

A PRELIMINARY STUDY OF HEAVY METAL LEACHABILITY FROM POLYETHYLENE ENCAPSULATED NITRATE SALT WASTE AT ROCKY FLATS

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ABSTRACT

Low level mixed wastes destined for disposal at the Nevada Test Site (NTS) must meet RCRA leachability requirements for hazardous constituents. The Rocky Flats Plant has several mixed waste forms that exceed these requirements and must be treated prior to shipment and disposal. Low density polyethylene encapsulation is one of several technologies under investigation for treatment of these wastes.

Leachability studies using the Toxicity Characteristic Leaching Procedure (TCLP) were conducted to determine whether the encapsulation process will meet RCRA leachability requirements for anticipated heavy metal concentrations in a low level mixed nitrate salt waste stream. Investigations into the feasibility of improving immobilization characteristics by incorporating metal-stabilizing additives were also conducted.

Results indicate that polyethylene encapsulation shows promise as a stabilization technique for the nitrate salt waste stream. Even with much of the salt liberated through an inappropriate TCLP size reduction technique, polyethylene encapsulated surrogate waste met TCLP requirements for five toxic metals. Metal immobilization by addition of chemical stabilizers (CaO) was also demonstrated on unencapsulated surrogate waste.

INTRODUCTION

Rocky Flats Plant (RFP) is considering polyethylene encapsulation as a stabilization technique for the treatment of several mixed waste streams. The primary focus of development activities has been on a polyethylene extrusion process for the nitrate salts, which is RFP's largest low level mixed waste stream. This waste stream is primarily composed of the nitrate salts of various metals, including trace concentrations of some metals that are land disposal restricted (LDR) under the Resource Conservation and Recovery Act (RCRA). Because the final disposal site for this waste is the Nevada Test Site (NTS), the waste form must meet NTS waste acceptance criteria and Department of Transportation regulations, including dispersible fines, solid oxidizer, and the TCLP.

Development activities completed to date indicate that polyethylene encapsulation produces a final waste form superior (in terms of waste loading, durability, and stability) to cementation processes. In order to determine the capabilities of this technique and to provide a basis for selecting the most appropriate technology for each waste stream under consideration, the ability of polyethylene encapsulation to pass the TCLP must be determined.

The nitrate salt waste stream is produced as a by-product of the treatment of aqueous waste at RFP. Aqueous waste streams from production operations at the plant are mixed and treated by hydroxide precipitation to remove radioactive metals. The effluent from the precipitation process is mixed with low specific activity aqueous waste streams from throughout the plant, such as laundry wastes and incidental waters from runoff and interceptor trenches. This solution is concentrated in an evaporation process, and then a portion of the concentrate is dried in a spray dryer. Currently, spray dried salt, brine and cement are combined to produce the "saltcrete" waste form.

The process generating this waste creates several difficulties in designing a stabilization process. First, aqueous wastes from several plant processes are combined. This forces the final waste form to meet the most stringent standards applicable to any of the initial wastes sent to the aqueous waste treatment system. Second, the composition of the nitrate salt

waste stream is highly variable. Thus, the stabilization process must be very robust with respect to chemical variations of the waste stream.

The polyethylene encapsulation process under investigation involves the mixing of dried waste with molten polyethylene in a commercially available extruder. The mix is deposited into a waste container where it solidifies into a solid monolith upon cooling of the melt. The polyethylene physically surrounds the salt, forming a water impermeable barrier. Maintenance of this physical barrier is essential to prevent dissolution of the salt and migration of the hazardous constituents. In the event of a breach of this physical barrier, additional waste stability can be achieved through chemical immobilization of the hazardous metals. This two-pronged attack uses both physical and chemical means to prevent migration of the heavy metals from the final waste form.

