SAND REPORT

SAND2002-0924
Unlimited Release
Printed June 2002

Thermal Treatment of Low-Level Radioactive Mixed Waste Using Molten Aluminum

Susan D. Carson, Phyllis K. Peterson and Eric M. Dinsmore

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

SAND2002-0924
Unlimited Release
Printed June 2002

Thermal Treatment of Low-Level Radioactive Mixed Waste Using Molten Aluminum

Susan D. Carson
International Environmental Analysis Department
Phyllis K. Peterson and Eric M. Dinsmore
Radioactive Waste/Nuclear Material Disposition Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0720

Abstract

A Clean Technologies molten aluminum waste treatment unit has been operated intermittently over a four-month period at Sandia National Laboratories' (SNL's) Radioactive and Mixed Waste Management Facility (RMWMF) at the SNL site in Albuquerque, New Mexico (SNL/NM). Nineteen surrogate samples and eight samples of mixed wastes stored at the RMWMF have been treated by immersion in a 900 °C molten aluminum bath. Items treated included small metal parts, personal protective equipment, circuit board samples, laboratory trash, and small batteries. Samples of the aluminum ingot, waste residues, scrubber water, scrubber activated charcoal, and system exhaust gases were collected and analyzed for radioactive and Resource Conservation and Recovery Act (RCRA) constituents. This report discusses these analytical results, the performance of the treatment unit, and the additional development efforts needed to successfully deploy this treatment technology for mixed waste.

Acknowledgment

The authors thank Robert Dinwiddie and Robert Specketer of Clean Technologies International Corporation for their invaluable contributions to equipment setup, modifications and operation.

Contents

Figures

Tables

Intentionally Left Blank

Executive Summary

Clean Technologies International Corporation of Houston, Texas has patented the use of molten aluminum to thermally (900 ^{o}C) treat hazardous waste. The treatment unit includes a waste delivery system, an electrically-heated, insulated ceramic crucible containing 50 lbs of aluminum, an off-gas scrubber system, consisting of two aqueous scrubbers followed by an activated carbon filter, and a sampling and analysis system for exhaust gases

SNL/NM was interested in this technology for treatment of items that are classified because of their shape and/or design details, and require destruction to prevent reverse engineering. Any residue from treatment of such items that did not remain in the bath as dissolved metal would be shapeless and therefore no longer classified.

SNL installed a 50-lb CTIC treatment unit at its Albuquerque facility to conduct a treatability study using samples of the types of mixed waste awaiting disposition at the RMWMF for which this treatment process is relevant. Nineteen surrogate samples representative of the types of mixed waste present at SNL and eight tritium-contaminated mixed waste samples were treated in the molten aluminum unit. Based on the results of these tests, the following statements can be made about the performance of the 50-lb molten aluminum treatment unit:

- Primary products of incomplete reduction during treatment of organic wastes are benzene, toluene, styrene, and naphthalene. Of these, only benzene is of regulatory concern.
- The process does not produce dioxins or furans.
- Aqueous scrubbers are not effective traps for either organic or metallic effluents. It is recommended that they be eliminated and multiple activated charcoal filters be used instead.
- Toxic metals with melting points above the 900 ^{o}C operating temperature (chromium and silver) are contained in the aluminum and slag.
- Toxic metals with boiling points below 900 ^{o}C (arsenic, cadmium, mercury and selenium) are not contained within the bath and are concentrated in the soot that forms within the top part of the furnace unit during sample treatment.
- Toxic metals with melting points below 900 ^{o}C and boiling points above 900 ^{o}C (barium and lead) will be distributed throughout the system based upon such factors as vapor pressure at 900 ^{o}C, solubility in molten aluminum, and the ability of the metal to agglomerate with soot.

This study demonstrated that this process is viable for destruction of classified items. However, the issues of volatile organic compound (VOC) generation during treatment of organic wastes and migration of volatile toxic metals need to be investigated further, both at the treatability study level and on a larger scale.

Acronyms and Abbreviations

AC	activated charcoal
ARCOCR	Analysis Request and Chain of Custody Record
bp	boiling point
CAM	continuous air monitor
CCD	catalytic combustion detector
cfh	cubic feet/hour
CTIC	Clean Technologies International Corporation
DOE	Department of Energy
DR	Disposal Request
EC	emergency coordinator
EPA	Environmental Protection Agency
ES&H	environmental, safety and health
GC	gas chromatograph
HA	Hazards Analysis
HEPA	high efficiency particulate air
LDRs	land disposal restrictions
LSC	liquid scintillation counting
MLLW	mixed low-level waste
mp	melting point
MSDS	Material Safety Data Sheet
ND	not-detected
NESHAPS	National Emission Standards for Hazardous Air Pollutants
PCBs	polychlorinated biphenyls
PHS	Primary Hazard Screening
PPE	personal protection equipment
ppm	parts per million
psi	pounds per square inch
QC	quality control
RCT	radiological control technician
RCRA	Resource Conservation and Recovery Act
RMWMF	Radioactive and Mixed Waste Management Facility
RWP	Radiological Work Permit
SCL	Sample Collection Log
SIH	Standard Industrial Hazard
SMO	Sample Management Office
SNL/NM	Sandia National Laboratories/New Mexico
SVOCs	semi-volatile organic compounds
TCLP	Toxicity Characteristic Leaching Procedure
TG	Treatability Group
TWD	Technical Work Document
VOCs	volatile organic compounds
WIPP	Waste Isolation Pilot Plant

Thermal Treatment of Low-Level Radioactive Mixed Waste Using Molten Aluminum

INTRODUCTION

Clean Technologies International Corporation (CTIC) of Houston, Texas has patented the use of molten aluminum to thermally (900 °C) treat hazardous waste. The process reduces organic compounds to primarily elemental constituents (carbon, hydrogen, nitrogen) in an inert atmosphere of argon gas containing less than 5% oxygen. Halogens form the corresponding aluminum salts and oxygen forms aluminum oxides and small amounts of water vapor. Non-volatile metal contaminants remain in the molten aluminum bath.

SNL/NM has a wide variety of small-volume mixed low-level waste (MLLW) streams for which there is currently no viable treatment and/or no disposal option, including approximately 40 drums of classified waste. The CTIC process is particularly attractive for treatment of classified waste because these items are in most cases classified because of their shape and/or design details. Classified items require destruction to prevent reverse engineering. In small treatment units, items to be treated are wrapped in aluminum foil prior to insertion in the molten aluminum bath; whole containers (boxes, drums) can be inserted into larger units. Any residue that does not remain in the bath as dissolved metal would be shapeless and therefore no longer classified.

SNL installed a 50-lb (of aluminum) CTIC treatment unit at its Albuquerque facility to conduct a treatability study using samples of the types of mixed waste awaiting disposition at the RMWMF for which this treatment process is relevant. Goals of the study were to:

- Determine the effectiveness of this thermal treatment technology for a wide variety of mixed wastes. Wastes that are characteristic mixed wastes should meet the Toxicity Characteristic Leaching Procedure (TCLP) standards for disposal as low-level waste after treatment; F-listed mixed wastes should meet the Land Disposal Restrictions in 40 CFR 268.40 for disposal in a mixed waste disposal facility.

- Evaluate the destruction and removal efficiency of waste hazardous constituents through sampling and analysis of waste residues and waste treatment effluents.

- Evaluate system reliability and maintenance requirements, recognizing that the unit at SNL is a research unit not designed for commercial waste treatment.

BACKGROUND

Mr. Anthony S. Wagner of CTIC began development of the molten aluminum waste treatment process in 1987. Process testing beyond the bench scale level was begun in November of 1989 using a mobile demonstration unit mounted on a 20-ft trailer. This system was used to process biomedical wastes and various types of liquid waste. The latter were added by subsurface pumping of the liquid into the molten aluminum.

Between 1990 and 1993, when CTIC was formed to commercialize the process, further technology demonstrations were conducted on various waste types, including organic refinery wastes and PCB (polychlorinated biphenyl)-contaminated pond sludge. Analytical results for the latter demonstrated that this treatment process effectively destroys PCBs. Additional tests in 1994 and 1996 using the unit to decontaminate soils contaminated with creosote, organic liquids, PCBs and toxic metals resulted in successful remediation at all sites. A test for Dow Chemical in 1997 demonstrated that the process does not produce dioxins or furans.

Ten years of testing the molten aluminum process successfully demonstrated that:

- the process destroys PCBs
- the process does not produce dioxins or furans
- toxic metals are alloyed with the aluminum.

In August 2000 the Department of Energy (DOE) supported a treatability demonstration of the CTIC process at a cleanup site in Ashtabula, OH. This was the first time the molten aluminum process had been used to treat radioactive waste. A 50-lb (of aluminum) unit similar to the one deployed at SNL/NM was used to test four waste streams:

- soil contaminated with PCBs and uranium
- soil contaminated with high levels of uranium
- pyrophoric uranium
- liquid organic stripper solvent.

The primary objective of this study was to demonstrate the ability of the process to destroy PCBs in the soil. A PCB destruction and removal efficiency of 99.9% was achieved [1]. X-ray fluorescence analysis results were 33 ppm uranium in untreated soil and 40 ppm in treated soil, indicating that no uranium was removed from the soil during treatment. Removal of uranium from the soil contaminated with "high levels" (1080 ppm) of uranium was also unsuccessful.

Approximately 6% of the pyrophoric uranium tested was alloyed with the aluminum before the solubility limit of uranium in 50 pounds of aluminum was exceeded. The remaining uranium formed a slag layer on top of the aluminum.

At a subsurface feed rate of 1 ounce per minute, the stripper solvent was destroyed to the extent that off-gas monitoring indicated no hydrocarbon emissions. However, treatment off gases exited through two aqueous scrubbers and an activated charcoal filter prior to emission to the atmosphere, and these were not sampled and analyzed for the presence of hydrocarbons.

The Ashtabula study provided several "lessons learned" that were incorporated into the study at SNL:

- Formation of significant amounts of uranium oxide during processing indicated that the system was not completely purged of oxygen prior to sample insertion. An oxygen sensor was incorporated into the SNL system to ensure oxygen concentrations in the atmosphere above the molten aluminum was <6% prior to sample treatment.

- The capabilities of the small treatment unit were overwhelmed by samples that were too large to be effectively treated by the 50 pounds of aluminum in the bath. SNL protocol for sample preparation specified that samples be no larger than one-half cup in volume, the sample size specified by CTIC for the 50-lb unit.

TECHNOLOGY DESCRIPTION

The treatment unit (see Figs 1 and 2) included a waste delivery system, an electrically-heated, insulated ceramic crucible containing 50 lbs of aluminum, an off-gas scrubber system, consisting of two aqueous scrubbers followed by an activated carbon filter, and a sampling and analysis system for exhaust gases. A Watlow Series 93 microprocessor-based temperature controller was used to maintain the 900 °C bath temperature. During sample treatment, argon flows through the system at a rate of approximately 2 cubic feet per hour (cfh) to maintain an inert atmosphere. This resulted in a positive operating pressure of approximately 4 psi within the unit.

The off-gas monitoring system (Fig. 3) consisted of an oxygen sensor, a hydrogen sensor, and a gas chromatograph (GC). The GC was an SRI Instruments Model 8610C unit that was customized for this project. It included a Carbosieve II column for sample collection in series with a standard GC separation column and a catalytic combustion detector (CCD) with a sensitivity of <1 ppm. The unit was a "gasless" chromatograph that used an internal compressor to produce the carrier gas from room air. A valve manifold (Fig. 4) was used to monitor either head space gases above the molten aluminum bath or off gases from the activated carbon filter. After passing through the monitoring system, exhaust gases exited through the building's High Efficiency Particulate Air (HEPA) filter system.

Head space gases were monitored for both hydrogen and oxygen. Hydrogen production during sample reduction was monitored with a DHC Technology, Inc. Model HH3-SB06Ps1 Robust Hydrogen Sensor that detected hydrogen gas from <0.5% to 100% in <2 seconds with an accuracy of $\pm$0.1%. An Illinois Instruments Model 910 oxygen analyzer that measures 0.01 – 100% oxygen in less than 30 seconds to an accuracy of $\pm$ 0.1% was used to monitor oxygen levels during system purging with argon gas.

In addition to the ability to collect and analyze samples of effluent gases prior to their emission to the atmosphere, the unit allowed sampling of the aluminum, scrubber water, and the activated charcoal, as shown in the schematic in Fig. 4. Samples of the molten aluminum were collected directly from the bath, scrubber water samples were taken at valves 8 and 9 in Fig. 4, and the activated carbon was sampled by removing the filter from the unit.

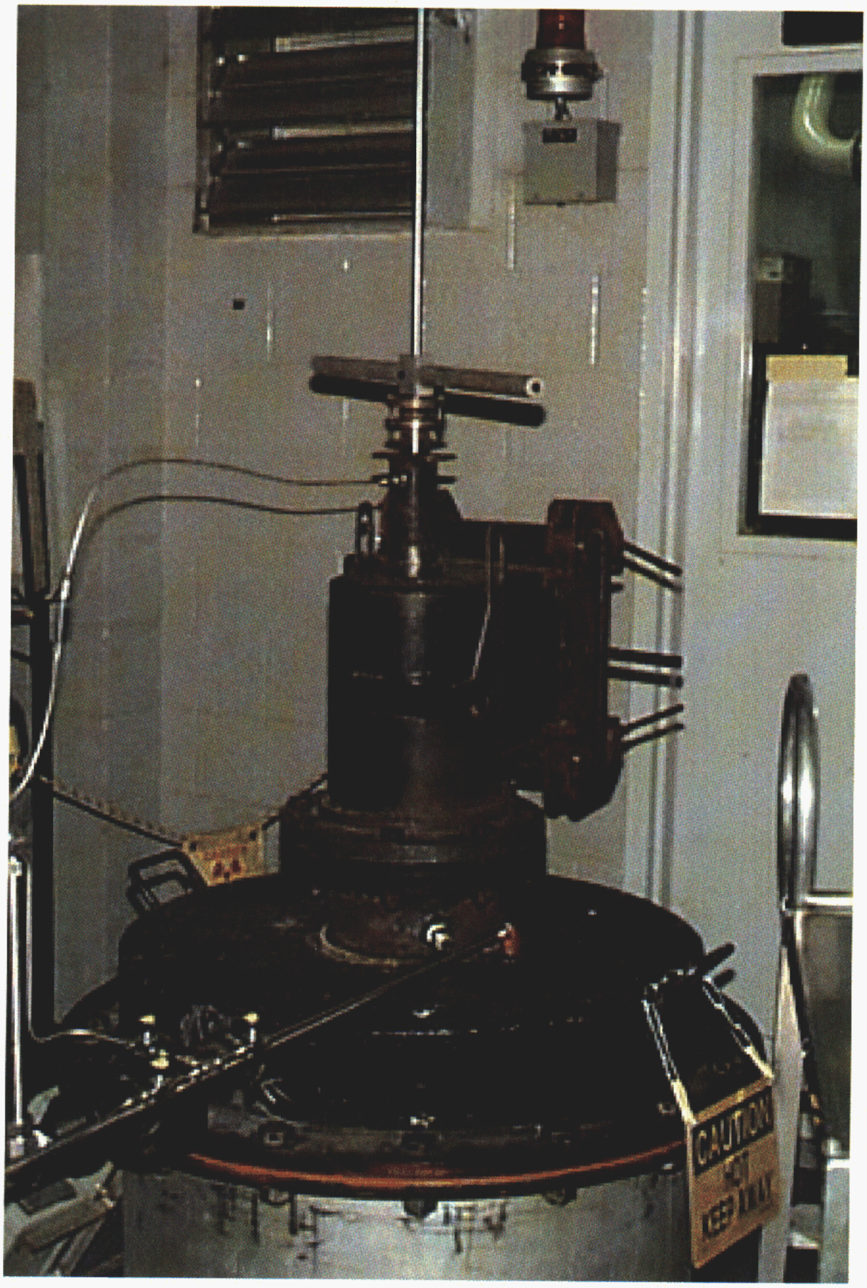

Fig. 1. Molten aluminum bath with the sample insertion head in place. Samples are inserted through the door on the back side of this view of the unit and pushed down into the bath using the handle on the rod at the top of the unit. In this picture, the rod is in the "down" position; a sample is being treated.

Due to the possibility of radioactive contamination being released into the room when the push rod was raised and lowered, the operator used a supplied air hood when radioactive samples were treated.

