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Trivalent Chromium Ion Removal from Aqueous Solutions Using Low-cost Zeolitic Materials Obtained from Exhausted FCC Catalysts[†]

Maximiliano R. González[1], Andrea M. Pereyra[1,2] and Elena I. Basaldella[1,2*] *(1) CINDECA, CCT- La Plata–CONICET, Universidad Nacional de La Plata, 47 N 257 (B1900AJK), La Plata, Argentina. (2) Universidad Tecnológica Nacional, Facultad Regional La Plata, 124 y 60, 1900- La Plata, Argentina.*

ABSTRACT: The hydrothermal treatment of exhausted FCC catalysts with zeolite was optimized by varying the chemical composition of the synthesis mixture. The zeolitic products obtained were used to evaluate their ability for the capture of Cr(III) cations from aqueous solutions. It was shown that the zeolitic product materials were capable of reducing the Cr(III) ion concentration to values lower than 1.2 ppm. The chromium ion-containing solids were afterwards solidified in cement mortars on which leaching studies of this cation were made. The results obtained showed that the synthesized solids acted as effective Cr(III) ion immobilizers and that their inclusion as additives in cement formulations could provide an environmental friendly disposal procedure.

INTRODUCTION

Water pollution caused by the presence of heavy metal ions represents one of the most frequent environmental problems widely known at present. Such heavy metal cations accumulate in living organisms and are considered harmful for human health because of their cytotoxic and carcinogenic effects (Bagchi *et al*. 2002).

The cation-exchange properties of zeolitic materials are one of their fundamental characteristics, allowing their application as selective ion sorbents in purification processes. To date, the ion-exchange processes of zeolites with uni- and di-valent cations have been widely studied. As far as trivalent cations are concerned, it is known that faujasite (FAU) zeolites are suitable materials for the removal of aquo-stabilized Cr(III) ion species generally present in the aqueous phase (Gazola *et al*. 2006). In addition, spent solid FCC catalysts are considered as being incapable of regeneration.

Large volumes of refinery catalysts are purchased to replace non-regenerable refinery catalysts, with the volume of the spent amount approaching that of the newly bought material. Such spent catalysts have been attracting the attention of environmental authorities in many countries for the past few years. There are some indications that all exhausted refinery catalysts might be classified as hazardous materials in the future (Furimsky 1996). Hence, special precautions should be taken during their storage, transportation and disposal to avoid future liabilities. Perhaps, the best solution would be the reclamation of all components of spent catalysts, but nowadays most exhausted catalysts are solidified with cement and buried in landfill sites. Exhausted FCC catalysts are also used as raw materials for manufacturing cement, ceramics, bricks or tiles (Hsu 1996; Su *et al*. 2001; Tseng *et al*. 2005; Zornoza *et al*. 2009).

We have previously analyzed the use of exhausted FCC catalysts as raw materials for zeolite synthesis (Basaldella *et al*. 1995, 2006, 2009). The fusion pre-treatment method proposed by Abdemeizien-Hamoudi and Siffert (1989) was used to improve the reactivity of the catalyst towards zeolitic conversion. These authors described a method by which the quartz present in clays could be eliminated by thermal treatment with Na_2CO_3 at 800 °C. It was found that such alkaline fusion increases the zeolitic nature of the solid phases (Basaldella *et al*. 2009). In addition, there are also reports regarding the incorporation of natural or artificial zeolites in cementitious materials (Caputo *et al*. 1999; Perraki *et al*. 2010).

The aim of the present work was the optimization of the conversion of exhausted FCC catalysts into zeolitic products. Additionally, the ability of these products to remove Cr(III) cations present in aqueous solution was tested, and the polluted solids obtained after chromium ion removal incorporated into cementitious matrices. The retention of Cr(III) cations inside these matrices was evaluated by performing normalized washing tests, while their matrix engineering properties were investigated to study the feasibility of using the mortar formulation as a chromium ion immobilizer, thereby providing a potentially safe construction material.

EXPERIMENTAL

Hydrothermal synthesis of zeolitic products

An equilibrium catalyst (CAT) was used as the source of silica and alumina for the hydrothermal synthesis. This catalyst was a waste material arising from a commercial unit employed for fluidized bed catalytic cracking (FCC). Synthesis of the zeolites was undertaken from mixtures of the catalyst and Na_2CO_3 (Baker, A.R. standard) as described by Basaldella *et al*. (2009).

