



Removal and cementitious immobilization of heavy metals: chromium capture by zeolite-hybridized materials obtained from spent fluid cracking catalysts



Maximiliano R. Gonzalez ^a, Andrea M. Pereyra ^{a, b}, Raúl Zerbino ^c, Elena I. Basaldella ^{a, b, *}

^a CINDECA, (CONICET-CIC-UNLP) 47 No. 257, B1900 AJK La Plata, Argentina

^b CITEMA, Universidad Tecnológica Nacional, 60 y 124, 1900 La Plata, Argentina

^c CONICET – Fac. Ing. UNLP, LEMIT, 52 entre 121 y 122, B1900AYB La Plata, Argentina

ARTICLE INFO

Article history:

Received 16 June 2014

Received in revised form

31 October 2014

Accepted 4 December 2014

Available online 12 December 2014

Keywords:

Zeolite

Mortars

Cr(III)

Mechanical strength

Leaching

ABSTRACT

An alternative for the reutilization of spent catalyst industrial residue for removal and immobilization of heavy metals is presented. A solid containing about 80% (w/w) of NaA zeolite was hydrothermally synthesized by reconversion of a spent catalyst discarded from a fluidized-bed catalytic cracking unit (FCC). The obtained material (ZFCC) was afterwards used for Cr(III) removal from aqueous solutions. Chromium cation was incorporated in the zeolitized structure by ionic exchange in liquid media, and the exchange level was determined by atomic absorption spectrometry. To analyze the viability of final disposal for the chromium sludge obtained using this methodology (Cr-ZFCC), cement mortars containing Cr-ZFCC in variable percentages were prepared and their mechanical and metal retention properties were evaluated. Mechanical strengths and drying shrinkage shown by mortars containing not more than Cr-ZFCC 5% (w/w) were similar to those corresponding to control mortars without zeolitic additions. Leaching tests indicated that mortars with Cr-ZFCC 5% (w/w) produce an effective immobilization of Cr(III) and should be considered as a viable alternative for safe chromium disposal.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Each year the petrochemical industry produces huge amounts of exhausted FCC catalyst, therefore the spent catalyst is a solid waste of difficult management. Currently, most of these catalysts are solidified and buried, although nowadays there is a strong interest concerning their use as an admixture to improve the mechanical properties of concrete (Al-Jabri et al., 2013; Morozov et al., 2013).

Moreover, zeolite syntheses from wastes are crystallization processes considered as environmentally friendly, promising ways for the reutilization of spent industrial products (Basaldella et al., 2006; Chareonpanich et al., 2011; Pimraksa et al., 2013).

In previous papers a process for obtaining a solid product enriched in NaA zeolite (ZFCC) through a hydrothermal treatment of spent FCC catalyst was described (Basaldella et al., 2006; Gonzalez et al., 2011). This very fine synthesized material can be

used for heavy metal cations removal from aqueous solutions. As pozzolanic reactivity and heavy metal encapsulation in zeolites are of much interest to cement chemists and concrete technologists, this study aims to evaluate the zeolite-rich material obtained after the cation exchange (Cr-ZFCC) as a cement additive. In this way, an alternative for the reutilization of spent catalyst industrial residue for removal and immobilization of heavy metals, including an evaluation of its potential pozzolanic properties when it is combined with portland cement, is presented in this paper.

2. Experimental

A sample of spent FCC catalyst was hydrothermally treated for obtaining a solid product enriched in NaA zeolite (ZFCC). The synthesized material was used in the removal of Cr(III) cations from aqueous solutions, generating a solid residue containing an appreciable percentage of the heavy metal. The properties of portland cement mortars with different contents of this waste containing the maximum Cr(III) level obtained by ion exchange were studied and compared with similar mortars incorporating pure A zeolite, a product possessing a very similar structure and

* Corresponding author. CINDECA, (CONICET-CIC-UNLP) 47 No. 257, B1900 AJK La Plata, Argentina. Fax: +54 221 4210711.

E-mail address: eib@quimica.unlp.edu.ar (E.I. Basaldella).

chemical composition, or silica fume, a high quality mineral addition widely used in high-performance concrete mixtures. The effects on fresh mortar properties, the evolution of strength and drying shrinkage were studied and finally, leaching tests of the heavy metal were performed to verify the viability of this process for Cr(III) immobilization.

