PYROLYSIS/STEAM REFORMING TECHNOLOGY FOR TREATMENT OF TRU ORPHAN WASTES

J. Bradley Mason, John McKibbin, Duane Schmoker, and Pat Bacala
THOR Treatment Technologies LLC
1135 Jadwin, Richland, WA 99352

ABSTRACT

Certain transuranic (TRU) waste streams within the Department of Energy (DOE) complex cannot be disposed of at the Waste Isolation Pilot Plant (WIPP) because they do not meet the shipping requirements of the TRUPACT-II or the disposal requirements of the Waste Analysis Plan (WAP) in the WIPP RCRA Part B Permit. These waste streams, referred to as orphan wastes, cannot be shipped or disposed of because they contain one or more prohibited items, such as liquids, volatile organic compounds (VOCs), hydrogen gas, corrosive acids or bases, reactive metals, or high concentrations of polychlorinated biphenyl (PCB), etc. The patented, non-incineration, pyrolysis and steam reforming processes marketed by THOR Treatment Technologies LLC removes all of these prohibited items from drums of TRU waste and produces a dry, inert, inorganic waste material that meets the existing TRUPACT-II requirements for shipping, as well as the existing WAP requirements for disposal of TRU waste at WIPP.

THOR Treatment Technologies is a joint venture formed in June 2002 by Studsvik, Inc. (Studsvik) and Westinghouse Government Environmental Services Company LLC (WGES) to further develop and deploy Studsvik's patented THOR^{SM} technology within the DOE and Department of Defense (DoD) markets.

The THOR^{SM} treatment process is a commercially proven system that has treated over 100,000 cu. ft. of nuclear waste from commercial power plants since 1999. Some of this waste has had contact dose rates of up to 400 R/hr. A distinguishing characteristic of the THOR^{SM} process for TRU waste treatment is the ability to treat drums of waste without removing the waste contents from the drum. This feature greatly minimizes criticality and contamination issues for processing of plutonium-containing wastes. The novel features described herein are protected by issued and pending patents.

INTRODUCTION

The THOR^{SM} process proposed for treatment of DOE orphan waste consists of two treatment stages, an in-drum pyrolysis process followed by a steam reforming process. In the first stage, TRU waste is heated in an inert environment to temperatures between 650°C and 750°C. Drums of waste are placed in an electrically heated pyrolysis chamber where water is evaporated, organics are volatized and pyrolyzed, and corrosives and reactive materials are converted into non-hazardous oxides or carbonate compounds. The pyrolyzed residue in the drums will be an inert, inorganic, carbon char containing radioactive metals.

A distinguishing characteristic of the THOR^{SM} process is that the system greatly minimizes criticality and contamination control issues for processing of plutonium-containing wastes. Moderate processing temperatures mitigate radioactive metal volatility, and very low off-gas flows essentially eliminate particulate carryover from the drummed wastes. Back-up protection to prevent radionuclides from going airborne is provided by replacing the existing drum lid with a lid that has a ceramic filter and an inorganic drum-to-lid sealing mechanism. The ceramic filter allows gas interchange, but prevents release of radioactive particles.

Stage two of the THOR^{SM} treatment process is used to treat the off-gases from the pyrolysis process, and consists of a steam reformer and a downstream scrubber for neutralization of acid gases. The off-gas produced by pyrolysis consists of water vapor, volatized organics, and acid gases from the decomposition of cellulosic materials (i.e., paper, wipes, anti-contamination clothing, etc.), plastics and other organics in the drums. The off-gas from the pyrolysis chamber is pulled by vacuum into the bottom of a steam reformer. The steam reforming process destroys residual organics in the off-gas, including RCRA and TSCA organic constituents. These organics are converted to carbon dioxide and water vapor in the steam reformer by a combination of steam reforming and oxidizing reactions.

