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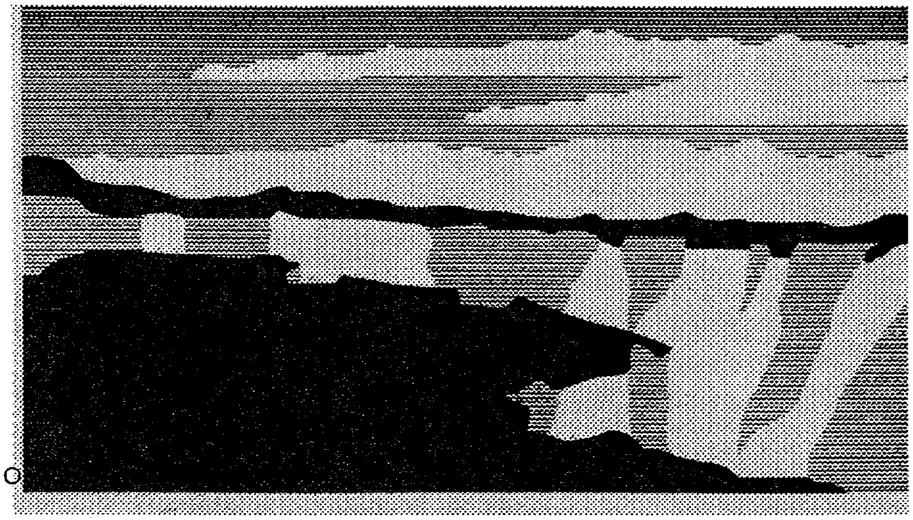

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A PORTABLE SYSTEM FOR THE TREATMENT OF WATER-REACTIVE MIXED WASTE

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INTRODUCTION

Los Alamos National Laboratory and other locations in the complex of experimental and production facilities operated by the United States Department of Energy (DOE) have generated an appreciable quantity of hazardous and radioactive wastes. The Resource Conservation and Recovery Act (RCRA) enacted by the United States Congress in 1976 and subsequently amended in 1984, 1986, and 1988 requires that every hazardous waste must be rendered nonhazardous before disposal. Many of the wastes generated by the DOE complex are both hazardous and radioactive. These wastes, called mixed wastes, require applying appropriate regulations for radioactive waste disposal and the regulations under RCRA. Mixed wastes must be treated to remove the hazardous waste component before they are disposed as radioactive waste.

This paper discusses the development of a treatment process for mixed wastes that exhibit the reactive hazardous characteristic. Specifically, these wastes react readily and violently with water. Wastes such as lithium hydride (LiH), sodium metal, and potassium metal are the primary wastes in this category. Besides their tendency to react with water, the wastes also produce alkaline hydroxides and hydrogen gas as products of the reactions.

$$LiH + H_2O \Rightarrow LiOH + H_2 \tag{1}$$
$$2Na + 2H_2O \Rightarrow 2NaOH + H_2 \tag{2}$$
$$2K + 2H_2O \Rightarrow 2KOH + H_2 \tag{3}$$

If in aqueous form and if the pH exceeds 12.5, the alkaline hydroxides must be further processed to lower the pH to the range of 2–12.5 to remove the corrosive hazardous characteristic. The hydrogen gas formed during treatment is not considered a RCRA hazardous waste, but the hydrogen poses a substantial safety hazard because it can form explosive mixtures with air. Tritium may also be substituted for hydrogen in the LiH. If tritium is present, special processing may be necessary to avoid exhausting tritium into the environment.

Because of the requirement to control environmental exposure to radioactivity contained in the wastes, the process design requires a reaction within enclosed vessels. These vessels require inert gas purging with subsequent off-gas scrubbing and high-efficiency particulate air (HEPA) filtration before discharge to the atmosphere. If tritium is present in the reaction gases, a better system to capture the tritium is necessary. The hydrogen-containing off-gas could be vented, flared, oxidized to water by combustion or electrochemical oxidation, or separated from the nitrogen purge and collected in gas cylinders or thermally regenerable hydride substrates. Any alkaline hydroxide reaction products would be neutralized and further treated for disposal.

