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Introduction to Studsvik's In-Drum Pyrolysis Technology

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Studsvik's In-Drum Pyrolysis Technology

Studsvik's In-Drum Pyrolysis Technology is applicable to thermal treatment of the types of wastes typically found in the nuclear industry. Studsvik has developed and continually improved upon this technology through many years of research and development and full-scale testing of the technology. Figure 1 shows the full-scale pyrolysis test unit.

Studsvik's In-Drum Pyrolysis System is a batch thermo-chemical system designed for the treatment of radioactive wastes to remove characteristics that make the drums unacceptable for shipping, long-term storage, and disposal. Key results of IDP are:

- Removal of free liquids
- Destruction of organics
- Deactivation of reactive and corrosive chemicals
- Breaching of sealed containers

Removing these prohibited materials from drums by sorting and repackaging is costly, time consuming, increases worker radiation exposure risk, and results in secondary waste streams that still require treatment.

Figure 1 In-Drum Pyrolysis System Test Unit – full scale pyrolysis chamber on left with modified off-gas system for testing purposes.

A single drum unit can process about 25 metric tons per year. A typical unit, with a four-drum treatment capacity and a common off-gas system, can treat about 100 metric tons per year. The system is small enough that it could be mounted on tractor-trailers and be transported from one facility to the next with minimal effort. The process will achieve a volume reduction (volume reduction = starting volume of waste divided by the final volume of the waste material to be disposed) of approximately greater than 10 depending on the type of wastes as well as the desired final form of the waste material to be disposed of.

1 Process Overview

The In-Drum Pyrolysis (IDP) process utilizes pyrolysis to treat containerized (bulk) radioactive wastes by means of in-container thermal treatment to breach sealed containers and remove the free liquids, organic materials, and reactive materials from the containers. The resultant product is a dry, inert, inorganic waste material. Treatment is achieved without removing or handling/sorting wastes from the container.

The IDP process consists of two main treatment systems – an in-container autoclave treatment system followed by an off-gas treatment system. In the autoclave system, containers of contaminated waste are electrically heated in a nitrogen-blanketed autoclave. The autoclave is heated to temperatures that result in the water evaporating, organics being volatized and pyrolyzed, and corrosives and reactive materials being converted into non-hazardous oxides or carbonate compounds. The steam-reformed residue in the drums is an inert non-reactive, non-volatile carbon char (it does not contain hydrocarbon compounds and is similar to non-activated carbon or graphite) containing radioactive metals. The injection of steam into the container following pyrolysis results in further conversion of residual carbon char into carbon monoxide and carbon dioxide along with the release of some hydrogen. Once the process is complete, the autoclave and waste container are pre-cooled using nitrogen gas and a water spray prior to transferring the container to a holdup chamber where the container cools down to near ambient temperatures. Refer to Figure 2 for images of a drum before and after treatment. If it is necessary to solidify the contents that remain in the waste container, additives can be used to produce the desired final waste form.

Figure 2: Before and After IDP Treatment – waste stream was oil and chlorinated organics absorbed on $CaSiO_3$ – waste was in a carbon steel drum with a high-density polyethylene liner

A distinguishing characteristic of the IDP process is that the system greatly minimizes criticality and contamination control issues for processing of wastes containing radioactive materials. The moderate processing temperatures mitigate concerns of radioactive metal volatility. The integral high temperature rated particulate filter essentially eliminates particulate carryover from the containerized wastes. Additional protection to prevent radionuclides from going airborne can be provided by placing an existing packaged drum inside a 320 L (85-gal) overpack drum that is provided with an integral high temperature rated particulate filter and a ceramic fiber drum-to-lid sealing mechanism (see Figure 3). Alternatively, the original 200 L drum lid can be removed, and a new drum lid with a ceramic seal and integral filter can be placed on top of the drums. The filter allows gas interchange but prevents release of radioactive particles during treatment. The process off-gas from the IDP vessel passes through a secondary filter housing containing catalytic ceramic filters that minimize the emissions of NOx gas as well as ensure that any particulates are captured.

