WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

STUDSVIK PROCESSING FACILITY PYROLYSIS/STEAM REFORMING TECHNOLOGY FOR VOLUME AND WEIGHT REDUCTION AND STABILIZATION OF LLRW AND MIXED WASTES

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ABSTRACT

Studsvik has completed construction, start-up testing, and has commenced commercial operation of a Low-Level Radioactive Waste (LLRW) processing facility in Erwin, TN. The Studsvik Processing Facility (SPF) has the capability to safely and efficiently receive and process a wide variety of solid and liquid LLRW streams including: ion exchange resins (IER), charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to 1.5 Sv/h (150 R/hr). The licensed and heavily shielded SPF can receive and process liquid and solid LLRWs with high water and/or organic content.

The SPF employs the THermal Organic Reduction (THOR^{sm}) process, developed and patented by Studsvik, which utilizes pyrolysis/steam reforming technology. THOR^{sm} reliably and safely processes a wide variety of LLRWs in a unique, moderate temperature, pyrolysis/reforming, fluidized bed treatment system. The THOR^{sm} technology is suitable for processing hazardous, mixed and dry active LLRW (DAW) with appropriate licensing and waste feed modifications.

Operations have demonstrated consistent, reliable, robust operating characteristics with consistent volume reductions of up to 70:1 and weight reductions of up to 30:1 when processing depleted, mixed bed, ion exchange resins with over 99.8% of all radionuclides in the waste feed incorporated in the final solid residue product. Final reformed residue comprises a non-dispersible, granular solid suitable for long-term storage or direct burial in a qualified container. THOR^{sm} effectively converts hexavalent chromium to non-hazardous trivalent chromium and can convert nitrates to nitrogen with over 99 percent efficiency in a single pass.

The paper provides an overview of the first 6 months of commercial operations processing radioactive ion exchange resins from commercial nuclear power plants. Process improvements and lessons learned will be discussed. Plans for new mixed waste and graphite steam reforming processing will be presented.

PROCESS OVERVIEW

Studsvik Inc., with offices in Columbia, SC and Erwin, TN, is a subsidiary of Studsvik Holding AB located near Stockholm, Sweden. Since 1947 Studsvik has been actively involved as a research center for nuclear power in Sweden. Studsvik operates a research test reactor and hot cell facility for production of medical isotopes, commercial nuclear fuel testing, and materials irradiation. Studsvik operates a Dry Active Waste (DAW) incinerator, which has been in commercial operation since the early 1970s. Full metal melting and recycling capabilities for carbon and stainless steels and aluminum have been in use for several years.

A five phase test program was implemented to develop a process that could effectively volume reduce and stabilize a wide variety of liquid and solid LLRWs that could not be processed by the Studsvik incinerator. The successful test program culminated in the decision to proceed with the licensing, design, and construction of a commercial LLRW processing facility that utilizes the patented THOR^{sm} process. The Studsvik Processing Facility (SPF) has completed construction, startup testing, and commenced commercial operations with processing of radioactive IER from nuclear power stations in July 1999.

The THOR^{sm} process utilizes two fluid bed contactors to process a wide variety of solid and liquid LLRWs. Figure 1 provides an overview flow diagram of the THOR^{sm} process. Radioactive waste feeds are received at the SPF and stored in holdup tanks. As waste is needed in the process, waste is transferred to the waste feed tanks for metering and injection into the first stage fluid bed pyrolyzer/reformer. Solid, dry, granular wastes such as charcoal, graphite, soil, etc are metered into the Pyrolyzer by the solids feeder. Liquids and slurry wastes such as IER, sludges, oils, antifreeze, solvents, cleaning solutions, etc are metered into the Pyrolyzer by a pump.

