

Title: A PROCESS FOR TREATING RADIOACTIVE WATER-REACTIVE WASTES

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Submitted to: Radioactive Waste Management and Environmental Remediation
Berlin, Germany
September 1995

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A PROCESS FOR TREATING RADIOACTIVE WATER-REACTIVE WASTES

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ABSTRACT

A considerable quantity of hazardous, water-reactive, and radioactive wastes is generated and stored within the complex of production and experimental facilities operated by the United States Department of Energy. According to Resource Conservation and Recovery Act (RCRA), every hazardous waste must be treated before it can be disposed. A hazardous waste that contains low level radioactivity is a mixed waste, and RCRA regulations and other appropriate regulations for radioactive waste apply. Water-reactive compounds react with water and generate hydrogen. The reaction is exothermic and sometimes extremely rapid. Hydrogen may easily ignite or even form an explosive mixture. The most abundant water-reactive waste at Los Alamos National Laboratory is lithium hydride; others include sodium, magnesium, calcium, and some finely divided metals.

A process was developed at Los Alamos National Laboratory to treat mixed, reactive wastes. An experimental program was the first step of process development. The chosen method was hydration by water at controlled reaction rate. At first, the use of humid nitrogen was investigated. Nitrogen was passed through a humidifier to gain appropriate humidity and then directed to the reactor with a reactive compound. The temperature of the reactor was controlled. The reaction kinetics was traced by measuring the concentration of hydrogen in the exit from the reactor. The investigated variables were temperature, percent humidity, and particle size of the reactive compounds. It has been demonstrated that the reaction follows the Unreacted Shrinking Core Model, which has become a classic model for heterogeneous fluid-solid reactions. The reaction rate proved to be appropriate for finely divided powders but too slow for larger chunks of water-reactive reactants.

Another set of experiments was conducted with direct contact of the reactive species with water at controlled conditions. A 1.7 L pressure reactor was used in the experiments. The addition rate of the reactants was controlled. Pressure buildup, temperature, and pH changes were used to determine the reaction rates. Use of Li_2SO_4 or other sulfate solutions at different concentrations rather than pure water was investigated as a means to slow the reaction rate. Applying polyvinyl alcohol water-soluble bags was used to contain fine powders, prevent elutriation, and slow down the reaction rate.

The results of the experimental program were used in the design of a full-scale equipment. In this design the water-reactive waste is introduced in intervals to a 2000-L reactor half-filled with water or a sulfate solution through a double valve entry at an

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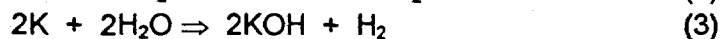
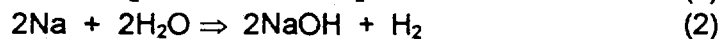
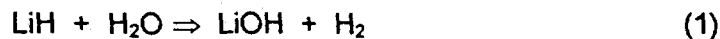
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average rate of 25 moles per minute. Hydrogen gas generated in the reaction exits through a venturi scrubber and a water seal and is vented to the atmosphere. The most common radioactive component of the waste is uranium, and it falls to the bottom of the reactor. If tritium is present in a hydride, however, hydrogen emission will be contained by hydrogen getters, such as rare earth elements or uranium, and directed to a tritium recovery unit. The feed, the reactor, and the scrubbing system are blanketed with constantly flowing nitrogen and operated at negative pressure. Nitrogen prevents hydrogen fires, and the vacuum ensures that there will be no emissions of radioactivity to the work area. The solution in the reactor is continually neutralized with sulfuric acid. The uranium from the bottom of the reactor is discharged once a shift.

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.



