# Effect of Latex Modification of Portland Cement Matrices on Properties of Heavy Metal Immobilized Products

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**ABSTRACT:** Solidification and stabilization are considered to be a successful method for the treatment of hazardous metal sludges because the properties of the end product and cheap methods of disposal. Although solidification often limits the undue leaching of metals, the highly porous nature of the cement matrices are susceptible to attack by various solutes after placement in landfills, thus reducing their strength and durability. Improved methods of treatment for the metal sludges are required. Modification of the physical properties, especially porosity, of the cement matrices can improve the properties of the final product. The objective of this research was to study the effect of polymer modification of the cement matrices on the strength and leachability of the solidified and stabilized product. The results of this preliminary study showed a 10-fold reduction in the leachability of the metals, although no noticable difference in strength values was noted. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2482–2487, 1999

**Key words:** solidification and stabilization; waste treatment; polymer modification; Portland cement; compressive strength; toxicity

## INTRODUCTION

The solidification and stabilization (S/S) of hazardous metal wastes in Portland cement matrices prevents the leaching and migration of some hazardous wastes deposited in landfills by "fixation" or "solidification" in a stable inert matrix. Improved physical handling properties of the waste and cheap methods of disposal have placed this method in the forefront for disposal of heavy metal sludges. These stabilized metal bearing wastes have been found suitable for use as a construction material and as a road subbase material.[1] Other stabilized wastes have also been successfully reused.[2] The strength and leachability of the S/S specimens has been subject to numerous studies.[3–9] A review of these studies indicates that little attention has been paid to the factors affecting the properties of the Portland cement matrix. Knowledge of the physical properties of the Portland cement matrix that affect the S/S process allows modification of those properties so that the matrix will perform more satisfactorily. Manipulation of the physical properties of the cement matrix will open more avenues and give new dimensions for disposal and reuse of the S/S waste.

The water/cement ratio and curing time play a very important role in influencing the strength, durability, and leachability of the S/S product. Strength and durability are directly related to the

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porosity of the hydrated cement-based composites. The permeability of the S/S product to aggressive agents that can travel through it is also related to its accessible pore structure. In addition, the permeability of the porous S/S materials to water is often the primary factor affecting the rate of deterioration.[10] If the porosity of the hydrated cement paste could be reduced by filling it with compatible materials, the strength, durability, and permeability of the Portland cement stabilized product would be greatly improved, thereby reducing the rate of deterioration of the S/S products. Organic polymers have exclusive corrosion resistance, good adhesive properties, and compatibility with Portland cement and have the potential to be used with ordinary Portland cement (OPC) for S/S of hazardous heavy metal sludges.

Polymer latexes are generally classified by the kind of electrical charges on the polymer particles, which are determined by the type of surfactants used in the production of latexes: cationic, anionic, and nonionic. In general, polymer latexes are copolymer systems of two or more different monomers; their total solid content including polymers, emulsifiers, stabilizers, and antifoaming agents (to reduce air entrainment) are 40–50% by weight. Some of the requirements of any polymer latex as a cement modifier are that it does not adversely influence the cement hydration process, forms continuous polymer films in mortar or concrete, has high adhesion of the polymer films to cement hydrates and aggregates, and has high chemical stability toward active cations liberated during cement hydration. Styrene-butadiene copolymer latex has been widely and successfully used commercially.

Polymers have been used for many years in construction to achieve high strength and improved physical properties.[11,12] Some polymers are highly resistant to chemical attack and can withstand extreme pH and temperatures. Polymers can be incorporated in cement mortar as an addition and can also be incorporated by impregnating them into the hardened concrete and curing in place.[13] Latex polymers are inexpensive and easy to handle dispersions that readily mix with the cement/sand mixture to form a smooth mortar. Upon hydration of the cement pastes, the latex particles form continuous membranes and fill the pores of the cement matrix. Generally, a polymer/cement ratio of 15% by weight is used to achieve this type of matrix. However, the ratio depends on the amount of polymer by weight in the dispersion. The discontinuity in the cement gel and reduced pores in the cement matrix allow less pathways for the attacking agents to pass through it and, as a consequence, increase the strength and durability of the product. This research was carried out to determine the effect of latex modification on the strength and leachability of heavy metals from the S/S product.

**Table I Characteristics of Air-Dried Electroplating Sludge**

| Parameters | Values |
|---|---|
| pH | 9.23 |
| Moisture content | >1% |
| Organic content | 7.4% |
| Loss on ignition | 2.9% |
| Fineness | 92.3% |
| Total metal concentration | 2% |

## MATERIALS AND METHODS

### Materials

#### *Cementitious Binder*

The cementitious binder used for the study was OPS (43 grade, Larson & Toubro, India Ltd.,). The cement was sieved prior to mixing with sludge. Sand with an effective size of 0.2 mm and a uniform coefficient of 2.5 was used for the entire study.