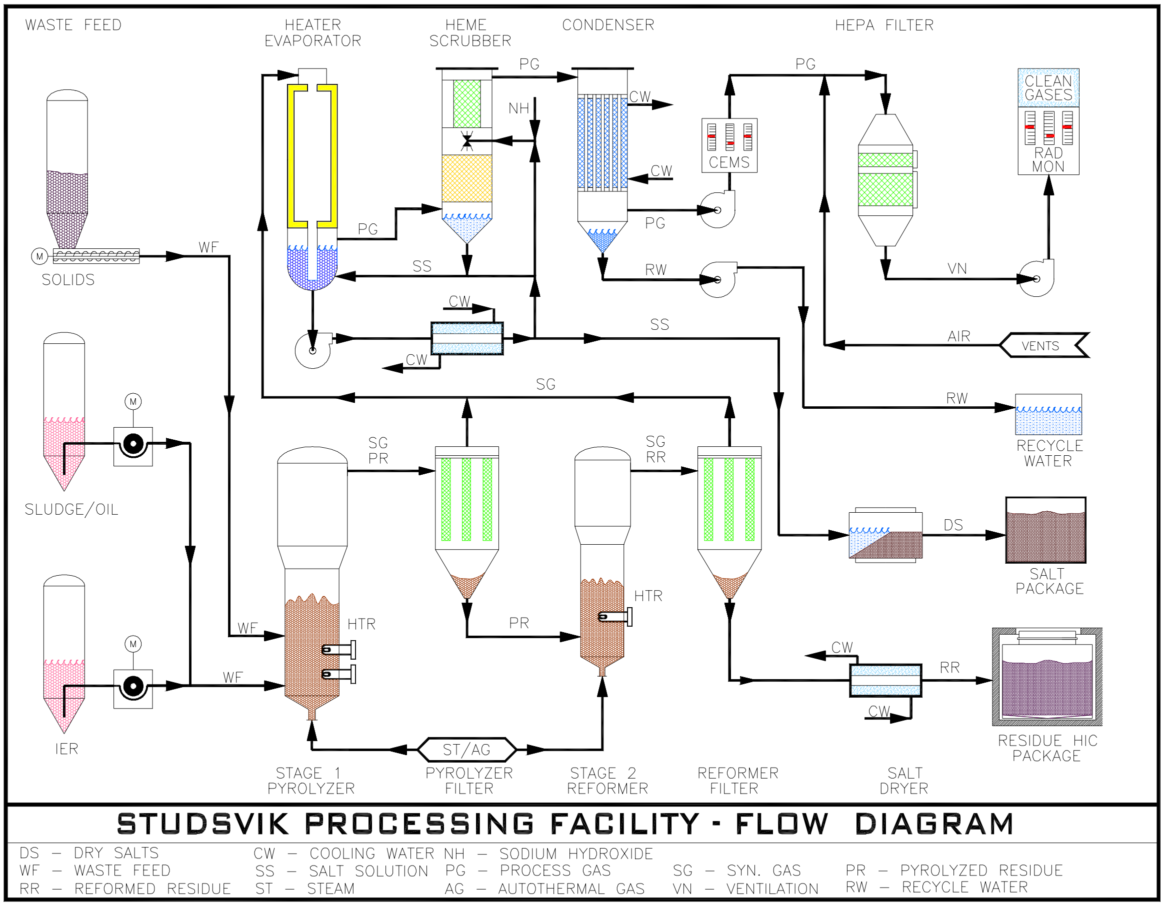

Figure 1 - THOR^{sm} Process Flow Diagram

The Pyrolyzer fluid bed serves to evaporate all water from the IER slurry and liquid waste feeds, and pyrolyze the organic components through destructive distillation. Fluidizing gases, volatile organic vapors, and steam released in the Pyrolyzer fluid bed comprise a synthesis gas which passes through the ceramic filters and to the gas handling system. The low-carbon, metal oxide-rich residue removed by the ceramic filter can be further processed in the second stage steam reformer to remove any final carbon or to convert the oxidation state of selected metals. The stage 2 Reformer can also be used as a primary waste processing unit by the direct injection of liquid wastes. The radioactive, volume reduced residue is packaged in qualified high integrity containers for burial at licensed burial sites or return to the generator. The final reformed residue volume is routinely only 1 to 4 percent of the incoming resin volume. For depleted, mixed-bed IER it is possible to achieve a volume reduction (VR) of 20-100 times with a corresponding weight reduction (WR) of 12-85 times.

Through selection of autothermal steam reforming operating conditions it is possible to produce an inert, inorganic final waste that consists of only the radioactive elements, metal oxides and inorganic calcium and silica compounds initially absorbed on the IER. It is possible to reach near theoretical mass reductions with the THOR^{sm} process. Another significant improvement realized by the THOR^{sm} process is the ability to process wastes with high water content. Aqueous wastes do not need to be dried prior to processing, but can be injected directly into the fluid bed using reliable slurry pumping equipment. Sodium nitrate slurry, oils, activated carbon, antifreeze solution, steam generator cleaning solvent and several types of IERs have all been successfully processed by the THOR^{sm} process.

