**Addendum to
"Expedited Demonstration of Molten Salt
Mixed Waste Treatment Technology"**

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**Addendum to "Expedited Demonstration of Molten Salt
Mixed Waste Treatment Technology" (TTP SF-2410-03 Final Report):
Supplemental Final Forms Results**

Introduction

The Final Forms portion (Section 4) of the TTP SF-2410-03 final report¹ was incomplete. This was noted under the subsection "Task Variances." The present report documents the work that was unfinished at that time, arranged in accord with the subsections of the Final Report. An assessment of the overall immobilization efficacy of polymer microencapsulation, as supported by this study, has been added.

The study and demonstration of the polyethylene microencapsulation of salt residues is continuing under other auspices. A stand-alone report combining the results of the continuation with the contents of this memorandum and of Section 4 of the Final Report¹ will be issued in later this year.

Experimental Methods and Results

Materials

Table A below is an extended version of Table 4.1, incorporating the internal (Rocky Flats and LLNL) designations and the specific surface area of the salt.

Table A. Characteristics of NaCl.

Rocky Flats & LLNL code	Morton commodity code*	Morton name	Anticaking agent*	Mean particle size (μm)	Specific surface area cm^2/g	Crystal form
TFCS460	1312	TFC 999 Salt	$\text{Na}_4\text{Fe}(\text{CN})_6$	460	62	cubes
TFCS290	1328	TFC 999 Fine Salt	$\text{Na}_4\text{Fe}(\text{CN})_6$	290	98	cubes
50/50FPS	1226	50/50 Flour Prepared Salt	$\text{Ca}_3(\text{PO}_4)_2$	200	140	cubes
FS120	1482	Flour Salt	$\text{Na}_4\text{Fe}(\text{CN})_6$ & $\text{Ca}_3(\text{PO}_4)_2$	120	330	jagged fragments of cubes
XF200	1255	Pulverized Salt, Extra Fine 200	$\text{Ca}_3(\text{PO}_4)_2$	35	1900	ditto
XF325	1247	Pulverized Salt, Extra Fine 325	$\text{Ca}_3(\text{PO}_4)_2$	25	2500	ditto

* Concentrations ~1-2 wt% $\text{Ca}_3(\text{PO}_4)_2$, ~5 ppm $\text{Na}_4\text{Fe}(\text{CN})_6$

Specimen Characterization and Immersion Tests

Table B below supplements Table 4.3 of the Final Report, which provided data on loading and on salt loss upon immersion testing of encapsulated MSO gray salt and FS120 NaCl. As there are no additional data on MSO salts, only the NaCl results are given here. All specimens were extruded using the volumetric feeder arrangement. FS120 salt was extruded on 1/11/95, the others on 1/19/95. Each ashing entry is an average of four replicate experiments. Attention may be called to specimen no. 20a. There was actually a slight weight *gain*. The cause is uncertain, but a plausible explanation is adsorbed water. If this is the case, then the actual salt loss may be slightly higher than inferred from the weight losses shown in Table B.

¹ Erica H. von Holtz, Robert. W. Hopper & Martyn G. Adamson, "Expedited Demonstration of Molten Salt Mixed Waste Treatment Technology." TTP SF-2410-03 Final Report, LLNL report UCRL-ID-119720, February 2, 1995.

Table B. Ashing and immersion test results.