Downstream of the steam reformer, wet scrubber technology is used to neutralize corrosive acid gases and particulates that are carried out of the reforming vessel with the off-gas. Scrubber liquids are concentrated, emptied into a 55-gallon drum, and then dried in the pyrolyzer; thus, the process produces no secondary liquid waste. Downstream of the scrubber, the off-gases are passed through a HEPA filter so that the emissions released to the atmosphere are carbon dioxide and water vapor. The THOR^{SM} process does not generate dioxins or furans, and is considered a non-incineration process by the Environmental Protection Agency (EPA). A conceptual representation of the THOR^{SM} pyrolysis and steam reforming processes is provided in Figure 1.

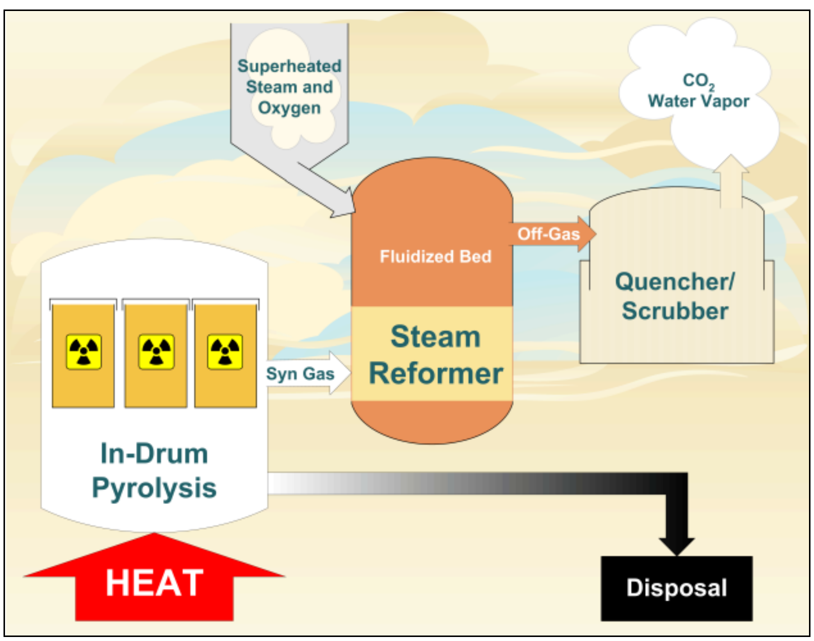

Fig. 1. Conceptual representation of the THOR^{SM} pyrolysis and steam reforming systems

The remainder of the paper provides detailed processing information, including discussions of pyrolysis and steam reforming chemistry, the neutralization of acid gases, the conversion of reactive chemicals, the conversion of RCRA and TSCA organics, and concludes with a discussion of non-toxic secondary waste generation, emissions, and discharges.

PYROLYSIS CHEMISTRY

Intact 55-gallon or 85-gallon drums of waste will be placed in a pyrolysis chamber, which is an electrically heated, double-walled pressure vessel. The inner chamber wall is fabricated of a high-temperature-resistant alloy suitable for contact with the pyrolysis gases and evaporated water from the drum contents. The outer chamber wall provides a secondary sealed barrier to the environment. Ceramic-insulated electrical heaters located between the inner and outer walls provide needed heat to the inner chamber and waste drums. The drums will be heated to pyrolysis temperatures between 650°C and 750°C. Before being introduced into the pyrolyzer, the original drum lids will be removed and replaced with a lid containing a ceramic filter and an inorganic drum-to-lid sealing mechanism. The new lid will keep radionuclides in the drum, but allow gases to escape from the drum during pyrolysis heating.

The pyrolyzer is designed to fully volatize and remove >99.9% of the organics from the waste streams, regardless of the organic composition. Organics with low to medium boiling points (less than 650°C), such as RCRA waste codes D018 through D043 and PCBs, will readily evaporate and form organic vapors that will flow out of the drum and pyrolyzer to the steam reformer. Organics with low boiling points are the source for VOCs found in the headspaces of many drums. VOCs and PCBs are, thereby, removed from the waste matrix. Typical pyrolyzer off-gases include water vapor, carbon monoxide, carbon dioxide, volatile hydrocarbons (organics), hydrogen, and hydrochloric acid.

