

SIMPLE AND EFFECTIVE CHEMICAL DECONTAMINATION OF RADIOACTIVELY CONTAMINATED LEAD

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ABSTRACT

Millions of pounds of lead has been used by the DOE and their contractors as radioactive shielding over the last fifty years. In the process, radioisotopes in different chemical forms have adhered or adsorbed into the surface corrosion matrices, making the lead metal a hazard and expensive to stabilize and bury at approved sites. Physical decontamination methods are generally applicable only to regular geometries. These physical methods also require high worker exposure and result in a relatively high volume of solid waste. Acid cleaning is difficult to control, is hazardous to workers, and will generally result in a high volume of solid and liquid waste.

A chemical decontaminating agent (tradenamed CORPEX[®]-982) apparently overcomes many of these difficulties of decontamination of lead surfaces. Comparison of CORPEX[®]-982 and nitric acid cleaning of oxidized lead surfaces reveals that the chelant formulation will only dissolve the corrosion layer, not the base lead metal, while the nitric acid consumes base lead. The temperature dependence and the concentration dependence of CORPEX[®]-982 is that expected for chelant formulations, with the only surprising result being the high speed decontamination even at room (20°C) temperature. Oxidation of the chelants to meet waste disposal criteria may be accomplished using a variety of chemical agents. Stabilization to a non-leachable final waste form can be accomplished using traditional cement-lime mixtures or with a newer alumino-silicate technology to lower total waste volume.

From project and lab data, a ratio of 230 ft² decontaminated lead to free release levels per ft³ of LLW generated is determined.

INTRODUCTION

Millions of pounds of lead has been used by the Department of Energy and their contractors as radioactive shielding over the last fifty years. In the process, radioisotopes in different chemical forms have adhered or adsorbed into the surface corrosion matrices, making the lead metal a hazard and expensive to stabilize and bury at approved sites. The documented lead waste inventory in the DOE complex is greater than 1,500,000 kilograms [DOE/RW-006]; other estimates for contaminated lead in storage at DOE sites range from 4,000,000 kg to 24,000,000 kg, with a like amount in current use [DOE/2006]. A similar problem exists in the commercial nuclear power industry.

Numerous methods have been considered in the surface decontamination of lead. Physical methods, such as shot or CO₂ blasting, shaving, scraping etc., are applicable only

to regular geometries. Even brick and sheet lead are not necessarily amenable to physical methods. For example, many lead bricks used in the construction of hot cells for shielding have non-regular shapes and holes used to line up the brick wall. These geometric features inhibit the line-of-sight required for blasting methods to be effective. Lead sheet has been used to wrap around piping and ducting; cracks are usually formed which can be contaminated; depending on the depth of these fissures, blasting techniques may not be able to reach the contamination. Blasting also generates high levels of airborne contamination by their very nature, so either special protective devices (forced air suits, etc.) or expensive and clumsy vacuum systems are required. Additionally, physical methods like blasting raise the possibility of peening the lead surface which could entrap radionuclides in the bulk metal, or, of greater environmental concern, shield the radionuclide from detection resulting in false survey and release. Shaving is potentially cost-effective only when one or two sides of a regular geometry lead piece is contaminated. This eliminates the bulk of the stored contaminated lead, as dusting from one surface to the other has occurred. These physical methods also generally require high worker radiation exposure and result in a relatively high volume of solid waste as, by necessity, more lead metal is removed than just that in the matrix binding the radionuclides.

Another possible approach has been to use mineral acids, usually nitric acid as chemical cleaning agents. Mineral acid cleaning of contaminated lead has several drawbacks. Mineral acids are very hazardous materials being corrosive to human tissue and require substantial personal protective equipment during use. The cleaning process itself is difficult to control, in that the nitric acid will continue to dissolve base lead as long as the acid is in contact with the metal. For example, the contamination level will vary on different lead surfaces, therefore in a batch mode of application, the mineral acid solution will continue to dissolve base lead metal on the lesser contaminated surfaces while the more contaminated surface continues to be decontaminated. This inability to distinguish between dissolution of contaminated matrices on the surface and dissolution of base metal by mineral acids leads to higher waste disposal volumes.

