RocTec Stabilization Treatment of WERF Ash

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EXECUTIVE SUMMARY

This report is an account of experiments performed for the U.S. DOE's Mixed Waste Focus Area (MWFA) using RocTec technology to stabilize fly ash generated by the WERF facility at the Idaho National Engineering & Environmental Laboratory. RocTec is a ceramic sintering process where the waste to be stabilized is first calcined at approximately 500 °C. The waste is then ground and mixed with inexpensive reagents and additives. This mixture is then pressed into briquettes and air dried. After being air dried, the briquettes are sintered to a hard, dense ceramic at approximately 1000 °C, which results in a volume-reduced waste form. Success is determined if the dense ceramic passes the standard Toxicity Characteristic Leaching Procedure (TCLP) for all RCRA metals.

RocTec ceramic fabricated with mixed metal oxides (that were believed to simulate the composition of the WERF ash before analytical results were available) successfully passed the TCLP test. However, it was later determined that the actual WERF ash contained large concentrations of volatile RCRA metal compounds which contained chloride and sulfate anions. When RocTec was applied to the WERF ash, the resulting ceramics could pass the TCLP tests, but a significant amount of the RCRA metals (particularly lead) volatilized during the calcining and sintering process. It was assumed that Pb was present either as volatile lead chloride (PbCl_2) or low volatility lead sulfate (PbSO_4). Subsequently, an extensive experimental effort was conducted to develop chemical pre-treatments to convert lead chloride to non-volatile compounds prior to undergoing the RocTec process. These pre-treatment experiments were successful in converting dissolved lead chloride into the desired low-volatility compounds. The RocTec ceramic production process was then used in conjunction with the pre-treatment procedures. Resulting ceramics then passed TCLP tests for all major RCRA metals comprising the ash (e.g. Pb, Cd, etc.) except sometimes for chromium (chromium was a minor constituent of the WERF ash). Evidently some pre-treatments changes the valence state of the chromium containing compound(s).

However, off-gas testing determined that, after pre-treatments, the volatility problem still existed. Later, a solubility test indicated that less than 1 % of the Pb found in the as-received WERF ash was being dissolved in the treatment water. About 19 % of the zinc in the ash was being dissolved. Therefore, it was concluded that the lead must be contained in water-insoluble, yet volatile compounds. Some of the other metals must be present as chlorides (e.g., zinc chloride). Evidence was presented to conclude that the majority of the lead must be chemically bound in a "glassy" amorphous phase that will not dissolve in the pretreatment processes tried, but decomposes at temperatures ≥ 550 °C.

For RocTec ceramic production process to be successful, more work is needed to develop a chemical pre-treatment procedure (at low temperatures) to convert this material into a compound exhibiting low lead volatility at temperatures used in the process. The complex chemistry of a fly ash such as this (large number of cations and anions) makes any single effort to modify the material for subsequent ceramic production very difficult. Furthermore, since the additional pre-treatment conversion steps complicates the RocTec process, and the resultant total process may be more costly than other options thought to be available, Starmet recommended to terminate its work on this material at this time. If other stabilization processes being investigated at INEEL are not successful, the data in this report can serve as a good starting point for subsequent studies.

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1. OBJECTIVE

The objective of this project is to demonstrate a process to stabilize mixed waste flyash generated by the combustion of mixed waste at the Idaho National Engineering & Environmental Laboratory's (INEEL's) Waste Experimental Reduction Facility (WERF) incinerator such that it will meet Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDRs) Universal Treatment Standards.

2. BACKGROUND

2.1 Statement of Mixed Waste Treatment Needs

The current technology for stabilizing characteristic mixed waste ash is via encapsulation in Type II - Portland cements. However, difficulties have been experienced in passing the TCLP test using Type II-Portland cement to encapsulate the flyash portion of the WERF ash. This is because of the significant concentrations of cadmium, lead and hexavalent chromium (up to 6 wt%) that become concentrated in the flyash, during incineration. These high concentrations of heavy metals in the WERF ash, upon solidification, result in a cementitious waste form that does not pass Toxic Characteristic Leaching Procedures (TCLP) for leachability of these metals. For this reason, there was a need to look at alternative means of waste form stabilization for the WERF flyash.

Glass or vitreous waste forms provide very good leach resistance but require melters to fuse the materials. Melter problems have proved challenging to DOE, and large scale production deployment on mixed low level waste matrices has not been accomplished at this time. Major melter problems at the DOE Fernald site have caused the DOE to reconsider other technologies. Typical problems for joule melters include performance limiting refractory and electrode corrosion and viscosity control of the melt. Plasma melters have similar problems as well as limited plasma torch lifetimes and torch failure modes that inject cooling water onto the surface of hot magma.

INEEL Needs: WERF incinerator ash is generated at the approximate rate of 15-20 tons/yr with 3-5 tons of that being fly ash and the remainder being bottom ash. The ash can have up to 6 wt % heavy metal content (Cd, Pb, Cr, etc.). The current method of encapsulation is to add the ash to Portland cement grout in a mass ratio of four parts cement to one part ash. This results in the estimated volume expansions described in Table 1. However, the heavy metals in the flyash can leach from the Portland cement to such an extent that there currently there is a difficulty in obtaining regulatory approval for this waste form. Encapsulation in glasses (e.g. borosilicate glass) via a melter produces good leach resistance, but the melting (vitrification) is prohibitively expensive.

Savannah River Needs: Current estimates indicate the CIF Incinerator at Savannah River will produce approximately 600 lb of ash per day. With the expected ratio of four parts cement to one part ash, this is expected to result in a stabilized waste form volume of 26 ft³/day, just for the ash alone. In addition, the highly-radioactive, mixed-waste nature of the CIF ash (radionuclide concentrations just slightly under the transuranic regulatory limit of 100 nCi/g) limits the availability of radioactive or mixed waste storage sites that may accept this waste. As a result, Savannah River is looking at alternative waste forms that may achieve substantial reductions in waste form volume.

Based on preliminary estimates, it appears that the RocTec process produces only 5 ft³ of stabilized waste form, per daily volume of 600 lb of ash. This would be a significant volume reduction.

Oak Ridge Needs: This project was expected to be applicable to ash stabilization at other Department of Energy (DOE) rad-waste incinerators such as the Oak Ridge TSCA incinerator, which currently uses grout stabilization for ash disposal.

2.2 Description of Process

The RocTec process is being developed as a low cost alternative to vitrification. The process is much superior, with respect to leaching of heavy metals, volume reduction and range of waste feed material, than cement based stabilization processes. RocTec waste forms are created using a ceramic manufacturing process that combines incinerator ash with suitable additives. A flow chart of the RocTec process is shown in Figure 1. At the end of the sintering step, the product is a rock-like ceramic that is leach resistant and has 80 to 90% of the crystal density of the constituents.

Figure 1. Flow Chart of Generalized RocTec Process

The process uses small quantities of additives compared to grout encapsulation (5% to 20% by weight versus 400%). For the RocTec process, a mixture ratio of four parts ash to one part additive by weight is typical. In contrast, based on discussions with WERF incinerator personnel, grout mixtures are typically one part ash to four parts cement. This small quantity of additive for making RocTec ceramic, combined with the densification associated with the process results in a volume reduction of 30-50 %, depending on the composition and initial density of the incoming material. This volume reduction would result in substantial savings in the disposal cost as shown in Table 1 below.

Table 1. Comparison of the Estimated Disposal Volumes and Costs for RocTec and Grout

Stabilization of 100 ft³ of Incinerator Ash (Assuming Initial Bulk Density of 80 lb/ft³)

<u>Parameter</u>	<u>RocTec Stabilization</u>	<u>Grout Stabilization</u>
Initial Volume/Mass of Ash	100 ft ³ /8000 lb	100 ft ³ /8000 lb
Mass of Additives	2000 lb	32,000 lb
Total Mass of Mixture	10,000 lb	40,000 lb
Density of Final Product	162 lb/ft ³	135 lb/ft ³
Post Treatment Volume	61 ft ³	297 ft ³
Disposal Cost at \$50/ft,	\$3,050	\$14,850

Initial results on RocTec waste forms [liquid phase sintered ceramic waste form] indicate performance characteristics (compressive strength, leach rate, etc.) similar to a vitreous waste form.

2.3 Stage of Development of Proposed Technology

The RocTec process was originated by scientists at Triox Technologies, Inc. of Murray, Utah. Work at Triox showed that low concentrations of radionuclides and chemically hazardous wastes could be contained in the RocTec structure (a mixed crystallized/vitrified product). Related work has been performed by Starmet, Inc., on multiple inorganic matrices including ash and, sludges. This project was performed as a joint undertaking of both companies.

During 1996, a subcontract of about \$31 K was signed between Triox and INEEL under the "Proof of Concept Research of Environmental Technologies" program. This RocTec study accomplished the following:

Five surrogates for hazardous and radioactive compounds were selected for study as a function of waste loading (up to 80 volume %) and contaminant composition. These compounds were cadmium oxide, cesium oxide, strontium oxide, cerium oxide as a surrogate for the transuranic compounds and rhenium oxide as a surrogate for technetium oxide. Additional tests were performed on the reagents used in processing RocTec.

Ash from a municipal waste incinerator was processed into a RocTec ceramic waste form and tested for leach resistance. Radioactive waste from the WERF incinerator was not available to TRIOX, Inc. during the short period of the 1996 contract. Reaction products of the major constituents in the ash were analyzed by X-ray diffraction. Individual batch operations in a modified ceramic extrusion process were investigated for scale-up potential for an eventual remote automated process line. Firing of the RocTec product was demonstrated where the pellets were free-standing (no support, no excessive slumping or melting).

The following processing steps were developed on a laboratory scale for a municipal incinerator ash and simulated Rocky Flats incinerator ash:

- i. Continuous Mixing and Milling
- ii. Chemical "Tailoring"
- iii. Extrusion of waste into an green dense, aggregate form
- iv. Liquid phase sintering
- v. Leach resistance

3. APPROACH

The primary goal of this project was to demonstrate the effectiveness of the RocTec process to stabilize ash from the WERF incinerator to meet the RCRA-LDR standards. The ash was to be stabilized in a ceramic waste form using the liquid phase sintering technology of the RocTec process.

The ceramic waste form was then leach tested according to SW846 Method 1311 TCLP and the results compared to leachability limits as specified in Table 1 of 40 CFR 268.48.

To achieve this purpose a careful analysis of the WERF ash was performed to set a baseline. Additives were then added to the ash and then stabilized using the RocTec process. This plan was broken down into four parts. A brief summary of each part is described below.

Task 0 – Surrogate Ash Testing: Starmet Inc. and its subcontractor Triox Technologies performed tests on surrogate ash to establish a reasonable range of process variable for stabilizing the WERF ash. This work was in the Triox ceramic laboratory located in Murray, Utah. No radioactive materials were used in these surrogate material tests. It was desirable to understand the behavior of such materials before Starmet began dealing with the radionuclides found in the actual WERF ash. The synthetic ash was formulated based upon data provided from the INEEL but as it turned out, the data was not adequate. There were no indications of the volatile compounds found subsequently after work on the actual WERF ash began. Task 0 is primarily described in Appendix A.

Task 1 – Ash Analysis: Chemical and physical analysis was performed on the WERF ash. Task 1 is described in the next section and also in Appendix A for some of the work associated with Phase 0 testing.

Task 2 – Developed RocTec Process using WERF ash: This task optimized RocTec procedures and compositions developed in Task 0, but using actual WERF ash. New processing approaches were developed to accommodate the unique nature and chemical composition of the WERF ash. Processing parameters that were developed included: composition of chemical additives, mixing and grinding times conditions and machinery, dry pressing methods, and sintering times, temperatures, and atmosphere. It was found that RCRA metals were vaporizing during the sintering treatment because they were present in the WERF ash as metal chlorides and sulfates. Therefore, extensive experiments were conducted to develop a chemical "pretreatment" that would convert the high vapor pressure metal salts into chemical compounds that exhibited low vapor pressures at temperatures up to the sintering temperature. Task 2 is described in the main body of this report.

Task 3 – Post Test Analysis: Samples from Task 2 were tested by SW846 Method 1311 TCLP for

leachability of ash hazardous metals constituents shown in Table 1 of 40 CFR 268.48. The leach characteristics from the samples were compared with the leach characteristics of the untreated ash and ash fired with no RocTec processing. Task 3 is described in the main body of this report.

Task 4 – Phase 1 Reporting: This report is the Final Report on Phase 1. In addition, an Interim Report was submitted and comprises the majority of Appendix A.

4. EXPERIMENTAL PROCEDURES

These experimental procedures are for Task 1, Task 2 and Task 3. The experimental procedure for Task 0 is found in Appendix A.