Figure 3 IDP Treatment Drum with Integral High Temperature Rated Particulate Filter and Ceramic Drum-to-Lid Seal

The off-gas treatment system consists of a thermal oxidizer (TOX) located directly downstream from the IDP vessel and a wet quench/scrubber (QSE) for neutralization of acid gases from the TOX. The off-gas produced from the IDP vessel consists of nitrogen, water vapor, volatized organics, and acid gases from the decomposition of cellulosic materials (i.e., paper, wipes, anti-contamination clothing, etc.), resins, plastics, and other organics in the waste containers. The off-gas from the IDP vessel is directed into the TOX, which operates at approximately 800ºC to 1000ºC to destroy organics in the off-gas.

Downstream of the TOX, the QSE is used to cool the hot gases and neutralize corrosive acid gases. A calcium-based neutralizer is used in the wet scrubber. The scrubber solution and suspended solids and are then metered into a collection drum. Once the drum is full it is placed in the pyrolysis autoclave chamber and the slurry is dried to produce solid salts such as calcium chloride, calcium sulfate, and calcium fluoride. Thus, the IDP process produces no secondary liquid waste. The dried calcium salts will have very low radioactivity and it should be practical to dispose of them as a low-level waste.

Downstream of the scrubber, the off-gases are heated by means of an electrical gas heater to dry any mist carryover from the scrubber. The heated off-gas is then filtered in a HEPA off-gas filter prior to discharging to the atmosphere.

A simplified flow diagram of the IDP process is shown in Figure 4. The handling of the drums to prepare them for storage and final disposal is simplified. Options for storage and disposal are discussed in a later section. The secondary filter shown in Figure 4 is a conservative design feature and may not be required.

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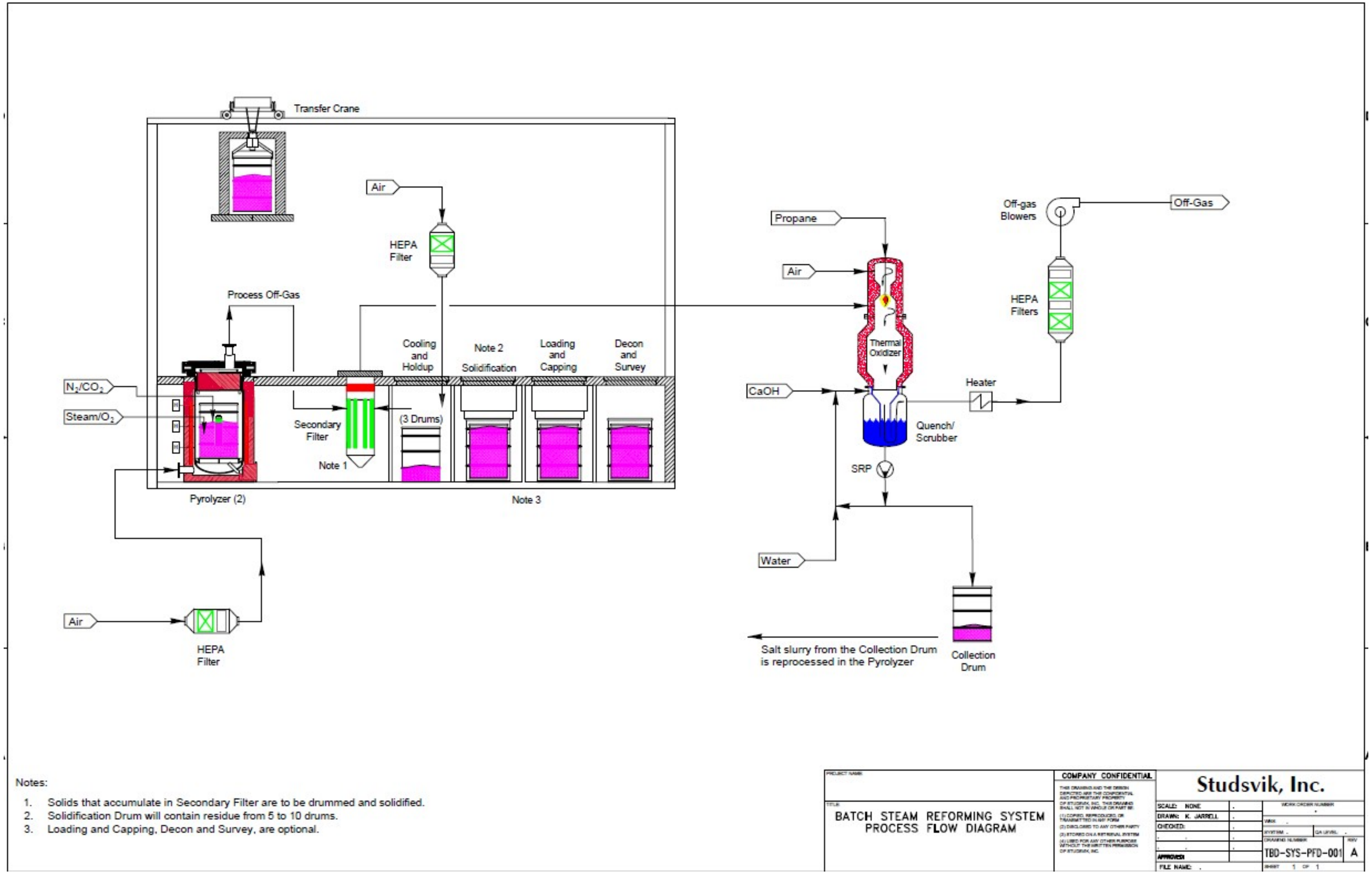