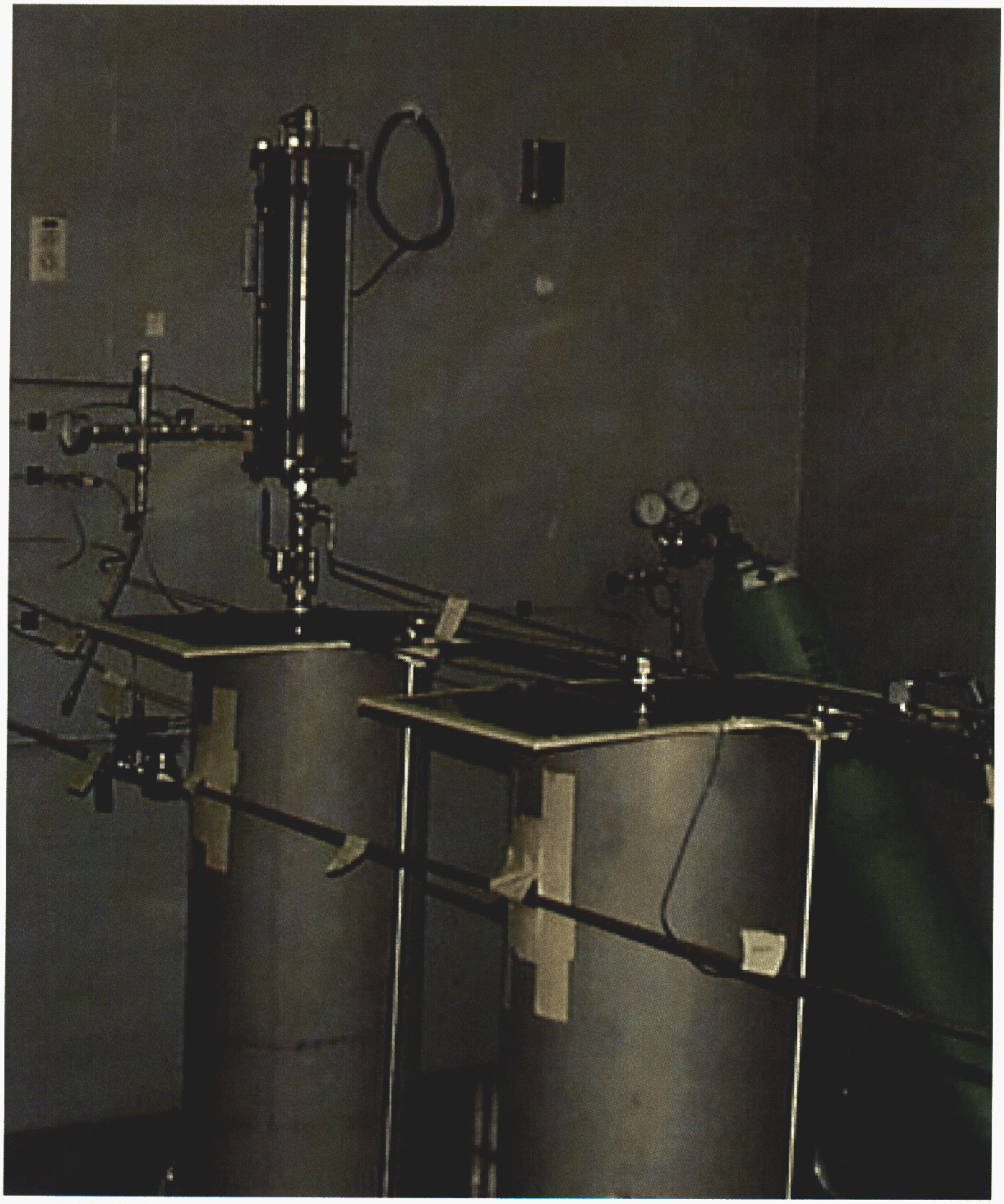

Fig. 2. Molten aluminum treatment unit off-gas scrubbers and activated charcoal filter.

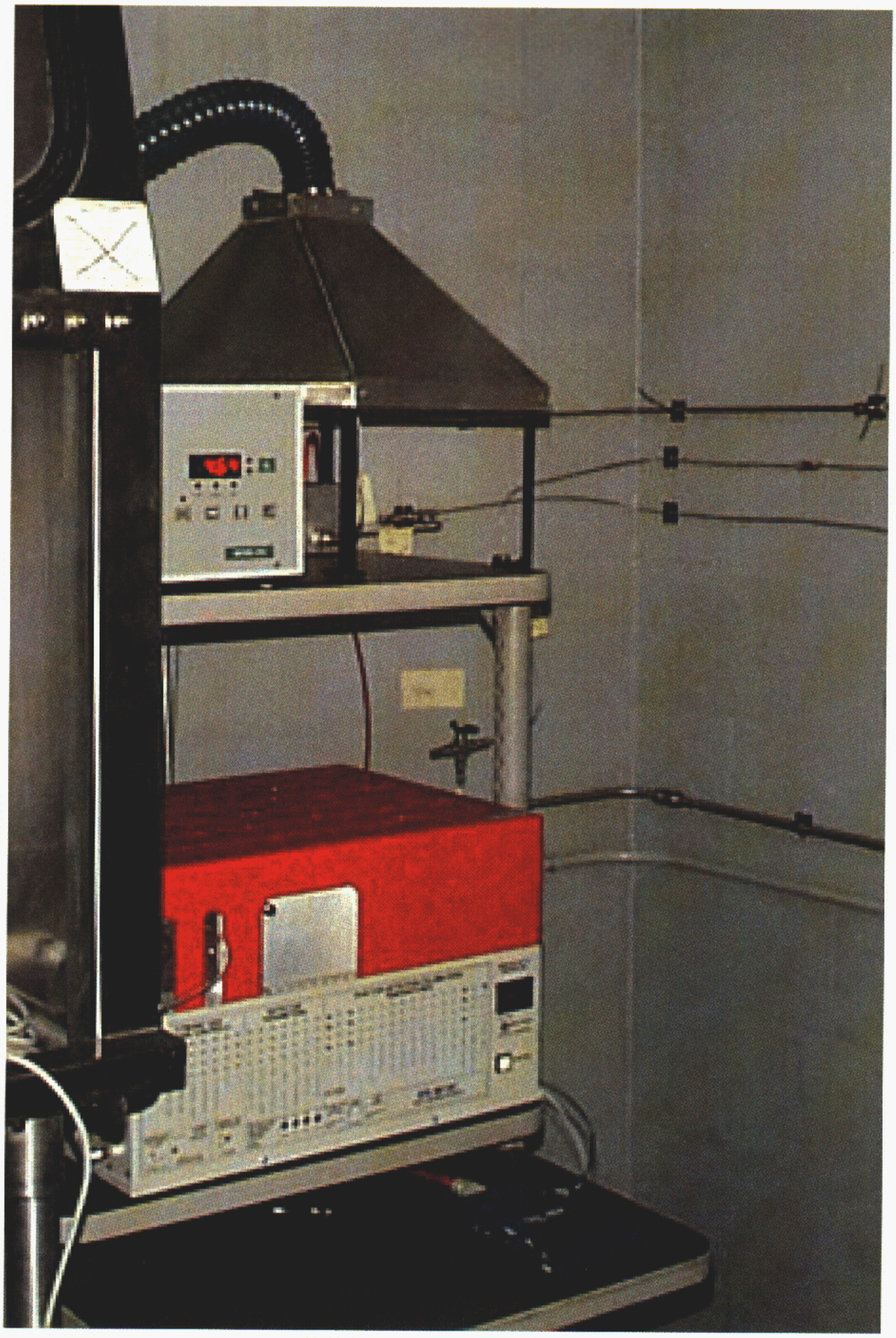

Fig. 3. Molten aluminum oxygen sensor (top shelf), gas chromatograph (below oxygen sensor), and hydrogen sensor (small blue box on table).

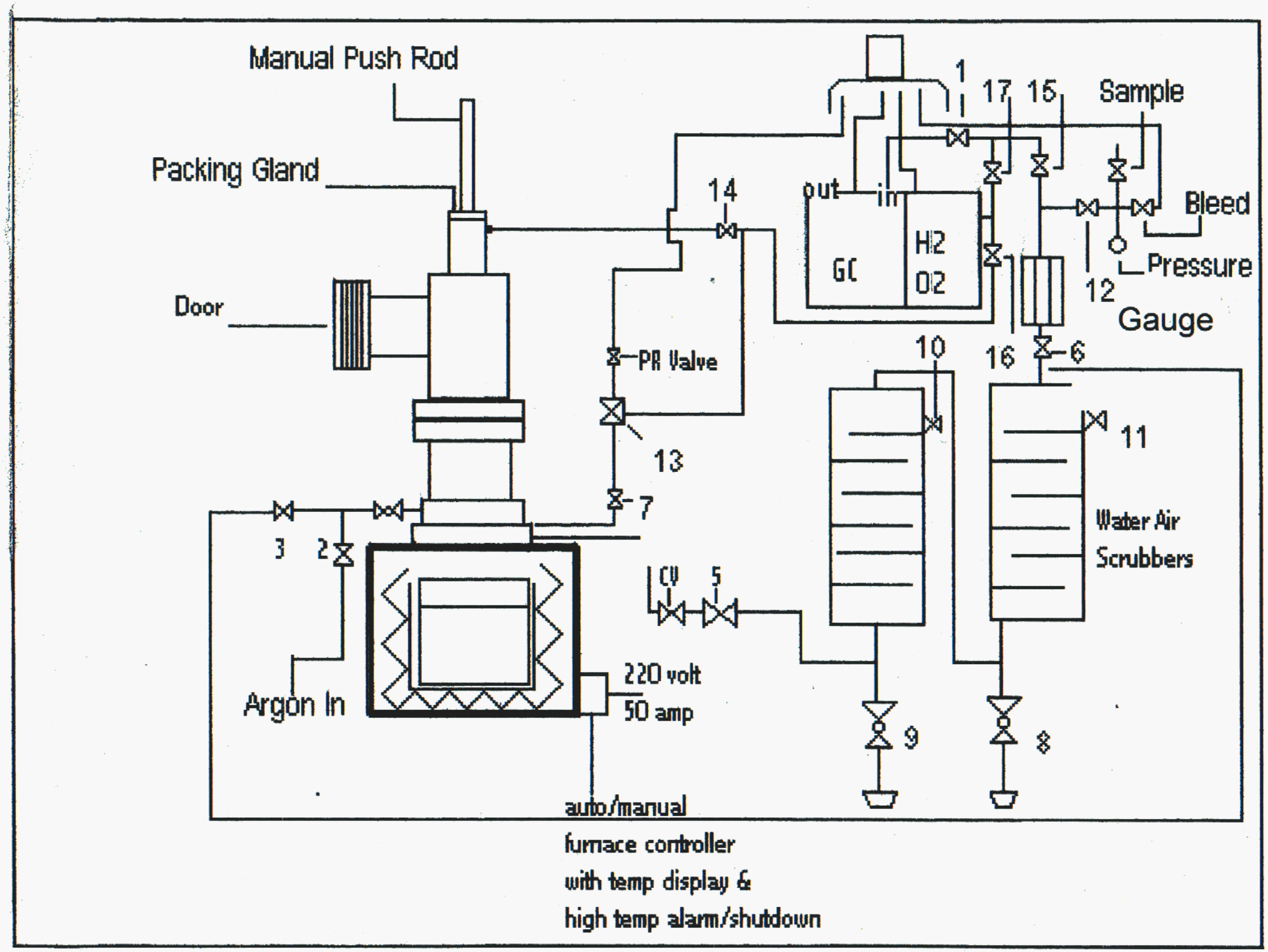

Fig. 4. Schematic of Clean Technologies' 50-lb molten aluminum treatment unit

Equipment Modification and Testing

During assembly of the molten aluminum unit at SNL, it was determined that, if valves were inadvertently opened in the wrong order, water from the scrubbers could backwash into the molten aluminum bath. To prevent this, a 6000 psig check valve was added between scrubber #1 and the bath (valve "CV" in Fig. 4). As designed, if excess pressure were to build up in the bath head space, it would be vented through the scrubber system. A 25 psi pressure relief valve ("PR Valve" in Fig. 4) was added to the head space off-gas line to allow excess pressure to vent directly to the building exhaust system.

The original activated charcoal filter on the system was replaced with a larger unit that was easier to dismantle for sampling. The unit shown in Fig. 2 is the replacement filter.

Since the system would be operated under a pressure of 4-10 psig argon, prior to startup, the aluminum furnace was pressure-tested to 18 psig. The vessel was held at this pressure for five minutes. There was no leakage and no damage to the vessel or ancillary parts.

Facility Modifications

The molten aluminum treatment unit was housed in Room 119, Building 6920, in Tech Area III at SNL/NM. The following facility modifications were made to be able to operate the unit efficiently and safely:

- A 220-volt, three-phase electrical outlet in the room was changed to single phase to meet the unit's electrical requirements.

- The amount of heat generated from extended operation of the 900 °C bath with the resultant possibility of worker heat stress was a health and safety concern for unit operators. The room ventilation system was modified to ensure rapid air change. During a dry run to test heat buildup in Room 119, the unit remained at 900 °C for approximately three hours. The room temperature remained at 80-82 °F during this time. Excessive heat buildup was never a problem during unit operation.

- Since it took 4-5 hours for the bath to heat up to 900 °C from a cold start, a timer was added to the 220-volt circuit to avoid the necessity of keeping the unit on 24 hours a day in order to have sufficient treatment time during a normal work day. Bath heaters came on at 0400 and the unit was up to temperature by 0800-0900.

- As shown in Fig. 5, the molten aluminum had to be ladled out at the end of each day's operation to prevent the crucible from cracking. This required removal of the furnace head (see Fig. 1), which weighed 143 pounds. A 250-lb chain hoist was installed in Room 119 for head removal.

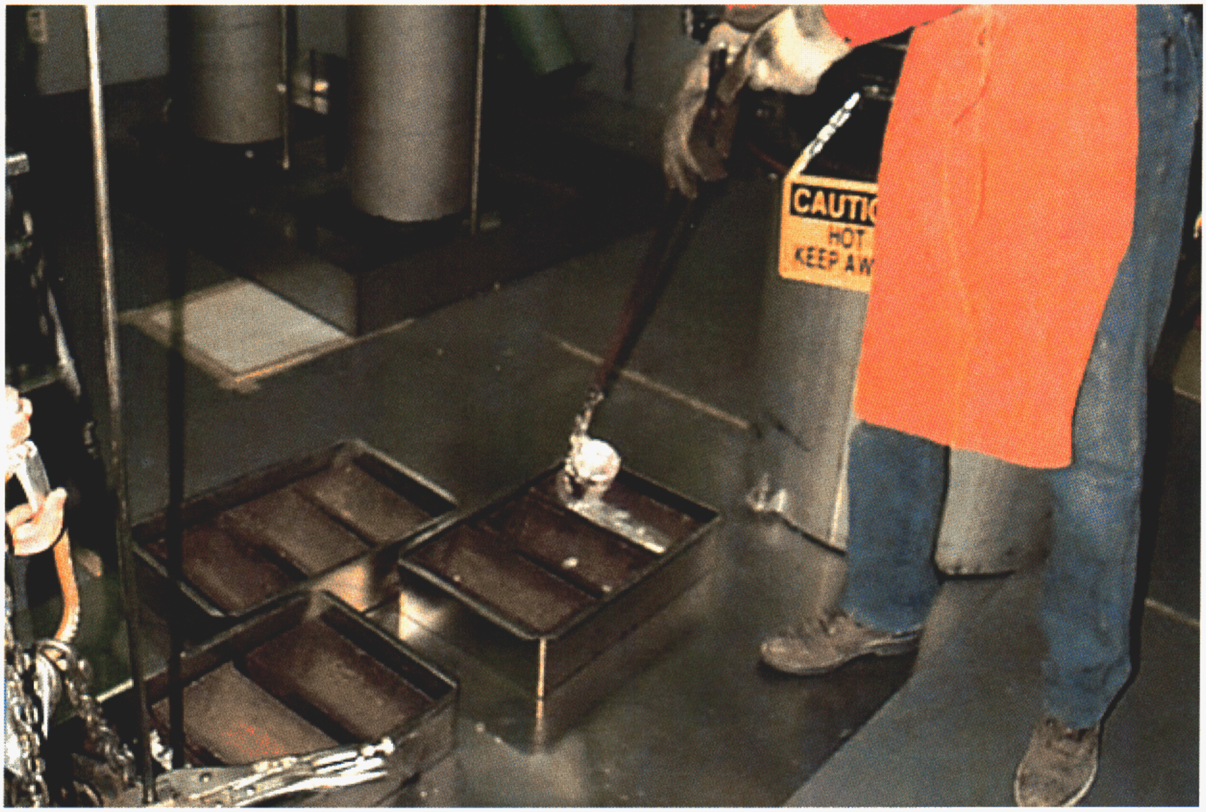

Fig. 5. Ladling out the molten aluminum at the conclusion of each day's operation.

- A small hood (see Fig. 3) was installed over the instrument table to duct exhaust gases from the sensors to the building exhaust system.

EXPERIMENTAL PROCEDURES

Due to the high operating temperature and the fact that the molten aluminum treatment unit is a pressure vessel, there are significant environmental, safety and health (ES&H) issues associated with its operation. Operational hazards were addressed through several SNL-required documents, two of which have been included as Appendixes to this report. Documents provided include a Test Plan that contains detailed operating, safety and quality control procedures (Appendix A) and the project Radiological Work Permit required to treat radioactive and mixed waste (Appendix B). The project Primary Hazard Screening (PHS) and Hazards Analysis (HA) documents (SNL1A00121-003) may be viewed at:

http://www-irn.sandia.gov/iss/isms_software/index.htm.

Prior to system startup, on October 24, 2001, an Operations Readiness Review was conducted in accordance with the SNL ES&H Manual requirements for startup of a "standard industrial hazard and low-hazard non-nuclear operation" [2].

SAMPLE TREATMENT

Nineteen surrogate samples representative of the types of mixed waste present at SNL (Table 1) and eight tritium-contaminated mixed waste samples (Table 2) were treated in the molten aluminum unit. Each sample was approximately one-half cup in volume, and was wrapped in a sufficient amount of aluminum foil to ensure the sample would sink when immersed in the bath. Samples were placed in a 4-inch diameter stainless steel mesh "cage" attached to a push rod (see Figs 1 and 4) through the door shown in Fig. 4. They were held above the bath while the system was purged with argon, and were manually inserted into the bath by pushing down on the rod when the oxygen sensor indicated <6% oxygen in the head space. (The system typically purged to <1% oxygen in 5 minutes.) Samples remained in the bath for 5 minutes, at which point the push rod was pulled up. The sample was then allowed to remain in the basket under argon for an additional 10 minutes to ensure all exhaust gases were purged from the head space above the bath prior to opening the sample insertion door. The system was then depressurized, the door opened, and a new sample was inserted. Any sample residue was collected for analysis.

Table 1. Surrogate samples treated in the molten aluminum unit

Sample #	Treatment Date	Sample Description
1	11/13/01	Plastic package with several fluted filter papers.
2	"	Yellow duct tape.
3	"	Several wooden cotton swabs and a Tyvek bootie.
4 & 5	12/04/01	Nitrile glove, plastic ear plugs, 2 plastic ties, duct tape.
6	12/05/01	Energizer industrial alkaline "C" battery, no. EN93; Energizer industrial alkaline 9V battery, no. En22.
7	"	Two EN93's; 2 EN 22's.
8	"	Car window crank.
9	"	Large metal binder clip, plus the plastic composition of samples 4 and 5.
10	"	Same metal clip as in sample 9, plus a new plastic mix with the composition of samples 4 and 5.
11	12/10/01	Circuit board samples.
12 & 13	12/11/01	Circuit board samples.
14 & 15	"	One-half a plastic bag for radioactive waste, high-density polyethylene bottle cap.
16 & 17	"	Paper towels soaked in ethanol.
18 & 19	12/12/01	One EN93; one EN22.

