

STABILIZATION/SOLIDIFICATION OF MUNICIPAL SOLID WASTE IN CEMENTED MATRICES

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Abstract

The exponential increase that has been unchained in the generation of municipal solid wastes, in these last years, and that they need to be treated and management appropriately, it has forced to act immediately as for the management of this type of wastes. One type of these wastes is the wastes coming from Municipal Solid Wastes Incineration. One of the most useful methods to management its, is by means of stabilization/solidification systems.

In that aspect it shows up this work in which has been used cement-based materials as immobilization system. Among the different kinds of cementitious materials to be employed in the solidification of wastes, the ordinary Portland cement is the most frequently employed. The main objective of this paper is to quantify the grade of immobilization grade of hazardous wastes, by means of the pore solutions analysis.

Keywords: pore solutions, cement matrix, solidification/stabilization systems.

INTRODUCTION

The industrial and technological development, as well as the demographic increase observed in some cities, it has unchained in a substantial increase of the municipal solid wastes that they are generated, and that they need to be treated and management appropriately to be able to complete all the environmental requirements of protection for the health and in general of the environment. In this sense a wide number of so much European Directive, national or autonomous legislations exist (1-6) that regulate all the definition aspects, manipulation, management and use of all type of wastes.

Many forms exist in those that different investigation groups are faced the problem of the climatic change, placing all them, a strong emphasis in the reduction of the greenhouse gas emission.

One of the words key in this whole lattice is the "wastes management" and concretely of those wastes that for their characteristics, treatment or nature; they go directly to landfill, occupying a very significant space of our environment. Centring us in them, special mention will give to the wastes coming from the incineration of municipal solid wastes that independently of the incineration system that has been carried out, they suppose a great number of ash and slag that can be valorised, or stabilized, so that they reduce its environmental impact.

The mentioned processes of stabilization/solidification are defined:

1. **Stabilization:** Includes those techniques that reduce the potential dangerous of waste, by means of the step from their polluting elements to a for of smaller mobility, solubility or toxicity.
2. **Solidification:** Includes those processes developed with the purpose of encapsulating waste in a monolithic solid of high structural integrity. It does not necessarily imply a chemical interaction between waste and solidifying reactants, but it can mechanically bind waste and monolith. Pollutant migration is restrained since the surface exposed to leaching decreases dramatically and/or waste is isolated in an impenetrable capsule.

Among stabilization/solidification treatment more common, can be appointment:

1. Sorption processes.
2. Organic processes
3. Processes that use: pozzolan, fly ash, lime and Portland cement.

4. Micro-encapsulation
5. Macro-encapsulation

One of the materials most used in these immobilization systems is the "System based of Portland cement". In this system waste is added to the cement in solid or aqueous form resulting in a more or less fluid consistency that can be poured in a mould or a container fitted for a safe transport to the storage place. Cementation of waste reduces the risk of external pollution by accidental spill.

Portland cement is representative of a group of materials that have practical and conceptual advantages when making matrices of waste immobilisation. These are constructions materials relatively well proved, and presented many advantages as:

1. Inexpensive raw materials.
2. Its setting and hardening reactions are well known, and also the fixation of metals in its body.
3. There are well-documented studies for modelisation of leaching of nuclear waste. Good durability in natural environment
4. Capacity for incorporating modifiers of the solid matrix (slag, fly ash, silicates, etc) to improve the waste immobilisation.
5. It allows aqueous wastes.
6. Its alkalinity discourages microbiological activity, and its provides chemical and physical immobilization.

The present paper is a part of an extensive investigation project study carries out in our laboratory (9-11), where we are used fly ash and bottom from two Spanish Incineration Plants. In this work we are present the influence of the type of cement on the components of the four municipal solid waste incineration. Due to the short time we are shown the efficiency of matrices of stabilise the minority toxic elements and dangerous salts, through analyses of extracted matrix pore solution.

