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NRC Research and Technical
Assistance Report

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NRC NUCLEAR WASTE MANAGEMENT TECHNICAL SUPPORT IN THE DEVELOPMENT OF NUCLEAR WASTE FORM CRITERIA:

TASK 2: ALTERNATIVE TRU TECHNOLOGIES

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Assistance Report

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Executive Summary

This interim report contains an assessment of certain transuranic (TRU) waste management technologies. The evaluation results from a review of, primarily, relevant DOE research and development efforts, although some foreign work has also been included. The topical reports, progress reports, and contributions to scientific and technical meetings reviewed to date, cover work done up to approximately mid 1979. The three specific areas of interest to NRC which are addressed within this report are alternate TRU waste forms for ultimate geologic disposal, management of TRU waste by decontamination, and the potential for gas generation of TRU bearing waste. The purpose of the effort is to provide NRC with information needed to support and develop regulations and criteria, and to identify research needed to reduce significant uncertainties.

Review efforts to date in the area of TRU waste forms indicate that most of the recently considered candidates have not proved adequate to meet NRC's proposed requirements for immobilization in a form suitable for geologic disposal. They include bitumen, urea-formaldehyde, and cast concrete. Concretes specially treated to remove most of the unbound water (e.g., FUETAP concrete and hot-pressed concrete), have been under development for only a short time. Data on release rates of TRU isotopes are insufficient to permit evaluation of these concretes, but preliminary testing indicates that they cannot be ruled out as acceptable candidates. The same situation exists with borosilicate glasses as specific TRU waste immobilization forms. Natural minerals, such as monazite and several mineral phases contained in various formulations of SYNROC, are known to incorporate Th and U into their crystal lattices, and to have low aqueous solubilities, and long term radiation stability. It is highly probable that synthetic forms incorporating TRU isotopes will also behave well. A small amount of work has been done with monazite to show that high quality synthetic forms can be made. Leaching studies on natural monazites indicate they will perform much better than glasses.

Decontamination of non-combustible TRU waste, particularly metallic, has the potential to greatly reduce the volume requiring disposal in a geologic repository. For this potential to be realized, the secondary waste stream of removed TRU contamination not only must be smaller than the original waste volume, but also must be compatible with an acceptable waste form. Decontamination methods such as electropolishing, vibratory finishing and liquid honing have been developed to the stage where equipment can be decontaminated to below the 10 nCi/g level (which defines TRU waste), and thus becomes non-TRU waste suitable for shallow land burial.

The major sources of gas production in TRU waste items are degradation of organic material containerized in its original form, and radiolysis of the matrix used to immobilize the ash from incineration of combustible waste. The degradation mechanisms discussed are bacterial, radiolytic, and thermal. Of these bacterial degradation can potentially produce larger quantities of gas than the other two. Disagreements and uncertainties in the existing data are pointed out. Depending on the choice of waste form, gas generation from degradation can be eliminated or greatly reduced by incinerating the combustible waste, followed by immobilization in a suitable waste form.

Recommendations are made on the basis of our review to date. It must be recognized that these recommendations may have to be modified as additional data become available.

1. It is recommended that combustible organic TRU waste not be allowed in repositories. Such material almost certainly will not meet 10 CFR 60 criteria for radionuclide release rate, and it has high potential for generation of toxic, explosive, and combustible gases. Since incineration techniques are well established, it seems reasonable to require that all organic waste be incinerated and the incinerator ash immobilized in a suitable waste form for repository emplacement. Further support of this position is obtained from volume reduction considerations.

2. In view of the major advantages associated with volume reduction which are achieved by decontaminating metallic waste, and since a range of well developed decontamination methods are available, it is recommended that removal of TRU contamination from metals be considered as the preferred disposal method.

3. In terms of process simplification and decreased risk to the public, there is merit to the idea of combining HLW and TRU waste. Because of this, and in light of the general tightening of criteria governing ultimate disposal of both HLW and TRU waste, the concept should be thoroughly evaluated.