CORPEX Technologies Incorporated recently invented a chemical decontaminating agent, tradenamed CORPEX[®]-982, which apparently overcomes many of the difficulties of decontamination of lead surfaces. CORPEX[®]-982 is a complex blend of organic acid chelating agents, redox modifiers, and surfactants. These chelating agents are organic compounds which have multiple sites on each molecule to bind to metal ions. This feature ensures a high entropic driving force toward complex formation; the result is highly stable metal ion complexes in solution. This formulation has been shown to dissolve the corrosion matrix and the radioisotopes on the surface of the lead without attacking the metal itself, thereby minimizing the solid waste generated and making the process very easy to control.

RESULTS

Performance versus Nitric Acid: The surface radioactive contamination is bound in the corrosion matrix of the lead shielding. This corrosion matrix is made of up one or more forms of lead oxide and any lead salts resulting from the use environment of the shielding. Ideally, the decontamination process would dissolve this corrosion matrix and not attack the base lead metal. The results of a laboratory experiment comparing 10% nitric acid with CORPEX[®]-982 in the dissolution of lead oxide from a lead sheet. Both chemicals were at 20°C and there was no agitation during the test. Aliquots of the chemicals were removed and later measured for dissolved lead on an Inductively Coupled Plasma Spectrometer (ICP).

The chelant formulation rapidly dissolves the lead oxide as indicated by the lead measured in solution, then no additional lead is measurable in the solution as the base lead metal is exposed. At the end of the 5 minutes, the lead sheet was rinsed with DI water, and appeared bright, metallic-looking. This sheet remained bright (no rapid reoxidation) for over 24 hours. The 10% nitric acid solution rapidly dissolved the lead oxide, but continued bring lead into solution by dissolution of the base metal. After 5 minutes and a DI water rinse, the lead rapidly re-oxidized in ambient air.

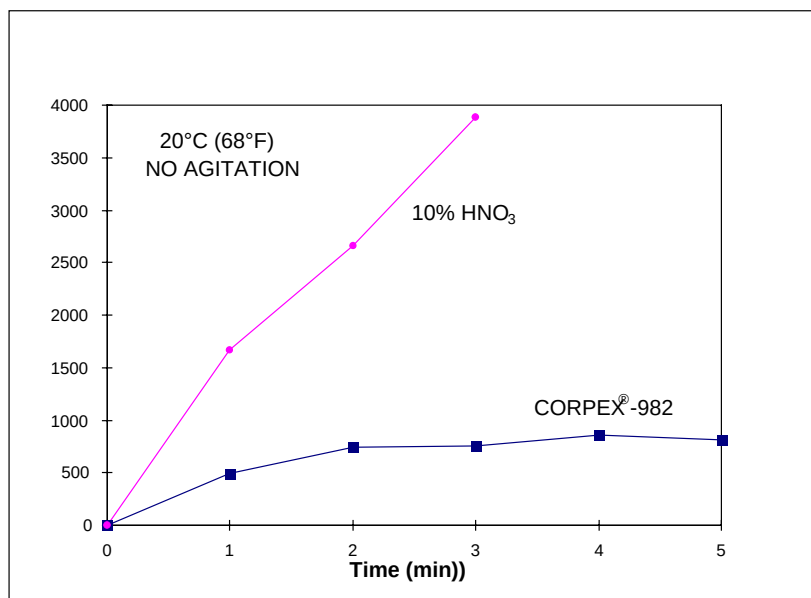


Figure 1.

Temperature Dependence of Lead Oxide Dissolution: Although CORPEX[®]-982 dissolves lead oxides and salts very quickly at room temperature, a cursory evaluation of the temperature dependence was done in the laboratory. Reagent lead monoxide was added to directly to 66% (v/v) CORPEX[®]-982 preheated to the appropriate temperature. The solutions were stirred throughout the experiment. At intervals, small samples were removed, filtered, and measured on the ICP for lead in solution. The first samples at 50°C and 70°C were already saturated at 5 minutes.

