Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

STABILIZATION OF A GALVANIC SLUDGE BY MEANS OF CALCIUM SULPHOALUMINATE CEMENT

R. Cioffi[1], M. Lavorgna[2], M. Marroccoli[3] and L. Santoro[2]

[1] Dipartimento di Ingegneria dei Materiali e della Produzione, Università di Napoli "Federico II", P.le Tecchio 80, 80125 Napoli, Italy.

[2] Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, 80134 Napoli, Italy.

[3] Dipartimento di Ingegneria e Fisica dell'Ambiente, Università della Basilicata, via della Tecnica 3, 85100 Potenza, Italy.

ABSTRACT

A solid waste containing heavy metals from galvanic treatment has been stabilized by means of a binding matrix containing β-$2CaO{\cdot}SiO_2$, $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ and $CaSO_4$ able to give calcium silicate and trisulphoaluminate hydrates upon hydration. Experiments have been carried out with mixtures containing up to 60% waste under three different points of view, as follows. The influence of the waste on the technical properties of the stabilized products, the leaching behaviour under four different conditions and the effect of the leaching medium on the binding matrix have been studied.

1. INTRODUCTION

In the light of the most recent directives of European Community regarding solid wastes management, stabilization/solidification processes will play in the near future a more and more important role because it will be only allowed to dispose of inert or stabilized residues. These directives have been acknowledge by the Italian Government by means of a specific act dated 5 February 1997.

This act gives high priority to the development of technologies addressed towards recycling and reuse of solid wastes as well as recovery of raw materials and energy from the wastes themselves. Among the available stabilization technologies, the most frequently applied are cement-based. They rely on the formation of a calcium silicate hydrate matrix and make use of a number of systems such as ordinary portland cement, blast furnace slag and mixtures of lime and coal fly-ash (or other pozzolanic materials). A wide range of residues is currently stabilized by means of these inorganic processes, that is industrial solid wastes containing heavy metals, nuclear wastes, municipal solid wastes incineration ashes, sludges from wastewater treatment plants and so on. In addition, this technology can also be applied to the stabilization of contaminated soils and sediments. In these cases the addition of bentonite can be helpful to reduce the amount of binding/stabilizing matrix.

Once a specific stabilization process has been selected as the most appropriate for a specific solid waste, a number of questions must be answered in order to assess its environmental feasibility. These questions belong to three different technical fields, as follows.

First of all, some interactions will arise between the binding/stabilizing matrix on one side and the waste components on the other. These interactions must be properly studied in order to understand how the binder performance changes in response to the waste admixture. This is particularly important if the ultimate scope is the reuse of the final product.

Furthermore, the process must be environmentally acceptable which means that the release of contaminants due to leaching must be studied in different conditions in order to get an understanding of what the long term behaviour of the stabilized product in the environment will be. The test conditions in which leaching should be carried out will have to be designed keeping in mind the ultimate scope of this aspect of the of the research.

Last but not least, and in addition to what just stated, emphasis should be given to the interactions which may arise in the environment between leaching media and the binding matrix itself. This aspect has been generally disregarded by the researchers in the field, but is particularly important because the long-term exposure to leaching media may result in complete release of contaminants if the stabilizing matrix undergoes substantial modification.

In this paper a solid waste from galvanic treatment containing heavy metals, mainly Cd, Cr, Cu, Ni, Pb and Zn, has been stabilized by means of a novel cementitious matrix based on calcium silicate β-$2CaO{\cdot}SiO_2$ and sulphoaluminate $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$. Upon hydration this matrix forms calcium silicate hydrate and calcium trisulphoaluminate hydrate (ettringite). It was tested in previous work for both physico-mechanical and stabilizing properties proving to be suitable for the application under study.

The study referred to in this paper deals with physico-mechanical properties of stabilized samples, release of metals in different leaching tests and matrix behaviour during leaching.

2. EXPERIMENTAL

The components β-$2CaO{\cdot}SiO_2$ and $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ of the binding matrix were synthesized in the theoretical ratio 1:1.5 by firing a raw mixture of $CaCO_3$ (45.37%), bauxite fines (31.09%), zeolitic tuff (13.27%) and $CaSO_4{\cdot}2H_2O$ (10.27%) at 1200°C for 90 min. The binder was obtained by adding anhydrous $CaSO_4$ to the fired mixture in the ratio 1:2.5. The chemical composition of the waste, bauxite fines and zeolitic tuff is reported in Table 1.