4. If NRC should decide not to require incineration of all organic waste, several problems in connection with gas generation would have to be solved. This would require research efforts to resolve uncertainties that exist in the areas of bacterial degradation, (such as the potential for methane production), and radiolytic degradation of cellulosics (effect of dose rate and matrix depletion).

5. Results of leaching studies on specially prepared concretes incorporating TRU waste have been inconclusive. More extensive and careful leach testing should be done in order to determine their suitability as waste forms to meet NRC requirements for radionuclide release rates.

6. Borosilicate glasses specifically designed for TRU have so far shown poor leach resistance. However, in view of some desirable qualities and a reasonable performance with HLW, they should be considered for further development as a TRU waste form.

7. A relatively large effort should be devoted to developing and characterizing a monazite waste form for TRU. Along with this development effort, a comprehensive program of leach testing should be carried out.

8. A simplified SYNROC based on the minerals perovskite and baddeleyite has potential to incorporate actual TRU waste in a very stable form, and a level of effort in characterizing and testing similar to that applied to monazite should be initiated.

9. Both the monazite and SYNROC waste forms should be tested for stability to alpha radiation under expected repository conditions

1. INTRODUCTION

Transuranic (TRU) waste is made up of materials which contain or are contaminated by transuranic elements. These elements characteristically emit alpha particles and have half-lives measured in thousands of years. Alpha particle radiation requires little shielding for biological protection but alpha emitters are dangerous if ingested or inhaled. Primary concern comes from the long lifetimes during which they remain radioactive.

Early practice allowed disposal of TRU waste by shallow land burial because the threat to health and safety was perceived as being small. Concern over long times required for containment and experiences with some leakage and migration resulted in a determination by AEC in 1970 that TRU wastes should not be placed in shallow land burial. It was decided that all waste containing more than 10 nCi/g of transuranics would be classified as TRU waste and stored retrievably. This storage has been primarily at the Idaho National Engineering Laboratory (INEL) and at the Hanford reservation in Washington State. Some 2,000,000 ft^3 are now stored, and the generation rate is 250,000 ft^3/year.[1] Before retrievable storage was begun, many times this amount had been generated and buried, the greater part of it from the defense program,[2] which alone has contributed more than 10,000,000 ft^3. These amounts indicate the magnitude of the problem faced in the management of this type of waste.

Ultimate disposal of the TRU waste will be in a mined geologic repository, using methods similar to those required for conventional high level waste (HLW). It had been planned to use the Waste Isolation Pilot Plant (WIPP) in New Mexico for this purpose, but now that WIPP has been at least temporarily terminated, these plans may have to be changed, and an alternate site or facility selected.

Whichever site is eventually chosen, NRC has the responsibility of evaluating all aspects of the geologic repository performance which could affect the public health and safety. The general performance requirements for waste packages in a repository are given in the Code of Federal Regulations, 10 CFR 60,[3] in Section III, Parts (c) and (d). These specify that the waste package provide reasonable assurance of containing the radionuclides for at least the first 1000 years, that release rate after this period be as low as reasonably achievable but at most one part in 10^5 per year of the radionuclide inventory, and that the option be maintained to retrieve the package during the operational period and for 50 years thereafter.

BNL's task on alternative TRU technologies includes review and evaluation of the methods proposed for processing TRU waste into suitable forms for geologic disposal, in the light of the above criteria and regulations. The task is divided into three areas:

1. Waste forms
2. Management of wastes
3. Gas generation

Although these subtasks are interrelated they are sufficiently independent that they may be discussed in separate sections of this report.

1.1 References

1. U. S. Department of Energy, "Report of Task Force for Review of Nuclear Waste Management," DOE/ER-0004/D, February 1978. Available for purchase from the National Technical Information Service, Springfield, Virginia, 22161.

2. A. F. Perge and V. G. Trice, Jr., "Management of Transuranium-Contaminated Solid Waste from the Department of Energy Nuclear Materials Production R&D Programs," Proceedings, NEA/IAEA Technical Seminar on Treatment Conditioning, and Storage of Solid Alpha-Bearing Waste and Cladding Hulls, Paris, France, December 1977. Available in public technical libraries.

