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Environmental and technological effectiveness of a process for the stabilization of a galvanic sludge

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Abstract

A binding matrix containing calcium silicate β -2CaO·SiO₂ and sulphoaluminate 4CaO·3Al₂O₃·SO₃, and CaSO₄ that gives calcium silicate and trisulphoaluminate hydrates upon hydration has been used for the stabilization of a solid waste from a galvanic treatment process. The waste is to be disposed of in a hazardous wastes landfill to prevent the risk of cadmium, chromium and nickel release. Anhydrous calcium silicate and sulphoaluminate of the binder have been synthesized using a mixture containing powdered tuff in addition to bauxite and calcium carbonate and sulphate. Powdered tuff is quarry dust and is, as such, a true residue. Experiments have been carried out with mixtures containing up to 60% waste and have been addressed towards the environmental and technological assessment of the effectiveness of the stabilization process. Specifically, the study has been carried out taking into account requirements from three different points of view, that is the influence of the waste on the hydration process and on the technological properties of the stabilized products, the leaching behavior under some selected conditions and the effect of the leaching medium on the binding matrix in the stabilized system. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The most recent directives of the European Community regarding solid wastes management give high priority to the development of technologies addressed towards recycling and reuse. In the former case, wastes are recycled to the same process from which they were generated, while in the latter case, they are reused in a different process. High priority is also given to the recovery of raw materials and energy from wastes. These requirements cannot always be satisfied because a proper technology may be too expensive or may not be available at all. When this happens, the last chance is given by treatment processes which are addressed to the reduction of the environmental impact of wastes. In the case of solid wastes, stabilization/solidification (S/S) processes are the most suitable.

S/S processes are already widely used for the treatment of hazardous industrial solid wastes, and those cement-based are most suited for wastes containing heavy metals. Although they are mainly employed for wastes safer disposal, they are also intrinsically able to give products which may have high potential to be used in the field of pre-formed building materials. This is due to the fact that often these processes lead to the formation of monolithic products.

In any case of a specific waste stabilized by means of a specific binding matrix, a fundamental study is required to assess the actual potential of the S/S process to be addressed towards the manufacture of building materials instead of safer disposal. First of all, the output of this type of fundamental study must be the understanding of the chemical interactions that occur between the hydrating binder and the waste components (pollutants). Then, it must be checked that the proposed process is environmentally acceptable through proper leaching tests which, in turn, can help understand whether the stabilization mechanisms are of physical or chemical type. Finally, a preliminary physico-structural characterization must be carried out through the determination of the unconfined compressive strength (UCS) which is the most important property to foresee a possible technological application. When all this develops successfully, it is possible to say that a novel way of reusing a specific waste has been found.

The available cement-based S/S technologies rely on the formation of a calcium silicate hydrate stabilizing matrix. A number of systems such as ordinary portland cement, blast furnace slag and mixtures of lime and coal fly-ash (or other pozzolanic materials) can be used.

In this paper, a solid waste from galvanic treatment containing heavy metals, mainly Cd, Cr, and Ni, has been stabilized by means of a novel cementitious matrix based on calcium silicate β -2CaO·SiO₂ and sulphoaluminate 4CaO·3Al₂O₃·SO₃. This matrix hydrates to calcium silicate hydrate and calcium trisulphoaluminate hydrate (ettringite) and offers some advantages in stabilization processes because heavy metals can be chemically entrapped by diadochy and isomorphic substitution. These phenomena may preferentially take place when ettringite is among the hydration products. This is proved by the occurrence of ettringite-like minerals (sturmanite Ca₆(Fe, Al)₂(SO₄)₂(B(OH)₄)(OH)₁₂·26H₂O and bentorite Ca₆(Cr, Al)₂(SO₄)₃(OH)₁₂·26H₂O) and also by the synthesis of ettringite derivatives reported by many authors [1–6].