Thus, the mixtures were calcined at 800 °C for 2 h under static conditions. Three Na_2CO_3/CAT ratios were used employing different weight proportions of Na_2CO_3 (0, 25 and 50 wt%). Synthesis leading to hydrothermal crystallization was undertaken in a closed vessel at 90–95 °C without stirring. Reaction mixtures were prepared by adding NaOH solution to the calcined mixture at room temperature, followed by stirring to achieve homogeneity.

Separately, commercial sodium aluminate (36.5% Al_2O_3, 29.6% Na_2O, 33.9% H_2O) was added to an aluminate/starting mixture at a 0.02 w/w ratio, again with stirring to achieve homogeneity. This mixture was allowed to rest for 48 h at room temperature without stirring. The weight of Na_2O added to the reaction mixture was calculated so as to attain a selected H_2O/Na_2O ratio.

The mixed gels were heated at 95 °C in closed propylene containers with samples being taken at different reaction times, the solid being separated from the liquid by centrifugation. The solid fractions were washed until the pH value of the wash water reached 10 and then dried at 110 °C. The compositions of the reaction mixtures and the synthesis conditions employed are detailed in Table 1.

In the data listed, the elapsed reaction time is indicated by adding the number of corresponding hours at the end of the sample. Thus, for example, 1279–2 h indicates that the sample consisted of mixture 1279 after remaining for 2 h at the reaction temperature.

Characterization

The composition of the starting catalyst was determinded via an electron microprobe (EDX) coupled to a scanning electron microscope. Such EDX chemical analysis gave the composition 50.6 wt% SiO_2, 47.8 wt% Al_2O_3, 1.4 wt% Na_2O and 0.2 wt% other metallic oxides.

TABLE 1. Initial Compositions, Products and Conversions Achieved in Different Tests

Test Conversion	Na_2CO_3 (w/w%)[a]	$NaAlO_2$ (w/w%)[b]	H_2O/Na_2O (w/w%)[b]	Zeolite type	(% XRD)[c]
1272–2 h	–	2	27	–	–
1272–3 h	–	2	27	–	–
1272–21 h	–	2	27	X > A	68
1272–2 h	50	2	27	A + trX	60
1272–3 h	50	2	27	A + trX	90
1272–21 h	50	2	27	trA + HS	10
1279–1 h	–	–	27	X > A	35
1279–2 h	–	–	27	X > A	40
1279–3 h	–	–	27	X > A	45
1280–1 h	25	–	27	X > A	40
1280–2 h	25	–	27	X > A	66
1280–3 h	25	–	27	X > A	68
1281–1 h	25	2	27	A ≥ X	60
1281–2 h	25	2	27	A ≥ X	70
1281–3 h	25	2	27	A ≥ X	70
4012–1 h	50	2	33	A > X	60
4012–2 h	50	2	33	A > X	70
4012–3 h	50	2	33	A > X	85
4016–1 h	50	2	45	–	–
4016–2 h	50	2	45	A + trX	70
4016–3 h	50	2	45	A + trX	85

Characterization of the initial solids used for the synthesis and of the reaction products was carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. The X-ray diffraction measurements were obtained using a Philips 3020 diffractometer (40 kV, 20 mA, Cu Kα radiation via a Ni filter, step width 0.04° and counting time 2.0 s/step). The types of zeolites and other crystalline phases obtained were determined by comparing their diffraction profiles with published data (Breck 1974). The Rietveld method (Rietveld 1969) was used for quantitative determination of the crystalline phases. This consists of refining a crystal structure by minimizing the weighted squared difference between the observed and calculated diffraction patterns.

The "FullProf" program (Rodriguez-Carvajal 1990) was used to perform the Rietveld analysis. The crystallographic data used for each phase were extracted from the literature. The size and morphology of the particles obtained were determined by scanning electron microscopy (Philips 505 instrument) using samples coated with a gold film.

Ion-exchange studies

Ion-exchange experiments were conducted under stirring by contacting 1–3 g of each zeolitic sample with 1 ℓ of chromium ion solution containing ~42 ppm of Cr(III) ions. The chromium ion solution was prepared by dissolving the appropriate amount of $Cr(NO_3)_3 \cdot 9H_2O$ (Anedra, p.a.) in distilled water. The pH value of the final solution was noted as 3.53. Samples of the suspension were collected at pre-determined times, with the liquid being separated from the solid by filtration. The solid phases were oven-dried at 110 °C and stabilized at room temperature at 35% relative humidity.

