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DISPOSAL OF TRANSURANIC SOLID WASTE
USING ATOMICS INTERNATIONAL'S
MOLTEN SALT COMBUSTION PROCESS, II

MASTER

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Rockwell International

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By

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I. SUMMARY

The Atomics International (AI) Molten Salt Combustion Process reduces the weight and volume of combustible transuranic (TRU) waste by utilizing a molten salt medium to combust organic materials, to trap particulates and fissile material, and to react chemically with any acidic gases produced during combustion.⁽¹⁾ The "ash" is retained by the molten salt. To control the amount of noncombustible substances in the melt, a portion of the molten salt is periodically drained from the combustor. There are two options following the combustion step: the salt-ash mixture can be cast into a metal canister for direct storage, which is preferred, or the salt-ash mixture can be processed to separate ash for disposal, to recover the salt for recycle and to recover fissile materials. Either option results in the rapid, complete, and nonpolluting destruction of the combustible waste.

Bench-scale (0.2 kg/hr) combustion tests with plutonium-contaminated waste showed that >99.9% of the plutonium is retained in the melt during combustion. The small amount of plutonium (<0.1%) found downstream of the melt was primarily particulates trapped on the prefilter. Very small amounts (<10⁻⁴%) of plutonium were found in either the off-gas condensate or on the High Efficiency Particulate Absolute (HEPA) filter. A similar test with uranium indicated that uranium and plutonium behave identically during combustion, i. e., >99.9% of the uranium remained in the melt.⁽¹⁾ Bench-scale plutonium recovery tests have shown that ~98% of the plutonium can be recovered from the ash-melt mixture with a single acid leach.

Pilot plant combustion tests were conducted with uncontaminated shredded waste consisting of paper, Kimwipes, cardboard, rubber, polyvinyl chloride, and polyethylene at feed rates up to 70 kg/hr. Hydrogen chloride (<5 ppm), sulfur oxide (<1 ppm), carbon monoxide (<0.1%), and hydrocarbon (<0.1%) emissions were below the detection limits of the instrumentation. The particulate loading varied from 0.1 g/m³ at ~790°C to 0.6 g/m³ at 1020°C before the venturi scrubber, and 0.01 to 0.04 g/m³, respectively, after the scrubber. Downstream of the HEPA filters, no particulates could be detected (<10⁻⁶ g/m³). The particulates consisted of ~80% sodium chloride, due to vaporization.

The developmental status of the process has progressed to the point where conceptual design of a TRU waste combustor without plutonium recovery is the next logical step. In this regard, conceptual design of a combustion unit for hazardous organic chemicals has been completed by AI; this design and required safeguards are very similar to a TRU waste combustion unit. Furthermore, AI is presently designing and constructing a 1000 kg/hr molten salt coal gasification unit, with many features similar to the TRU waste combustor. Further research and development is required before a plutonium recovery system can be designed to reclaim the plutonium from the spent salt.

II. INTRODUCTION

Atomics International has been investigating a process for the oxidation of combustible materials in a molten salt medium since 1969. The process reduces the weight and volume of the waste while utilizing the molten salt medium to combust organic materials, to trap particulates, and to react chemically with any acidic gas produced during combustion.⁽¹⁾ The process was successfully tested for such diverse combustion problems as destruction of chlorinated organic liquid wastes,⁽²⁾ destruction of toxic and lethal chemicals, and combustion of x-ray film with subsequent recovery of silver metal.⁽³⁾ By feeding less than the stoichiometric requirement of air, the process can also be utilized to gasify coal,⁽⁴⁾ organic waste, high-sulfur oil, etc., to produce a source of clean combustible gas.

Development of the process to reduce the volume and weight of transuranic waste began in 1974 when bench-scale combustion tests on uncontaminated waste were carried out. Subsequently, combustion tests of plutonium-contaminated waste in a bench-scale combustion unit were made followed by combustion tests of uncontaminated typical TRU waste on a pilot-scale (50 kg/hr). The results of the latter tests are described in this report.

In the initial program, all process steps were verified and engineering and economic evaluations of the process, with and without plutonium recovery, were made. This data showed that volume reduction factors of 57 with plutonium recovery, and of 45 without plutonium recovery were obtained by the process. A brief review of the process description and economics is given in the following text. This is followed by the results obtained during combustion of plutonium-contaminated waste and the recovery of plutonium from the spent salt-ash mixture. Then, a description of the Molten Salt Test Facility is given, followed by the results obtained during combustion of uncontaminated waste in this facility. The report concludes with a summary of the status of the process.

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III. PROCESS DESCRIPTION AND ECONOMICS

In the Molten Salt Combustion Process, the shredded waste is fed, with air, to the molten salt combustor. Initially, the molten salt consists of sodium carbonate, an inexpensive natural mineral, and about 10 wt % sodium sulfate. Rapid and complete (>99.999%) combustion of the organic material, producing steam and carbon dioxide, occurs in the melt. As the combustion products rise through the melt and are scrubbed by it, the melt reacts chemically with any acidic pollutants such as hydrogen chloride, sulfur oxides, and phosphorus oxides. The noncombustible inorganic matter such as oxides of aluminum, silicon, iron, and transuranics, are trapped in the melt. The molten salt, which contains a dissolved catalyst, completely oxidizes the waste; no incomplete combustion products such as hydrogen, hydrocarbons, or carbon monoxides are observed as long as excess air is fed with the combustible waste.

