X-Ray Diffraction study of particulate tannery waste solidified in cement

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Abstract - The leather industry creates a large quantity of organic and inorganic waste containing chromium. This research examines stabilization of particulate tannery waste in type II Portland cement. Several clays, Brazilian polycationic smectite modified in laboratory and commercial clays, were used as additives with the aim of optimizing chromium adsorption. Tannery waste was added in quantities of 10, 15 and 20% relative to cement mass. The solidification components were analyzed separately and in combination in the solidified mixes using X-ray diffraction. The analysis showed that reactions between the waste and the cement occurred, and that the tannery waste modified the final compounds of the system. Calcium sulfate present in the waste increased ettringite formation. Chromium also reacted with cement, since compounds with chromium and calcium were identified. Substitution of aluminum and silicon by chromium was also observed.

Introduction

The tannery wastewater contains organic and inorganic compounds. Among the inorganic compounds present in high concentrations, there are ammonia, sulfides and chromium that are inhibiting factors for any kind of biological treatment[1]. Leather tanning is a major consumer of chromium. Of all chromium used for commercial purposes in 1996, the fraction used for leather tanning was 40% in the Western world and 13% in the USA [2]. In leather tanning much of the chromium appears to complex with proteins after chromium penetrates the hide.

One study of the characteristics of two major tannery complexes in different districts in Turkey was performed [3]. One of the districts, containing 107 tanneries processing cattle hide and sheepskin, had wastewater flow of 13000-14000m³.d⁻¹. Characterization of the wastewater showed high concentrations of total chromium, ranging from 58 to 213mg/L.

There are several technologies available for treatment or removal of chromium from waste streams or contaminated soil. Solidification/Stabilization is one treatment process, which immobilizes the material with respect to potential leaching into the environment [4; 5].

Stabilization has been defined by as a technique that reduces the hazardous potential of a waste by converting the contaminants into their least soluble, mobile or toxic form[6]. In addition to chemical modifications, solidification encapsulates the waste in a solid of high structural integrity. Portland cement is the most common solidifying agent, but cement-based systems may contain many additives mainly for control of setting, physical property development and metal
and/or organic immobilization. Clay sorbents have been used widely by waste generators, treaters or in landfill operations[7].

Numerous studies related to encapsulation of chromium by cement [8-10] have been described, with wastes ranging from aqueous Cr species to chromite ore processing residue to tannery wastes. An issue identified very early was the differences in behavior between Cr(III) and Cr(VI) species, with the latter generally being more water soluble and more toxic. Our previous work in the area has involved mechanistic studies of aqueous Cr species solidified by Portland cement [11] and solidification of tannery waste [12]. The former work centered around determining the extent of reduction of Cr(VI) to Cr(III) using FeSO₄ as a reducing agent during solidification. The tannery waste studies were principally aimed at development of thermal analysis techniques as a tool for investigation of waste solidification in systems that contained cement, clay, and an organic-containing waste. The work showed that thermogravimetry and derivative thermogravimetry were fast and accurate methods for quantitative determination of the cement phases formed during hydration. In addition, it was shown that thermogravimetry can give a quantitative determination of organics present, in this case the organics were part of the tannery waste. The presence of Wyoming bentonite and tanning wastes resulted in a considerably higher extent of cement hydration over 28 days of cure as compared to cement alone or cement plus bentonite.

Methodology

Commercial Portland cement Type II E-32 was used, identified as C. Two different sodium bentonites were used: Wyoming sodium bentonite, identified as S, and a modified bentonite (Na), obtained from verde-claro polycationic bentonite by cation exchange with sodium carbonate [13]. The verde-claro clay is from Paraíba State, Brazil. A commercial organoclay, identified as Ti, and a modified organoclay (O) were also used. In both cases the modified clays were prepared from a polycationic bentonite by cation exchange with alkylbenzyldimethylammonium chloride [13].

The waste, identified as T, was collected after its industrial drying process, in a tanning facility located at City of Franca, São Paulo State, Brazil. In the laboratory the material was dried at 60°C and ground using mortar and pestle. The particle size of the waste allowed 100% to pass through sieve number 100.

The control specimens were prepared with a water/total dry material ratio of 0.6. The percentage mass used with the samples containing waste was related to the dry cement mass. The clays percentage used was 5%. To allow minimum workability, the water/cement (w/c) ratio was different according to the quantity of waste used. For 10 and 15% by mass of tannery waste used, the w/c ratio was of 0.6; for 20% by mass of tannery waste, the w/c ratio was of 0.7. The dry material was mixed initially followed by addition of water and manual mixing until a homogeneous paste was formed.