EXPERIMENTAL

1. Materials

To carry out the present study the cement used were:

- Ordinary Portland Cement type I-55A, namely here as: OPC.
- Fondu Calcium Aluminate Cement, namely here as: CAC.

- A mixture of Ordinary Portland Cement and Granulated Blast Furnace Slag (OPC/BFS) in a proportion of 20/80, namely here as: BFS/OPC.

We have used for wastes that belong to taken samples of two Spanish Incineration Plants: one of Comunidad Autónoma de Madrid: Valdemingomez Incineration Plants; and others of Ciudad Autónoma de Melilla; in the first of them weekly samples were picked up during four serial weeks, of each one of the silos in those that the ashes are deposited, calling you to the same ones:

- Cenizas de silo 1 (R1): Ash from fluidised bed combustion of MSWI of Valdemingomez Incineration Plant, in Madrid, contains a great amount of SiO₂.
- Ash of silo 2 (R2): fly ash from cleaning-gas device of MSWI of Valdemingomez Incineration Plant, in Madrid.
- Fly ash (R3): from cleaning-gas device of MSWIR of Melilla Incineration Plant.
- Slag (R4): Coming from the furnace from Melilla Incineration Plant.

The chemical composition and the mineral characterisation of the wastes used here and the cements are shown in Table 1 and Figure 1. The X-ray diffraction (XRD) patterns were recorded with a diffractometer (Model PW-1730 Philips Research Laboratories, Eindhoven, The Netherlands) using a graphite monochromator and Cu K α ₁ radiation.

Table 1. Chemical Composition of Starting Materials: wastes and cement (% by weight)

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	Cl	S ²⁻	LOI	IR
OPC	65,3	20,1	5,3	2,9	1,3	3,1	0,2	1,0	-	-	1,5	0,8
CAC	38,3	3,5	41,2	15,3	0,4	>0,1	0,1	0,1	-	-	0,4	0,9
OPC/B	40,2	37,6	12,5	1,2	8,2	-	0,2	0,6	-	1,2	1,4	0,8
FS												
R1	21,9	34,1	19,3	6,6	2,6	3,3	2,1	1,9	3,6	-	4,6	5,2
R2	44,9	11,4	11,3	1,1	1,9	3,9	2,1	1,9	13	-	17,6	0,1
R3	23,4	12,8	10,0	1,8	3,1	7,6	9,4	4,9	16,8	-	16,6	0,5
R4	20,6	46,2	9,3	7,2	1,9	1,1	5,8	1,6	0,7	-	7,5	1,5

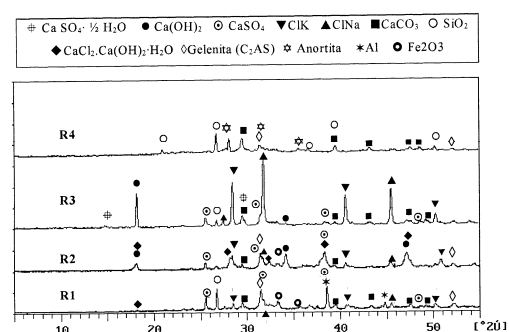


Figure 1. X-ray Diffraction Patterns of Starting Wastes

The concentration of minority toxic elements (Zn^{2+} , Cd^{2+} and Pb^{2+}) of the wastes and the different cement materials using in this study are given in the following figure 2. Zn^{2+} and Pb^{2+} , are the most abundant ions in the wastes and in the cement. In all cases, the content of these toxic elements in wastes are 10 times high that in the cement.