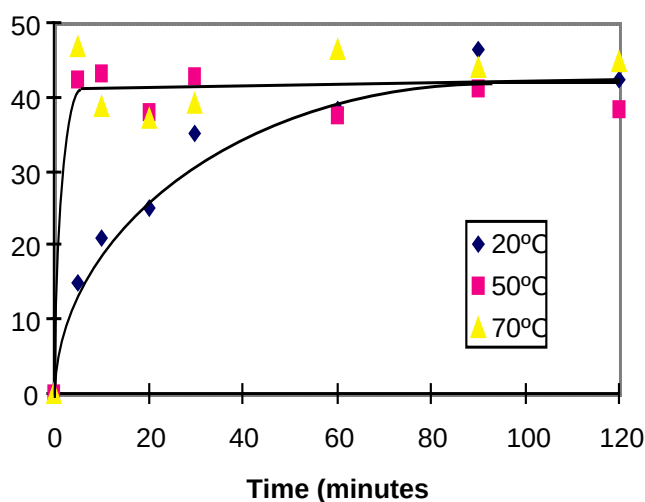


Figure 2.

Concentration Dependence of Lead Oxide Dissolution: For active concentrations above about 1%, chelant formulations in general do not display strong concentration effects on the dissolution kinetics. This observation holds true for CORPEX[®]-982, with the speed of dissolution of lead oxides identical within the noise of measurement for concentrations from 100% to 10% by volume. Unlike acid systems, the amount of lead which can be put into solution by CORPEX[®]-982 can be adjusted by dilution. In Table 1, the capacity of the solution for lead is shown versus the concentration of CORPEX[®]-982. The theoretical capacity is based on molar quantities of chelants in the formulation. The solutions were stirred for 3 hours with excess PbO at 20°C, filtered, and the filtrate analyzed for lead with the ICP.

Solvent	%Pb in Solution	%Pb (Theory)
100% CORPEX [®] -982	6.3%	6.6%
50% CORPEX [®] -982	3.3%	3.3%
25% CORPEX [®] -982	1.7%	1.6%
10% CORPEX [®] -982	0.7%	0.7%

Process Engineering

Lead item decontamination is done in a series of vats and sequenced to optimize the CORPEX[®]-982 chemical decontamination. Vat sizes are determined by component sizes and/or throughput required.

Application system

The application system consists of the following components:

<u>Component</u>	<u>Comment</u>
Chemistry Tank	Size based on equipment or component to be decontaminated and the required throughput. Additionally method of agitation may impact size
Rinse Tank(s)	Sized based on equipment or component to be decontaminated and throughput required.
Destruction Tank	Size based on volume of the chemistry tank and destruction method used. At a minimum, this tank is at least three times the size of the chemistry tank to hold both rinse water and CORPEX [®] - 982 solution. The tank could be larger based on destruction method.
Agitators, Aerators	Agitate chemical solution to ensure that all component surfaces are wetted.
Filter	Prevents reintroduction of suspended solids into the system.

Materials of construction for the application system are typically welded stainless steel and chemistry resistant materials such as Teflon[®]. Portions of the system that are exposed to oxidizers used to destroy the chelant need to be fabricated of stainless steel and Teflon[®].

Components may be introduced into the decontamination solution via baskets or continuous conveyor system depending on throughput and material handling preferences. The CORPEX[®] -982 solution is held near 20°C, to minimize airborne and safety issues and reduce the cost and downtime associated with heating chemical solutions. After decontamination, the lead is removed from the CORPEX[®] -982 tank, chemicals allowed to drip back into the tank, then the lead is placed in the rinse tank. After rinsing, the lead is removed for survey and release.

