USE OF ADMIXTURES IN ORGANIC CONTAMINATED CEMENT-CLAY PASTES

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Abstract

In this work microstructure, porosity and hydration degree of cement-based solidified/stabilized wasteforms were studied before assessing their leaching behaviour. 2-Chloroaniline was chosen as a model liquid organic pollutant and included into cement pastes which were also modified with two different admixtures for concrete: a superplasticiser based on acrylic modified polymer and a synthetic rubber latex. An organoclay, modified with an ammonium quaternary salt (benzil-dimethyl-tallow-ammonium, BDMA), was added to the paste as pre-sorbtent agent of the organic matter.

Two different experimental procedures were adopted for the contaminated pastes. In the former one the organoclay, the pollutant and some water were mixed together to obtain a homogenous slurry, then the cement powder and the remaining water were added; finally, liquid admixtures, i.e. superplasticiser and/or rubber latex, were poured into the mixture. The whole process lasted about 15 minutes. In the latter, the organoclay and the pollutant suspended in water were maintained in contact for 24 hours before admixing them with the cement powder, the remaining water and the admixtures.

For each procedure four series of samples were prepared: without admixture, with superplasticizer, with latex and with superplasticizer and latex. For each series, reference samples without pollutant were also prepared, for a total of twelve sets of specimens.

All the samples were dried up to constant weight in order to stop hydration at different times during the first 28 days of curing (typically, after 24 hours, one week and 28 days). Then, microstructural characterization of the hardened cement-clay pastes was investigated by powder X-ray diffraction (XRD). Hydration degree and porosity were studied by thermal analysis (TG/DTA) and Mercury Intrusion Porosimetry (MIP), respectively. On samples cured for 28 days, the organic waste immobilization process performance was assessed by the short term leach test set by Italian regulation for industrial waste recycling (D.M. 5 February 1998).

Keywords: organic waste, cement pastes, admixtures, organoclay, hydration degree

1. Introduction

Solidification and stabilization (S/S) is a well-known technique of disposal of a wide range of hazardous wastes; in particular, cement-based S/S technology is currently used in the treatment of hazardous inorganic (e.g. heavy metals) or radioactive wastes before landfilling (Glasser, 1997). However, when the wastes have a high content of organic matter, cement matrices might reveal unsuitable for retaining organic pollutants because most of these compounds have adverse effects, such as retardation or inhibition, on the hydration processes of cement pastes (Montgomery et al., 1991a; Natali Sora et al., 2002). To neutralize these negative effects, it was suggested to use pre-sorbent materials like activated carbons or organophilic clays (Gong and Bishop, 2003; Montgomery et al., 1991b). Nevertheless, the use of organoclays as a pre-solidification adsorbent material could be not yet satisfactory, because of the reversibility of the adsorption process (Natali Sora et al., 2005). The consequent

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release could be mitigated by drastically reducing the porosity/permeability of the cement matrix. This result could be achieved in a number of different ways, mainly reducing the water-to-cement ratio.

The aim of this work was to assess the effectiveness of the addition of commercial admixtures, normally used in concrete, to reduce porosity/permeability. To this purpose, it was studied the leaching behaviour of cement–clay pastes, modified with superplasticizer and/or rubber latex, and contaminated with a model organic pollutant, i.e. 2-chloroaniline.

2. Experimental

2.1 Materials

All the cement pastes were prepared using Ordinary Portland Cement (OPC) Type I 52.5 R (CementiRossi Piacenza), an organoclay (Laviosa Chimica Mineraria, Livorno), as pre-sorbent for the organic liquid waste and different types of commercial admixtures for concrete, i.e. a superplasticiser based on acrylic modified polymer and a synthetic rubber latex (Mapei). The model organic pollutant was 2-chloroaniline, (2-CA), Fluka (99.5% purity).

2.2 Sample preparation

The organoclay, used as supplied by the producer, was a montmorillonite modified with an ammonium quaternary salt (benzil-dimethyl-tallow-ammonium, BDMA); the basal spacing, determined by XRD analysis, was $22.7 \pm 0.2$ Å and the amount of organic matter (om), estimated from the weight loss measured by thermogravimetric analysis, was $0.32$ kg om/ kg s.