Binder-waste mixtures were prepared containing 0 (pure binder), 20, 40 and 60% of waste and hydrated at 25°C, 100% RH, and water/solid ratio equal to 0.4, 0.46, 0.5 and 0.56 for the systems containing 0, 20, 40 and 60% waste, respectively. These values were chosen in order to get constant workability. The hydration time ranged between one hour and 28 days (672 hours).

Small samples (about 3 g) of each system have been used to study the kinetics of hydration. This part of the study has been carried out by determining the amount of chemically combined water by ignition at 1000°C for the time required to reach constant weight. In addition, the formation of hydrated products has been monitored by differential thermal analysis (DTA).

Table 1
Chemical composition of waste, bauxite fines and zeolitic tuff (wt%)

	Waste	Bauxite fines	Zeolitic tuff
LOI*	34.60	25.40	9.93
SiO_2	-	4.70	52.93
Al_2O_3	48.12	51.50	17.21
CaO	7.62	0.02	3.54
K_2O	-	-	7.26
Na_2O	-	-	2.97
SO_3	-	-	0.13
Fe_2O_3	0.15	15.3	3.71
MgO	0.44	0.04	1.44
Cr_2O_3	6.57	-	-
NiO	0.98	-	-
CdO	0.04	-	-
ZnO	0.04	-	-
CuO	0.02	-	-
PbO	0.01	-	-
MnO	0.03	-	-

*LOI = Loss on ignition

Samples of the three mixtures containing 20, 40 and 60% of waste have been submitted to the following three leaching tests: (a) the dynamic TCLP test [1],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 on monolithic cylindrical samples dxh=2x3 cm^2; (b) the same test as (a) but with pH 3.86 CO_2-saturated solution instead of acetic buffer and renewals up to 672 hours; (c) the static US-EPA test [2] with pH 5 acetic acid solution and ratio liquid/solid equal to 16 ml/g on granulated sample (size < 9.5 mm) and (d) the availability test [3] carried out on 3 g of pulverized sample (size < 180 μm) with 150 ml of pH 7 nitric acid solution for 3 hours plus additional 150 ml of pH 4 HNO_3 solution for 3 hours.

Following these tests, the leaching solutions have been analysed by means of atomic absorption spectroscopy and the solids before and after leaching have been characterized by means of DTA and scanning electronic microscopy (SEM).

3. RESULTS AND DISCUSSION

Figure 1 shows the amount of normalized chemically combined water. The absolute values have been divided by the fraction of binder present in each mixture to get the normalized values. It is seen that only the mixture containing 20% of waste behaves like the pure binder, while in the cases of the 40 and 60% mixtures the waste does not simply dilutes the binder but its components inhibit the binder hydration. This effect increases as the content of waste in the mixtures increases.

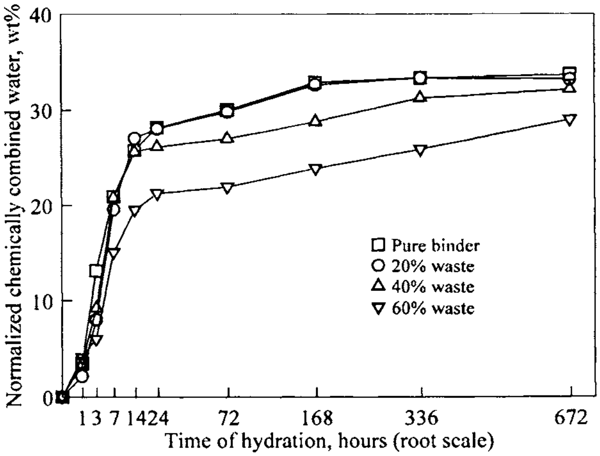

Figure 1. Normalized chemically combined water for the pure binder and the three mixtures binder-waste.