To determine the chromium(III) ion concentration, the liquid phases were analyzed by atomic absorption spectrometry (AAS) employing an IL 457 model double-beam spectrophotometer. Solid phases were analyzed by X-ray diffraction (XRD) methods.

Stabilization tests

The product obtained after cation exchange of the 1273–3 h test sample (1273–3 h/Cr) was stabilized in a cementitious matrix obtained from natural siliceous sand and normal Portland cement CPC 40. A series of cement mortars (prisms of size $40 \times 40 \times 160$ mm) were prepared. The series included four mortars, a reference mortar (Z0, without the zeolitic product) and three mortars in which 8 wt%, 20 wt% and 30 wt% cement was replaced by 1273–3 h/Cr. The samples are referred to below as Z8, Z20 and Z30, respectively. The mix proportions used were a water/cement w/w ratio of 0.45 and a sand/cement w/w ratio of 2.6. These matrices were cured for 28 d at 25 °C and 100% relative humidity. The hardened mortars were subjected to compressive and flexural strength measurements. A leaching test was also performed with the aim of analyzing the environmental impact of incorporating the chromium-bearing zeolite in cementitious materials. The release of Cr(III) ions from the cured mortars Z10, Z20 and Z30 was estimated by performing the leaching test with the crushed mortar in acidic media employing standard methods (US EPA, Method 1311, 1992). The solid compact was first ground (grain size < 125 μm) and the powdered sample then placed in contact with an acetic acid solution at pH = 5.0 (liquid/solid ratio = 20). The Cr(III) ion concentration was determined in the liquid phase by atomic absorption spectroscopy (AAS) after 18 h contact time.

RESULTS AND DISCUSSION

Figures 1 and 2 overleaf show the X-ray diffraction patterns for solid samples taken during selected experiments of zeolite synthesis. These characterizations were carried out in order to analyze the influence of sodium aluminate addition and alkaline fusion. At short reaction times (< 1 h), the diffractograms obtained indícate that all the samples examined exhibited sharp peaks in the $20 < 2\theta < 25$ region, being typical of silica glasses. At longer times, the conversion of the zeolitic phases was appreciable, with many of the reaction products exhibiting high percentages of NaA (LTA) and NaX (FAU) (see data listed in Table 1). Another general feature was that allowing the reaction to proceed further led to the conversion of NaA to hydroxysodalite (HS), as can be seen from the X-ray diffraction pattern depicted in Figure 2. In addition, some samples also exhibited traces of natrite, nepheline, low carnagieite, mullite and anatase. Comparing the results for samples obtained with or without alkaline fusion pre-treatment (Figures 1 and 2, respectively) shows that the production of zeolitic products was faster when such pre-treatment was applied. Furthermore, the crystallization of NaA zeolite was favoured when higher percentages of sodium carbonate were employed and additional aluminium was added (Table 1, samples 1273–3 h, 4012–3 h, 4016–4 h). Test 1279, which was carried out in the absence of both fusion and extra aluminium addition, led to a very low conversion percentage. The mixture which presented a high conversion to zeolitic materials containing a higher content of zeolite X was obtained using 25 wt% sodium carbonate and adding sodium aluminate (Table 1, sample 1281–3 h). Comparison of the results for series 1273, 4012 and 4016 indicates that a higher water/silica ratio had little effect on the synthesis process.