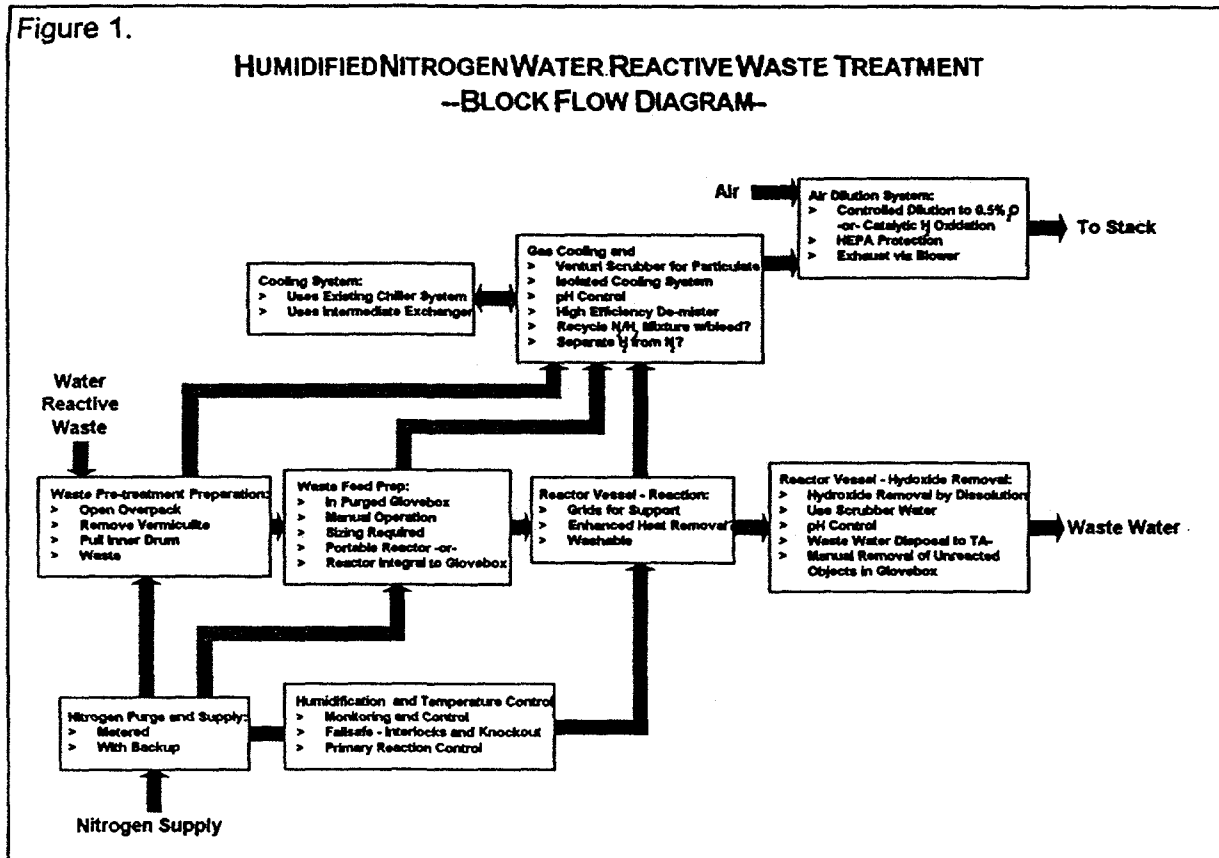
If in aqueous form and if the pH exceeds 12.5, the alkaline hydroxides must be further processed to lower the pH to the range of 2–12.5 to remove the corrosive hazardous characteristic. The hydrogen gas formed during treatment is not considered a RCRA hazardous waste, but the hydrogen poses a substantial 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

Initial investigations of process development focus on the idea that a stream of humidified nitrogen could be used. Figure 1 shows the block flow diagram for this process.



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% N₂ 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.