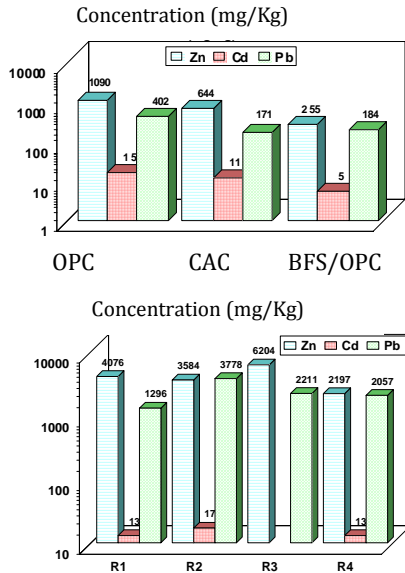


Figure 2. Concentration of Minority Toxic Elements in Cement and in Wastes

2. Methodology of Study

Mixtures of cements and solid wastes were prepared at a waste to cement ratio of 40:60. Matrices were fabricated with de-mineralized water at water to solid ratio of 0.6, and stored in sealed plastic cylinder at 100% relative humidity and 21°C up to 28 days. Also, it was prepared matrices without wastes, using as reference. An aspect of the different matrices appeared in the figure 3. As can be seen in this figure, an special attention could be done for the porosity of this matrices, specially matrices with the waste 2.



Figure 3. Aspect of different Cement Matrices

The stabilisation of minority toxic metals and dangerous salts contained in the wastes was

evaluated from analyses of the matrix pore solutions which were extracted by applying high mechanical pressure (500 MPa) with equipment that is presented in Figure 4.



Figure 4. Extracted Pore Solution Equipment

The elements analysed were: SO_4^{2-} , Cl^- , Na^+ , K^+ , Ca^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} . The pH and the conductivity were also measured. The concentration of Na^+ , K^+ and Ca^{2+} , was determined by atomic absorption spectroscopy, SO_4^{2-} and Cl^- by gravimetric method and automatic titration against $AgNO_3$, and those of Zn^{2+} , Cd^{2+} and Pb^{2+} by Anodic Solution Voltamperometry (ASV).

The microstructure and mineral characterization of matrices were studied by mercury intrusion porosimetry (MIP) (Model 9320 Pore size Micromeritics Instrument Corp., Norcross, GA) and X-ray diffraction (XRD) patterns were recorded with a diffractometer Model PW-1730 Philips Research Laboratories, Eindhoven, The Netherlands) using a graphite monochromator and $Cu K\alpha_1$ radiation.

RESULTS AND DISCUSSION

1. Matrix Pore Solution

Analyses of matrix pore solutions, extracted after 28 days from mixing, appeared in Figures 5 and 6. As shown, when matrices contained the wastes the pH decreases from 13.14 for OPC until 13,04; 11,67; 11,97 and 11,95 for OPC with different wastes and for 12,61 for OPC/BFS to 12,03 and 11,52 in the case of this cement with R1, R2 and R3, but in the case of R4 the pH increase.

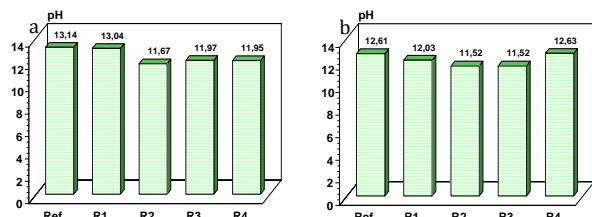


Figure 5. pH values of a) OPC matrix and b) BFS/OPC matrix.

So, to evaluate with more rigour the efficiency of matrices to stabilise any ionic species it is necessary to know two parameters:

Co: initial concentration in each sample provided by the mixture: waste to cement; and

c: concentration in the aqueous phase analyzed after 28 days of hydration.

The difference between Co and c, is the amount retained in the solid phase.

As can be seen in the Figure 6, the percentage of chloride ion retained in the solid phase is higher in general, in the case of OPC matrix. In the case of sulphate its behaviour is different, in the matrix BFS/OPC with the wastes, practically all the content of sulphate is retained in solid phase. The behaviour for the alkaline ions ($\text{Na}^+ + \text{K}^+$) is similar to the chloride ions.

