

TANNERY WASTE SOLIDIFICATION AND STABILIZATION

Thermal and mechanical characterization

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(Received: October 13, 2003; in revised form; April 23, 2004)

Abstract

The stabilization/solidification of tannery waste containing chromium was studied as an option for its treatment and final disposal, by using a Portland cement type II and two different commercial bentonites (sodium and organophilic) as additives. Different compositions were evaluated by compressive strength analysis, porosity measurement, leaching tests and thermal analysis. The effect on the compressive strength is directly related to the resulting effect of the components present in the original paste on the hydration degree of the cement, which can be evaluated by thermogravimetric analysis from the dehydration steps of tobermorite and ettringite phases of the pastes. The results show that this process is suitable for the treatment of the tanning waste and that the best conditions of stabilization are obtained when both additives are used.

Keywords: mechanical characterization, solidification, tannery waste, thermal analysis

Introduction

The industrial waste management is facing an increase of pressure from environmental legislation. New treatments have been studied in several researches mainly related to the presence of heavy metals in hazardous wastes, as in the tannery industry.

The stabilization/solidification process consists on mixing the cement and water with the waste and additives. When the system is solidified, a rigid block is obtained with low hazardous of contamination of soil and groundwater after its disposal into landfill [1]. Chemical fixation of toxic and hazardous waste using cement has been practiced for many years as a way to stabilize the waste in landfill. Cement-based stabilization/solidification aims either to bind and to turn the original metal components

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of the hazardous waste into non-soluble compounds within the solid cement matrix, which main phases may be quantified by thermal analysis [2, 3]

The effect of heavy metal oxides (Cr, Cu, Zn, As, Cd, Hg, Pb) on the physical properties of cement, according to Barth and Percin [4], have shown that metals interact with the hydration and the microstructure of the hydrated cement in the early stages of setting, affecting seriously its strength development. Some metals have been found to promote the growth of ettringite crystals and induce significant changes in the microstructure of the hydrated products obtained from the tricalcium aluminate (C_3A) phase [5].

The use of adsorbents, such as organoclays, to solidify wastes containing up to 15% of organic compounds, has been shown to be effective in overcoming adverse organic-cement interactions. The presence of clay in cement paste has been known to affect its strength [6, 7].

According to Lo and Liljestrand [8], clays have high sorption capacity and low hydraulic diffusivity, which minimize the rate of contaminant transport retarding the diffusive fluxes of pollutants on leaching. Sodium bentonite has been used in order to reduce the waste permeability through the soil and groundwater [9].

Organoclays may be obtained from clays submitted to the exchange of the sodium cation for an organic one. Normally it is used a quaternary organic ammonium salt for this exchange, and the organoclay thus formed presents the property to adsorb organic compounds [10].

The replacement of exchangeable inorganic cations by organic cations reduces the hydration of the resulting clay, increases the original interlamellar spacing and simultaneously decreases the exposed aluminosilicate mineral surface area. As the inorganic cations are progressively replaced by the organic cations, the surface properties of the clay may change considerably from a highly hydrophilic condition to an increasingly hydrophobic one [11].

Cement, water, sodium bentonite, organoclay and tanning waste were used in the several compositions studied in the present work. The clays adsorb the waste, which is fixed in the cement matrix, decreasing the possibility of waste leaching, which is also mainly due to the fact that the original hazardous metal salts in the waste are transformed to metal hydroxides by the calcium hydroxide formed during cement hydration. X-ray diffraction was used to characterize the waste and the clays used as additives. The following experiments were done to study the effect of each component on the final properties of the cement solidified pastes: compressive strength and porosity were measured to analyze the mechanical and structural properties of the solidified matrix, thermal analysis was used to evaluate the cement hydration degree and the leaching tests were performed to see the effects on the stabilization of the waste.

Materials and methods

The tannery waste was collected after its industrial partial drying process at ambient air, in a tannery industry located at Franca, SP, Brazil.