Table 2. Mixed waste samples treated with the molten aluminum unit *

Sample #	Sample Wt., g	Treatment Date	Sample Description
1	46	01/31/02	Plastic bag.
2	49	02/05/02	Polyvinyl chloride gloves.
3	37	01/31/02	Paper filters.
4	80	"	Gloves, paper.
5	61	02/05/02	Circuit board sample.
6	78	"	"
7	85	"	"
8	104	"	"

* Samples 1 through 4 were lab trash from operations with tritium-contaminated mercury waste; therefore, they were considered to be contaminated with trace amounts of both these constituents. Samples 5 through 8 contained chromium and lead and were from a waste package whose total listed activity was 2.31 E-08 Ci of tritium.

The molten aluminum was dipped out of the crucible at the end of each day's operation. After cooling, the ingots were placed back in the bath, and the timer was set to bring the unit to operating temperature by 0800 the next day.

RESULTS

In the following sections, test results and analytical data are discussed in terms of specific waste types and the overall performance of the treatment unit.

System Performance

Overall, the 50-lb unit performed in accordance with expectations; however, there were several operational issues that were inherent in the design of this research unit. The principal difficulty was the limited lifetime of the stainless steel sample "cages". Since they were stainless steel, they were slowly melted into the aluminum bath during sample treatment. Depending upon sample immersion time, a basket would last for an average of five samples before either the bottom of the basket was eaten away or the connection to the stainless steel push rod failed. (The tests at Ashtabula also averaged about five samples per basket.) Attempts to use a ceramic sample "basket" instead were unsuccessful; the material proved to be brittle and subject to cracking. However, this is not a problem that would occur with a commercial treatment unit, since whole waste containers would be directly immersed in the bath.

For samples requiring immersion times longer than five minutes, a ceramic disc was attached to the push rod. Two holes were drilled in the disc such that solid samples could be wired to the disc and immersed in the bath. This method worked well for samples such as batteries, but prevented residues from being recovered for analysis.

The large amount of soot and aerosol carbon generated during treatment of organic samples left an oily carbon film on the push rod, which made it difficult to raise it from the bath. This problem was alleviated by the addition of a lever arrangement that allowed the rod to be mechanically raised after each sample run. On two occasions the fine carbon particles present in soot spontaneously oxidized when the sample insertion door was opened after treatment of an organic sample. This resulted in a small flash or explosion analogous to the dust explosions that occur in grain elevators; however, the problem was eliminated by opening the door slowly. The hazards associated with fine particle carbon could be especially significant for larger treatment units, and will need to be addressed.

Sample treatment also generated a significant amount of slag in the bath. While at least some of this can be attributed to the gradual melting of the sample cage, on average, treatment of 3-5 samples, each weighing approximately 100 grams, resulted in the production of 1 to 1.5 kilograms of slag, exclusive of the sample cage.

An unexpected problem occurred with the treatment of alkaline batteries. (This waste type was of interest because there are a large number of radioactively contaminated batteries across the DOE complex.) The sodium hydroxide in the batteries proved to be corrosive to the ceramic crucible holding the molten aluminum, causing it to crack and damage some of the thermocouple heating elements. The crucible was replaced prior to treatment of the mixed waste samples. Again, this is not a problem that would occur in a commercial unit, since a much thicker refractory material impervious to acids and bases would be used.

The GC monitored head space and effluent gases during the argon purge when the sample was suspended in the cage above the bath, during treatment, and after treatment when the sample again remained above the bath to ensure all effluent gases were purged to the off-gas scrubber system. No effluent peaks were observed during any of these treatment phases. Since the GC response was tested using n-hexane, acetone and benzene samples, the lack of peaks indicated any treatment by-products were effectively trapped by the scrubber system. A typical GC spectrum is shown in Fig. 6. The initial spike is the sample entering the column.

Surrogate Samples

The samples in Table 1 can be generically classified as organic lab trash (paper, plastic, etc.) and inorganic metallic debris (car window crank, metal clip, batteries). The circuit board samples are "hybrids" in the sense that they have both organic (the board) and inorganic (circuitry) constituents. As stated earlier, all organic samples produced finely divided aerosol carbon that spread throughout the system, from the bath to the activated charcoal filter; however, air particulate stack monitors for the building where the unit was housed did not register any particulate release to the atmosphere. In every case, sample treatment produced hydrogen at an average concentration of 0.5-1% in the exhaust gas. Average hydrogen concentration increased to 2-3% when the alkaline batteries were treated, due to the presence of sodium hydroxide, which is reduced to elemental constituents in the reducing atmosphere.

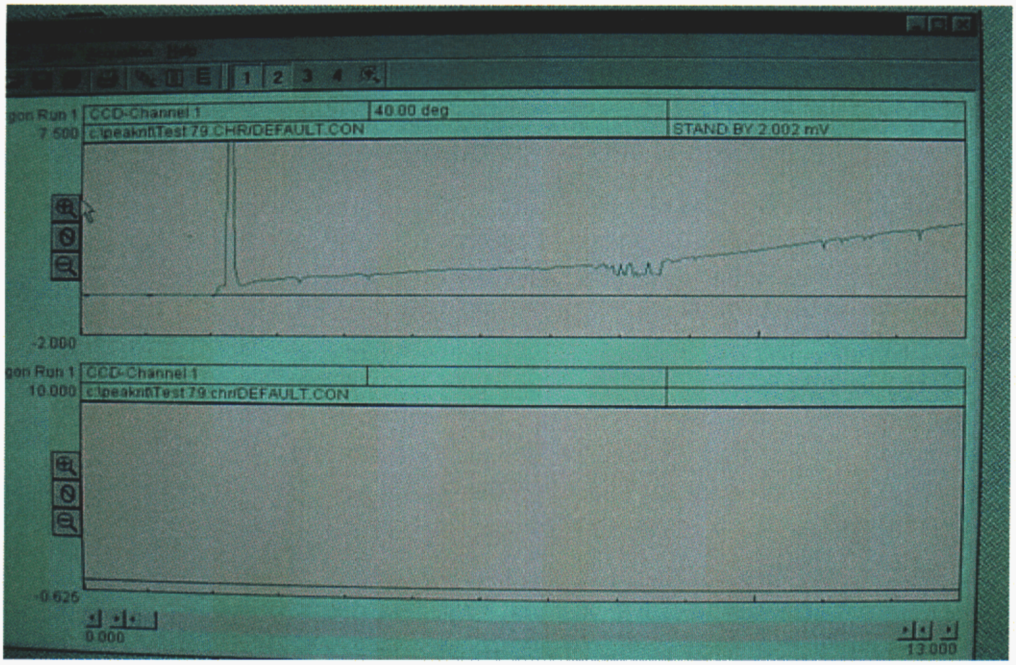

Fig. 6. GC plot of off-gases during surrogate waste treatment.

The large metal clip and the car window crank (found in the parking lot, no claimers) served as surrogates for excess nuclear components classified because of shape. Both samples required ten minutes of treatment, but were completely absorbed into the metal melt with no residue.

The only samples that produced an identifiable residue other than carbon and ash were the circuit boards and the batteries. The fiberglass mesh that is embedded in the board matrix remained in the basket after circuit board treatment. Batteries were readily destroyed once the outer shell was penetrated; however, this sometimes proved to be difficult. On one occasion, after being immersed for 45 minutes, intact batteries remained in the bath when the aluminum was ladled out.

Mixed Waste Samples

The distribution of tritium among the various treatment effluents after treatment of the eight radioactive samples is summarized in Table 3. From these data, it is obvious there was more tritium present in these samples than was indicated by the radiological data provided in the waste characterization data. Therefore, it was not possible to attempt to do a mass balance analysis for tritium.

The bulk of the tritium captured in the waste effluents was in the activated charcoal. Data from the tritium monitor on the building exhaust system are summarized in Table 4. Tritiated waste was treated on January 31 and on February 5, resulting in a ten-fold increase in HTO concentration

Table 3. Tritium concentration in waste treatment effluents

Sample	Activity	2σ	Units
Slag from 01/31/02	0.809	0.124	nCi/g
Slag from 02/05/02	1.57	0.204	nCi/g
Activated Charcoal	122	11.6	nCi/g
Water, scrubber #1	205	21.0	nCi/L
Water, scrubber #2	72.1	7.37	nCi/L
Soot from furnace head	4.70	0.557	nCi/g

Table 4. Tritium bubbler results, EPA Method B-5 [3], SNL stack exhaust monitor

Week, 2002	HTO Conc., μCi/mL	HTO Conc., μCi/mL
1/17 – 1/24	1.67 E-10	1.13 E-11
1/24 – 1/31	1.13 E-10	1.05 E-11
1/31 – 2/7	1.29 E-09	1.16 E-09
2/7 – 2/14	2.65 E-10	1.69 E-11
2./14 –2/21	1.88 E-10	1.24 E-11

and a 100-fold increase in HT concentration in the monitoring system for that week. However, these levels are still orders of magnitude below SNL's allowable release limits for tritium.

Alpha, beta and gamma analyses indicated that tritium was the only radionuclide present in waste effluents.

Analytical Data

After treatment of the nineteen samples in Table 1, samples of the aluminum, slag, scrubber water and activated charcoal were sent out for the analyses listed in Table 5. The activated charcoal (AC) filter was replaced on 12/10/01; hence the designation "old AC" and "new AC" in Table 5. Since a larger amount of slag was generated from battery treatment on 12/12/01, it was kept separate from the slag from previous tests. The latter is labeled "<12/12 Slag" in Table 5.

Analytical results from surrogate sample treatment are summarized in Table 6. It can be seen from the data that, in addition to carbon and hydrogen, aromatic hydrocarbons were produced during the reduction of organic samples. These are "products of incomplete reduction", analogous to the "products of incomplete combustion" seen in incineration. Since the benzene concentrations exceed the RCRA TCLP limit of 0.5 ppm [4], the scrubber water and the activated charcoal are hazardous wastes that will have to be treated to meet RCRA standards prior to disposal. While the aluminum and slag contain large amounts of chromium and lead, the

TCLP results indicate they are effectively alloyed with the aluminum and are not hazardous waste.

The presence of bromine in the "<12/12 Slag" indicates at least one of the plastics treated was a brominated polymer. The presence of arsenic in the activated charcoal was not surprising, since it sublimes at 613 °C [5]. What was not expected was the amount of barium and chromium present in this effluent; however, they are effectively bound to the charcoal, which passes the TCLP test and is therefore not a mixed waste.

Table 5. Treatment effluent analyses

Effluent	Analysis	EPA Test Procedure [3]
Aluminum, <12/12/ slag,	TCLP [1] metals	1311/6010B/7471A
12/12 slag	Total RCRA [2] metals	6010B/7471A
	Major anions	300.0
Scrubber #1, scrubber #2	VOCs [3]	8260B
	SVOCs [4]	8270C
	Total RCRA metals	6010B/7471A
	Major anions	300.0
	Dioxins & furans	8280
Old AC, new AC	VOCs	8260B
	SVOCs	8270C
	TCLP metals	1311/6010B/7471A
	Total RCRA metals	6010B/7471A
	Total organic halogens	9020B
	Dioxins & furans	8280

[1] Toxicity Characteristic Leaching Procedure
[2] Resource Conservation and Recovery Act
[3] Volatile Organic Compounds
[4] Semi-Volatile Organic Compounds

No dioxins or furans were detected in either the scrubber water or the activated charcoal.

Analytical results from treatment of mixed waste samples are summarized in Table 7. Since the aqueous scrubbers were not emptied and refilled prior to treatment of mixed waste, analytical data for scrubber samples are cumulative. The activated charcoal was changed out prior to mixed waste treatment. Samples of the slag were taken at the end of each day's treatment.

The data in Tables 6 and 7 are consistent. In both cases, the primary VOC products are benzene, toluene and styrene. Naphthalene is the only significant SVOC produced. Since these compounds are not from a spent solvent source, from a regulatory standpoint, the only contaminant of concern is benzene, which exceeds the RCRA TCLP limit of 0.5 ppm in all scrubber and charcoal samples. Since the VOCs and SVOCs are concentrated in the activated charcoal, and are not effectively trapped by the aqueous scrubbers, one could argue that the latter are superfluous. A simpler and safer design would be to only have a bank of two or three

Table 6. Analytical results – surrogate samples.[1] Units are ppm.

Analysis	Compound/ Element	Scrubber #1	Scrubber #2	Old AC	New AC	Al	<12/12 Slag	12/12 Slag
VOCs	Acetone	-	-	-	5.17	N/A	N/A	N/A
	Benzene	16.400	7.630	80.300	83.300			
	Chlorobenzene	-	-	-	0.504			
	Chloromethane	0.227	-	-	-			
	Ethylbenzene	-	-	-	0.205			
	Styrene	1.720	0.548	-	-			
	Toluene	3.830	2.170	1.28	10.100			
	Total xylenes	0.538	0.317	-	0.502			
SVOCs	Acenaphthene	-	0.001	-	-	N/A	N/A	N/A
	Acenaphthalene	0.104, 0.108 [2]	0.013	0.163	-			
	Anthracene	-	0.003	-	-			
	4-Chloroaniline	-	-	4.14	-			
	Fluorene	0.030, 0.028 [2]	0.007	-	-			
	2-Methylnaph-thalene	0.210, 0.227 [2]	0.028	1.280	4.840			
	Naphthalene	0.942, 2.17 [2]	0.115	14.800	36.100			
	Phenanthrene	0.052, 0.057 [2]	0.016	-	0.351			
Total RCRA Metals	Arsenic	0.00601	-	2.20	-	-	-	-
	Barium	0.0281	0.0052	42.2	30.3	-	16.6	-
	Chromium	0.00902	1	2.55	-	3490	7880	3810
	Lead	0.0156	0.0506 -	-	-	115	103	109
TCLP Metals	Arsenic	N/A	N/A	0.0722	0.0561	0.0517	-	-
	Barium			0.566	-	-	0.544	0.744
	Chromium			-	-	0.0152	0.0913	-
	Lead			-	-	0.0532	-	-
Major Anions	Bromide	-	0.149	N/A	N/A	-	2630	-
	Chloride	30.5	31.8			-	-	-
	Fluoride	0.505	0.481			-	-	-
	Sulfate	32.0	32.0			-	-	-
Total Organic Halogens		N/A	N/A	56.1	33.8	N/A	N/A	N/A

[1] Values that were below the detection limit and therefore estimates are not included.
[2] 1:20 dilution.

Table 7. Analytical results – mixed waste samples. [1] **Units are ppm.**

Analysis	Compound/ Element	Scrubber #1	Scrubber #2	AC	Al	1/31/02 Slag	2/5/02 Slag
VOCs	Benzene	19.6, 28.0 [2]	11.0, 12.5 [2]	197 [4]	N/A	N/A	N/A
	Styrene	2.35, 2.20 [2]	0.898, 0.835 [2]	-			
	Toluene	4.31, 4.63 [2, 3]	2.84, 2.88 [2, 3]	11.2 [4]			
	Total xylenes	0.578, 0.593 [2]	0.419, 0.412 [2]	-			
SVOCs	Acenaphthene	0.00876	-	-	N/A	N/A	N/A
	Acenaphthalene	0.120	0.0200	0.0425			
	Anthracene	0.0145	0.00388	-			
	Fluoranthene	0.00401	0.00142	0.109			
	Fluorene	0.0361	0.0116	-			
	2-Methylnaph-thalene	0.224	0.0336	0.918			
	Naphthalene	2.14	0.197	11.5			
	Phenanthrene	0.0557	0.0194	0.274			
	Phenol	0.0607	0.0201	-			
	Pyrene	0.00496	0.00175	0.0969			
Total RCRA Metals	Barium	0.0068	-	25.1	0.996	8.69	5.12
	Cadmium	-	-	-	2.07	1.35	18.5
	Chromium	-	0.042	-	11,600	7510	11,400
	Lead	0.00983	0.0172	-	502	985	841
	Mercury	0.0271	0.00227	2.43	-	0.0914	-
	Selenium	0.00512	-	1.65	-	-	-
	Silver	-	-	-	32.3	2.04	58.5
TCLP Metals	Barium	N/A	N/A	0.0894	0.0722	0.0707	1.32
	Chromium			-	0.0616	0.0839	0.116
	Mercury			0.0209	-	-	-
	Lead			-	0.533	0.319	0.460
Major Anions	Bromide	-	-	N/A	-	-	-
	Chloride	33.0	32.3		-	-	214,000
	Fluoride	0.450	0.394		-	-	143,000
	Sulfate	31.3	28.7		-	-	-
Total Organic Halogens		N/A	N/A	71.9 [5]	N/A	N/A	N/A

[1] Values that were below the detection limit and therefore estimates are not included.
[2] First number is a 1:50 dilution; second number is a 1:500 dilution.
[3] Toluene was detected in the trip blank at 0.436 ppb.
[4] 1:1000 dilution.
[5] Blank had ~1 ppm Cl.

charcoal filters, which would eliminate the potential hazard of scrubber water backwashing into the molten aluminum.

Although aluminum and 2/5/02 slag samples contain about 3 times more chromium and 5-9 times more lead than the corresponding samples in Table 6, all samples still easily pass the TCLP test and are therefore not hazardous.

The concentrations of fluoride, chloride and sulfate are essentially identical in scrubber samples from both surrogate and mixed waste samples. These numbers are essentially identical with the average concentration for these anions in Albuquerque's water: 30-32 ppm for choride, <1 ppm for fluoride, and 30-32 ppm for sulfate [6].

Bromide, chloride and fluoride from waste samples form the corresponding aluminum halide salts and are captured in the slag. It is interesting to note that bromine was apparently the only halogen present in surrogate waste samples, none of the plastic waste treated on 1/31/02 contained halogens, and that the circuit board samples contained a fluorinated polymer. Most of the chloride present is most likely from the polyvinyl chloride gloves.

