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Ceramic Stabilization of Hazardous Wastes:
A High Performance Room Temperature Process

Presented by

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Paper	Ceramic Stabilization of Hazardous Wastes: A High Performance Room Temperature Process
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Abstract	<p>Argonne Laboratory has developed a room-temperature process that converts hazardous materials to a ceramic structure. The performance is similar to vitrification but is achieved at low costs similar to conventional cement stabilization. The waste constituents are both chemically stabilized and physically encapsulated, producing very low leaching levels and the potential for delisting. The process, which is pH-insensitive, is ideal for inorganic sludges and liquids, as well as mixed chemical-radioactive wastes, but can also handle significant percentages of salts and even halogenated organics. High waste loadings are possible and densification occurs, so that volumes are only slightly increased and in some cases (e.g., incinerator ash) are reduced. The ceramic product has strength and weathering properties far superior to cement products.</p>
Introduction	<p>Extensive research has been funded at the Argonne National Laboratory by the Office of Technology Development, U.S. Department of Energy, in an effort to develop a cost effective method of stabilizing low level radioactive materials and mixed chemical-low level wastes. Thermal processes for managing these wastes are problematic in that such processes are not only expensive, but the presence of volatile metals and pyrophoric compounds in many low-level and mixed wastes has significant unwanted effects. The metals must be controlled and recovered in an off-gas treatment system whose residue frequently requires secondary processing. Furthermore the intended product of the primary thermal system may not achieve its required uniformity and strength. In the course of its research into a non-thermal alternative method of treatment, the Laboratory has developed a stabilization process that applies to very broad classes of waste, notably hazardous and toxic chemical wastes, incinerator and coal ash, contaminated soils, and many other heterogeneous materials. The Argonne ceramics group has designed several materials that require no heat treating, that can incorporate large percentages of these varied waste types, and that yield such low levels of contaminants that the products are no longer hazardous and in many cases obviate the need for controlled land disposal. As such, this new process appears to outperform not only thermal processes but also conventional stabilization.</p>
Background	<p>Conventional room temperature stabilization has been applied to a wide variety of waste materials, and has proven to be the economic choice in many cases. The equipment is not particularly expensive and the process controls do not have to be highly sophisticated. The formulation of reagents for a given waste is designed to immobilize certain chemical components in the waste. Success of the process is</p>

measured by a prescribed extraction procedure to determine the extent of chemical leaching under conditions expected to occur from land disposal. The leachate tests are targeted at certain chemicals, and therefore the stabilization formula targets those same chemicals. These processes are limited by the types or combinations of waste materials that they can handle. Certain metals may be immobilized within a certain range of pH, while others are not. Alkaline processes are commonly employed since they stabilize a number of volatile heavy metals such as lead, cadmium, chromium, nickel, etc. However, these processes are retarded by salts such as those commonly formed in air pollution control systems, and by significant concentrations of organics.

Industrial wastes and contaminated materials requiring remediation are not the only candidates for treatment by ceramic stabilization. Incinerators and coal-fired power plants every day produce very large quantities of ash containing a broad spectrum of metals and metallic salts. In addition, while incinerators are regulated at very low carbon levels, utilities continually have to address the carbon issue. In both cases this is adding considerably to the cost of operations.

As regulations have tended to impose ever tightening restrictions, an increase in the more difficult materials requiring treatment may be expected, more materials will require treatment before they can be landfilled, allowable leachate concentrations may be reduced, and/or more waste material recovery will be required. Whether by regulation or by economics and liability issues, the drivers will continue to be there for higher performance in terms of non-leachable treatment residues, recovery of useful products from wastes, and the avoidance of land disposal where at all feasible. At the same time, market economics dictate an equally strong force for lower cost treatment processes, favoring innovative stabilization concepts over thermal treatment.

While the Argonne process was originally developed for the stabilization of low-level and mixed radioactive-chemical wastes at room temperature, the comparatively low costs involved indicate that other hazardous but non-radioactive chemical wastes could also be treated very economically. Also, the process, as an alternative to vitrification, was designed to produce a non-leachable material. The process has proven to stabilize waste streams so effectively that the resultant by-products in principle would not require land disposal. Furthermore, the physical properties of the stabilized material are such that its use as a structural product is being considered.

Process

Stabilization is obtained by converting chemical wastes and contaminated materials into chemically bonded phosphate ceramics. The waste streams are mixed sequentially with basic and acidic reagents to cause chemical reactions that yield a ceramic material in which the hazardous constituents are both physically encapsulated and chemically bonded. The ceramics produced are dense, highly leach-resistant, impermeable, and very strong.