The Portland cement was a Brazilian commercial type II code E-32 supplied by Votorantim, Sao Paulo, Brazil, with 86% of its particles passing through the 325 ASTM sieve. The compressive strength for a water/cement ratio of 0.5 paste after 28 days of setting was 33.2 MPa (according to the Brazilian Standard Procedure ABNT 7215/96 – Portland cement – Compressive strength determination) and presents a specific mass of 1.84 g cm^{-3} .

The sodium bentonite, produced from a polycationic bentonite, was supplied by Bentonit União Nordeste S.A., State of Paraíba, Brazil. According to Valenzuela Diaz [12] who previously characterized the original clay, it has a cation exchangeable capacity of 51 meq/100 g on 110°C dried clay basis, with 32 meq corresponding to the sodium cation, it presents Foster swelling of 12 mL g^{-1} , a loss of ignition (LOI) of 10.80% and the following oxide mass composition: SiO_2 – 64.40%, Al_2O_3 – 12.50%, Fe_2O_3 – 7.85%, CaO – 0.87%, MgO – 1.30%, Na_2O – 2.29 %, K_2O – 1.91%. Its mineralogical composition indicates also the presence of illite, kaolinite, and quartz.

The organoclay, known as Tixogel-A, is produced in Brazil by Stauce–Produtos Químicos Ltda. Its Foster swelling analysis presented low swelling in kerosene and soy-bean oil (about 5 mL g^{-1}); medium swelling in hydrated ethanol and absolute ethanol (9 mL g^{-1}) and high swelling in toluene (20 mL g^{-1} without mixing and 27 mL g^{-1} with mixing) [12].

The X-ray diffraction patterns were obtained by using a Philips, X-ray diffractometer – 1880 model. The radiation was K_α of copper, with 0.04° steps (2 theta) and time for each step of 0.5 s.

Simultaneous thermogravimetry and differential thermal analysis TG/DTA analysis were performed from 35 to 1000°C , after a previous drying step at 35°C , by using 100 mL min^{-1} of air, as the purge gas, with a heating rate of $10^\circ\text{C min}^{-1}$, in a simultaneous TG/DTA, TA Instruments equipment, model SDT2960. The reference sample was alpha-alumina and a sample mass of about 15 mg was used in each analysis.

The compositions of the samples used for compressive strength and porosity tests are shown in Table 1. By using a water/cement mass ratio of 0.5, each system was homogenized in a beaker, initially adding the solid components and after adding water, mixing manually until a homogeneous paste was obtained. The paste was

Table 1 Compositions used for compressive strength and porosity tests. Contents of each component are referred to the initial cement mass

| Composition | Water W | Sodium Bentonite-B | Organoclay O | Tannery waste T |
|-------------|------------|-----------------------|-----------------|--------------------|
| CW | 50% | | | |
| CWB | 50% | 5% | | |
| CWO | 50% | | 5% | |
| CWBO | 50% | 5% | 5% | |
| CWBOT | 50% | 5% | 5% | 10% |
| CWT | 50% | | | 10% |

poured in cylindrical molds with 100 mm of height and 50 mm of diameter, where each sample remained during 24 h and was kept afterwards in a wet chamber at 22°C (99% of humidity) for 28 days.

The strength was measured applying a compressive tension charge with a velocity of 0.25 MPa s⁻¹ until the rupture of the sample. The rupture charge was measured and the individual strength (*IS*) is calculated by the expression $IS = P/S$, where *P* is the rupture charge (kgf) and *S*, the sample sectional area.