4.1 Experimental Procedures for Treatment of WERF Ash using the RocTec Process

ASH ANALYSIS: A 500 g sample of WERF ash was sent to Mountain States Analytical (MSA) for analysis. The tests performed included loss on ignition, metals analysis, and an anion scan. Three types of metal analyses were performed. The first was a lithium metaborate fusion (in-house MSA technique) for metals. The second was EPA Method SW846-3050 (Acid digestion/Flame ICP). The third test was EPA Method SW846-1311 (Toxicity Characteristic Leaching Procedure – TCLP). Anion content was determined using Loss on Ignition (ASTM D-482) and Ion Chromatography (EPA 300 MOD).

ROCTEC PROCESS: The original RocTec procedure called for calcining (in air) the as-received WERF ash at 550 °C. This was to drive off any water and oxidize residual carbon not combusted in the incinerator. An experiment was performed to capture and analyze the off-gas from the calcination process. Porcelain crucibles were filled with ash and weighed. They were then placed in a tube furnace and the ends of the tube sealed with end-plates. One end-plate had a port for plant air supply while the other end-plate was connected to a bubbler filled with deionized water. While the furnace was at 550 °C, air was forced through the system and carried volatile materials into the bubbler's water. After a run, the ash was weighed and the water analyzed.

Based upon the analysis of Task 0 results, a mixture of 50% kaolin to 50% WERF ash was selected for the beginning composition for Task 2 experiments.

A Union Process S-1 attrition mill was filled with ½" diameter chrome steel grinding media. Deionized water was added to the mill jar. The water level just covered the top of the grinding media. The mill was turned on at a low setting and 200 g of kaolin was then added to the mill, followed by 200 g of calcined WERF ash. The speed of the mill was then increased and run for 60 minutes. The resulting slurry was poured into a drying pan, and the pan placed in a drying oven set at 110 °C for about 12 hours. The dried cake was then crushed using a mortar and pestle. The powder was then placed in crucibles and calcined at 950 °C for 5 hours in a tube furnace. The mixture was then crushed again in the mortar and pestle and placed in the attrition mill for 1 hours. Then 1 wt% organic binder was added and the attrition mill ran for 15 minutes. The slurry was poured into a pan and dried at 110 °C for 12 hours. The dried cake was crushed and pushed through a No. 70 screen. Pellets were then pressed in a 13 mm diameter metal die at 6,000 psi in a uni-axial hydraulic press (12 ton Carver). The thickness of each pellet was about ¼". Samples were placed on a porcelain plate

and put into the tube furnace.

For sample #1 pellets, the temperature was ramped at about 10 °C/min up to about 1070 °C and then held for 1 hour. Sample #2 pellets were ramped to 1100 °C and held for 1 hour while sample #3 pellets were ramped to 1170 °C and held for 1 hour. TCLP testing was performed on all the pellets.

4.2 Experimental Procedures for Pre-treatment of WERF Ash + RocTec

The first pre-treatment procedures, performed on the WERF ash, were to convert the metal chlorides to metal hydroxides or carbonates. The pre-treatment was performed by mixing the ash into a slurry with de-ionized water. Then concentrated hydrochloric acid was added until the pH stabilized below a value of 3. The purpose of this was to digest any metal chlorides and sulfates. This practice was halted in later experiments due to the solubilization of undesirable cations. Then a base (e.g. ammonium hydroxide, sodium hydroxide, sodium carbonate, or calcium carbonate) was added. Initially, the addition was until the pH stabilized above 10.5. This was done to precipitate the metals as metal hydroxides or metal carbonates that would transform into metal oxides during calcination or sintering. It was later discovered that this pH value was too high, and the procedure was modified to a much lower pH value. The solids were then allowed to settle to the bottom of the beaker. The excess solution (supernatant liquid) was poured off the solids and a sample of the solution was taken for analysis. The solids were dried at 110 °C for 12 hours.

Pre-treated WERF ash and kaolin were both calcined at 950 °C for 5 hours. In later samples this practice was discontinued due to worries about PbO volatilization. The ash was crushed in a mortar and pestle and a 50 wt% kaolin/50 wt% pre-treated ash mixture was made. Both the ash and the kaolin were added to an attrition mill. The remainder of the procedure then followed that already explained in Section 4.1.

A separate off-gas experiment was also performed on the pre-treated ash per Section 4.1. The ash was calcined at 550 °C for 5 hours. A white powder was discovered in the tubing between the furnace and the bubbler. A sample of this powder was analyzed.

Further development of ash pre-treatment experimental procedures was quite extensive, and are reported in Appendix B.

5. RESULTS

5.1 Task 1 and Task 0 Results

5.1.1 WERF Ash Analysis (Task 1)

Some analysis of WERF ash is given in Appendix A. Table 2 shows the most recent results of chemical analyses conducted for metals on as-received WERF ash.

Table 2. WERF Ash Analyses

Analyte	Fusion (Molten lithium metaborate) (mg/kg)	Method SW846-3050 (Acid dissolution) (mg/kg)	TCLP 3010 Leach (mg/L)
Aluminum	1668.	1651.	5.284
Antimony	676.8	3228.	11.30
Arsenic	3.56	51.97	0.2351
Barium	40.24	140.0	0.1431
Beryllium	0.09	0.18	0.001
Calcium	2089.	10400.	315.5
Cadmium	ND	691.1	38.84
Chromium	414.2	420.1	0.2494
Cobalt	29.9	---	0.4880
Copper	245.6	1679.	37.92
Iron	3369.	12180.	0.1879
Lead	150.	46420.	28.63
Magnesium	258.4	983.5	26.72
Manganese	132.8	578.9	9.740
Molybdenum	51.61	169.0	0.0156
Nickel	213.0	625.1	4.512
Phosphorus	589.3	2496.	8.611
Potassium	28600.	---	2231
Selenium	ND	7.06	ND
Sodium	24985.	---	1049
Strontium	23.	---	0.3671
Silver	16.03	158.1	0.6669
Silicon	5120.	432.7	10.35
Tin	18.83	188.8	ND
Titanium	338.2	638.3	0.0078
Thallium	ND	8.14	0.0845
Vanadium	3.63	8.78	ND
Zinc	34910.	172700.	8112

By comparison, the metal levels measured after the lithium metaborate fusion were significantly lower than when using the 3050 acid digestion preparation. The analytical chemists at MSA believed that there was a loss of analyte by a volatility mechanism in the fusion preparation. Therefore, although the 3050 preparation is not considered to be a total dissolution preparation, the results from the 3050 test is thought to be the best cation analysis of the WERF ash sample.

The volatile compound content was revealed by ASTM D-482 Loss on Ignition (LOI) experiments at 550 °C for 12 hours. The LOI was determined to be 32.1 wt % of the as-received sample with only 2.5 wt % of the as-received sample being moisture.

The nature of the volatile compounds was further revealed using Ion Chromatography Anion Scan testing (EPA 300 MOD) as shown in Table 3.

Table 3. Anion Scan (Ion Chromatography)

Compound	Amount (mg/kg)	Limit of Detection (mg/kg)
Fluoride	ND	100
Bromide	376	100
Orthophosphate phosphorous	ND	100
Nitrate Nitrogen	ND	50
Nitrite Nitrogen	ND	1,000
Chloride	169,000	20,000
Sulfate	122,000	20,000

Table 3 reveals that almost all of the volatile material (29.2 wt % of WERF ash) consists of metal chlorides and metal sulfates. It is not known which metals are found as chloride and sulfate salts, but the highest metals found in test 3050 were zinc (172,700 mg/kg), lead (46,200 mg/kg), copper (12,180 mg/kg), iron (12,180 mg/kg), calcium (10,400 mg/kg), and antimony (3,229 mg/kg).

The X-ray diffraction conducted at Southwest Research Institute gave some indication of the complex mixture of chemical compounds constituting WERF ash after it had been calcined to 450 °C, and 550 °C.

The 450 °C sample was about 80 % crystalline. The crystalline portion of the sample consisted of about 30 % cotunnite (PbCl_2), 30% KAlSiO_4 , 10% wurtzite (ZnS), 10% Pb_3SiO_5 , 10% willemite (Zn_2SiO_4), 5 % lead metal, and a trace (<5%) each of susannite [$\text{Pb}_4(\text{CO}_3)_2\text{SO}_4(\text{OH})_2$] and litharge (PbO).

The 550 °C sample was about 80% crystalline. The crystalline portion of the sample consisted of 50% willemite (Zn_2SiO_4), 25% K_2ZnCl_4 , 10% $\text{K}_2\text{Pb}_3\text{O}_6$, 5% $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ and a trace (<5%) each of cotunnite (PbCl_2), $\text{Pb}_3\text{C}_2\text{O}_7$, $\text{Zn}_3\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$, Zn_2PbO_4 , and $\text{Pb}_3\text{C}_2\text{O}_7$.

5.1.2 Task 0 RocTec Results (Task 0)

The entire description of Task 0, where the WERF ash was simulated with mixed metal oxides, is given in Appendix A. A summarized version of some results is given below.

Table 4 contains an abstract of leach resistance results from Appendix A. This compilation is important since leach resistance is the primary qualification factor for RocTec ceramics made with WERF ash. Information was received from INEEL that zinc wasn't part of the RCRA group; therefore, there would not be a UHC-threshold leaching requirement. Consequently, experimental results were selected for Table 4 where TCLP numbers for lead were less than 1.0 mg/L (requirement of <0.370 mg/L).

Table 4. Experiments with less than 1.0 mg/L lead in TCLP leach test

Sample #	Dopant	% Conc.	Firing Temp. °C	Lead (Need <0.370)	Other RCRA levels OK ?	Zinc (for reference only)
1049	EPK	20	1100	0.690	Yes	22.00
1050	EPK	30	1100	0.700	Yes	17.00
1051	EPK	50	1100	0.340	Yes	3.30

1057	Soil	50	1100	0.680	Yes	18.00
1058	Soil	50	1000	0.810	Yes	14.00
1088	EPK	20	1000	0.310	Yes	109.00
1104	Bentonite	30	NA	0.830	Yes	27.00
1105	N.S.	30	NA	0.860	Yes	23.00
1092	Al ₂ O ₃	10	1200	0.960	Yes	36.00
1093	Al ₂ O ₃	20	1200	0.960	Yes	16.00
1052	Al ₂ O ₃	30	1100	0.710	Yes	9.60

Appendix A shows that there was little difficulty in achieving the UHC threshold requirements for RCRA metals, except for zinc and lead. Table 4 shows that there were a number of significantly different additives and additive levels that nearly achieved the leach resistance standard for lead. Significantly, two of the RocTec samples made with the kaolin clay (EPK) additive met the TCLP standard.

However, there were indications of variances within the data:

- (1) Sample # 1089 had conditions very close to a sample (#1088) that passed the lead standard, but the Pb leach level for sample # 1089 was quite high (10.0 mg/L) as shown below in Table 5.

Table 5. Sample #1089 Data Showing high Pb Content

Sample #	Dopant	% Conc.	Firing Temp. °C	Lead (Need 0.370)	Other RCRA OK ?	Zinc (for reference only)
1089	EPK	30	1100	10.00	Yes	252

5.2 Task 2 and Task 3 RocTec Results

5.2.1 RocTec Results using WERF Ash

Table 6 gives the TCLP leach results for RocTec samples made with 50% Kaolin and 50% calcined (to 550 °C) WERF ash. The threshold values represent the upper leach limit allowed for a given metal for the sample to pass the TCLP test. Sample 2 was omitted because the sintering temperature (1170 °C) was too high and the sample completely melted.

Table 6. TCLP Leach Analysis of RocTec Samples made with Kaolin + WERF Ash

Element	Threshold (mg/L)	Sample #1- fired 1070 °c (mg/L)	Sample #3- fired 1100 °c (mg/L)
Antimony	2.1	0.004	0.012
Arsenic	5.0	ND	ND
Barium	7.6	0.13	0.18
Beryllium	0.014	ND	0.007
Cadmium	0.19	0.14	0.067
Chromium	0.86	0.009	0.003
Lead	0.37	3.4	0.18

Mercury	0.025	---	---
Nickel	5.0	ND	ND
Selenium	0.16	ND	ND
Silver	0.30	0.009	ND
Thallium	0.078	---	---
Vanadium	0.23	0.008	ND
Zinc	NA	49	1.2

Table 6 illustrates that RocTec samples can pass the TCLP tests (for every metal) when the samples are fired to 1100 °C (sample #3). Sample # 3 was visually superior to sample # 1; sample #3's surface was slightly glassy and it had only slumped slightly. Sample # 1 was friable and failed the TCLP test with regard to lead and was also approaching the limit in leached cadmium.