Systems able to generate ettringite and calcium silicate hydrate upon hydration were tested in previous work for both physico-mechanical and stabilizing properties. They proved to be suitable for the proposed application [7–9].

2. Materials and methods

2.1. Synthesis of binder

Clinkers containing β -2CaO·SiO₂ and 4CaO·3Al₂O₃·SO₃ were synthesized in previous work starting from different sources of CaO, SiO₂, Al₂O₃, and CaSO₄. Specifically, reagent grade chemicals, commercial materials (limestone, bauxite, etc.) and industrial by-products and wastes (phosphogypsum, coal fly-ash, etc.) were used [9,10]. The results of this work showed that, depending on the nature of the raw materials, the temperature and time required for the synthesis of the clinker varied considerably. Also, other products form beside β -2CaO·SiO₂ and 4CaO·3Al₂O₃·SO₃, namely, gehlenite (2CaO·Al₂O₃·SiO₂) and calcium aluminates (3CaO·Al₂O₃ and/or 12CaO·7Al₂O₃).

The choice of the raw materials required for the synthesis may depend on the local availability of materials (especially industrial by-products and wastes) containing the above oxides. In all Southern Italy there is wide availability of zeolitic tuff quarries, as well as in the United States, Japan and other countries of Eastern Europe. Tuff dust is produced during the cutting of shaped stones for the manufacture of building elements. It is a true solid waste that must be disposed of, unless some way of reusing is found. As zeolitic tuff contains mainly SiO₂ and Al₂O₃, it was judged that its quarry dust could be usefully employed for the clinker synthesis. The tuff dust employed contained SiO₂ (52.93%), Al₂O₃ (17.21%), K₂O (7.27%), Fe₂O₃ (3.71%), CaO (3.54%), Na₂O (2.97%) and MgO (1.44%).

The clinker composition was designed to have β -2CaO·SiO₂ and 4CaO·3Al₂O₃·SO₃ in the theoretical weight ratio 1:1.5. According to previous findings, binders of good mechanical properties can be produced starting from a clinker of such a composition [7]. The composition of the raw mixture for the synthesis was computed to get the above theoretical composition. Then, mixtures of zeolitic tuff dust (13.27%), bauxite fines (31.09%), reagent grade CaCO₃ (45.37%) and CaSO₄·2H₂O (10.24%) were fired at 1200°C for different times from 15 to 360 min. The addition of bauxite fines was required to increase the ratio Al₂O₃/SiO₂. Alumina content was 51.50% in this material.

Fig. 1 shows the results of the clinker synthesis in terms of X-ray diffraction (XRD) counts of the strongest peaks of the main components of the fired product. It is seen that 2CaO·Al₂O₃·SiO₂ and 3CaO·Al₂O₃ form beside β -2CaO·SiO₂ and 4CaO·3Al₂O₃·SO₃. Furthermore, the concentrations of 4CaO·3Al₂O₃·SO₃, 2CaO·Al₂O₃·SiO₂ and 3CaO·Al₂O₃ increase with firing time, while that of β -2CaO·SiO₂ passes through a maximum. Based on these results, the firing time of 90 min was used for the clinker synthesis.

The binder was obtained by mixing the clinker and anhydrous CaSO₄ in the weight ratio 2.5:1. Anhydrous CaSO₄ was obtained by firing reagent grade CaSO₄·2H₂O at 850°C for 2 h [7]. The presence of anhydrous CaSO₄ in the binder is necessary for the formation of non-expansive ettringite [11].