During equipment dismantlement, a sample of soot from the furnace head was collected and sent for VOC, total RCRA metals and TCLP analyses; however, there was only sufficient sample to perform the VOC and total metals tests. These results are shown in Table 8.

Table 8. Analytical results – furnace head soot. [1]

Analysis	Compound/Element	ppm
VOCs [2]	Benzene	4.42
	Styrene	0.263
	Toluene	0.707
Total RCRA Metals [3]	Arsenic	9.93
	Barium	48.4
	Cadmium	1040
	Chromium	516
	Lead	3250
	Mercury	6160
	Selenium	2.91
	Silver	6.33

[1] Values that were below the detection limit and therefore estimates are not included.
[2] 1:50 dilution.
[3] 1:50,000 dilution for mercury; 1:2 dilution for remaining metals.

Given the high level of mercury in this sample, it is unlikely that the head soot would pass TCLP; however, since all of the material was consumed in analyses, there was no mixed waste soot that required disposal.

All metals that were detected in any of the samples were present in the soot, which accumulated over the entire test program. Table 9 shows the distribution of RCRA metals between the aluminum (2 samples), slag (4 samples), soot (1 sample) and activated charcoal (3 samples) and the melting point (mp) and boiling point (bp) for each metal. As expected, metals that vaporize below 900 °C (arsenic, cadmium, mercury and selenium) are found primarily in the soot and activated charcoal, and the chromium and silver are concentrated in the aluminum and slag. What is somewhat surprising, is the amount of lead present in the soot and the rather uniform distribution of barium throughout the system. Given the unknown nature of the samples tested, these results demonstrate the need for quantitative mass balance tests to determine exactly where various treatment products are likely to be concentrated.

Table 9. RCRA metals distribution. Concentrations are ppm.

Metal	mp, °C [5]	bp, °C [5]	Al	Slag	Soot	AC
Arsenic	817	613 [1]	ND [2], ND	ND, all samples	9.93	2.20, ND, ND
Barium	725	1640	ND, 0.996	16.6, ND, 8.69, 5.12	48.4	42.2, 30.3, 25.1
Cadmium	320.9	765	ND, 2.07	ND, ND, 1.35, 18.5	1040	ND, all samples
Chromium	1857 ± 20	2672	3490, 11,600	7880, 3810, 7510, 11,400	516	2.55, ND, ND
Lead	327.502	1740	115, 502	103, 109, 985, 841	3250	ND, all samples
Mercury	-38.842	356.68	ND, ND	ND, ND, 0.914, ND	6160	ND, ND, 2.43
Selenium	217	684.9 ± 1.0	ND, ND	ND, all samples	2.91	ND, ND, 1.65
Silver	961.93	2212	ND, 32.3	ND, ND, 2.04, 58.5	6.33	ND, all samples

[1] Arsenic sublimes at this temperature.
[2] ND = not detected.

The fact that mercury is concentrated in the soot, rather than the activated charcoal can be explained by the fact that mercury alloys directly with other metals to form amalgams. At 20 °C, the solubilities of barium and lead in mercury are 0.33 wt./% and 1.5 wt./%, respectively, and the solubility of mercury in cadmium is approximately 37 wt./% at 25 °C [7]. Since these three metals are present in high concentration in the soot, and the measured temperature in the furnace head space is approximately 160 – 180 °C, the mercury would be expected to readily amalgamate and remain in the head space.

Based on the data in Tables 6-9, the following statements can be made about the performance of the 50-lb molten aluminum treatment unit:

- Primary products of incomplete reduction during waste treatment are benzene, toluene, styrene, and naphthalene. Of these, only benzene is of regulatory concern.
- The process does not produce dioxins or furans.
- Aqueous scrubbers are not effective traps for either organic or metallic effluents. It is recommended that they be eliminated and multiple activated charcoal filters be used instead.
- Toxic metals with melting points above the 900 °C operating temperature (chromium and silver) are contained in the aluminum and slag.
- Toxic metals with boiling points below 900 °C (arsenic, cadmium, mercury and selenium) are not contained within the bath and are concentrated in the soot within the sample insertion head. (See Fig. 1 and Table 9.)
- Toxic metals with melting points below 900 °C and boiling points above 900 °C (barium and lead) will be distributed throughout the system based upon such factors as vapor pressure at 900 °C, solubility in molten aluminum, and the ability of the metal to agglomerate with soot.

DISCUSSION

The incomplete reduction of organics and the rather large amount of slag produced are felt to be primarily due to inefficient contact between the solid waste and the aluminum, due to the lack of stirring in the bath. Significant slag production was also seen in the Ashtabula study during treatment of uranium-contaminated soil and pyrophoric uranium [1]. In this same study, an organic liquid, floor stripper, was also treated; however, scrubber water and activated charcoal were not analyzed for VOCs and SVOCs. The floor stripper was injected below the surface of the molten aluminum, and argon was bubbled through the aluminum at the same time. The fact that the sample was a liquid would provide more efficient contact with the aluminum, and both the subsurface injection process and the bubbling of the argon would generate currents within the mix analogous to that produced by stirring. However, since the effluents were not analyzed, it is not known if more efficient contact between the waste and the aluminum reduced or eliminated aromatic hydrocarbon production.

Due to its small size, there is no practical way to stir the aluminum in the 50-lb unit when solids are treated. The issue of the effectiveness of treating solid organic waste using the molten aluminum process needs to be investigated further using a unit where the bath is stirred. CTIC is building a 1500-lb (of aluminum) unit that will stir the bath. Treating items similar to those treated in this study and analyzing the scrubber water and activated carbon for VOCs and SVOCs should answer the question as to whether or not stirring is sufficient to prevent the production of aromatics, particularly benzene, during the treatment of solid organic waste. If regulated (>0.5 ppm) levels of benzene continue to be present in treatment effluents, then activated charcoal filter media would have to be changed out on a regular basis and treated as a hazardous or mixed waste.

Even if small amounts of aromatics are produced during treatment of organic solids, this does not necessarily preclude using the molten aluminum process for certain applications, particularly when no other viable alternative exists. A specific example is a need at DOE's Savannah River site to separate plutonium oxide from organic lab trash so the former can be shipped to the Waste Isolation Pilot Plant (WIPP) for disposal without having to worry about hydrogen generation. A treatability study using a 50-lb molten aluminum unit and cerium oxide as a surrogate for plutonium oxide will be conducted to determine if the aluminum effectively traps the cerium while destroying the organic waste. If successful, this will be followed by a test using plutonium oxide. If the molten aluminum process successfully traps the plutonium while destroying the trash, having to treat scrubber water and/or activated carbon contaminated with hazardous constituents, is a reasonable tradeoff for being able to ship waste to WIPP.

The tests using the car door crank, metal clip, battery and circuit board samples, while admittedly on a small scale, indicate the molten aluminum process could be used to demilitarize weapon components. Given enough time and aluminum, parts would be reduced to their elemental constituents. In the results presented here, samples of both the waste aluminum and slag that contained high levels of chromium and lead passed the TCLP test. However, the fact that six out of the eight RCRA characteristic toxic metals were not effectively contained in either the aluminum or slag means that soot which builds up on interior surfaces would eventually also be a hazardous or mixed waste requiring further treatment prior to disposal. It is expected that both process and unit design improvements will reduce soot production; however, the volatile toxic metals will still have to be trapped and treated, or recycled if they are not mixed waste.

CONCLUSION

While this study has demonstrated the feasibility of using the molten aluminum treatment process to declassify excess weapons components that are classified because of their shape, it has also raised issues regarding the treatment of wastes using this process; specifically, the generation of aromatic hydrocarbons as a result of incomplete reduction of organic waste and the migration of volatile toxic metals that may be present. Use of the molten aluminum process in these and other applications needs to be investigated further, both at the treatability study level and on a larger scale.

REFERENCES

1. Earthline Technologies, *Treatability Report of Clean Technologies International Corporation's Molten Aluminum Alloy Waste Treatment Process*, 2001, p. 9.

2. Attachment 13D-1, "Guidelines for Planning Standard Industrial Hazard (SIH) and Low-Hazard Reviews", *ES&H Manual*, Sandia National Laboratories, MN471001, Issue A, October 25, 1999.

3. U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846*, 3rd ed., USEPA, Washington, D.C., 1990.

4. Maximum Concentration of Contaminants for the Toxicity Characteristic, 40 CFR Part 261.24, Table 1.

5. *Handbook of Chemistry and Physics*, 70th ed., CRC Press, Boca Raton, Florida, 1990.

6. Conversation with Mr. Bill Lindbergh of the Albuquerque Water Department, 6/10/02.

7. B. J. Aylett, "Table 55. Mercury Alloy Systems", in *Comprehensive Inorganic Chemistry,* vol 3, J.C. Bailar, Jr., H. J. Emeleus, Sir Ronald Nyhorn and A. F. Trotman-Dickenson, eds., New York, Pergamon Press, 1973, pp. 283-285.

APPENDIX A

Test Plan

SANDIA NATIONAL LABORATORIES
NEW MEXICO

RADIOACTIVE WASTE/NUCLEAR MATERIAL DISPOSITION DEPARTMENT

TEST PLAN FOR EVALUATION OF CLEAN TECHNOLOGIES' MOLTEN ALUMINUM TREATMENT UNIT

Effective Date: October 24, 2001

Author:

Susan D. Carson International Environmental Analysis Department	Date

Reviewed by:

Ernest Sanchez, ES&H Support Team, Facilities Safety	Date
Randey Colgrove, RWNMDD Site Safety Officer	Date
Mark Wong, ES&H Support Team Industrial Hygienist	Date
Martin Brennan, RWNMDD Radiation Safety Officer	Date

Approval:

James J. Thompson, Manager Radioactive Waste/Nuclear Material Disposition Department	Date

CONTENTS

1.0 PROJECT DESCRIPTION

This test plan provides guidance, instructions and data quality requirements for a performance evaluation of a Clean Technologies molten aluminum waste treatment unit. The unit will be operated at Sandia National Laboratories' (SNL's) Radioactive and Mixed Waste Management Facility (RMWMF) at the SNL site in Albuquerque, New Mexico (SNL/NM) for a period of one year from date of installation. Samples of mixed wastes currently stored at the RMWMF will be treated by immersion in a 900 °C molten aluminum bath. Samples of the aluminum ingot, waste residues, scrubber water, scrubber activated charcoal, and system exhaust gases will be periodically collected and analyzed for radionuclides using gamma spectroscopy and/or liquid scintillation counting (LSC; tritium), as appropriate, and Toxicity Characteristic Leaching Procedure (TCLP) metals, polychlorinated biphenyls (PCBs), volatile organics (VOCs), semi-volatile organics (SVOCs), dioxins, and furans, as appropriate.

1.1 Background

SNL/NM has a wide variety of small-volume mixed low-level waste (MLLW) streams for which there is currently no viable treatment and/or no disposal option, including approximately 40 drums of classified waste. Clean Technologies International Corporation (CTIC) of Houston, Texas has patented the use of molten aluminum to chemically reduce hazardous waste to primarily elemental constituents. This process is particularly attractive for treatment of classified waste because these items are in most cases classified because of their shape. Items to be treated will be wrapped in aluminum foil prior to insertion in the molten aluminum bath, and any residue that does not remain in the bath as dissolved metal will be shapeless and therefore no longer classified.

SNL has installed a CTIC treatment unit at its Albuquerque facility for an initial treatability study using samples of all the types of mixed waste awaiting disposition at the RMWMF for which this treatment process is relevant. This will be followed by a one-year performance evaluation of the unit. If both short and long-term tests are successful, this project will result in an initial validation of an environmentally benign treatment alternative to incineration.

1.2 Goals and Objectives

This study will:

- Determine the effectiveness of this thermal treatment technology for a wide variety of mixed wastes. Wastes that are characteristic mixed wastes should meet the TCLP standards for disposal as low-level waste after treatment; F-listed mixed wastes should meet the Land Disposal Restrictions in 40 CFR 268.40 for disposal in a mixed waste disposal facility.

- Evaluate the destruction and removal efficiency of waste hazardous constituents through sampling and analysis of waste residues and waste treatment effluents.

- Determine system reliability, maintenance requirements, and operating costs during the one-year performance evaluation.

1.3 Technology Description

Clean Technologies International Corporation of Houston, Texas has patented the use of molten aluminum to thermally (900 °C) treat hazardous waste. The process reduces organic compounds to primarily elemental constituents (carbon, hydrogen, nitrogen) in an inert (argon) atmosphere containing ≤5% oxygen. Halogens form the corresponding aluminum salts and oxygen forms aluminum oxides and small amounts of water vapor. Non-volatile metal contaminants remain in the molten aluminum bath. Because treatment is carried out in an inert atmosphere, formation of dioxins and furans has not been observed.

The treatment unit (see Figure A-1) consists of a waste delivery system, an insulated molten aluminum bath containing 50 lbs of aluminum, an off-gas scrubber system, consisting of two aqueous scrubbers followed by an activated carbon filter, and a sampling and analysis system for exhaust gases. A gas chromatograph (GC) is used to monitor off gases for volatile organics.

In addition to the ability to collect and analyze samples of effluent gases prior to their emission to the atmosphere, the unit is designed to allow sampling of the aluminum, scrubber water, and the activated charcoal, as shown in Figure A-2. Samples of the molten aluminum will be collected directly from the bath, scrubber water samples will be taken at valves 8 and 9 in Figure A-2, the activated carbon will be sampled directly, and off-gas samples will be collected at the air sample tee after the activated carbon filter.

Figure A-1. 50-lb Molten Aluminum Treatment Unit.

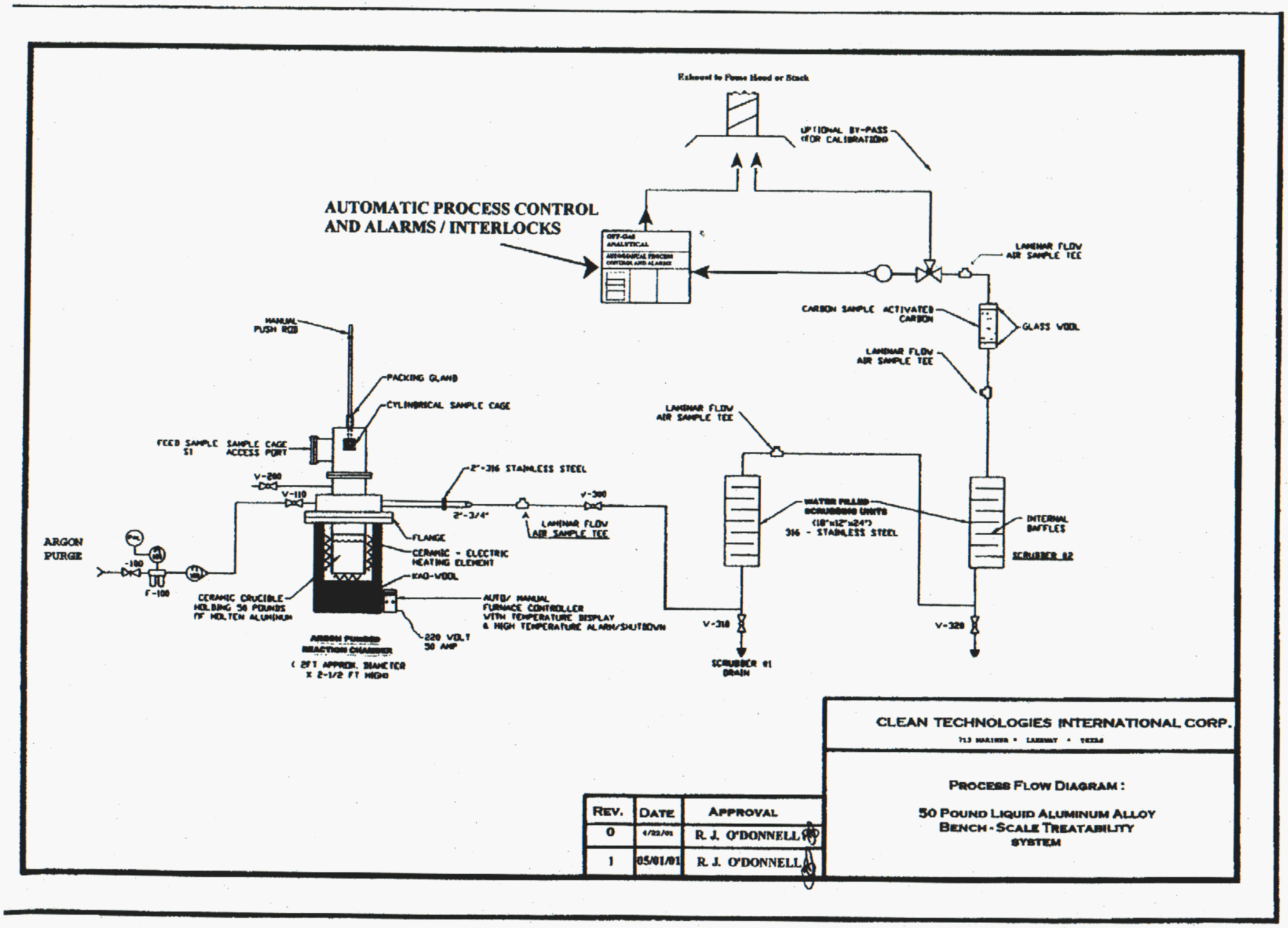

Figure A-2. Schematic of Clean Technologies Molten Aluminum Treatment Unit.

The electrically-heated furnace contains a ceramic crucible that holds the molten aluminum. Solid waste samples wrapped in aluminum foil are placed in a 4-inch diameter ceramic "cage" and manually inserted into the bath using a push rod. Samples are held above the bath until the oxygen in the atmosphere above the bath is ≤5%, as indicated on the oxygen sensor, which is part of the sensor package shown in Figure A-2. The push rod is sealed with a packing gland to maintain the argon atmosphere within the unit. Liquid samples are injected into the bottom of the bath using a positive displacement feed pump; however, Sandia does not currently plan to treat any liquid samples. Argon flows through the system at a rate of approximately 2 cubic feet per hour (cfh), to maintain a positive operating pressure of approximately 4 psi within the unit. A hydrogen sensor monitors the atmosphere above the bath for hydrogen that may be generated during waste reduction.