3. Code of Federal Regulations, 10 CFR 60, "Disposal of High Level Radioactive Wastes in Geologic Repositories," (Proposed), Advance Notice of proposed rule making, Appendix II.

2. WASTE FORMS

2.1 General Considerations

2.1.1 NRC Requirements

In the general performance requirements for the individual barriers of a nuclear waste repository given in 10 CFR 60,[1] the waste package is considered as a system. The current task area covers only the waste form since, for a conservative approach, it may be assumed that the overpack and canister are of limited help in retarding radioactivity. Hence, the waste form may be considered as being the only significant barrier for the migration of TRU elements.

One arrives at a similar position from consideration of the half-lives of TRU isotopes. In most TRU wastes, Pu-239, Pu-240, and Am-241 will be the dominant radionuclides. In 1000 years, Am-241 will have decayed only to a quarter of its original activity, and Pu-239 and Pu-240 hardly at all. So the thousand-year criterion for HLW, geared to the 30 year half-lives of the dominant fission products Cs-137 and Sr-90, has limited significance for TRU waste. Protection of the public from the effects of TRU migration is taken into consideration through the required slow release rate of one part in 10^5 per year.[1]

Several parts of 10 CFR 60 describe requirements to be met by the waste form and its associated packaging. These include:

Waste Form, Packaging, and Emplacement Environment

(1) General requirements

(i) The physical waste form and its associated packaging shall be considered as the primary barrier to the release of radionuclides, and shall take into account the leachability, solubility, and other potential physical and chemical interactions between the physical waste forms, packaging, emplacement media and the surrounding groundwater, so as to minimize the potential for release, dispersion and migration of the radionuclides.

The waste form itself has the following requirements:

(2) Waste form requirements

(i) Solidification

Pursuant to 10 CFR Part 50 Appendix F, all high-level liquid radioactive wastes shall be converted to a dry solid and placed in a sealed canister prior to transfer to a Federal repository. This criterion shall extend to all radioactive wastes (including TRU wastes and other non-high-level wastes) emplaced in a waste repository. Further, finely divided waste forms (calcine etc.) shall be stabilized by incorporation into a containing matrix so as to minimize the production and availability of respirable fines during any accident condition.

(ii) Waste components

(a) Radioactive wastes containing free liquid shall not be accepted at the repository.

(iii) Chemical, Thermal, and Radiological Stability

The waste form and its associated packaging shall be chemically non-reactive to the maximum extent practicable (including leachability and solubility) when exposed to the emplacement environment. The stability of the waste package shall be analyzed considering the characteristics and properties of the waste form itself, the primary containment and subsequent packaging, the emplacement medium, the surrounding ground water, and the high radiation and thermal fields.

The stability requirements are of prime importance in developing, testing and evaluating waste forms.

2.1.2 Thermal and Radiation Conditions

In the stability requirement of the previous section, an important concern is "high radiation and thermal fields." It should be borne in mind that unless HLW and TRU are stored in the same repository these fields, particularly the thermal, are much lower for the TRU waste. Because of this NRC is contemplating the position that TRU waste packages may well be able to meet more stringent requirements than HLW and spent fuel. If HLW and TRU are stored in the same repository, high integrity containerization may be necessary to isolate the TRU waste form from the repository environment (higher temperatures are anticipated for HLW). Although low heat generators, TRU waste forms heated externally by the HLW waste form presumably are susceptible to accelerated degradation.

Assuming TRU waste and HLW are not in the same repository, the TRU waste form temperature will be relatively low, with the temperature at the container surface expected to be no more than 40-50°C.[2] Radiation fields will also be lower for TRU waste. The ionization density caused, per curie, by α-radiation from TRU isotopes, is considerably greater than that of the β,γ-radiation from fission product isotopes. However, total energy deposition in TRU waste will be much lower because of the much lower total number of curies. Also, due to the essentially complete absorption of the α-particles inside the waste form, no adverse effects on leach resistance will be caused by irradiation of surrounding ground waters or brines.