The material porosity is defined by the ratio between the pore volume and the apparent volume of the samples. The test was carried out according to the Brazilian Standard Procedure ABNT 9778/87 – Mortar and Cement hardened – Water absorption determination, by immersion; empties index and specific mass. After the test, the water absorption (*Abs*) and the empties index (*EI*) were calculated respectively by Eqs (1) and (2).

$$Abs = \frac{M_{sat} - M_s}{M_s} \times 100 \quad (1)$$

$$EI = \frac{M_{sat} - M_s}{M_{sat} - M_i} \times 100 \quad (2)$$

where: M_{sat} – sample mass with dried surface after water saturation in water and boiling (g), M_s – dried sample mass (g), M_i – mass sample immersed in water after saturation in boiling water.

Leaching tests were performed according to the Brazilian Standard Procedure NBR-10005/87, with all the samples shown in Table 1 containing the tanning waste, using a water/cement ratio of 0.6 instead of 0.5 to have more critical conditions for the tests. After been ground, the samples were mixed for 24 h with acetic acid (pH 5.5) in a ratio of 100 g of solidified waste per liter of acetic acid. After filtering, the leachate composition was measured by atomic absorption spectrometry.

Results and discussion

X-ray diffraction

Figure 1 shows the X-ray diffraction pattern of sodium bentonite, which interlamellar d_{001} spacing is characterized by the peak at 14.5 Å. Illite, kaolinite, and quartz peaks were also identified, respectively at 10.0, 7.15 and 3.35 Å. The organoclay XRD pattern presents an interlamellar spacing of 17.9 Å, increased by the organic cation presence there adsorbed.

Figure 2 shows the tannery waste X-ray diffraction pattern. The main peaks are due to the presence of Cr(OH)₃ at 2.81 Å, Cr₄(SO₄)₅(OH)₂ at 1.98 Å, CaSO₄ at 4.25 Å and Na₂SO₄ at 1.62 Å. The peak at 7.56 Å (near 2 theta = 10) is due to the presence of CaSO₄·2H₂O, which also has a characteristic peak at 4.25 Å.

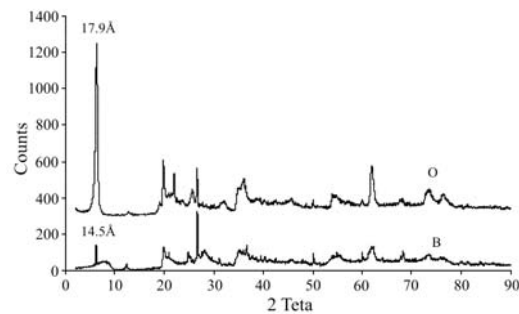


Fig. 1 X-ray diffraction patterns of sodium bentonite (B) and organoclay (O)

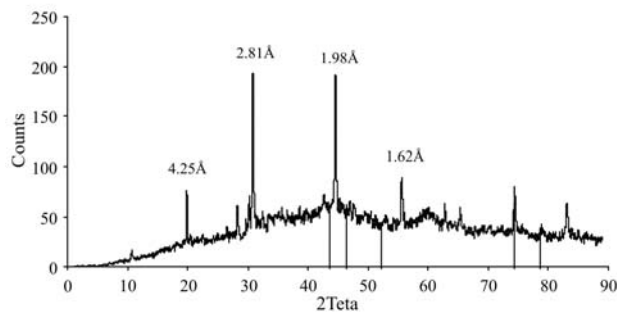


Fig. 2 X-ray diffraction pattern of the tannery waste containing chromium

Compressive strength

Table 2 shows the compressive strength, water absorption and porosity measurements. The results, compared to the CW sample case (the paste prepared only by cement and water), show that when only sodium bentonite is present it increases the compressive strength in 11.5%. The organoclay presence decreases it in 4.8%. When both clays are present, there is an increase in the compressive strength of 7.5%. The compositions containing the waste show a decrease of the mechanical resistance: the CWBOT sample strength reduced in 16% and the CWT one in 48.8%.

