the amount of spinel-structure formed. Results given in Tables 1 and 2 reveal that γ-radiation enhances the amount of spinel structure in samples heated up to 1200ºC.

Figure 2 shows some large differences in the relative intensities of the s(220) and s(111) spinel reflections. The ratios of the integrated spinel intensities s(220)/s(111) are shown in Table 3. The differences between the HT-Al and HT-Cr samples can be explained by the different spinels they form. On the other hand, the ratio of the integrated spinel intensities s(220)/s(111) increases from 0.51 for HT-Cr-1200 to 0.66 for 1000 kGy irradiated HT-Cr-1200 and to 0.72 for 6000 kGy irradiated HT-Cr-1200 (Table 3), revealing non-uniform intensities which, in turn, show that the structure of the solid has been modified. There are two possibilities that can explain this modification: the first one is to consider that γ-radiation leads to the development of orientation texture by high temperatures produced during the irradiation process, *i.e.* the material may attain a preferential crystallite orientation rather than a purely random one, changing the solid from a specimen whose crystallites are randomly oriented to asymmetric crystallites, oriented preferentially. The second possibility that can explain the modification in the solids is that defect centers formed in the irradiated material promote the mobility of Cr, changing its population in some planes and developing new locations of Cr ions. These results are similar to those observed in the crystalline rocks and minerals which develop orientation texture in crystallizing from the melt and/or from mechanical operations such as stretching which also increases the orientation effects (Klug and Alexander, 1974).

Table 2. Ratio of the integrated intensity s(311)/o(200) for samples heated at 1200ºC, non-irradiated and γ-irradiated at 1000 or 6000 kGy.

Samples	HT-Al-1200	HT-Cr-1200	HT-Cr-1200 1000 kGy	HT-Cr-1200 6000 kGy
s(311)/ o(200)	0.59	0.74	0.75	0.78

Table 3. Ratio of the integrated intensity s(220)/s(111) HT-Al and HT-Cr samples for samples heated at 1200ºC, non-irradiated and γ-irradiated.

Samples	HT-Al-1200	HT-Cr-1200	HT-Cr-1200 1000 kGy	HT-Cr-1200 6000 kGy
s(220)/ s(111)	1.51	0.51	0.66	0.72

IR spectroscopy

Figure 3 shows the IR spectra of the HT-Al, HT-Cr and γ-irradiated HT-Cr samples, the broad band at 3442–3467 cm^{-1} resulting from an overlapping of hydrogen vibrations: stretching vibrations of structural OH^- physically adsorbed water and vibrations of OH^- bonded with carbonate ions in Mg and Al environments. The low-intensity band at 1637–1639 cm^{-1} is assigned to bending vibrations of strongly adsorbed water (solvation water of compensating anions). Carbonate ions are observed at ν_3, 1350–1380 cm^{-1}; ν_2, 850–880 cm^{-1} and ν_4, 670–690 cm^{-1} (Nakamoto, 1978). In the present paper, only ν_3, 1359–1389 cm^{-1} and ν_4, 603–636 cm^{-1} are clearly distinguished. In HT-Cr samples a new band appears at 885 cm^{-1}, which, according to Nakamoto (1978), can be assigned to the chromate ion.

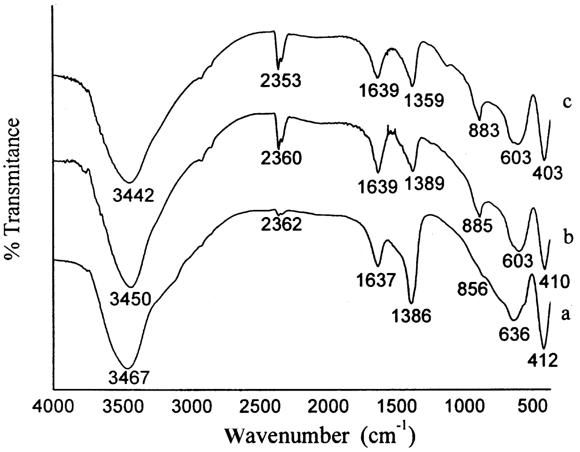

Figure 3. IR spectra of non-heated samples (a) HT-Al, (b) HT-Cr, and (c) HT-Cr γ-irradiated at 6000 kGy.