2.1.3 Candidate TRU Waste Forms

Most of the work on waste forms specifically applied to TRU waste has been based on rather simple concepts. A number have involved mixing solid TRU waste (including organics) in a steel drum with a liquid or slurry, such as bitumen urea-formaldehyde resin or concrete, and letting the mixture set. Borosilicate glasses have been extensively studied as HLW forms, and development of processes for fabricating TRU waste forms of borosilicate glasses is now under way in this country. These forms will be described and evaluated in the following sections.

2.1.4 Waste Forms Based on Natural Minerals and Other Alternatives

Several more sophisticated forms have been suggested for TRU waste, and others which are being considered for HLW would be equally suitable for TRU. The latter include porous glass and coated ceramics. In the first category are forms based on natural mineral phases such as monazite, supercalcine, and SYNROC. Work on monazite has already been started in at least two places in the U.S. Use of SYNROC and supercalcine for TRU waste forms does not seem to be under investigation yet, but both are potentially useful since actinide oxides are readily incorporated into the host lattices of their mineral phases.

2.2 Traditional Forms

This section deals with the waste forms presently in use for immobilizing ash waste from the incineration of combustible TRU wastes and some wet TRU waste for which information has been collected and reviewed. These waste forms include bitumen, cement/concrete, and urea-formaldehyde resins. Bitumen solidification systems are not used in the U. S. but find widespread application in foreign nuclear facilities. Some of the waste types that are treated by these immobilization technologies are listed in Table 2.1. Typical incinerator ash compositions are given in Table 2.2 for ash generated at the Rocky Flats Plant (RFP) from the fluidized bed incinerator (FBI) system and the conventional incinerator. No TRU contaminated waste has been incinerated in the fluidized bed incinerator.[3]

Table 2.1

Fuel Reprocessing Plant Particulate and Wet Wastes

Source	Description
Fuel receiving and storage facility	Mostly non-TRU, intermediate-level solutions and slurries of ion exchange resins, filter aids, and concentrated solutions
Separations facility	Primarily intermediate-level TRU concentrated solutions and slurries
PuO_2 conversion facility	Low-level TRU solutions and slurries (volumes would be combined with separations facility wastes)
UF_6 conversion facility	Low-level; little or no TRU content· low water content; composed of oxides, hydroxides, and fluorides
Waste treatment facilities	Secondary wastes arising from waste treatment operations, including incinerator ashes, off-gas scrub solutions, and decontamination solutions

Table 2.2

Composition of Incinerator Ash

	Quantity in Ash	
Component	Fluidized Bed (wt%)	Conventional (wt%)
Pu	b	4.6
Am	b	5.4×10^{-3}
SiO_2	9	48
C	26	17
Fe_2O_3	0.5	5.7
MgO	1.0	4.0
CaO	1.0	4.0
Al_2O_3	4.9	c
Na salts	23	d
Other	35	16

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[a] Single determination.
[b] Low level; total count $<10^3$ dpm/g ash.
[c] Negligible; large amounts in FBI ash from catalyst in afterburner.
[d] Negligible; large amounts in FBI ash from Na_2CO_3 (fluidized medium).

2.2.1 Bitumen (Asphalt)

2.2.1.1 Physical and Chemical Properties

Bitumen is a mixture of high molecular weight hydrocarbons commonly obtained as a residue in petroleum and coal-tar refining. The elementary composition of asphalts free of minerals, water, and gases is as follows: carbon (80-86%), hydrogen (9-11%), oxygen (1-17%), sulfur (1-9%), nitrogen (1%), and ash (0.1-1%). These elements occur in four major components: saturated hydrocarbons, resins, cyclic hydrocarbons, and asphaltenes in various proportions.