However, based upon the WERF ash chemical analysis (See Table 3 and Table 4) and Loss on Ignition results, there was serious concerns that volatile species like lead chloride could be volatilizing in both the calcining and high temperature sintering steps. Table 7 shows the results of the chemical analysis of the water in the off-gas bubbler that trapped volatile gases when the WERF ash was calcined to 550 °C.

Table 7. Analysis of Water in Bubbler - from WERF Ash Calcined to 550 °C.

Element	Concentration(µg/L)	Element	Concentration(µg/L)
Antimony	8.6	Mercury	---
Arsenic	1.5	Nickel	ND
Barium	0.1	Selenium	10
Beryllium	ND	Silver	0.3
Cadmium	4.2	Thallium	---
Chromium	0.1	Vanadium	ND
Lead	497	Zinc	1216
		LOI	18.4 %

The results of Table 7 indicate that lead and zinc salts are the primary volatile components of WERF ash when calcined to 550 °C in air. The LOI (18.4 %) was not as high as the 32.1% LOI measured (at the same temperature) by Mountain States Analytical on WERF ash. However, Starmet considered the 18.4 % LOI to be undesirable because it would create a secondary waste stream of RCRA metals through contaminated furnace linings and off-gas systems. Thus, a modified process step was deemed necessary to eliminate this volatility.

5.2.2 RocTec Results when using Pre-treatment Procedures for the WERF Ash

The first pre-treatment experiments utilized ammonium hydroxide to precipitate various RCRA metal as hydroxides with the concurrent formation of soluble ammonium chloride. The ammonium chloride can be removed by de-canting the supernatant water solution or by drying the slurry followed by volatilization during calcination or sintering. Table 8 gives resulting data on the first ammonium hydroxide pre-treated samples for: (a) chemical analyses of off-gases, (b) chemical analysis of supernatant liquid after the precipitation, (c) TCLP leach analysis of the final sintered pellets.

Table 8. Analyses of Ammonium hydroxide Pre-treated RocTec Processed WERF Ash

Element	Calcine Off-Gas (μ g/L)	White Powder Found in Tubing from Calcining (mg/L)	Supernatant Liquid (mg/L)	TCLP Test of Pellet (mg/L)
Antimony	26,900	57,000	<1	0.021
Arsenic	77	70	<1	ND
Barium	ND	ND	<1	0.20
Beryllium	40	ND	ND	ND
Cadmium	<1	48	239	ND
Chromium	ND	ND	<1	0.003
Lead	10,800	13,000	18	0.21
Mercury	---	---	---	---
Nickel	ND	56	24	0.031
Selenium	15	37	ND	ND
Silver	<1	ND	15	0.006
Thallium	---	---	---	---
Vanadium	ND	ND	ND	ND
Zinc	6800	9,200	13,400	1.1
LOI	34.4 %			

The results of Table 8 indicated that the samples made with WERF ash pre-treated with ammonium hydroxide will pass the TCLP test. However, antimony, lead, and zinc were still volatilizing during the calcining step; indicating they were still present as volatile salts. The reason for this volatilization was unclear since the supernatant liquid analysis indicated that the precipitation step was removing a great deal of the lead and chromium. However, the precipitation was leaving some cadmium and lots of zinc in the supernatant water solution.

One possible explanation of the continued volatility problem was that the lead salts never completely dissolved in the water prior to precipitation. This could have been because of lack of solubility or because too little water was used. An additional speculation was that some metals (e.g. zinc and perhaps cadmium) were forming complexes with the ammonium ions in the solution since a lot of ammonium hydroxide was added to reach the high pH value of 10.5. It was noted that this solution retained a dark blue color. It was also debated that acidifying the liquid prior to raising the pH might have been counterproductive since it could put metal ions into solution that might be difficult to precipitate.

Consequently, experiments were conducted on lead chloride and lead sulfate salts to determine their water solubility and solubility versus pH characteristics. It was found that lead sulfate was fairly insoluble in water at room temperature (0.00425 g/100 cc of water- CRC Handbook value). This low solubility did not increase when lowering the pH to 2.4 - 2.5 by using HCl acid. It was found that lead chloride was considerably more soluble in water at room temperature (0.99 g/100 cc at RT –CRC Handbook value), but it took about 1 hour to completely dissolve 1 g in 200 cc of water (5 g lead chloride/L of water). When raising the pH of this solution, with concentrated ammonium hydroxide, it visually appeared that all of the lead precipitated as lead hydroxide between a pH of about 5.1 and 6.3. Further raising the pH to about 10.3 did not seem to re-dissolve any lead hydroxide.

When raising the pH of a lead chloride (1 g in 200 cc of water) solution with sodium hydroxide, it appeared that the lead precipitated more quickly than when using ammonium hydroxide and the precipitate was a very voluminous lead hydroxide. All the lead chloride was precipitated between a pH of about 5.1 and 6.0. Table 9 tabulates some of the dissolution/precipitation quantification results.

Table 9. Dissolution and Precipitation of lead chloride.

Sample	Starting amount of PbCl₂ (g)	Equivalent amount of Pb(OH)₂ (g)	Weight of dried residue (g)
PbCl ₂ / NaOH	1.068	.926	.960
PbCl ₂ / NH ₄ OH	0.945	.820	.840

The weight of the dried residue was slightly higher than the expected amount. A possible explanation is that some of the Pb(OH)₂ was hydrated to Pb(OH)₂ · xH₂O. The hydrate would weigh more than Pb(OH)₂, and the drying temperature was not high enough to drive off the additional water. Table 9 indicates that if PbCl₂ is dissolved it completely precipitates when the pH is lowered to about 5.1 to 6.0.

Based upon the visual observations, and the results in Table 9, it was tentatively concluded that the previous difficulty of lead volatilization, after pretreatment, was insolubility rather than incomplete precipitation. A likely cause might be due to the use of insufficient water to completely dissolve the maximum amount of lead chloride that might be present in the WERF ash. Less likely problems could be low-temperature volatility of Pb(OH)₂ · xH₂O or perhaps lead sulfate (PbSO₄). Lead sulfate is not thought to be a problem since it should have a volatility (vapor pressure) at high temperatures that is much less than lead chloride. Based upon melting points, lead sulfate (melts 1170 °C) should be less volatile than lead hydroxide. Lead hydroxide should decompose to PbO; PbO has a melting point of 888 °C, but a relatively low vapor pressure¹. Lead oxide (PbO) has a vapor pressure of 0.015 psia at 930 °C. By comparison, lead chloride has a vapor pressure of 0.6 psia at 593 °C, 1.5 psia at 763 °C, and 15 psia at 930 °C. Any lead sulfate present in the WERF ash may partially convert to lead oxide at high temperatures during the RocTec process and become part of the glass structure or it may be trapped within the structure as relatively insoluble lead sulfate inclusions.

Recommendations were made to adjust the WERF ash pretreatment process to facilitate the dissolution of any PbCl₂ that might be found in the WERF ash. After grinding of the WERF ash, at least 4.68 L (1.24 gallons) of water should be used for a 500 g sample of WERF ash. Heating the water and holding the ash in the water for longer periods of time was also recommended to assure dissolution. It was also recommended that the initial addition of hydrochloric acid to lower the pH to about 3.0 should be eliminated. This step does not help to dissolve lead sulfate and may solubilize other cations that need a high pH (higher than needed to precipitate lead hydroxide) to precipitate back as metal hydroxides into the solid sample. It was further recommended that the pH should not be raised above about 6.3 in order to minimize the amount of ammonium chloride that later needs to be volatilized or sodium chloride that would stay in the sample and possibly lower the melting point of the final sample. The use of sodium hydroxide was recommended over the use of ammonium hydroxide. This is for two reasons: (a) Ammonium hydroxide seems to be forming complexes with certain cations (other than lead) and keeping them in solution. This problem would be worse at high pH values (e.g. 10.5) that were previously used. (b) Sodium hydroxide appears to precipitate lead

hydroxide more quickly when raising the pH than ammonium hydroxide.

New batches of WERF ash were pre-treated using sodium hydroxide, sodium carbonate and calcium carbonate. The carbonates were used in order to precipitate metal carbonates that were hoped to be less volatile than the $\text{Pb}(\text{OH})_2 \cdot x \text{H}_2\text{O}$, during heating, until they convert into metal oxides (lead carbonate decomposes to PbO at 315°C). These new batches used at least 4.68 L (1.24 gallons) of water for a 500g WERF ash sample and the ash was held in the water for at least 12 hours to dissolve as much soluble lead salts as possible. The previously-used acid solubilizing treatment was not part of the new process.

About 500 g of Na_2CO_3 or 650 g of CaCO_3 were used per 1 kg of raw ash. The slurry was stirred for at least 12 hours during the precipitation step. This was an attempt ensure the carbonates were dissolved completely enough to cause precipitation of “bad” RCRA cations to compounds like lead carbonate. The procedure did not utilize a fire and regrinding step. After drying, the pellets were pressed and fired fairly quickly (especially at temperatures above 800°C) to the final sintering temperature. This was to minimize volatilization of lead containing species (e.g., PbO).

When the Na_2CO_3 was added to the ash, bubbles formed in the slurry. They were visible through the sides of the beaker and on top of the slurry. There was no obvious bubbling when CaCO_3 was added the other ash slurry. These pellets appeared to sinter well at 1100°C .

The TCLP results shown in Table 10 show that RocTec samples made with either CaCO_3 or Na_2CO_3 passed for all metals. However, there were still concerns regarding volatility.

Table 10. TCLP Analysis results from first set of Carbonate pre-treatments.

Component	Threshold (mg/L)	CaCO_3 Exp.1 Fired 1100°C (mg/L)	Na_2CO_3 Exp.1 Fired 1100°C (mg/L)
Ag	0.03	ND	ND
As	5.0	ND	ND
Ba	7.6	0.37	.037
Be	0.014	ND	ND
Cd	0.19	0.022	0.005
Cr	.86	ND	ND
Ni	5.0	ND	ND
Pb	0.37	0.087	0.078
Sb	2.1	ND	ND
Se	0.16	ND	ND
Ti	0.23	-	-
V	0.23	0.080	ND
Zn	5.3	19	1.1

ND = Not Detected.

Both non-precipitated metal chlorides and some of the metal carbonates could have volatilized during sintering and would not show up in the TCLP results. An off-gas test was performed to look for volatile species and the supernatant liquid was analyzed for RCRA metal salts that dissolved in the water but were not precipitated by the pre-treatment.

The analysis results of the supernatant liquids from the pretreatments are shown in Table 11. Table 11 shows that, on the average, NaOH did the best job of precipitating the tested metal cations. The Na_2CO_3 also precipitated most of the metals. The CaCO_3 results were high on cadmium, nickel, lead, and zinc. All of the liquids appeared to be a little high in silver.

Table 11. Cation Analysis of Carbonate Pre-treatment Supernatant liquids.

Element	CaCO ₃ (µg/ml) Exp. 2	Na ₂ CO ₃ (µg/ml) Exp. 2	NaOH (µg/ml) Exp. 2
Ag	2.3	2.6	1.0
As	ND	0.42	ND
Ba	0.01	0.01	0.29
Be	ND	ND	ND
Cd	101	0.06	0.34
Cr	ND	0.13	0.02
Ni	8.3	ND	ND
Pb	25	ND	0.06
Sb	ND	1.4	ND
Se	0.04	0.06	0.05
V	ND	ND	ND
Zn	4136	0.14	0.19

When the pellets made from these pretreated powders were sintered at 1100°C, they melted badly. This was due to the addition of large amounts of sodium or calcium fluxes to the mixture from the precipitation pre-treatment. There were no identifiable pellets left, and the puddle was stuck to the porcelain sintering plate. A change was made to alumina sintering plates instead of the porcelain plates. This was done to prevent the sintering plate from participating in the melting. The sintering temperature was lowered in 50C° decrements until good sintering temperature were found. The CaCO₃ pre-treated pellets sintered well at 1000°C. At this temperature the pellets still slumped slightly, but they did not melt entirely. It was also observed that the surface contacting the plate shrunk more than the exposed surface. There is no record of which surfaces were top and bottom during pressing. However, it is unlikely that all ten pellets were oriented the same way. Therefore, it is believed to be a sintering phenomenon. The Na₂CO₃ and the NaOH pre-treated pellets displayed less and less evidence of melting as the temperature was lowered. However, the melting did not drop to an acceptable level until 700°C. At this temperature the pellets did still slump some in the center and around the edges. These lower melting temperatures obviously are the result of adding large amounts of calcium or sodium, which are fluxing materials. The additional metal carbonates and hydroxides precipitated by these pretreatments may have also lowered the melting points.