2.2. Stabilization technique

The waste employed in this study comes from the treatment of spent galvanic liquor. It contains the heavy metal oxides Cr₂O₃ (10.05%), NiO (1.50%) and CdO (0.06%). The main component is Al₂O₃ (73.58%), due to the use of aluminium salts as flocculants in the

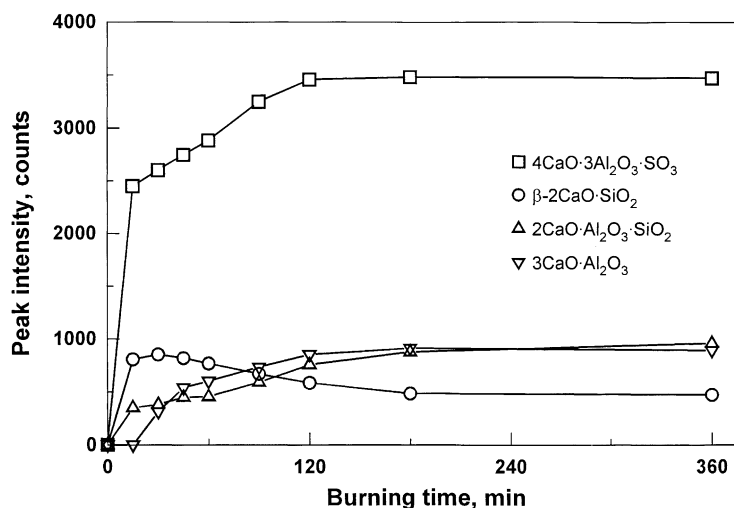


Fig. 1. Clinker synthesis from XRD.

spent liquor treatment process. According to Italian regulation (Ministry of Environment, Act of 5 February 1997), this waste is not classified as hazardous. Despite of this, it must be disposed of in a hazardous waste landfill because the release of heavy metals exceeds established limits in the compliance leaching test. The waste is classified in the European Waste Catalog with the code 06.05.01.

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 1 h and 28 days (672 h).

Small samples (about 3 g) of each system were used to study the kinetics of hydration. This part of the study was 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 was monitored by differential thermal analysis (DTA) and XRD.

Cubic samples 4 cm × 4 cm × 4 cm of all the systems were tested for UCS.

Samples of the three mixtures containing 20, 40 and 60% of waste were submitted to the following three leaching tests: (a) a dynamic test 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 h on monolithic cylindrical samples $d \times h = 2 \text{ cm} \times 3 \text{ cm}$; (b) the same test as (a) but with pH 3.86 CO₂-saturated solution instead of acetic buffer and renewals up to 672 h and (c) the availability test carried out on 3 g of pulverized sample (size < 180 μm) with 150 ml of pH 7 nitric acid solution for 3 h plus additional 150 ml of pH 4 HNO₃ solution for 3 h. In test (b) the initial pH in each step was 3.86 and the solution was kept constantly saturated by continuous feeding of gaseous CO₂. Despite this, the pH increased during each step due to interactions with the solid. In test (c) the pH was

controlled at 7 for 3 h and at 4 for additional 3 h by adding, when necessary, the proper amount of HNO_3 1 M solution. The choice of leaching tests was not made for the sake of compliance to some regulation, but to get better understanding of the process effectiveness and stabilization mechanisms.

Following the above tests, the leaching solutions were analyzed by means of atomic absorption spectroscopy and the solids before and after leaching were characterized by means of DTA, XRD and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Hydration chemistry

Fig. 2 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. Specifically, when the waste content is 40%, only the ultimate value of chemically combined water is negatively influenced, as the amount up to 14 h hydration time is almost the same as those for the pure binder and the 20% waste mixture. On the other hand, when the waste content is raised to 60%, not only the ultimate value, but also those at very early hydration times are lowered.

The results of XRD carried out on the samples of all the systems aged 28 days are reported in Fig. 3. This figure shows the presence of the main $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$ hydration product, that is $6\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$ (ettringite). The presence of $2\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2$,