Organics with high boiling points, such as high molecular weight polymers and plastics, are fully pyrolyzed. Exposure to temperatures above 650°C causes the organic polymer structure to break. The long carbon-hydrogen chain molecules break into smaller, more volatile organics, thereby gasifying the organic constituents. For this reason, pyrolysis is often referred to as destructive distillation or thermal desorption. The thermal breakup of long polymers leaves behind a carbon-rich, inorganic char that is inert and non-volatile (similar to non-activated carbon). This carbon pyrolysis residue is an inert inorganic that has only an extremely small hydrogen content. The pyrolyzed residues are, therefore, practically inert to alpha particle interaction. Typical chemical reactions that occur during pyrolysis of high boiling point organics and plastics are shown in Table I.

Table I. Removal of Organics from Typical TRU Waste Streams

Original Material	Pyrolysis Chemistry
Polyvinylchloride	$(-CH_2-CH(Cl)-) + H_2 + Heat \rightarrow CH_4 + HCl + C$
Polypropylene	$(-CH_2-CH(CH_3)-) + H_2 + Heat \rightarrow 2CH_4 + C$
Polystyrene	$(-CH_2-CH(C_6H_5)-) + H_2 + Heat \rightarrow CH_4 + C_6H_6 + C$
Polyethylene	$(-CH_2-CH_2-) + Heat \rightarrow CH_4 + C$
Cellulose	$C_6H_{10}O_5 + Heat \rightarrow 5CO + 5H_2 + C$

STEAM REFORMING CHEMISTRY

In the steam reformer, superheated steam (750^{o}C to 900^{o}C) is used to oxidize and reform the off-gas from the pyrolysis process. The steam reformer is operated in an autothermal mode at 800^{o}C to 1,000^{o}C, whereby the energy needs of the reformer are supplied by the incoming superheated steam and by the oxidation of organics in the waste. Additional energy can also be supplied by oxidation of carbonaceous materials that can be added to the steam reformer.

Off-gases from the pyrolysis process consist of water vapor (steam), volatized organics, and acid gases from the decomposition of plastic and other organics in the drums. The pyrolysis gases are subjected to reformation and oxidation reactions in the steam reformer, which fully convert all organics to carbon dioxide and water vapor via the typical chemical reactions shown in Figure 2. Off-gases from the steam reformer are water vapor (steam), carbon dioxide, and small quantities of acid gases. Acid gases are neutralized by the wet scrubber process described in the next section.

$$CH_4 + H_2O = CO + 3H_2$$
$$C_2H_4 + 2H_2O = 2CO + 4H_2$$
$$C_6H_6 + 6H_2O = 6CO + 9H_2$$
$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$

Fig. 2. Conversion of Volatized Hydrocarbons into Carbon Dioxide and Water Vapor

NEUTRALIZATION OF ACID GASES

Off-gases from the steam reformer are composed of water vapor (steam), carbon dioxide, and acid gases. The acid gases from the pyrolyzer pass through the steam reformer largely unreacted and are neutralized in a downstream scrubber/quencher. The quantity and makeup of the acid gases depend on the type and quantity of plastics and other organics in the original drums. For example, polyvinyl chloride (PVC) and most RCRA organics contain significant quantities of chlorine that are volatized in the pyrolyzer. A scrubber/quencher downstream of the steam reformer instantly cools the hot reformer off-gases, and the acid gases are adsorbed by the scrubber solution. The scrubber solution is neutralized by the injection of metered quantities of caustic materials to form stable salts, as shown in Figure 3. The recirculating salt solution in the scrubber/quencher is periodically transferred to a drum where the salt solution is dried in the pyrolyzer.