At ordinary temperatures, bitumen appears to be a lyophilic colloid made up of asphaltenes, resins, and hydrocarbons. As the temperature of asphalt is increased (25° to about 500°C), colloidal structure is changed and the fluidity of the substance increases. When cooled to 25°, the product is normally more prone to be brittle than it was originally. This is important if this waste form is subjected to changes in ambient temperature under repository or possible interim storage conditions. The density of bitumen ranges from 1.1 to 1.5 g/cm^3. The waste form, loaded with 40 to 60% solids, has high mechanical strength and no residual free water. Little detailed information has been accumulated on the leach resistance of bitumen. However, since its constituents are highly insoluble in water, low rates are expected. The ranges that have been published for rare earths and actinides are 10^{-3} to 10^{-7} g/cm^2-day,[4] and 10^{-7} to 10^{-8} g/cm^2-day.[5] Parameters such as percent loading, temperature, type of leach test, etc., were not available. Release rates for bitumen can be estimated if one assumes a geometry for the monolith. A typical waste container might be a 55-gal. drum (24 in. x 35 in.) that is filled to 90% of its volume. For a bitumen/waste matrix of density 1.3 g/cm^3 and a leach rate of 10^{-7} g/cm^2-day, an initial annual fractional release rate of 2.5×10^{-6} is estimated.

2.2.1.2 Stability

The thermal stability of bitumen products is good at ambient to moderate temperatures, fair at moderate temperatures, and poor (ignition results) at high temperatures. Certain salts were found to have adverse effects on the thermal stability of bitumen. Nitrates and nitrites, which are known oxidants, have been investigated because of their use in fuel reprocessing. It was found that the bitumen containing 40 to 75% (w/w) sodium nitrate/nitrite salts lowered the ignition temperature. The bitumen, although demonstrated not to be explosive,[6] burned more vigorously when significant amounts of oxidants that decompose at the combustion temperature were present.[4] Ignition temperatures for various grades of bitumen range from 260° to over 400°C.[6] Tests were conducted to determine if combustion of bitumen was possible by ignition of hydrogen-air mixtures resulting from the radiolysis of the bitumen. Initial small-scale experiments with H_2 contents between 4 and 11% (v/v) did not result in inflammation of the bitumen sample. The working temperature range for waste bitumenization processes is 150° to 230°C. This operating range is a disadvantage because of the generation of volatile organic compounds (potential fire hazard)[6] and because the resultant condensate is an additional waste stream that requires disposal treatment.[5]

Insufficient data exist for assessment of the long term chemical stability of bitumenized radioactive wastes under geologic repository conditions (potential leaching scenarios, waste/container and waste/rock interactions, etc.).

Various bitumen types and bitumen/salt mixtures (about 40% by wt. salt) were subjected to gamma-radiation.[6] A marked increase in the softening point was observed for blown bitumen and its corresponding product when irradiated to 5×10^8 rad. All pure bitumen and bitumen/salt samples showed significant swelling under these same exposure conditions. The increase was as high as 70% (v/v), presumably caused by radiolytic gas generation. As will be discussed in Section 4, hydrogen and methane are generated by the α-radiolysis of bitumen and carbon dioxide by microbial degradation. Preliminary results indicated that significant quantities of methane could potentially be generated by microbial degradation of this waste form under appropriate conditions (see Reference 7 of Section 4). ZoBell and Molecke[7] have addressed several areas that concern the possibility of radionuclide migration due to microbial metabolic processes involving bitumen.

At this time, much information on the performance of bitumen as a suitable waste form for TRU immobilization is incomplete and/or inconclusive. The volumetric efficiency (waste loading), waste types applicable, and leach resistance of bitumen argue in favor of its use. However, based on its stability to thermal, radiolytic, and microbial attack, it does not appear that bitumen is capable of meeting repository criteria. It is also felt that further research on this waste form should be discontinued because its chemical and physical properties and flammability preclude the successful development of techniques that might make it an acceptable form.

2.2.2 Urea-Formaldehyde Resins

The immobilization of radioactive wastes in urea-formaldehyde (U-F) is a well developed technology that is widely applied in U. S. nuclear facilities. The resin is used to incorporate aqueous waste solutions, filter sludge and ion exchange resins. No information has yet been received on the incorporation of TRU incinerator ash into U-F.