It is possible for the CORPEX[®] -982 solution to be tested for loading at a specific interval to determine the extent of chemical depletion. Upon depletion, the CORPEX[®] - 982 is removed to the destruction tank for oxidation and stabilization processing.

Results of a Project

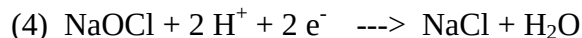
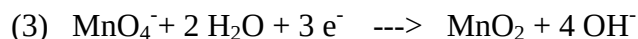
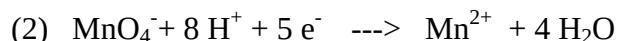
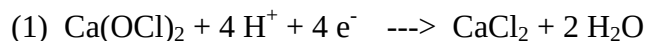
The chemical decontamination of lead bricks and shot was performed for Rockwell Aerospace/ETEC using CORPEX[®] -982 [Moore]. Lead brick (220,000 lbs.) and 3/32" lead shot (17,000 lbs.) were decontaminated using 1100 gallons of CORPEX[®] -982 in a dip tank application. As 24,500 pounds of the bricks had been housed for some time in corroded stainless steel cladding, an estimated 100 mil thick iron oxide layer was present on them, which had to be removed to achieve the free release goal. The maximum immersion time for these bricks with the thick rust layer was 2 hours; usual immersion

times were 30 - 45 minutes. At the end of the process, over 99% by weight of the lead was surveyed as free releasable.

OXIDATION OF CHELANT SOLUTIONS

A second critical factor in using chelant containing solution in decontamination solutions is understanding how to eventually dispose of these solutions. The stabilization of metal ions in solution provided by chelating agents puts restrictions on their radiological storage. The State of Washington, for example, requires that waste with between 0.1 and 8 weight percent chelant be segregated from other wastes and have special containment facilities. [State of Washington, Radioactive Materials License, WN-I019-2]. These special waste disposal considerations are very expensive. This chelant solution can be treated with oxidizing agents to destroy the chelant to less than 0.1 weight percent of the final waste form.

The chemical oxidation reactions using calcium hypochlorite, acidic permanganate, alkaline permanganate and sodium hypochlorite are straightforward:



Stoichiometric reaction of these oxidizing agents with chelant formulations can achieve very low levels of total organic carbon (TOC) in solution, and low (<0.1 wt %) chelant concentrations.

Calcium Hypochlorite

A series of oxidations of CORPEX[®]-982 saturated with lead oxide was performed using technical grade calcium hypochlorite. The destruction of the chelant functionality in the formulation was measured by the decrease in lead remaining in solution. At these near neutral pH values, any lead remaining chelated would stay in the aqueous phase. Therefore measuring the lead remaining is a direct measure of the remaining chelant level in the solution. The chelant concentration in neat CORPEX[®]-982 is 12 weight %. After addition of an aliquot of (technical grade, 60% active chlorine) calcium hypochlorite (technical grade, 60% active chlorine), the aqueous layer was measured for lead concentration using the ICP; the concentration of lead remaining in solution is directly proportional to the chelant concentration remaining. The data are displayed in Figure 3. below. At levels above 900 grams per liter, the chelant concentration is below the 0.1 weight percent level.