As shown in Table 12, the TCLP analysis for the three samples showed significant variations. The CaCO₃ pellets were the only group that passed the test for lead content. However, they were high on the chromium. The leachate had a yellowish-gold tint to it. This is a typical color for a chromium solution. The high amount of lead left in the supernatant liquid means that there would have been less lead oxide in the CaCO₃ pellets than in the Na₂CO₃ or the NaOH pre-treated RocTec pellets.

The Na₂CO₃ pellets were over the threshold for lead content. They were also a little over on cadmium, and barely below the threshold for selenium. The Na₂CO₃ appeared to be the best pretreatment, based upon the supernatant liquid and TCLP results. Modifications to this pretreatment may be the best avenue for future experiments. The NaOH pellets were well over the threshold for cadmium and lead. Offgas tests were then performed to determine which metals were volatilizing during heating.

Table 12. TCLP Analysis results from the second set of pretreatments.

Element	Threshold	CaCO ₃ Exp.2 Fired 1000 °C (mg/L)	Na ₂ CO ₃ Exp. 2 Fired 700 °C (mg/L)	NaOH Exp.2 Fired 700 °C (mg/L)
Ag	0.30	0.15	ND	0.034
As	5.0	0.004	0.029	0.003
Ba	7.6	0.50	0.57	0.094
Be	0.014	ND	ND	ND
Cd	0.19	0.046	0.53	10
Cr	0.86	8.9	ND	0.021
Ni	5.0	ND	ND	ND
Pb	0.37	0.11	8.7	153
Sb	2.1	0.76	0.28	0.32
Se	0.16	0.085	0.15	ND
V	0.23	ND	ND	ND
Zn	5.3	2.5	56	538

Table 13 shows the results of the off-gas tests for both the first and second sets of carbonate pre-treatments. The off-gas tests involved sealing both ends of the furnace and then air was forced in through one end and out the other through a bubbler of deionized water. The ash was heated at 10°C/min to 550°C, and was held at 550°C for 4 hours. Table 13 also shows results of a water leach test performed on the raw ash. This experiment was performed by mixing 25g of ash in 235 ml of water overnight, then de-canting the supernatant liquid for chemical analysis. The water leach test indicated that the lead was not dissolving well in the pre-treatment water. The implication is that the lead is not available in solution, such that the various pre-treatments cannot convert the majority of the lead into a less-volatile compound.

Table 13. Off-gas Test Results after NaOH, Na₂CO₃, or CaCO₃ Pre-treatments

Element	Off-gas Results (µg/ml)					Water Leach (µg/ml)
	NaOH Exp.2	CaCO ₃ Exp.1	CaCO ₃ Exp.2	Na ₂ CO ₃ Exp.1	Na ₂ CO ₃ Exp.2	
Ag	ND	ND	3.7	ND	ND	1.9
As	3.0	ND	4.3	ND	0.6	ND
Ba	0.15	ND	ND	ND	ND	0.04
Be	ND	ND	ND	ND	ND	ND
Cd	1.1	10	0.07	1.2	0.2	95
Cr	ND	ND	ND	ND	0.3	ND
Ni	ND	ND	1.8	1.0	ND	9.3
Pb	353	2134	13	192	118	29
Sb	151	5.7	27	27	129	ND
Se	ND	ND	ND	1.9	ND	ND
Ti	ND	ND	ND	ND	ND	ND
V	ND	ND	ND	ND	ND	ND
Zn	5.0	1651	36	35	22	3476

6. DISCUSSION OF RESULTS

6.1 Discussion of Task 0 (Mixed Oxide Surrogates) Results

The variations noted in the Task 0 mixed oxide data may be an indication that experimental parameters are varying within the system to cause the lead leach level to go up by a factor of 30 X when the dopant level was only adjusted by a relatively small amount. These experimental factors might include: (a) Degree of mixing, (b) Firing temperature, (c) Unknown factors.

There are five dopants that gave fairly good results: (a) EPK = kaolin clay, (b) Bentonite clay, (c) Soil, (d) Al_2O_3 , (e) Nepheline seynite.

Which of the five are the best additive candidates ? These additives are fairly disparate in chemical composition, yet the Zn and Pb leach tests do not vary significantly from one disparate composition to another. It is reasonable to think that the total amount leached would show trends that depend upon a given major component (e.g. SiO_2 , Al_2O_3), fluxes (Na_2O , K_2O , etc.) or ratios among the major components. There is the possibility that the relatively high concentration of ZnO (and perhaps PbO) is acting as a mild flux on the SiO_2 (always present in high amounts) and is overwhelming the contributions of the stronger fluxing agents (present in much lower concentrations). Otherwise, the lack of definite trends likely is a clue that a factor or factors other than overall chemical composition is governing the leach rate.

In order to systematically contrast the overall chemistry, all of the 11 formulations in Table 4 were considered on a molar basis. A molar accounting for example mixes are shown in the Table 14, Table 15 and Table 16 (below). For clarity, the trace (present at less than about 0.1%) components were not included in the tables.

Table 14 . 80 % Surrogate Ash + 20% Kaolin Clay (mole fractions of components)

RO & R₂O Fluxes- Network Modifiers	R₂O₃ –Intermediate Glass formers	RO₂ – Network (glass) formers
Na_2O .031	Al_2O_3 .053	SiO_2 .689
K_2O .030	ZnO .150	
CaO .016	PbO .015	
MgO .004	Others:	
ZnO .150	Fe_2O_3 .009	
PbO_2 .015	CuO .001	

Network (glass) formers include the oxides: SiO_2 , B_2O_3 , P_2O_5 , and As_2O_5 . The intermediates may under suitable conditions enter the glass network itself as partial substitutes for the network former, and includes the oxides: ZnO (coordination of 2), PbO (coordination of 2), Al_2O_3 , ZrO_2 , and CdO. The network modifiers (fluxes) cannot form glasses but can enter into the holes in the network and lower the viscosity by terminating the network, and includes the oxides: Na_2O , K_2O , CaO, MgO, ZnO (coordination number of 4), and PbO_2 (valence of +4 and coordination number of 6).

Notice that Pb in the +2 valence state (reduced) is an intermediate, while Pb in the +4 valence state (oxidized) is a network modifier and should have a higher bond strength with the silica network when it is reduced. This argument suggests that the sample should be fired in air (oxidized) to achieve

maximum stability of Pb within the network.

Table 15. 50 % Surrogate Ash + 50% Kaolin Clay (mole fractions of components)

RO & R₂O Fluxes- Network Modifiers	R₂O₃ –Intermediate Glass formers	RO₂ – Network (glass) formers
Na ₂ O .029	Al ₂ O ₃ .139	SiO ₂ .668
K ₂ O .018	ZnO .099	
CaO .016	PbO .010	
MgO .001	Others:	
ZnO .009	Fe ₂ O ₃ .016	
PbO ₂ .010	CuO .001	

Table 16. 70 % Surrogate Ash + 30% Alumina (mole fractions of components)

RO & R₂O Fluxes- Network Modifiers	R₂O₃ –Intermediate Glass formers	RO₂ – Network (glass) formers
Na ₂ O .025	Al ₂ O ₃ .221	SiO ₂ .549
K ₂ O .028	ZnO .141	
CaO .013	PbO .014	
MgO .004	Others:	
ZnO .141	Fe ₂ O ₃ .003	
PbO ₂ .014	CuO .001	

According to established “fritting” rules, a well-formulated glass should be able to tie up large amounts of Pb and still mature at about 1100 °C. Some fritting rules are:

- (a) R₂O/RO ratio should be approximately 1 for viscosity control, PbO is excepted from this rule.
- (b) RO/SiO₂ ratio should be in the range of 1/1 to 1/3, or higher if B₂O₃ is present.
- (c) B₂O₃/SiO₂ ratio should be less than or equal to about 1 /2
- (d) Al₂O₃ should be kept low (less than about 0.4 equivalent).

Analysis of the molar ratios with regard to fritting rules yielded the following conclusions:

- (1) The best samples were those that utilized kaolin (EPK) clay at levels between 20 and 50 %.**
- (2) Mixtures generally could tolerate considerably more flux (e.g., Na₂O, K₂O, and CaO) content.**

Analysis of molar ratios indicated that all the mixtures were short on network modifiers in order to satisfy fritting rule (b) above. Even when using nepheline seynite (sample # 1105), the mixture was short on powerful network modifiers like Na₂O, such that we have to count both the ZnO and PbO₂ (by firing oxidizing) as modifiers in order to achieve the minimum 1 /3 ratio. However, if we add too much of the powerful modifiers to make a good glass, the sample could easily slump and “puddle”; which goes against the general RocTec “free standing” concept.

(3) Leach tests were inconclusive in pointing out compositional trends. It was concluded that there was no distinct trend with regard to how the ratios of network modifiers, intermediate glass formers, and network glass forming metal oxides affect the TCLP leach results.

There probably were several reasons for this: (a) Leach tests were only conducted for samples that did not slump. Therefore, dopant levels and firing temperatures or times that resulted in complete melting were not measured. It can be argued that complete melting should result in samples with more complete reactions and formation of glassy and/or crystalline phases that have better leach resistance. However, complete melting gives a sample that is hard to contain (may react with the sample container and not release without chipping or breaking of the sample and/or the container). Also, complete melting goes against the RocTec philosophy of a “free standing” waste form. The “free standing” requirement is to avoid operating conditions and equipment associated with complete melting, i.e., vitrification. (b) Inhomogeneous mixing during processing probably leads to pockets of material that never completely dissolve in the glass matrix structure. The PbO level in the ash is quite high at 5.76 weight %. This level was the second highest metal component after ZnO (25.13 %); (not counting SiO₂ at 53.72 %) and if not mixed properly, unreacted pockets of PbO could be left within the sample. Therefore, processing parameters that give variations that need strict control are: (a) Degree of mixing of PbO with the other components, (b) Particle size of all components being small enough (degree of grinding) to ensure good reactivity.

6.2 Discussion of Task 2 and Task 3 Results

It was known, from information provided by the INEEL, that there was a high lead and zinc content in WERF ash. This analysis placed the lead content at about 4.5 % with zinc at 19.5 % which is in good agreement with the analysis conducted by Starmet at Mountain States Analytical. However, it was not well known how the lead content was distributed among the various possible lead compounds. X-ray

Diffraction (XRD) analysis at INEEL (reported by Vince Maio – dated 9/17/97) indicated most of the ash was amorphous (possibly some sort of glass), but minor amounts of Anorthite [Na₆Pb₄Cl₂(SO₄)₆], Spencerite [Zn₄(PO₄)₂(OH)₂ · 3 H₂O], KNaPb₈(PO₄)₆, Zn(SiO₄)₇, and PbCl₂ were present. Anions of Cl, SO₄, and PO₄ were identified (analysis assumed to be via a dissolution technique, but solution type was not stated). XRD data from analysis performed at the Southwest Research Institute indicated that calcination in air to 450 °C caused some of the amorphous (glassy) majority to crystallize since the 450 °C sample was about 80 % crystalline. The crystalline portion of this sample consisted of about 30 % cotunnite (PbCl₂), 30% KAlSiO₄, 10% wurtzite (ZnS), 10% Pb₃SiO₅, 10% willemite (Zn₂SiO₄), 5 % lead metal, and a trace (<5%) each of Susannite [Pb₄(CO₃)₂SO₄(OH)₂] and litharge (PbO).

The 550 °C sample was about 80% crystalline. The various components of the sample seems to be reacting since it consisted of 50% willemite (Zn₂SiO₄), 25% K₂ZnCl₄, 10% K₂Pb₃O₆, 5% Pb₃(CO₃)₂(OH)₂ and a trace (<5%) each of cotunnite (PbCl₂), Pb₃C₂O₇, Zn₃CO₃(OH)₆ · H₂O, Zn₂PbO₄, and Pb₃C₂O₇.

The “EPA Method SW846-3050” (digestion in nitric and hydrochloric acid followed by ICP) analyses performed by Mountain States Analytical (MSA) yielded a high level of lead (46,420 mg/kg = 4.64 %) and 172,700 mg/kg (17.2 %) for zinc. The lithium metaborate fusion analyses by MSA yielded a lower lead value of 258.4 mg/kg, but lead salts could have been volatilizing from this test. In addition, we know from the anion scan performed by MSA that there is a high chloride (169,000 mg/kg) and sulfate (122,000 mg/kg) content in WERF ash.

We originally assumed, since lead was volatilizing when calcining untreated WERF ash, that the volatile lead most probably was in the form of lead chloride rather than lead sulfate, anorthite $[\text{Na}_6\text{Pb}_4\text{Cl}_2(\text{SO}_4)_6]$, $\text{KNaPb}_8(\text{PO}_4)_6$, or lead oxide (or hydroxide). This was because lead chloride has a lower melting point than the other probable lead compounds, and lead chloride is known to be very volatile (has a high vapor pressure). But we also knew that some lead was present in one or more of the less volatile compounds.