Salt type	Sample no.	Nominal loading wt%	Loading by ashing wt%	Weight per cent of salt lost	Salt type	Sample no.	Nominal loading wt%	Loading by ashing wt%	Weight per cent of salt lost
XF325	7a	50	46.74	5.01	50/50FPS	14a	50	50.03	7.74
	7b	50		5.30		14b	50		7.97
	7c	50		5.91		14c	50		7.81
	8a	60	59.18	31.81		15a	60	60.85	16.19
	8b	60		30.68		15b	60		14.88
	8c	60		28.19		15c	60		15.38
	9a	70	63.03	72.13		16a	70	71.72	36.81
	9b	70		78.89		16b	70		36.12
	9c	70		84.93		16c	70		36.21
XF200	20a	50	49.57	-1.77	TFCFS290	11a	50	50.74	10.53
	20b	50		-0.22		11b	50		10.36
	20c	50		1.95		11c	50		9.96
	21a	60	59.62	22.37		12a	60	60.90	20.66
	21b	60		19.33		12b	60		21.19
	21c	60		22.79		12c	60		22.37
	22a	70	70.48	62.30		13a	70	70.77	72.11
	22b	70		64.33		13b	70		72.836
	22c	70		67.13		13c	70		69.22
FS-120	4a	50	50.6	7.9	TFCFS460	17a	50	49.85	11.74
	4b	50		7.7		17b	50		9.89
	4c	50		7.6		17c	50		10.86
	5a	60	60.8	16.1		18a	60	60.55	23.62
	5b	60		17.2		18c	60		25.18
	5c	60		17.4		19a	70	70.02	66.43
	6a	70	70.7	46.5		19b	70		65.60
	6b	70		45.2		19c	70		64.25
	6c	70		47.3					

TCLP Tests

TCLP test results for encapsulated and unencapsulated MSO gray and MSO green salt were reported in Table 4.4 of Reference 1. Chemical analysis for total RCRA metal content of the salts were unavailable at the time of the Final Report. Table C gives the analysis of MSO green salt. For convenience of comparison, the Table D repeats the MSO green salt TCLP results for Cr reported earlier in Table 4.4 of Reference 1. As mentioned in Reference 1, TCLP leachant concentrations for the unencapsulated salt were below detection limits for Ag, Cd and Ni. This, as discussed, is a result of the high pH of the final solution. Since the total levels of Ba and Pb in the salt were well below the regulatory limit (Table C), no TCLP analyses was performed for these elements.

Table C. Total RCRA metal content of MSO green salt

Element	Concentration ppm	Regulatory level, ppm
Ag	118	5
Ba	1.43	100
Cd	<1	1
Cr	6480	5
Ni	629	[20]*
Pb	<1	5

Table D. TCLP leach test results for MSO green salt

wt % salt (nominal)	Cr conc. ppm	Final pH
40	9.84	4.08
50	22.4	4.57
60	60.7	6.44
100	254	9.37
100	288	9.34
100	300	9.35

* California STLC level (Ni is not Federally regulated).

There had been some concern (Ref. 1, p. 30) regarding interferences in the atomic absorption analyses used in these TCLP tests. The atomic emission spectroscopy in progress at the time of the Final Report confirmed that there was in fact no problem and that the analyses were correct.

Ongoing Work

Some theoretical work intended to elucidate isolated aspects of microencapsulation waste form was undertaken. As discussed in Reference 1 (p. 22), if the salt particles are largely isolated from one another, leaching should dissolve the salt only to an average depth on the order of the mean particle size, at least in the short run. When the particles are geometrically similar, but not necessarily of the same size, the quantitative result can be expressed as follows:

$$\text{mass fraction of salt leached} = \text{const} \times \left(\frac{\text{specimen area}}{\text{per specimen mass}} \right) \left(\frac{\text{specific surface}}{\text{area of waste}} \right)^{-1} \left(\frac{\text{waste loading,}}{\text{mass fraction}} \right)^{-1} \quad [1]$$

(Particle size is inversely proportional to specific surface area.) For isolated spheres, the constant is 3.