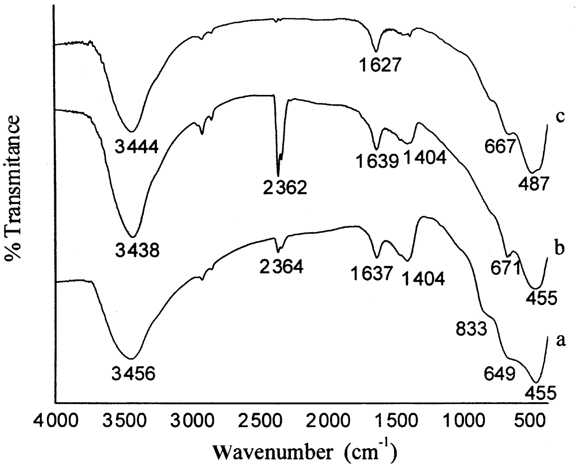

Figure 4. IR spectra of samples: (a) HT-Al-800, (b) HT-Cr-800, and (c) HT-Cr-800 γ-irradiated at 6000 kGy.

Figure 4 shows the IR spectra of oxide solid-solutions produced by calcining HT-Al, HT-Cr-800 and γ-irradiated HT-Cr-800 samples. The chromate ion-vibration band disappears in samples heated at 800°C, showing that Cr(VI) is reduced by heating, as already proven by the change of color of the HT-Cr-800 sample. The presence of the CO_3^{2-} main vibration band (1404 cm^{-1}) in samples HT-Cr-800 and irradiated HT-Cr-800 is less intense, as expected, than in sample HT-Al-800.

Figure 5 shows the IR spectra of HT-Al-1200, HT-Cr-1200 and γ-irradiated HT-Cr-1200. ν_3 IR CO_3^{2-}, the main vibration band (1404–1431 cm^{-1}), is present mainly in the calcined HT-Al-1200 sample but not in the γ-irradiated HT-Cr-1200 samples that display a very weak CO_3^{2-} main vibration band showing that γ-irradiation decomposes CO_3^{2-} ions. Infrared spectroscopy spinel bands were reported by Ross (1972), 690 and 538 cm^{-1} for $MgAl_2O_4$ and 645 and 535 cm^{-1} for $MgCr_2O_4$. The characteristic spinel IR vibration bands of the HT-Al-1200 sample are not shown because they are probably hidden under the CO_3^{2-} vibration bands; however, in the HT-Cr-1200 γ-irradiated (6000 kGy) sample, CO_3^{2-} vibration bands are weak and $MgCr_2O_4$ bands at 663–675 cm^{-1} and 507–511 cm^{-1} can be clearly observed. These values are similar to those reported by Ross (1972) for spinel structures.

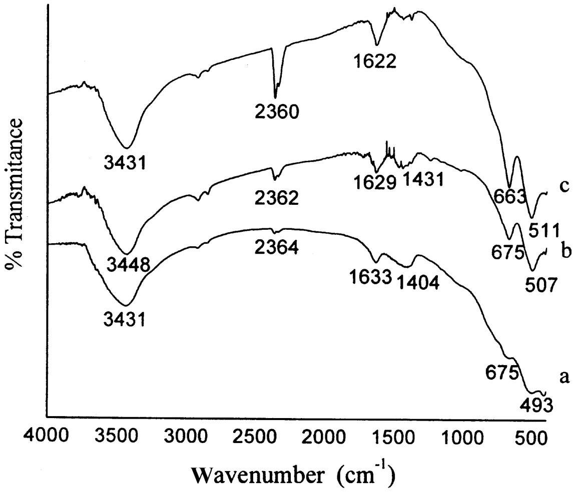

Figure 5. IR spectra of samples: (a) HT-Al-1200, (b) HT-Cr-1200, and (c) HT-Cr-1200 γ-irradiated at 6000 kGy.

Cr immobilization

Chromium immobilization was measured through Cr desorption from the samples when lixiviated with 1 N and 5 N NaCl solution as shown in Figure 6a and b, respectively. These results are valid only for short contact periods between the solids and the NaCl solutions. In order to establish the degree of immobilization for long periods, additional experiments need to be performed.