#### *Molds*

Different types of molds were used to test the unconfined compressive strength (UCS) and flexural strength (FS) of the solidified sludge samples. For compressive strength, mild steel cube molds with 50-mm edges as specified by ASTM C109-86 were used. For the FS and leaching tests, $60 \times 40 \times 20$ mm rectangular molds made of teak wood were used. The inside of the molds was oiled with motor oil before filling with the mortar to ensure that the mortar did not stick to the sides of the molds.

#### *Hazardous Metal Sludge*

The metal sludge from an electroplating industry had the characteristics listed in Table I. The metal concentration of the sludge used for the study was ascertained by a Jobin Yuon-Model

**Table II Mixture Formulations of Solidified and Stabilized Specimens**

| | Percent Ratio | | | |
|---|---|---|---|---|
| Sample Code | Cement/Sand | Water/Cement | Sludge/Cement | Polymer/Cement |
| $^{1}Ia^{1}$ | 1 : 3 | 0.50 | 25 | 15 |
| $Ib^{1}$ | 1 : 2 | 0.43 | 25 | 15 |
| $Ic^{1}$ | 1 : 3 | 0.50 | 10 | 15 |
| $Id^{1}$ | 1 : 2 | 0.43 | 10 | 15 |
| $Ia^{2}$ | 1 : 3 | 0.50 | 50 | 15 |
| $Ib^{2}$ | 1 : 2 | 0.43 | 50 | 15 |
| $Ic^{2}$ | 1 : 3 | 0.50 | 25 | 15 |
| $Id^{2}$ | 1 : 2 | 0.43 | 25 | 15 |

Superscript 1s and 2s represent, respectively, samples with the weight percent of the cement replaced by the electroplating sludge and samples with the weight percent of the sludge added by the weight of the cement.

JY24 sequential inductively coupled plasma emission spectroscope after nitric/hydrofluoric acid digestion. The concentrations of the individual metals were as follows: Cu, 532 mg/kg; Cr, 8200 mg/kg; Pb, 152 mg/kg; Cd, 432 mg/kg; Fe, 86,000 mg/kg; Ni, 332 mg/kg; and Zn, 93,000 mg/kg.

### *Polymer Latex*

Commercially available styrene-butadiene rubber (SBR) latex was used for this study. The solids content of the SBR latex was 45 ± 1% and its specific gravity was found to be 0.98.

### Methods

Each mix was prepared by proportioning, on a weight basis, amounts of cementitious binders, heavy metal sludge, sand, latex, and water in the ratios given in Table II. The polymer/cement ratio was calculated based on the polymer solids in the SBR latex. The amount of water present in the polymer dispersion was deduced from the amount of water added to the mortar in order to maintain the water/cement ratio. Dried sludge and cement were thoroughly mixed in a mechanical Hobart-like mixer for a few minutes. The determined quantity of water and latex was added to the mixing bowl for further mixing until a uniform consistency was achieved. The mortar was poured into molds as described above and vibrated on a vibration table to remove voids, if any. Samples were air dried in ambient conditions for 1 day, demolded, and cured in a relative humidity controlled chamber maintaining room temperature and 50% relative humidity for 28 days. In order to compare the effect of latex modification, solidification of samples with formulations as in Table II but with no latex addition was also carried out.

### *Physical and Chemical Evaluation*

To evaluate the physical integrity, two physical tests were performed on the S/S samples: UCS and FS. A toxicity characteristic leaching procedure (TCLP) was carried out to evaluate the leachability of the metals from the S/S samples according to the standard procedure.[14] Polymer-modified and unmodified samples $Ia^{1}$, $Ib^{1}$, $Ic^{2}$, and $1d^{2}$ were selected for the TCLP studies.

## RESULTS AND DISCUSSION

A film of latex nearly immediately formed on the surface of the S/S specimens. Formation of such films was previously recorded.[12,13]

### Effect on Strength

The results of UCS and FS test (Table III) showed no noticable difference in the UCS of the latex-modified samples compared to that of the unmodified ones (without latex). In fact, a slight decrease in the UCS values was noticed for some samples. There was a very minor increase in the FS values for samples $Ia^{1,2}$, $Ic^{1,2}$, and $Id^{1,2}$; however, other samples had the same flexural strength as that of the unmodified mortar. This behavior could be attributed to the inhibition of the rates of cement hydration due to the presence of high concentrations of Zn, Cd, Cr, and Pb in the sludge used for the present study. The presence of

**Table III Unconfined Compressive Strength (UCS) and Flexural Strength (FS) of Polymer-Modified and Unmodified Specimens**

| | UCS ($N/mm^2$) | | FS ($N/mm^2$) | |
|---|---|---|---|---|
| Sample Code | Unmodified | Modified | Unmodified | Modified |
| $^{1}Ia^{1}$ | 30.6 | 30.1 | 5.1 | 5.1 |
| $Ib^{1}$ | 33.6 | 32.8 | 6.0 | 6.0 |
| $Ic^{1}$ | 36.1 | 34.0 | 6.6 | 6.8 |
| $Id^{1}$ | 41.2 | 41.0 | 8.0 | 7.9 |
| $Ia^{2}$ | 8.9 | 8.8 | 2.9 | 3.0 |
| $Ib^{2}$ | 14.3 | 14.1 | 3.6 | 3.7 |
| $Ic^{2}$ | 34.1 | 34.0 | 5.7 | 5.8 |
| $Id^{2}$ | 38.0 | 37.9 | 7.4 | 7.7 |

Cd in the mortar reduces the UCSs of the solidified sludge,[15] and the strengths were affected to a significant extent by the presence of heavy metals in the cement mortar.[16] Poisoning of the cement and the effects of metals on cement hydration were previously observed.[17–20] The reduction in UCSs was consistent with previous results.[13] By contrast, no reduction in the UCS was observed in another study[21] with polymer modification of the cement matrices.