STUDSVIK PROCESSING FACILITY

Studsvik has completed construction and start-up testing of a Low-Level Radioactive Waste (LLRW) processing facility in Erwin, TN. The SPF has all applicable licenses and permits for operation including a radioactive materials license from the State of Tennessee. Commercial operation of the Studsvik Processing Facility (SPF) began in July 1999. The SPF and THOR^{sm} process systems are described below. The SPF is designed to meet all laws, codes, and standards related to processing LLRW. A photograph of the SPF is shown in Fig. 2.

Figure 2 - SPF Overview

The SPF is designed to meet the following criteria:

Facility Curie Inventory:	up to 2,000 Ci (74 TBq)
LLRW Input Curies:	up to 2.0 Ci/cu.ft. (2.6 TBq/m^3) Contact dose of up to 150 R/h (1.5 Sv/h)
LLRW Inputs:	Ion Exchange Resins, Charcoal, Graphite, Organic Solvents and Oils, Aqueous Decon and Cleaning Solutions, Slurries, and Sludge

The SPF consists of a heavily shielded Process Building, unshielded Ancillary Building, and an Administration Building. The Process and Ancillary Buildings are licensed for receipt, handling, processing, and packaging of LLRW.

Process Building

The Process Building contains all radioactive processing, handling, and packaging systems for volume and weight reduction of incoming LLRW. Major areas include Truckbays, LLRW Input Holding Tank Vault, Pyrolysis/Reforming Vault, Gas Handling Vault, Salt Dryer Room, Final Residue Packaging Vault, and Auxiliary Equipment Rooms.

Truckbays

LLRW is shipped to the SPF in DOT or NRC qualified non-shielded containers and/or shielded casks. Most LLRW is received in the Truckbay where containers and casks are surveyed, opened and the waste transferred to shielded Waste Input Holding Tanks located in shielded vaults. Cask maintenance activities are performed in the Truckbay where an overhead bridge crane provides lifting capability. Figure 3 is a photograph of the dual station truckbay.

Waste Input Holding Tanks

Three large stainless steel Slurry Holding tanks are provided for receipt and holdup of incoming liquid and slurry wastes. A separate Liquid Waste tank is used to receive more volatile organic solvents, cleaning solutions, and oils. A Lockhopper Feeder is used to receive and feed granular and powdered LLRW, such as charcoal. A separate Waste Feed tank with Injection Pumps is used to meter slurry and liquid wastes from the Slurry Holding tanks into the stage one Pyrolysis vessel. Figure 4 is a photograph of the Slurry Holding tank vault.

Figure 3 – Truckbay

Figure 4 – Slurry Holding Tanks

Pyrolysis/Reforming System

The Pyrolysis/Reforming THOR^{sm} system comprises: stage one Pyrolysis contactor (Pyrolyzer), stage two Reformer contactor and associated Filters. The Pyrolyzer is a vertical, cylindrical fluid bed gasifier designed to operate at up to 800°C. LLRW is injected into the electrically heated, fluidized Pyrolyzer where: 1) water is instantly vaporized and superheated, and 2) organic compounds are destroyed as organic bonds are broken and resulting synthesis gas (principally carbon dioxide, carbon monoxide, and steam) exits the Pyrolyzer. Residual solids from the pyrolysis of the LLRW (including fixed carbon, >99.8 percent of the incoming radionuclides, metal oxides and other inorganics and debris present in the LLRW feed) are removed from the Pyrolyzer and collected in the stage one Ceramic Filter vessels. The Pyrolyzer is fluidized with superheated steam and additive gas. Figure 5 is a photograph of the Reformer Process Area.

Figure 5 - Process Area - Reformer

The stage two Reforming contactor is a vertical, cylindrical fluid bed designed to operate at up to 800°C. Pyrolyzed solid residues from the stage one filters or additional LLRW feed can be transferred to the Reformer, which is an electrically heated, fluidized bed. The reformed, low-carbon, final residue is collected in the stage two Ceramic Filter vessel. The Reformer is fluidized with superheated steam and additive gas.

Gas Handling System

The Gas Handling system comprises an Energy Recovery Heater, Submerged Bed Evaporator, Scrubber/Mist Eliminator, Condenser, CEMS, Process Blower, HEPA filter, Vent Blower and Radiation Monitor. The purpose of the Gas Handling system is to convert synthesis gas constituents to carbon dioxide and water, recover energy from the synthesis gas, convert acid gases to stable salts, control water content of exiting process gases, and control negative pressure levels throughout the THOR^{sm} pyrolysis/reformer system.