2.2.2.1 Physical and Chemical Properties

U-F is a condensation product of urea and formaldehyde which react under neutral or alkaline conditions to yield monomethylol or dimethylol urea. As a solidification agent, the cross linked U-F polymer entraps the waste (about 50% loading) within its structure. Because the hardening reaction is acid catalyzed, the trapped water is acidic (pH 1 or 2) and, hence, corrosive. The U-F emulsion is completely miscible with water but immiscible with non-polar solvents.

The density of U-F is 1.3 g/cm^3 (25°C) and the density range for the immobilized U-F waste product is 1.0 to 1.3 g/cm^3. U-F is slightly basic (pH of 7.4 to 7.8) and has a low free formaldehyde content. Significant amounts of free water (that not bound by the solid waste form) have been observed for some U-F formulations under certain conditions. As much as 26% (w/w) free water was found for decontamined waste (waste/U-F ratio = 0.5).[8] Free standing water can potentially lead to nuclide migration and container corrosion, not to mention radiolytic gas generation. The mechanical strength (i.e., compression and impact strength) of U-F, compared to cement, is rated as fair.[4,8] Also, it has generally been found that the U-F product strength decreases and leachability increases as the rate of liquid to U-F increases.[9] At this time, no leach rate data for TRU elements from U-F have been published. However, recent results from experiments conducted at BNL appear to indicate that leach rates for TRU elements are at least a few orders of magnitude greater for U-F than for concrete.*

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*R. M. Nielson, Jr., BNL, personal communication to G. Bida, BNL, April 21, 1980.

2.2.2.2 Stability

Several samples of various water/U-F emulsion ratios underwent rapid and complete dewatering within five days on exposure to ambient air (20°C) and 50% relative humidity. The effect of water loss on mechanical properties and leachability has been discussed elsewhere.[8] Potential concerns over the release of water in a geologic repository are addressed below in Section 4.2.2. Various U-F formulations were subjected to a standardized flammability test and found to undergo minor surface charring; no sustained burning for any length of time was observed.[8] This is partially due to the water content of the resin.

Hydrogen gas was generated due to gamma-radiolysis of the water contained in U-F. Hydrogen yield decreased with increasing total dose, probably due to attainment of steady-state conditions. This phenomenon is observed in the gamma-radiolysis of water (see Reference 12 of Chapter 4). Although no information is available on the alpha radiolysis of U-F, hydrogen is expected from the radiolysis of water. However, due to mechanistic differences, the hydrogen pressure will most likely continue to increase with increasing total dose. The accumulation of explosive atmospheres within waste containers due to hydrogen formation is an area of concern that is discussed in Section 4.2.1.4.

It has not been determined if U-F products undergo bacterial degradation and concomitant gas production. Bacterial growth can be supported by nutrients that are leached from the waste matrix by groundwater. The analysis of leachant from a U-F sample showed that a significant amount of organic carbon is leached from this waste material (about 4% of the total carbon content after only ten days of static leaching).[8] The form of the organic carbon and whether it was capable of supporting microbial growth were not determined. The microbial degradation of waste matrices can result in generation of explosive gas mixtures with dispersion of radionuclides, increased leachability, and loss of waste package integrity.

Urea-formaldehyde resin is not an acceptable waste form for immobilization of TRU wastes. Because of its water content (which is corrosive), instability toward radiolytic degradation and gas production, potential for microbial degradation, mechanical strength and relative leach resistance, this waste form cannot (and probably would not with additional R&D) meet repository acceptance criteria.

2.2.3 Concretes

The use of concrete for immobilization of low-level and intermediate-level radioactive wastes (LLW and ILW) has found wide application in the U.S. for many years. This waste form is considered attractive because the raw materials are inexpensive, ambient temperatures are used for processing, and processing operations are fairly simple. The literature reviewed to date deals with incorporation of liquid concentrates and solid waste (generated as by-products of the liquid radwaste treatment in LWR's) into concrete, process sludges into FUETAP, and TRU incinerator ash into cold-pressed concrete.