Table 2 Results for compressive strength and porosity tests

| Composition | Compressive strength/MPa | Porosity/% | |
|-------------|--------------------------|------------------|---------------|
| | | Water absorption | Empties index |
| CW | 33.2 | 29.8 | 43.8 |
| CWB | 37.0 | 28.6 | 42.2 |
| CWO | 31.6 | 29.9 | 42.8 |
| CWBO | 35.7 | 28.1 | 41.3 |
| CWBOT | 28.9 | 32.2 | 44.9 |
| CWT | 17.1 | 37.5 | 50.0 |

The study of stabilization/solidification of phenol using cement and organoclay, by Oliveira and Büchler [13], showed that the presence of phenol decreases the compressive strength. The increase of phenol solution concentration decreases the compressive strength measurements for the same hydration time.

This occurrence can be confirmed through the study of Wan and Vipulanandan [14], which focused the behavior of chromium in K_2CrO_4 form, which was being stabilized by cement with a water/cement ratio of 0.5. The compressive strength analysis showed that the presence of chromium in this form in the cement matrix reduces its value, because it delays the hydration of the cement, resulting in a low compressive strength as well.

Porosity

In terms of water absorption, the results obtained for the porosity tests, when compared to the cement/water system, showed that the presence of the sodium bentonite reduces the porosity. The presence of the waste increases significantly the porosity, either when comparing the cases of CWBOT and CWBO compositions, or the CW and CWT samples. As also shown by Tango [15], the higher is the excess of water regarding to that necessary to cement hydration, the higher is the porosity and the lesser is the compressive strength.

Leaching tests

The results of the leaching tests, in term of the chromium concentration in the extract, in ppm, were the following: CWT – 2.07; CWBT – 1.85; CWOT – 1.47 and CWBOT – 1.06. Samples CWBT and CWOT, have the same composition than CWBOT as defined in Table 1, without using, respectively, the organoclay (O) and sodium bentonite (B). They were additionally prepared to evaluate the effect of each additive on the stabilization of the waste. Comparing the last three cases to the case without any additive (CWT), it can be seen that when both B and O are present (CWBOT), there is a decrease in 49 % of the chromium content, which is higher than when only B or O are used (CWBT and CWOT), which respectively decrease the chromium content in 11 and 30%. It is important to note that from the results, all the above compositions would be indicated and approved by environmental legislation, which accepts a maximum chromium content in the leachate of 5 ppm.

Thermal analysis

Figure 3 shows the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves of the tanning waste.

From TG and DTG curves it can be seen that during the first mass loss step at 35 and up to 100°C, during the heating rate at $10^\circ C \text{ min}^{-1}$, there is a mass loss due to the residual water present in the waste. The asymmetric endothermic DTA peak between 120 and 160°C, is due to the water loss from the two overlapped decomposition steps of the dihydrated calcium sulfate present in the waste [2], which are more evidenced

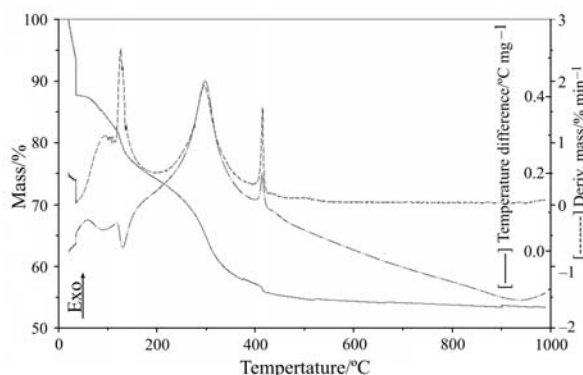


Fig. 3 TG, DTG and DTA curves of the tanning waste

by the respective DTG peaks. Between 200 and 500°C, there is a mass loss caused by organic material decomposition and to chromium hydroxide dehydroxylation seen in the respective DTG peak that occurs from 400 to 450°C. As the exothermal effect from the organic material burnout is higher than the endothermal effect of its decomposition and that of the chromium hydroxide dehydroxylation, it is observed only a large exothermal peak from 200 to 400°C. After this temperature there is a very sharp DTA exothermal peak characteristic of the burnout of organometallic compounds [16, 17], which in the present case are the organic compounds containing chromium present in the tanning waste, which decomposition presents a very high mass loss weight rate, as seen by the correspondent DTG peak.