The unit has successfully treated non-radioactive samples of circuit boards, laboratory trash (rags, paper towels, cardboard, latex gloves), oil absorbed on kitty litter, polyvinyl chloride (pvc) pipe, and oil-soaked ceramic clay chips ("boiling chips"). Each sample is approximately 1/2 cup in volume. Residue after treatment was limited to inorganic material; a small amount of ash from the circuit board, charred kitty litter, and clean boiling chips. The laboratory trash and pvc pipe samples, which were 100% organic materials, produced no visible treatment residues.

For further details on unit design and operation, see the patents listed in Appendix A-1.

1.4 Schedule

The schedule for FY01 and FY02 activities is shown in Figure A-3. Initial testing using surrogate, non-radioactive waste samples will begin in mid-November. This will be followed immediately by the first mixed waste treatment campaign, which will treat characteristic mixed waste.

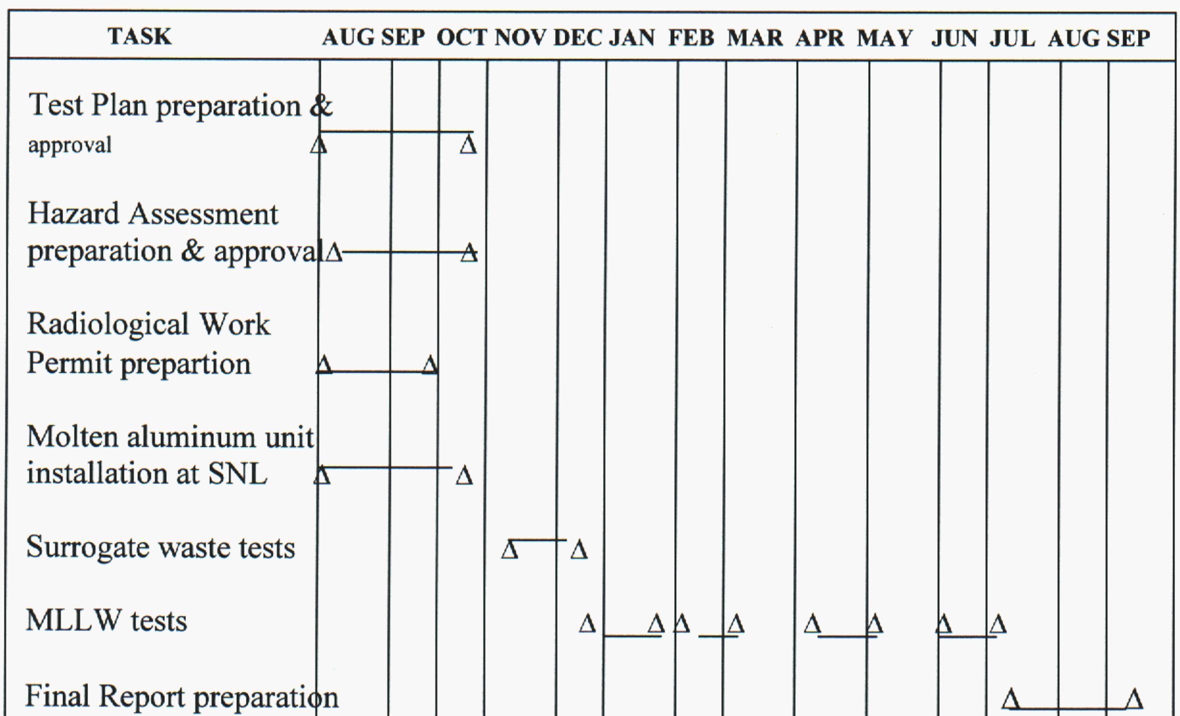

Figure A-3. Schedule of Key Activities, FY01/02

Subsequent FY02 activities will include additional treatment campaign, long-term performance evaluation of the unit and development of an operating and troubleshooting manual.

At least three waste treatment campaigns will be conducted during FY02. The first campaign will treat samples of characteristic mixed low-level waste. The second campaign will treat samples of classified mixed waste. The third campaign will treat samples of listed mixed waste. If, during the course of the evaluation, additional waste streams suitable for this treatment are identified, a final 2-week treatment campaign will be completed by 6/30/02. The unit will then be disassembled and parts that can be decontaminated will be returned to CTIC. A Final Report documenting system performance and waste treatment results will be completed by 9/30/02.

The above schedule is tentative and subject to change based upon equipment performance (downtime for repairs/upgrades) and SNL/NM Site Treatment Plan waste treatment milestones which have priority over this project.

1.5 Ownership

The Radioactive Waste/Nuclear Material Disposition Department, 3125, is responsible for the structure and content of this test plan. Recommendations and comments regarding its modification should be forwarded to this department.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The following sections define organizational responsibilities and establish training requirements for project personnel.

2.1 Project Leader

The Project Leader is responsible for the overall implementation of this plan. Specific duties include:

- Ensure:

  - This procedure complies with all applicable SNL/NM policies and procedures.
  - The procedures outlined in this document are carried out according to the quality control standards described in the Department 3125 Quality Assurance Plan, PLA 96-15.
  - This document is reviewed, approved and updated as required by the author and/or as suggested by personnel on the Authorized Users List.
  - The treatment activity is listed on the RWNMDD Plan-of-the-Day and Plan-of-the-Week.
  - Only personnel who have the training and experience for a Treatment Supervisor/Planner specified in the Weston Training Matrix shall implement this procedure.

- Approve and implement this plan and all other documentation associated with this project.

- Evaluate plan changes and nonconformances and approve corrective actions, as needed.

- Evaluate data for compliance with program objectives and regulatory compliance.

- Review and approve analytical data and associated reports.

- Ensure data and records are properly maintained in accordance with SNL/NM policy.

- Chair weekly project planning sessions. During these meetings, the project team will:

  - Discuss any problems that have occurred during the previous week's operation of the unit.

  - Identify and resolve any waste-specific hazard/control issues associated with wastes to be treated.

  - Develop the work plan for the next week's work.

- Conduct daily pre-job briefings that review the issues identified in the weekly work plan.

- Conduct ongoing hazard and control evaluation to assure that operations remain safe and within the scope of the Technical Work Documents (TWDs) for the project, specifically, this document and Radiological Work Permit (RWP) 1416.

- Notify the Emergency Coordinator (EC) in case of any off-normal event that may constitute an emergency. It is the responsibility of the EC to perform additional notifications.

2.2 Project Safety/Quality Assurance Supervisor

A Project Safety and Quality Assurance Supervisor shall be available at all times during waste treatment and collection of analytical samples. Specific duties include:

- Ensure waste treatment and sampling operations are conducted in accordance with this test plan, Environmental, Safety and Health (ES&H) documents referenced herein, and the requirements of the Radiological Work Permit (RWP).

- Attend project weekly planning sessions.

- Interface with the SNL/NM Sample Management Office (SMO) to obtain appropriate sample containers and documentation forms.

- Oversee sampling activities.

- Ensure sampling activities are properly documented, sample containers are labeled correctly, and initiate chain of custody documents.

- Interface with the Project Manager during normal operations to ensure routine activities, changes and nonconformances are communicated.

- Ensure samples are sent to the SMO in a timely manner such that hold times are not exceeded.

2.3 ES&H Support Team

The Team shall:

- Review general and job-specific work documents for ES&H adequacy.

- Prepare the project RWP.
- Provide radiological support for the project, including, but not limited to, radiological surveys, personnel monitoring, evaluation of radiological conditions and the need for TWD/RWP modification(s).
- Provide general industrial hygiene and OSHA support.

2.4 Clean Technologies International Corporation

CTIC shall:

- Provide to SNL a 50-lb (of aluminum) waste treatment unit that has been leak-tested and certified as leak-free.
- Install the unit at the SNL/NM RMWMF. Unit will be leak-tested again when installation is complete.
- Train SNL personnel to operate the unit using surrogate waste samples.
- Have a representative present during all SNL/NM molten aluminum waste treatment campaigns.

2.5 Unit Operation Personnel

All personnel who will operate the waste treatment unit are required to have the following training:

HAZ101I, Employee Basic Hazcom
HAZ127, Laboratory Spill Cleanup
RAD230, Radiological Worker II Training
ENV189, SNL/NM Mixed Waste Generator Training
24-Hour OSHA Hazards and Protection Training, with an 8-hour refresher course within the past calendar year
Unit-specific training in the operation of the argon gas transfer system to be provided by SNL personnel
HAZ103, Site-specific Hazcom. Specific hazards will be discussed as part of the daily pre-job briefing.

Unit operators shall have been trained by CTIC or by an SNL staff member who has been trained by CTIC and has operated the unit. They must be listed in, read, and have signed the RWP for this program. Operators shall have read this test plan and so signified by signing the Authorized Users List, Appendix A-2 of this document.

Unit operation personnel shall also:

- Read, understand and comply with any additional job-specific work plans that may be required.
- Review waste Disposal Requests prior to waste treatment and verify that the results of any chemical or radiological analyses are present as part of the waste data package.

- Attend weekly project planning sessions and daily pre-job briefings during waste treatment campaigns.

- Ensure that all safety precautions specified in this document are followed.

- Notify the Project Leader when:

  - Incidents occur that are not covered by this procedure or supplemental job-specific work plans.
  - Modifications to this procedure are necessary.
  - Waste does not match the description given on the Disposal Request.

Only personnel who meet the qualifications of Treatment Supervisor/Planner of the Weston Training Matrix shall implement this procedure.

2.6 Sample Collection Personnel

Sample collection personnel are subject to all the requirements listed in section 2.5.

2.7 Sample Management Office (SMO)

The SMO is responsible for the following:

- Provide sample identification numbers, sample bottles, chain of custody form numbers and sample shipping coolers.

- Verify sample numbers and chain-of-custody documentation.

- Provide sample packaging and shipping to an Environmental Protection Agency (EPA) certified analytical laboratory.

- Interface with the analytical laboratory to ensure samples arrive safely at the laboratory, analyses are performed according to standard EPA SW 846 procedures, and analytical reports are prepared according to SNL requirements.

3.0 OPERATING PROCEDURES

The following sections define procedures for installation and checkout of the treatment unit, surrogate waste tests and MLLW tests.

3.1 Treatment Unit Installation and Checkout

Items discussed in this section include unit assembly, RMWMF infrastructure requirements, general unit operating instructions, and hazards associated with unit operation and their mitigation.

3.1.1 Unit Assembly

The molten aluminum treatment unit is being assembled at the SNL/NM RMWMF by Clean Technologies personnel. After the unit is assembled, all joints and connections will be leak-tested under a

2 cfh argon atmosphere using concentrated soap solution. Clean Technologies personnel will then conduct a performance check of the unit to verify that all systems are functioning correctly.

3.1.2 RMWMF Infrastructure Requirements

The molten aluminum treatment unit is housed in Building 6920, Room 119, at the RMWMF. The room has been equipped with single-phase 220-volt 50-amp electrical service, which is required to operate the unit. A timer on the 220-volt outlet enables the bath heater to turn on automatically so that the unit is at 900 °C at the start of each day's waste treatment. The unit off-gas system has been connected to the Room 119 exhaust system, which ties into the main RMWMF exhaust system. The latter includes a High Energy Particulate Air (HEPA) filtration system and particulate and tritium monitors.

A hoist has been added to the cross beam in Room 119 for the placement and removal of the 141-lb treatment unit sample insertion compartment. This compartment is removed after each day's treatment to enable the molten aluminum to be ladled out. A separate lid is placed on the unit when it is not in operation.

3.1.3 General Unit Operating Instructions

The following sections outline the procedures for system startup, operation and shutdown.

3.1.3.1 System Startup - Initial Operation

1. The off-gas monitoring system (GC and oxygen sensors) calibration needs to be checked daily during a waste treatment campaign. Calibration procedures are provided in Appendix A-4 of this document.

2. The 25 psi pressure relief valve (see Section 3.1.5.4) needs to be tested prior to each day's operation using the procedure in Appendix A-5, Section 1.0.

3. Place ~40 lbs of aluminum ingots into the crucible, place the lid on the bath. and start the crucible heating system. The system will take about three hours to melt the ingots.

4. After the initial ingots melt, using a ladle, carefully add additional ingots to fill the crucible to the full mark. Adjust the addition rate to avoid over-filling the crucible or excessive cool-down of the crucible. This step should result in a total of about 50 lbs of aluminum being used, and should take about an hour.

   (**NOTE:** CTIC will fill the bath initially; during the one-year operating time frame at SNL, aluminum will need to be added periodically as the bath is sampled during waste treatment.)

5. Using the procedure in Appendix A-5, section 2.0, place the sample insertion compartment on the bath and tighten bolts.

6. Leak check all joints and seals with concentrated soap solution.

3.1.3.2 System Startup - Subsequent Operation

The molten aluminum is ladled out at the end of each day's operation. (See Section 3.1.3.4.) After the bath is filled and emptied the first time, the ingots will be put back in the bath as soon as they are cool enough to handle, the lid will be placed on the bath, and the heater timer will be set to come on at 0400 the next day.

1. Calibrate the off-gas monitoring system using the procedures in Appendix A-4.

2. Test the pressure relief valve as per the procedure in Appendix A-5, Section 1.0.

3. Remove the bath lid.

4. At this point, the level of aluminum in the bath should be checked daily and verified by initialing line 1 of the System Operation Checklist. (A sample checklist is provided in Appendix C.) Add aluminum ingots as necessary to keep the molten aluminum level at the "full" mark. Record any aluminum additions on line 2 of the System Operation Checklist.

5. Using the procedure in Appendix A-5, section 2.0, place the sample insertion compartment on the bath and tighten bolts.

6. Leak check all joints and seals with concentrated soap solution at the start of each treatment campaign and once a week during a treatment campaign.

3.1.3.3 System Operation

The following steps summarize system operation during sample treatment. The detailed procedure is presented in Appendix A-5, Section 3.0.

1. Verify that the off-gas monitoring equipment has been calibrated and is operational by initialing line 3 of the System Operation Checklist. (See sample checklist, Appendix A-3.) If calibration has not been performed, calibrate the instrumentation using the procedures in Appendix A-4.

2. Verify that the Room 119 ventilation system is connected to the unit exhaust hood and is operational. Initial line 4 of the System Operation Checklist. If the ventilation system is not operating, i.e., there is no noticeable air flow in Room 119, this is a Stop Work condition. Proceed to System Shutdown, Section 3.1.3.4.

3. Verify that the pressure relief valve is operational by initialing line 5 of the System Operation Checklist. If the valve is not operational, this is a Stop Work condition. Proceed to System Shutdown, Section 3.1.3.4.

4. Record the initial argon gas cylinder pressure on line 6 of the System Operation Checklist. If pressure is below 200 psig, change out the cylinder as per the procedure in Appendix A-6. Record the initial pressure of the new cylinder on line 7 of the Checklist. Allow the argon to flow through the system until the oxygen sensor in the molten aluminum bath atmosphere indicates an oxygen concentration $\leq$ 5%, about ten minutes.

5. Verify that the temperature monitor is at 900 $\pm$ 20 °C and initial line 8 of the Checklist. System is now ready for operation.

   NOTE: A temperature reading outside this range after the unit has been on for at least four hours is an indication that the temperature controller is not functioning properly. This is a Stop Work condition. Proceed to System Shutdown, Section 3.1.3.4.

6. Record the sample type, weight, and date of treatment in the Waste Treatment Logbook. Add the waste sample to the molten aluminum in accordance with the instructions in section 3.0 of Appendix A-5.

7. Allow the sample to remain in the bath for at least five minutes. (Surrogate tests will determine bath times for various waste types.) Remove sample cage from the bath in accordance with the instructions in section 3.0 of Appendix A-5 and place in a stainless steel tray on the stainless steel table in Room 119 and allow to cool. Collect any sample residue in accordance with the instructions in 5.0 of Appendix A-7. Record the physical characteristics of any waste treatment residue in the "Comments" column in the Waste Treatment Logbook. If waste is completely consumed, note this in the "Comments" column.

8. Purge the system with argon between samples until readings on the off-gas monitoring system are zero and the oxygen monitor reads $\leq 5\%$, about ten minutes. Steps 6 through 8 are repeated for each sample.

9. Collect samples of the aluminum bath, scrubber water, activated carbon, and off gases in accordance with the procedures in Appendix A-7 weekly.

3.1.3.4 System Shutdown During a Treatment Campaign

1. Allow the argon purge to continue until all off-gas monitoring system readings are zero, approximately 10 minutes.

2. Turn off the argon flow and record the time on line 9 of the System Operation Checklist.

3. Shut down the off-gas monitoring system using the procedures in Appendix A-4 and initial line 10 of the System Operating Checklist.

4. Turn off the bath heaters and remove the sample compartment using the procedure in Section 4.0 of Appendix A-5. Ladle the molten aluminum into the ingot molds provided by CTIC. Initial line 11 of the System Operation Checklist.

5. Once the ingots have cooled, return them to the bath, place the lid on the bath, and set the timer for a 0400 startup. Initial line 12 of the System Operation Checklist.

3.1.3.5 System Shutdown at the End of a Treatment Campaign

1. Complete steps 1 through 4 in section 3.1.3.4.

2. Once the ingots have cooled, return them to the bath, place the lid on the bath, and initial line 13 of the System Operation Checklist.

3.1.3.6 Power Outage

No special precautions are required if the system should lose power. If a power loss should occur during treatment, treatment of the sample in the bath should continue. The bath is insulated and will retain sufficient heat to allow treatment of the sample to be completed. At that point treatment should cease until power is restored. If power is off for long enough that the bath temperature drops below 800 °C, the unit should be completely shut down as per the procedure in section 3.1.3.4.

3.1.4 Operational Hazards

Operational hazards associated with the molten aluminum treatment unit include radiation, hazardous materials, high temperatures, pressure, hydrogen generation, the potential for a fire, spills, and system leaks.