## Effect on Leachability

The results of TCLP tests of the latex-modified and unmodified samples (Table IV) show a 10-fold reduction in the leachability of the metals from the matrices. The retention (%) of metals in the polymer-modified cement matrix for all metals was to the extent of 99%. Zn, Cd, Fe, and Ni were 100% immobilized and were not detected in the solution. However, the immobilization of Zn and Fe could not be solely attributed to the latex modification, because all the matrices showed exceptional retention properties of these metals. Cu and Cr were not totally immobilized, even with latex modification; however, a 10-fold reduction in the concentrations of these metals leaching into the solution, compared to the unmodified matrices, was observed. A 100% immobilization of Ni was observed for samples $Ia^1$, $Ib^1$, and $Ic^2$. There was an increase in the concentration of Ni in the leachate of sample $Id^2$ and unreacted sludge particles in the matrix.

It was interesting to note that the leachability of the metals decreased with polymer modification, although there was no significant change in the strength of the samples. This was found to be the reverse in most of the unmodified samples in which the strength could be directly related to the solidification potential of the samples. The results

**Table IV Effect of Polymer Modification of Cement Matrix of TCLP Leaching Toxicity of Metals**

| | Concentration of Metals in TCLP Leachate (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Ia^1$ | | $Ib^1$ | | $Ic^2$ | | $Id^2$ | |
| Metals | Unmod. | Modified | Unmod. | Modified | Unmod. | Modified | Unmod. | Modified |
| Cu | 0.0832 | 0.0098 | 0.0676 | 0.0089 | 0.1248 | 0.0101 | 0.1014 | 0.0132 |
| Cr | 0.1352 | 0.0469 | 0.0312 | 0.006 | 0.0728 | 0.0081 | 0.0343 | 0.0024 |
| Pb | BDL | BDL | BDL | BDL | 0.0018 | BDL | BDL | BDL |
| Cd | 0.0072 | BDL | 0.0035 | BDL | 0.0117 | BDL | 0.0037 | BDL |
| Fe | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| Ni | 0.0176 | BDL | 0.0177 | BDL | 0.0104 | BDL | BDL | 0.0089 |
| Zn | 0.0031 | BDL | 0.002 | BDL | 0.0031 | BDL | 0.0062 | BDL |

BDL, below detectable limits.

of the TCLP studies were consistent with previous TCLP studies.[13] The increase in the FS and the reduction in leachability of the metals in latex-modified mortars could be explained by the effect of latex modification on the hydration of the cement. During hydration of latex-modified cement paste the latex forms threadlike membranes throughout the matrix. These membranes increase the bonding between the cement paste particles and the waste substances physically trapped in the cement matrix. The polymer fills the small pores and capillaries without creating discontinuity in the cement gel.[13] This decrease in porosity of the latex-modified mortar contributes to the impermeability and durability of concrete. Wagner[22] studied the influence of polymer modification on the rate of specific surface area development of latex-modified matrices. Reduced porosities of latex-modified mortars and concretes, compared to the unmodified ones, were previously reported.[23] The leaching solution had fewer pathways to reach the reaction site because of reduced porosities and the continuous gel system created by the latex dispersion, hence the reduced leachability. A study of the micromorphological characteristics of these matrices with a scanning electron microscope showed highly reduced porosities in latex-modified matrices, the results of which will be published elsewhere. This confirms the fact that the reduction in leachability was due to the reduced porosity of the latex-modified cement matrices. The sealing effect due to polymer films or membranes formed in the structure considerably increases waterproofness or water tightness, moisture transmission, chemical resistance, and so forth, further reducing or preventing the leachability of the metals.

## CONCLUSIONS

This study investigated the effects of polymer modification on the strength, durability, and leachability of Portland cement matrices containing heavy metals. The results of this study showed that, although fixation of the metals in the metal bearing sludge in an OPC admixture provide a very good degree of immobilization, polymer additions offer excellent immobilization of the heavy metal ions. Although the presence of the polymer materials did not significantly alter the strength characteristics of the S/S product, a 10-fold decrease in leachability as compared to unmodified matrices was observed. No correlation between the strength and leachability was observed in this study. In conclusion, polymer treatment of concrete/waste mixtures provides an excellent multiple barrier system (involving stabilization, physical and chemical adsorption, and isolation), ensuring excellent immobilization of toxic sludge and preventing any undue leaching out of the toxic metal ions into the surrounding environment. Further studies are to be conducted to arrive at precise conclusions and the significance of latex modification on the final properties of the S/S product.

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