Synthesis gases from the Pyrolyzer and Reformer are filtered and then oxidized in the Energy Recovery Heater to carbon dioxide and water. The Heater recovers energy from the synthesis gas and provides heat to the Submerged Bed Evaporator where excess water is evaporated from the scrubber water. The Heater is a vertical, refractory lined vessel that operates at up to 1200°C.

The Submerged Bed Evaporator is an energy recovery system that channels the hot Heater outlet gases through a volume of scrubber water, thereby evaporating excess water. The Evaporator concentrates scrubber solution to 10 to 20 percent salts. The wet evaporator gases pass through the rotary atomizer Scrubber where sulfur and halogen gases are efficiently converted to salts. Sodium hydroxide is metered into the Scrubber to neutralize sulfur and halogen gases that are absorbed by the scrubber solution. The outlet of the Scrubber is fitted with a Mist Eliminator that removes particulates and mists from the Scrubber outlet.

The clean, moisture-laden gases exit the scrubber and excess moisture is condensed for recycle/reuse in the process. The Condenser serves as the process heat sink and serves to control water balance in the SPF. The cool, clean gases are then compressed to atmospheric pressure by the Process Blower. A Continuous Emissions Monitoring system (CEMs) is provided on the Process Blower outlet to monitor and record the release of any traces of carbon monoxide, acid gases, total hydrocarbons, and NOx.

The clean, cool process gases commingle with the building ventilation airflow. The combined gases flow through a HEPA filter bank, Vent Blower and are then released through a monitored vent stack. A complete Radiation Monitor system measures and documents any trace radionuclides that may pass through the stack. The Radiation Monitor system includes gamma, beta, alpha, iodine, carbon^{14}, and tritium samplers and detectors.

Salt Handling System

The salts that are formed in the scrubber and concentrated in the evaporator are transferred to the Salt Handling system, which comprises a filter, an ion exchange system and Salt Dryer. The concentrated salt solution is filtered to remove any trace particulates that may pass through the Pyrolyzer and Reformer filters. Any trace radioactive species are removed from the scrubber solution by a high-efficiency, metals selective ion exchange medium. The Salt Dryer dries the purified salt solution to form a salt cake suitable for direct disposal at a licensed landfill. The dry salt is very low in activity.

Residue Handling System

The reformed, low-carbon residue from the Pyrolyzer and Reformer is transferred to the High Integrity Container (HIC) packaging vault. Qualified HICs are filled with the solid, inert residue. Filled HICs are transferred from the packaging vault to a shipping cask be means of a shielded transfer bell. Dual containment and seals are provided on residue handling components. The packaging vault is provided with separate HEPA filtered ventilation system and water washdown capability.

The HIC packaged residue is suitable for direct burial at either the licensed Barnwell or Hanford LLRW burial sites. The packaged residue is also suitable for long-term storage due to its solid, inert, all inorganic nature. The packaged residue is not subject to common problems with long-term storage including bacterial activity and radiolysis of organic compounds.

It is possible to package the low-volume residue in any of the following forms:

- stabilized in High Integrity Containers (HIC);
- compacted, cold-sintered, high-density, metal oxide monolith;
- solidified monolith using polymer sulfur cement, portland cement, thermoplastics, or polymers;
- vitrified monolith using borosilicate or phosphate glass; or
- melted metal monolith.

Spill Protection and Contamination Control

All interior surfaces of the SPF are provided with durable, easy-to-decon coatings. The interior wall and roof panels are of interlocking and sealed construction to eliminate leakage paths from the inside of the SPF to the outdoors. Interior concrete and steel surfaces have a special multi-layer coating to prevent migration of spills or contaminants from the SPF to the environment. The HVAC system also maintains the inside of the SPF at a slight negative pressure relative to the ambient outdoors, effectively eliminating potential airborne releases. Dikes, berms and sumps are located so as to prevent tank leaks and even potential large firewater events from escaping to the outdoor environment.