Figure 4 Flow Diagram of the In-Drum Pyrolysis Process

2 In-Drum Pyrolysis Chemistry

The IDP is an electrically heated vessel into which the intact drums of waste are placed. Ceramic-insulated electrical heaters are located on the exterior of the IDP vessel and the vessel is heated to the setpoint temperature which is dependent on the composition of the wastes. The IDP vessel provides energy to heat the waste materials in the drum to the evaporation and pyrolysis temperatures. The vessel wall is fabricated with a high-temperature resistant alloy suitable for contact with the evaporated liquids and pyrolyzed organic gases from the drum contents.

The IDP vessel is designed to fully volatize and remove >99.9% of the organics from the waste streams – regardless of the organic composition – and vaporize liquids. Many hazardous chlorinated organics, which have low to medium boiling points (less than 350ºC) readily evaporate and form organic vapors that flow out of the waste container and into the off-gas treatment system.

Organics with high boiling points, such as high molecular weight polymers and plastics, are fully pyrolyzed to a carbon char. Exposure to temperatures above 500ºC causes the organic polymer structure to break down into smaller, more volatile organics, thereby gasifying the organic constituents. For this reason, pyrolysis is often referred to as destructive distillation or thermal desorption. If steam is injected into the container following pyrolysis, the carbon char is converted to carbon monoxide and carbon dioxide.

Typical IDP process gases include nitrogen cover gas, water vapor, carbon monoxide, carbon dioxide, volatile hydrocarbons, short chain organics (mostly methane), hydrogen, hydrochloric acid, chlorine, and hydrogen sulfide. Small amounts of NOx gas may also be present if nitrates are present in the waste. Example chemical reactions that occur during pyrolysis of high boiling point organics and plastics are shown in Table 1.

Table 1 Typical Pyrolysis Reactions for High Boiling Point Organics During IDP Treatment

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

3 Conversion of Reactive Chemicals

The IDP process converts reactive chemicals with reactivity and ignitability hazards into stable compounds that can be disposed of safely. Examples of reactive wastes include metallic sodium, potassium, calcium, magnesium, metal shavings, and cyanide compounds that have the potential to burn, ignite, or even explode when exposed to certain other materials or when exposed to varied environmental conditions.

The IDP process thermally treats and stabilizes these reactive materials by converting them into stable compounds. The reactive metals in the waste container are usually present as shavings and/or fine powders that are highly reactive when heated above 500^{o}C. The strongly reducing metals 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 2. Gasses are injected in a controlled manner specifically for the purpose of deactivating the metals. Ideally, the reactive metals need to be in small concentration relative to the total waste in each container to prevent excessive heat generation during treatment.