The hydrated samples have been submitted to DTA stowing that in all the systems the main hydration product is ettringite. As in similar systems studied previously [4-6], other hydration products are calcium silicate hydrate, aluminium hydroxide gel and traces of calcium monosulphate hydrate. Significant differences were only observed at short hydration times as shown by the thermograms of Figure 2, relative to 1 hour hydration. In this figure the thermogram relative to the pure binder shows the main endotherm at 82°C that reveals the presence of ettringite. The three minor endotherms at 128, 205 and 260°C are related to dehydration of $CaSO_4 \cdot 2H_2O$, calcium monosulphoaluminate hydrate and aluminium hydroxide gel, respectively. The thermograms relative to the systems containing 20, 40 and 60% of waste show that neither ettringite, nor calcium monosulphate hydrate form at 1 hour hydration when the system contains the waste. In these thermograms the endotherms related to dehydration of $CaSO_4 \cdot 2H_2O$ show that the waste catalyses the conversion of anhydrous $CaSO_4$ to $CaSO_4 \cdot 2H_2O$, according to previous findings relative to similar systems [7]. The endotherms relative to dehydration of aluminium hydroxide are of higher intensity in the cases of the waste-binder mixtures because this compound is simultaneously a hydration product and a component of the waste. The particular baseline shape of the thermograms relative to the waste-binder mixtures is due to the

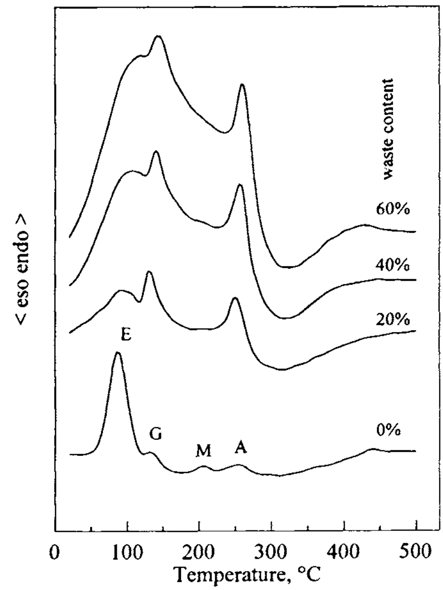

Figure 2. Thermograms of samples aged 1 hour. E: ettringite G: gypsum; M calcium monosulphate hydrate; A: aluminium hydroxide.

presence of waste.

The values of unconfined compressive strength are 25 MPa for the pure binder and 21, 16 and 2 MPa for the mixtures containing 20, 40 and 60% of waste, respectively. These values are such that recycling the stabilized products in the field of building materials is possible for waste content up to 40%. The value of 2 MPa observed for the mixture containing 60% waste exceeds the value of 0.44 MPa recommended by Stegemann and Coté for segregated landfill disposal [8].

Figures 3 and 4 report the results of the dynamic leaching tests carried out with the acetic buffer and CO_2-saturated solution, respectively. Table 2 shows the results of US-EPA leaching test and availability test. The data are relative to the metals Cd, Cr and Ni, whose presence is of greater environmental concern, and are expressed as percentages of the initial quantity present in the sample. These results show that the leaching behaviour depends strongly on the nature of the metal as Cr, Ni and Cd are released in steeply increasing amount in each test. The chemical nature of the leaching medium has also a strong effect inasmuch as quite larger amounts are released in TCLP test compared to CO_2-saturated solution test. To this regard, it is important to point out that pH does not have the effect that one would expect. In fact each step in the CO_2-saturated solution test starts with a pH value of 3.86 and ends at about 5. These values, compared to the value of 4.94 of the acetic buffer make clear that pH is not the most important factor that characterize the leaching

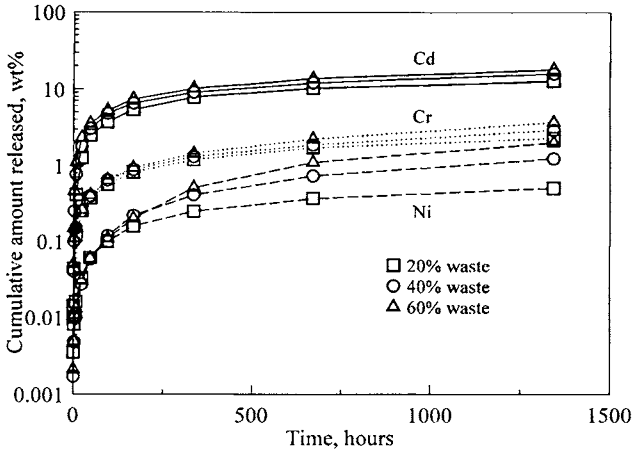

Figure 3. Results of TCLP test.