Inorganic combustion products can build up to different levels before the physical and chemical properties of the melt are altered significantly. Ash such as aluminum or iron oxides can build up to 20 wt %. If the melt becomes viscous due to too high a buildup of insoluble materials, the hydraulics become impaired and the melt must be changed, more salt must be added, or the temperature must be increased. Soluble products such as sodium chloride can build up to 85 wt %. About 5 wt % sodium carbonate and sulfate must remain in the melt to assure complete combustion and removal of all acidic gases from the off-gas.

To control the amount of noncombustible substances in the melt, a portion of the molten salt is periodically drained from the combustor. The product salt-ash mixture is cast directly into a metal canister for retrievable storage (Figure 1). Alternatively, it is possible to process the salt-ash mixture to separate ash for disposal, to recover the salt for recycle, and to recover fissile materials (Figure 2). Either option results in the rapid, complete, and nonpolluting destruction of the combustible waste. No liquid wastes are produced.

A preliminary process evaluation for a 90 kg/hr (200 lb/hr) combustor was made and reported previously for the two process options, i.e., with and

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Figure 1. Flow Diagram of Molten Salt Combustion Process

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Figure 2. Alternate Molten Salt Combustion Process Flow Diagram with Plutonium Recovery

without salt and plutonium recovery. The capital costs were \$2,050,000 and \$675,000, respectively; annual operating costs were \$1,029,000 [$\$95/\text{m}^3$ ($\$5.92/\text{ft}^3$)] and \$578,000, [$\$53/\text{m}^3$ ($\$3.31/\text{ft}^3$)], respectively, volume reduction was a factor of 57 with salt recovery and a factor of 45 without. Process effectiveness is given in Table 1, which shows that the entire cost of the plant (675,000) can be recovered during the first year of operation if typical current disposal costs of $\$128/\text{m}^3$ ($\$8/\text{ft}^3$) and 70% load factor are assumed.

TABLE 1
MOLTEN SALT SYSTEM EFFECTIVENESS*

Parameter	Without Treatment Plant	With Treatment Plant		Effectiveness	
		Without Salt or Pu Recovery	With Salt and Pu Recovery	Without Salt or Pu Recovery	With Salt and Pu Recovery
Weight (kg/yr)	5.49×10^5	2.27×10^5	1.04×10^5	58% Reduction	80% Reduction
Volume (m^3/yr)	1.08×10^4	0.02×10^4	0.02×10^4	97% Reduction	98% Reduction
Cost (\$/yr)	1.39×10^6	0.58×10^6	1.03×10^6	58% Reduction	26% Reduction

*90 kg/hr (200 lb/hr) plant with 70% load factor using the $\$128/\text{m}^3$ ($\$8/\text{ft}^3$) disposal cost figure.

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IV. BENCH-SCALE COMBUSTION TESTS WITH PLUTONIUM-CONTAMINATED WASTE

The combustion tests with plutonium-contaminated wastes were conducted in the AI Plutonium Facility. In this facility, all plutonium is handled inside gloveboxes at negative pressure. Therefore, the bench-scale combustion system was incorporated inside a glovebox and designed to operate at negative (12 to 20 cm H₂O) pressure.

A. DESCRIPTION OF EQUIPMENT

1. Flow Description

Figure 3 is a schematic diagram of the combustion equipment; the completed combustion system is shown in Figure 4. The pulverized waste was placed in the conical feed hopper which contained a stirring device that prevented the bulky feed material from bridging over the hopper outlet. The feed was transferred from the hopper outlet to the combustor inlet tube by a screw-feeder driven by a variable-speed motor. Combustion air conveyed the feed from the screw-feeder outlet into the bed of molten salt through the 2.5-cm-ID stainless-steel-lined alumina feed tube. The feed tube was positioned so that feed material would enter the center of the molten salt bed about 2 cm from the bottom.

The combustion gases exited through the 2.5-cm-diameter stainless-steel off-gas line into a 18-cm-diameter by 60-cm-high water trap. The water trap was a safety measure to prevent water from the water-cooled heat exchangers from entering the combustor. The water trap had a sufficient capacity to contain all of the water (~18 l) in the primary heat removal system if the primary heat exchanger should rupture. The water trap and all hot lines leading to and from it were insulated to prevent the gloves from touching a hot metal surface. The off-gas was cooled in the primary heat exchanger system (see below) and passed to a prefilter. The string-wound pre-filter served to de-entrain condensed water and to protect the HEPA filters from condensate droplets and large particulates. The gas passed through two sets of HEPA filters before leaving the glovebox and passing into the facility radioactive (RA - potentially radioactive) exhaust. Provision was made to valve a fraction of the HEPA-

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Figure 3. Bench-Scale Radwaste Combustor
Flow Diagram

Figure 4. Bench Scale Radwaste Combustion System

filtered off-gas through the analytical train after it exited from the box and before it passed into the main facility RA exhaust.