Selected products of such hydrothermal syntheses were tested in the Cr(III) ion-exchange reaction, employing an initial Cr(III) ion concentration in the liquid phase of 40.3 ppm. In all
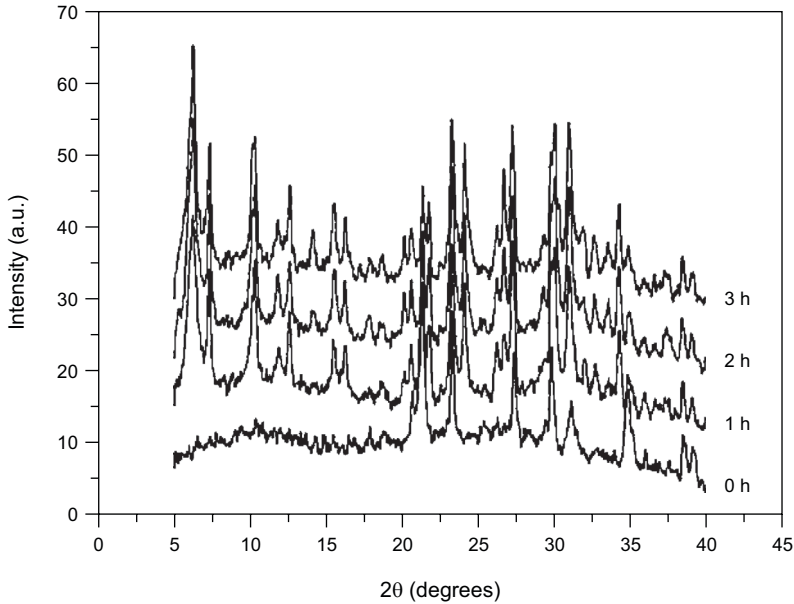
Figure 1. X-Ray diffraction patterns for the products of test 1272.

cases, excellent cation retentions were observed after 10 min contact time, with the Cr(III) ion concentration in solution being reduced to < 1.2 ppm. Figure 3 overleaf shows the development of the amounts of Cr(III) ions retained with time. The best results were achieved with the NaA sample containing the greatest amount of zeolite (1273–3 h), whose use led to Cr(III) ion
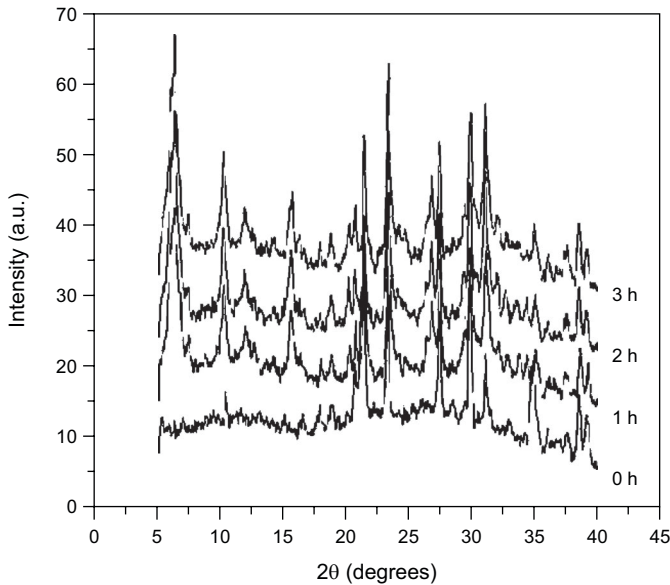

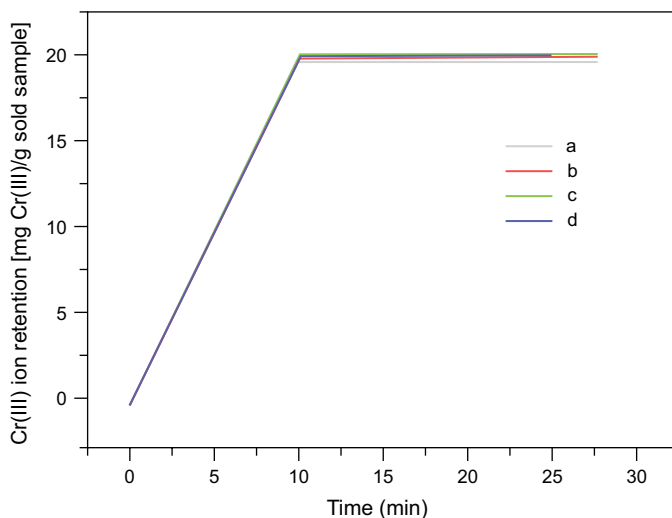**Figure 2.** X-Ray diffraction patterns for the products of test 1273.

Figure 3. Evolution of Cr(III) ion concentration in the solid phase employing different products obtained in the hydrothermal synthesis during the exchange reaction: (a) sample 1272–21 h; (b) sample 1273–3 h; (c) sample 1280–3 h; (d) sample 1281–3 h. Experimental conditions: Cr(III) ion conc. in solution at zero time = 40.3 ppm; weight of solid phase = 2 g.