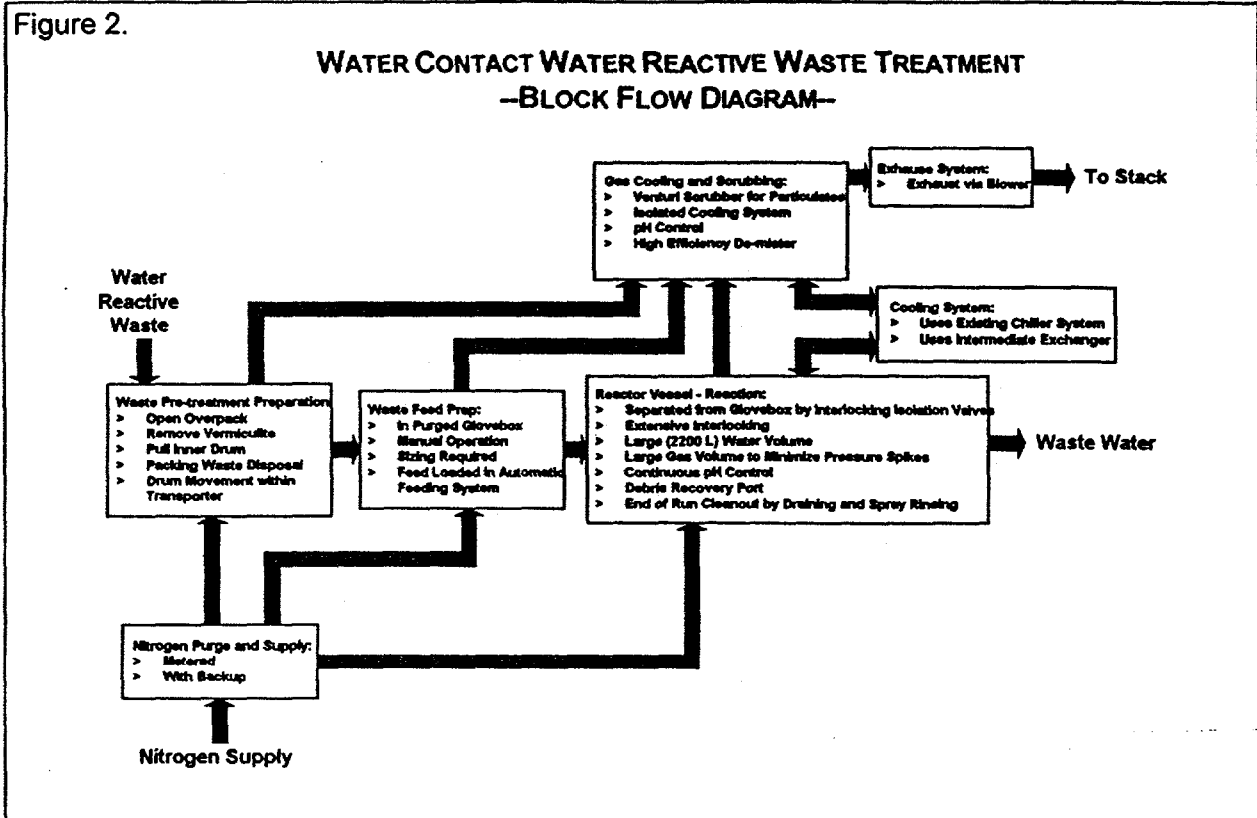
water-reactive waste or product	melting temperature (°C)	maximum inlet temperature of saturated nitrogen with 5 °C superheat	maximum water concentration in nitrogen stream (mole fraction)
LiH	688	65	0.28
LiOH	471	50	0.13
Na	98	~15	~0.02
K	63	~10	~0.01

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

1 J. Dziejewski and G. Lussiez, "Development of a Process to Neutralize Water-Reactive Wastes," Los Alamos National Laboratory report LA-UR 94-363, presented at the Waste Management International Symposium, Tucson, Arizona (March 1994).
 2 O. Levenspiel, *Chemical Reaction Engineering* (Wiley, 1972), pp. 357-400.

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 2 shows the basic process block flow diagram.



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.

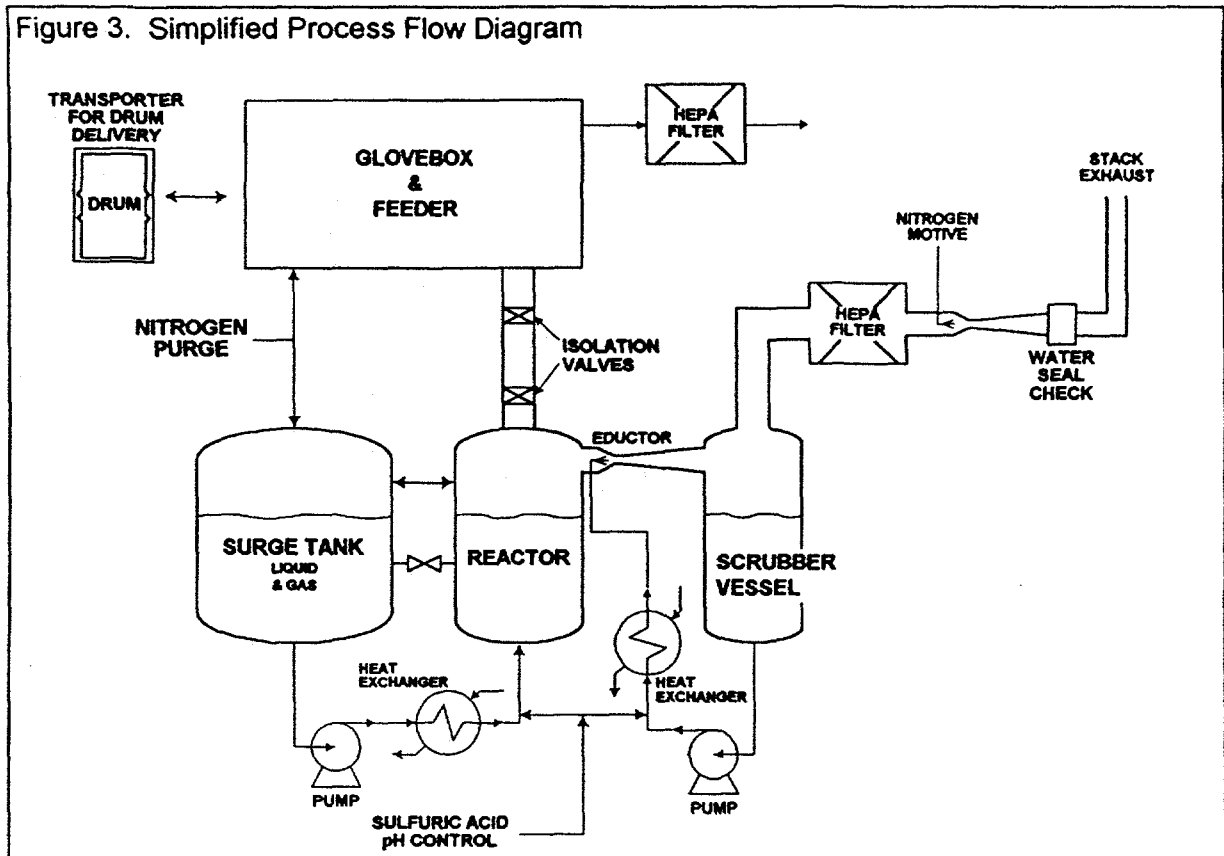
Experiments were performed to determine reaction characteristics and to validate the process concept. Details about the results of this experimentation are not within the scope of this paper; however, these generalizations are made.

