

SOLIDIFICATION/STABILIZATION OF HEAVY METALS IN LATEX MODIFIED PORTLAND CEMENT MATRICES*

S. DANIALI

Civil Engineering Department, Lamar University, P.O. Box 10024, Beaumont, TX 77710 (U.S.A.)

Summary

Immobilization of hazardous waste substances in a portland cement matrix is considered a major solidification method, which is no doubt due to the simplicity of the process and its low cost. However, the relatively high porosity of the cement matrix, which could lead to considerable leaching, has created a demand for improved portland cement matrices. In this regard, a research project has been sponsored by the Gulf Coast Hazardous Waste Substance Research Center. The overall objective of this study is to develop latex modified cement systems to treat inorganic and organic wastes. A preliminary study on stabilizing/solidifying inorganic waste (lead and chromium) with latex modified cement has shown very encouraging results.

Introduction

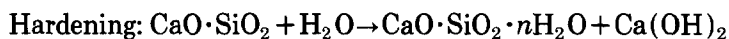
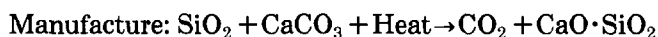
Solidification/stabilization (S/S) of hazardous waste substances in portland cement matrices prior to landfill disposal is the most commonly used process by disposal industries. Basically, the cement solidification technique involves mixing prepared waste with cement to produce slurry, which sets in about three days and attains its maximum strength in about six months. The leachability of solidified substances in portland cement matrices has been the subject of numerous studies [1-6]. The emphasis of these studies has focused primarily on the fundamental chemistry involved in the S/S and leaching mechanisms, but comparatively little attention has been paid to the factors affecting the properties of the portland cement matrix.

A knowledge of the compound composition of portland cement makes it possible to predict the properties of the cement paste. More important, it is possible, by suitable adjustment of the compound composition, to modify certain properties of the cement so that it will perform more satisfactorily.

Portland cement is produced by grinding together clay-bearing and lime-

*Paper presented at the GCHSRC Second Annual Symposium: Mechanisms and Applications of Solidification/Stabilization, Lamar University, Beaumont, TX, U.S.A., February 15-16, 1990.

bearing materials (usually clay and limestone) and heating them to about 1500°C. At 650°C, the limestone separates into CO₂ gas and CaO. When the silica reaches the point of fusion, it combines chemically with CaO and small amounts of Al₂O₃ and Fe₂O₃, producing portland cement clinker. The clinker is then ground to a fine powder and a small amount of gypsum is added. When the cement is mixed with water, it hydrates and produces calcium silicate crystals. About 75% of portland cement clinker is composed of calcium silicates. Calcium compounds of aluminum (Al₂O₃), iron (Fe₂O₃), and gypsum (CaSO₄) are of secondary importance. The principal reactions in the manufacture and hardening of portland cement are as follows:



The water/cement ratio is the most important parameter, influencing properties of hardened cement paste, such as strength, durability, and porosity. When portland cement paste is prepared and cured in the normal way, considerable capillary porosity is present in the paste, and some of this porosity is considered to be a part of the calcium silicate hydrate [7,8]. If the water present in the capillary pores of cement were removed and replaced with compatible materials, the strength, durability, and permeability of portland cement paste would greatly improve, thereby reducing the leachability of cement matrices. Organic polymers, with their high corrosive resistance and good adhesive properties, have the potential to be used with portland cement for S/S of hazardous waste substances.

Latices

Polymers have been used in concrete constructions for more than twenty years. They have been used to improve the properties of concrete and cement mortar, especially when these materials are subjected to severe chemical attack in applications such as sewage plants and chemical processing plants. Polymers can be incorporated in cement matrices in two ways: they can be added to the fresh cement paste, or they can be impregnated into the hardened cement matrix and cured in place [9–12]. Only those types of polymers which are added to the cement matrix in its fresh state are considered in this research study. Polymer additives can be classified into three groups: latices, liquid resins, and water soluble polymers. Of these, the latex polymers have been widely used with cement. Latices are dispersions of solid polymer particles in water. The polymers can be either elastomeric (rubbery) or amorphous thermoplastics, and the dispersion usually contains about 50% of the polymer by weight. Latices are usually formed by polymerization of an emulsion of the liquid monomer particles in water. Examples of polymers used in latices are natural rub-