TABLE 2. Rietveld Analysis of Sample 1273–3 h

Zeolite	Content (wt%)
LTA zeolite	5
Sodium nepheline	13
Low carnagieite	4
Mullite	1
Hydroxysodalite	6
Anatase	< 1

concentration values in the aqueous phase of < 0.3 ppm. The Rietveld compositional analysis results obtained for this sample are detailed in Table 2.

The morphology and particle size of the reaction products were estimated via scanning electron microscopy. The product obtained without alkaline fusion retained the morphology of the starting catalyst, since spherical particles of ca. 60–100 μm in diameter were observed even after reaction [Figure 4(a)]. These spheres were composed of zeolitic crystals whose morphology is depicted in Figure 4(c). When the fusion treatment was used for activation, the integrity of the starting catalyst was partially lost [Figure 4(b)]. The corresponding analysis for the solid obtained in one of the tests with a high LTA percentage (1273–3 h) indicated that the product was mainly composed of cubic crystals whose sizes were smaller than 1 μm [Figure 4(d)].

The results of lixiviation studies undertaken on the Z10, Z20 and Z30 mortars are shown in Table 3. The Cr(III) ion concentration values in the supernatant liquid at the end of such tests were always less than 0.5 ppm. Such results enable these materials to be classified as non-hazardous wastes suitable for landfill or construction (Zornoza *et al*. 2009).
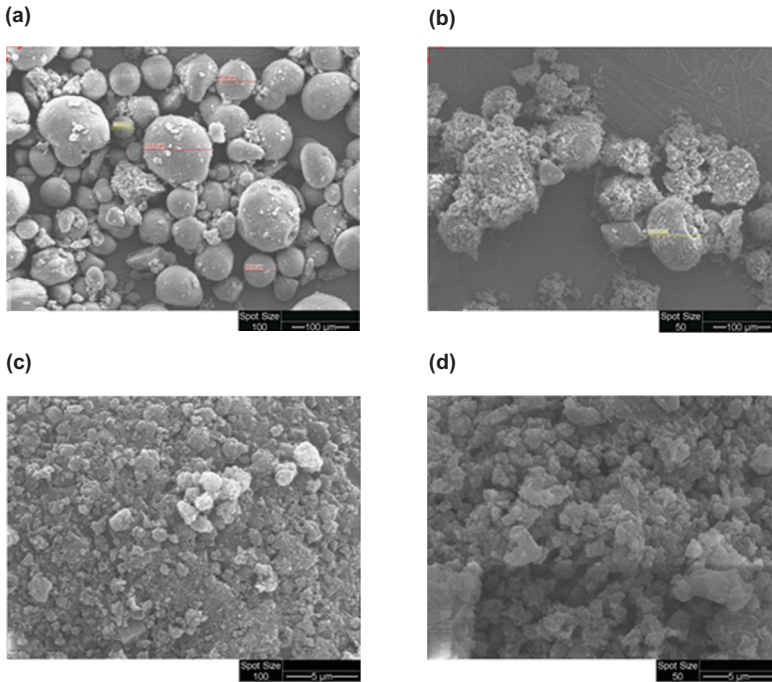
Figure 4. SEM micrographs of test products with and without alkaline fusion: (a) and (c), sample 1271–21 h, magnification ×200 and ×5000, respectively; (b) and (d), sample 1273–3 h, magnification ×200 and ×5000, respectively.

TABLE 3. Results of Leaching Tests for Different Mortars[a]

Sample	% Zeolite	Conc. (mg/ℓ)
Z8	8	0.061
Z8	8	0.064
Z20	20	0.077
Z20	20	0.072
Z30	30	0.105
Z30	30	0.135

[a] Leaching time for all samples = 18 h.

CONCLUSIONS

The conversion of exhausted FCC catalysts to zeolitic products of commercial interest provides a valid alternative for their disposal. Activation by alkaline fusion has been shown as an appropriate method for improving such transformation to provide a solid with a high content of zeolitic phases. The results obtained in cation-exchange experiments indicate that such products could be used for the removal of Cr(III) ions from aqueous media.

Additionally, the feasibility of including such Cr(III) ion-bearing zeolitic materials in cementitious blocks was studied. It was found that ca. 20 wt% of the zeolitic product could be used to replace the Portland cement without altering the engineering properties of the resulting

matrices. In this case, mortars with acceptable mechanical strength levels were obtained which gave appropriate performances in the leaching test.

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