2. Combustor

The combustor was located in the cylindrical extension below the box (Figures 3 and 4). It consisted of a 10-cm-diameter by 90-cm alumina round-bottomed tube which contained the 10 to 15-cm-deep bed of salt; the alumina tube was retained in a 12.7-cm stainless steel enclosure. Electrical clam shell heaters (8800 W) around the stainless steel enclosure were used to melt the salt and to maintain it in the molten condition. These heaters and electrical leads were cast with ALFRAX 3449-2D within a second round-bottomed alumina tube which acted as a secondary salt containment vessel in event of a primary salt containment vessel rupture. The can surrounding this second alumina tube is dual walled and is shown as the metal extension below the glovebox in Figure 4. Cooling air was directed between the dual walls of this can to remove approximately one-third of the heat generated by waste combustion. Sufficient electrical heating capacity was provided to maintain the salt in the molten state even with cooling air blowing through the cooling shroud. The power to the heaters was controlled by Variacs; an off-on temperature controller which maintained the heaters at a preset temperature was also provided. In general, the Variacs were set to maintain the temperature about 25 °C below the on-off setpoint to provide a constant heat input from the heaters.

3. Heat Exchanger

About two-thirds of the heat of combustion is contained in the off-gas and must be removed to protect the HEPA filters; the hot off-gas must be reduced in temperature from about 800 °C to about 60 °C. Thus, a heat-exchange system was required to remove the heat from the glovebox combustion system. The volume of water in the heat-exchanger had to be limited due to facility regulations and system restraints. Therefore, a dual heat-exchange system was required. The primary system with limited volume (~18 l) of water coolant was used to remove the heat from the combustion off-gas in the box, and the second heat exchanger was used to reject this heat to the facility cooling water system. The system contained a primary heat exchanger bypass and was valved so that the cooling water entering and exiting temperature could be controlled.

4. Feed System

The ground waste material, consisting of paper (Kleenex, Kimwipes, and magazines), plastic (80 wt/% polyethylene and 20 wt/% polyvinyl chloride), and rubber (50% surgeon's gloves and 50% black rubber gloves), was a fluffy difficult-to-feed material that tended to separate. The heavier plastic particles tended to fall through the lighter paper particles and concentrate at the bottom of the hopper. The heat of combustion of the plastic, as well as the amount of air required for complete combustion, is much greater than that of paper. Therefore, a constant-speed feed system designed for the mixed feed would tend to overfeed initially and underfeed at the end of a hopper full of waste. To overcome this problem, variable-speed motors were used to drive both the screw-feeder and the hopper-agitator and small quantities of feed (250 g) were placed in the hopper at a time. In addition, the amount of air added with the feed in the feed tube was varied to maintain the oxygen level of the off-gas at about 12%.

5. Analytical System

The combustion off-gas was monitored continually for carbon monoxide, carbon dioxide, hydrocarbons, and oxygen. The hydrocarbon and oxygen readings were recorded continuously on a two-pen recorder. It was found that these two off-gas components would register any feed upset before either of the other two monitors would register a change. The hydrocarbon meter was particularly sensitive to system upsets and was used as the primary control system to change the air-feed ratio. With complete combustion, no hydrocarbons would be present in the off-gas; the meter was sensitive to 1 ppm of hydrocarbons.

B. TEST PROCEDURE

Several combustion tests were made with uncontaminated waste to check out the system and determine the proper operating parameters. The salt in the combustor was heated electrically to about 100°C above the melting point and the waste (~250 g) was added to the feed hopper. The feed hopper was closed and combustion air flow through the combustor was started. The screw feeder was started and increased in speed until the predetermined level (14 rpm) was obtained. The hopper agitator was started whenever the carbon dioxide

content of the off-gas started to drop off. Towards the end of the run, the hopper agitator operated continuously. During each test, the temperatures of the combustor (melt and heater) and of the off-gas (before and after cooling), the flow rates, the feed rates, the pressure drops, valve settings, and the off-gas compositions were recorded periodically. The condensate was drained from the prefilter about twice per hour; normally about 200 cc/hr was collected.

A similar procedure was followed when three combustion tests were conducted with plutonium-contaminated waste. The waste was contaminated with plutonium by adding a known volume of a plutonium nitrate, sulfate and chloride solution to the waste. After contamination, the waste was mixed thoroughly by kneading it in the plastic containment bag before it was added to the feed hopper. At the conclusion of each test, the prefilter and the first set of HEPA filters were changed. The prefilter and HEPA filters were sectioned and counted in a low background counter to determine the activity present. A portion of the condensate was evaporated to dryness on a planchet and counted to determine the activity present.