2.1. Materials and methods

ZFCC and pure A zeolite (NaA) were prepared in our laboratory. ZFCC was synthesized using an exhausted FCC catalyst from a cracking unit at YPF oil refinery in La Plata, Argentina, as raw material. The methodology used and the starting material characterization are detailed in (Gonzalez et al., 2011). Pure NaA was obtained following the procedure described in (Basaldella et al., 2006). To estimate the pozzolanic activity, commercially available silica fume (SF) was used as reference material.

The size and morphology of samples were observed by scanning electron microscopy (Philips 505 SEM), using samples covered with Au film. SEM micrographs corresponding to ZFCC, NaA and SF are shown in Fig. 1 (a–c, respectively). ZFCC presents rounded particles about 60–80 μm in size, whereas smaller particles are observed for NaA (2–4 μm) and SF (0.2–0.4 μm). For mortar preparation, portland cement type CPC40 and natural siliceous sand (modulus of fineness 2.4) were used.

Chromium was incorporated according to (Gonzalez et al., 2013), by adding 3 g of ZFCC or NaA to 1 L solution containing 130 mg/L of Cr(III). The solution was obtained by dissolving $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Carlo Erba, pa/p.a.) in demineralized water (pH between 3.7 and 4). Chromium concentrations in the solids were calculated by determining the remaining chromium in the liquid phase by atomic absorption spectroscopy (AAS).

Table 1 shows the chemical composition of the zeolitic materials after chromium exchange, the portland cement and silica fume. SF presents 99% of SiO_2 and both Cr-NaA and Cr-ZFCC have similar chemical compositions. The semiquantitative chemical analysis of samples was carried out by energy-dispersive X-ray spectroscopy (EDX), using an Apex 2 EDAX model Apollo X coupled to the scanning electron microscope.

2.2. Cement mortar preparation and mechanical tests

Seven types of mortars were prepared using water/cement ratio 0.47 and cement/sand ratio 1:3, by weight. Cr-NaA, Cr-ZFCC and SF were used to replace cement by weight at 5% and 10% (Z5, Z10, ZC5, ZC10, S5 and S10); a reference mortar without mineral additions (P) was also prepared. Fresh mortars were characterized by the slump using a 150 mm height cone (with the same geometrical proportions as the Abrams cone) and the unit weight. Two set of samples were cast: prisms of $40 \times 40 \times 160 \text{ mm}^3$ in size for flexural and compression strength measurements and prisms of $30 \times 30 \times 220 \text{ mm}^3$ to evaluate the drying shrinkage. The mortars

Table 1

Chemical analysis of chromium-bearing zeolite products, silica fume and portland cement.

Oxide (%)	Cr-NaA	Cr-ZFCC	SF	Portland cement
SiO_2	46.84	42.84	99.15	30.85
Al_2O_3	34.85	38.85		2.69
Na_2O	15.84	15.74		
K_2O			0.85	0.41
CaO				63.31
MgO				1.79
TiO_2		0.75		
Cr_2O_3	1.60	1.82		
Fe_2O_3				0.96

were compacted by external vibration, selecting the vibration time in accordance with the measured slump. The samples were removed from the molds after 1 day.

The flexural and compression strengths were evaluated at 28 and 90 days. In this case, the mortars were cured in water at 23 °C up to the age of testing. For drying shrinkage measurements, the mortars were cured in water at 23 °C during 8 days and then exposed to dry room air/conditions (22 °C and 55% RH) during six months. All runs were performed in triplicate and the results were averaged.

2.3. Leaching tests

Leaching tests were performed following US EPA standard method 1311. The extraction solution was prepared using 5.7 cm^3 of glacial $\text{CH}_3\text{CH}_2\text{OOH}$ dissolved in distilled water up to 1 L volume. Mortars with zeolites (ZC5, ZC10, Z5, Z10) were ground and the fraction <1 mm was selected. The samples were put in contact with the extraction fluid, and the mixtures were transferred to a glass container and submitted to stirring in a rotary shaker at 30 rpm for 18 h [Cr(III)] in the remaining liquid was determined by AAS. In addition [Cr(III)] in the curing water was also determined in order to evaluate the possible occurrence of chromium leaching during the curing process.

