Environmental and technological assessment of recycling exchanged zeolitic tuff

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Abstract

In this paper Cd\textsuperscript{2+}, Cr\textsuperscript{3+} and Pb\textsuperscript{2+} exchanged tuff has been used in mixtures with lime and gypsum in order to assess the potentiality of this type of binding system for the manufacture of pre-formed building elements. Exchanged zeolitic tuff can be obtained as a solid waste from ionic exchange processes of industrial acid wastewaters containing heavy metals. This type of treatment can be a cheaper alternative to traditional precipitation processes and this work has the scope to assess the feasibility of recycling the exchanged tuff from both the technological and environmental points of view. Experiments were carried out to study the effect of the above heavy metals on the hydration behaviour and mechanical strength of the hardened products. To this regard, curing at 40\degree C up to 28 days gives in all cases unconfined compressive strength higher than the minimum value required in Italy for pre-formed building elements. From the environmental point of view, the TCLP test has been used for the assessment of leaching behaviour of the hardened samples. Leaching results have shown that the effectiveness of stabilization of the three metals is in the order Cr>Pb>Cd. In any case, however, the metals are released in low amount. Indeed, the release of cadmium, which is the highest, does not exceeds about 10\% of the initial quantity. Finally, the system tuff-lime-gypsum has proven to offer better performance in respect to cement-based stabilization systems from the environmental point of view.
Introduction

In these last few years the management of solid wastes has been addressed towards recycling on site and off site. In this way, wastes can be returned to the original process or reused as substitutes for raw materials in other processes.

It is obviously very difficult to consider solid waste recycling from a general point of view, due to extremely wide range of physico-chemical properties of these residues. Often, their properties are such that the processes to which specific residues can be recycled are easily found. In other cases it may be necessary to develop innovative processes in order to ensure some form of reuse of a specific residue, or, alternatively, the processes from which a residue is produced should be properly modified in order to get a different one more easily re-processed.

The treatment of acid wastewaters containing heavy metals is an example of a process whose modification could be of considerable environmental advantage. It is usually operated by means of an alkaline reagent that rises the pH and promotes the precipitation of the metals in the form of hydroxides. Coagulants and flocculants are generally added as aiders of the process. The solid residue from such a type of process is a gelatinous sludge which is difficult to filter and de-water in many cases. Furthermore, this residue contains mixed heavy metals hydroxides in high concentration and then it is very difficult either to identify established processes, or to develop innovative ones to which it can be recycled. Evidently, the process should be modified in order to overcome these difficulties and get a more easily reusable residue.

The abatement of heavy metals by means of ionic exchange processes making use of powdered natural zeolitic tuffs can give an answer to this problem.

In previous work by Albino et. al. [1] and Cioffi et. al. [2] it was established that the zeolitic fraction of powdered natural tuff has good exchange capacity against some heavy metals, and also that the vitreous fraction retains its pozzolanic activity, which means that the silica originally present in the material reacts with lime to give calcium silicate hydrate (C-S-H). However, zeolitic tuff contains also reactive alumina which, in hydratory mixtures with calcium hydroxide and sulphate (lime and gypsum), gives calcium trisulphoaluminate hydrate (ettringite) [3].

The scope of this work is to assess the feasibility of a process that, starting from a powdered zeolitic tuff pre-exchanged with Cd^{2+}, Cr^{3+} and Pb^{2+} and mixed with lime and gypsum, gives products useful for the manufacture of building materials.

First of all, the effects of the above heavy metals on the chemical processes that convert the reactive silica and alumina into C-S-H and
ettringite are studied. Then, the technological properties of the products must be assessed and finally it must be checked that the process is environmentally acceptable.

The above three parts of the whole work have been respectively carried out by means of quantitative determination of chemically combined water, unconfined compressive strength and metal release in the Toxicity Characteristic Leaching Procedure (TCLP).

**Experimental**

The zeolitic tuff employed in this work comes from a quarry located in the Neapolitan area (Licola, Italy). Its characterization in terms of chemical composition, particle size distribution and main mineralogical phases present has been reported in a previous paper [3]. The cationic exchange capacity of this tuff is due to the presence of chabazite and phillipsite, as in all the tuffs from Central-Southern Italy.

The raw tuff was exchanged by means of concentrated solutions of Cd(NO$_3$)$_2$, Cr(NO$_3$)$_3$ and Pb(NO$_3$)$_2$. The solid-liquid mixture was well stirred for the time required to reach equilibrium. The results of these exchange processes of Cd$^{2+}$, Cr$^{3+}$ and Pb$^{2+}$ are, respectively, 42.1, 13.0 and 137.0 milligrams of exchanged metal per gram of raw tuff.