Chemical stabilization can be accomplished in several ways. One method is to chemically react the hazardous metals to produce an insoluble compound. This mechanism is commonly used for the removal of heavy metals from industrial waste waters. Production of this insoluble compound can be accomplished by the addition of a buffer or a base (such as calcium oxide-CaO) to raise the pH of the solution contacting the salt. An insoluble metal hydroxide precipitate is formed. Sufficient buffer must be added to neutralize the acidity of the contacting solution and prevent redissolution of the precipitate. This provides chemical stabilization as a backup to the physical stabilization of the polyethylene.

The TCLP requires size reduction of the waste form to less than 0.95 cm. The normal method of size reduction (developed for cemented waste forms) is crushing. The Building 881 laboratories at RFP accomplish this task by using a hydraulic press. In the case of polyethylene waste forms, several thousand psi of pressure are required to adequately crush the waste form. Since pressures of this magnitude are highly unlikely in the disposal environment, crushing is an unrealistic size reduction method. When exposed to high pressures, the polyethylene tends to fail along the polyethylene-salt interface. This breaks the physical barrier enclosing the salt and exposes it to the leaching solution. Therefore, crushing the

polyethylene effectively reverses the encapsulation process and prevents realistic testing of the actual waste form. Alternative methods of size reduction, such as cutting or pelletizing, must be established to allow a realistic determination of the stability of polyethylene encapsulated waste. Such alternative methods are currently being investigated at RFP. Meanwhile, because exposure of the waste to the leaching solution also exposes the chemical stabilizers, the hazardous constituents can be immobilized through chemical means.

After size reduction, the TCLP requires about one hundred grams of the waste to be placed in twenty times that weight of a 0.1 molar acetic acid solution and agitated for eighteen hours. The leachate is then filtered and the filtrate analyzed for listed hazardous constituents. Chemical stabilization with a buffer must both neutralize the acetic acid and raise the pH to approximately 11 to precipitate the metals. The amount of buffer required to achieve this can be calculated from the reaction stoichiometry; however, occlusion of the buffer within the polyethylene may prevent neutralization of the acid. Therefore, for the encapsulated waste, the concentration of CaO required for chemical immobilization of the waste must be determined experimentally.

OBJECTIVES

The objectives of this study were:

1. To determine if the polyethylene extrusion process will meet RCRA leachability requirements for the anticipated concentrations of heavy metals in the nitrate salt waste stream without chemical stabilization,
2. To investigate the feasibility of chemical immobilization of the waste's hazardous constituents in the event that the physical barrier of polyethylene is broken,
3. To identify the maximum concentrations of target heavy metals that can be successfully immobilized by polyethylene extrusion in order to aid in technology ranking for several Rocky Flats radioactive mixed waste streams,
4. To establish a technology baseline to assist in the identification and planning of future development efforts.

EXPERIMENTAL

The experimental plan was conducted in three phases. The first phase was to conduct a preliminary screening of polyethylene encapsulated surrogate salt waste spiked with six of the land disposal restricted (LDR) metals to establish a baseline and to determine which metals should be included in a more detailed study. The second phase was to demonstrate the potential for chemical stabilization of the nitrate salt waste without polyethylene encapsulation. The third phase was to investigate the stability of polyethylene encapsulated and crushed salt mixtures from phase two. The second and third phases focused on two selected LDR metals and used a simplified surrogate salt mixture to streamline experimental efforts.

Phase 1. In this phase six LDR metals (Ba, Cd, Cr, Pb, Se, and Ag) were spiked into a surrogate salt mixture. The surrogate salt mixture was based on 1989 characterization data (Table I). This mixture was then encapsulated in polyethylene and submitted for TCLP analysis along with a sample of the unencapsulated mixture. The metals and the corresponding TCLP concentration criteria are listed in Table II. All eight LDR metals were originally considered for investigation; however, it was decided to eliminate mercury (Hg) and arse-

nic (As) from the study because of health and safety considerations and because As and Hg are not anticipated in the nitrate salt waste. The salts were spiked with each of the metals to levels of 50 ppm, 500 ppm, and 5000 ppm by weight. The 50 ppm spike was to simulate the metal concentrations expected in the salt. Metal loadings of 500 and 5000 ppm were included to simulate excursions of metal concentration in the salt and to identify the limits of the technique to assist in technology down-selection for other wastes. Because of the preliminary nature of this study, only one sample of each mixture was submitted for TCLP analysis with full CLP protocol. This is sufficient for future direction of the project, but confirmation of the results will be required before final conclusions can be drawn.