The solubility tests on lead chloride and lead sulfate indicated that the first set of pretreatment tests at Starmet CMI dissolved some of the lead, but more water probably was needed to be sure that all the lead chloride, that might be present, would be dissolved. We estimated (1 gallon mill jar about 70 vol % filled with steel media packed at 60 vol % packing density) that a maximum of about 2 Liters of water was used in the previous tests for 500 grams of WERF ash. The highest chemical analysis data obtained from Mountain States Analytical showed 46,420 mg/kg of lead in WERF ash. We assumed the analyte was reported as lead oxide (223.2 g/mole) which is approximately the weight for lead chloride (278.1 g/mole). By doing some simple math, we find that the solubility level of 0.990 g lead chloride per 100 cc of water translates into 2.34 L of water needed to dissolve all the lead from a 500 g sample of WERF ash (4.6 % lead chloride). The water needed might be as high as 4.68 L (1.24 gallons), based on our experimental observations of needing 200 mL of water for a 1 g sample of lead chloride for certain dissolution within 1 hour.

Using the chemical analyses, we concluded that experiments, after the first set, needed to use more water (at least 4.68 L for a 500 g WERF ash sample) to assure dissolution of the maximum predicted amount of lead chloride. The dissolution/precipitation experiments conducted at Starmet CMI gave no evidence for incomplete precipitation of soluble lead from the water solution when ammonium hydroxide or sodium hydroxide was used.

More water was used in the second set of experiments. However, no marked improvement was noted in the off-gas tests. The Table 2 value for Pb (46,420 mg/kg = 46.42 mg/g) can be compared to the amount of lead dissolving in the water leach step in the pre-treatment procedure (see Table 12). This amount of Pb can be calculated as:

$29 \mu\text{g of Pb /ml} \times 235 \text{ ml} = 6815 \mu\text{g of Pb} \div 25 \text{ g of ash} = 272.6 \text{ g of Pb/g of ash} = 0.273 \text{ mg/g of ash.}$

The amount of Pb dissolving / Pb present in ash = $0.273 \text{ mg/g} \div 46.42 \text{ mg/g} = 5.87 \times 10^{-3} = 0.587 \text{ \%}.$

This calculation is a very strong indication that the lead probably was present in the WERF ash as a relatively insoluble compound [such as glass, lead sulfate (PbSO_4), anorthite $[\text{Na}_6\text{Pb}_4\text{Cl}_2(\text{SO}_4)_6]$, $\text{KNaPb}_8(\text{PO}_4)_6$, or lead oxide (or hydroxide)]. The chloride content most likely is due to other very soluble compounds [such as zinc chloride (ZnCl_2)] as verified in the following calculations:

$3476 \mu\text{g of Zn /ml} \times 235 \text{ ml} = 816,860 \mu\text{g of Zn} \div 25 \text{ g of ash} = 32674.4 \text{ g of Zn/g of ash} = 32.67 \text{ mg/g of ash.}$

The amount of Zn dissolving / Zn present in ash = $32.67 \text{ mg/g} \div 172.70 \text{ mg/g} = 0.1891 = 18.91 \text{ \%}.$

7. CONCLUSIONS

The RocTec process was used to successfully treat a simulated WERF ash made from a mixture of metal oxides. The resulting ceramic pellets passed the TCLP test when the simulated WERF ash was mixed with from 20 to 50 % kaolin clay and fired to 1100 °C. Consideration of “fritting rules” indicated the mixtures generally could tolerate considerably more flux (e.g., Na₂O, K₂O, and CaO) content. The TCLP leach results were inconclusive in pointing out compositional trends with regard to ratios of network modifiers, intermediate glass formers, and network glass forming metal oxides.

The RocTec process was then used to treat real WERF ash using kaolin clay, and ceramic pellets were produced that passed the TCLP test. However, unacceptable amounts of RCRA metals (e.g. lead) were volatilized during the high temperature firing portions of the RocTec process. Chemical analyses pointed to problems with high lead and zinc metal content in the ash as well as high chloride and sulfate anion content. It was originally assumed that the volatile lead most probably was in the form of lead chloride rather than lead sulfate, or other minority crystalline phases identified in the WERF ash using x-ray diffraction. However, subsequent water-based chemical pre-treatments (using ammonium hydroxide, sodium hydroxide, sodium carbonate, or calcium carbonate) intended to convert the lead chloride into less volatile forms (such as lead hydroxide or lead carbonate) failed to greatly improve the gas phase losses during firing. Precipitation experiments showed the pre-treatments should have been effective in the conversion if the lead was actually being dissolved in the water.

A water solubility test indicated that less than 1 % of the Pb found in the as-received WERF ash was being dissolved. About 19 % of the available zinc was being dissolved. Therefore, it was concluded that the lead must be contained in water-insoluble, yet volatile form. Other metals were present as the chlorides (e.g., zinc chloride). It was further concluded that the Pb must be primarily trapped in a water-insoluble amorphous “glass” or in crystalline phases of low water solubility. This was based upon x-ray diffraction evidence that revealed large amorphous (i.e., glassy) peaks and only minor amounts of Pb containing compounds (e.g., anorthite [Na₆Pb₄Cl₂(SO₄)₆] and [KNaPb₈(PO₄)₆]). The x-ray diffraction did not detect lead sulfate (PbSO₄) but did detect minority amounts of other crystalline compounds (anorthite [Na₆Pb₄Cl₂(SO₄)₆] and [KNaPb₈(PO₄)₆]) that contained lead. The lead sulfate has low water solubility and the other compounds should also be much less soluble in water than lead chloride. Based upon melting points, the lead sulfate and anorthite are predicted to have low Pb vapor pressures.

Upon calcination the glassy phase crystallizes into a variety of compounds, some of which are lead containing compounds (e.g. Pb metal, cotunnite (PbCl₂), Pb₃SiO₅, susannite [Pb₄(CO₃)₂SO₄(OH)₂], litharge (PbO), K₂Pb₃O₆, Pb₃(CO₃)₂(OH)₂, Pb₃C₂O₇, Zn₂PbO₄, and Pb₃C₂O₇). It is obvious from the water trap analyses that some of these compounds are decomposing and evolving very volatile lead species during calcination.

Therefore, it was concluded that, in as-received WERF ash, the majority of the lead is chemically bound in a water insoluble amorphous “glassy” phase. This amorphous phase is either volatile itself, or decomposes into some crystalline phases that are quite volatile at temperatures 550 °C. More work would be needed to develop procedures to convert the as-received WERF ash material into a compound of low lead volatility. Assuming considerable lead is trapped in a water-insoluble “glass”, this glass did not release the Pb when the pH was reduced to 3.0 using HCl acid (based upon the first set of ammonium hydroxide precipitation experiments).

As a result of these complications in dealing with the WERF fly ash, Starmet recommends termination of this program at this stage of progress. If one of the other low temperature

stabilization techniques involved in this comparative evaluation program is successful, then the added complexity of the RocTec process pre-treatment steps is not justified. If the low temperature stabilization techniques do not prove successful, further development of the RocTec pre-treatment process could be investigated.

APPENDIX A

Task 0 - Surrogate Ash Testing

This task was accomplished at TRIOX, Inc. of Murray, Utah.

A.1 Experimental Procedures

An analysis of WERF Ash was obtained from INEEL. The majority constituents along with the RCRA metals are shown in Table A1. The second column contains data obtained from INEEL on Drum 96-WERF-097.

Table A1: The Composition Of WERF Fly Ash

Elemental Composition		Concentration (ppm on an elemental basis) ¹	Composition of Surrogate Ash (%) ²	UHC Allowable Levels (mg/liter)
Alumina	(Al ₂ O ₃)	1,540	0.29	
Antimony	(Sb ₂ O ₃)	3,680	0.44	2.100
Arsenic	(As ₂ O ₃)	59	0.01	5.000
Barium	(BaO)	180	0.02	7.600
Beryllium	(BeO)	0.04	NA ³	
Cadmium	(CdO)	875	0.10	0.190
Calcium	(CaO)	7,870	1.11	
Chromium	(Cr ₂ O ₃)	517	0.08	0.860
Cobalt	(CoO)	29	NA	
Copper	(CuO)	1,570	0.20	
Iron	(Fe ₂ O ₃)	17,400	2.50	
Lead	(PbO)	53,200	5.76	0.370
Magnesium	(MgO)	1,020	0.17	
Manganese	(MnO)	605	0.10	
Mercury	(HgO)	0.31	NA	
Nickel	(NiO)	701	0.09	
Potassium	(K ₂ O) ⁴	55,800	6.75	
Selenium	(SeO ₂) ⁵	8	0.01	0.160
Silica	(SiO ₂)	537,200	53.72	

Silver	(AgO) ⁵	163	0.02	0.300
Sodium	(Na ₂ O)	25,900	3.51	
Thallium	(Th ₂ O)	3	NA	0.078
Vanadium	(V ₂ O ₃)	9	NA	
Zinc	(ZnO)	201,000	25.13	5.300
Carbon	(C)	~20%	NA	
LOI		~3%	NA	

Notes For Table A1: The Composition Of A WERF Fly Ash

1. The composition is given on an elemental basis.
2. Carbon and LOI are deleted from the surrogate composition that was formulated. Also, all metal ions are assumed to be present as oxides.
3. NA indicates that this compound was not added to the surrogate ash
4. Added as the hydroxide.
5. Added as the compound AgSe₂.

Table A2, as shown below, uses the batch composition from Table A1 to recalculate the metal ion concentration on a parts per million weight basis, (ppm). This recalculation is necessary so that the numbers shown in the batch composition will correspond with the TCLP leach values, which are usually given in milligrams of metal ion per kilograms of total weight of sample. Thereby, the leached amount of RCRA metal can be compared directly with the total amount of RCRA metal in the surrogate batch.

Table A2: Metal Ion Concentration In The Surrogate Ash

	Batch	Molecular	Molecular		Weight	Weight	Weight of	Weight of
	Weight %	Weight of	Weight of	Total	Fraction of	Fraction of	Metal Ion	Oxygen Ion
Metal Ion	(as oxide)	Metal Ion	Oxygen Ion	Weight	Metal Ion	Oxygen Ion	(ppm)	(ppm)
Aluminum	0.29	54	48	102	0.53	0.47	1535	1365
Antimony	0.44	244	48	292	0.84	0.16	3677	723
Arsenic	0.01	150	48	198	0.76	0.24	76	24
Barium	0.02	137	16	153	0.90	0.10	179	21
Beryllium	0.00	11	16	27	0.41	0.59	0	0
Cadmium	0.10	112	16	128	0.88	0.13	875	125
Calcium	1.11	40	16	56	0.71	0.29	7929	3171
Chromium	0.08	104	48	152	0.68	0.32	547	253
Cobalt	0.00	59	16	75	0.79	0.21	0	0
Copper	0.20	64	16	80	0.80	0.20	1600	400
Iron	2.50	112	48	160	0.70	0.30	17500	7500
Lead	5.76	106	16	122	0.87	0.13	50046	7554
Magnesium	0.17	24	16	40	0.60	0.40	1020	680

Manganese	0.10	55	16	71	0.77	0.23	775	225
Mercury	0.00	201	16	217	0.93	0.07	0	0
Nickel	0.09	59	16	75	0.79	0.21	708	192
Potassium	6.75	78	16	94	0.83	0.17	56011	11489
Selenium	0.01	79	32	111	0.71	0.29	36	14
Silicon	53.72	28	32	60	0.47	0.53	250693	286507
Silver	0.02	108	16	124	0.87	0.13	131	19
Sodium	3.51	56	16	72	0.78	0.22	27300	7800
Thallium	0.00	204	16	220	0.93	0.07	0	0
Vanadium	0.00	51	48	99	0.52	0.48	0	0
Zinc	25.13	65	16	81	0.80	0.20	201660	49640
	<u>100.00</u>						<u>622297</u>	<u>377703</u>

Table A3 shows the expected radiological components in the WERF ash.

Table A3: Isotopic Composition Of WERF Fly Ash

<u>Radiologic Components</u>	<u>Activity (micro curies/gram)</u>
Alpha	0.00401
Am-241	0.0000209
Beta	0.0185
C-14	0.000001
Co-58	0.0000428
Co-60	0.0138
Cs-134	0.000031
Cs-137	0.00913
Eu-152	0.000233
Eu-154	0.000177
Fe-55	0.0061
Mn-54	0.0000601
Nb-95	0.0000163
Ni-63	0.0341
Pu-238	0.000215
Pu-239	0.0000228
Sb-125	0.000163
Sr-90	0.00418
Tc-99	0.00217
Th-228	0.00000325
Th-230	0.000018
Th-232	0.0000053
U-233	0.00135
U-234	0.000882
U-235	0.000079
U-236	0.0000291
U-238	0.00535
Zn-65	0.0000918

The radiologic components were not added to the surrogate ash, but are given here for reference.