ber, styrene-butadiene, polyvinyl acetate, and acrylates. During hydration of latex-modified cement paste, the latex forms thread-like membranes throughout the matrix. These membranes increase the bond within the paste particles and the waste substances, which are simply physically trapped in the cement matrix. The maximum effects of latex in cement are obtained with a polymer/cement ratio of 15–20%, by weight. This amount of polymer fills the small pores and capillaries without creating discontinuity in the cement gel [9–12].

Materials

Cement: A single source of Type I portland cement was used. The chemical composition of the cement is shown in Table 1. This information has been obtained from the manufacturer.

Polymer latex: The Union Carbide latex 413 has been used as a modifier for the cement matrix. This product is an acrylic emulsion polymer and is designed to improve properties of materials containing portland cement. The cement paste modified with UCAR 413 demonstrates higher compressive, flexural, and bond strengths compared with unmodified paste. The physical properties of UCAR Latex 413 are shown in Table 2.

Inorganic hazardous substances: Lead and chromium are considered to be priority pollutants [5,6]. The aqueous solutions of lead and chromium nitrate,

TABLE 1

Constituent	wt. %
SiO ₂	22.0
Al ₂ O ₃	4.1
Fe ₂ O ₃	3.1
CaO	65.8
MgO	0.9
SO ₃	2.7
Ignition loss	0.9
Insoluble residue	0.9

TABLE 2

Physical properties of UCAR latex 413

Parameter	Value
Solids, wt. %	47 + 1.0%
pH	9.0–9.5
Viscosity, mPa·s	50
Weight	8.8 lb/gal (~ 1.06 kg/l)

TABLE 3

Mix ratios by weight of cement

Mix no.	Water (W/C)	Pollutant (Pb/C) or (Cr/C)	Latex (solid) (Lx/C)
Pb-1 ^a	0.35	0.033	0.075
Pb-2	0.35	0.033	0.10
Pb-3	0.35	0.033	0.125
Pb-4	0.35	0.033	0.15
Pb-5	0.35	0.00	0.10
Pb-6	0.35	0.01	0.10
Pb-7	0.35	0.10	0.10
Pb-8	0.35	0.15	0.10
Pb-9	0.35	0.0	0.0
Cr-1 ^b	0.35	0.05	0.075
Cr-2	0.35	0.05	0.10
Cr-3	0.35	0.05	0.125
Cr-4	0.35	0.05	0.15
Cr-5	0.35	0.00	0.10
Cr-6	0.35	0.01	0.10
Cr-7	0.35	0.10	0.10
Cr-8	0.35	0.15	0.10
Cr-9	0.35	0.0	0.0

^aSamples containing lead nitrate.^bSamples containing chromium nitrate.

with concentration up to 15% by weight of cement, were used in preparing the specimens.

Sample preparation

A total of 18 sets of samples with different water/cement (W/C), latex/cement (Lx/C), and pollutant/cement (P/C) ratios was prepared. Table 3 shows the composition of each mix. Water, latex, and pollutant substance were mixed thoroughly prior to mixing with cement. Thousand grams of cement were used for each mix. The final mix was prepared using a bench model mixer. Mixing was continued until uniformity was assumed. The mix was cast in cylindrical teflon molds (30 mm diameter, 68 mm height). The curing procedure for latex-modified cement pastes is different from that for ordinary pastes since the latex component must be allowed to dry out. The simplest method of curing is to allow the paste to air dry. Therefore, the samples were kept at ambient condition for two days and then removed from their molds.

Test results

A film of latex was almost immediately formed on the surface of the specimens containing lead and chromium, sealing in the water. The water was then

TABLE 4

TCLP test results for three sets (ppm)

Sample ^a	Lx/C (solid%)	Pb/C (wt.%)	Set 1 (4 weeks)	Set 2 (5 weeks)	Set 3 (6 weeks)
Pb-1	7.5	2	10.06	9.96	8.94
Pb-2	10.0	2	7.38	5.76	2.44
Pb-3	12.5	2	6.75	4.81	2.53
Pb-4	15.0	2	9.66	3.20	2.98
Pb-6	10.0	0.066	1.76	0.85	0.75
Pb-7	10.0	0.66	16.85	-	-
Pb-8	10.0	0.92	33.33	-	-

^aSamples containing lead nitrate.