As far as the minority toxic elements is concerning both OPC/Waste and OPC/BFS/Waste matrices immobilise Zn^{2+} , Cd^{2+} and Pb^{2+} ions, as manifested their very low values (Fig. 6) of concentration after 28 days. Also, the presence of the wastes: R1, R2, R3 and R4, it is very important to retain Cd^{2+} ions in both matrices.

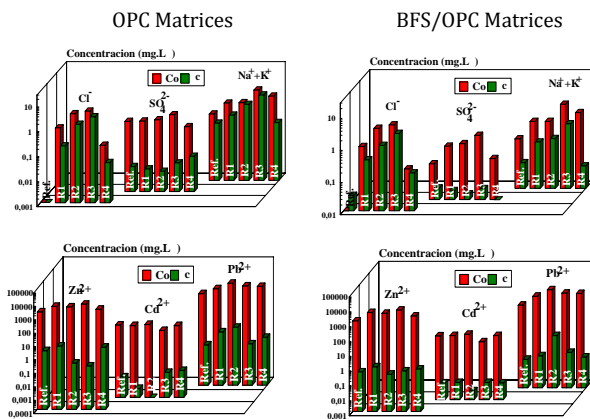


Figure 6. Concentration of the ions before and after 28 days of hydration

CONCLUSIONS

- System based of Portland cement, is a good method to immobilize heavy metals coming from municipal solid wastes.
- However, they have been able to observe phenomena, like increase in the porosity, formation of crystalline phases with expansive character, etc. that would be harmful for the

mechanical properties of the cement-based materials.

- For this reason, it is of interest to continue deepening in the improvement of the dosifications and study methodology for the application of these residuals in the construction materials

REFERENCES

1. Directiva 75/442/CEE, de 15 de julio de 1975, relativa a los residuos (con las modificaciones de la directiva del consejo 91/156/CEE, de 18 de marzo de 1991). Es la norma marco que sirve de base al desarrollo de las posteriores normativas europeas y nacionales
2. Directiva del Consejo, de 18 de marzo de 1991, por la que se modifica la Directiva 75/442/CEE relativa a los residuos, (91/156/CEE). Doce 78/l, de 26-03-91
3. Directiva 96/61/CE, de 24 de septiembre de 1996, relativa a la prevención y el control integrados de la contaminación (IPPC).
4. Resolución del Consejo, de 24 de febrero de 1997, sobre una estrategia comunitaria de gestión de residuos.
5. Directiva del Consejo 1999/31/CE, 26 de abril, relativa al vertido de residuos.
6. Ley 10/1998, de 21 de Abril, de Residuos, BOE 96, de 22-04-98, Resolución de 13 de enero de 2000, de la Secretaría General de Medio Ambiente, por la que se dispone la publicación del Acuerdo de Consejo de Ministros, de 7 de enero de 2000, por el que se aprueba el Plan Nacional de Residuos Urbanos.
7. Intergovernmental Panel on Climate Change: Special report on Emissions 2001. <http://www.grida.no/climate>.
8. McCaffrey, R. 2002. *Climate change and the cement industry*. Global Cement and Lime Magazine: Environmental Special Issue.
9. Macías, A., Goñi, S., Guerrero, A and Fernández, E. 1999. *Immobilization/Solidification of Hazardous Wastes in Cement Matrices*, vol. 49, nº 254, p. 5-16. Materiales de Construcción.
10. Macías, A., Fernández, E., Goñi, S. y Guerrero, A. 2001. *Valorización y Tratamiento de Cenizas y Escorias de Incineración de Residuos Sólidos Urbanos*, p. 39-46. Química e Industria.
11. Goñi, S., Guerrero, A., Macías, A., Peña, R. y Fernández, E. 2001. *Empleo de Materiales Secundarios como Materia Prima de Nuevos Tipos de Cemento*, vol. 51, p. 5-18. Materiales de Construcción.

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