Sample Preparation

Using the composition given in Table A1, a surrogate ash was formulated by normal ceramics processing techniques (The process was previously described in the Test Plan.). The same processing steps and treatments were used with the surrogate ash: mixing of reagents, calcination, grinding, pressing, and finally sintering of a freestanding waste form.

There are three primary process variables that can be used in making a leach resistant product:

1. **Inorganic reagent.** These reagents are selected from various aluminosilicates and the composition is usually determined by the composition of the waste being treated. The goal is to select reagent that will react with the waste to form thermodynamically stable crystalline phases or glasses that are not susceptible to leaching by ground water. The high levels of silica, zinc, soda and potassium in the WERF ash means that low viscosity glass phases will be preferred over crystalline phases.
2. **Quantity of Reagent.** The amount of these reagents additions can also be varied to force the overall composition into a phase region that is more stable. In addition, if there is difficulty dealing with a particular RCRA metal a reagent can possibly be selected to bind that metal in a leach resistant phase.
3. **Firing Temperature.** The maximum firing temperature can also be adjusted to impart stability to the waste.

For this study we selected three inorganic reagents, a plastic kaolin, alumina, and a basaltic type soil. The percent waste loadings varied from 100% down to 50%. (Waste loading is defined as the weight of surrogate ash divided by the sum of the weight of surrogate ash plus the weight of reagent additions.) The range of temperatures investigated was between 800°C and 1,200°C.

Test samples were prepared by mixing the reagents and the surrogate ash by aqueous ball milling. The mixing time was 30 minutes. After drying the slurry, this powder was ground in an attritor mill for 2 hours. An organic binder was added to the batch during the last 10 minutes of grinding. This powder was dried, screened, and pressed into pellets at 8,000 psi uniaxial pressure. The pellets were then fired in an air furnace. Heating rates were controlled at 10°C / minute. The time at temperature was 1 hour.

The following measurements were used to evaluate the process and the quality of the compositions tested:

1. final density by the Archimedes technique
2. volume reduction of the waste
3. weight loss to determine if waste components are volatile during any process step
4. leach resistance using the TCLP Leach test

A.2 Test Results

The physical property measurements which include compositions, maximum firing temperatures, density, volume reduction and weight loss measurements are shown in Section 3.1. The leach resistance results are shown in Section 3.2. In addition to these measures a phase analysis has begun on a limited number of samples along with optical microscopy and scanning electron microscopy. The results of the phase analysis work is shown Section 3.3.

A2.1 Physical Property Data

The physical property data taken to date is shown below in Table A4.

Table A4: Physical Property Data On Processed Surrogate Ash

Sample Number	TCLP Sample #	Composition % Additives ¹	Temperature (°C)	Density (grams/cm ³)	% Weight Loss	% Volume Reduction
404	1042	0% Additive	800	2.03	12.3	12.9
405	1043	5% E	800	1.98	10.3	8.9
406		10% E	800	1.71	9.9	3.3
407		20% E	800	1.53	10.7	0.1
408		30% E	800	1.49	11.6	0.3
409		50% E	800	2.15	12.6	3.0
410	1044	5% A	800	2.33	9.7	12.9
411	1045	10% A	800	2.29	8.8	12
412	1064	20% A	800	2.29	8.3	10.8
413	1065	30% A	800	2.13	8.0	9.0
414	1066	50% A	800	1.85	6.7	2.6
426	1071	0% Additive	900	1.56	12.7	6.2
427	1053	5% E	900	2.49	10.5	15.4
428	1054	10% E	900	2.04	9.9	8.5
429		20% E	900	1.75	11.2	4.1
430		30% E	900	1.62	11.9	2.4
431	1055	50% E	900	1.70	12.9	5.2
432	1073	5% A	900	2.54	9.4	15.1
433		10% A	900	2.68	8.6	16.7
434		20% A	900	2.63	9.0	14.4
435	1056	30% A	900	2.57	7.3	13.6
436	1074	50% A	900	2.14	5.1	5.0
437	1067	0% Additive	850	1.70	13.1	8.9
438	1068	5% E	850	2.10	10.3	10.8
439		10% E	850	1.78	9.6	4.8
440		20% E	850	1.60	9.8	1.2
441		30% E	850	1.51	11.9	1.0
442		50% E	850	1.60	12.9	4.4
443		5% A	850	2.39	8.6	13.4
444		10% A	850	2.41	9.2	13.8
445	1046	20% A	850	2.41	8.2	12.3
446	1047	30% A	850	2.39	7.7	11.3
447	1070	50% A	850	2.09	6.2	4.4
450	1083	0% Additive	1000	1.69	14.8	9.8
451	1086	5% E	1000	2.36	10.3	14.8
452	1087	10% E	1000	2.74	9.9	18.1
453	1088	20% E	1000	2.77	10.6	17.4
454	1089	30% E	1000	2.06	11.6	10.6
455		50% E	1000	2.13	12.5	12.4
456	1090	5% A	1000	1.67	9.0	4.4
457	1094	10% A	1000	1.91	9.0	9.1
458	1095	20% A	1000	2.69	8.3	16.4

459	1096	30% A	1000	2.60	7.9	15.2
460	1097	50% A	1000	2.02	7.0	5.4
472	1075	0% Additive	1100	N/A ²	12.77	N/A
473	1077	5% E	1100	N/A	10.23	N/A
474	1078	10% E	1100	N/A	9.88	N/A
475	1049	20% E	1100	1.90	10.90	9.7
476	1050	30% E	1100	2.37	11.67	16.5
477	1051	50% E	1100	2.66	12.76	18.5
478	1079	5% A	1100	N/A	9.08	N/A
479	1080	10% A	1100	N/A	9.14	N/A
480	1081	20% A	1100	1.87	8.45	7.3
481	1052	30% A	1100	2.79	7.94	15.8
482	1082	50% A	1100	2.15	5.76	4.9
483		0% Additive	1200	N/A	N/A	N/A
484		5% E	1200	N/A	1.11	N/A
485	101	10% E	1200	N/A	9.80	N/A
486		20% E	1200	N/A	10.70	N/A
487		30% E	1200	N/A	11.60	N/A
488		50% E	1200	N/A	12.80	N/A
489		5% A	1200	N/A	9.10	N/A
490	1092	10% A	1200	N/A	9.10	N/A
491	1093	20% A	1200	N/A	8.30	N/A
492		30% A	1200	1.93	8.00	7.5
493	1048	50% A	1200	2.53	5.80	11.1
520	1061	5% S	800	2.42	9.00	14.3
521	1062	10% S	800	2.73	8.00	15.6
522	1063	20% S	800	2.17	7.00	12.2
523		30% S	800	N/A	6.00	8.8
524		50% S	800	N/A	5.00	3.2
525		5% S	900	N/A	9.00	5.1
526	1072	10% S	900	N/A	8.00	9.6
527	1059	20% S	900	N/A	7.00	15.6
528	1060	30% S	900	2.67	6.00	16.6
529		50% S	900	N/A	5.00	5.7
530		5% S	1000	N/A	9.00	6.9
531		10% S	1000	N/A	8.00	4.5
532	1084	20% S	1000	N/A	7.00	5.3
533	1085	30% S	1000	N/A	6.00	9.4
534		50% S	1000	2.70	5.00	17.1
535		5% S	1100	N/A		N/A
536		10% S	1100	N/A		N/A
537		20% S	1100	N/A		N/A
538	1076	30% S	1100	N/A		N/A
539		50% S	1100	1.89		N/A

Notes for Table A3:

1. The three different reagents added to the surrogate as are designated as “A”, “E”, and “S” correspond with alumina, EPK, and a basaltic soil.

2. A “N/A” indicates that the measurement could not be performed. The most common cause was sample distortion coupled with a “sponge” like internal structure.

There are several trends that can be seen in the tabulated data in Table A3:

1. The sample that contain no inorganic reagents have measured weight losses of 12.3, 12.7, 13.1, 14.8 and 12.8 percent respectively; for an average weight loss of 13.14%.
2. There is a trend towards lower weight loss with increasing amounts of reagent additives. (This is expected since the reagents do not add to the observed weight loss.)

To understand the weight loss data an experiment was conducted on the surrogate ash composition. The ash contained no binders. The weight loss trend is shown in Figure A1.

Figure A1: Weight Loss On Firing The Surrogate Ash

From Figure A1 two weight loss regions can be seen. The first region extends from room temperature to about 400°C and the second weight loss region extends from about 400°C to about 600°C. Above 600°C we cannot detect any significant weight loss. This result is significant in that the components of the fly ash, some of which are volatile, are stabilized by the RocTec process.

We have now identified three principle sources of weight loss:

- the binder content in each pellet
- the adsorbed water in the powder
- the chemically bound water in the potassium hydroxide and the sodium hydroxide

A2.2 Leach Tests and Results

The leach test results are shown in Table A5 for the RCRA metals actually included in the surrogate ash.

Table A5. Surrogate Ash TCLP Results

#	Dopant	% Conc.	Temp. °C	Antimony 2.100 ¹ 3,677 ²	Arsenic 5.000 ¹ 76 ²	Barium 7.600 ¹ 179 ²	Cadmium 0.190 ¹ 875 ²	Chromium 0.860 ¹ 547 ²	Lead 0.370 ¹ 17,500 ²	Selenium 0.160 ¹ 36 ²	Silver 0.300 ¹ 131 ²	Zinc 5.300 ¹ 201,660 ²
1042	O ³	0	800	0.280	0.054	0.088	0.320	0.076	7.400	0.018	0.021	344.00
1043	E ⁴	5	800	0.240	ND	0.220	0.440	0.036	16.000	0.007	0.045	179.00
1044	A ⁵	5	800	0.350	0.014	0.180	0.420	0.086	12.000	0.042	0.023	172.00
1045	A	10	800	0.330	0.012	0.220	0.380	0.100	10.000	0.043	0.009	143.00
1046	A	10	850	0.120	ND	0.100	0.140	0.055	5.800	0.024	ND	48.00
1047	A	20	850	0.120	ND	0.120	0.230	0.098	8.300	0.048	ND	57.00
1048	A	50	1200	0.061	ND	0.130	0.022	0.002	1.300	0.015	ND	0.84
1049	E	20	1100	ND	ND	0.780	0.034	ND	0.690	0.031	ND	22.00
1050	E	30	1100	ND	ND	1.600	0.029	ND	0.700	0.030	ND	17.00
1051	E	50	1100	ND	0.006	0.120	0.007	ND	0.340	0.007	ND	3.30
1052	A	30	1100	0.028	ND	0.090	0.021	ND	0.710	0.033	ND	9.60
1053	E	5	900	0.027	0.007	0.092	0.088	0.053	5.000	0.031	ND	27.00
1054	E	10	900	0.063	0.130	0.190	0.360	0.052	2.100	0.022	ND	52.00
1055	E	50	900	0.068	0.006	0.120	0.072	0.006	2.900	0.022	ND	3.30
1056	E	30	900	0.024	ND	0.100	0.070	0.012	2.400	0.025	ND	27.00
1057	S ⁶	50	1100	ND	ND	0.300	0.023	ND	0.680	0.053	ND	18.00
1058	S	50	1000	ND	ND	0.190	0.031	ND	0.810	0.010	ND	14.00
1059	S	20	900	0.025	0.021	0.110	0.059	ND	1.900	0.011	ND	30.00
1060	S	30	900	ND	ND	0.270	0.086	0.002	2.500	0.013	ND	42.00
1061	S	5	800	0.097	ND	0.160	0.220	0.043	6.500	ND	ND	154.00
1062	S	10	800	0.088	ND	0.120	0.240	0.049	8.700	0.012	ND	132.00

1063	S	20	800	0.043	ND	0.340	0.360	0.093	13.000	0.004	0.011	134.00
1064	A	20	800	.14	ND	0.13	0.43	0.085	9.6	0.038	0.012	158
1065	A	30	800	.2	ND	0.17	.68	.045	15	.005	ND	239
1066	A	50	800	.23	ND	.14	.58	.058	14	.13	ND	226
1067	O	0	850	.024	ND	.15	.7	.031	5.2	ND	ND	103
1068	E	5	850	.063	ND	.13	.29	.065	9.3	.015	.015	111
1069	A	30	850	.018	ND	.15	.29	.086	8.4	.009	ND	66
1070	A	50	850	.069	ND	.12	.64	.047	19	ND	ND	177
1071	O	0	900	.01	ND	.15	.078	.014	3	.011	ND	55
1072	S	10	900									
1073	A	5	900									
1074	A	50	900									
1075	O	0	1100									
1076	S	30	1100									
1077	E	5	1100									
1078	E	10	1100									
1079	A	5	1100									
1080	A	10	1100									
1081	A	30	1100									
1082	A	50	1100									
1083	O	0	1000									
1084	S	20	1000									
1085	S	30	1000									
1086	E	5	1000									
1087	E	10	1000									
1088	E	20	1000	ND	ND	.097	.2	.012	.31	ND	.021	109
1089	E	30	1000	ND	ND	.076	.71	.006	10	ND	ND	252
1090	A	5	1000	ND	ND	.19	.21	ND	2.7	ND	ND	189
1091	E	10	1200	ND	ND	.16	.14	.024	2	ND	ND	16.3
1092	A	10	1200	.012	ND	.085	.029	ND	.96	.095	ND	36
1093	A	20	1200	.034	ND	.078	.022	ND	.96	ND	ND	16
1094	A	10	1000	.021	ND	.12	.066	ND	1.8	ND	ND	41
1095	A	20	1000	.026	ND	.2	.059	ND	1.5	ND	.013	28
1096	A	30	1000									
1097	A	50	1000									

Notes for Table A5:

1. UHC allowable levels of RCRA metals.
2. Actual ppm levels of metal ions added to the surrogate ash. These levels are proportionally lower with the weight % additions of reagent additives.
3. Beryllium; Mercury; and Vanadium were not included in the surrogate ash and therefore not included in Table A1.
4. Thallium also was not added to the batch, but in five samples there was a detectable amounts found.