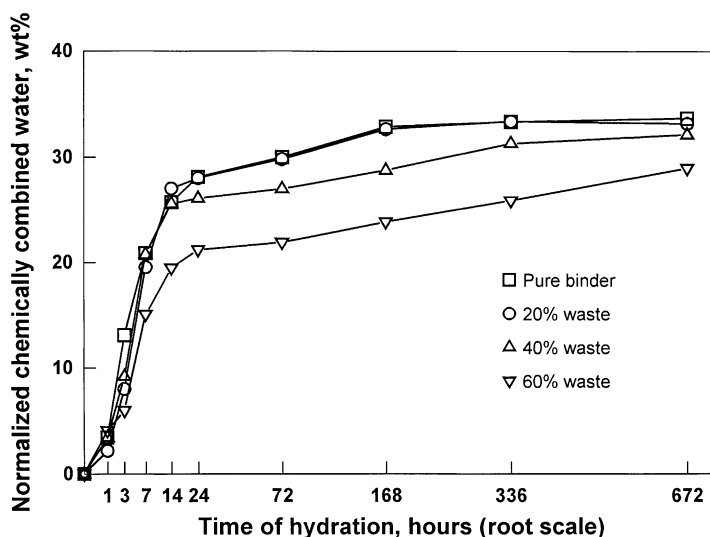


Fig. 2. Kinetics of hydration for pure binder and binder–waste mixtures.

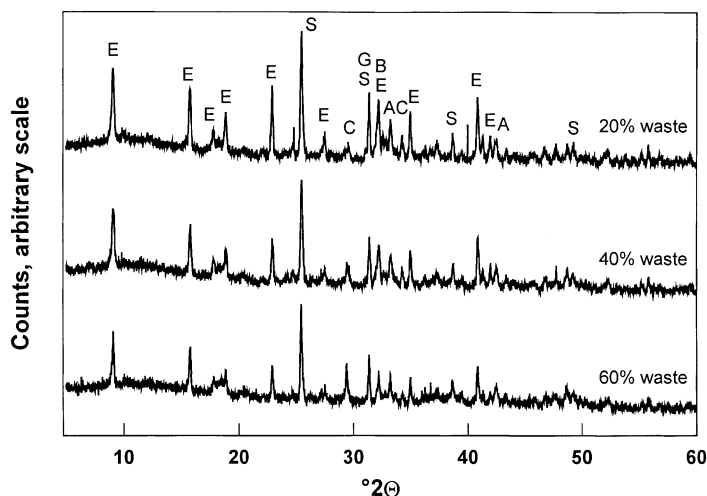


Fig. 3. Results of XRD carried out on binder-waste mixtures aged 28 days (A: Al_2O_3 ; AC: $3\text{CaO}\cdot\text{Al}_2\text{O}_3$; B: $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$; C: CaCO_3 ; E: ettringite; G: $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$; S: CaSO_4).

$\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and CaSO_4 is well documented by the numerous peaks linked to the above components. The absence of $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot\text{SO}_3$ peaks indicates that in all the systems this reactant is converted to such a degree that the residual quantities are below the detection limit of the XRD. Calcium silicate hydrate, the other hydrated phase that forms in systems of the type of those studied in this paper, cannot be detected by means of this analytical technique, due to its amorphous structure [12]. DTA is able to detect this hydration product as shown in a previous paper [13]. Comparing the three XRD patterns with each other makes clear that the presence of galvanic sludge in the systems does not alters the binder hydration from the qualitative point of view.

3.2. Mechanical strength

The histograms of Fig. 4 show the values of UCS for the pure binder and the three mixtures containing 20, 40 and 60% waste. The values found for the pure binder and mixtures with 20 and 40% waste are 25, 21 and 16 MPa, respectively. They are high enough to foresee the possible utilization of sulphoaluminate cement-waste mixtures as a binder for the manufacture of concrete blocks. As UCS is usually lower for the binder than for concrete blocks, there are good potentialities to get, at least, medium-high mechanical properties. In Italy, pre-formed blocks manufactured as above could well lay within the class C20/25. This means that at least 95% of UCS determinations must be greater than 20 MPa for cylindrical samples of size $d \times h = 10 \text{ cm} \times 15 \text{ cm}$, or greater than 25 MPa for cubic samples of size $L^3 = 15 \text{ cm}^3$. According to Italian classification, nine classes of concrete blocks exist ranging from C12/15 to C50/60 [14].