3.1.4.1 Radiation/Radioactive Material

Waste samples are mixed low-level waste, i.e., they contain radionuclides and materials considered hazardous under the Resource Conservation and Recovery Act (RCRA). Waste may contain virtually any radionuclide; however, uranium isotopes and decay products, Co-60, Cs-137, Sr-90 and tritium are expected to be the primary radioactive materials present. Most samples will contain radionuclides at activity levels ranging from picocuries to microcuries; however, samples contaminated with tritium may contain as much as 100 mCi.

A complete list of radionuclides that may be present in waste to be treated is shown in Table A-1.

Table A-1. Total Activity of Radionuclides Found in Candidate Waste Streams for Molten Aluminum Treatment

Radionuclide	Total Activity, Ci	Radionuclide	Total Activity, Ci
H-3	8.31 E-02	Ni-63	5.92 E-03
C-14	3.20 E-04	U-238	4.37 E-05
Cs-137/Sr-90	1.48 E-05	Co-60	7.38 E-06
U-234	4.89 E-06	Th-228	2.83 E-06
Ra-226	4.50 E-07	Kr-85	3.14 E-07
Th-232	2.73 E-07	U-235	2.03 E-07
Sb-125	1.22 E-07	Eu-152	4.48 E-08
Eu-154	1.32 E-08	Ra-228	8.13 E-09
Te-132	3.96 E-09	Pb-210	3.96 E-09
Th-230	3.83 E-09	Th-234	1.73 E-09
Cs-134	1.46 E-09	U-236	8.28 E-10
Pb-214	5.62 E-10	Co-57	5.52 E-10
Co-56	3.78 E-10	Mn-54	3.76 E-10
Fe-55	7.55 E-11	Ce-144	5.52 E-11
K-40	3.95 E-11	Nb-95	3.57 E-11
Ru-106	1.20 E-11	Ce-141	7.12 E-12
Ba-133	4.73 E-12	Pm-147	3.68 E-12
Ru-103	3.52 E-12	Zn-65	3.44 E-12
Fe-59	2.04 E-12	Pu-241	1.14 E-12
Pu-238	5.26 E-13	Pu-239	5.68 E-14
Pu-240	4.76 E-14	Am-241	3.80 E-14
Np-237	1.19 E-16	Am-242m	4.10 E-17
Pu-242	1.18 E-17	Cm-243	7.63 E-18
Am-243	4.06 E-18		

3.1.4.2 Hazardous Materials

Waste samples may contain any combination of RCRA metals and listed organic contaminants. Waste types include debris, granular solids, sludges and soils. At the present time, only solids will be treated. The wastes being considered for this treatability study are listed in Table A-2. In addition to these 40 wastes, samples of classified wastes will also be treated.

Table 2. Candidate Wastes for CTIC Treatment

DR# *	TG **	Vol., m^3	Wt., kg	RCRA Codes	Waste Description
204280	8	0.005	28.2	D006, 8, 10; F002, UHC	Soft debris (sorbent, paper filters)
204010	8	0.008	1.4	F002, F003	Organic debris, respirator filter medium
204302	8	0.21	18.2	D001, 6, 7, 8, 9, 11; F001, 2, 3, 5	WERF composite sample for TG-8
204357	8	0.003	2.3	F003	PPE (2 small bags)
900036	8	0.003	0.45	F003	Grease on a paper towel
960488	8	0.25	16.8	F002	PPE, gloves, packing
960489	8	0.076	4.5	F002	PPE/soft debris
981186	8	0.11	2.0	D006, F005	PPE, gloves, cardboard, paper towels
981247	8	0.085	2.0	F005	Soft debris
981345	8	0.038	0.91	D001	Ethanol wipes
990061	8	0.076	12.7	F002, 5; UHC	PPE and wipes
994100	8	0.019	2.7	F002, 3	Airline filters
994169	8	0.028	0.45	F002, 5; D008, UHC	PPE, gloves
994285	8	0.011	2.7	F002	Filter media
204225	9	0.057	37.8	D006	Crushed NiCd batteries
204374	9	0.002	0.45	D008	Spark gap switches used in laser research
981152	9	0.026	15.7	D007, 8	Circuit boards
994090	9	0.014	0.91	D008, UHC	Switch tubes
994136	9	0.23	0.91	D008	Meter with sealed source
994186	9	0.001	0.91	D008, UHC	NiCd AAA batteries
994515	9	0.003	0.45	D007, 8	Electronic tubes in epoxy
930401	9	0.002	0.09	D004	U phosphide, U phosphate, U arsenide in glass bottles
950125	9	0.019	3.2	D008	Activated lamp ballast
940197	9	0.014	2.3	D008	Circuit board, tape dispenser, lens
994303v	9	0.004	2.3	D001, 2, 6, 9	NiCd battery; HgO batteries
994107	10	0.020	5.9	D004, 7, 8, 9; F002, 3; UHC	Soil and mica flakes
994162	10	0.007	0.45	D003, UHC	Aerosol can of dry lubricant/release agent

Table 2, cont

DR# *	TG **	Vol., m^3	Wt., kg	RCRA Codes	Waste Description
014093	10	0.014	0.45	D011	Two D flashlight batteries
950039	12	0.0003	0.45	D009	Gloves, paper
204445	12	0.057	1.4	D008, 11	Wipes, gloves, towels, plastic container
204459	17	0.002	1.3	D008	Charcoal
204009	18	0.002	0.45	F003	Charcoal from respirators
204010	18	0.002	0.45	F002	Charcoal
204213	18	0.019	4.1	F003	Resin and soil
204292	18	0.004	0.91	F002	Vermiculite
204307	18	0.003	0.68	F002	Vermiculite
204309	18	<0.001	0.68	F003, 5	Vermiculite
204358	18	0.085	2.3	F005	Vermiculite
970899	18	0.014	0.68	F003, 5	Charcoal filter sample
994043	18	0.003	2.27	F001, 2, 3, 5	Vermiculite

* DR# = Disposal Request Number ** TG = Treatability Group

Total Mass, ~183 kg Total Vol., ~1.53 m^3

3.1.4.3 High Temperatures

The molten aluminum treatment unit operates at a temperature of 900 °C. While the molten aluminum bath is well insulated, unit operation will cause the ambient room temperature to rise.

3.1.4.4 Pressure

Excessive pressure in the system could occur in three ways: 1) a sample could generate large amounts of gas during treatment, 2) water from the scrubbers could backwash into the molten aluminum bath, producing a sudden burst of steam, or 3) the argon pressure regulator could fail.

3.1.4.5 Hydrogen Generation

Since the unit operates under an argon atmosphere, minimal amounts of oxygen ($\leq$5%) are present. As a result, waste is chemically reduced by the aluminum and hydrogen gas is one of the off-gas products.

3.1.4.6 Fire

The molten aluminum unit operates in an inert argon atmospheres that contains $\leq$5% oxygen. Therefore, organic materials are chemically reduced, not oxidized as they would be during incineration. If excessive oxygen should come in contact with waste in the bath melt, the waste could catch fire. Due to the size of the waste samples (~4 oz.) such a fire would be small and localized, and would last only until the waste was consumed.

3.1.4.7 Spills

Spills can occur during molten aluminum transfer or sampling, scrubber water sampling, or during removal of treatment sample residues (if any) from the bath.

3.1.4.8 System Leaks

The molten aluminum treatment unit contains seals and joints where leaks could occur during operation (see Figure A-2).

3.1.5 Operational Hazards Mitigation

The following sections outline the measures that will be used to mitigate the operational hazards discussed in Section 3.1.4.

3.1.5.1 Radiation/Radioactive Materials

Operations and sampling personnel will wear the following Personal Protection Equipment (PPE):

- For sample preparation in Room 120, collection of scrubber water and activated charcoal samples, and handling of aluminum ingots, standard PPE for radiological work; i.e., coveralls, booties, gloves and goggles.
- For sample treatment, a "bubble suit" with full-face respirator.
- For ladling out molten aluminum, a Kevlar fire protection suit with full-face respirator.

Room 119 is a radiological work area, with appropriate postings and barriers to limit access to only authorized personnel. Waste treatment and sample collection will be conducted under the supervision of a RMWMF radiological control technician (RCT). Dosimetry will be used in accordance with RWP requirements. Routine and special (at the discretion of the RCT) surveys will be performed to control radiological contamination and dose rates. Continuous air monitors (CAMs) will be used to monitor airborne radioactivity as deemed appropriate by the RCT and the RWP. Personnel monitoring will be required upon exiting the Room 119/120 work area.

The molten aluminum unit is connected to the Room 119 air exhaust system, which ties into the main RMWMF exhaust system. This system is equipped with particulate and tritium monitoring systems. Tritium will exhaust directly to the outside atmosphere, minimizing exposure of other building personnel. It is estimated that the entire treatability study will result in a maximum release of <10 curies of tritium to the atmosphere. The maximum tritium inventory evaluated in the original RMWMF radiological NESHAPS (National Emission Standards for Hazardous Air Pollutants) assessment was 176 curies per year released to the atmosphere. Therefore, the tritium releases associated with this project do not exceed 40 CFR Part 61, Subpart H thresholds. Most of the tritium released during waste treatment should be trapped in the scrubber water.

If a monitoring alarm should sound, work will cease and the bath will be placed in standby or shutdown mode, at the discretion of the RCT. The RCT will determine when work will resume.

3.1.5.2 Hazardous Materials

The PPE that all operations and sampling personnel are required to wear for radiation protection will also protect workers from contact with RCRA metals and organic contaminants in the waste to be treated. Treatment will destroy the organics and metals will remain either in the bath melt or in the scrubber water, depending upon their solubility and volatility. Daily sampling and analysis of effluents will verify the isolation and destruction of waste hazardous constituents.

3.1.5.3 High Temperatures

The PPE required for waste treatment is designed to minimize worker heat stress. However, tests have demonstrated that Room 119 does not become excessively warm. During about seven hours of operation, including about three hours at 900 °C, the temperature in Room 119 rose from about 73 °F to about 82 °F. During the twenty minutes when the molten aluminum was being transferred from the bath to ingot molds, the temperature rose to 89 °F in the room, exclusive of the area directly over the open bath, which was about 120 °F. Total temperature rise during operation will be limited by the fact that the unit will be turned off at the end of each day and will turn on at 0400 the next morning. The unit will never operate continuously for more than 10-11 hours, about 7 hours of which will be at 900 °C.

The molten aluminum bath is insulated with a 14-inch thick layer of ceramic fiber insulation; but the outside surface of the bath will become hot during unit operation. Therefore, the unit will be labeled as hot and barriers that will protect against accidental contact will be erected around it. The unit is programmed to automatically shut down if the bath temperature reaches 1000 °C.

The operator who collects samples of the molten aluminum will wear an aluminized Kevlar fire protection suit during sample collection.

The external surface temperature of the molten aluminum bath, the room temperature and the operating technician's heart rate will be monitored. If the operator shows signs of heat stress, he will cease work and another operator will take over.

3.1.5.4 Pressure

The molten aluminum bath is equipped with a one-half-inch, 25 psi pressure relief valve. Should the pressure in the bath exceed this value during sample treatment, the valve will open automatically and exhaust the gases directly to the unit exhaust system, and, from there, through the Building 6920 air exhaust system. The bath has been certified as leak-tight to 25 psi by SNL pressure safety personnel.

The bath is doubly protected from scrubber water backwash. The unit valve system (see Figure 2) and system operating procedures (Appendix E, section E3.0) prevent backwash. If an operator should inadvertently open and close valves in the wrong sequence, a backwash check valve between the bath and the scrubber valve system (see Figure 2) will close automatically to prevent scrubber water from backing up into the bath. If the check valve should fail, the steam would vent through the 25 psi pressure relief valve.

3.1.5.5 Hydrogen Generation

Hydrogen gas in the atmosphere above the molten aluminum is monitored automatically in real time by a hydrogen sensor that will sound both an audio and visual alarm if the hydrogen concentration (by volume) reaches 1%. Due to the small size of treatment samples, no significant amounts of hydrogen have been generated in previous studies with this unit. Should hydrogen concentrations rise above 1% (the lower explosive limit for hydrogen in air is 4%), the bath heater would be shut down. Argon gas would continue to flow through the system and would dilute and exhaust the hydrogen to the atmosphere. Work would cease until the hydrogen concentration returned to <1%.

3.1.5.6 Fire

An oxygen monitor will be used to ensure that the oxygen concentration in the bath melt atmosphere does not exceed 5% during unit operation. Depending upon the waste composition, "spikes" exceeding 5% may occur during waste treatment; however, samples will only be placed in or removed from the unit when oxygen concentration is $\leq$5%. While the risk of a fire is small, an ABC dry chemical fire extinguisher is available in Room 119 if needed.

3.1.5.7 Spills

Ingot molds will be placed in a Type 316 (or equivalent) stainless steel spill pan to contain any spills that may occur during molten aluminum sampling or transfer to the ingot molds. Scrubbers have been placed in a stainless steel pan of sufficient volume to contain the ~75 gallons of water in the two scrubbers. Treatment residues will be cooled in a stainless steel pan and placed in tared sample containers for weighing.

A spill is a Stop Work condition. All spills will be immediately reported to the RCT in charge, who will supervise cleanup, conduct post-cleanup surveys and determine when work may resume. Special instructions and/or a special RWP will be issued, as appropriate, to handle such situations.

3.1.5.8 System Leaks

If a system leak were to occur during unit operation, it is likely to be detected by one or more of the following:

- excessive use of argon
- a rise in the oxygen concentration
- release of radioactivity to the work area, which would set off area monitors

If a leak is small, it might not be detected by any of the system monitors listed above; however, during extended operation, the unit will be leak-checked weekly, or, if the unit has been completely shut down, a leak check is required as part of system startup. (See Section 3.1.3.1, Step 4.) If a leak is detected, the unit will be shut down immediately. Work will cease (Stop Work condition) until the leak is repaired and the area is declared safe for work to resume by the supervising RCT. Special instructions and/or a special RWP will be issued, as appropriate, to handle such situations.

3.2 Surrogate Waste Tests

Prior to treatment of mixed waste samples, a series of non-radioactive, non-hazardous samples will be treated to verify all systems are operating correctly and to train SNL personnel who will operate the unit.

3.2.1 Surrogate Waste Sample Preparation

Since mixed waste samples are primarily granular solids and solid debris, representative samples of each waste class will be treated. Clean oil on "kitty litter" will represent a granular solid, and samples of items such as pvc pipe, copper fittings and rags will be treated as representative of debris wastes.

Surrogate waste samples will be prepared outside the treatment area. They will be weighed and wrapped in a sufficient amount of aluminum foil to allow the edges of the foil to be tightly folded to prevent thermal decomposition from occurring until the waste is completely submerged in the molten aluminum.

3.2.2 Surrogate Waste Treatment

Samples will be treated according to the procedure in Section 3.1.3.3, System Operation.

3.2.3 Surrogate Waste Sample Disposal

Residues (if any) remaining after treatment will be weighed and the weights will be recorded in the Sample Treatment Logbook. Since sample residues are non-radioactive and non-hazardous, and radioactive waste has not been treated in the unit, residues may be disposed of as part of the ordinary lab trash.

3.3 Treatment of Mixed Low-Level Waste Samples

3.3.1 Waste Sample Preparation

Prepare waste samples in the hood in Building 6920, Room 120 in accordance with the procedures in Work Plan CT02-01. Samples should be approximately 1/2 cup in volume and should easily fit in the treatment unit sample holding basket when wrapped in aluminum foil. Wrap samples in a sufficient amount of aluminum foil to allow the edges of the foil to be tightly folded to prevent thermal decomposition from occurring until the waste is completely submerged in the molten aluminum. At least three samples from each DR will be treated, unless the waste is completely consumed in one or two samples.

Assign an identification (ID) number to each sample. ID numbers will consist of the waste package number, followed by a dash and an integer for each sample from that package; e.g., 930401-1, 930401-2, etc. For each sample, record the sample ID number, sample weight, type of waste, associated Disposal Request (DR) number, and the date of treatment in the Waste Treatment Logbook.

The types of wastes that will be treated are listed in Table A-2.

3.3.2 Waste Treatment

Treat waste samples according to the procedure in Section 3.1.3.3, System Operation. Since wastes that are characteristic mixed waste should be able to be disposed of as low-level waste after treatment, these wastes will be treated first in treatment campaigns 1 and 2. Samples of F-listed wastes, whose treatment residues will have to be disposed of as mixed waste, will be treated in campaign 3 after all characteristic mixed waste samples have been treated.

3.3.3 Analytical Sample Collection

Prior to treatment of any mixed waste, baseline samples of the aluminum, the water in each scrubber, and activated charcoal will be collected for analysis of VOCs, SVOCs, total halogens,TCLP metals, PCBs, dioxins, furans, and radionuclides. Samples of these effluents will also be collected weekly during treatment campaigns. Sampling and analysis requirements for the aluminum, scrubber water, activated carbon and off gases are summarized in Table A-3.

Table A-3. Sampling and Analysis Requirements for Molten Aluminum Treatment Effluents

Effluent	Analysis [a]	Sample Container	Max Holding Time	Test Procedure [b]
Aluminum	TCLP Metals Total RCRA Metals Major Anions (F, Br, Cl, SO_4)[c]	TBD, based on ingot size; 100-150 g required for analysis	6 Months	1311/6010B/7471A 6010B/7471A 300.0
Scrubber #1 Scrubber # 2	VOCs [c]	3 40-mL glass vials, HCl preservative	14 Days	8260B
	SVOCs [c]	2 1-L amber glass bottles	7 Days to extraction	8270C
	Total RCRA Metals	250-mL poly bottle, HNO_3 preservative	6 Months	6010B/7470A
	Dioxins & Furans [c]	4 1-L amber glass bottles	30 Days	8280
	Major Anions (F, Br, Cl, SO_4)[c]	500 mL poly bottle		300.0
Activated Charcoal	VOCs [c] SVOCs [c] TCLP Metals Total RCRA Metals Dioxins & Furans [c] Total Organic Halogens[c]	50 g One 150-g sample for all remaining analyses (SVOCs, TCLP metals, total RCRA metals, dioxins & furans, total organic halogens)	14 Days 14 Days to extraction 6 Months 30Days	8260B 8270A 6010B/7471A 8280 9020B
Off-Gases	VOCs [c]	Summa canister	14 Days	TO14A

[a] Samples will only be analyzed for PCBs when these are known to be present in the untreated waste.