At the conclusion of the third test, the system was dismantled so that the salt could be removed. The salt was pulverized and portions of it were transferred to a planchet with water and evaporated to dryness to determine the plutonium present by counting. Swabs and washing were taken from various parts of the off-gas system to determine how much activity was present. From the counting rates of the various samples, the plutonium disposition in the system was determined at the conclusion of each test.

C. COMBUSTION RESULTS

The combustion and feed parameters during each test, and the test results are given in Table 2. The feed rate was maintained at about 180 ± 20 g/hr throughout all three tests. Two concentrations of plutonium in the waste were used (9×10^{-5} g/g and 1.1×10^{-3} g/g); these correspond roughly to the level of plutonium expected in low-level and intermediate-level TRU waste, respectively.

TABLE 2
TEST PARAMETERS FOR PLUTONIUM WASTE COMBUSTION TESTS

Test No.	Average Pu Concentration in the Salt* (wt %)	Pu Concentration in Waste Feed (wt %)	Feed Rate (g/hr)	Average Combustion Temperature (°C)	Off-Gas Analysis				
					CO ₂ (%)	CO (%)	HC (ppm)	O ₂ (%)	ΔP HEPA Filters (cm H ₂ O)
1	5×10^{-4}	9×10^{-3}	190	895	7	0.1	5	12.0	11.3
2	7×10^{-3}	1.1×10^{-1}	180	892	6.3	0.1	5	12.0	10.8
3	1.3×10^{-2}	9×10^{-3}	170	880	6.0	0.02	5	13.0	10.8

*If all plutonium in the feed remained in the salt.

The low concentration of plutonium in the waste was used in Tests 1 and 3; the intermediate concentration was used in Test 2.

The concentration of carbon dioxide in the off-gas during all three runs averaged between 6 and 7%, and the oxygen content of the off-gas averaged between 12 and 13%. Hydrocarbon content of the off-gas averaged about 5 ppm while the carbon monoxide content of the off-gas averaged 0.02 to 0.1%. The temperature averaged 880 to 895°C during each of the three tests and varied from 850 to 905°C throughout the three test periods.

The plutonium disposition at the end of each test in each of the off-gas components is given in Table 3. Less than 0.1 wt % of the plutonium in the feed could be detected downstream of the melt, indicating that greater than 99.9% of the plutonium was retained by the melt in all three tests. Analyses of the melt itself indicated that $99.0 \pm 1.3\%$ of the plutonium was retained by the melt. Most of the plutonium found downstream of the melt was found in the prefilter; very little ($<10^{-4}$ wt %) plutonium was found either in the HEPA filters or in the condensate coming from the prefilter. This would suggest that the plutonium on the prefilter was an insoluble particulate, probably plutonium oxide. The plutonium found in the combustion off-gas line (Column 6, Table 3), and in the water trap may have been due to finely divided melt droplets carried out of the combustor or to plutonium dioxide deposits on the walls.

TABLE 3
DISPOSITION OF PLUTONIUM IN BENCH-SCALE
RADWASTE COMBUSTION TESTS

Plutonium Found in Various Components (Percent of Total)						
Test No.	HEPA Filters	Pre-Filter	Condensate	Water Trap	Combustor Off-Gas Line	Melt *
1	$<10^{-4}$	0.07	$<10^{-4}$	—	—	(99.9)
2	$<10^{-4}$	0.01	$<10^{-4}$	—	—	(99.9)
3	$<10^{-4}$	0.02	$<10^{-4}$	0.01	0.009	(99.9)

*By difference, melt analysis indicated that $99.0 \pm 1.3\%$ of the plutonium was in the melt.

D. PLUTONIUM RECOVERY

For some waste feeds, plutonium recovery may be important, therefore, a method to recover this plutonium was developed (see Figure 2). Normally, the salt would be drained from the combustor and cast directly into retrievable storage canisters. However, if plutonium recovery is desired at some future date, the plutonium can easily be recovered from the salt in the storage canisters.

To show that plutonium could be recovered from spent salt, 11 plutonium reclamation tests were made using the following procedure. The solidified sodium carbonate-sulfate-chloride salt was dissolved in water and filtered. The insoluble ash which contained the plutonium was leached with acid (HNO_3 , HCl , or $\text{HNO}_3\text{-HF}$). This leach readily dissolved the plutonium; only ~ 30 min of refluxing was required. It was also found that direct acidification of this ash with HNO_3 or HCl forms a colloidal solution that is extremely difficult to filter. The colloid which is formed by the hydrolysis of sodium silicate was destroyed by either of two very effective means: (1) the addition of HF which volatilized the silica as SiF_4 , or (2) evaporation to dryness to dehydrate the

silica. The latter technique provides a satisfactory ash-plutonium separation and eliminates the hydrofluoric acid recovery system. Additional work is required to optimize plutonium recovery by any of these acid leaches.