The first step in the investigation was preparation of approximately five kilograms of the surrogate salt mixture. This was done by dissolving all the salts together (including the metal salts) in a single solution and evaporating the solution to dryness. Some separation of the salts occurs during this process due to differences in the crystallization rates of the salts. The separation was remedied by thorough mixing during the crushing process. Finally, the salt was crushed in a ten inch ball mill. The salt was then encapsulated in polyethylene and submitted for TCLP analysis.

Phase 2. Based on results from Phase 1 of the investigation, it was decided to narrow the focus of the study to Cd and Cr. At this time it was also decided to use pure sodium nitrate

TABLE I
Surrogate Nitrate Salt Waste Based on
1989 Characterization Data

Compound	Symbol	%Comp
Sodium Nitrate	NaNO ₃	53.9%
Potassium Nitrate	KNO ₃	33.9%
Sodium Chloride	NaCl	3.2%
Potassium Chloride	KCl	2.2%
Sodium Sulfate	Na ₂ SO ₄	2.8%
Potassium Sulfate	K ₂ SO ₄	1.8%
Sodium Phosphate	Na ₃ PO ₄	0.9%
Potassium Phosphate	K ₃ PO ₄	0.6%
Sodium Fluoride	NaF	0.4%
Potassium Fluoride	KF	0.3%
	Sum	100.0%

TABLE II
Constituent Concentration in Waste Extract
(CCWE, 40 CFR 268) for the Six LDR Metals Tested

Metal	Symbol	CCWE
Barium	Ba	100.0 ppm
Cadmium	Cd	0.066 ppm
Chromium	Cr	5.0 ppm
Lead	Pb	0.50 ppm
Selenium	Se	5.7 ppm
Silver	Ag	0.072 ppm

as the surrogate for RFP salts instead of the mixture of salts. There are several reasons for this switch. First, the composition of the nitrate waste stream is constantly changing; therefore, the salt composition determined by the 1989 characterization is not a realistic estimate of the current waste stream. Second, the mixture of salts used to imitate the RFP nitrate salt stream unnecessarily increased the complexity of the study. This mixture of salts made even simple equilibrium calculations difficult. Third, several of the anions in the salt mixture can cause some of the metals to precipitate. This can result in an overestimation of the effectiveness of the stabilization technique. Finally, using pure nitrate salts should be a worst case situation. Therefore, if the waste can be stabilized using sodium nitrate as the surrogate salt, the addition of other compounds in the actual waste should only act to increase the waste stability.

The salt was prepared as in phase one with the following exceptions: 1) Only sodium nitrate was used as the matrix, 2) only Cd and Cr metals were used to spike the sodium nitrate, and 3) instead of crushing to a powder in a ball mill, the salt was crushed and sieved by hand to attain the 20-40 mesh fraction.

Chemical stabilization was attempted by mixing the surrogate waste with various loadings of CaO. CaO loadings used were: 0, 2.5%, 5%, 10%, 20%. After mixing with CaO, the surrogate salt samples were submitted for TCLP. For improved confidence in the results, three samples of each composition of the chemically stabilized salts were submitted for TCLP.

Phase 3. In the final sequence of tests, the mixtures from Phase 2 were encapsulated in polyethylene at a salt loading (including the CaO) of 50%. These were then submitted for TCLP with size reduction by crushing. As in phase 2, three samples of each composition were submitted for TCLP analysis.