[b] U.S. Environmental Protection Agency (EAP), 1990. "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," SW-846, 3rd ed., USEPA, Washington, D.C.

[c] Will only be performed if wastes treated contained organic compounds.

Samples will be placed on ice in a shipping cooler immediately after collection, and will be maintained at 4 °C until delivery to the analytical laboratory. Samples will undergo gamma and/or LSC (liquid scintillation counting) analyses, as appropriate, prior to shipment off-site for chemical analyses.

Sampling personnel will obtain sample identification numbers, chain-of-custody numbers, sample labels and containers from the SMO. Sample labels and the Analysis Request and Chain of Custody Record (ARCOCR) are to be typed or completed using indelible ink. Errors are corrected by drawing a single line through the error, such that the stricken text remains legible. The correct information is entered along with the date and initials of the person recording the information.

See Appendix A-7 for detailed sample collection procedures for molten aluminum, scrubber water, activated charcoal and off gases.

3.3.4 Sample Shipping

Upon completion of sampling activities and associated documentation, after release by the RCT, the samples will be delivered to the SMO Shipping and Receiving Facility. Sample custody will be assigned to the SMO at that time. SMO shipping technicians will package the samples for shipment and deliver the package to the SNL/NM Shipping/Receiving Department for assignment to an overnight carrier. Upon shipping, the shipper's waybill documents the transfer of custody to the shipper. The ARCOCR accompanies the samples to the laboratory. Sample storage, packaging and shipment are the responsibility of the SMO and will be performed in accordance with the "Sample Management Office User's Guide," AOP 94-22.

3.3.5 Sample Disposition

Samples will be disposed of only at the conclusion of all laboratory analytical work and in accordance with all federal and and state regulations. Samples will be returned to SNL for treatment and disposal.

4.0 EXTENDED OPERATION

The molten aluminum treatment unit will remain at SNL/NM for one year after installation. The unit will be used on a regular periodic basis in order to evaluate long-term performance. A Unit Operation Log will be kept during this time. In addition to the System Operation Checklists, the log will contain records of system maintenance and repairs or parts replacement that may be required.

5.0 UNIT SHUTDOWN AND DECONTAMINATION

After the one-year performance evaluation, the unit will be decontaminated and dismantled. A separate procedure will be written for unit disassembly and decontamination. All parts that can be decontaminated will be decontaminated and returned to CTIC. Parts that are not practical to decontaminate will be disposed of as mixed waste debris.

Treatment residues requiring disposal will include the solidified aluminum from the bath, scrubber water, and activated charcoal. Since these waste streams come from a unit used to treat listed mixed waste, they will have to be treated to meet RCRA Land Disposal Restrictions (LDRs) and disposed of as mixed waste. If the scrubber water meets LDRs as is, it can be solidified for disposal. If organic concentrations exceed LDR limits, the water will have to be incinerated. If the activated charcoal meets LDRs, it can be disposed of as is. If it exceeds LDR limits for organic contaminants, it will require thermal treatment, such as thermal desorption. If TCLP limits for toxic metals are exceeded, the charcoal will have to be stabilized prior to disposal.

If the aluminum ingots pass TCLP, they can be disposed of as is. If ingot samples fail TCLP, the standard treatment for the solidified aluminum would be to grind it up and stabilize the ground material. However, since the ingots are already monoliths with metals alloyed in them, the logical treatment would be to macroencapsulate the ingots. If treatment of the waste aluminum is required, SNL will apply for a treatment variance from the New Mexico Environment Department to be able to macroencapsulate the aluminum.

Slag may form on top of the ingot. This can be scraped off, sampled, and sent for analysis. If it meets LDRs, it can be disposed as is, otherwise, stabilization is required prior to disposal.

6.0 EMERGENCY PROCEDURES

- If a fire occurs, alert co-workers in the area, evacuate Room 119, initiate a fire alarm, and proceed to the designated assembly area. Do not remove PPE if danger is imminent. If you have had fire extinguisher training and, in your judgement, you can handle the fire, proceed with extinguishing the fire. **You are not required to fight a fire.** If at any point you decide not to fight the fire, follow evacuation procedures.

- Dial 911 for a medical emergency. Immediately contact the 3125 Emergency Coordinator after making the call.

- If an evacuation alarm sounds and it is safe to do so, ensure all chemical containers are closed and all waste containers are sealed or covered prior to building evacuation.

- If a worker becomes radiologically contaminated, immediately notify the RCT so decontamination procedures can be implemented as quickly as possible. All personnel must remain in the area and await further instructions from the RCT.

- If a worker becomes chemically contaminated, decontamination procedures will be initated as per the Material Safety Data Sheet (MSDS) for the chemical involved, including the use of the emergency shower and eyewash located directly outside Room 119. The RCT will be notified and all personnel must remain in the area and await further instructions from the RCT. Industrial Hygiene will be notified to address issues associated with skin absorption of chemicals.

- Report all emergencies to the Emergency Coordinator and the 3125 Department Manager.

- Fire/Emergency/Alarm - In case of a fire alarm or other emergency alarm, follow the emergency procedures for the facility defined in the RMWMF Contingency Plan. This includes alerting others, putting work in a safe condition if it does not endanger you or others to do so, evacuating the area, assembling at the designated location, and contacting response personnel.

7.0 QUALITY CONTROL

To maintain an accurate record of system operation, a Unit Operation Log and a Waste Treatment Log will be maintained. To document the integrity of samples from the time of collection through data reporting, sample collection and custody records shall be maintained. Standardized SNL/NM forms, the Sample Collection Log (SCL) and the ARCOCR, will be used to document sample collection and custody. These forms will be completed as specified in AOP 95-16, following instructions provided on the back of each form. All documentation must be legible, identifiable, and typed or recorded in permanent black ink. Operations and sampling personnel will complete documentation at the job site during or immediately after sample collection.

7.1 Unit Operation Log

The Unit Operation Log is a bound notebook that will contain a running daily record of system operation that includes items such as routine and corrective maintenance, calibration records for the off-gas monitoring system, abnormal occurrences, the total weight of waste treated each day, and the names of the operating personnel for the day. The System Operation Checklists (see Section 3.1.3.2) shall be kept in a separate loose-leaf notebook. The notebook and log will be kept in the South Bay of Building 6920.

7.2 Waste Treatment Log

The Waste Treatment Log is a bound notebook that will contain a running daily record of the waste streams treated. For each waste, the following data will be recorded:

- Waste name and sample ID number(s)
- Treatment date
- Names of operating and sampling personnel
- Weight of each sample
- Total weight of waste treated
- Weight of any waste residue from each sample
- Physical characteristics of waste residue
- Problems (if any) associated with waste treatment

The following data will be recorded for both waste and effluent analytical samples:

- Type of and identification numbers for analytical samples collected
- ARCOCR identification number for analytical samples
- Date analytical results received
- Summary of analytical results

Copies of official analytical reports will be kept in a separate loose-leaf notebook. Original data will be kept by the SMO. The notebook and log will be kept in the South Bay of Building 6920.

7.3 Sample Collection Log

A standard SNL/NM SCL and attachments will be used to record pertinent sample collection information for each sample collected. The log will be completed at the time of collection and becomes part of the permanent record describing sample collection conditions and sample disposition. Information recorded shall be sufficient to ensure the entire sampling event can be reconstructed from the recorded information. Sample collection documentation may be supplemented through the use of log sheets to record additional sampling details not entered on the SCL. Copies of the SCL and attachment log sheets will be attached to the analytical report as an appendix.

7.4 Analysis Request and Chain of Custody Record

The ARCOCR is used to record the possession and handling of a sample from collection through analysis and disposal and to relay analysis request information to the laboratory. The ARCOCR is initiated at the time of sample collection and must accompany all samples to the analytical laboratory. The record must clearly state the analysis to be performed, including laboratory QC analyses and any special handling required.

7.5 Quality Control Samples

Quality control samples and frequency of analysis are summarized in Table A-4. A trip blank sample will be provided by the laboratory to accompany VOC samples from collection to delivery at the laboratory. Duplicate samples will be submitted for analysis as blind samples. Relative percent differences for duplicate samples that exceed laboratory QA objectives shall be cause for evaluation of the sampling and analysis system

Table A-4. Quality Control Sample Requirements

Field QC Sample	Purpose	Min Frequency	Corrective Action
Trip Blank	Monitor sample contamination during holding and transport	1 per shipping cooler with VOC samples	Evaluate holding and shipping process to determine contamination source and correct. Evaluate data for usability.
Duplicate Sample	Determine precision associated with sampling process	1 per 5 samples	Evaluate sampling process and revise as necessary. Evaluate data for usability.
Laboratory QC			
Method Blank	Determine contamination associated with analytical process	1 per analytical batch	Correct problem in accordance with laboratory Quality Assurance (QA) plan.
Laboratory Control Sample	Determine accuracy and precision associated with analytical process	1 set per 20 samples or analytical batch, whichever is most frequent	Correct problem in accordance with laboratory QA plan.
Matrix Spike	Determine matrix bias	1 per 10 samples for all inorganic and non-gas chromatography/ mass spectrometry organic parameters	Evaluate data for usability; repeat analyses as necessary.

7.6 Data Reduction, Validation and Reporting

All data reduction will be performed at the analytical laboratory in accordance with the analytical method and the laboratory's data reduction procedure and QA plan. Since treatment waste residues may be disposed of at Envirocare, Inc. of Utah, the contract laboratory must be certified by the state of Utah.

7.7 Records Management

Completed records generated during sampling and analysis will be submitted to the SNL/NM Environmental Operations Record Center (EORC). The EORC will maintain these records in accordance with "Sandia National Laboratories/New Mexico Records Center Customer Manual".

Upon completion of this project, the Unit Operation Log, System Operation Checklist notebook, Waste Treatment Log and Analytical Reports notebook will placed in the RMWMF Records Center.

8.0 RMWMF REPORTING AND DOCUMENTATION

- SF 2042-RTF, RMWMF Treatment Form, must be completed for each DR treated and all items should be completed. All unused entries should be crossed out and initialed.

- SF2042-DRX, Radioactive/Mixed Waste DR Change Request form must be completed for each DR treated.

- Both the completed treatment form and DR change request should be attached to the original DR and submitted to records personnel once treatment is complete.

- The Rad Track electronic mixed waste treatment log must also be updated.

- A separate disposal request will be written for empty waste containers. The radiological content of the empty containers will be assumed to be 10% of the original waste in the container.

9.0 REFERENCES

Radiological Work Permit (RWP) 1416 to treat mixed waste in a 900 deg. C molten aluminum treatment unit.

Sandia National Laboratories/New Mexico, Department Quality Assurance Plan, PLA 96-15.

Sandia National Laboratories/New Mexico, Radioactive Waste/Nuclear Material Disposition Department, "Non-Nuclear Operations Safety and Health Program".

Sandia National Laboratories/New Mexico, Radioactive Waste/Nuclear Material Disposition Department, Work Plan CT02-01, "Sample Preparation for Clean Technologies, Phase I, September 20, 2001.

Appendix A-1. Clean Technologies Patents

1. "Hazardous Waste Reclamation Process," U.S. Patent No. 5,000,101, March 19, 1991.
2. "Waste Treatment and Metal Reactant Alloy Composition," U.S. Patent No. 5, 167, 919, December 1, 1992.
3. "Equipment and Process for Medical Waste Disintegration and Reclamation," U.S. Patent No. 5,271,341, December 21, 1993.
4. "Equipment and process for Waste Pyrolysis and Off Gas Oxidative Treatment," U.S. Patent No. 5,359,947, November 1, 1994.
5. "Equipment and Process for Molten Alloy Treatment of Hazardous Liquids and Slurries," U.S. Patent No. 5,431,113, July 11, 1998.
6. "Equipment and Process for Ultra Hazardous Liquid and Gas Molecular Decomposition," U.S. Patent No. 5,452,671, September 26, 1998.
7. "Equipment and Process for Molten Alloy Pyrolysis of Hazardous Liquid Waste," U.S. Patent No. 5,461,991, October 31, 1998.
8. "Equipment and Process for Surface Treatment of Hazardous Solids and Slurries with Molten Alloy, " U.S. Patent No. 5,553,558, September 10, 1999.
9. "Equipment and Process for Molecular Decomposition of Chlorinated Hydrocarbons," U.S. Patent No. 5,564,351, October 15, 1999.
10. "Equipment for Using Molten Metal Reactive Media for the Treatment of Hazardous Waste," U.S. Patent No. 5,832,845.
11. "Waste Treatment Process and Reactant Metal Alloy," U.S. Patent No. 6,037, 517.
12. "Reactant Metal Alloy and Treatment Process for Radioactive Waste," U.S. Patent No. 6,069,290.

Appendix A-2. Authorized Users List

Document Title: **Test Plan for Evaluation of Clean Technologies' Molten Aluminum Waste Treatment Unit**

By my signature below, I affirm that I have read and understood this procedure and all References called out in procedural steps, and I agree to operate within the stated constraints.

Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date
Name (printed)	Signature	Org./Company	Date

THIS PROCEDURE IS TO BE REVIEWED EVERY 12 MONTHS.

Appendix A-3. Sample System Operation Checklist - Molten Aluminum Treatment Unit

DATE: ____________________

OPERATOR: ____________________________

<u>SYSTEM STARTUP:</u>

Operator's Initials

1. **Aluminum level is / is not (circle one) at the bath "full" mark.** ______________

2. **If bath is not full, record the amount of aluminum added:**

   ____ ______________

3. **Off-gas monitoring system is operational and calibrated as per procedure in Appendix D.** ______________

4. **Room 119 ventilation system is operational and connected to the treatment unit off-gas exhaust line.** ______________

5. **Pressure relief valve is operational.** ______________

6. **Argon gas cylinder pressure, psig** _______________ ______________

   If the pressure is <200 psig, change out the cylinder.

7. **New cylinder pressure, psig** _______________ ______________

8. **Time system at 900 °C:** ________________________ ______________

<u>SYSTEM SHUTDOWN:</u>

9. Time argon flow shut off: __________________________ ________________

10. Off-gas monitoring system shut off. ________________

11. Bath heaters turned off, sample compartment removed, aluminum ladled into molds.

Time: ______________ ________________

COMPLETE STEP 12 <u>OR</u> STEP 13, NOT BOTH.

12. Cooled aluminum ingots returned to bath, lid placed on bath, timer set for 0400 starup.

Date: _______________ Time: ______________ ________________

13. Cooled aluminum ingots returned to bath, lid placed on bath.

Date: _______________ Time: ______________ ________________

Appendix A-4. Procedures for Calibration, Operation and Shutdown of the Off-Gas Monitoring System

The off-gas monitoring system consists of an oxygen sensor, a hydrogen sensor, and a gas chromatograph. The following sections outline procedures for calibration, operation and shutdown of each component. For more detail, see the operations manual for each instrument.

1.0 Gas Chromatograph

The gas chromatograph (GC) is an SRI Instruments Model 8610C unit that has been customized for this project. It includes a Carbosieve II column for sample collection in series with a standard GC separation column and a catalytic combustion detector (CCD). The unit is a "gasless" chromatograph that uses an internal compressor to produce the carrier gas from room air. The GC is operated using SRI's PeakSimple software, which uses Windows NT as its operating system.

Prior to operation, any user should read the instrument manual, paying special attention to the tutorials on the use of PeakSimple.

1.1 Calibration

The unit calibrates automatically when PeakSimple is started. At the start of each day's operation, a baseline chromatogram should be generated by running the sample program with valve 1 closed. If any peaks are observed, due to incomplete desorption of sample from the Carbosieve II column during the previous run, flip the "trap filter bakeout switch" on the GC control panel. This will run automatically for five minutes. After bakeout, repeat the blank program run with valve 1 closed. Trap filter bakeout should remove any "leftover" peaks.

1.2 Operation

During a programmed sample collection run, gases from either the molten aluminum unit head space or off-gases from the activated charcoal effluent filter are collected on the Carbosieve II column for two minutes. A solenoid valve then opens, and the absorbed gases are sent to the separation column. As currently programmed, a complete run takes 13 minutes. The sampling program is initiated by pressing the space bar on the computer.

1.2.1 Head Space Sample Collection

1. To obtain a head space sample, close valve 15 and open valve 1 to the GC.

2. Press the space bar on the computer.

3. At the end of the 2-minute sample collection period, close valve 1 and open valve 15 after the solenoid valve opens. A light on the GC control panel comes on when this occurs.

1.2.2 Off-Gas Sample Collection

1. To obtain and off-gas sample, close valve 17 and open valve 1 to the GC.

2. Press the space bar on the computer.

3. At the end of the 2-minute sample collection period, close valve 1 and open valve 17 after the solenoid valve opens. A light on the GC control panel comes on when this occurs.

1.3 Shutdown

If the GC is going to be used for several successive days, it should be left on. Other than turning the unit off at the end of the week, there are no special shutdown procedures.

2.0 Hydrogen Sensor

The hydrogen sensor is a DHC Technology, Inc. Model HH3-SB06Ps1 Robust Hydrogen Sensor that detects hydrogen gas from <0.5% to 100% in <2 seconds with an accuracy of $\pm$ 0.1%. Operating temperature range is 0 to 40 °C. The unit includes a low alert alarm that activates at 1% hydrogen and a high level alarm that activates at 2% hydrogen.

2.1 Calibration

The unit is calibrated at the factory. The manufacturer recommends that it be sent back annually for re-calibration.

2.2 Operation

Turn on the instrument and allow 1 to 2 minutes for the sensor to stabilize before taking readings. Reset the sensor after each time hydrogen is sensed by clearing the display with compressed air:

a) Open the valve on the compressed air cylinder and set the pressure at ~10 psi.
b) Open valve 13.
c) Close valve 14.
d) Reverse steps c) through a) when the sensor reads zero.