PROCESS DEVELOPMENT

Innitioal process development investigations centered around the idea that a stream of humified nitrogen could be used. This approach has many apparent advantages including

- the ability to control the reaction rate by limiting the humidity level in the nitrogen purge gas;
- the nitrogen provides a carrier for the water vapor and acts as the purge blanket; and
- the possibility to control the hydrogen content in the off-gas to below explosive limits by maintaining +96% N_2 by hydrogen/nitrogen separation and nitrogen recycle.

An experimental program focused on the humidified nitrogen process. In the experiment, nitrogen was passed through a humidifier and then contacted with the water-reactive substance in a reactor. The reaction kinetics were determined for LiH by measuring the gas flows and the amount of hydrogen exiting the reactor. The primary investigation variables were temperature, percentage of humidity, and particle size of the water-reactive substance. Specific results of these tests have been previously presented (1). Essentially, the results showed that the reaction follows the Unreacted Shrinking Core Model (2). Acceptable control and reaction rates were achieved with finely divided powders. Rates were prohibitively slow for larger pieces of LiH.

The humidified nitrogen process was abandoned because of these factors.

- The formation of an alkaline hydroxide layer on the particle surface slowed the reaction appreciably. Therefore, there was no foolproof way to ensure that the reaction had gone to completion.
- Heat removal from the reacting solid is critical because melting can occur at relatively low temperatures. Because melting would quickly plug most reactor designs, operation would be below the maximum saturated temperature. Table I shows that for LiH, operation would be fairly reasonable because saturated nitrogen at 50° C would carry enough water to the reaction without consuming too much nitrogen. Sodium and potassium metals would require recycling the reactor off-gas or would consume excessive nitrogen.

Table I. Water-Reactive Waste Melting Temperatures and Maximum Saturate Reactant Temperature.

water-reactive waste or product	melting temperature (°C)	maximum inlet temperature of saturated nitrogen with 5 °C superheat	maximum water concentration in nitrogen stream (mole fraction)
LiH	688	65	0.28
LiOH	471	50	0.13
Na	98	~15	~0.02
K	63	~10	~0.01

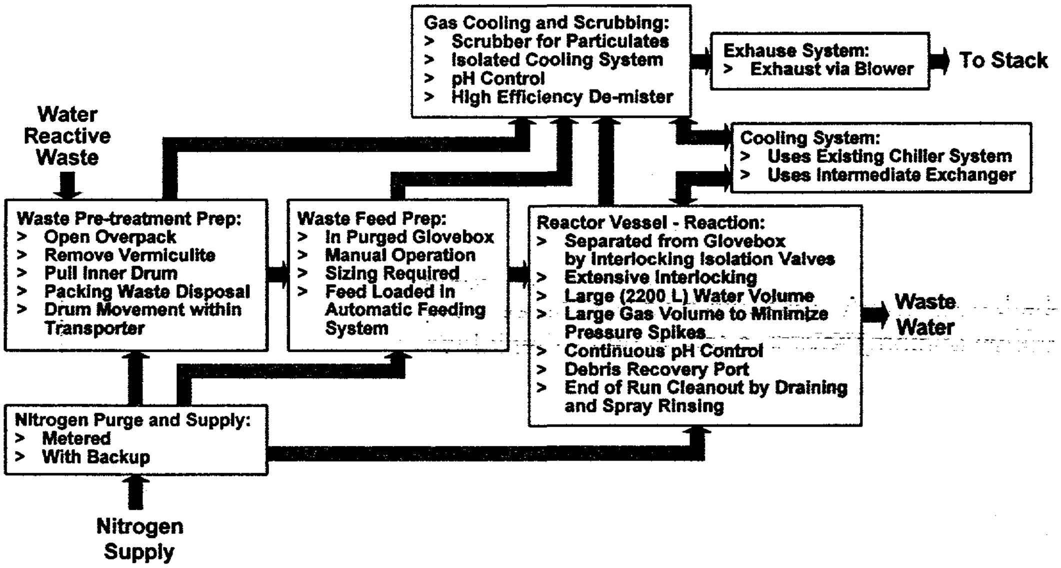
- The reaction rate for large particles was too slow to be practical. Grinding would be necessary to ensure complete and reasonable reaction rate.