The samples were kept in cylindrical plastic molds, with dimensions 5 cm diameter × 10cm height. Each mold with the sample was tapped on the ground to eliminate possible air bubbles. The molds were capped. The samples had a cure time of 28 days in a wet chamber at 25°C with 100% humidity. After this period the samples were removed from the molds and ground in an agate mortar and pestle to a particle size passing through sieve #100.

The raw samples used in this research were analyzed also by XRD. The samples, with the exception of the cement and the organoclays, were micronised in ethanol to obtain a particle size
up to 5µm using a McCrone Micronising Mill. The samples then were centrifuged for 20 min. at 2000 rpm and the liquid phase was removed. The raw samples were dried at 60 ºC for 24 h before being placed in the round molds.

The samples were analyzed by X-ray diffraction using a Siemens D5000 diffractometer. The radiation was K-α of copper, with steps of 0.040º (2θ) and time for steps of 0.500 s. The compounds were analyzed according to the d-spacing values, with 2θ between 2º and 70º.

Results

Table 1 presents the nomenclature used to identify the compounds by XRD. All the raw samples were analyzed separately. The samples containing either organoclays or cement were not micronized in order to avoid any reaction or structure change during the material characterization. The main peaks were identified for all samples.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Compound</th>
</tr>
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<tbody>
<tr>
<td>Q</td>
<td>Quartz</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum sulfate hydrated</td>
</tr>
<tr>
<td>CC</td>
<td>Calcite</td>
</tr>
<tr>
<td>G</td>
<td>Gypsum</td>
</tr>
<tr>
<td>C₃S</td>
<td>Tricalcium silicate</td>
</tr>
<tr>
<td>AO</td>
<td>Aluminum oxide hydrated</td>
</tr>
<tr>
<td>CO</td>
<td>Calcium oxide</td>
</tr>
<tr>
<td>SAS</td>
<td>Sodium aluminum silicate hydrated</td>
</tr>
<tr>
<td>CMA</td>
<td>Calcium magnesium aluminum oxide silicate</td>
</tr>
<tr>
<td>NC</td>
<td>Sodium chromium oxide</td>
</tr>
<tr>
<td>CS</td>
<td>Chromium sulfate hydrated</td>
</tr>
<tr>
<td>CrO</td>
<td>Chromium oxide</td>
</tr>
<tr>
<td>AS</td>
<td>Aluminum silicate</td>
</tr>
<tr>
<td>FS</td>
<td>Iron sulfate</td>
</tr>
<tr>
<td>SCS</td>
<td>Sodium calcium sulfate hydrated</td>
</tr>
<tr>
<td>P</td>
<td>Portlandite</td>
</tr>
<tr>
<td>E</td>
<td>Ettringite</td>
</tr>
<tr>
<td>CAS</td>
<td>Calcium aluminum silicate hydrated</td>
</tr>
<tr>
<td>CSH</td>
<td>Calcium silicate hydrated</td>
</tr>
<tr>
<td>S</td>
<td>Smectite</td>
</tr>
<tr>
<td>K</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>M</td>
<td>Mica</td>
</tr>
<tr>
<td>CCO</td>
<td>Calcium chromium oxide hydrated</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium hydroxide hydrated</td>
</tr>
<tr>
<td>CCC</td>
<td>Calcium chromium carbonate hydrated</td>
</tr>
</tbody>
</table>

XRD analysis (Figure 1) of the unhydrated Type II Portland cement used in the present studies showed the compounds typically present in cement: CaSO₄, tricalcium silicate, CaCO₃, calcium magnesium aluminum oxide silicate and calcium oxide. Aluminum oxide and quartz were also identified as low intensity peaks. This cement is usually referred to as blended cement; that is, it contains added calcium carbonate and it was already characterized by thermal analysis by the authors [14]. The only surprise in the analysis was the absence of peaks that could be identified as dicalcium silicate (C₂S). After 28 days of hydration the cement showed the known products ettringite(trisulfate), calcite and calcium hydroxide. Other hydrated compounds that
could be observed were calcium aluminum silicate, calcium silicate and sodium aluminum silicate.

Fig. 1. X Ray Diffraction of unhydrated Portland cement Type II and tannery waste.

The XRD for the tannery waste, also represented in Figure 1, showed as main peaks calcium sulfate (probably due to sodium sulfide used in the peeling process and the use of calcium hydroxide to precipitate chromium during the pretreatment), chromium oxide, sodium carbonate and chromium hydroxide.