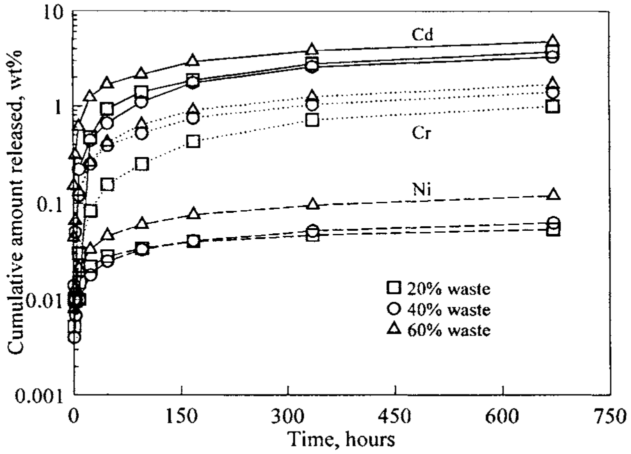

Figure 4. Results of CO_2-saturated solution leaching test.

medium.

Table 2
Results of US-EPA leaching test and availability test (wt%)

	Type of test and waste content					
	US-EPA			Availability		
	20%	40%	60%	20%	40%	60%
Cd	2.29	1.78	3.54	58.93	56.96	55.66
Cr	0.16	0.05	0.05	0.70	0.47	0.56
Ni	0.30	0.22	0.42	17.47	10.76	10.37

The results of Figures 3 and 4 show that the percentage of metal released increases with the amount of waste in the mixtures and this means that the binder does not simply physically segregate the waste from the attack of the leaching media, but that chemical interactions take place between the binder and the waste components whose extent decreases as the binder content decreases.

Finally, the data of Table 2 confirm that the results of a leaching test depend strongly on the chemical nature of both the metal and the leaching medium, and also on the physical nature of the solid sample.

The effect of the leaching medium on the binder in the stabilized samples has been studied only in the two dynamic tests carried out with the acetic buffer and CO_2-saturated solution. The monolithic cylindrical samples submitted to these tests underwent significant modification which could be evidenced by cutting the samples themselves orthogonally to the cylinder axis. In this way it was possible to distinguish between an external leached layer of increasing thickness and an internal unleached shrinking core. The thickness of the leached layer increased with time and with the amount of waste in the mixture and reached the values of about 2, 3, and 7 mm at the end of both tests in the cases of 20, 40 and 60% waste, respectively.

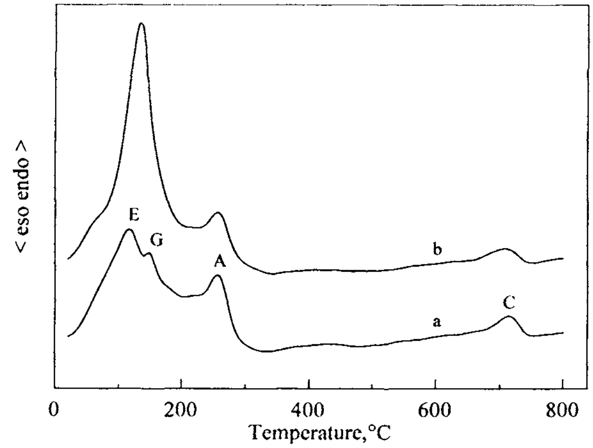

Figure 5. Results of DTA carried out on samples from external layer (a) and inner core (b) of system containing 40% waste after CO_2-saturated solution leaching test.

Figure 5 shows the results of DTA carried out on samples of the leached layer and the unleached inner core in the case of the mixture containing 40%

waste submitted to the CO_2 -saturated solution test. It is seen that ettringite undergoes substantial decomposition to gypsum, aluminium hydroxide and calcium carbonate. This observation can also explain why lower amounts of metals are leached in the CO_2 saturated solution test. The formation of metal carbonates can limit metal ions solubility even if the pH is lower than in the TCLP test. This chemical modification of the system implies also substantial morphological modification, as it can be seen in Figure 6 where two micrographs of samples of the external leached layer and the inner unleached core are shown. The system of Figure 6 is that containing 20% waste submitted to TCLP test. The needle-like ettringite crystals visible in micrograph (a) completely disappear after leaching, as seen in micrograph (b). This observation, relative to the sample submitted to TCLP test, is not in contrast with the results that ettringite decomposes in CO_2-saturated solution giving calcium carbonate among the other products. In fact, in a previous work carried out on systems similar to those studied in this paper [5], the acetic buffer attack caused ettringite decomposition into calcium acetate pentahydrate, gypsum and aluminium hydroxide.