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 LiSO₄ 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 worked well as a powder-control device, 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 3 shows a simplified process flow diagram of the process.

Figure 3. 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 water-reactive waste treatment system is designed to receive an inspected, sampled, and sorted drum of waste. The drum is enclosed in a specially designed nitrogen-purged transporting container that connects and seals to the feed glovebox. Operators receive the waste into the 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

3 The National Electrical Code as developed by the National Electrical Code Committee of the American National Standards Institute (ANSI), sponsored by the National Fire Protection Association (NFPA). NFPA 70-1993 (1993).

- a) A Class I location is one in which gases or vapors may be present in sufficient quantities to be explosive or flammable.
- b) Division 1 locations are those in which ignitable concentrations of flammable gases or vapors are present in the air under NORMAL operating conditions.
- c) Division 2 locations are those in which ignitable concentrations of gases or vapors are present in air under ABNORMAL operating conditions such as accidental rupture, breakage, or unusual, faulty operation.
- d) Group B is the classification for gases or vapors, which includes the presence of HYDROGEN.

grams for powders, the system is stopped while the operator reloads the feeder with the proper weighed feed. This system provides a check against overpressuring the reaction system.

The nitrogen-purged reactor vessel is then 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. The valve positions are sensed. If correct valve position is not sensed, the feeding operation stops until the operator corrects the problem. Mechanical barriers and control system interlocks ensure separation of glovebox and reactor atmospheres. For example, feeding operations cannot begin before the nitrogen purge totalizer has reached a minimum value; all four oxygen meters 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.