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 [15].

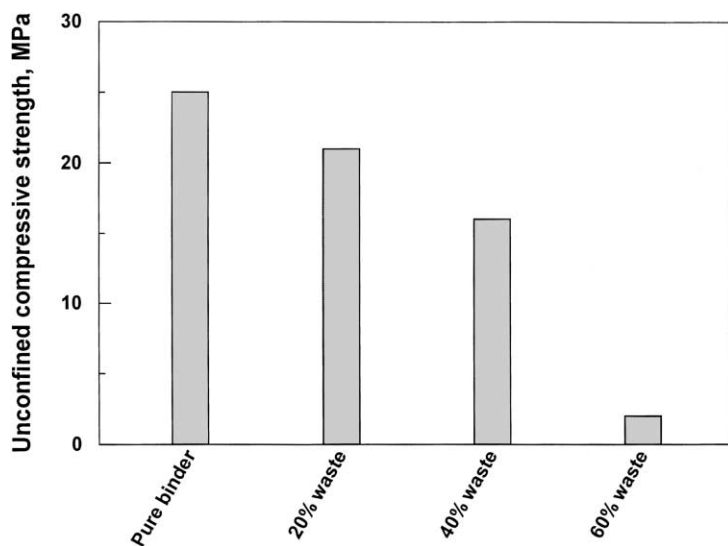


Fig. 4. Unconfined mechanical strength for pure binder and binder–waste mixtures.

3.3. Leaching behavior

Fig. 5 shows the results of the three leaching tests carried out on the stabilized samples. Specifically, for the two dynamic tests, the ultimate cumulative values are reported. All the results are in terms of percentages of metal released in relation to the amount originally

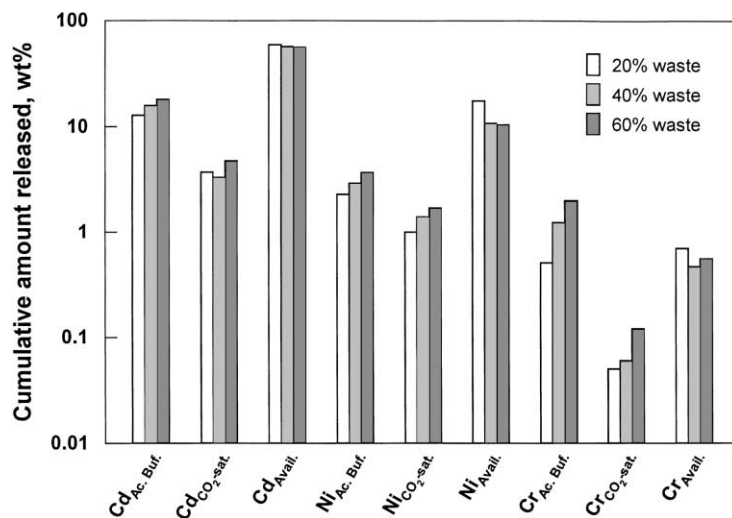


Fig. 5. Results of the three leaching tests carried out on binder–waste mixtures aged 28 days.

Table 1
pH-values at the end of each leaching step

Waste (%)	Time (h)									
	1	3	8	24	48	96	168	336	672	1344
Acetic buffer test										
20	4.90	4.90	4.94	4.96	4.97	5.02	5.03	5.15	5.32	5.50
40	4.90	4.90	4.96	4.97	4.98	5.03	5.06	5.23	5.34	5.78
60	4.92	4.94	4.96	4.99	5.01	5.03	5.09	5.31	5.44	5.82
CO ₂ -saturated solution test										
20	4.63	5.00	5.02	5.45	5.56	5.67	5.76	5.90	5.99	–
40	4.76	5.05	5.06	5.67	5.74	5.81	5.91	6.04	6.12	–
60	4.84	5.20	5.34	5.84	5.90	5.96	6.03	6.09	6.22	–