The composition of the hydratory mixtures used in this work, on an unexchanged tuff equivalent basis, is tuff 41.3%, lime 25.7%, gypsum 24.8% and Portland cement 8.2%. The presence of Portland cement in the mixtures is not strictly necessary, inasmuch as systems containing tuff and calcium hydroxide and sulphate are able to generate both C-S-H and ettringite. However, Portland cement, when added in small amount, shows catalytic activity on the hydration of the above systems [3].

The system containing raw tuff and those containing Cd$^{2+}$, Cr$^{3+}$ and Pb$^{2+}$ pre-exchanged tuff were hydrated at 25 and 40°C, 100% R.H., for 1, 3, 7, 14 and 28 days and at 70 and 85°C, 100% R.H., for 2 days. In any case the water/solid ratio was 0.53. The time-temperature hydration conditions were chosen because in a previous paper [4] they were found to be suitable for the development of good mechanical properties in systems similar to those studied in this paper.

At any pre-fixed hydration time, samples were taken, ground under acetone and rinsed with diethyl ether to stop the reaction.

Specimens of the samples were analysed for the amount of chemically bonded water by means of loss on ignition at 1000°C for two hours.

Cubic samples 4x4x4 cm$^3$ aged 28 days at 25 and 40°C and 2 days at 85°C were tested for unconfined compressive strength.
Cylindrical samples \((d \times h = 2 \times 3 \text{ cm}^2)\) of the three mixtures containing pre-exchanged tuff aged 28 days at 25 and 40°C and two days at 80°C were used for the dynamic TCLP leaching test \([5]\) with pH 4.94 acetic acid/sodium acetate buffer, liquid/solid ratio equal to 20 ml/g and leachant renewals at 1, 3, 8, 14, 24, 48, 96, 168, 376, 672 and 1344 hours.

**Results and discussion**

Tables 1 and 2 show quantitative data of chemically combined, non-evaporable water determined in all the experimental conditions tested. It is seen that temperature has a positive effect on the amount of chemically combined water, but the extent to which this positive effect is observed decreases as temperature increases. In fact, the values detected at 85°C are only slightly higher than those found at 70°C. The data after two day hydration at both 70 and 85°C are very similar to the values found at 25°C after 28 days, according to previous results obtained with systems of similar nature \([4]\).

**Table 1 - Chemically combined water at 25 and 40°C, wt%**

<table>
<thead>
<tr>
<th>Temperature 25°C</th>
<th>Time, days</th>
<th>Raw tuff</th>
<th>Cd tuff</th>
<th>Cr tuff</th>
<th>Pb tuff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.66</td>
<td>3.98</td>
<td>3.52</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.21</td>
<td>8.03</td>
<td>6.43</td>
<td>5.53</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>10.04</td>
<td>10.42</td>
<td>8.61</td>
<td>7.67</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>12.62</td>
<td>13.00</td>
<td>11.20</td>
<td>10.04</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>15.45</td>
<td>16.31</td>
<td>15.16</td>
<td>13.40</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>16.30</td>
<td>17.00</td>
<td>15.60</td>
<td>15.20</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature 40°C</th>
<th>Time, days</th>
<th>Raw tuff</th>
<th>Cd tuff</th>
<th>Cr tuff</th>
<th>Pb tuff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.68</td>
<td>7.10</td>
<td>5.59</td>
<td>4.73</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11.57</td>
<td>11.95</td>
<td>10.02</td>
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<tr>
<td>7</td>
<td>13.45</td>
<td>14.30</td>
<td>11.70</td>
<td>12.35</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>15.80</td>
<td>16.32</td>
<td>14.70</td>
<td>15.34</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>19.00</td>
<td>20.34</td>
<td>18.50</td>
<td>19.80</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>21.10</td>
<td>22.56</td>
<td>19.30</td>
<td>21.65</td>
<td></td>
</tr>
</tbody>
</table>
Table 2 - Chemically combined water after two day hydration, wt%

<table>
<thead>
<tr>
<th></th>
<th>70 °C</th>
<th>85 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw tuff</td>
<td>14.8</td>
<td>15.1</td>
</tr>
<tr>
<td>Cd tuff</td>
<td>15.4</td>
<td>15.5</td>
</tr>
<tr>
<td>Cr tuff</td>
<td>12.1</td>
<td>12.5</td>
</tr>
<tr>
<td>Pb tuff</td>
<td>12.5</td>
<td>13.5</td>
</tr>
</tbody>
</table>

The effect of the presence of the heavy metals Cd, Cr and Pb is different from each other. In all the experimental conditions tested, the presence of cadmium causes an increase of the amount of chemically combined water in respect to the undoped system. On the other hand, chromium has always the opposite effect. Lead shows a negative effect with the exception of the longer times (28 and 56 days) at 40°C, when the amount of chemically combined water reaches values slightly greater than the undoped system. This is quite an unexpected result inasmuch as it is well known that lead is a strong hydration retarder of Portland cement [6] and systems able to generate ettringite [7]. Finally, it is to be pointed out that the differences in behaviour caused by the presence of the heavy metals decreases as hydration temperature increases.