PCB, PVC	→ HCl	→ $NaCl$
Resin, Rubber	→ SO_x	→ Na_2SO_4
Teflon	→ HF	→ NaF
Mercury	→ HgO, Hg, $HgCl_2$	

Fig. 3. Scrubber Chemistry Neutralizes Acid Gases by Forming Low-Volume Salts

DESTRUCTION OF RCRA AND TSCA ORGANICS

A tremendous advantage of the pyrolysis/steam reforming process is that it can destroy the RCRA and TSCA constituents of organic wastes. Specifically, the pyrolysis/steam reforming processes will destroy RCRA organic waste codes D018 through D043, and F001 through F005. TSCA organic wastes, such as PCBs, will also be destroyed.

Essentially all of the RCRA D018 through D043 organics are relatively volatile chlorinated organics that will readily evaporate at pyrolysis temperatures. The volatized organic vapors from the pyrolyzer will flow to the steam reformer, where they will be fully converted to carbon

dioxide and water vapor. Other RCRA waste codes, such as F001 through F005, can also be fully thermally treated in the pyrolysis/steam reforming processes.
Other listed organics, such as TSCA-listed PCBs, are often less volatile, but will be gasified in the pyrolyzer. The thermal breakdown products of PCBs are composed of volatile aromatic ring compounds, such as RCRA waste codes D021, D027 through D029, D032, and D037 that are chlorinated aromatic benzene compounds. The volatized pyrolysis gases from the destruction and evaporation of PCBs and related toxic organics are fully converted to carbon dioxide and water vapor in the steam reformer.

CONVERSION OF REACTIVE CHEMICALS

The pyrolysis/steam reforming system provides another tremendous advantage for treating TRU wastes in that it converts reactive metals, which are prohibited from disposal at WIPP, into stable compounds that can be disposed of at WIPP. Specific reactive chemicals excluded from disposal at WIPP include RCRA waste codes D003, for reactivity hazard, and D001, for ignitability hazard. The RCRA waste codes list metallic sodium, potassium, calcium, magnesium and cyanide compounds as potentially reactive materials that have the potential to burn, ignite, or even explode when exposed to certain other materials or when exposed to varied environmental conditions.

The pyrolyzer will thermally treat and stabilize these reactive metals by converting them into stable compounds. The reactive metals in the drums of TRU wastes are fine powders that are highly reactive when heated above 500^{o}C. The strongly reducing metals will bond or react with oxygen, steam, carbon oxides, chlorine, or fluorine in the solid inorganic waste or gases near the reactive metals, producing one or more stable compounds, as shown in Table II. Cyanides, if present, will volatize from the drums and will oxidize in the reformer to water, carbon dioxide, and nitrogen.

RCRA waste code D001 also lists oxidizers, such as nitrates, due to their ability to release oxygen and augment a potential ignitability hazard. Nitrates are the only oxidizer that is expected to be in the TRU wastes. Nitrates will thermally decompose into gaseous NOx at pyrolysis temperatures. The nitrates will be converted to nitrogen gas in the reformer.

RCRA waste code D001 also lists ignitable compressed gases due to a potential ignitability hazard. The incoming wastes with potential for containing gas bottles will undergo x-ray examination for process safety reasons. Compressed gas cylinders will be manually removed prior to placement of the drums inside the pyrolyzer. (Note: For safety purposes, the pyrolyzer/steam reforming process equipment is designed to accommodate a rapid excursion [pressure surge] in the event of a liquid-filled container flash evaporation).

RCRA waste code D001 also lists liquids with a flash point less than 60^{o}F due to their ignitability hazard. All such low flash point liquids will be evaporated and removed from the drummed waste at pyrolysis temperatures.