The Brazilian verde-clara clay, which is considered to be polycationic, was subjected to cation exchange with sodium carbonate to adjust the clays to optimize waste adsorption. The cation exchange can be confirmed by observing the first smectite peak (\(d_{001}\)). In the verde-clara natural clay, the first peak was at 14.5Å. The modified bentonite, which was submitted to a cation exchange for sodium presented this peak at 12.4 Å, a typical value expected for a sodium bentonite. This value was confirmed in the commercial sodium bentonite that showed a spacing of reflection of 12.3Å. Sodium bentonite typically shows a spacing of reflection at 12-13Å[15]. For an organoclay a higher spacing of reflection is expected. In this case the modified Brazilian clay showed a smectite peak at 24.1Å, and the commercial organoclay had a \(d_{001}\) at 18.24Å. The modified clays showed kaolinite and quartz as impurities. The commercial sodium bentonite and organoclay had quartz and mica as impurities. These results are represented at Figure 2.

Fig. 2. X Ray Diffraction of sodium bentonites, Na and S and organoclays, O and Ti.

The XRD patterns for the hydrated Portland cement and a cement sample containing 10% by weight tannery waste are shown in figure 3. Formulations containing clays in addition to cement and waste are shown in figure 4. Compared to hydrated cement alone, it can be noticed
that the ettringite peaks show higher intensity in all the samples containing waste. Higher ettringite formation is probably due to the high quantity of calcium sulfate present in the waste, and calcium sulfate is known to promote the hydration of tricalcium aluminate forming ettringite [16]. Previous studies have shown that both trivalent and hexavalent Cr react with cement. Due to the high pH, the waste can form insoluble hydroxides, react with cement components to form a variety of compounds, or result in mixed-metal systems in which Cr substitutes for other metal ions [17-22].

![Fig. 3. X Ray Diffraction patterns for hydrated Type II Portland cement and the hydrated cement with 10% waste (CT) after 28 days of curing time.](image)

Chromium present in the tannery waste showed resulted in major differences in the present samples. Hydrated calcium chromium oxide appeared in the XRD analysis as a result of chromium oxide reaction with the high concentration of calcium ions in hydrating cement. Hydrated calcium chromium carbonate was also identified in the tannery solidified samples. This compound showed that chromium substitution occurred for either aluminum or silicon. Calcium hydroxide (P) appeared at lower relative intensity in all the waste-containing samples, showing that the waste retards Portlandite formation. This observation confirms previous research which had shown that chromium inhibits C3S hydration [23].

Solidified samples were also prepared containing 15% and 20% by mass tannery waste, and the XRD patterns for the 20% samples are shown in Fig. 5. XRD patterns for both sets of samples allowed the identification of the same compounds as those in the 10% samples. The ettringite peaks were more intense than the sodium aluminum silicate peaks due to the increased amount of calcium sulfate arising from the waste. The samples containing clays showed a high
calcite peak, which represents an increased inhibition of calcium hydroxide formation by the increase of tannery waste mass added.

Fig.5. X Ray Diffraction solidified sample with CT20, CT20STi and CT20NaO, after 28 days of curing time.

Conclusions

Several components of the tannery waste resulted in significant modifications of the chemistry of the cement system. Cement-solidified samples containing tannery waste showed a higher intensity for ettringite when compared to hydrated cement alone, probably due to the high quantity of calcium sulfate present in the waste. Reactions occurred between the waste and the cement, particularly chromium present in the waste. The presence of hydrated calcium chromium oxide confirmed that chromium oxide reacted with calcium ions. Hydrated calcium chromium carbonate was also identified in the tannery solidified samples, showing that chromium substitution occurred for either aluminum or silicon. Calcium hydroxide appeared at lower intensity in all the waste-containing samples, showing that the waste retards Portlandite formation.

The same compounds were identified in all samples containing clays but in different intensities. Commercial clays showed a higher intensity for calcite than for calcium hydroxide. Solidified samples containing 15% and 20% of tannery waste had ettringite peaks at higher intensity than the sodium aluminum silicate peaks due to the increased quantity of calcium sulfate, from the waste, in the system. The samples containing clays all showed a high calcite peak, which represents an increased inhibition of calcium hydroxide formation by the increase of tannery waste mass added.

It is beyond the scope of the present paper, but all tannery waste solidified samples examined in the present work showed very low chromium leachability, indicating the practicality of using cement solidification for treatment of this category of waste.

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