The amount of plutonium dissolved in the initial step was dependent on the sodium carbonate concentration of the solute. In order to minimize the plutonium dissolution, the carbonate concentration must be near the solubility limit of 30 wt % salt; under these conditions, ~1% of the plutonium will dissolve. However, in 15 wt % salt solutions, up to 10% of the plutonium dissolved. It is expected that the plutonium that does dissolve with the carbonate would be recrystallized out of solution with the carbonate and recycled to the furnace. Very little plutonium should appear with the sodium chloride crystals. With low-level waste combustion, it is anticipated that the chloride product will contain (or readily can be decontaminated to) less than 10 nCi/g so that nonretrievable disposal can be used. The results with three different acid leaches are given in Table 4 for comparison; they show that from 90 to 98% of the plutonium can be recovered in a single acid leach of 30 min refluxing. It would appear that either hydrochloric or nitric-hydrofluoric acids are more effective leach acids than pure nitric acid. However, these are the results of only 11 preliminary exploratory tests and basic parameters such as acid contact time and refluxing temperature have not been adequately evaluated. About 60% of the plutonium in the residue was dissolved in a second acid leach.

TABLE 4
RECOVERY OF PLUTONIUM FROM ASH-MELT MIXTURE

Plutonium Leach Solution		Plutonium Distribution* (%)	
Acid	Concentration	Leach Solution	Insoluble Residue†
HNO ₃ - HF	3N, 2N	98.0	1.0
HCl	3N	97.9	1.1
HNO ₃	2N	90.7	8.3

*The aqueous sodium carbonate extraction always contained some plutonium. The minimum amount observed was 0.67%; the average of four tests was 0.97% of the plutonium.

†A second acid extraction dissolved about 60% of the plutonium remaining in the insoluble residue.

E. DISCUSSION OF RESULTS

The plutonium-contaminated waste was burned on a continuous 0.2 kg/hr rate to determine the plutonium disposition in the system at the completion of three molten salt combustion tests. Although a small amount of plutonium (<0.1%) was found in the prefilter and water trap (Table 3), essentially all (99.9%) of the plutonium was retained in the melt in all three tests. A similar test with uranium⁽¹⁾ indicated that uranium and plutonium behave identically during combustion, i.e., >99.9% of the uranium remained in the melt.

The volume and weight of contaminated waste can be further reduced after combustion by processing the melt-ash mixture to recover the sodium carbonate and sulfate for recycle to the combustor, and to produce an ash and sodium chloride fraction for disposal (see flow diagram, Figure 2). This is accomplished by leaching the soluble sodium carbonate, sulfate, and chloride from the quenched melt-ash mixture. About 98% of the plutonium is readily dissolved from the insoluble residue (~30 min reaction time) with either nitric-hydrofluoric or hydrochloric acid; pure nitric acid dissolved only about 91% of the plutonium in comparable preliminary tests. Additional tests are required to optimize the plutonium recovery process. After leaching, the plutonium can then be separated and purified by the conventional solvent extraction and ion exchange techniques.

V. PILOT PLANT TESTING OF UNCONTAMINATED WASTE

A. DESCRIPTION OF TEST FACILITY

The Molten Salt Test Facility (MSTF) consists of a refractory-lined combustion vessel along with the following auxiliary components: air compressor, solid material feed systems, vessel preheater, process air heater, combustion air blowers, particulate removal system, control equipment, secondary combustor, and gas analysis equipment. A schematic flow diagram of this facility is shown in Figure 5. Except for the HEPA filters, all of the test equipment utilized for this test was equipment permanently installed at the MSTF. Pre-filter and HEPA filter banks to filter the exhaust before exhausting it through the stack were installed specifically for this test.

The combustion vessel is 3.6 m (12 ft) high and has a 1.2 m (4 ft) OD. It is fabricated of Type 304 stainless steel and conforms to Section VIII of the ASME Boiler and Pressure Vessel Code. The vessel is lined with 6 in. (15 cm) thick high purity alpha alumina blocks (Monofrax A, a product of Carborundum Company) blocks. The vessel is shown in Figure 6. This vessel is preheated by a natural gas-fired 1.1×10^6 kcal/hr (4.5×10^6 Btu/hr) excess air burner. The hot air flows from this preheater to the reactor vessel through a 30 cm OD (20 cm ID) refractory-lined pipe and a refractory-lined gate valve, which is pneumatically activated. The valve is utilized to isolate the preheater from the vessel during the negative pressure operation used in this test. During the pilot plant tests of TRU waste combustion, the combustor was operated at negative pressure (20 cm H₂O) to assure that any leak that might develop would draw air into the vessel and through the HEPA filters. This type of operation would also be used in actual radioactive waste combustion.

The MSTF has two solids feeding systems; a pressurized feed system for operation up to 6.8 atm (100 psig), and an atmospheric feed system for operation up to 1 atm (15 psig). The pressurized feed system is used to feed the sodium salt mixture to the vessel at slightly above atmospheric pressure. The system is a multichambered lock hopper which allows the feeding of coal, coke, or salt to the vessel through a 2.5 cm pneumatic conveying line. This feed system is shown in Figure 5 as the pressure feeder. The solids material is

Figure 5. Molten Salt Test Facility Pilot Plant

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Figure 6. Molten Salt Pilot Plant Combustor

metered into the conveying line by controlling the speed of a solids conveying screw at the bottom of the lower lock hopper.