A2.3 Phase Analysis

Selected samples were submitted for powder x-ray diffraction analysis. A representative x-ray diffraction plot is shown in Figure A2, on the next page. The peak intensities and 2-theta values were then compared with the library values. The following crystalline phases were identified: silica in the form of quartz; zinc silicate in the mineral form of Willemite. About 92% of the crystalline components can be accounted for by these two phases. The remainder is probably composed of an aluminosilicate.

There is a glassy phase also present in the samples as seen by the amorphous hump in Figure A2 between 2-theta values of 20 to about 40 degrees 2-theta. The glass is estimated to accounts for about 25% of the sample.

Lead oxide, potassium oxide, sodium oxide are present in quantities greater than 5%, but X-ray diffraction could not detect the presence of these compounds or phases containing these compounds. And, since there is excess silica, as evidenced by the quartz in the sample, it is presumed that these compounds are dissolved in the glass phase.

Figure A2: X-ray Diffraction Pattern For A Fired Sample

A.3 Discussion of Results

The results as shown in the previous section are mostly tabulated values. However, there are trends that can be seen in the data. The specific measures or variables that were investigated are listed below:

- a. Composition and amount of reagent additions to the surrogate ash
- b. Maximum firing temperatures
3. Density of the fired waste
- d. Volume reduction
5. Weight loss measurements
- f. Leach resistance by TCLP

As expected, each of these variables are not independent. So, the firing temperature, density, volume reduction, and weight loss experiments will be discussed together.

A3.1 Composition

The large amounts of silica present in the WERF ash (> 50 weight %) suggest that no additional silica should be needed to form a network glass structure or for the formation of crystalline aluminosilicates.

Indeed, it was found that even 50% alumina additions to the surrogate ash there was still free silica present in the final waste form as crystalline quartz. Therefore, the compositions containing the basaltic soil and the plastic kaolin clay did not add significantly to the stability of the waste.

The alumina additions did seem to balance the large amounts of silica and proved to be a useful reagent. Except for a minor phase, the x-ray diffraction data shows that the alumina did not appear in any crystalline form. The bulk of the alumina is certainly contained in the glass phase. Generally, alumina additions to glass impart durability (less susceptible to chemical reaction with water), lower viscosity, and a wider range of processing temperatures.

Further investigations on surrogate ash will be conducted with alumina as the primary inorganic reagent. Minor glass modifiers will be added to enhance further the durability of glass phase.

A3.2 Firing Temperature, Density, Volume Reduction, and Weight Loss

The maximum firing temperature for a particular sample is limited by the temperature when the sample can no longer hold its shape and the sample slumps or even melts. As reagents are added to the surrogate ash the maximum firing temperature increases. This was the case for all three reagents. Alumina was the most effective at extending the temperature range of the samples.

In general, the sample with the highest densities were the ones fired at the highest temperatures and contained the largest amount of reagent additions. Under fired samples contained a large amount of porosity. The overfired samples also showed significant porosity. This led to the fact that the volume reduction that we had expected was not seen in the data. In every sample there was some significant amount of porosity. The weight loss data shows that the weight loss was essentially complete by 500°C. That meant that the conditions leading to porosity was a processing issue; one that occurred at low temperatures.

When the firing cycle was interrupted there was small amounts of large size porosity evident at 400°C. This kind of porosity was the cause of excessive bloating at temperatures greater than 1,000°C. As the glass formed, at relatively low temperatures, the gas filled pockets could expand as the temperature increased.

The fix for this problem is in understanding the low temperature portion of the firing process. Even though the surrogate ash contained small quantities of volatiles (water and organic binders), these volatiles along with the glass from the sample interfere with the firing process. Recognizing these factors a new batch of surrogate ash was formulated by the same techniques as the first batch, but involved a more rigorous and detailed calcination step. The first sample had a waste loading of 70%, with alumina as the reagent composing the rest of the sample fired to a density of 2.95 grams / cm².

Under 100x in a microscope the sample surface showed some porosity the interior showed only a minor amount of porosity. Three phases can be identified visually, but there is very little contrast between the phases to reproduce here.

3.3 Leach Resistance As Measured By TCLP

The leach resistance of the samples is effected principally by temperature and composition. Table A5 shows some trends in the data. In general, it is observed that the leach rate decreases with as the firing temperature increases. This is particularly the case for temperatures 1,000°C and above. At temperatures below 1,000°C the leach results seem more random.

In all cases the leach rate of the RCRA metals decrease significantly with increasing temperature.

A.4 Conclusions

It has been demonstrated that this process can deal with relatively large quantities of UHC metals.

A summary of the conclusions are listed below:

1. Sample number 1051 passed all UHC requirements.
2. Excluding zinc, for which there are separate land disposal regulations, the following metals passed the UHC requirements in all 38 tests: Antimony, arsenic, barium, selenium, and silver. Chromium passed in 37 of the 38 tests. Cadmium passed in one half of the tests. Lead passed in 2 of the tests, which is rather remarkable since it was present in large quantities. A change in calcination procedures and a change in reagent additives is expected to more easily stabilize lead. This will be confirmed shortly.
3. Increasing the firing temperature lowers the leach rate of the samples.
4. Increasing the concentration of additives lowers the leach rate of the samples.
5. Calcination is an important processing step. If properly performed the density and volume reduction along with enhanced leach behavior is expected.

APPENDIX B

Development of Additional Pretreatment Procedures

This work was accomplished at Starmet Corporate Research Labs in Concord, MA. It was intended to develop a pre-treatment method for WERF ash to supplant the pre-treatment methods.

B.1 Background

The WERF material to be investigated in this program is a mixed waste containing radioactive isotopes and toxic heavy metals. The results from chemical analysis of the material indicates that 15% of the material is chlorine, present as chloride ion and 20% of the material is a mixture of toxic heavy metals. The remainder of the WERF material is radioactive isotopes and inert materials.

In prior efforts to produce an aggregate, meeting the requirement for safe waste disposal, there was a significant loss of toxic heavy metals at the ignition temperature of 1250 °C that is necessary to produce a stable unleachable aggregate. To prevent the loss of the toxic heavy metals, a significant secondary waste treatment would be necessary. Other investigators have looked at procedures involving prior partial dissolution and reprecipitation to prepare the material for high temperature ignition.

B.2 Objective

The basic premise of the investigation at Concord, is that the loss of the toxic heavy metals is because the toxic metals are present in the form of chlorides. Many of the metal chlorides have significant vapor pressures at well below the required 1100°C ignition temperature to produce a stable, unleachable aggregate. Since volatile toxic metal chlorides may be the key to the solution of the WERF material, this investigation has concentrated on eliminating the chloride ion in the WERF material. Procedures to be investigated, were the oxidation of chloride ion to either chlorine gas or an oxychloride or the formation of hydrogen chloride gas and its volatilization.

B.3 Experimental Procedures

The necessary equipment was obtained from Ace Glass. The following is a listing of the equipment and catalogue numbers:

1. Adapter, Gas Inlet - #5190-10 (24/40)
2. Flask, Filtering, Heavy Wall, 500ml #6979-10 or 250ml #6979-05
3. Funnel, Pressure Equalizing (1:5) 125ml #7285-35(24/40)
4. Stopper, Full Length #8250-12 (24/40)
5. Bottles, Gas Washing (2) (29/42) 250ml #7166
6. Hot Plate with Magnetic Stirrer

Because of time constraints some of the experiments were run before the optimum equipment was available.

Since the Concord Starmet facility is not licensed to work with radioactive isotopes, this program will use surrogate materials in its investigation. The surrogate material will contain the chlorides of four toxic heavy metals - Sb, Cd, Pb and Zn. In two of the surrogates the radioactive isotopes and inert materials will be represented by either Na_2SiO_3 or Na_2SO_4 .

The following three WERF surrogates were prepared.

WERF Surrogate #1:	SbCl_3	46.84 gms
	CdCl_2	40.77
	PbCl_2	33.56
	ZnCl_3	52.12
	Na_2SiO_3	<u>326.71</u>
		500.00

WERF Surrogate #2:	SbCl_3	46.84 gms
	CdCl_2	40.77
	PbCl_2	33.56
	ZnCl_2	<u>52.12</u>
		173.29

WERF Surrogate #3:	SbCl_3	9.37 gms
	CdCl_2	8.15
	PbCl_2	6.71
	ZnCl_2	10.42
	Na_2SO_4	<u>65.35</u>
		100.00

This program was limited to investigating the elimination of the chloride in surrogate WERF materials. If the investigation of the surrogate WERF material indicates that the chloride ion elimination is a viable pretreatment, further investigation can be carried out at CMI using actual WERF material.

It was decided to investigate four chemical agents. The chemicals investigated were: ammonium persulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, potassium persulfate $(\text{K}_2\text{S}_2\text{O}_8)$, hydrogen peroxide (H_2O_2) , and concentrated sulfuric acid (H_2SO_4) . The investigation was limited to these four chemicals based on time constraints and prior experience with these chemicals. Chemical thermo-dynamic¹ data indicated the feasibility of these reagents.

Place a weighed portion of an appropriate WERF surrogate into the filtering flask. If using either of the two persulfates add appropriate weighed portions and mix by shaking the filtering flask. Connect the filtering flask into the apparatus assembly. Make the flexible tubing connection from the Nitrogen (N_2) tank to the gas inlet adapter. Add 100ml of distilled water to each of the gas washing bottles and connect the flexible tubing to the bottles to the side arm of the filtering flask. Flush the system gently with N_2 observing a small stream of bubbles in the gas washing bottles. Start the magnetic stirrer. Add the appropriate amount of liquid reagent or distilled water to the pressure equalizing funnel or other funnel. Seal the top of the funnel, using the pressure equalizing funnel, completely open the side arm valve. Then slowly open the delivery valve to make dropwise additions of the water or liquid reagents. Control the dropwise addition as needed to continue a bubbling action in the gas washing bottles. When the liquid reagent or water has been totally added, shut all valves on the addition funnel. When the reaction seems to subside, increase the flow of N_2 to

¹ Data supplied by J. Bulko

provide a steady flow through the gas washing bottles. Continue flushing for 0.5 hrs. A minimum of heating can be used in the last time stage. The system is disassembled, the water in the gas washing bottles are transferred separately to plastic bottles labeled scrubber #1 and #2. These samples are sent to CMI for analysis for Sb, Cd, Pb, Zn and Cl. The solids and liquid phase, as completely as possible, are transferred to a beaker for drying. The contents in the beaker are dried at a temperature to drive off the water. Two portions of the dried solid residues are preserved for chemical analysis² of Sb, Cd, Pb, Zn, and Cl at CMI and the second sample is analyzed by XRD³ at Concord. All the pertinent data is included in this report.

There are two cautionary items that must be noted. Using magnetic stirrers in this apparatus did not give good mixing to the semi-solid slurry. Secondly since most of chlorides are soluble in water, if they remain unreacted they may be in the aqueous phase and must be dried with the solid residue.