RESULTS AND DISCUSSION

Phase 1. The results of the Phase 1 investigation are shown in Figs. 1-6. These figures show the concentration of the metal in the TCLP leachate spiked at different levels. The results indicate that polyethylene encapsulation increased the stability of all the metals. This improvement of stability varied from slight for barium and lead to significant for cadmium and silver. After encapsulation, barium, chromium, and silver were and would pass the TCLP at all metal loadings. Lead would pass at lower concentrations, but not at the 5000 ppm level. Selenium was stabilized at the 50 ppm level; however, its stability at higher loadings is questionable. Even though Se passes the TCLP at 5000 ppm, little confidence can be placed in its immobilization because it failed at the lower 500 ppm loading. The reason for this unexpected behavior is not known. Cadmium was not successfully immobilized at any concentration; however, the polyethylene encapsulation decreased the amount of Cd leached by a factor of 25. It should be noted that polyethylene encapsulation achieved this stabilization despite the fact that size reduction through crushing exposed much of the salt to the solvent.

These preliminary results can be explained to some extent by the equilibrium of species in solution. The complex mixture of the salts used to make up the surrogate waste is capable of precipitating several metal species from solution. For example, chloride ions cause silver to precipitate. This effect accounts for the large variation in stability of the metals.

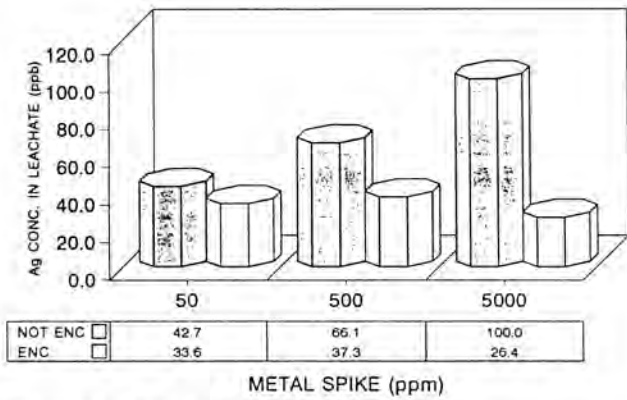
Additional complications occur in the polyethylene encapsulated salt. In this case the precipitation of some ions from solution can block the pores containing the salt. This prevents access of the solution to the remaining species that would otherwise dissolve. Until accurate characterization data is available on the current salt waste, only NaNO_3 will be used as this represents the worst case for leachability. Simplifying the surrogate salt to sodium nitrate eliminates this confusion by removing the troublesome anions from consideration.

It was decided at this time to simplify the system by reducing the number of metals to be tested to two: cadmium and chromium. Cadmium was chosen because the results show it to be the most difficult metal to immobilize. The solubilities of all the expected cadmium salts are high, and cadmium's levels of acceptance are the lowest of the LDR metals. Chromium was included for two reasons: 1) Cr is expected to be present at high levels in other wastes that may be stabilized by PE encapsulation, and 2) Cr produces strongly colored compounds and can act as a visible tracer for the metals. This provides a visual indication of the presence of the metals.

Phase 2. The results of the TCLP and analysis are shown in Fig. 7. The concentrations of Cd and Cr in the leachate for the 20% CaO sample were below the instrument detection limit (IDL), which is 20 ppb for Cd and 10 ppb for Cr. For those results below the IDL, a value of half the IDL was used. The actual concentration, however, may have been much lower. This investigation demonstrates the effect of increasing CaO loading on Cd and Cr leaching from the unencapsulated surrogate waste. The Cd and Cr concentrations in the leachate initially increase then decrease with increasing CaO loading. This initial increase may indicate unexpected reactions are occurring between species in solution. As the CaO loading increased further, the amount of Cd in solution declined to less than the IDL and Cr declined to 0.08 ppm at 20% CaO. This demonstrates that chemical immobilization of the metals was successful.

Phase 3. Due to a disruption of analytical support, the results of the TCLP on the polyethylene encapsulated, 20% CaO spiked sample are unavailable. Again, the effect of CaO addition to the nitrate salt is demonstrated (See Figure 8). In the polyethylene encapsulated salt waste form, the initial increase in leachability was absent for Cd and very slight for Cr. This indicates that the interactions causing this increase were dampened either by the lower waste concentrations or by decreased availability of the metals. As the CaO loadings increased further, the solubilities decreased. The results of TCLP tests on CaO loadings above 10% are not available and, therefore, the CaO levels required for chemical stabilization of the polyethylene encapsulated waste form were not determined.