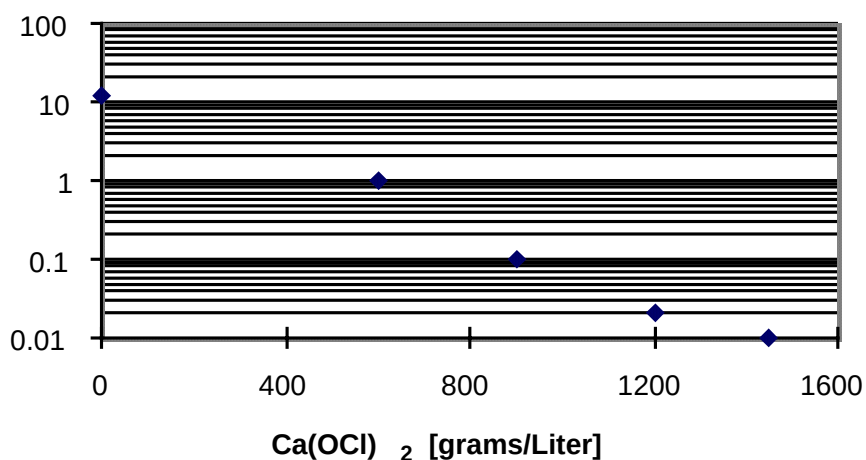
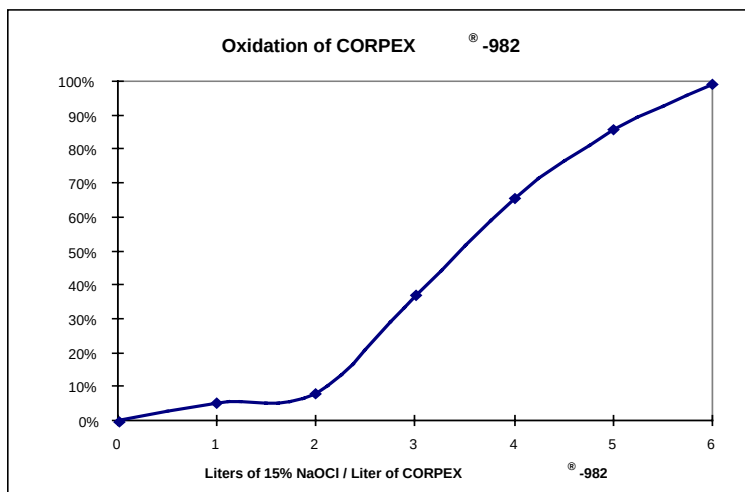


Figure 3.

As a safety factor, we currently recommend 1200 grams/Liter (10 pounds/gallon).

Sodium Hypochlorite

A similar series of oxidations of lead saturated CORPEX[®]-982 was performed using 15% sodium hypochlorite solution. After addition of the oxidizing agent, each solution was allowed to react for 24 hours. The lead remaining in solution was then measured by ICP. The percentage of lead precipitating as a function of volume ratio (NaOCl/ CORPEX[®]-982) is shown in Figure 4. below. This demonstrates that at 6 volumes of 15% NaOCl to one volume of CORPEX[®]-982, the chelant concentration is <0.1 weight %, even when



volume corrected back to the original CORPEX[®]-982 volume (no dilution effects).

Potassium Permanganate

Likewise, 172 g of potassium permanganate was added to 200 mL of lead-saturated CORPEX[®]-982 slowly. After allowing 24 hours for full reaction, the concentration of lead remaining in the aqueous phase proved that the chelant concentration was less than 0.1 weight percent.

STABILIZATION METHODS

The third important part of the chemical decontamination process is the stabilization of the waste product after oxidation. Before stabilization, the sludge has the properties of a mixed waste; in addition to the radiological waste, there is leachable lead above the regulatory limit (5 ppm) due to the necessary dissolution of the lead oxide by the decontamination chemical. Stabilization techniques need to be incorporated and optimized into the chemical decontamination process.

Cement and Lime

Portland cement has historically been a common stabilization medium for hazardous metals. The cementing process physically (as opposed to chemically) binds the metals. For lead solidification, calcium hydroxide (lime) is usually added to the matrix. The calcium hydroxide adjusts the pH to approximately 9 - 10, which is the pH range of minimum solubility of lead salts. Baseline testing of waste out of the oxidation processes defined above solidified with Portland cement/lime blends. Testing procedures will include leaching testing (TCLP), compression strength, and weatherability testing.

A partially depleted sample of CORPEX[®]-982 was oxidized with calcium hypochlorite. The resultant slurry was solidified in five different compositions.