Auxiliary Equipment and Utility Services

The Process Building contains all auxiliary and utility subsystems required to support SPF operations and THOR^{sm} operations including:

Steam Supply
Steam Superheaters
Steam Condensate
HVAC and Ductwork
Natural Gas Supply
Motor Control Center
Sluice Water
Demineralized Water
Potable Water
Dryer Condensate
Cooling Water
Hot Laboratory
Nitrogen Supply
Service Air
Instrument Air
Breathing Air
Additive Gas
DAW Compactor

ANCILLARY BUILDING

The Ancillary Building is designed for storage of spare parts, empty waste shipping containers and equipment for use at customers’ locations. A spray dryer and collector are being installed to provide additional salt drying capability for the process. Full salt containers are accumulated for shipment for disposal. Low activity LLRW can also be received and offloaded in the Ancillary Building. Maintenance of plant equipment is also performed in a controlled area. A modular, skid-mounted, pilot-scale THOR^{sm} system can be located in the Ancillary or Process Building to perform testing on surrogate and low activity wastes.

ADMINISTRATION BUILDING

The Administration Building has: offices for plant staff and management, control room, switchgear and UPS, health physics and personnel contamination monitoring areas, and count room. The THOR^{sm} control room provides remote readout of all process parameters. Trained operations personnel utilize the fully automated Supervisory Control and Data Acquisition (SCADA) system to monitor and control all system operations. The SCADA provides a comprehensive human-machine-interface that monitors the PLC panels, instruments, and equipment located in the Process and Ancillary Buildings. Automated safety systems, alarms, and interlocks are provided together with real-time data acquisition and trending. The SCADA provides the operators automated flow diagram windows to monitor and control the process through graphical interfaces.

START-UP ACTIVITIES

SPF start-up activities commenced in February 1999 with the performance of a series of subsystem tests and hot functional tests. Process and SCADA control systems were tested over a several month period to demonstrate reliable performance and to verify that all systems work together as an integrated facility.

Operations personnel training was certified on actual operating plant systems. Operating procedures were also verified to be accurate.

Testing activities uncovered several design and equipment deficiencies that were corrected throughout the testing and subsequent operational periods. The main problems encountered during the start-up activities as well as successes are discussed below.

The IER unloading system worked very well. The incoming resin containers were opened and the dried or wet resins inside were slurried out using remote devices with very low personnel dose accumulation or direct hands-on effort required. Special stainless steel shipping containers were developed that allowed fully remote removal of incoming resins. Many resins were shipped to the facility in disposable plastic or metal containers that were not compatible with full remote slurrying operations. Such containers required manual intervention to remove the final contents from the container. The IER unloading system has worked very well.

The water-slurried IER is transferred to the Slurry Holdup tanks where the resins are allowed to settle and excess water is then decanted off the top of the settled resin. The original tank manufacturer provided decant devices that did not work as the floats sank and the decant hoses became tangled. A modified, larger decant device with positive alignment guides was installed in each tank with good success. Decant operations require no operator intervention.

The settled IER from the Slurry Holdup tanks is transferred to the Resin Feed tank and then the low-water content resin slurry is injected directly into the Pyrolyzer. The IER transfers and feed operations have worked very well except when substantial charcoal is commingled with the IER. Additional water flush connections were added to facilitate handling and injection of IER commingled with granular charcoal. Slurry injection lines were modified to remove excess bends.

The Pyrolyzer has performed as designed for drying, pyrolyzing and steam reforming the various LLRW feeds processed. A problem was encountered in the superheated steam system that provides fluidizing gases to the Pyrolyzer. The steam system did not have adequate condensate removal capability that allowed condensate to enter the electrically heated superheaters. The presence of liquids in the superheater caused crack formation of the heater shell due to thermal stresses. The steam system was corrected to provide thorough condensate removal. The super heated fluidizing gas systems have worked very well.

The Pyrolyzer experienced several agglomeration events during testing and initial radioactive operations that have required process shutdowns to remove accumulated deposits in the fluid bed. The Pyrolyzer operating parameters have been adjusted and the design of the IER injector and internals inside the Pyrolyzer have been changed with good success. A unique fluid bed media washing station (patent pending) has been added to allow the sand in the fluid bed to be automatically removed and washed to dissolve accumulated low-melting point salts on the sand media, without disturbing Pyrolyzer on-line operations. The clean sand media is then returned to the Pyrolyzer. No significant agglomerations have occurred for several months.