Figure 4 shows the TG curves for the same samples after 28 days of setting, which were analyzed in the leaching tests. All the curves present the initial drying step at 35°C, where free water is lost, followed by a very similar continuous mass loss behavior occurring during the 10°C min⁻¹ heating rate up to 1000°C. The sample that does not have any additive (CWT) presents the highest free water loss, due probably

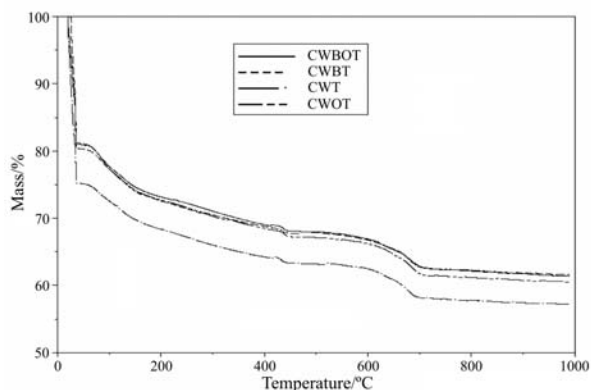


Fig. 4 TG curves of CWT, CWBT, CWOT and CWBOT samples

to a lower hydration degree. Up to 200°C, the mass loss is due to the dehydration of the tobermorite and ettringite phases present in the cement matrix [3], after which the other hydrated phases decompose. From 400 to 450°C, dehydroxylation of the calcium hydroxide occurs. The mass losses between 500 and 700°C correspond, according to Dweck *et al.* [18] to the non-well-crystallized and crystallized calcium carbonate phase decompositions, the former occurring at the beginning of this temperature range. Some of these phases can be formed during the thermal analysis, by the reaction of the carbon dioxide formed during the burnout of the organic material of the waste and/or of the organoclay, with the original calcium hydroxide present in the hydrated paste [2]. This fact does not allow one to estimate the hydration degree by the calcium hydroxide content of the paste, as usually is done for water cement pastes. For this purpose, the hydration degree can be evaluated by the corresponding DTG curve peaks of the tobermorite and ettringite dehydration [3] as plotted in this case in Fig. 5, which in turn give much more information than the TG curves, about the decomposition stages that occur during the analysis.

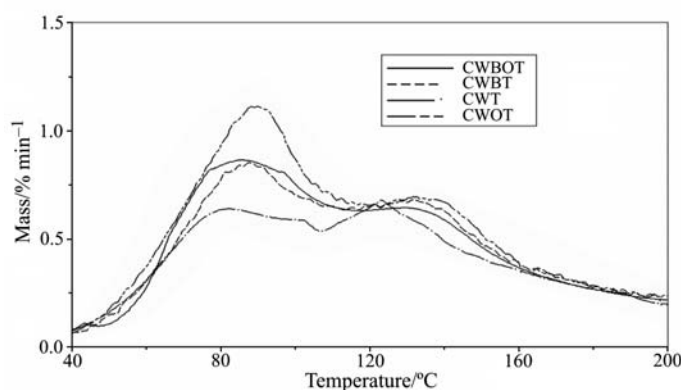


Fig. 5 DTG curves of the CWT, CWBT, CWOT and CWBOT pastes in the dehydration temperature range of tobermorite (first peak) and ettringite (second peak)

As shown in Fig. 5, which represents the water loss after the 35°C drying step of respective pastes, the first large DTG peak is due to tobermorite dehydration, which is partially overlapped at its end part by the ettringite dehydration DTG peak, which occurs subsequently [18, 19].