An analysis of the effects of polyethylene encapsulation can also be made (Figs. 9 and 10). In the case of Cd, encapsulation followed by crushing has little effect. While encapsulation reduced the Cd in the TCLP leachate by approximately 50%, the waste loading of the salt in the final waste form was 50%, thus reducing the waste available for leaching by 50%. Therefore, size reduction by crushing effectively destroys the containment of Cd by polyethylene and defeats the purpose of the waste form. On the other hand, the fraction of Cr dissolved from the PE encapsulated salt is much less than that dissolved from the unencapsulated form. This indicates that immobilization of Cr by the polyethylene is much better than



1989 MIX-NITRATE SALTS, 50% SALT-50% PE
 PASSES TCLP AT 72 ppb

Fig. 1. TCLP results - Ag.

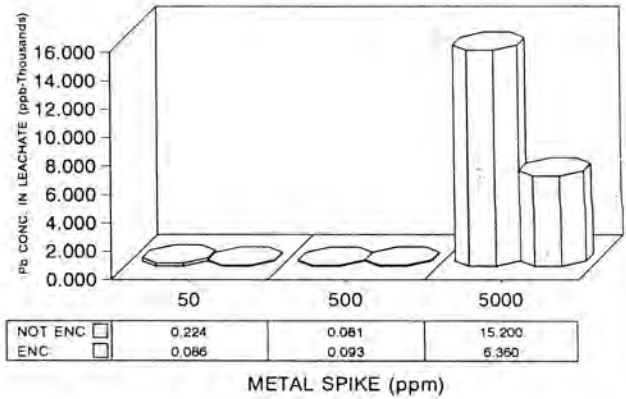
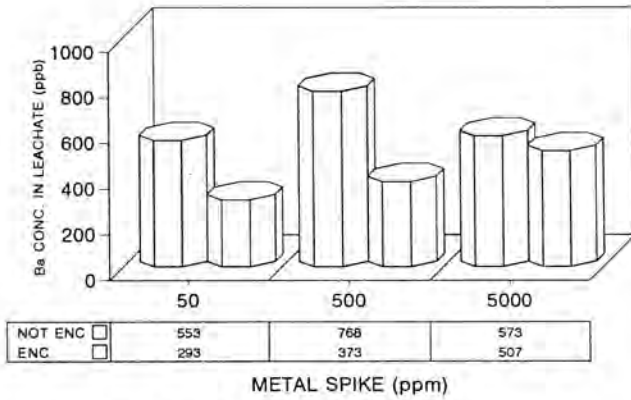
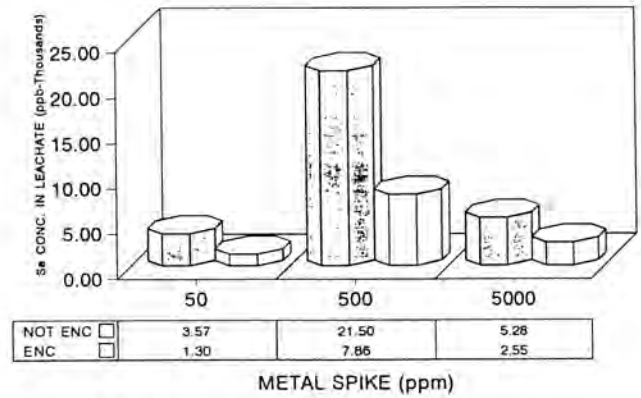


Fig. 4. TCLP results - Pb.