2.3 Shutdown

Before turning the instrument off, be sure the system is operated in air or nitrogen until the display reads zero. It is then safe to power down the instrument. Failure to observe this precaution may result in sensor damage, which is not covered by the warranty

3.0 Oxygen Sensor

The oxygen sensor is an Illinois Instruments Model 910 oxygen analyzer that measures 0.01 – 100% oxygen in less than 30 seconds to an accuracy of $\pm$ 0.1% It is suitable for all gaseous atmospheres except corrosive gases and operates at temperatures of –5 to 50 °C at sample pressures of 0.25 to 2 bar.

3.1 Calibration

The oxygen analyzer will be calibrated daily using compressed air in accordance with the instructions on page 19 of the Model 910 manual.

3.2 Operation

1. Open the instrument sample outlet valve.

2. With the argon flow on, open the sample inlet valve to obtain a flow rate of 100-150 cc/min on the flow meter on the front of the instrument.

3. Turn on the analyzer and follow the operating instructions in Section 8, pp12-16 of the Model 910 manual.

3.3 Shutdown

1. Close the instrument sample inlet valve.

2. Close the instrument sample outlet valve.

3. Turn off the instrument.

Appendix A-5. Procedures for Testing the Pressure Relief Valve, Sample Compartment Insertion, Sample Addition, and System Shutdown

1.0 Testing the Pressure Relief Valve

1. Close Valve 7. (See Figure 2, Section 1.3.)
2. Open the air cylinder valve and set the regulator at 25 psi.
3. Valve 13 should be open to the pressure relief line.
4. Slowly open the air line valve. Check that air is coming out of the pressure relief line.
5. Close the air cylinder valve.
6. Allow the air regulator to depressurize.
7. Close the air line valve.

2.0 Sample Compartment Insertion

1. Remove the bath lid.
2. Check the level of aluminum, add aluminum if necessary (see Section 3.1.3.2).
3. Place the sample compartment gasket on the rim of the bath.
4. Check that the vice grip is secured to the push rod to immobilize it during movement of the sample compartment. Using the lift points on the top of the unit, pick up the sample compartment with the Room 119 chain hoist.
5. Set the sample compartment on top of the gasket.
6. Install the eight bolts that hold the sample compartment in place and hand-tighten.
7. Using a speed wrench, hand-tighten the four push rod nuts.

3.0 Sample Addition to the Molten Aluminun

1. Using tongs, place the sample to be treated in the sample "cage".
2. Close the door, hand-tighten the four clamps that secure it, then tighten each clamp an additional three-quarter turn. If this is the first sample of the day, go to Step 4. If this is a subsequent sample, go to Step 6.
3. Verify that Valves 1 through 13 (see Figure 2, Section 1.3) are closed.

4. Verify that Valves 14 through 17 are open.

5. Open the valve on the argon cylinder.

6. Open Valves 2, 4, 5, 6 and 7.

7. Purge the system with argon until the oxygen sensor readout is $\leq 5\%$, approximately 10 minutes.

8. Remove the vice grip from the push rod. Using the push rod, insert the sample into the molten aluminum bath. Allow the sample to remain in the bath at least 5 minutes.

9. Reattach the vice grip to the push rod and use it to raise the sample cage out of the bath.

10. Continue to purge the system with argon for approximately 10 minutes.

11. Close Valve 5, then close Valves 2 and 6.

    NOTE: ALWAYS CLOSE VALVE 5 FIRST!

12. Open Valve 3 and allow the system to come to atmospheric pressure, approximately 10 minutes.

13. Open the sample compartment door and, using tongs, remove the sample cage.

14. If hydrogen has been sensed, purge the sensor using the procedure in Appendix A-4, section 2.2.

15. For the next sample, return to Step 1 and repeat the sequence.

    NOTE: Once the first sample of the day has been treated, Valves 4 and 7 will remain open for the day's treatment sequence.

4.0 System Shutdown

At the end of the day,

1. Close the valve on the argon cylinder.

2. Open the argon regulator and allow the system to depressurize.

3. Close all valves when the system has returned to atmospheric pressure.

4. Turn off the bath heater.

5. Remove the sample compartment bolts.

6. Remove the sample compartment with the chain hoist. Remove the sample compartment gasket. Store the compartment and gasket in the designated stainless steel pan.

7. Place the aluminum ingot molds in stainless steel pans. Ladle the molten aluminum into the

molds. Allow to cool for approximately 1.5 hours.

8. Return the solidified ingots to the bath.

9. Place the lid on the bath and set the bath heater timer for 0400.

Appendix A-6. Gas Cylinder Changeout - Argon, Methane or Air

1. Close the valve on the empty gas cylinder.
2. Open the regulator valve to purge residual gas.
3. Remove the regulator at the gas cylinder fitting.
4. Cap and remove the empty cylinder.
5. Attach the regulator to the new cylinder.
6. Open the valve on the new cylinder.

Appendix A-7. Sample Collection

Prior to sample collection,

- Obtain a chain of custody (COC) number, sample labels, sample containers, and the appropriate number of sample numbers from the Sample Management Office (SMO).

- Fill out the Sample Collection Log, the COC form, and sample labels.

- Attach labels to sample containers.

1.0 Molten Aluminum Sample Collection

A sample of the molten aluminum is to be collected at the end of each day of waste treatment during a treatment campaign. The ingot will be analyzed for total RCRA metals and TCLP metals.

Required Materials: Stainless steel or ceramic ladle
Ingot mold
Stainless steel spill pan to hold mold
Marinelli for solidified ingot

Procedure:

1. Complete system shutdown as per Section 3.1.3.4.2.

2. Place sample ingot mold in the stainless steel spill pan.

3. Fill the sample ladle approximately 1/2 full of molten aluminum.

4. Pour the molten aluminum into the ingot mold.

5. When the ingot is cool enough to handle, place it in the sample Marinelli.

2.0 Scrubber Water Sample Collection

At least one sample set from each scrubber is to be collected at the end of each day of waste treatment during a treatment campaign. Duplicate samples from each scrubber will be collected one day each week. If only wastes containing RCRA metals were treated, samples will be analyzed for total RCRA metals. If wastes treated contain organics, samples will be analyzed for total RCRA metals, VOCs, SVOCs, dioxins, and furans. If wastes containing tritium were treated, a sample will be sent for tritium analysis.

Required Materials: VOC samples, three 40-mL glass vials, HNO_3 preservative, per sample.
SVOC samples, two 1-L amber glass bottles per sample.
Total RCRA metal samples, one 250-mL poly bottle, HNO_3 preservative, per sample.
Dioxin and furan samples, four 1-L amber glass bottles per sample.
Tritium sample, one 100-mL glass jar.

Procedure:

Fill sample containers, as appropriate, from Valve 8, scrubber -1 sample and drain valve, and Valve 9, scrubber -2 sample and drain valve, at the bottom of each scrubber.

3.0 Activated Carbon Sample Collection

Activated carbon analyses (VOCs, SVOCs) require a total of about 200g. Since the activated carbon filter assembly hold approximately 275-300 g, the unit will be completely emptied each time the activated carbon is sampled. This procedure will be carried out in the Room 120 fume hood. If waste containing tritium has been treated, a sample of the activated carbon will be sent for tritium analysis.

Required Materials: Container for ~50-g sample
Container for ~150-g sample
Container for tritium sample.

Procedure:

1. Unscrew the activated carbon filter assembly from the off-gas line.

2. Remove either end of the filter assembly.

3. Pour about 1/4 of the activated carbon into the 50-g sample container.

4. If a tritium sample is not required, pour the remaining activated carbon into the 150-g sample container. If a tritium sample is required, pour a small amount (~10%) of the carbon into a separate container and pour the rest into the 150-g sample container.

5. Collect a swipe from the inside of the filter assembly for radiological analyses.

6. Fill the filter assembly with fresh activated carbon and replace the end of the filter asssembly.

7. Attach the filter assembly to the off-gas line.

4.0 Off-Gas Sample Collection

Off-gases will be continuously monitored during treatment using a gas chromatograph. If the detector should indicate that the off-gas from a particular waste sample contains VOCs, additional samples of that waste will be treated and off-gas samples will be collected for laboratory VOC analysis. At least one, and, if there is a sufficient amount of waste, two gas samples will be collected.

Required Materials: Summa gas sample collection bottles
Soap solution for leak testing

Procedure:

1. Connect the end of the gas sample collection line to the Summa collection bottle.

2. **Keeping the valve on the collection bottle closed,** turn Valve 12 toward the Summa collection bottle and allow argon to flow through the system.

3. Leak-check the gas sample bottle/Valve 12 connection with soap solution. If necessary, tighten/re-do connection.

4. When connection is leak-free, turn Valve 12 to its normal operating position and open the valve on the Summa collection bottle.

5. After the sample has been immersed in the molten aluminum bath, turn Valve 12 toward the Summa collection bottle.

7. When the pressure gauge on the Summa collection bottle reaches zero (bottle is under a vacuum), close the valve on the collection bottle and turn Valve 12 to its normal operating position.

5.0 Waste Residue Samples

It is anticipated that treated waste will: 1) be completely destroyed, 2) remain as part of the bath melt, either alloyed with the aluminum or as slag, or 3) leave a residue. Wastes of the latter type, such as PCB-contaminated soil, will be sent for analyses based upon the contaminants in the untreated waste. Due to the small size of the waste samples to be treated, residues from the same waste type will be combined and sent as a single sample for analysis.

If, upon raising the sample cage, a residue is observed:

1. Using tongs, remove the sample residue from the cage and in a stainless steel spill pan on the stainless steel table in Room 119.

2. Allow the cage to cool, then scrape the reside into a sample container (glass or plastic) with a spatula.

APPENDIX B

Radiological Work Permit

RADIOLOGICAL WORK PERMIT

SF 2001-RWP# (9/99)

☒ General ☐ Job Specific

RWP No.: RWP1416

Start Date: 10-01-01 **End Date:** 9-30-02	**Location:** Building 6920 Room 119

Description of Work

Treat mixed waste in a 900 deg. C molten aluminum waste treatment unit.

RADIOLOGICAL CONDITIONS

* Indicates an estimated value

Radiological Source(s)	Airborne Radioactivity	Surface Contamination
☐ Pu ☐ ^{235}U ☐ DU ☐ ^{3}H ☐ Activation Products ☐ Mixed Fission Products ☐ RGD# _____ ☒ Other: See attached list	Source Concentration ____ ____ µCi/ml ____ ____ µCi/ml ☒ Not Applicable	☐ None Detectable ☐ Unknown Levels Fixed: ____ dpm/____ cm^2 Alpha Fixed: ____ dpm/____ cm^2 Beta/Gamma Removable: Special inst 2 dpm/____ cm^2 Alpha Removable: Special inst 2 dpm/____ cm^2 Beta/Gamma Radionuclide(s): See attached list ☐ See Latest Survey

Radiation Levels	Pre-Job Survey Information
General Area: <5 mR/hr Contact: TBD per job Other: _____	Detailed survey information contained in the following: Review surveys from last entry

ALARA

Level of ALARA Review Required: ☒ None

☐ Department Manager ☐ ALARA Coordinator ☐ RPSC Date Completed: _____

Type of ALARA Job Review Required ☒ None

☐ Pre-Job Review ☐ Pre-Job Briefing ☐ In-Progress Review ☐ Post-Job Review

RADIOLOGICAL PROTECTION REQUIREMENTS

Protective Clothing	Respiratory Protection	Training
☐ None Required ☐ Level I: (coveralls, cotton glove liners, gloves, shoe covers, rubber over shoes, hood) ☐ Level II: (two pairs of coveralls, cotton glove liners, two pairs of gloves, two pairs of shoe covers, rubber overshoes, hood) ☐ Specific: ☐ Lab Coat _____ ☐ Surgeon-Style Gloves _____ ☐ Coveralls/Tyvek _____ ☐ Shoe Covers _____ ☐ Plastic Suit _____ ☐ Plastic Shoe Covers _____ ☐ Rubber Boots _____ ☐ Hood _____ ☐ Work Gloves _____ ☒ Other: See special instruction 1	☒ None Required ☐ Full Face Air Purifying (APR) ☐ SCBA ☐ Airline (Supplied Air) ☐ Other: _____	☐ GERT ☐ Radiological Worker I ☒ Radiological Worker II ☐ Respiratory Protection ☐ RGD Safety or Radiological Worker I/II ☐ Containment ☐ Other: _____
	Dosimetry	**Monitoring**
	☐ None Required ☒ Routine TLD ☐ Additional TLD(s): _____ ☒ Extremity: see special instruction 3 ☐ Self-Reading Dosimeter Bioassay ☐ Pre-job ☐ Post-job ☐ Frequency: _____ ☐ Lapel Air Sampling ☐ Other: _____	☒ Notify RCT at Job Start ☒ Intermittent ☐ Continuous ☒ Notify RCT at Job Completion ☐ RCT required at Control Point ☐ Undress by RCT ☐ Portable CAM ☐ Portable Air Sampling During Job ☒ Other: See Special instruction 4

RADIOLOGICAL WORK PERMIT

SF 2001-RWP# (9/99)

☒ **Special Instructions Page(s) Attached**

RWP No.: RWP1416

RADIOLOGICAL PROTECTION REQUIREMENTS—CONTINUED

Containment	Radiological Posting	
☐ None	☐ Controlled Area	☐ Radioactive Materials Area
☐ Glove Bag/Box	☒ Contamination Area	☐ High Contamination Area
☐ Tent/Enclosure	☐ Airborne Radioactivity Area	☐ Soil Contamination Area
☒ HEPA Filtered Ventilation	☐ Radiation Area	☐ High Radiation Area
☐ Hood	☐ Very High Radiation Area	☒ Other: RBA
☒ Other: Scrubber system for process ventilation	☒ See Radiological Hold Points	☒ See Special Instruction 6

Entry Control

☐ Not Required ☐ Facility Established Effectiveness & Operability Criteria Necessary? ☐ No ☐ Yes (Explain)

☒ Administrative Control: RWP sign in sheet

☒ Signs & Barricades: on all posted areas where treatment is being performed.

☐ Visual/Audible Alarm:

☐ Entrance Control Device:

☐ Locked Entrance:

RWP Sign-In/Out	Personnel Contamination Frisk
☐ Initial Entry ☐ Daily ☒ Each Entry	☐ None ☒ On Exiting Area:
☐ Other:	☐ Hands & Feet ☒ Whole Body
	☐ Other:

RADIOLOGICAL HOLD POINTS

The following Radiological Hold Point(s) apply to this RWP:

1. Any unexpected radiological conditions stop working and notify RCT.
2. In case of a spill notify RCT, perform actions required by RPO-07-701.
3. If contamination levels exceed the value prescribed by the RCT, stop working and decon below these limits. Work will not be restarted until the situation has been evaluated to determine if different controls will be necessary, or if the need exists to change posting of an area to reflect current levels.
4. If any non-radiological IH concerns arise, the workers will stop working and contact an IH representative to determine what actions should be taken
5. If contamination is found on gloves during work, replace gloves prior to continuing.
6. Prior to initiating any maintenance activities or equipment part replacement, pause work and contact RCT.
7. If elevated exposure rate conditions are suspected or verified, pause work and contact RCT.
8. If spill involves molten aluminum stop working and exit area, follow guidance provided by treatment supervisor.
9. In case of fire or sprinkler system activation, exit the area and contact RCT. Follow the instruction of the RCT and job supervisor.

SIGNATURES

Prepared by (RCT): JAMES L MILLS [signature]	Date: 9-6-01
Reviewed by (RP Line Support Project Leader): M Brennan for R Seyler	Date: 09/11/01
Approved by (Line Manager(s)): Earl Conway	Date: 9/18/01

TERMINATION

RWP Termination Date:

RADIOLOGICAL WORK PERMIT

RWP No.: RWP1416

SPECIAL INSTRUCTIONS

1) Protective Clothing

a) PPE will be determined by the RCT on a daily basis. Due to the nature of the treatment being performed, normal PPE may not be advisable due to the heat being generated. All PPE decisions will take into account IH concerns.

b) Handling of liquids may also require some type of face shield.

c) Preparing treatment samples inside the Room 120 fume hood will require coveralls, booties and gloves.

2) Surface Contamination

a) Review of the list of nuclides, Contamination limits will be determined on a case by case basis, due to the wide range of nuclides and expected nuclide activity level present.

3) Dosimetry

a) TLDs will be worn.

b) Extremity dosimeters will be used if the conditions warrant as per RPO-06-625.

4) Monitoring

a) Coverage for this job will be intermittent.

b) Refer to the most resent survey of the area for current radiological conditions

c) CAMs will be used to begin with. Continued use or campaign specific use will be evaluated as appropriate by RP staff. Lapels may be required during certain maintenance activities and as otherwise decided by RP staff.

5) Surveys

a) Notify the RCT prior to the removal of anything from the area to determine type and need for survey.

b) Surveys will be performed on the loading assembly each morning prior to work start. This will allow time for the unit to cool. This survey will not prevent work to begin on this day, but will establish a baseline and trending for how contamination is being controlled.

c) Contamination control limits will be established on a campaign basis as noted under # 2 above.

6) Posting

a) Room 119 will be posted as a RBA.

b) A contamination area will be set up in a corner of room 119 for storage of the loading assembly when removed.

c) The crucible and scrubber system will be posted Potential Internal Contaminated.

DISTRIBUTION:

1		Robert S. Dinwiddie P.O. Box 308 Rowe, NM 87562
1		Darrell Lainhart 7600 Hwy 107, Suite "D" Sherwood, AR 72116
2		Vincent Maio Bechtel/INEEL P.O. Box 1625 Idaho Falls, ID 83415-3875
6	MS 0719	C. F. Heise, 6131
5	0720	S. D. Carson, 6804
1	0720	D. D. Drayer, 6804
1	1149	E. M. Dinsmore, 3125
1	1151	P. K. Peterson, 3125
1	1151	M.T. Spoerner, 3125
1	1151	J. J. Thompson, 3125
1	9018	Central Technical Files, 8940-2
2	0899	Technical Library, 4916
2	0619	Review & Approval Desk, 12690 For DOE/OSTI