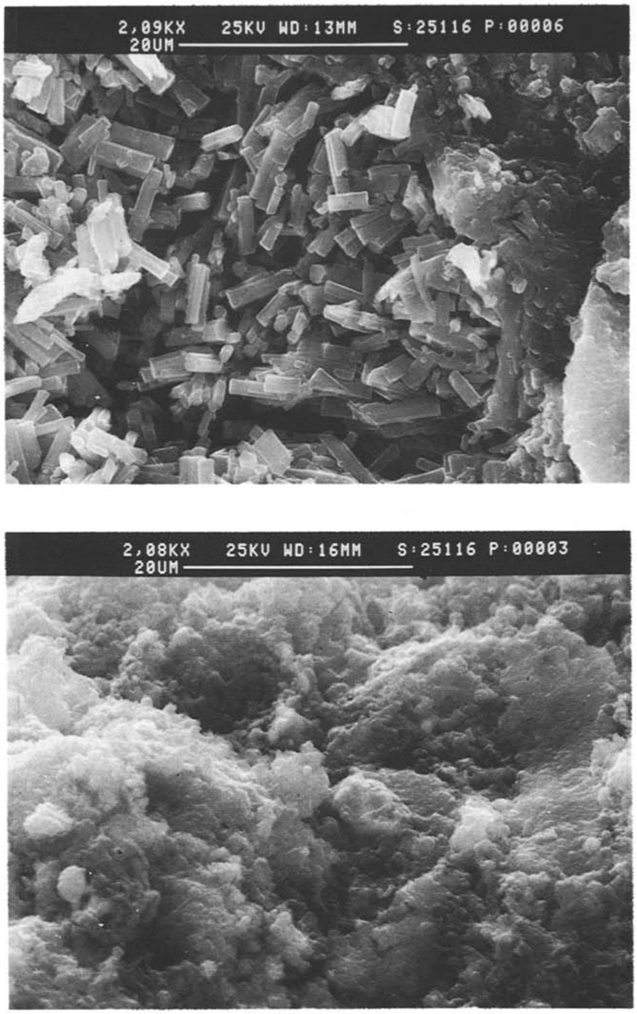

Figure 6. SEM micrographs of samples of external layer (below, b) and inner core (above, a) of system containing 20% waste after TCLP test.

4. CONCLUSIONS

The results of the experiments can be summarized as follows with respect to the three aspects of the study emphasized in the introductory part.

From the point of view of binder performance, the addition of waste to an extent greater than 20% inhibits the hydration process. On the other hand, mechanical performance is reduced starting from 20% waste addition.

The leaching behaviour is strongly influenced by the chemical nature of both the metal and leaching medium. Other parameters that greatly influence metal release are the physical nature of the stabilized samples and type of liquid-solid contact. Of the two tests carried out under the same conditions, namely TCLP an CO_2-saturated solution, the latter gives rise to lower amounts of metals released.

Finally, it has been found that the attack of the leaching medium to the stabilized samples causes severe modification of the binder. This modification has been characterized from both the chemical and morphological points of view, showing that ettringite decomposes to gypsum, aluminium hydroxide and a calcium compound.

The possibility that metal carbonates precipitate during the CO_2-saturated solution test can explain the lower metal ions release observed in this test in comparison to TCLP test.

REFERENCES

1. Toxicity characteristics leaching procedure, Federal register, Vol. 51, No. 261 (1990).
2. U.S- EPA Test method for evaluating solid waste, SW-846. Washington, DC: Office of Solid Waste and Emergency Response (1986).
3. NEN 7341 (formerly NWN 2508), Determination of leaching characteristics of inorganic components from granular (wastes) materials. NNI, Delft (1993).
4. J. Beretka, B. de Vito, L. Santoro, N. Sherman and G.L. Valenti, Cement and Concrete Research, 23 (1993) 1205.
5. V. Albino, R. Cioffi, M. Marroccoli and L. Santoro, Journal of Hazardous Materials, 51(1-3) (1996) 241.
6. R. Berardi, R. Cioffi and L. Santoro, Journal of Thermal Analysis, in press.
7. V. Albino, R. Cioffi, L. Santoro, and G.L. Valenti, Waste Management and Research, 14 (1996) 29.
8. J.A. Stegemann and P.L. Coté, Science of the Total Environment, 178(1-3) (1996) 103.