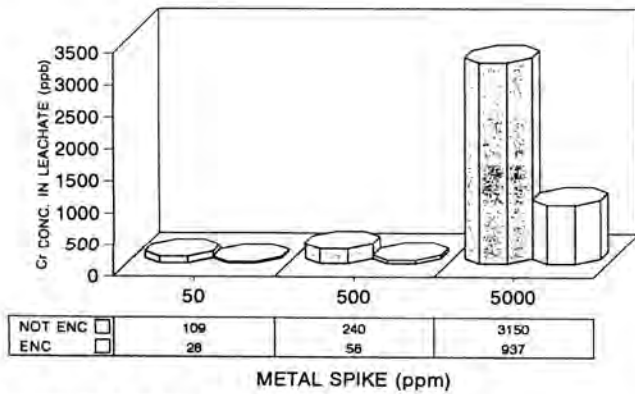
1989 MIX-NITRATE SALTS, 50% SALT-50% PE
 PASSES TCLP AT 100,000 ppb

Fig. 2. TCLP results - Ba.



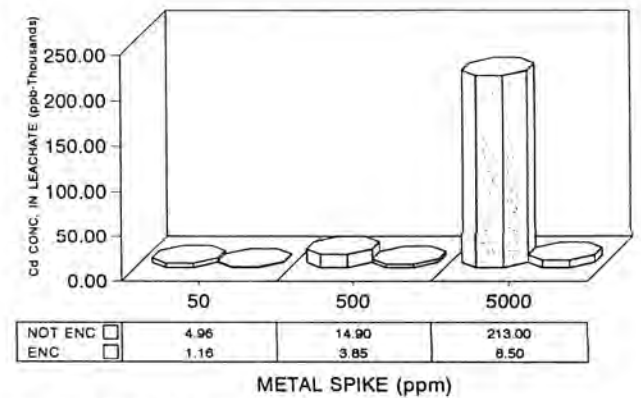
1989 MIX-NITRATE SALTS, 50% SALT-50% PE
 PASSES TCLP AT 5700 ppb

Fig. 5. TCLP results - Se.



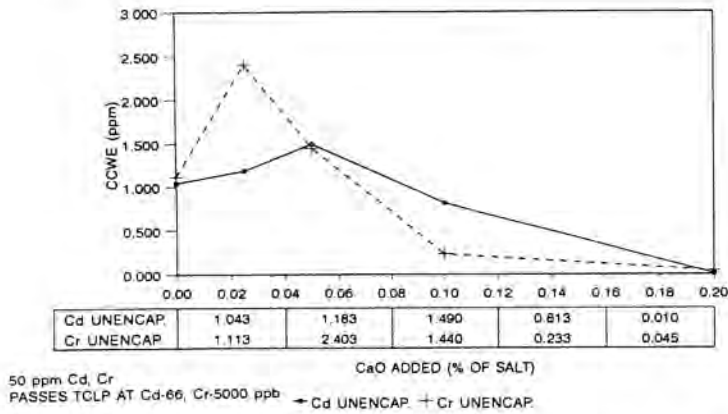
1989 MIX-NITRATE SALTS, 50% SALT-50% PE
 PASSES TCLP AT 5000 ppb

Fig. 3. TCLP results - Cr.



1989 MIX-NITRATE SALTS, 50% SALT-50% PE
 PASSES TCLP AT 66 ppb

Fig. 6. TCLP results - Cd.



50 ppm Cd, Cr
 PASSES TCLP AT Cd-66, Cr-5000 ppb
 → Cd UNENCAP + Cr UNENCAP

Fig. 7. Effect of CAO addition on TCLP - unencapsulated.

that of Cd. As the CaO loading increased, the effects of the CaO began to dominate over the effect of polyethylene encapsulation, until at 10% CaO the fraction of the metals leached was nearly equal for both encapsulated and unencapsulated salts.