The Ceramic Filters have performed with high efficiency except during the initial non-radioactive tests. It was determined that several of the special high temperature seals were not large enough to seal the filter element tubesheet penetrations thereby allowing some reformed residue to bypass the filters elements and enter the Gas Handling System. Corrected seals have been installed on the tubesheet. Filter removal efficiency is now very high with typical particulate radionuclide removal efficiencies exceeding 99.999 percent.

The Gas Handling System has performed well except for the carryover of small quantities of salt from the Scrubber to the HEPA filters and lower than specified performance of the Process Blower. A filter baghouse has been added just upstream of the HEPA filters to prevent rapid blinding of the HEPA filters with salt. Larger drive motors have been provided on the Process Blowers so that process pressures can be adequately maintained during all processing operations.

The Salt Dryer did not provide the required throughput capacity. Extensive revisions have been performed to the Salt Dryer system to provide full production throughput capacity and to significantly reduce the hands-on maintenance required of the initial system. A new spray dryer is being installed to provide improved salt drying capacity and to reduce the hands-on maintenance needs of the current salt dryer.

OPERATIONS SUMMARY

Commercial radioactive operations commenced on July 19, 1999. Initial operations were limited for several weeks to processing only very low activity IER at low waste feed rates. This allowed operations staff to gradually implement and perform maintenance activities on system components with full radiological controls but with only very limited radiation and contamination levels. Several plant hardware corrections were identified and accomplished during this period as discussed above. The initial low feed rates of 1 to 2 cubic ft per hour (0.03 to 0.05 cubic meter/hour) have been progressively improved up to the current 8 to 12 cubic ft per hour (0.22 to 0.34 cubic meter/hour) processing rate. Continued efforts are being made to reduce downtime for maintenance activities.

Higher activity IER and charcoal have been progressively received and processed. Table 1 provides a summary of SPF processing throughput and waste processing parameters from the start of commercial operations through January 19, 2000.

Quantity of Radioactive Resin Processed:	>4,000 cuft (>113 cu meter)
Current Processing Rate:	8 to 12 cuft/h (0.22 to 0.34 cu meter/h)
Highest Activity Resin Processed:	150 R/h (1.5 Sv/h) On Contact
Volume Reductions Achieved:	Incoming Resin Volume : Final Residue Volume
Condensate Polisher Resin:	64:1 to 74:1 (1.3% to 1.5% Remaining)
Cleanup/CVCS/Radwaste System Resin:	15:1 to 58:1 (1.7% to 6.7% Remaining)
Torus Cleanup – High Inorganic Sludge:	5:1 to 8:1 (12.5% to 20.0% Remaining)

Table 1 - Processing Throughput and Parameters

The volume reduction of the incoming waste is dependent on the inorganic content of the resin. Resins that are not fully depleted or have been ultrasonically cleaned to remove particulates will have VR factors exceeding 60:1. Typical water cleanup and radwaste resins will have VR factors of 20:1 to 60:1 depending upon the quantity of metals and particulates on the resin. Resins that have a very high inorganic loading, mainly particulates from floor drains and torus sludge removal efforts, may have VR factors as low as 5:1. Pyrolysis and steam reforming can only remove the water and organic fraction of the incoming waste feed. Essentially all inorganic cations (metals) including all non-volatile radionuclides will be in the final, low-volume residue. It is possible however, to change the oxidation state of various metal ions if desirable, e.g. hexavalent chromium is converted to non-hazardous trivalent chromium.

The processing rate has been increased and is anticipated to be at the annualized design throughput of over 60,000 cubic ft (1,700 cubic meter) of incoming IER when the new spray dryer is commissioned in April, 2000.

CONCLUSION

The THOR^{sm} process, as implemented in the SPF, has the following features and provides the following significant advantages over other current LLRW processing technologies.

- VR of 20 to 100 for IER wastes;
- WR of 12 to 85 for IER wastes;
- Atom-for-atom processing mode is possible;
- Inert, inorganic, homogeneous, final waste form;
- Direct disposal in qualified HICs;
- Accept IER with contact dose rates up to 150 R/h (1.5 Sv/h);
- Accept LLRW including: IER, graphite, charcoal, SGOG solvents, antifreeze, oils, sludge, high-water content wastes, and high-organic content wastes;
- Packaged final waste form suitable for long-term storage with no risk of gas generation due to bacterial or radiolysis action (residue has no organic content);
- Final waste form is reprocessable to alternative waste forms including vitrification, solidification, encapsulation, cold-sintering, and melting.