B.4 Results

B.4.1 Potassium Persulfate ($K_2S_2O_8$)

Weigh 50g of WERF surrogate #1 and transfer it to the filtering flask. Then weigh 29g of $K_2S_2O_8$ and transfer it to the filtering flask. Mix the solids by vigorous shaking, (because the crystalline powders are not uniform in size they will be less than homogeneously distributed.) Assemble the apparatus as previously described. The pressure equalizer funnel was not available, so a standard 125ml separatory funnel was used to deliver 75ml of distilled water dropwise. There was back pressure and some generated gases were released through the separatory funnel instead of to the scrubbers.

Table B1. CMI Chemical Analysis for $K_2S_2O_8$

	Scrubber Solutions / ppm						Solids, Wt%				
	Sb	Cd	Pb	Zn	Cl		Sb	Cd	Pb	Zn	Cl
A-1	0.28	0.02	0.02	0.08	152	A	0.44	3.6	2.8	3.6	4.0
A-2	0.41	<0.01	0.03	0.08	7						

B.4.2 Experiments Using Ammonium Persulfate ($(NH_4)_2S_2O_8$)

Experiment-A

Weigh 50g of WERF surrogate #1 into the filtering flask containing a stirring bar. Add 100ml of distilled water to each of the gas washing bottles. Connect the apparatus as shown in the apparatus diagram and slowly flush the system with N_2 , (pressure equalizing funnel not available). Dissolve 12g of $(NH_4)_2S_2O_8$ in 50ml of distilled water and place in a separatory funnel. Slowly add the reagent while stirring the slurry. Maintain slow bubbling in the gas washing bottles. There is some loss of the generated gas through the separatory funnel. When all the reagent solution has been added maintain the bubbling in the gas washing bottles using N_2 . Add a small amount of heat and continue N_2 flushing

² CMI analysis provided by J.C. Cornwell

³ X-Ray analysis provided by B. Smyser

for 0.5 hrs. Disassemble the apparatus. Preserve the gas washing solutions (scrubbers) for chemical analysis at CMI and the second sample for XRD analysis at Concord.

Experiment-B

Repeat of Experiment A.

Experiment-C

Weigh 50g of WERF surrogate #1 into the filtering flask. Add 25g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and mix the solids by vigorous shaking. Add a stirring bar. Add 100ml of distilled water to each of the gas washing bottles. Connect the apparatus as shown in the apparatus diagram. Connect the N_2 tank and slowly flush the system with the pressure equalizing funnel. Open the side valve fully. Then slowly open the bottom valve and allow the dropwise addition of the water. Control the addition of water as needed to maintain a steady stream of bubbling in the gas washing bottles. When the addition of water is completed, shut both valves in the pressure equalizing funnel. Continue the N_2 flushing for 1.0 hr., adding a small amount of heating in the last 0.5 hrs. Preserve the scrubber solutions for chemical analysis at CMI. Preserve two portions of dried solid, one for chemical analysis at CMI and the second sample for XRD analysis at Concord.

Experiment-D

Repeat of Experiment C except add 20g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and flush with N_2 for 1 1/2 hrs.

Table B2. CMI Chemical Analysis for $(\text{NH}_4)_2\text{S}_2\text{O}_8$

Scrubber Solutions / ppm					Solids, Wt%						
	Cl	Sb	Cd	Pb	Zn		Cl	Sb	Cd	Pb	Zn
A-1	25	18	0.01	<0.01	0.03	A	4.0	0.44	3.6	2.8	3.6
A-2	<0.02	0.61	10.01	0.05	0.12						
B-1	64	0.12	0.02	ND	ND	B	4.7	4.9	61	4.2	6.2
B-2	12	0.30	<0.01	ND	0.03						
C-1	41	0.11	0.11	0.06	0.09	C	0.15	0.74	6.7	11.3	6.5
C-2	9	0.05	0.02	0.01	0.06						
D-1	70	5.4	0.09	0.21	0.10	D	0.37	0.84	4.8	4.1	7.9
D-2	5	0.23	<0.01	0.02	<0.01						

B.4.3 Experiments Using Hydrogen Peroxide (H₂O₂)

Experiment-A

Weigh 50g of WERF surrogate #1 into the filtering flask containing a stirring bar. Add 100ml of distilled water to each of the gas washing bottles. Connect the apparatus as shown in the apparatus diagram and slowly flush the system with N₂ (pressure equalizing funnel not available). Add 50ml of 10% H₂O₂ using a 125ml separatory funnel to deliver the H₂O₂ dropwise while stirring the slurry. When the reaction appeared to be slowing down as indicated in the gas washing bottles. Flush the system with N₂ for 0.5 hrs., while gently warming. Disassemble the apparatus. Preserve the gas washing solutions (scrubbers) for chemical analysis at CMI. Dry the solid sample by low temperature heating (125-150°C). Preserve two solid samples, one for chemical analysis at CMI and the second sample for XRD analysis at Concord.

Experiment-B

Repeat of Experiment A except that a 500ml filtering flask and a larger stirring bar was used. Additionally 25ml of distilled water was used in an effort to improve stirring. Reserve samples for chemical and XRD analysis.

Experiment-C

Repeat of Experiments A and B except that the pressure equalizing was available, and 60ml of 12% H₂O₂ was used. A significant orange-yellow was observed in the liquid layer. After the 0.5 hrs. of N₂ flushing the color faded. The solids were white after flushing. Reserve samples for chemical and XRD analysis

Experiment-D

Repeat of Experiment C and reserve samples for chemical and XRD analysis

Table B3. CMI Chemical Analysis for H₂ O₂

Scrubber Solutions / ppm					Solids, Wt%						
	Cl	Sb	Cd	Pb	Zn		Cl	Sb	Cd	Pb	Zn
A-1	73	0.80	0.56	0.33	0.59	A	13.5	0.75	5.3	3.4	4.7
A-2	8	0.34	<0.01	<0.01	0.09						
B-1	38,000	9.4	0.70	12	0.89	B	8.3	0.46	6.6	4.8	6.5
B-2	4	1.1	0.20	1.7	0.35						
C-1	10,500	15	0.33	0.99	1.2	C	5.0	0.60	11.2	7.4	8.2
C-2	<2	0.07	0.02	0.11	0.8						
D-1	420	3.0	0.06	0.24	0.13	D	6.5	0.57	11.1	7.5	8.9
D-2	3	0.09	<0.01	0.05	0.01						

B.4.4 Experiments Using Concentrated Sulfuric Acid (H₂SO₄)

Experiments using concentrated H₂SO₄ on dry chlorides is a familiar procedure for generating hydrogen chloride gas. It was hoped that the surrogates would be a suitable source for generating HCl gas.

Experiment-A

Weigh 50g of surrogate #1 into the filtering flask containing a stirring bar. Add 100ml of distilled water to each of the gas washing bottles. Connect the apparatus as shown in apparatus diagram and slowly flush the system with N₂. Add 25ml of H₂SO₄ (conc.) to the pressure equalizing funnel. Open the side valve and very slowly, dropwise add H₂SO₄ from the lower valve. The gas evolution was very vigorous in both of the scrubbers for 0.75 hrs. The flask was very warm. When the reaction slowed down the system was flushed for 0.75 hrs. The sample residue solidified preventing further stirring. Disassemble the apparatus. Preserve the scrubber solutions for chemical analysis at CMI and the second sample for XRD analysis at Concord.

Experiment-C

Weigh 17g of surrogate #2 into the filtering flask containing a stirring bar. Add 100ml of distilled water to each of the gas washing bottles. Connect the apparatus as shown in the apparatus diagram. Flush the system with N₂ with both valves of the pressure equalizing funnel closed. Add 25ml of H₂SO₄ to the funnel. Open the upper valve and slowly open the lower valve to allow dropwise addition of the acid. Continue as in Experiment A. Preserve samples for analysis.

Table B4. CMI Chemical Analysis for H₂SO₄ - Surrogate #1 & #2

Scrubber Solutions / ppm					Solids, Wt%						
	Cl	Sb	Cd	Pb	Zn		Cl	Sb	Cd	Pb	Zn
A-1	115,000	76	0.94	2.5	1.8	A	1.2	2.1	2.0	2.3	3.6
A-2	5	0.22	0.07	0.48	0.11						
C-1	70,000	6.4	0.12	1.3	1.6	C	0.13	6.5	17.1	8.1	21.8
C-2	3	0.18	0.05	1.4	0.12						

B.4.5 Experiment Using H₂SO₄ and Surrogate 3 (Na₂SO₄ replacing Na₂SiO₃)

Experiment-A (H₂SO₄-Na₂SO₄)

Weigh 50g of surrogate #3 into the filtering flask containing a stirring bar. Add 100ml of distilled water to each of the gas washing bottles. Assemble the apparatus and start the stirrer. Start flushing the system with N₂ with both valves closed in the pressure equalizing funnel. Add 25ml of H₂SO₄ (conc.) to the funnel. Open the upper valve, then make dropwise additions from the lower valve until all the acid has been added. Close both valves. When reaction subsides continue N₂ flushing 0.75 hrs. Disassemble apparatus and preserve scrubber sample and solid for chemical and XRD analysis.

Experiment-B (H₂SO₄-Na₂SO₄)

Repeat as in Experiment A.

Table B5. CMI Chemical Analysis for H₂SO₄ - Surrogate #3

Scrubber Solutions / ppm					Solids, Wt%						
	Cl	Sb	Cd	Pb	Zn		Cl	Sb	Cd	Pb	Zn
A-1	83,000	17.4	0.04	0.10	0.12	A	0.08	0.89	6.1	1.6	6.2
A-2	5,000	0.07	0.01	0.05	0.05						
B-1	22,000	11.8	0.11	0.52	0.46	C	0.33	0.78	6.9	2.2	5.8
B-2	8,000	0.10	<0.01	<0.01	<0.01						

B5. Conclusions

This investigation was limited to determining the feasibility of eliminating chlorides from surrogate WERF materials as a preliminary to high temperature (1250°C) ignition, to produce a safe to handle, unleachable aggregate. The reagents used were two persulfates, hydrogen peroxide and concentrated sulfuric acid. The persulfate concentrated on was ammonium in preference to potassium because of its greater solubility.

The $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was presumed to react with the chloride ion to produce oxides of chlorine such as chlorite (ClO_2), Chlorate (ClO_3) or perchlorate (ClO_4). The H_2O_2 was presumed to react with chloride to produce nascent chlorine gas. The use of concentrated sulfuric acid was to generate hydrogen chloride gas.

The experiments using persulfates and H_2O_2 were applied to WERF surrogate #1 which was a 500g mix containing 5% each of the toxic metals as their chloride and the remainder was sodium silicate (Na_2SiO_3). These were lightly pulverized using a mortar and pestle and transferred to a plastic bottle. The bottle was shaken vigorously for a total of 0.5 hrs. It was noted that the SbCl_3 was very hygroscopic. It might be desirable to store SbCl_3 in a desiccator. If this work were to be repeated, each experiment should use a fresh, individually prepared surrogate portion.

The chemical analysis results for Cd, Pb and Zn showed $(\text{NH}_4)_2\text{SO}_4$. The Sb and Cl data differed radically in the A and B from C and D. The temperature of the dissolution of the solids in an oxidizing environment must be held close to room temperature, since SbCl_5 boils at 140°C. Therefore both Sb and Cl could be lost.

The chemical analysis results for Cd, Pb and Zn were reasonable using H_2O_2 , although somewhat high for Cd. Using H_2O_2 to eliminate Cl as chlorine gas could reduce the weight basis of the original material. Again the analysis for Sb is somewhat suspect since it could be lost in drying to remove the water or in the dissolution for chemical analysis.

Three different WERF surrogates were used in the tests using concentrated H_2SO_4 . In test A the reaction was very vigorous, such that there was concern that there was a reaction between H_2SO_4 and the Na_2SiO_3 . However the chemical analysis showed that most of the HCl was collected in the first gas washing bottle. A second surrogate containing only the four toxic metals as their chlorides, showed that HCl gas was absorbed in the scrubber and very little chloride left in the solid.

The last two experiments using H_2SO_4 , used surrogate #3 which included the four toxic metals as their chlorides and the remainder was Na_2SO_4 . Again the chloride was mainly in the scrubbers. Again the Sb was low and the Pb somewhat low. The reasons as previously noted.

In summation, of the problem is the volatility of the toxic metal chlorides, then the chlorides could be eliminated using either concentrated H_2SO_4 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$. I believe the Sb loss, if important, is controllable with careful handling of the drying procedure and the chemical analysis.

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J. Cornwell Chemical Analysis

B. Smyser XRD Data

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¹ *Handbook of Vapor Pressure, vol.4. Inorganic Compounds and Elements*, Carl L. Yaws, Gulf Publishing Company, Houston, page 232.