present in the samples. This helps to understand the effectiveness of the stabilization process. First of all, it is seen that in each test metals are released in the order Cd > Ni > Cr. Furthermore, an important observation is that in both the dynamic tests the amount released slightly increases with the amount of waste in the mixture, showing that metal release is not limited by metal solubility in the liquid phase, but by the intrinsic stabilizing properties of the matrix. In a previous work [16], it was found that this is not always the case, as copper was found to be leached in amount limited by solubility in the leaching medium from stabilized model systems.

The results of the two dynamic tests are different from each other as the cumulative amounts released in the acetate buffer test are invariably higher than those released in the CO₂-saturated solution test. The pH-values observed at the end of each leaching test are reported in Table 1 for both the dynamic tests. It is seen that pH is lower in the case of acetate buffer test and this could explain the difference observed. However, also the effect of the leaching medium on stabilizing matrix can have significant influence on the leaching results, as it will be shown later. Another important observation from Fig. 5 is that release ranges between about 0.05 and 18% of the initial quantity in both the dynamic tests. This, in conjunction with the slight increase of metal released with increasing waste content, makes clear that the matrix retains a good stabilization capacity even when the waste content is as high as 60%.

The overall effectiveness of the stabilization process, as argued from the results of the dynamic tests, does not make clear what the roles of physical and chemical stabilization mechanisms are. To this scope, the results of the availability test are to be examined and discussed keeping in mind that this test makes use of powdered samples in which the matrix is physically destroyed.

As far as cadmium is concerned, it is seen that the amount released increases from low values of about 3–5% (CO₂-saturated leaching test) and about 12–18% (acetate buffer test) to quite high values of about 56–59%. This makes clear that this metal is stabilized by prevailing physical mechanism, meaning that no respeciation leading to incorporation or micro-encapsulation within the neo-formed hydrated phases takes place after cadmium precipitation in the alkaline environment of cement [17–20]. Specifically, Yousuf et. al. [20] found evidence that cadmium is present in cementitious S/S systems in the form of calcium

hydroxocadmiate $\text{CaCd}(\text{OH})_4$ which results from the reaction of $\text{Cd}(\text{OH})_4^{2-}$ with calcium ions at or on the surface of cement grains.

In cement-based S/S systems, cadmium release can be almost complete due to lack of chemical mechanisms of stabilization for this metal [21]. In our case, however, the release of cadmium in the availability test, although high, is still far from total release, and this may be due to some form of cadmium entrapment by mechanisms like diadochy or isomorphic substitution in the presence of ettringite.

In the case of nickel, the availability test results are greater than those found in the two dynamic tests, but of the order of 10%. Then, it can be concluded that chemical mechanisms strongly prevail over physical ones, but the latter occur to some extent. A comparison with literature data for nickel leaching [17] confirms that there is no difficulty in fixing nickel by means of effective S/S systems.

Finally, in the case of chromium, the results of the availability test are of the same order of magnitude as those for the acetate buffer test and higher than those for the CO_2 -saturated solution test. This means that the stabilization mechanism is exclusively of chemical type. This result is in agreement with those reported by other authors [17,18,21] in the case of portland cement-based stabilization processes of this metal. Evidence was found that chromium is incorporated in the calcium silicate hydrate matrix. In our case, chemical stabilization can take advantage by the substitution of aluminum with chromium in ettringite. The particularly low values observed for chromium release in the CO_2 -saturated solution test may be due to higher pH-value (Table 1).

3.4. Effect of leaching on the matrix

It is well known that acidic leaching media can have significant effects on stabilizing matrices. Some authors found that acid attack on calcium silicate hydrate matrix leads to increased polymerization degree of calcium silicate hydrate with increased porosity and loss of mechanical properties [22]. Previous studies on stabilizing matrices based on calcium sulphoaluminate only also showed significant decomposition following an acid attack [9,23]. The leaching media used in this work are surely much more acidic and aggressive than those which are being proposed and used for compliance purposes in both European Union and Italy. For this reason they are much more useful for understanding the stability of the hydrated phases in contact with leaching media, and then their stabilization capacity.