As in any system containing lime, gypsum and reactive silica and alumina [8-10], the main hydration products in the system tuff-lime-gypsum are calcium silicate hydrate and ettringite. This has been found by means of differential thermal analysis (results not shown).

Figure 1 shows the results of unconfined compressive strength determination. It is seen that 40°C is the optimum hydration temperature that maximizes mechanical strength. This condition is suitable for the manufacture of pre-formed building elements for which Italian rules state a minimum value of 12 MPa (dashed line in Figure 1).

The effect of heavy metals on mechanical strength is scarce, with the exception of lead doped system at 40°C for which mechanical strength is seen to be quite higher than for the other systems.

The results of the TCLP leaching test are reported in Figure 2 and shows that the metals are released in the order Cd>Pb>Cr. Hydration temperature has a little effect on metal release and the maximum amount released is not higher than about 10% in the case of the system doped with cadmium. Best results have been obtained with the system doped with chromium, where the amount released is well below 1%.
Figure 1: Mechanical strength of systems with raw and Cd\textsuperscript{2+}, Cr\textsuperscript{3+} and Pb\textsuperscript{2+} exchanged tuffs.

Figure 2: Release of cadmium, chromium and lead in TCLP test.
It is reported in the literature that chromium is stabilized by the occurrence of chemical mechanisms in traditional systems. Bishop in a study on a cement-based stabilization system [14] found that even after all of the alkalinity had been leached from the stabilized sample, chromium was still largely retained (85%) in the silicate matrix. This gave rise to the theory that chromium, originally present as the hydroxide, had been respeciated in a complex silicate form, probably as metal-hydrated oxide/silicate structures of indeterminate composition. Our data show that chromium is retained in the matrix to an extent greater than that reported in the literature, and this proves that the stabilizing system studied in this paper offers better performance in comparison to cement-based systems. This may well be due to the incorporation of chromium in complex metal silicates, but the occurrence of a further chemical mechanism in the system under investigation can be more powerful in respect to chromium stabilization. In fact, the zeolitic fraction of the tuff exchanges chromium irreversibly [15]. Then, despite the high calcium concentration in the pore solution, chromium is not given off during hydration being kept within the zeolite crystal lattice by strong ionic bonds. The occurrence of this mechanism can also explain why chromium is best retained in respect to lead and cadmium in the hydrated system tuff-lime-gypsum. Cadmium and lead exchange processes are reversible and then these metals can be given off during hydration. The consequence is that processes such as respeciation in the form of some insoluble compounds or incorporation within the hydration products are required for stabilization of lead and cadmium to take place. The new chemical bonds that form in the cases of lead and cadmium may well be weaker than the ionic one that binds chromium in the zeolite crystal lattice.

Cadmium stabilization relies only on the precipitation as the hydroxide. Butler et. al. [16] attribute cadmium entrapment to early formation of Cd(OH)$_2$ which provides nucleation sites for hydration products. This results in cadmium being in the form of the hydroxide with an impervious coating. When the sample is monolithic cadmium is retained within the matrix provided that pH does not drop to the acid range. Bishop [14] found a dramatic cadmium release in the case of a cement-based system using a sequential batch acid leaching test. The onset of cadmium release coincided exactly with the sudden decrease of final leachant pH from 11 to about 5 and after fifteen extractions about 75% of cadmium leached out. Again, the system tuff-lime-gypsum studied in this paper proves to offer better performance in respect to cement-based ones. In fact, cadmium release reaches a maximum cumulative amount of only about 10% after ten extraction in the TCLP test carried out with a monolithic sample and an acid buffered leachant.
Conclusions

The use of pre-exchanged zeolitic tuff does not worsen the technological properties of the system tuff-lime-gypsum. On the contrary, when Pb-loaded tuff is used, mechanical strength improves significantly after curing at 40°C. At this temperature, all the system give products suitable for the manufacture of pre-formed building elements.

The TCLP leaching test carried out in this paper has shown that lead and chromium are effectively stabilized by means of prevailing chemical mechanisms, as in other cement-based stabilization systems. In addition, in the case of chromium, a relevant contribution to stabilization can be given by the ionic exchange process being irreversible.

Cadmium, which is fixed by prevailing physical mechanisms, leaches out to an extent of about 10% which, when compared to other cement-based stabilization systems, proves that in our case this metal is retained more effectively.

From the environmental point of view, in relation to the leaching behavior of all the three metals studied, the system tuff-lime-gypsum has proven to offer better performance than other cement-based stabilization systems. This may be due to the parallel formation of ettringite beside calcium silicate hydrate.

References


