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Safe immobilization of Cr(III) in heat-treated zeolite tuff compacts

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Abstract

The possibility to remove chromium ions from a simulated electroplating wastewater by a discontinuous ion-exchange process based on phillipsite-rich Neapolitan yellow tuff (NYT) has been investigated. The immobilization of the pollutant cation in the resulting sludge through a heat-treatment has been realized, demonstrating that compacts made of Cr-loaded NYT powder, fired at temperatures of 1000 °C or over, are safe materials with negligible Cr^{3+} leaching. The set up overall process allows, in addition, a volume reduction of the waste with associated lower disposal costs or, better, the obtainment of a ceramic material, whose physical and mechanical properties are comparable to those of similar ordinary ceramics, such as bricks. In summary, the proposed strategy looks at the polluted sludge as a resource to be exploited, instead of a dangerous material to safely dispose of.

Keywords: Electroplating wastewater; Chromium removal; Ion-exchange; Natural zeolite; Ceramization

1. Introduction

Hexavalent chromium is a powerful carcinogenic agent, because of its ability to modify the DNA transcription process causing important chromosomal aberrations [1]. However, the presence of chromium in environment, whatever its oxidation state and the possibility of variations by redox reactions, is a source of serious problems and harmful health effects [2].

Chromium removal from water is part of the wider problem of heavy metals abatement. Various procedures have been set up to remove heavy metals from water, based on chemical precipitation, membrane filtration, carbon adsorption and ion-exchange [3]. Ion-exchange, in particular, has proven to be one of the most useful techniques to remove polluting cations from water, since it allows: (1) good performances, (2) reasonable costs and, in favourable cases, (3) metal recovery [4]. As regards chromium, various exchangers have been tested, e.g., ion-exchange resins [5], natural hydrothermal zeolites [6], natural sedimentary zeolites [7] and synthetic zeolites [8].

Ion-exchange is usually operated by continuous processes in fixed bed plants. This procedure involves, however, good cation exchange selectivity for the noxious species to overcome the negative effects of interfering cations on the overall process performance. An alternative way to operate is to opt for a discontinuous process, i.e., the direct addition of a low cost natural zeolite to wastewater. Selecting a proper water–zeolite ratio allows to exhaustively remove the toxic cation from water in times of practical significance, transferring the polluting cation from water to a zeolitic sludge. Stabilization–inertization of the sludge in a cement matrix is usually a successful procedure to safely and irreversibly entrap the cation. This technique has proven to be suitable to remove and safely dispose chromium either using natural [9] or synthetic zeolites [10].

Previous research pointed out that ceramization of zeolitic sludges entrapping polluting cations may be a possible alternative procedure to safely dispose harmful species. In particular, it has been proven that pre-formed compacts of zeolitic sludge can be transformed by firing into stable alumino-silicate structures, which are highly resistant to leaching and possibly also of interest as ceramic materials [11].

On the basis of previous results pointing out the reasonable selectivity of phillipsite for chromium [9], this work aims to evaluate the ability of a phillipsite-rich tuff to steadily entrap chromium through a two stage process: (a) cation removal from water by ion-exchange and (b) stabilization of the resulting Cr-bearing sludge by thermal conversion of pre-formed compacts into ceramic materials.

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2. Experimental

2.1. Tuff sample

A phillipsite-rich tuff powder sample from Marano (Naples, Italy), belonging to the huge formation of *Neapolitan yellow tuff* (NYT), marketed by IZ, Italiana Zeoliti, Pigneto (MO, Italy) as PHIL-75, whose chemical composition has been reported previously [12], was selected as the natural exchanger. Its mineral composition was as follows: phillipsite 46%, chabazite 5%, analcime 9%, smectite 10% plus 30% of non-exchanging phases, including feldspar, pyroxene, biotite and amorphous compounds [12]. The cation exchange capacity (CEC), measured through the cross-exchange procedure [13], turned out to be 2.03 meq g^{-1}. Table 1 reports the results of the screen analysis of the tuff sample.

It is to be observed, that the choice of using a marketed product, costing US$ 0.08–0.10 per kg, is convenient, but not limitative, as more specific products, with higher zeolite content, may be easily found in the numerous tuff quarries operating in the same area [14]. Products richer in zeolite could also be obtained from the parent rock, by mineral enrichment processes, based on simple grinding and screening [15].