TABLE 5

TCLP test results

Sample ^a	Lx/C (solid%)	Cr/C (wt.%)	TCLP (ppm)
Cr-7	10	2	<0.5
Cr-8	10	3	<0.5

^aSamples containing chromium nitrate.

used up in hydrating the cement. Formation of such film was previously observed and reported [12]. Final setting time of different mixes was measured using a Vicat apparatus. All mixes containing inorganic pollutants reached their final setting within 6 to 14 hours. Results of the freeze/thaw durability tests conducted on specimens with inorganic pollutants were very good, showing little or no weight loss after 50 cycles. The compression test of specimens containing lead and chromium indicated no loss of strength due to the presence of these materials; the compression strength at 28 days ranged from 950 to 1000 psi (or 660–700 kPa).

The U.S. Environmental Protection Agency Toxicity Characteristic Leaching Procedure (TCLP) and Extraction Procedure (EP) are in progress. The preliminary results of TCLP tests are summarized in Tables 4 and 5.

Conclusions

In this study the efficiency of the solidification/stabilization technique using latex modified portland cement matrices containing lead or chromium was investigated. The concentration of pollutants varied from 0.2% up to 15% of total weight (20,000 to 150,000 ppm). The preliminary results of the physical

tests (setting time, compression, freeze/thaw) and TCLP of specimens made of latex modified portland cement indicated considerable improvement relative to those made of regular portland cement. However, more data are needed to derive a solid conclusion.

Acknowledgement

The author wishes to thank the Gulf Coast Hazardous Substance Research Center, Lamar University, for supporting this research project.

References

- 1 W. Shively, P. Bishop, D. Gress and T. Brown, Leaching tests of heavy metals stabilized with Portland cement, *J. Water Pollut. Control Fed.*, 58 (1986) 234.
- 2 P. Bishop and D. Gress, Evaluation of the Potential for Marine Disposal of Stabilized/Solidified Inorganic Wastes, report Office of Sea Grant, National Oceanographic Administration, Washington, DC, 1986.
- 3 W. Lowenback, Compilation and evaluation of leaching test methods, report EPA-600/2-79-095, U.S. EPA, Cincinnati, OH, 1979.
- 4 U.S. Environmental Protection Agency, Solid waste leaching procedure manual, SW-924, U.S. EPA, Cincinnati, OH, 1985.
- 5 E.J. Calabrese, P. Kostecki, Soil contaminated by petroleum. In: *Environmental and Public Health Effects*, Wiley, New York, NY, 1988, p. 458.
- 6 J.L. McArdle, M.M. Arozarena and W.E. Gallagher, Treatment of Hazardous Waste Leachate. Unit Operation, and Costs. Noyes Data Corp., Park Ridge, NJ, 1988, p. 110.
- 7 S. Mindess and J.F. Young, *Concrete*, Prentice-Hall, Englewood Cliffs, NJ, 1989, p. 76.
- 8 W.A. Cordon, *Properties, Evaluation, and Control of Engineering Materials*, McGraw-Hill, New York, NY, 1979, p. 68.
- 9 S.A. Frondistou-Yannas and P.S. Shah, Polymer latex modified mortar. *J. Am. Concr. Inst.*, 69 (1) (1972) 61-65.
- 10 S. Cardone, M. Brown and A. Hill, Latex modified mortar in the restoration of bridge structures, *Highway Res. Board Bull.*, 260 (1960).
- 11 J. Hosek, Properties of cement mortars modified by polymer emulsion. *J. Am. Concr. Inst.*, 63 (12) (1966) 1411-1423.
- 12 V.R. Riley and I. Razi, Polymer latex modified mortar - a review. *Composites*, Ann Arbor Publ., Ann Arbor, MI, 1979.