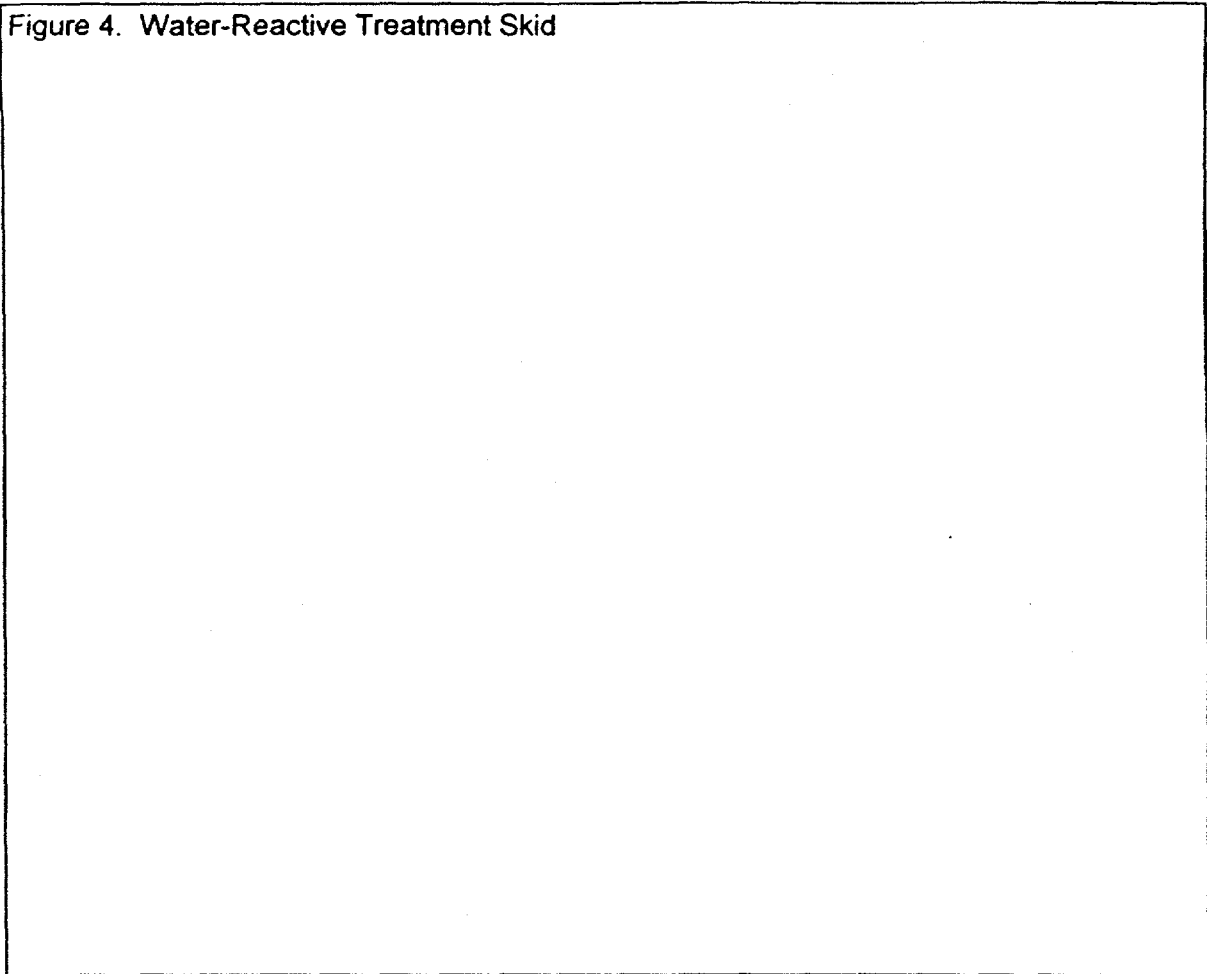
The reaction produces hydrogen gas and an alkaline metal hydroxide solution that is continuously neutralized with sulfuric acid. Reactor vent off-gases are scrubbed with water in a venturi-eductor scrubber before passing through a HEPA filter to the stack. Cooling water is applied to the reactor and scrubber cooling exchangers using an intermediate heat-transfer loop. An intermediate cooling loop prevents environmental contamination by ensuring that the main cooling system is isolated. The nitrogen-hydrogen mixture is vented to atmosphere. All waste water is collected and processed at the Radioactive Liquid Wastewater Treatment Facility at Los Alamos National Laboratory.

Any debris separated in the glovebox—such as plastic bags, filter media, or tools—will be stored in air-tight containers until enough accumulation requires processing this material to remove trace amounts of water-reactive waste. This debris is processed by reintroducing the container contents into the glovebox for “washing.”

Debris such as depleted uranium, tools, metal pieces, and reaction containers will be removed from the base of the reactor after the reactor is drained and rinsed. This operation will be done under a nitrogen blanket. The debris will be placed directly into a plastic bag for immediate transport to the sampling glovebox for repacking if necessary.

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 4. 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.

Figure 4. Water-Reactive Treatment Skid



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 treatment⁴ 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

4 Santa Fe Engineering, Ltd., "Depleted Uranium Oxidation Process for Mixed Waste Treatment at the Hazardous Waste Treatment Facility," under contract # 9-XY2-Y9590-1 for Los Alamos National Laboratory (September 29, 1992).

5 Santa Fe Engineering, Ltd., "Chemical Plating Waste Treatment Process for Mixed Waste Treatment at the Hazardous Waste Treatment Facility," under contract # 9-XY2-Y9590-1 for Los Alamos National Laboratory (April 22, 1994).

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-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 skid⁶ 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.
- The drum transporter concept requires using an additional glovebox for sampling, feed sorting, drum transfer, bagout, and sorting. This glovebox is currently under design.

6 Santa Fe Engineering, Ltd., "Utility Skid at the Hazardous Waste Treatment Facility," under contract #9-XY2-Y9590-1 for Los Alamos National Laboratory (October 4, 1993).

Figure 4.
Dzieninski, Lussier, Mungar
A Process for Treating Radioactive Water Reactive Waste