The atmospheric feed system was used to feed the (uncontaminated) simulated radioactive waste materials into the molten salt. This system consists of a conveyor belt which feeds material to a hammermill (Williams Pulverizer) where it is reduced to a less than 1.25 cm size. The feed particulates are pneumatically conveyed from the hammermill to a cyclone separator, where the solids material is separated from the transporting air stream. The solids material then drops into a rotary valve, which meters the ground material into a pneumatic conveying line for transportation into the combustion vessel below the molten salt level. This conveying line is 5 cm diameter piping with special wide-radius turns. The rotary valve has an SCR variable speed drive to change the flowrate of feed into the conveying air. All of the pneumatic conveying air and process air for combustion is supplied by a 222 l/s (470 scfm), 7.5 atm (110 psig) air compressor; combustion air for the vessel preheater is supplied by a centrifugal blower rated at 1086 l/s (2300 cfm). Only a fraction (1/2 to 2/3) of the combustion air is used to convey the solid waste into the combustor. The remainder of the combustion air is fed into the vessel near the point where the solid waste enters the combustor. This process air, prior to entering the vessel, passes through an electric heater which is capable of preheating this air to 760°C (1400°F) when required. The process air lines and side nozzle arrangement are fabricated of stainless steel.

The exhaust gas generated from the combustion in the vessel leaves through two ports in the vessel head. These ports are 25 cm OD (15 cm ID) refractory-lined 45° elbows which direct the gas to a baffle chamber positioned horizontally above the reactor vessel. This refractory-lined chamber, which is 120 cm long by 50 cm OD by 27.5 cm ID, contains a baffle arrangement which traps entrained melt droplets from the vessel.

Various sample ports for gas and particulate analyses are located downstream of the baffle chamber. Farther downstream is the exhaust gas flow orifice for monitoring the exhaust gas flow rate from the vessel. After Traversing an expansion bellows section, the exhaust gases pass into a refractory-lined

secondary combustor, which was not operated in these tests. From the secondary combustor, the gases flow through a venturi scrubber system where they are scrubbed with water to remove any particulate matter. The scrubbing liquid is removed from the cleaned gas stream in a gas-water separator and returned to a 2275 l (500 gal.) recirculation tank. The cleaned gases pass through an induced-draft blower which maintains the vacuum on the venturi and the slight negative pressure on the combustor. A second induced-draft blower draws the gas through HEPA filter banks before it is exhausted to the atmosphere. The feed system and off-gas system are shown in Figure 7.

B. ANALYTICAL INSTRUMENTATION

All of the analytical instruments, with the exception of the Dynasciences SO_2 Analyzer, received sampling gas from a port connected to the off-gas piping upstream of the secondary combustor. The sampling probe extended into the center of the off-gas piping from the vessel. After filtration and dehumidification, a portion of the gas stream was diverted to a Bailey, continuously recording oxygen and total hydrocarbon analyzer. The balance of the gas flowed past a sampling port of a Honeywell process chromatograph which automatically sampled and analyzed for H_2 , N_2 , O_2 , CO , CO_2 , CH_2 , CH_4 , and C_2H_6 every 100 sec. From the chromatograph, the gases passed through a Thermal Electron Chemiluminescence Analyzer for NO and NO_2 analysis.

The Dynasciences system was used primarily for SO_2 analysis, but also monitored O_2 and NO_x . This unit had its own sampling ports and sampling system and, therefore, was independent of the other analytical instrumentation. The three sample ports were located upstream of the off-gas orifice, downstream of the off-gas orifice, and downstream of the secondary combustor. The unit automatically sampled from each port for 15 min before switching to the next port. A Perkin-Elmer gas chromatograph was used to analyze melt samples for carbonate. This instrument was located in a hot lab so that contaminated melts could be analyzed.

C. TEST PROCEDURE

A relatively small amount of low-melting-point alkali carbonate mixture (395°C melting point) was used to start up the vessel. This salt was conveyed

Figure 7. Feed and Off-Gas System for the Molten Salt Test Facility

into the vessel through a feed lance extending down from the top of the vessel. The conveying air flow was set at 14.2 l/s (30 scfm). After the low melting salt mixture was added, an additional 68 kg of 90% Na_2CO_3 - 10% Na_2SO_4 was fed into the vessel to increase the salt bed depth to about 23 cm. After the salt bed reached 600°C, 100% polyethylene feed was started. The bed temperature increased rapidly to about 750°C but would not continue to increase to the desired 850 to 900°C until the feed was switched to petroleum coke. It was found that only a portion of the polyethylene was burning within the shallow bed and high heating value pyrolysis gases were burning above the bed. The coke, which burned entirely within the shallow bed, increased the bed temperature to the desired 850 to 900°C. When the bed temperature reached 900°C, an additional 900 kg of salt (90 wt % Na_2CO_3 - 10 wt % Na_2SO_4) was added. This brought the quiescent melt depth up to 1 m. Simulated radwaste mix consisting of 33 wt % paper, 20 wt % Kimwipes, 32 wt % polyethylene, 8 wt % polyvinylchloride (pvc), and 7 wt % rubber was then fed into the 1 m deep bed. At this bed depth, all of the waste combustion occurred within the bed, so that the bed temperature could be changed (increased or decreased) at will by changing the solid waste feed rate.