3. Results and discussion

3.1. Properties of fresh mortars

Table 2 shows the effect of incorporation of the different mineral additions on the slump and air content. The air content was estimated from the measurements of the unit weight. Mortars with 5% zeolite (Z5, ZC5) or silica fume (S5) replacement showed similar slump values to those of the reference mortar. As expected, a decrease in workability appears when 10% replacement of additions is used; the high surface area of these mineral additions increases the water demand for maintaining the workability. However, it can be noticed that the reduction in slump is smaller in ZC10 than in the other cases (Z10, S10), which can be associated with the larger

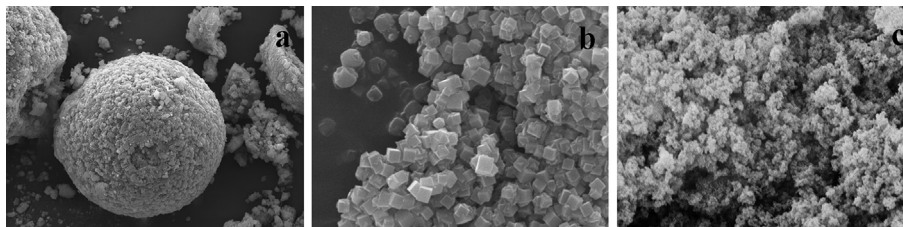


Fig. 1. SEM micrographs of the materials used. a) Rounded ZFCC particles covered by small zeolite crystals, magnification 500 X. b) NaA crystals obtained by using the conventional synthesis methodology, magnification 5000 X. c) Silica fume, magnification 4000 X.

Table 2
Fresh mortar properties.

Mortar	Slump (mm)	Air content (%)
P	30	6.0
Z5	35	5.0
Z10	5	7.5
ZC5	35	7.0
ZC10	25	5.5
S5	25	5.5
S10	5	4.5

Table 3
Mechanical properties.

Mortars	Bending strength (MPa)		Compressive strength (MPa)	
	28 days	90 days	28 days	90 days
P	6.7	6.8	33.1	35.2
Z5	6.4	6.4	24.9	32.6
Z10	5.9	6.0	24.6	28.5
ZC5	6.8	6.8	31.2	35.8
ZC10	5.5	6.6	26.2	32.7
S5	7.2	7.0	39.4	41.7
S10	7.5	7.9	45.6	51.5

particle size of ZFCC. In the same way, a small decrease in the air content was observed in mortars incorporating the highest dosages of mineral additions, coincident with the decrease in the fluidity of the mortars.

3.2. Flexural and compressive strength

The results of bending and compressive strength at 28 and 90 days are given in Table 3. It appears that the Z5 and ZC5 mortars reach almost the same level of flexural strength as the reference mortar (P) at the age of 90 days. In the case of compressive strength, the results show that strength evolution between 28 and 90 days was higher in mortars incorporating zeolite-containing materials than in the reference mortar, indicating that there is some pozzolanic action of these additions. Although this is not seen in bending, it should be noted that, as is well known, the flexural strength increases faster than the compressive strength.

Fig. 2 shows the results of flexural and compressive strengths as relative values of the reference mortar. When 10% of zeolitic materials were used, although the gain of strength between 28 and 90 days was again higher than in the reference mortar, a decrease in mechanical properties occurred. At 90 days, Z5 and Z10 achieved a compressive strength of 93% and 81% of that of the control mortar. Although the mechanism of the pozzolanic action of zeolites is not yet well understood, it can be assumed that consumption of silica

from the zeolite by reaction of dissolved calcium hydroxide leads to the formation of C–S–H-type phases. Nevertheless, experimental data reported in previous papers (Caputo et al., 1999; Perraki et al., 2003) indicated that less C–S–H formation was obtained when cement was replaced by zeolitic materials.

The present results also show that the pozzolanic activity is significantly smaller for zeolitic materials when compared to silica fume, a high quality mineral addition. In fact, SF addition increases the compressive strength in the order of 20% and 40% at the ages of 28 and 90 days, respectively.