	Slurry (g)	Portland Cement (g)	Lime (g)
1	50	37.8	7.27
2	50	37.8	4.36
3	50	37.8	10.2
4	50	22.7	7.27
5	50	52.9	7.27

Each sample was made up in a small plastic cup by adding the CORPEX[®]-982 sludge to the well-mixed cement plus lime mixture and mixing thoroughly with a glass rod. The cement was allowed to harden for 19 days before testing. The weight was taken as the sum of the weights of the lime, cement and CORPEX[®]-982 sludge. The volumes were approximated by filling a small plastic cup to the same level and then pouring into a graduated cylinder. Strength testing was to 125 lbs on a surface area of 0.77 in² (162 lb/in²). All exceeded this value except for #4 which was still moist and crumbled when removed from the cup. TCLP testing was done by weighing 5.00 g of the crushed monolith (all pieces smaller than 1 cm largest dimension) into a 125 mL Nalgene bottle. A solution of acetic acid was made up by adding 5.7 mL of glacial acetic acid to a 1 L

volumetric flask and making up to volume with deionized water. The pH of the solution was 2.50. To each Nalgene bottle, 100.0 g of this solution was added and the solutions capped tightly and mixed for 18 hours. The lead content of each solution was measured by ICP. Passing is less than 5 ppm. The water test was done by taking a larger chunk of the monolith and soaking in deionized water for 5 days. All were stable except #4 which crumbles, even without the soak.

	Weight (g)	Volume (mL)	Strength	TCLP	Water
	95	52	>160 lb/in ²	Pass	Stable
	92	52	>160 lb/in ²	Pass	Stable
	98	52	>160 lb/in ²	Pass	Stable
	80	48	0	Pass	Crumbles
	110	56	>160 lb/in ²	Pass	Stable

Alumino-Silicate Binders

Alumino-silicate binders are comprised of soluble alkali polysilicates which can be activated to form tetrahedra of SiO₄ and AlO₄. These are cross-linked by shared oxygen molecules to form inorganic polymeric networks. A mildly exothermic reaction in the alkali activated mixture is accompanied by hardening and polycondensation. During this condensation reaction, the crystal structure of the final monolith forms. By variation of the conditions of the condensation reaction, the crystal structure can be varied to accommodate various metal ions. For example, high atomic volume ions, such as barium need larger lattice spaces to incorporate into the matrix. Smaller ions (e.g., lead) need a more closely packed pore structure. In this technology, the metals are chemically bound by replacing the shared oxygen atoms in the alumino-silicate lattice. This chemical bonding strongly inhibits the solubility and mobility of metal ions in aqueous media.

A series of laboratory scale tests were done by Dr. Steve Prewett of Krystal Bond Ohio, manufacturer of alumino-silicate binding chemicals. The oxidation was performed as usual, using calcium hypochlorite. The calcium oxide (used to raise the pH of the final waste form) was replaced by magnesium oxide (at three levels). Then the sludges were treated with the alumino-silicate binder KC102. All three stabilized materials passed TCLP testing for lead.

The total volume of the stabilized form of the alumino-silicate structure is about 1.4 X the total volume of the CORPEX[®]-982 chemical used. This compares with 2.1 X for the lime/cement system.

WASTE VOLUME PER AREA CLEANED

A common unit used in comparing decontamination systems is square feet of surface decontaminated per volume unit of waste generated. From historical data, 5 grams of lead is in the oxide layer of typical shielding. From the capacity of CORPEX[®]-982 for lead, and the volume changes due to oxidation and stabilization with the alumino-silicate binder, we can calculate a ratio of **230 ft² decontaminated lead to free release levels per ft³ of LLW generated.**

CONCLUSIONS

A patented chemical formulation, tradenamed CORPEX[®]-982, has been shown to be an effective decontamination agent for surface contaminated lead brick, shot and sheet. Laboratory and field studies indicate a rapid decontamination effect even a moderate temperature (20°C). The chemical formulation may be treated by chemical oxidation and stabilization techniques to make the final waste form acceptable to Low Level disposal sites.

LITERATURE CITED

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Moore, R. Decontamination of Radioactive Lead for Recycling, Rockwell Aerospace/ETEC, **1994.**