A rough model of a plausible mechanism of waste form degradation was investigated. The basic notion is that if the waste form is immersed in water, the water can diffuse through thin polyethylene barriers to an encapsulated salt grain. The driving force for this is the decrease in free energy which then occurs upon dissolution of the still-encapsulated salt. Were the polyethylene itself of great strength, the diffusion would cease when the pressure in the capsule reached the osmotic pressure of water *vs.* salt-saturated water. This osmotic pressure at ambient temperatures is ~380 bar, however, which would induce stresses far above the tensile strength of LDPE. One therefore expects that as the water diffuses in, the capsule expands as the polyethylene near the external surface of the body yields and creeps. The polyethylene eventually breaks, the salt in that capsule quickly dissolves in the surrounding water, and the next capsule into the waste form is exposed to the same process. The salt grains were modeled as spherical, and it was assumed arbitrarily that the capsule would burst when a volume of water equal to the initial volume of the capsule had diffused into it. This is depicted in following figure:

Using readily available permeability data, the rate at which this process penetrates a monolith was estimated. The estimated rate depends, of course, on the size of the spheres and of the gaps separating them. For spheres of diameter 100 μm separated by gaps of 1 μm , the calculated rate is ~1 mm/yr. The assumptions of the model are obviously crude, and such estimates are probably only of order-of-magnitude accuracy.

More significant is the parametric trend predicted. For reasonable ranges of diameters and gaps, the penetration rate is nearly proportional to the reciprocal of the sphere diameter. Surprisingly, the dependence on the gap is very weak for gaps > ~1 μm and is never as important as the sphere diameter. This result has implications for waste form design: For a given loading level, this osmosis-driven degradation is reduced by *increasing* the salt particle size. In contrast, as discussed in Reference 1, the rapid initial leaching of salt grains exposed

at the surface of the waste form is minimized by *reducing* the particle size. Theoretical analyses showed that this trend holds for shapes other than spheres.

Of course, if the rate of salt diffusion through the polyethylene is comparable to that of water, then the rupture mechanism would not apply. Long-term observation of leaching of NaCl microencapsulated in LDPE, by optical microscopy on a polished section, was undertaken. Initial observations seem to indicate that diffusion of NaCl through the LDPE is indeed dominant, and no direct evidence for the rupture mechanism was found. A more controlled and systematic experiment is required to confirm this result. The transport rate of the hazardous constituents would in general be quite different from that of the NaCl.

Assessment of the Utility of Polymer Microencapsulation of Salt

As a *demonstration* of polymer microencapsulation, the results of this study did not provide the clear-cut encouragement one might have wished. In particular, the waste form prepared from "MSO green" salt failed the TCLP criterion for Cr. Also, the volumetric loading levels at which leach resistance began to deteriorate were disappointingly low (~30 vol%). Significantly better combinations of loading and immobilization may reasonably be expected to result from process innovation and optimization, preferably guided by fundamental studies. Even at the present state of the art, however, we maintain that polyethylene microencapsulation is an adequate final form for MSO salt residues. The following discussion is intended to clarify and place in perspective the experimental leaching results.

The MSO green salt had a very high concentration of Cr. As noted in Ref. 1, an MSO treatment train would almost certainly separate the NaCl and/or ash for disposal, and recycle the Na_2CO_3 . The separation entails dissolving the used salt in water, so a simple precipitation step (e.g., by pH adjustment) prior to filtration would be natural. This would yield a residual salt having far lower concentrations of RCRA metals than existed in our MSO green salt. The efficacy of such a procedure is reflected in the relatively low Cr concentrations observed TCLP measurements on unencapsulated MSO green salt (Table D). As discussed in Ref. 1 (p. 29), the salt raises the pH of the leachant to a level where the Cr solubility is low, and most of the Cr is therefore removed when the leachate solution is filtered (a part of the TCLP).

Control of the particle size distribution is crucial. The MSO green salt was simply pulverized and ball milled to a fine size: there was no attempt to control the size, nor to remove the "fines" (which tend to agglomerate). Controlling the particle size distribution, which would involve only simple and industrial standard procedures, may be expected to improve waste form performance significantly. The extremely low leaching of NaCl observed with 40 wt% loadings of XF200 (diameter ~35 μm) salt supports this optimism.

The general context should not be forgotten: The problem of immobilizing salt waste is generic to the destruction of waste halogenated hydrocarbons, the usual products of which are CO_2 , H_2O , NaCl and NaF. The MSO process merely adds Na_2CO_3 to the list.