Figure 6a reveals that Cr is leached from HT-Cr samples with 1 N NaCl solution, Cl$^-$ ions partially displacing partially CrO_4^{2-} ions present in the HT-Cr

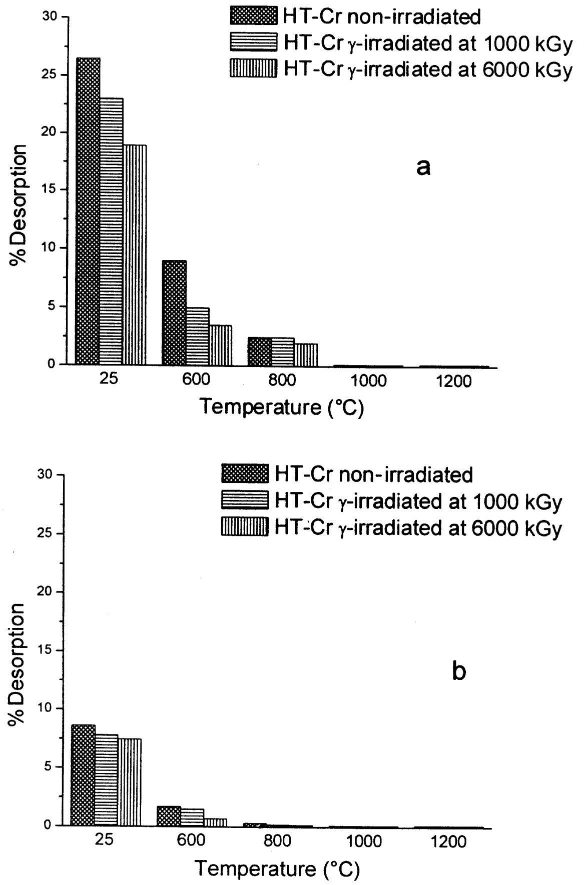

Figure 6. Chromium desorption by lixiviation with (a) 1 N and (b) 5 N NaCl solutions through HT-Cr, HT-Cr γ-irradiated at 1000 kGy, and HT-Cr γ-irradiated at 6000 kGy; samples heated at several temperatures.

interlayer space. Samples heated at 600 and 800ºC retain more Cr than unheated samples, since Al^{3+} (Miyata, 1980) and probably Cr^{3+} remain inside the MgO formed. Chromium desorption with 1 N NaCl solution from HT-Cr samples heated from 600 to 1200ºC decreases constantly, from 23% to 0%, demonstrating that heating at 1000 and 1200ºC completely immobilizes Cr in the solid. Differences between the results obtained by Goswamee *et al*. (1998) who suggested that Cr(VI) adsorbed Mg-Al layered double hydroxide calcined up to 1250ºC did not immobilize the Cr in the solid and those obtained in the present paper may be explained by the different spinel composition of the samples, $MgAl_2O_4$ and $MgCr_2O_4$, respectively.

The γ-radiation damage in the solids containing the immobilized Cr is also shown in Figure 6a,b. Figure 6a shows that Cr lixiviated through non-irradiated, and through γ-irradiated at 1000 kGy and at 6000 kGy HT-Cr are 9, 6 and 3%, respectively, when the samples are heated at 600ºC, and 2, 2 and 1.5%, respectively, when heated at 800ºC. Hence, in samples heated up to 800ºC, Cr is partially immobilized in the solid, and immobilization increases in γ-irradiated samples because of the increase in the amount of $MgCr_2O_4$ spinel as shown by the XRD patterns.

Chromium is not lixiviated at all through HT-Cr samples heated at 1000 and 1200ºC, non-irradiated or irradiated at 1000 and 6000 kGy (Figure 6a). Accordingly, Cr strongly immobilized in these solids and γ-radiation (1000 or 6000 kGy) does not affect these results in spite of the irradiation texture or new location of Cr ions developed during irradiation as exhibited by XRD.

The effect of the concentration of NaCl solution utilized for the lixiviation is given in Figure 6b. Even in the presence of very strong NaCl solutions (5 N), Cr is strongly immobilized in the solid, in fact more firmly than when lixiviation is performed with 1 N NaCl solution, probably because of the low mobility of Cl^- ions in the very concentrated solutions.

CONCLUSIONS

(1) Cr(VI) adsorbed in calcined hydrotalcite, heated at 1200ºC forms mainly $MgCr_2O_4$ spinel.

(2) γ radiation enhances the amount of spinel in the solids heated up to 1200ºC.

(3) γ radiation effects on HT-Cr samples heated at 1200ºC modify the structure of the solid developing a γ radiation texture, a preferential crystallite orientation rather than a purely random one or promoting the mobility of Cr ions.

(4) Chromium is partially immobilized in HT-Cr samples heated up to 800ºC; γ radiation increases Cr immobilization in these samples as a consequence of the $MgCr_2O_4$ spinel increase.

(5) Chromium is strongly immobilized in HT-Cr samples calcined up to 1200ºC either non-irradiated or γ-irradiated at 1000 or 6000 kGy, in spite of the γ-radiation effects developed in the solids.