D. TEST RESULTS

A total of 660 kg (1456 lb) of waste was burned. The combustion temperature was varied from 790°C to 1020°C during the test. At the end of the test, the melt composition was ~75 wt % Na_2CO_3 , 6 wt % NaCl , 8 wt % Na_2SO_4 , and 11 wt % ash.

Several particulate samples were taken during the test. Four sets of particulate loadings obtained during the test are given in Table 5. The three particulate sample ports in the off-gas line were located (1) in the off-gas line between the combustion vessel and the venturi scrubber, (2) between the venturi scrubber and HEPA filter banks, and (3) in the stack downstream of the HEPA filter. These samples are designated "before venturi," "after venturi," and "after HEPA," respectively. As expected from bench-scale test results, the particulate loading varied directly with the combustion temperature since the particulates consisted of 80 to 90% salt and the salt vapor pressure increased with temperature. In general, the particulates were white or grey and similar to those found in the bench-scale tests. Before the venturi, the particulate loading varied from 0.1 to

TABLE 5
PARTICULATE LOADING FOR COMBUSTION OF SIMULATED
TRU WASTE IN THE MSTF PILOT PLANT

Sample No.	Feed Material	Feed Rate (kg/hr)	Average Melt Temperature [°C(°F)]	Particulate Loading (g/m ³)		
				Before Venturi	After Venturi	After HEPA Filter
1	PVC	16	975 (1787)	0.31	0.014	(ND; <10 ⁻⁶) [†]
2	Radwaste* + 40% PVC	50	1020 (1868)	0.62	0.043	(ND; <10 ⁻⁶) [†]
3	Radwaste* + 40% PVC	50	845 (1553)	0.11	0.016	(ND; <10 ⁻⁶) [†]
4	Radwaste* + 45% PVC	43	790 (1454)	0.10	0.014	(ND; <10 ⁻⁶) [†]

*Radwaste consisted of 33 wt % high ash paper, 20 wt % Kimwipes, 32 wt % polyethylene, 8 wt % PVC, and 7 wt % rubber

[†](ND) = not detected

0.6 g/m³; downstream of the venturi, the particulate loading varied from 0.014 to 0.043 g/m³. The average efficiency of the venturi scrubber was about 93%. This was less than expected, and was probably due to an insufficient water flow to the venturi. Downstream of the HEPA filters, no particulate could be detected, i.e., <10⁻⁶ g/m³.

Typical off-gas analyses are given in Table 6. The oxygen and carbon dioxide content of the gas was directly related to the air/feed ratio and varied from 5 to 12% for O₂, and from 10 to 15% for CO₂. Hydrogen chloride content (<5 ppm) of the off-gas was below the detection limit of the apparatus even when pure PVC was burned. Sulfur dioxide (<2 ppm), carbon monoxide (<0.1%), and hydrocarbons (<0.1%) were all below the detection limit of the apparatus used to monitor these gases. Nitrogen oxides (nearly 100% nitrogen monoxide) were detected in the off-gas and varied with the magazine content of the waste being burned. This is to be expected since the nitrogen oxide content of the off-gas has been shown to be directly related to the nitrogen content of the waste

TABLE 6
TYPICAL OFF-GAS ANALYSIS FOR SIMULATED
TRU WASTE COMBUSTION IN THE MOLTEN
SALT TEST FACILITY

Major Off-Gas Constituents	Quantity
N ₂	76-78%
O ₂	5-12%
CO ₂	10-15%
Minor Constituents	Quantity
HCl	ND* (<5 ppm)
SO ₂	ND (<2 ppm)
CO	ND (<0.1%)
HC	ND (<0.1%)
NO _x	30-500 ppm

*ND = not detected

combusted. The magazines in the waste contained colored dyes which contained nitrogen.

Although it was originally planned to add depleted uranium to the waste and determine its disposition during combustion, an equipment failure precluded this portion of the test. This portion of the equipment has been replaced and the system modified to eliminate the cause of failure.

E. DISCUSSION OF RESULTS

Large scale (50 kg/hr) combustion tests were performed at AI's Molten Salt Test Facility. In the test, typical waste was shredded in a hammermill with a 1.25 cm screen. An air flow rate of 2500 l/min (90 scfm) was used to convey the waste in the 5 cm line. Feed rates from 20 to 70 kg/hr were used in the test, and the feed was varied from pure PVC to typical waste consisting of paper, plastic, and rubber. Results of the test off-gas analyses were in approximate agreement with the results from bench-scale tests. Even with

pure PVC feed, the hydrogen chloride content of the off-gas was less than the detection limit (<5 ppm). As expected, the particulate loading varied directly with combustion temperature and ranged from 0.1 to 0.6 g/m³ upstream of the venturi scrubber. Also, no particulates were found downstream of the HEPA filter. The particulates collected consisted of 80 to 90 wt % salt, with a small amount of ash and carbon. The particulate loading at the design combustion temperature of 800 to 850°C (0.1-0.2 g/m³) is so small that omission of the venturi scrubber will probably be cost effective in the demonstration plant. These results were also consistent with the results of the bench-scale tests. Although some components such as the feed system and the drain system require further engineering for remote operation, the basic design of the combustion system would not be modified in an actual waste reduction plant.