It is interesting to note that the case that presents the highest cement hydration degree, which is evaluated by the total area of both tobermorite and ettringite DTG dehydration peaks [20], is when only the organoclay and the waste are present in the solidified paste (CWOT). As the organoclay is hydrophobic, probably more water is available than in the other cases to react with the original tricalcium silicate and aluminate present in the original cement, producing respectively more tobermorite ($3\text{CaO}\cdot 2\text{SiO}_2\cdot x\text{H}_2\text{O}$) and ettringite ($3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) phases during the

28 days of setting. It is important to note that the ettringite formation is due to the presence of the gypsum present in the waste and in the original cement [21, 22]. From respective total DTG peak areas, the cement hydration degree of the samples decreases in the following order: CWOT > CWBOT > CWBT > CWT.

This indicates that in the presence of the waste, the organoclay enhances cement hydration more than the sodium bentonite, which is hydrophilic, but at the same time, the waste stabilization action, by respective adsorption of the chromium organic and inorganic compounds present in the waste, decreases their retarding effect on cement hydration, as seen when no additives are present.

All the previously discussed thermal analyses were done with samples after 4 weeks of hydration, taken from pastes, which were kept in sealed plastic bags, since their preparation. Right after taking out the sample, the remaining part of the paste is maintained sealed in the plastic bag, to allow further analysis of the hydration degree at higher hydration times. In order to better evaluate the cement hydration evolution of the case that presented the best stabilization (CWBOT), a thermogravimetric analysis of another sample of the same original hydrating paste was also done after 9 weeks of hydration. As shown in Fig. 6, which presents the results on calcined mass basis, the respective curves are practically coincident and there are not significant differences between respective TG curves in terms of mass losses due to the several phases present in the paste. This fact indicates that, by using the operational conditions and compositions detailed in this work, after 4 weeks, the cement hydration degree of the best stabilized waste paste practically does not change.

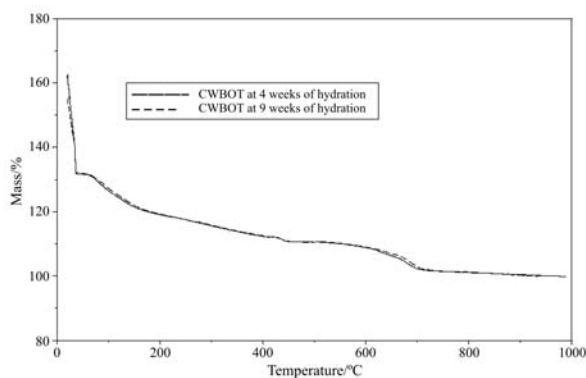


Fig. 6 TG curves of the CWBOT paste after 4 and 9 weeks of hydration

Conclusions

The presence of sodium bentonite increases the final compressive strength of the hydrated cement and consequently decreases its porosity. On the other hand, the presence of organophilic clay affects in a lesser but opposite way the mechanical properties of the block containing cement and water.

The tannery waste containing chromium, when mixed alone with cement promotes a significative reduction of the compressive strength of the solidified matrix. When both clays and water are present this effect is decreased.

The effect on increasing or decreasing the compressive strength is directly related to the resulting effect of the components that are present in the original paste on the hydration degree of the cement, which can be evaluated by the respective derivative thermogravimetry plots from the dehydration of tobermorite and ettringite phases of the paste.

The stabilization of the waste is significantly affected by the adsorptive properties of the sodium and organophilic clays on, respectively, the inorganic and organic chromium containing compounds present in the waste, affecting also the available water for cement hydration.

The best stabilization of the waste occurs when both additives are present and by thermogravimetry, it can be seen that for this case, the cement hydration degree practically does not change after 4 weeks of setting.

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Our acknowledgments to the Brazilian Research Council (CNPq), Brazilian Ministry of Education (CAPES) and to the Thematic Project - São Paulo State Foundation for Endowment of Research (FAPESP), Process n° 1995/0544-0, for financial support.

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