- Controlling a large volume of a dusty reactant within a reactor while contacting with a moving gas stream would be a difficult design task. This task is made even more difficult because LiH has a very low density.

An alternate contacting method was developed. This process involves directly immersing the water-reactive waste in a volume of water. Reaction rate is controlled by the rate of addition of the waste to the reactor. In this system, a nominal amount of nitrogen is introduced as purge gas, but there is no attempt to maintain the hydrogen content 4%. The possibility of explosion is avoided by excluding oxygen. All off-gas is scrubbed, filtered, and discharged. During processing, the liquid volume charged gradually accumulates alkaline hydroxide strength. After pH adjustment, the waste water is sent to a wastewater processing plant. Figure 1 shows the basic process block flow diagram.

Figure 1.

WATER CONTACT WATER REACTIVE WASTE TREATMENT
--BLOCK FLOW DIAGRAM--



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The advantages of this approach are the following.

- Either powdered or large solid pieces of water-reactive waste can be fed, with acceptable reaction rates. Simple solids introduction methods can be used.
- Extraneous materials can be processed with the water-reactive waste. For instance, if lithium hydride is bonded to another non-water-reactive substance, the whole mass can be introduced to the reaction system to reliably remove the water-reactive waste from the nonreactive substrate.
- The volume of water in the reaction system provides an effective heat sink for the exothermic reaction. The reaction system is sized to limit the temperature rise to 20° C if the cooling system fails.

- Accumulations of solid alkaline hydroxide layers that could stop the reaction are minimized because the excess water dissolves the accumulations. This factor also eliminates the need for separate dissolution and rinse procedures.
- The amount of water-reactive waste treated per run is limited only by the liquid volume in the reaction system and the solubility of the alkaline hydroxide or neutralized hydroxide, and not by the volume of the reactor itself.

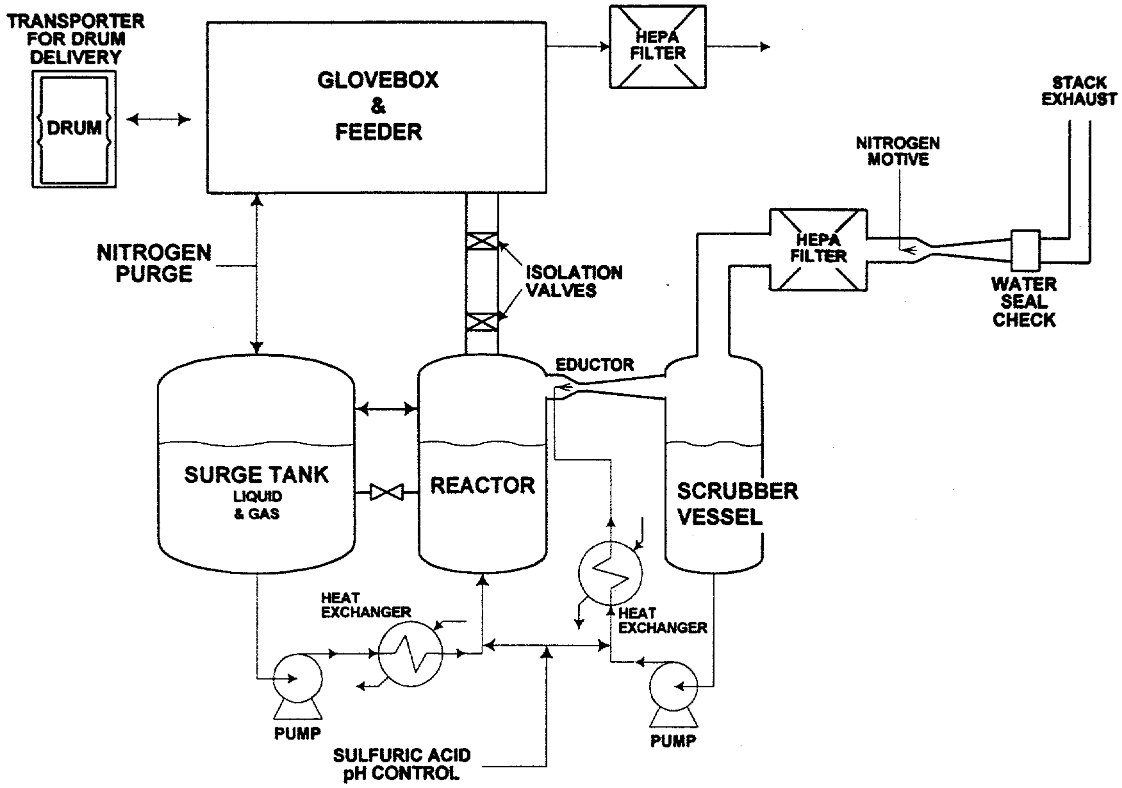
Experiments were performed to determine reaction characteristics and to validate the process concept. Details about the results of this experimentation are not within the scope of this paper; however, these generalizations are made.