The contaminated pastes, whose compositions are reported in Table 1, were prepared following two different procedures:

- in the first one the organoclay, 2-chloroaniline and some water were mixed together for some minutes to obtain a homogenous slurry, then the cement powder and the remaining water were added; finally, liquid admixtures, i.e. superplasticiser and/or rubber latex, were poured into the mixture; the whole process lasted about 15 minutes (samples marked with letter I),
- in the second one, the organoclay and 2-chloroaniline suspended in water were maintained in contact for 24 hours on a rotating arm; then the slurry was admixed with cement powder, the remaining water and the admixtures (samples marked with letter I*)

<table>
<thead>
<tr>
<th>Sample</th>
<th>w/c</th>
<th>w/sm</th>
<th>s/c</th>
<th>sp/c</th>
<th>af/l</th>
<th>rl/c</th>
<th>2-CA/c</th>
<th>os/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.85</td>
<td>0.70</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>0.22</td>
</tr>
<tr>
<td>A-I/A-I*</td>
<td>0.85</td>
<td>0.70</td>
<td>0.30</td>
<td>/</td>
<td>/</td>
<td>0.08</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.68</td>
<td>0.55</td>
<td>/</td>
<td>0.015</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>0.22</td>
</tr>
<tr>
<td>B-I/B-I*</td>
<td>0.67</td>
<td>0.55</td>
<td>0.30</td>
<td>0.015</td>
<td>/</td>
<td>/</td>
<td>0.08</td>
<td>0.22</td>
</tr>
<tr>
<td>C</td>
<td>0.85</td>
<td>0.70</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>0.05</td>
<td>/</td>
<td>0.22</td>
</tr>
<tr>
<td>C-I/C-I*</td>
<td>0.85</td>
<td>0.70</td>
<td>0.30</td>
<td>/</td>
<td>0.05</td>
<td>0.08</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.56</td>
<td>0.46</td>
<td>0.28</td>
<td>0.015</td>
<td>0.002</td>
<td>0.14</td>
<td>0.08</td>
<td>0.20</td>
</tr>
<tr>
<td>H-I/H-I*</td>
<td>0.56</td>
<td>0.46</td>
<td>0.28</td>
<td>0.015</td>
<td>0.002</td>
<td>0.14</td>
<td>0.08</td>
<td>0.20</td>
</tr>
</tbody>
</table>

For each procedure four series of samples were prepared: without admixture (series A), with the superplasticizer (series B), with latex (series C) and with the combined use of superplasticizer and latex (series H). For each series, reference samples without pollutant were also prepared, for a total of twelve sets of specimens. Polluted samples of each series are marked with letter −I.
The fresh pastes were cast into polyethylene cylindrical moulds (3.2 cm height and 2.2 cm diameter), only partially filled and sealed. All samples were cured at a constant temperature of 23±1°C. One specimen for each group was demoulded at 1, 7 and 28 days and dried up to constant weight (at 85°C the samples with 2-CA and at 105°C the references) in order to stop hydration. Then the solidified monolith was cut and ground in a grinding mill to obtain the powders used for XRD and TGA analyses. A second series of specimens was demoulded after 28 days and used for the Mercury Intrusion Porosimetry (MIP). Another series was demoulded after 28 days and used to perform a dynamic leach test.

2.3 Leaching test

The leaching test adopted in this work was indicated by the Italian regulations (D.M. 5-1998) which assess whether a waste can be considered hazardous or not. It is a dynamic leach test which has to be performed on monolithic samples using deionized water as leachant. The leaching was started after 28-day curing: the solidified samples were smoothed, cleaned and each of them hung in a 60mL jar filled with 35 mL of water, completely immersed and maintained at 24°C without agitation; the liquid to solid ratio was 5:1. Water was periodically renewed at 2, 8, 24, 48, 72, 102, 168, 384 hours (16 days). Concentration of 2-CA in the leachates was determined at each leachant renewal, according to the test procedure; the amount of 2-CA was gas-chromatographically determined after isoctane extraction. GC analyses were performed with a Carlo Erba Mega mod. 5100 instrument, equipped with an on-column injector, flame ionization detector and HP fused silica capillary column 0.32 mm internal diameter and 50m length, coated with 5% phenylmethylsilicone rubber, 0.5 µm thickness. The temperature was linearly raised from 70°C to 130°C at 4°C/min; then to 250°C at 10°C/min. A final isothermal time of 5 min at 250°C was maintained.