3.3. Drying shrinkage

Fig. 3 shows the evolution of drying shrinkage. The reference mortar showed drying shrinkage of 0.09% after 6 months, and similar values were measured on mortars incorporating SF or Cr-ZFCC. In the case of mortars incorporating Cr-NaA (Z5 and Z10) an increase in shrinkage was observed, which was more significant as the Cr-NaA content increased. It was noticed that pure NaA plays an important role in the shrinkage properties of mortars when its percentage is higher than 5%. The increasing tendency can be attributed to the characteristics of the zeolitic materials used, which have a small particle size, high specific surface area, porosity and water adsorption properties. In the case of FCC-based replacement, a minor influence could be attributed to its larger particle size and lower zeolite content, which can restrain water mass movement (Zhang et al., 2013). It is interesting to note that higher shrinkage may result in the cracking of monolithic waste forms.

3.4. Leaching tests

Table 4 shows the results of the leaching tests. The analysis was done using samples taken from the hardened mortars Z5, Z10, ZC5 and ZC10 previously used in the mechanical strength tests. A slight increase in the chromium concentration in the leaching phase was observed as the zeolite content in the solid phase increased, but its value was always lower than the allowable limits (2 mg/L) established by Resolution 336/2003 of the Water Authority of Buenos Aires, Argentina. It is worth noting that [Cr(III)] was also determined in the final curing waters. Measurements indicated the absence of leaching during the curing process.

4. Conclusions

A solid containing about 80% (w/w) of NaA zeolite (ZFCC) was obtained by reconversion of a spent catalyst discarded from a

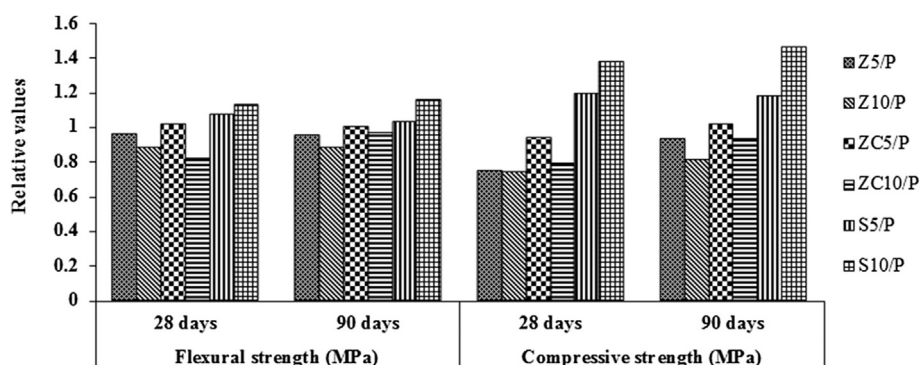


Fig. 2. Results of flexural and compressive strengths as relative values of the reference mortar.

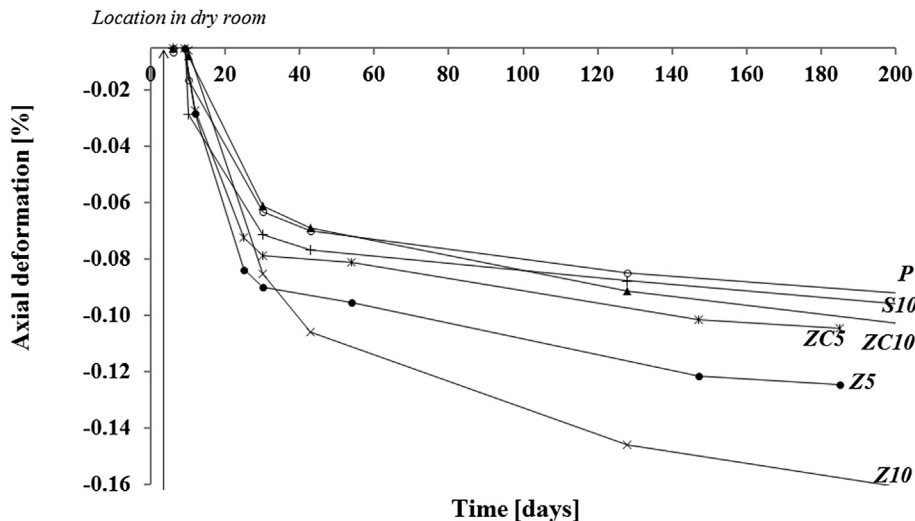


Fig. 3. Results of drying shrinkage tests.