CONCLUSIONS

Several conclusions can be drawn from this study:

1. Polyethylene encapsulation shows promise for the stabilization of the RFP nitrate salt waste stream with regard to immobilization the hazardous constituents. Even using a size reduction technique that liberated most of the salt from occlusion by polyethylene, five of the six LDR metals tested (Ba, Cr, Pb, Se, and Ag) would pass TCLP at concentrations near those expected in the waste. With a more appropriate size reduction method, better stability is expected. The data used for this conclusion is preliminary and requires additional work for confirmation.
2. The feasibility of chemical immobilization of the waste's hazardous constituents through the addition of CaO has been demonstrated. This was shown by the ability of the

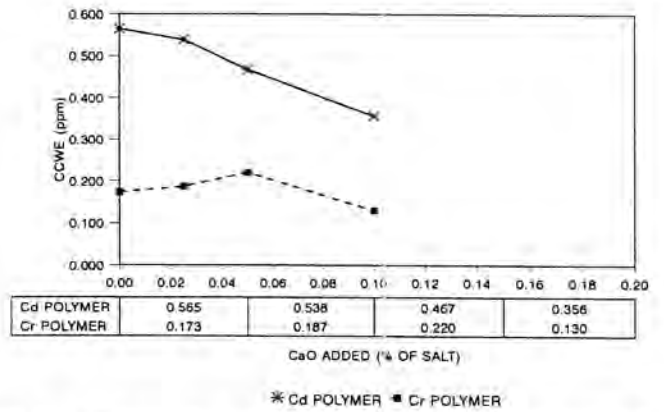


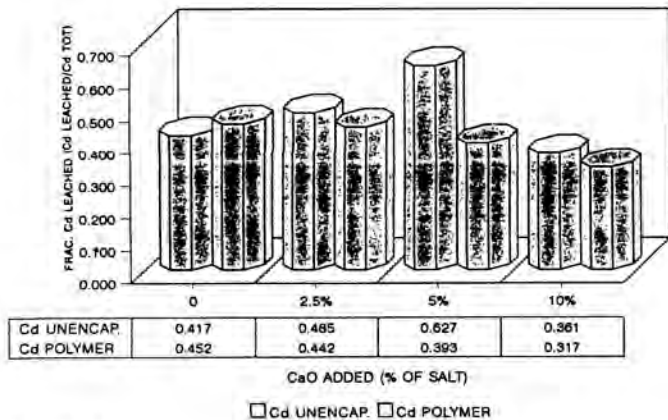
Fig. 8. Effect of CAO addition on TCLP - PE encapsulated.

unencapsulated surrogate salt spiked with 50 ppm Cd and Cr to pass the TCLP when stabilized with CaO. Testing of the encapsulated and crushed waste form was not completed, but expectations are high that it will also pass the TCLP. It should be pointed out that this need not reduce the waste loading in the final waste form because CaO addition may allow use of less polyethylene.

3. Crushing is an inappropriate method of size reduction for polyethylene encapsulated salts because of the unreasonable pressures required. These pressures, in excess of 12,000 psi, are much greater than those expected in the final repository. Polyethylene encapsulation stabilizes the waste by surrounding it with an impermeable barrier. Crushing the waste breaks this barrier and effectively reverses the encapsulation process. For an effective method of testing this waste form, a different method of size reduction for the TCLP must be used.

ACKNOWLEDGEMENTS

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50 ppm Cd, Cr

Fig. 9. Effect of PE encapsulation on fraction of Cd

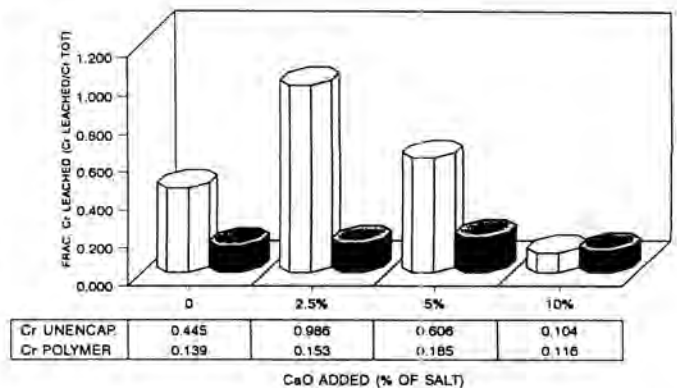


Fig. 10. Effect of PE encapsulation on fraction of Cr leached.