Wastes having a broad range of chemical and physical properties have been tested, as have a large number of potential reagents. In most cases, the important reagents are magnesium oxide and phosphoric acid. Liquid wastes are first mixed with phosphoric acid solution and magnesium oxide powder is added to the mixture. In the case of solid wastes, the powder is first mixed together with the waste and then the acid solution is applied. For sludges, the two reagents are combined to form a slurry that is mixed with the waste. There are variations in the reagents and their percentages in the final mixture, and other additives may be used, depending on the waste stream, but the process steps are always essentially the same. While the bonding is invariably effective insofar as environmental performance is concerned, research is undertaken with each waste type in an effort to identify the most economic mixture.

From photo micrographic inspection on a scale of 1 to 10 microns, it is evident in every case that the particles of waste constituents are uniformly distributed, coated or encapsulated with magnesium phosphate binder, converted to insoluble phosphates as chemically possible, and bonded in a dense ceramic matrix. Depending on the waste/formula, the ceramic sets on the order of hours and cures in one to a few days. The material has low porosity (typically 10% to 30%) and densities range from 1.3 to 1.9 for the products tested to date. Static compressive strength is very high: from 1 to 2 times that of cement.

In contrast with conventional stabilization, the new ceramic process is not subject to limitations in a number of key areas. It is insensitive to pH. Metals are bonded into the matrix regardless of the solubility of their alkaline or other salts. Salts in high concentrations do not affect the binding process. Carbon at high levels (up to 6% as been tested) and hazardous organics similarly have no effect on the ceramic properties. This can be important for incinerator ash when burnout is incomplete, and also for scrubber residue when the presence of metals/salts precludes land disposal. Regarding waste loadings, hazardous wastes have been stabilized in ceramics having from 50 to 80% waste by weight. Loadings were initially attempted at 50% and have been increasing as the research continues. Recent tests on some benign wastes at 90% loading have been successful in terms of reaction, encapsulation, and bonding. Due to the densification that occurs during the process and the high waste loadings, waste volume increases in many cases are much less than those of conventional stabilization. For ash the volume of the ceramic product is reduced relative to the volume of the waste.

As indicated by the process description, the equipment required for ceramic stabilization would be similar to that for current stabilization processes. Equipping or retrofitting a waste treatment facility or a waste generator for stabilization using the Argonne ceramic process would be very inexpensive. Due to the simplicity of the system, a facility could be erected on-site for remediation work and thereby eliminate any concern about the transportation of hazardous materials.

Findings

Three of the surrogate waste streams that were prepared to verify the ceramic process are described in Table 1 (here adapted from a prior publication). The wastes comprise a range of consistencies and compositions designed to test the formation and structural integrity of the ceramic. None of the parameters had any adverse impact on the process. The hazardous metals and organics were identical in all three samples. Leachate results are presented in Table 2 (also adapted). The results show a reduction to levels at least an order of magnitude lower than the U.S. regulatory threshold, or to non-detectable levels, and in all cases lower than the Universal Treatment Standard (UTS) limits.

Another sample from a commercial incinerator is shown in Table 3, with similar results. One incinerator ash sample was doped with 0.5 wt. % mercury chloride; leachate extraction tests yielded a level of only 0.0003 ppm mercury. This is two orders of magnitude lower than the UTS limit of 0.025 ppm.

In view of the very low leachate levels and what is known about the chemistry of the ceramic bonding, it is reasonable to consider the Argonne process as a potentially viable alternative to many chemical waste problems in the future. The unit costs of reagents exceed that for conventional cement stabilization, but the quantities are considerably smaller. The result is that the costs are very similar, yet the ceramic process may apply to wastes that are more hazardous or difficult to stabilize, and can be expected to yield lower leachate levels. In cases where the waste can be exempted from regulation, the added costs of testing, interim storage, reprocessing as needed, and land disposal can be avoided. Indications are that superior environmental performance, in terms of long term duty of care or liability, will persist over time. In 90 day immersion tests, there is a short-term loss of about 10% by weight, followed by stable weight for the duration of the tests. Measurements indicate this loss is actually excess unreacted magnesium oxide and phosphoric acid on the surface of the ceramic. Strength tests after immersion indicate no significant change in material bonding.

Applications

This paper contemplates the application of the phosphate bonded ceramic stabilization process to hazardous chemical wastes, low level radioactive wastes, incinerator ash (more so in the future), and contaminated soils, dredge spoils and debris from demolition activities. The process may also be considered for mining and mill processing wastes, for example, red muds and other waste mineral matrices. Coal ash is another candidate, in that these materials contain metals and 15-20% unburned carbon that in some instances is difficult to separate.