Table 4

Results of leaching tests (leaching time = 18 h).

Mortar	Concentration of Cr(III) (mg/L)
ZC5	0.054
ZC10	0.062
Z5	0.053
Z10	0.065

fluidized-bed catalytic cracking unit and the synthesized material was used for Cr(III) removal from aqueous solutions.

After the exchange reaction, a chromium-bearing solid waste was obtained (Cr-ZFCC). Mechanical strengths and drying shrinkage of cement mortars containing a fraction lower than Cr-ZFCC 5% (w/w) were similar to those corresponding to control mortars without zeolitic additions. Contents of Cr-ZFCC up to 5% can be incorporated in these materials without affecting their workability. As compared to mortars containing 5% of silica fume, the values of flexural and compressive strength were lower, thus a high pozzolanic activity must not be expected in Cr-ZFCC.

Leaching tests indicated that in mortars of 0.47 water/cement ratio, using Cr-ZFCC contents lower than 5% (w/w), an effective immobilization of Cr(III) cations occurs.

Nowadays, the incorporation of diverse mineral additions in portland cement formulations is a common practice of the industry due to their technical and/or ecological implications. This paper shows that the highly contaminated solid phase obtained after ion exchange could be included in cement formulations without altering the usually required cement properties, acting simultaneously as an efficient heavy metal retainer. Incorporation of Cr-ZFCC in concrete and other cement-based materials can be considered as a valid option for chromium disposal.

Acknowledgements

M. R. Gonzalez thanks CONICET for a doctoral scholarship.

References

- Al-Jabri, K., Baawain, M., Taha, R., Al-kamyani, Z.S., Al-Shamsi, K., Ishtieh, A., 2013. Potential use of FCC spent catalyst as partial replacement of cement or sand in cement mortars. *Constr. Build. Mater.* 39, 77–81.
- Basaldella, E.I., Paladino, J.C., Solari, M., Valle, G.M., 2006. Exhausted fluid catalytic cracking catalysts as raw materials for zeolite synthesis. *Appl. Catal. B Environ.* 66, 186–191.
- Caputo, D., De Gennaro, B., Pansini, M., Colella, C., 1999. Chromium removal from water by ion exchange using zeolites and solidification of the resulting sludge in a cement matrix. *Stud. Surf. Sci. Cat.* 125, 723–730.
- Chareonpanich, M., Jullaphan, O., Tang, C., 2011. Bench-scale synthesis of zeolite A from subbituminous coal ashes with high crystalline silica content. *J. Clean. Prod.* 19, 58–63.
- Gonzalez, M.R., Pereyra, A.M., Basaldella, E.I., 2011. Trivalent chromium ion removal from aqueous solutions using low-cost zeolitic materials obtained from exhausted FCC catalysts. *Adsorpt. Sci. Technol.* 29, 629–636.
- Gonzalez, M.R., Pereyra, A.M., Torres Sánchez, R.M., Basaldella, E.I., 2013. Chromium removal by zeolite-rich materials obtained from an exhausted FCC catalyst: influence of chromium incorporation on the sorbent structure. *J. Colloid Interf. Sci.* 408, 21–24.
- Morozov, Y., Castela, A.S., Dias, A.P.S., Montemor, M.F., 2013. Chloride-induced corrosion behavior of reinforcing steel in spent fluid cracking catalyst modified mortars. *Cem. Concr. Res.* 47, 1–7.
- Perraki, T., Kakali, G., Kontoleon, F., 2003. The effect of natural zeolites on the early hydration of portland cement. *Microporous Mesoporous Mater.* 61, 205–212.
- Pimraksa, K., Chindapasirt, P., Huanjit, T., Tang, C., Sato, T., 2013. Cement mortars hybridized with zeolite and zeolite-like materials made of lignite bottom ash for heavy metal encapsulation. *J. Clean. Prod.* 41, 31–41.
- US EPA, 1992. Method 1311. Toxicity Characteristic Leaching Procedure. US Environmental Protection Agency, Washington, D.C., U.S.A.
- Zhang, W., Zakaria, M., Hama, Y., 2013. Influence of aggregate materials characteristics on the drying shrinkage properties of mortar and concrete. *Constr. Build. Mater.* 49, 500–510.