FUTURE PLANS

Studsvik has further developed the THOR^{sm} process for efficient handling of graphite and mixed wastes by utilizing a simplified single-stage Reformer process (patent pending). A modular fluid bed Reformer is now being designed for implementation in processing additional IER feed at the SPF. In addition, the modular THOR^{sm} reforming system can be transported and or modified to process significant quantities of LLRW and Mixed wastes at other sites. Figure 6 illustrates the capabilities of the THOR^{sm} process.

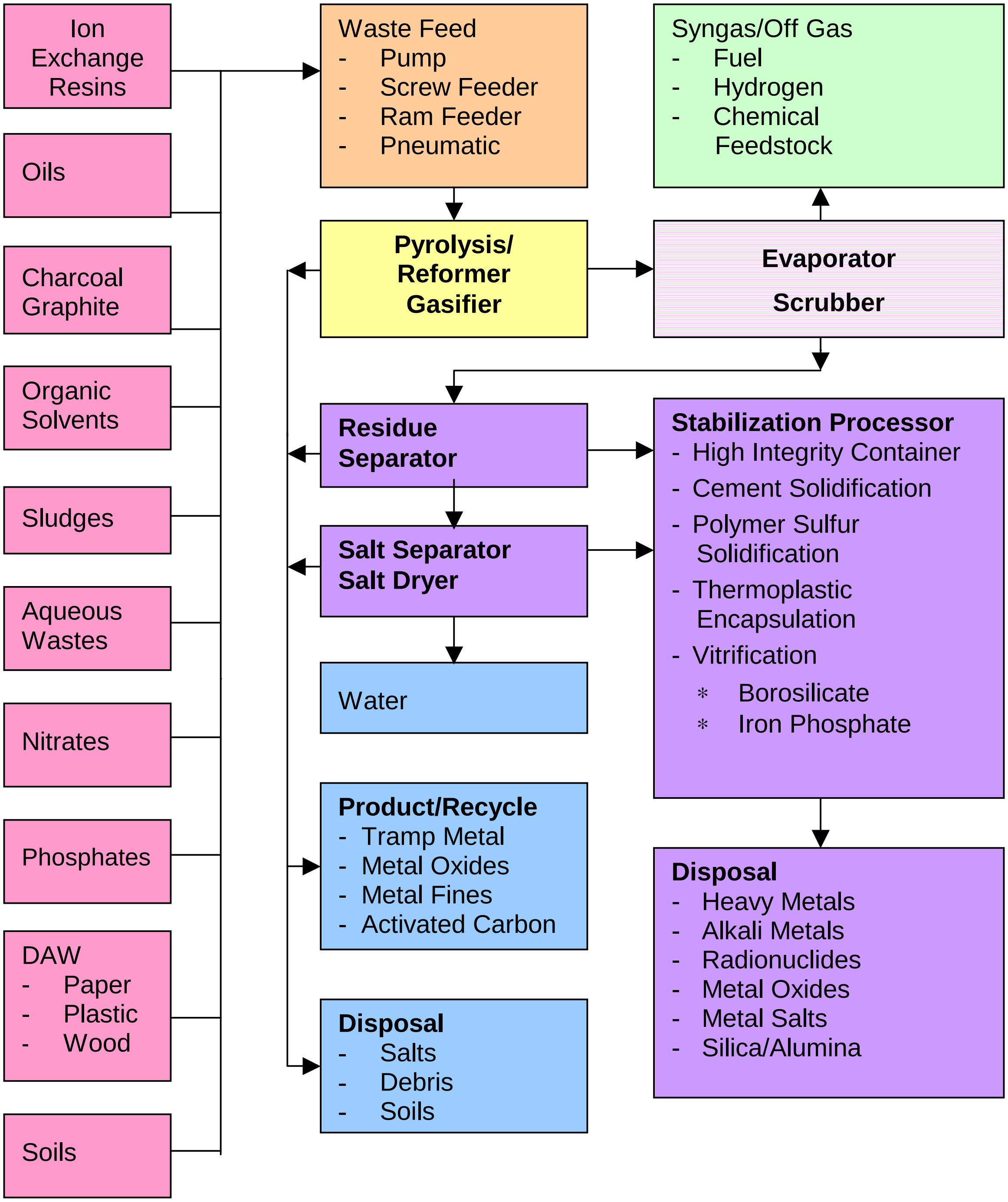

Figure 6 - Block Flow Diagram