1. Water-reactive solids larger than 1/4 in. tend to complete reaction in a reasonable time and do not react instantaneously. Tests on 1/4-in. pieces of LiH resulted in reaction times between 20 and 40 seconds.
2. Finely divided water-reactive material tends to react very quickly. Tests on LiH powders showed that reaction rates equivalent to 50% reaction within 0.5 seconds were attainable.
3. Attempts to regulate the reaction rate of powders showed some success:
    - Raising the solution strength to saturation of LiOH or $LiSO_4$ had little effect on reaction rate for small samples.
    - Forcing water to access the LiH through orifices controlled the reaction rate. The mechanism for control is the rate of water accessing the LiH, which is controlled by the escaping hydrogen gas. With fine orifices in metal bombs or cloth bags, the reaction rate was relatively steady for several minutes. An attendant problem is plugging the orifices with undissolved LiOH. Tuning the powder containers in the process unit will be necessary. An additional advantage of using a rate-controlling container or bag is that a delivery method controlling the powder rate is possible.
    - Water-soluble bags were tried as a delivery method and as a rate-controlling method. Although the soluble bags contained powders well, the rate controlling aspect did not work well. Once a spot on the bag dissolved, the whole bag would quickly empty because of hydrogen pressure buildup. Another problem encountered with the bags was they lost their ability to dissolve as the ionic strength increased in the reaction liquor. Suppression began as the concentration approached 20% of saturation of LiOH.

PROCESS DESIGN

A process design was completed in early 1995. The water-reactive waste treatment system will remove the RCRA reactive characteristic by contacting the solid waste with water. The treatment process is a skid-mounted system designed with maximum flexibility to treat the anticipated water-reactive wastes. The treatment skid consists of individual modules. Each module weighs a maximum of 4000 pounds and has maximum dimensions of 5 feet wide x 10 feet long x 12 feet high. The structural system is designed so that it can be easily cleaned for removal to storage. This requirement necessitates welded stainless steel construction that greatly minimizes cracks, crevices, and corrosion products such as rust. All reasonable effort has been given to meeting this goal with standard industrial equipment. When stainless construction is not possible, epoxy painting for nonstainless metal parts is specified. Figure 2 shows a simplified process flow diagram of the process.