When the cylindrical solidified samples were submitted to the attack of the acetic buffer and CO_2 -saturated solution, a strong structural modification could be observed. In fact, the external part of the sample became more porous and friable, while the internal core was left unchanged. The boundary between these two parts moved inwards and the thickness of the external layer was equal to 2, 3 and 7 mm after 28 days for the systems containing 20, 40 and 60% waste, respectively. This was independent of the type of leaching medium.

Samples from both the internal core and the external layer were submitted to specific analysis to verify the chemical modifications induced by the attack.

Fig. 6 shows the results of XRD carried out on samples of the system containing 40% waste. It is seen that the peaks relative to ettringite disappear in the external layer, giving decomposition products which are somehow different from one medium to the other. Specifically, in the case of acetic buffer, calcium sulphate dihydrate and aluminium hydroxide are

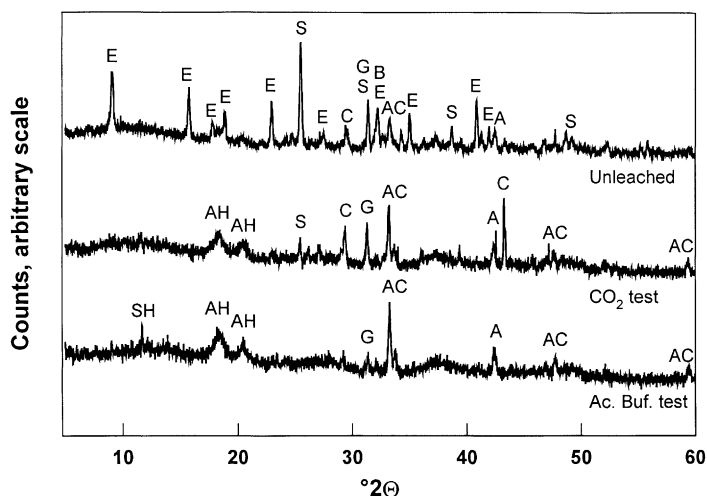


Fig. 6. Effect of leaching media on stabilized products (A: Al_2O_3 ; AC: $3\text{CaO}\cdot\text{Al}_2\text{O}_3$; AH: $\text{Al}(\text{OH})_3$; B: $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$; C: CaCO_3 ; E: ettringite; G: $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$; S: CaSO_4 ; SH: $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$).

the observed decomposition products, while in the case of CO_2 -saturated solution, calcium carbonate appears beside aluminium hydroxide.

Starting with a 1:1.5 ratio between $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ and $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot\text{SO}_3$ in the clinker, one gets a 1:4 ratio between calcium silicate hydrate and calcium trisulphoaluminate hydrate. Hence, the latter hydration product is present in amount equal to 80% of all the hydrated phases. Then, its contribution to chemical stabilization must be significant. Such contribution is due to diadochy and isomorphic substitution and it is supposed that it remains active even when the above hydration products decompose. In other words, the metals are still chemically retained by diadochy and isomorphic substitution within the decomposition products.

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 hydration chemistry, it has been shown that the addition of waste up to 60% does not alter the nature of hydration products. However, the extent to which hydration takes place is reduced when the waste content is greater than 20%.

The UCS starts from 25 MPa for the pure binder and reduces to 21 and 16 MPa when the waste content is 20 and 40%, respectively. It falls down to only 2 MPa when the waste content is further increased to 60%. Then, the use of binder–waste mixtures for the manufacture of pre-formed building blocks can be taken into consideration for waste content up to 40%.