The test results confirm that the molten salt combustion process is effective in reducing the volume of combustible waste on a large-scale production basis.

VI. STATUS OF DEVELOPMENT

A. EXPERIMENTAL

The applicability of the process to TRU waste has been demonstrated through bench-scale cold, bench-scale hot, and pilot-plant scale cold (50 kg/hr) tests.

Bench-scale tests have shown that typical TRU waste can be burned rapidly and completely in the molten salt process, with acidic gaseous combustion product emissions below the detection limits. The ash can build up to 20 wt % before the melt fluidity is too low, and the sodium chloride content can build up to at least 85 wt % before detectable hydrogen chloride emissions are obtained. The test also showed that at 800°C, the particulate level is about 0.2 g/m³ (0.1 grain/scf) and that the particulates consist of 80 wt % NaCl, i.e., the particulate level in the off-gas is directly related to the NaCl vapor pressure at the combustion temperature.⁽¹⁾

Actual plutonium-contaminated waste was burned at a continuous rate of 0.2 kg/hr. These tests showed that essentially all (>99.9%) of the plutonium was retained in the melt during combustion. A similar test with uranium indicated that uranium and plutonium behave identically during combustion, i.e., >99.9% of the uranium also remained in the melt.⁽¹⁾ Approximately 98% of the plutonium can be recovered from the spent salt by a single hydrochloric or nitric-hydrofluoric acid leach of the aqueous insolubles in the ash-melt mixture.

In the large scale (50 kg/hr) combustion tests, waste consisting of paper, Kimwipes, cardboard, PVC and polyethylene was disposed of at a rate up to 70 kg/hr. No hydrogen chloride, sulfur oxide, carbon monoxide, or hydrocarbon emissions were detected in the off-gases. Particulate loading in the off-gas from the combustor varied from 0.1 g/m³ at 790°C to 0.6 g/m³ at 1020°C. Downstream of the HEPA filters, no particulates could be detected (i.e., <10⁻⁶ g/m³). The particulates were ~80% salt.

B. ENGINEERING

A 50 kg/hr Molten Salt Test Facility has been operating for 5 years at the AI Field Laboratory. This unit is about one-half the size of the TRU waste

combustor considered in the design and economic studies. A conceptual design of a Molten Salt Combustor for TRU wastes was completed in 1975.⁽¹⁾ The design indicated that further engineering studies on the shredder and off-gas system would be cost effective. Conceptual design of a similar Molten Salt Combustor System for toxic wastes has been completed. Design and construction of a similar 500 kg/hr Molten Salt Coal Gasification System is in progress.

Although these engineering studies and operational experience have indicated that further engineering trade-offs would be cost effective, no problems have been uncovered that cannot be solved by the application of existing technology. Therefore, it appears that molten salt combustion of TRU waste is a feasible non-polluting method of reducing waste volume by approximately 98%.

C. FURTHER DEVELOPMENT REQUIRED

In addition to the design studies previously mentioned, further areas of experimentation should be conducted. A large fraction of TRU waste is contaminated with β - γ fission products. Combustion tests on waste containing fission product elements have been conducted as a part of AI's internal research and development program. The tests were made in the bench-scale equipment (0.5 kg/hr) with nonradioactive simulated fission products using conventional analytical chemistry means for detection. Excellent results were obtained. Much higher concentrations of fission product (up to 1.7 wt % iodine) were used than expected in actual β - γ contaminated waste to obtain the required analytical sensitivity. Large-scale (50 kg/hr) combustion tests of fission-product contaminated waste should be made to confirm the observed fission product disposition.

There are also applications for which a liquid off-gas scrubber is unsatisfactory. The particulate data indicate that a baghouse filter will provide satisfactory cleanup of the gas and can be substituted for the venturi scrubber. A pilot plant test (50 kg/hr) is planned for such an off-gas train.

REFERENCES

1. D. E. McKenzie, et al, "Disposal of Transuranic Solid Waste Using Atomics International Molten Salt Combustion Process," AI-ERDA-13151 (May 1975)
2. L. F. Grantham, et al, "Disposal of Organic Pesticides," U.S. 3,845,190 (1974)
3. L. F. Grantham and S. J. Yosim, "Noble Type Metal Recovery Process by Use of Molten Salt Bath," U.S. 3,899,322 (1975)
4. C. A. Trilling, "Coal Gasification by the Atomics International Rockgas Process," Paper Presented at November 1974 ASME Meeting