(6) Chromium lixiviation with 5 N NaCl solution is less than the corresponding lixiviation with 1 N NaCl; this effect is probably due to the poor mobility of the ions in the highly concentrated NaCl solution.

ACKNOWLEDGMENTS

We thank Dr J. Amonette and Dr P. Bosch for useful discussions and recommendations; we also acknowledge M. Espinosa for the XRD studies and M. Villa-Tomasa for the IR spectroscopy. The investigation forms part of a program supported by CONACYT, project 32096-E. M. S. Martínez-Gallegos thanks CONACYT for financial assistance.

REFERENCES

Bosch, P. García, I., Solache, M. and Bulbulian, S. (1995) Co^{2+} ion exchange in zeolite NaA. *Separation Science and Technology*, **30**, 3399–3403.

Bulbulian, S. and Bosch, P. (2000) Vitrification of gamma irradiated $^{60}Co^{2+}$ zeolites. *Journal of Nuclear Materials*, **295**, 64–72.

Châtelet, L. Bottero, J.Y., Yvon, J. and Bouchelaghen, A. (1996) Competition between monovalent and divalent anions for calcined and uncalcined hydrotalcites: anion exchange and adsorption sites. *Colloid Surface*, **A 111**, 167–175.

Földeslová, M., Lukác, P., Majling, J. and Tomoková, V. (1996) Deposition of cesium and cobalt sorbed on zeolite in matrices of blast furnace slag. *Journal of Radioanalytical and Nuclear Chemistry Letters*, **212**, 293–302.

Goswamee, R.L., Sengupta, P., Bhattacharyya, K.G. and Dutta, D.K. (1998) Adsorption of Cr (VI) in layered double hydroxides. *Applied Clay Science*, **13**, 21–34.

Hibino, T. and Tsunashima, A. (1998) Characterization of repeatedly reconstructed Mg-Al hydrotalcite-like compounds: gradual segregation of aluminum from the structure. *Chemical Materials*, **10**, 4055–4061.

Hibino, T., Uchisawa, J. and Tsunashima, A. (1999) Synthesis and applications of hydrotalcite-type anionic clays. *Report of the National Institute for Resources and Environment*, Tsukuba, Japan, pp. 1–20.

Klug, H.P. and Alexander, L.E. (1974) Investigation of Preferred Orientation and Texture. Pp 709–754 in: *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials* (Wiley-Interscience editor). John Wiley & Sons, New York.

Labajos, F.M. and Rives, V. (1996) Thermal evolution of chromium (III) ions in hydrotalcite-like compounds. *Inorganic Chemistry*, **35**, 5313–5318.

Miyata, S. (1980) Physico-chemical properties of synthetic hydrotalcites in relation to composition. *Clays and Clay Minerals*, **28**, 50–56.

Nakamoto, K. (1978) Inorganic compounds. Pp. 101–165 in: *Infrared and Raman Spectra Inorganic and Coordination Compounds* (Wiley-Interscience editor). John Wiley & Sons, New York.

O'Dwyer, T.F. and Hodnett, B.K. (1995) Recovery of chromium from tannery effluents using a redox-adsorption approach. *Journal of Chemical and Technology Biotechnology*, **62**, 30–37.

Rao, C.N. and Gopalakrishnan, J. (1997) *New Directions in Solid State Chemistry*. Cambridge University Press, Cambridge, UK, pp. Pp. 30–32.

Ross, D.S. (1972) Spinels. Pp. 112–117 in: *Inorganic Infrared* *and Raman Spectroscopy* (P. Sykes, editor). McGraw Hill, London, New York.

Sato, T., Fujita, H., Endo, T., Shimada, M. and Tsunashima, A. (1988) Synthesis of hydrotalcite-like compounds and their physico-chemical properties. *Reactivity of Solids*, **5**, 219–228.

Thamzil, L. (1997) *Waste treatment immobilization technologies involving inorganic sorbents*. Final Report, a Coordinated Research Program 1992–1996. International Atomic Energy Agency, Vienna, Austria.

Ulibarri, M.A., Pavlovic, I., Barriga, C., Hermosín, M.C. and Cornejo, J. (2001) Adsorption of anionic species on hydrotalcite-like compounds: effect of interlayer anion and crystallinity. *Applied Clay Science*, **18**, 17–27.

Yui, M., Rai, D., Ochs, M. and Shibata, M. (2003) Applicability of thermodynamic database of radioactive elements developed for the Japanese performance assessment of HLW repository. *Journal of Nuclear Science and Technology*, **40**, 356–362.

(*Received 3 April 2003; revised 28 April 2004; Ms. 779; A.E. James E. Amonette*)