2.4 Sample characterization

X-ray diffraction data were collected with a Philips diffractometer at room conditions using graphite monochromated Cu-Kα radiation. The step scan was 0.02° and the measuring time 10 seconds per step. The phase analysis was made using the Diffrac Plus Evaluation software (Bruker AXS). TGA/DTA analysis was carried out in nitrogen using about 20 mg of powdered dried samples heated to 900°C at 10 °C/min rate. The amounts of portlandite, Ca(OH)_2, and calcite, CaCO_3, were determined considering the weight-loss between 400 and 500 °C and 500 and 800 °C, respectively; all values are reported as grams per 100 grams of dried sample and the amounts of calcite and portlandite were corrected for the weight loss of cement powder.

Pore structure of the different systems was determined by means of mercury intrusion porosimetry (MIP) for pressures of up to 400 MPa (r = 0.2 nm according to Washburn model). The samples (fragments of 1.5-2 grams) were previously dried at 110°C in oven for 12 hours and then placed in an dryer-vessel until a constant weight to be reached.

For thermal analysis and mercury intrusion porosimetry the values of the samples prepared with pre-adsorption are not reported; but all the considerations can be done even for the series –I*

3. Results and discussion

Since the interactions between the organoclay and the organic pollutant are relatively weak and reversible (Natali Sora et al., 2005), it is vital to reduce the porosity/permeability of the matrix to decrease the release of the pollutant; so two organic admixtures were used. Indeed, it is known that the superplasticizer drastically lowers the water amount (and consequently the porosity), whereas rubber latex develops a polymeric film around cement particles that should hinder the pollutant mobility.

A schematic representation of this line of reasoning is reported in figure 1: first of all, a set of samples was prepared using two different admixtures, i.e. superplasticizers and rubber latex; then two different procedures were adopted to slow down the release of 2-chloroaniline. In the former one the pastes were prepared after a 24-hour pre-adsorption process, in the latter the two admixtures were used in combination.
3.1 Leaching behaviour

In figure 2 the cumulative amount of 2-chloroaniline, released after 16 days, is shown for the sample with (-I*) and without (-I) pre-adsorption. At the end of the leaching test the sample without any admixture (A-I) released 16.5% of 2-CA, while those prepared using the superplasticizers (B-I) and the rubber latex (C-I) released 12.8% and 14.3%, respectively. The use of the admixtures shows a slight improvement (about 3.0%). The process of pre-adsorption yielded better results: 13.4%, 9.5%, 11.2% of 2-CA released in samples A-I*, B-I* and C-I*, respectively. If compared with sample A-I, there was a further improvement of 3.2%, 7.1% and 5.4%, respectively. However, the results obtained by the combined use of the superplasticiser and the latex were more encouraging having reduced the release by 11.4% (H-I) and 10.2% (H-I*) with respect to the reference (A-I).
3.2 Thermal analysis

A quantitative determination of the amounts of portlandite and calcite was performed by TGA and the results were reported as grams of substance per 100 grams of dried sample in Table 2. From the experimental data it could be observed that neither the pollutant nor the admixture greatly influenced the hydration process. In particular, comparing the amount of portlandite, we observed that already at 24 hours of hydration all the samples, contaminated and uncontaminated, had a consistent amount of portlandite. Comparing the amount of portlandite in the A and B series, the same trend could be observed: portlandite slightly decreased in the first 28 days of hydration as a consequence of the normal carbonation process. Some anomalies were observed in the samples containing the latex (series C and H), rising some doubts on the usual way adopted to estimated the amount of portlandite, i.e. from the weight loss in the range of 400-500 °C. Indeed, the calcium hydroxide interacts with the polymer (Al-Noaimi et al., 2000) making difficult the dehydration process; as a consequence, it was reported that two endothermic peaks appear in the usual dehydration area of portlandite (Chandra et Ohama, 1994).