2.2. Preliminary Cr^{3+} exchange tests

Ion-exchange kinetic runs were carried out by putting 5–25 g of NYT powder into contact at room temperature, under continuous stirring in a batch reactor system, with a Cr^{3+} solution, simulating an electroplating wastewater, having the following cation composition: $[Cr^{3+}] = 45\,mg\,l^{-1}$, $[Na^+] = 20.3\,mg\,l^{-1}$, $[K^+] = 9.2\,mg\,l^{-1}$, $[Ca^{2+}] = 150\,mg\,l^{-1}$, $[Mg^{2+}] = 21\,mg\,l^{-1}$. The simulated solution was obtained dissolving, in bidistilled water, chromium and magnesium nitrates, provided by Baker Analyzed, and sodium, calcium and potassium nitrates, provided by Carlo Erba Analyticals. Cr^{3+} uptake by the NYT sample was monitored by drawing small solution samples at fixed times and measuring, after filtration, Cr^{3+} concentration by atomic absorption spectrophotometry (AAS, AA2100 Perkin-Elmer apparatus). pH was occasionally measured by a Radiometer mod. PHM220 pH meter, to be sure of the absence of any precipitate ($pH \leq 6$).

2.3. Preparation and firing of the Cr^{3+}-loaded tuff sample

A model tuff sludge, whose chromium amount was fixed on the basis of the results of above mentioned kinetic tests, was obtained by contacting, under continuous stirring, at room temperature, for 24 h 100 g of NYT sample with a 178 mg l^{-1} Cr^{3+}solution. Chromium content in the experimental Cr^{3+}-loaded tuff sample, estimated by AAS, after a suitable dissolution with a hydrofluoric–perchloric acid mixture, was 1.67 mg g^{-1}.

Cr^{3+}-bearing NYT samples were dry-formed into cylindrical compacts (i.d. = 10 mm; height = 3 mm), using a suitable steel mould and a Carver Lab press. Compaction pressure was fixed at 120 MPa. Firing of the compacts was carried out in an electric furnace. Green compacts were brought at temperatures ranging from 800 to 1100 °C (heating rate, 10 °C min^{-1}), kept at the selected temperature for 1 h, and finally slowly cooled down to room temperature inside the furnace.

Reference heat-treatments of Cr^{3+}-loaded powder tuff samples were also performed in a wide range of temperatures to investigate the thermal evolution of the zeolite (phillipsite) structure.

Table 1
Screen analysis of the tuff sample utilized

Screen size (μm)	Cumulative passing (wt%)
180	100.0
125	98.5
90	94.5
63	82.0
38	57.2

2.4. Characterization of Cr^{3+}-loaded tuff samples after firing

Changes in mineral composition of the samples after thermal treatments were investigated by X-ray diffraction (XRD, Philips PW 1730 apparatus, rad. Cu $K\alpha_1$).

Scanning electron microscopy (SEM, Oxford-Cambridge S440) was used to analyze the ceramic microstructure of the fired compacts.

Thermodilatometric analyses (Netzsch 402 E/7) were carried out in air on cylindrical Cr^{3+}-loaded tuff compacts (i.d. = 10 mm; height = 10 mm), obtained using a isostatic press (150 MPa). Heating rate was fixed at 10 °C/min; Al_2O_3 was used as reference material.

Physical properties of the fired compacts, such as open porosity and bulk density, were estimated using a mercury porosimeter (Micromeritics Autopore 9400). Linear shrinkage was determined, estimating with a gauge the variation of the compacts diameter after firing. Compressive strength measurements were performed using an Instrom 4204 instrument. All the physical measurements were carried out in triplicate and the results averaged.

2.5. Leaching tests

To test the safety of chromium immobilization, two procedures were used:

(a) Hundred milligram samples of unfired Cr^{3+}-loaded powder tuff were contacted, under continuous stirring, for 3 days with 50 ml of a 1 M NaCl solution, to evaluate the amount of back exchangeable Cr^{3+}.
(b) Samples of Cr^{3+}-loaded powder tuff, both fired and unfired (reference sample), were subjected to the so-called “availability test”, which is a measure of the extent of a given species (e.g., a cation) that is not tied up in poorly soluble mineral phases and can potentially be released into environment [16]. Accordingly, leached Cr^{3+} was estimated