Other properties of the ceramic product make it reasonable to consider using the process to manufacture structural materials from wastes. Research, and in some cases demonstrations, have been carried out in a number of areas. One is the fabrication of waste containment structures or vaults for waste storage and/or disposal. Another is the use of these ceramic materials to form slurry walls for

control of contaminated groundwater migration, since the materials indicate a higher resistance to weathering than conventional cement-based materials. Still others include conventional construction materials, due to the apparent strength advantage the ceramic has over cement. The same binder material has been used in low concentrations to convert benign wastes into high volume recycled products. For example, waste wood products have been converted into a high strength particle board, replacing the currently used polymer binders that emit noxious fumes. Ceramic slurries mixed with Styrofoam or other insulating wastes have been used to retrofit older structures or to fabricate insulating board. These ceramic bonded building materials are not only resistant to weathering and chemical attack, but are non-flammable and their thermal resistance exceeds that of fiberglass by 50% to 100%. All indications are that the new ceramic binders for stabilizing wastes have the added value of offering an economic way to achieve a high level of material recovery and recycling.

References

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Table 1 Hazardous Waste Stream Test Compositions (wt%)					
Sample 1: Ash-Based		Sample 2: Salt-Based		Sample 3: Sludge/Cement-Based	
Fly ash	37.5	Na ₂ (CO) ₃	58	Fly ash	10
Vermiculite	18.7	Cation exch. resin	5	Concrete	50
Coal ash	30.9	Water	10	Water	10
Carbon (activated)	4.7	NaCl	5	Plaster of Paris	10
Metals		NaNO ₃	10	Haematite(Fe ₂ O ₃)	3
Cr(NO ₃) ₂ .6H ₂ O	2.6	Na ₂ (PO ₃)	5	Alumina	3
Ni(NO ₃) ₂ .6H ₂ O	2.3	Na ₂ (SO ₄)	5	Perlite	1.5
Pb(NO ₃) ₂	0.75	Carbon (activated)	5	Carbon (activated)	10
Cd(NO ₃) ₂ .4H ₂ O	1.3	Metals		Metals	
Organics		Cr(NO ₃) ₂ .6H ₂ O	2.6	Cr(NO ₃) ₂ .6H ₂ O	2.6
Naphthalene C ₁₀ H ₈	0.47	Ni(NO ₃) ₂ .6H ₂ O	2.3	Ni(NO ₃) ₂ .6H ₂ O	2.3
Dichlorobenzene C ₆ H ₄ Cl ₂	0.47	Pb(NO ₃) ₂	0.75	Pb(NO ₃) ₂	0.75
Radionuclides (surrogate)		Cd(NO ₃) ₂ .4H ₂ O	1.3	Cd(NO ₃) ₂ .4H ₂ O	1.3
CsCl	0.3	Organics		Organics	
		Naphthalene (C ₁₀ H ₈)	0.47	Naphthalene (C ₁₀ H ₈)	0.47
		Dichlorobenzene (C ₆ H ₄ Cl ₂)	0.47	Dichlorobenzene (C ₆ H ₄ Cl ₂)	0.47
		Radionuclides (surrogate)		Radionuclides (surrogate)	
		CsCl	0.3	CsCl	0.3

Note: Adopted from Proceedings of the American Chemical Society Symposium on Emerging Technologies in Hazardous Waste Management VI.

Table 2 Leachate Extraction (TCLP) of Ceramic Stabilization Product From Samples 1, 3 in Table 1					
		Parameters-Concentrations (ppm)			
Sample	Loading (wt%)	Pb	Cd	Ni	Cr
1	Unstabilized	99.7	40.4	186	196
1	50	<0.2	0.09	0.21	<0.05
	60	<0.2	0.12	1.27	<0.05
	70	<0.2	0.06	3.71	<0.05
3	50	<0.2	0.03	0.13	<0.05
	60	<0.2	0.04	0.26	<0.05
	70	<0.2	0.06	0.74	<0.05
Regulatory limits		5.0	1.0		5.0

Note: Adopted from Proceedings of the American Chemical Society Symposium on Emerging Technologies in Hazardous Waste Management VI.

Table 3 TCLP Results on Air-Pollution Control Residue (ppm)

	Concentration in Waste	TCLP Concentration	Treatment Standard
Ba	400	<0.05	7.6
Cd	70	<0.01	0.19
Cr	200	0.02	0.86
Cu	900		
Pb	900	<0.2	0.37
Ni	100	<0.02	5.0
Zn	10,300	0.02	5.3