Figure 2. Simplified Process Flow Diagram



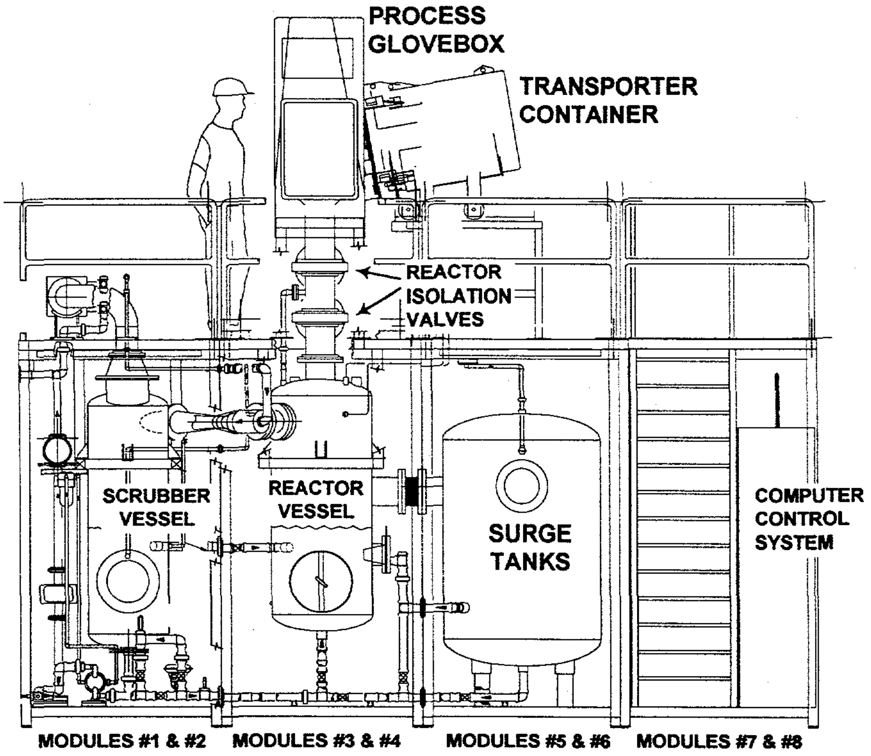
The skid design conforms to the standards of the National Electrical Code for explosion-proof operations in Class I Division 2 or Class 1 Division 1 Group B (3). Explosion-proof design uses a combination of explosion-proof enclosures, purging, and intrinsic safety barriers. The instrument and control portion of the skid design allows local and remote control of all critical portions of the process. Further, the skid system is mobile for use outside the Hazardous Waste Treatment Facility (HWTF) at Los Alamos National Laboratory or can interface with the central control system of the HWTF.

The process equipment is designed as several transportable modules that will be connected together to form an integrated skid. This allows moving of the equipment to various locations at the Laboratory, including movement of the skid in and out of the HWTF. Figure 3. shows the overall appearance of the skid. The four main process modules are on the lower level. A fifth module, which holds the processing glovebox, is on the second level.

Several design features are noteworthy because of the requirements of the process:

- Every attempt is made to minimize the complexity of the design.
- Multiple layers of operator and process protection are provided. For example, the preliminary safety analysis has determined that no single failure of equipment or procedure can lead to a catastrophic event. Much attention has been paid to ensure that water cannot accidentally contact water-reactive waste during handling operations; operators will not be exposed to water-reactive waste; explosive mixtures cannot form within the reaction or venting vessels; and radioactive materials are not released to the environment.
- A computer-based process control system is specified. This control system provides maximum flexibility for necessary future changes, simplicity in operation and design, explosion-proof design, capability for logging data, and capability for remote operation. Control system components are compatible with those used in the previously designed process skids for depleted uranium treatment (4) and chemical plating waste treatment (5).
- Every attempt was made to specify 304L, 316L, or higher alloy. This specification is for corrosion control and easy decontamination. Exterior surfaces not constructed of stainless steel or other material that cannot be decontaminated will be painted with approved epoxy paint.
- Because of the explosion-proof requirement and the size and weight limitations, the number of electrical devices is minimized. For example, to avoid electric motors on the main process skids, pumps driven by nitrogen gas will be specified. The processing skids adhere to NEC Class I Division 2 design code for explosion protection in the liquid-

Figure 3. Water-Reactive Treatment Skid Module Layout



handling areas. The gas-handling areas adhere to the NEC Class 1 Division 1 Group B code.