RCRA waste code D002 is excluded from disposal at WIPP because aqueous liquids with a pH less than 2 or greater than 12.5 are highly corrosive and corrode steel at a rate greater than

0.25 inches per year. Essentially all corrosives, including both organic and inorganic acids and bases, will evaporate, thermally decompose, or be converted to stable compounds at pyrolysis temperatures, as shown in Table II. It is anticipated that the thermally treated TRU waste residues will have pH levels ranging from 5 to 10, and will not be considered corrosive.

In summary, the chemical compounds referenced in RCRA waste codes D001 (ignitability hazard), D002 (corrosive hazard), and D003 (reactive hazard) will be thermally stabilized or removed from the pyrolyzed residue, making it possible for waste contaminated with these compounds to be disposed of at WIPP. Table II outlines the stabilization method for each of the listed wastes.

Table II. Stabilization of Reactive Materials

RCRA Code	Material	Stabilization Method
D001	Liquids with flash points <60^{o}F	Evaporated from waste converted to CO_2 and water in steam reformer
D001, D003	Sodium	Converted to NaCl, Na_2CO_3, or Na_2SO_3
D001, D003	Potassium	Converted to KCl, K_2CO_3, or K_2SO_3
D001, D003	Calcium	Converted to CaO, $CaCl_2$, $CaCO_3$, or $CaSO_3$
D001, D003	Magnesium	Converted to MgO, $MgCl_2$, $MgCO_3$, or $MgSO_3$
D001	Compressed gas	Removed prior to treatment
D001	Nitrate	Decomposed to NO_x by pyrolysis. NO_x is then converted to nitrogen in the reformer
D002	Corrosives	Stabilized by one of three methods: • Decomposed to volatile gas • Evaporated from waste • Converted to stable, non-corrosive Cl, CO_3 or SO_3 compound
D003	Cyanide	Evaporated from waste converted to CO_2 and water in steam reformer
D003	Chromium	Converted to non-hazardous tri-valent oxide

SECONDARY WASTE GENERATION, EMISSIONS, AND DISCHARGES

The pyrolysis/steam reforming processes generate very little secondary waste because most of the secondary waste streams can, themselves, be collected and fed into the pyrolyzer for drying, organic destruction, or volume reduction. Waste streams generated from process and maintenance operations are shown in the bulleted list below.

- Chemicals, oils, and solutions used for maintenance and decontamination activities
- High Efficiency Particulate Absolute (HEPA) filter elements and process filter elements
- Personal protective equipment

- The scrubber salts will be mainly NaCl and Na_2SO_4 from the pyrolysis of chlorinated organics, plastic, and rubber in the incoming waste streams.

The wastes streams listed above will be processed in the pyrolysis chamber to minimize all secondary waste stream generation from the THOR^{SM} process. After pyrolysis, the residue from the secondary waste streams will be disposed of.

A significant benefit of the THOR^{SM} pyrolysis/steam reforming system is that it results in zero liquid releases. All water is discharged from the plant as water vapor out the ventilation system stack.

The quantity of gaseous water and carbon dioxide releases is dependent on the quantity and type of organics in the drums of the incoming waste stream. For example, approximately 30-40% of the carbon of long-chain hydrocarbons, such as polystyrene, will remain in the waste residue as a fixed, inorganic carbon char. The balance of the carbon is gasified and converted to carbon dioxide. Volatile organics, such as most RCRA waste code organics, are readily evaporated, and essentially all the carbon content will be gasified and converted to carbon dioxide. Plastics such as PVC and polyethylene are almost totally gasified as well. After the syngas undergoes thermal reduction treatment, hydrocarbon emissions from the process are de minimus.

SUMMARY

The THOR^{SM} pyrolysis and steam reforming system provides a disposal path for TRU orphan waste because the system removes liquids, VOCs, corrosive acids and bases, reactive metals, high concentrations of PCBs, and organics that produce hydrogen gas. These items currently prohibit either shipment or disposal of TRU waste, but once removed, the waste will meet the current TRUPACT-II requirements for shipment, as well as the WIPP WAP requirements for disposal.