<table>
<thead>
<tr>
<th>Sample</th>
<th>1 d</th>
<th>2 d</th>
<th>28 d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH</td>
<td>Calcite</td>
<td>CH</td>
</tr>
<tr>
<td>A</td>
<td>16.8</td>
<td>9.0</td>
<td>14.7</td>
</tr>
<tr>
<td>A-I</td>
<td>17.2</td>
<td>11.3</td>
<td>15.3</td>
</tr>
<tr>
<td>B</td>
<td>15.3</td>
<td>8.8</td>
<td>18.2</td>
</tr>
<tr>
<td>B-I</td>
<td>17.8</td>
<td>11.8</td>
<td>13.4</td>
</tr>
<tr>
<td>C</td>
<td>19.2</td>
<td>10.4</td>
<td>21.3</td>
</tr>
<tr>
<td>C-I</td>
<td>22.2</td>
<td>12.3</td>
<td>26.8</td>
</tr>
<tr>
<td>H</td>
<td>23.6</td>
<td>11.8</td>
<td>21.9</td>
</tr>
<tr>
<td>H-I</td>
<td>16.7</td>
<td>12.4</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Table 2: Amounts of portlandite(CH) and calcite determined by TGA for all the samples

In figure 3 typical DTA curves are shown: all the samples of series H and H-I in the first 28 days of hydration are reported. The broad endothermic peak (•) at low temperature (around 200°C) is due to the decomposition of calcium silicate hydrates, while the sharp one at about 450°C (♦) corresponds to the dehydration of calcium hydroxide. However, at 28 days it is clearly visible a second peak at about 400°C (●) which originates from the calcium hydroxide bonded to the polymer, as suggested in the literature.

Figure 3: Comparison of DTA curves of samples H and H-I at 24 hours, 1 week and 28 days.
3.2 XRD analysis

Figure 4 shows a typical XRD powder pattern for the 28-day-old paste of series H-I. Tricalcium silicate, β-
dicalcium silicate, portlandite, calcite, small amounts of dolomite and quartz, modified montmorillonite and
amorphous hydrated calcium silicate (C-S-H) were found in pastes of series A, B, C and H, respectively. The
patterns of 7-day-old pastes are similar to the 28-day-old pastes.
In contaminated pastes carbonate phases, mainly Ca₄Al₂O₆(CO₃)₀.₅(OH)·11.5H₂O (PDF # 410221) were found as
products of the hydration reactions. These carbonate phases might have been present in very small quantities also
in uncontaminated samples, but due to the overlapping of the strongest peaks in the range 10°<2θ<12°, their
identification was difficult. Crystalline ettringite was not detected as a consequence of the drying treatment
performed to stop hydration reactions after curing, which might have damaged the ettringite crystals.
The OPC hydration was roughly estimated from the XRD patterns, by measuring the integrated intensity of the
portlandite peaks at d = 4.89, 2.62 and 1.79Å, respectively. The comparison of the integrated intensities of
portlandite peaks highlighted that the lower water to cement ratio due to the addition of the superplasticiser, led
to some delay in the hydration kinetics, while the other series showed similar behaviour. No significant
differences were found between contaminated and uncontaminated samples of a same series except for series C.

3.2 The porosimetric investigations

The samples investigated exhibit generally a great value of the total porosity (35÷45 %) related to an high a/c
ratio and to the presence of the clay minerals in the mixture. The fig. 4 shows a representative pore size
distribution for the system B with superplasticizer (total open porosity = 42%; mean radius = 0.05 µm ) and for
the H system with superplasticizer and latex (total open porosity = 38 %; mean radius = 0.03 µm) the last one
giving the best results in the leaching tests. Therefore the use of superplasticizer shows by itself to be suitable to
producing significant effect on the microstructure of the cement matrices. Although the samples maintain high
porosity values, their pore size distribution shifts towards extremely small pore size classes when the a/c ratio is
reduced; so suggesting that system H can be considered less permeable than the other systems (A and C in
particular). Further investigation have to be carried out in order to obtain more information about the active
permeability and the related leaching of the pollutants.
4. Conclusions

The addition of the two admixtures did not affect the phase composition of the hydration products, as confirmed by XRD analysis. However, DTA revealed the presence of interaction between portlandite and the latex in the series H, which alter the normal dehydration behaviour of portlandite.

The leaching test pointed out that the addition of the admixtures had improved the leaching behaviour of the solidified monoliths, if compared with the sample without any admixture. The results obtained using two admixtures are more encouraging having reduced the release by about 10% with respect to the reference (A-I). In any case, the pre-adsorption process seems to be more efficient when there is only one admixture; the results obtained for series H are better than the others, but in this series there are no differences between the samples prepared in the two different ways.

Although some improvements in the leaching behaviour of these monoliths were achieved, the amount released seemed to be still quite high for safe environmental applications.

References