- Careful component selection results in a long term operation assuming normal maintenance. The ASME piping specifications (ASME 31.3-1993) call for a 20-year piping life.
- A separate utility skid (6) is provided to supply chilled water to remove the heat generated during reaction. The utility skid is designed to be set up outside potentially contaminated process areas. The utility skid also provides heated water to desaturate scrubber off-gas for HEPA protection.

Operating flexibility is incorporated into the design. Examples of this flexibility are:

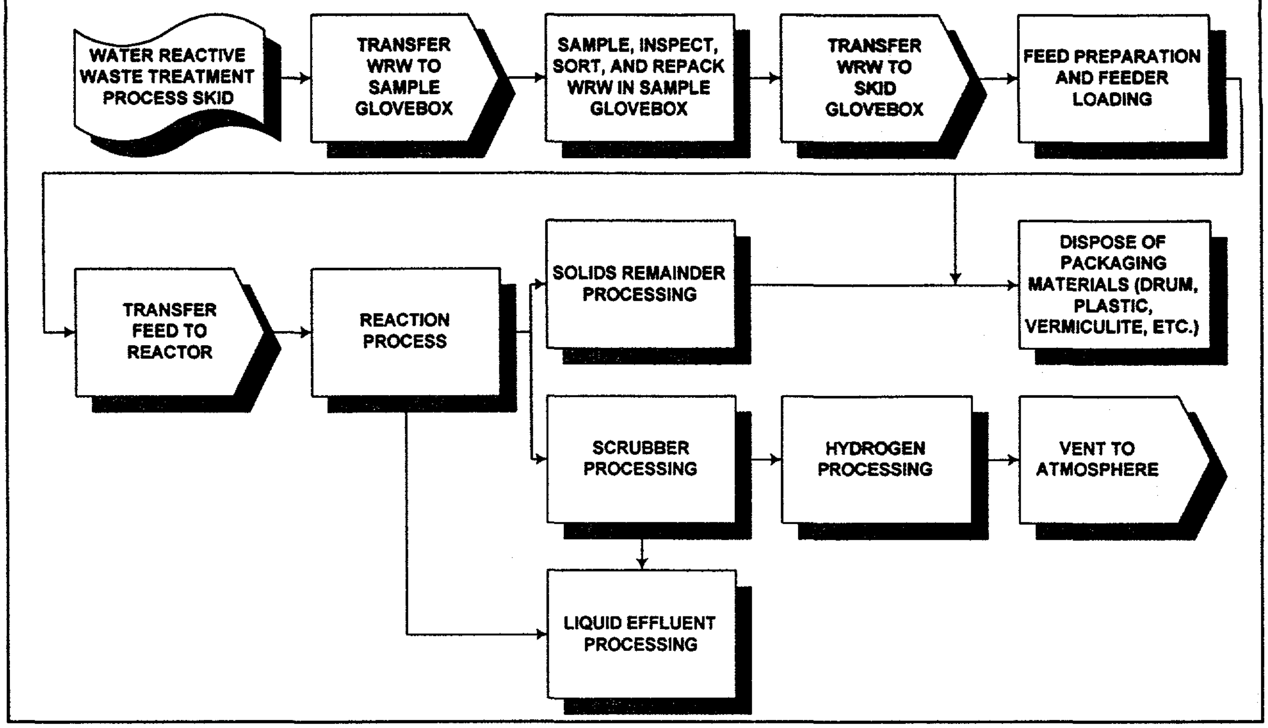
- Some flow directions can be changed to enable the operator flexibility. For instance, the operator can change the reactor circulation/cooling loop flow to clear inlet restrictions.
- The control software is capable of supporting various operating modes such as normal interlocking or bypass selected interlocks, etc.
- There is spare capacity for additional control and monitoring equipment. The unit has at least 20% analog I/O, discrete I/O and wiring spares.
- All interlocking and control functions are done within the software of the control system. With the exception of new equipment additions, any control logic changes can be accomplished by programming changes with no need for hard-wiring modifications.