Cyanides, if present, volatize from the waste container and oxidize in the TO to form water, carbon dioxide, and nitrogen.

Limited amounts of oxidizers, such as nitrates, can also be treated to reduce potential ignition hazards. Nitrates thermally decompose into gaseous NOx at IDP operating temperatures. The reducing environment within the IDP vessel combined with the use of catalytic ceramic filters in the secondary filter vessel significantly reduces the NOx concentration in the process gas.

Essentially all corrosives, including both organic and inorganic acids and bases, evaporate, thermally decompose, or are converted to stable compounds at the operating temperatures, as shown in Table 2. Most thermally treated contaminated waste residues have pH levels ranging from 5 to 10 and are not considered corrosive. If necessary, gasses are injected in a controlled manner specifically for the purpose of removing the corrosive characteristic of the waste.

Table 2 Stabilization of Reactive Materials during IDP Treatment

Material	**Stabilization Method**
Liquids	Evaporates from waste in autoclave and converts to CO_2 and water in TO
Sodium	Converts to Na_2CO_3, NaCl, or Na_2SO_3
Potassium	Converts to K_2CO_3, KCl, or K_2SO_3
Calcium	Converts to $CaCO_3$, CaO, $CaCl_2$, or $CaSO_3$
Magnesium	Converts to $MgCO_3$, MgO, $MgCl_2$, or $MgSO_3$
Nitrate	Decomposes to NO_x by pyrolysis. NO_x is then converted to nitrogen in the reducing environment by the catalytic secondary filtration system.
Corrosives	Stabilized by one of three methods: • Decomposes to volatile gas • Evaporates from waste • Converts to stable, non-corrosive Cl, CO_3 or SO_3 compound
Cyanide	Evaporates from waste is converted to CO_2, nitrogen, and water in steam reformer
Chromium	Converts to non-hazardous tri-valent oxide

4 Conversion of Reactive Chemicals

Figure 5 shows the off-gas hydrogen, total acid gases, and total VOCs concentration in the IDP offgas along with the average temperature of the centerline drum core thermocouples as a function of time. The plot is for the waste shown in Figure 2. VOCs evolution started essentially at the beginning of the test and peaked when the pyrolysis autoclave core temperature reached the normal boiling points of compounds contained within the waste drum.