The leaching behavior under the conditions of the three tests employed has proved that cadmium is stabilized by prevailing physical mechanism and that chemical entrapment

plays a secondary role. Chemical mechanisms prevail in the case of nickel and are almost exclusively active in that of chromium. From the qualitative point of view, leaching results agree with those for cement-based stabilization processes.

Finally, it has been found that the attack of the leaching media to the stabilized samples causes severe structural modification of the binder due to ettringite decomposition into gypsum, aluminum hydroxide and a calcium compound. Despite of this, chemical stabilization is retained in those cases in which it occurs and it is inferred that metals are chemically entrapped even in the decomposition products.

References

- [1] J. Bensted, S.P. Varma, *Cement Technol.* 2 (3) (1971) 73.
- [2] J. Bensted, S.P. Varma, *Silica Ind.* 37 (12) (1972) 315.
- [3] R. Wenda, H.J. Kuzel, in: *Proceedings of the 8th International Congress on the Chemistry of Cement*, Vol. III, Rio de Janeiro, 1986, p. 307.
- [4] H. Pöllmann, H.J. Kuzel, *Cement Concr. Res.* 20 (1990) 941.
- [5] H. Pöllmann, S. Auer, H.J. Kuzel, R. Wenda, *Cement Concr. Res.* 23 (1993) 422.
- [6] J. Csetenyi Laszlo, F.P. Glasser, *Mater. Res. Soc. Symp.* 294 (1993) 273.
- [7] J. Beretka, B. de Vito, L. Santoro, N. Sherman, G.L. Valenti, *Cement Concr. Res.* 23 (1993) 1205.
- [8] J. Beretka, R. Cioffi, L. Santoro, G.L. Valenti, *J. Chem. Technol. Biotechnol.* 59 (1994) 243.
- [9] R. Berardi, R. Cioffi, L. Santoro, *Waste Manage.* 17 (1997) 535.
- [10] J. Beretka, B. de Vito, L. Santoro, N. Sherman, G.L. Valenti, *Res. Cons. Recycl.* 9 (1993) 179.
- [11] G.A. Mudbhalkar, P.S. Parmeswaran, A.S. Heble, B.V.B. Pat, A.K. Chatterjee, in: *Proceedings of the 8th International Congress on the Chemistry of Cement*, Vol. IV, Rio de Janeiro, 1986, p. 364.
- [12] H.F.W. Taylor, *Cement Chemistry*, Academic Press, London, 1997.
- [13] G.L. Valenti, R. Cioffi, L. Santoro, S. Ranchetti, *Cement Concr. Res.* 18 (1) (1988) 91.
- [14] Italian Standard UNI 9858, Milan, 1991.
- [15] J.A. Stegemann, P.L. Coté, *Sci. Total Environ.* 178 (1–3) (1996) 103.
- [16] V. Albino, R. Cioffi, B. de Vito, M. Marroccoli, L. Santoro, in: J.J.J.M. Goumans, H.A. van der Sloot, Th.G. Aalbers (Eds.), *Environmental Aspects of Construction with Waste Materials: Studies in Environmental Sciences*, Vol. 60, Elsevier, Amsterdam, 1994.
- [17] J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.
- [18] R.D. Spence (Ed.), *Chemistry and Microstructure of Solidified Waste Forms*, Lewis Publishers, Boca Raton, FL, 1993.
- [19] D.L. Cocke, *J. Hazard. Mater.* 24 (1990) 231.
- [20] M. Yousuf, A. Mollah, Y.N. Tsai, D.L. Cocke, *J. Environ. Sci. Health: Part A A27 (5) (1992) 1213.*
- [21] P.L. Bishop, *Hazard. Wastes Hazard. Mater.* 5 (1988) 129.
- [22] J.D. Ortego, Y. Barroeta, F.K. Cartledge, H. Akhter, *Environ. Sci. Technol.* 25 (6) (1991) 1171.
- [23] R. Cioffi, L. Santoro, *Environ. Technol.* 21 (2000) 815.