TREATMENT SYSTEM OPERATION

Figure 4., below presents the simplified operating sequence for treating water-reactive mixed waste. Each step represents a unit operation or series of operations in the treatment of a generic water-reactive waste. Some steps depend on the nature of the specific waste being treated. For instance, the hydrogen treatment step is necessary only if appreciable amounts of tritium are present.

The water-reactive waste treatment system is designed to receive an inspected, sampled and sorted drum of waste. These operations are performed in a sample/sorting glovebox separate from the process. The waste drum is introduced into the nitrogen purged, sample glovebox where it is opened and inspected. If further inspection, sampling, sorting, repacking or consolidation is required, the sample glovebox is equipped with multiple ports for these operations. Once introduced into the sample glovebox, the waste drum is isolated from the atmosphere until it is empty and clean. The drum with the prepared waste is placed into a transporter vessel. The transporter is designed to transfer the waste drum between the sample glovebox and the process glovebox while maintaining a nitrogen blanket for the waste drum. The transporter is designed to survive a fall from 20 feet without rupture and subsequent release of waste.

Figure 4. Simplified Operating Sequence



Operators receive the waste into the process glovebox, sort the waste according to size and load the feeding device. The feeding device is an air powered bucket conveyor. The buckets on the conveyor are first manually loaded and then an automatic, interlocked system feeds one bucket every five minutes. The buckets place the feed material on a check weigh scale. If the weight is greater than 1000 grams for large solids or 250 grams for powders, the system is stopped while the operator reloads the feeder with the proper weighed feed. This system provides a check against feeding the reaction system at too high a rate.

The nitrogen purged reactor vessel is fed directly from the glovebox. Isolation valves are placed between the glovebox and the reactor. These valves are sequenced for minimum open time and to never be open simultaneously. This avoids the potential for a broken glove causing air intrusion into the reaction system sufficient to cause ignition.. Additionally, the valve positions are sensed. If correct valve position is not maintained, the feeding operation ceases until the operator corrects the problem. Mechanical barriers and control system interlocking are used to assure separation of glovebox and reactor atmospheres. For instance, feeding operations cannot commence before the nitrogen purge totalizer has reached a minimum value, the oxygen meters (4 total) all confirm the elimination of oxygen to less than 0.5% O2, all doors and valves are positioned correctly and the process itself is functioning correctly.

The reaction produces hydrogen gas and an alkaline metal hydroxide solution which is continuously neutralized with sulfuric acid. Cooling water is applied to the reactor and scrubber cooling exchangers using an intermediate heat-transfer loop. An intermediate cooling loop is used to prevent environmental contamination by insuring isolation of the main cooling system. All waste water is collected and processed at the Los Alamos National Laboratory's Waste Water Treatment plant.

Reactor vent off-gases are scrubbed with water in a venturi-eductor scrubber before passing through a HEPA filter to the stack. The nitrogen-hydrogen mixture is vented to atmosphere after passing through water seal device. The water seal, which is located adjacent to the vent stack, is designed to allow the process gasses to exit while preventing the backflow of air into the reaction system which could potentially lead to ignition of hydrogen.

Any debris separated in the glovebox such as plastic bags, filter media, tools, etc., is stored in air-tight containers until sufficient accumulations require processing of this material to remove trace amounts of water-reactive waste. This debris is processed by reintroducing to the container contents into the glovebox for "washing". Protection against ignition of any hydrogen generated includes elevated nitrogen purge rates, standard interlocking and relative trace amounts of water-reactive waste present. All transfers make use of the transporters and the sample glovebox. Any bagout operation uses the bagout port on the sample glovebox.

Debris items such as depleted uranium, tools, metal pieces, reaction containers, etc., that were introduced to the reactor with the water-reactive waste, is removed from the base of the reactor after reactor draining and rinsing. This operation is done under a nitrogen blanket to prevent the potential ignition of depleted uranium. The debris is place directly into a plastic bagout bag for immediate transport to the sampling glovebox for repacking if necessary. Any recovered depleted uranium is packed under fuel oil for later treatment.

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