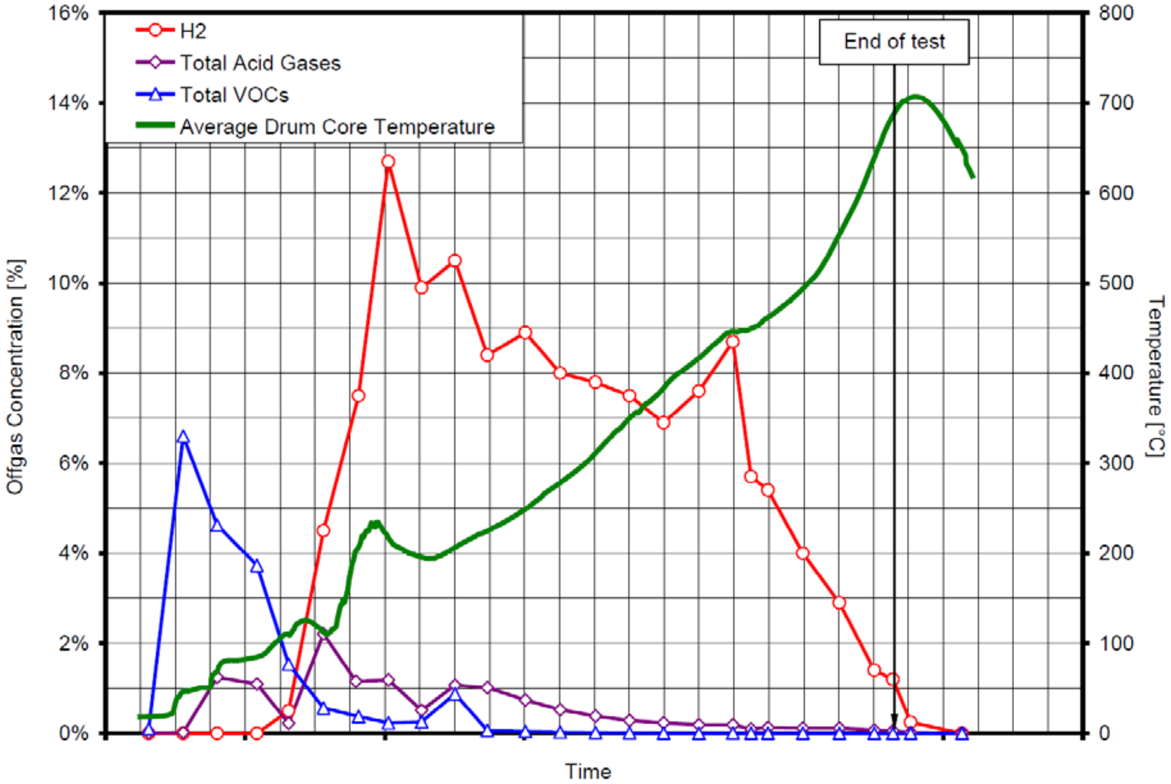

Figure 5 Full Surrogate Waste Drum Test – off-gas H2, total acid gases, and total VOCs concentrations and average drum core temperatures as a function of time.

5 Storage and Disposal

To be able to further volume reduce and/or stabilize IDP residues, it is possible to employ one or more of the following volume reduction and stabilization techniques:

- **Compact and Store**: Compact post-treatment waste containers with contents inside into a lower volume, compacted metal disk filled with compacted residues. The compacted disks, commonly called pucks, are placed into larger containers or boxes for storage and disposition. This option has very low storage risk as the organics and liquids would have been removed, and the dry, inert, post-treatment residues are safely stored for long periods of time with no risk of hydrogen and other flammable gas generation. Corrosion of the storage container would be minimal due to absence of corrosive materials and liquids. This method would eliminate additional handling of the drums, as no segregation would be required. Volume reduction for this approach is dependent on the input waste stream – (the volume reduction numbers provided here are calculated as [volume of incoming waste] / [volume of processed waste], overpack not included) examples are:

- Combustible waste is greater than 5 and is limited by either volume of carbon char or volume of crushed drum;
- Mixed waste (combustible and non-combustible) 2 to 5;
- Non-combustible waste 1-2 – only small amounts of organic waste are present (for example plastic bags and liners) and volume reduction by compaction is limited.

- **Compact and Grout/Solidify**: Compact post-treatment container with contents into a lower volume, compacted metal disk filled with compacted residues. The compacted pucks are placed into disposal boxes or storage containers, and the voids are filled with qualified grout or cement. This method would eliminate additional handling of the waste containers, as no segregation would be required. If macro-encapsulation is acceptable for final disposal, this option provides the lowest final waste volume. Volume reductions before placement in the disposal container are the same as those for the previous option.

- **Segregate and Grout/Solidify**: Open waste containers and encapsulate with a grout/cement mixture that consists of the particulate residues, cement additives and water. This option provides the best stabilization of treated residues as each particle is individually micro-encapsulated. If the volume-reduced contents of drums are combined before solidification, the volume reduction is similar to that for the other two process; with no combining, the volume reduction for this approach is <1.

Additional methods for volume reduction and stabilization are possible; however, the three techniques above have been used with success by several organizations in commercial and government facilities.

6 Studsvik's Unique Experience

Studsvik has developed and tested the IDP process over a period of several years. A deep understanding of what is possible has been developed. Studsvik has confirmed that the IDP process has the capability to remove water, destroy organics, convert reactive chemicals into stable compounds that can be disposed of safely, breach sealed containers, and reduce the volume of waste.

The unique treatment technologies associated with Studsvik's In-Drum Pyrolysis System are protected by issued and pending US and international patents.