2.2.3.1 Hydraulic Cement/Concrete

2.2.3.1.1 Physical and Chemical Properties

A mixture of hydraulic cement, water, and aggregate is known as concrete. Three commonly used types of cement are portland cement, portland-pozzolanic cement, and high alumina cement. The major constituents are various calcium silicates and aluminates. Five types of portland cement have been defined and consist mainly of tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). Relative compositions of types I-V portland cement are given in Table 2.3. Type I-P cement is a standard portland-pozzolanic cement with 80% type-I plus 20% fly ash (SiO_2). Fly ash enhances the cementitious properties of portland cements by reacting with the calcium hydroxide formed during the hydration of cement. High-alumina cement (HAC) is composed primarily of monocalcium aluminate ($CaO \cdot Al_2O_3$).[10] Hydration reactions are responsible for the setting and hardening of cement paste into concrete. For portland type cements, cementitious hydrates and calcium hydroxide are the reactants. In portland-pozzolanic cements, the pozzolan (fly ash) reacts with $Ca(OH)_2$ to form compounds that possess cementitious properties. High-alumina cement reacts with water to form cementitious, hydrated calcium aluminate and aluminum hydroxide.[10]

Table 2.3

Relative Composition of Portland Cements

	Composition, wt%			
Cement Type	C_3S[a]	C_2S[b]	C_3A[c]	C_4AF[d]
I	45	27	11	8
II	44	31	7	13
III	53	19	10	7
IV	20	53	6	14
V	38	43	4	8

---

[a] Tricalcium silicate - $3CaO \cdot SiO_2$
[b] Dicalcium silicate - $2CaO \cdot SiO_2$
[c] Tricalcium aluminate - $3CaO \cdot Al_2O_3$
[d] Tetracalcium aluminoferrite - $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

Before additional properties are discussed, some mention of the types of wastes that are being incorporated into concrete will be made. As was indicated above, LWR liquid concentrates and wet solids from radwaste treatment constitute the LLW and ILW requiring disposal. The wet solid waste is comprised of spent resins, filter sludges, evaporator concentrates and miscellaneous liquids. Hanford Engineering Development Laboratories has conducted studies on the immobilization of TRU contaminated dehydrated residue (from acid digestion processing), filter residue, and ion exchange resin. Savannah River Laboratory (SRL) has studied the incorporation of simulated sludges and actual radioactive sludge into concrete. Sludge compositions are given in Table 2.4.[11] The gross alpha activity ranged from 0.1 to 0.3 mCi/g. Incorporation of simulated Hanford wastes in concrete has also been studied. The compositions of these simulated sludges are given in Table 2.5.[10] The work being conducted at SRL and Hanford is directed at the disposal of defense high-level waste.

Table 2.4

Composition of Washed, Dried SRP Waste Sludges

	Wt% Element in Sludges From SRP Tanks		
	Tank 5	Tank 13	Tank 15
Fe	27.5	27.9	3.1
Mn	10.8	8.8	2.3
Al	1.5	7.1	33.5
U	15.4	4.0	0.9
Na	6.1	3.1	1.2
Ca	0.6	2.3	0.2
Hg	0.1	2.1	0.9
Ni	5.1	0.5	0.5

Table 2.5

Composition of Simulated Sludges, Wt%

	Hanford Redox Sludge	Hanford Purex Sludge
Fe	2.7	22.4
Al	22.6	8.3
Mn	0.09	2.5
Sr	1.8	1.0
Na	3.9	4.8
Cr	1.9	
Si	5.2	6.4
Ca		0.5
PO_4^{3-}		2.2
H_2O	30.0	26.0
O_2[a]	31.0	26.0

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[a] Calculated

2.2.3.1.2 Stability

Cement/waste composites must exhibit sufficient strength to withstand handling, transportation, and accident situations with only marginal resultant damage. Neat cement pastes exhibit compressive strengths of approximately 69 MPa with portland cements developing about 90% ultimate strength after 30 days and high-alumina cements developing about 75% after only 3 days. Compressive strengths of cement-sludge samples progressively decrease with increasing sludge content; the decreases are primarily due to the lack of strength of the sludge particles. Compressive strengths for simulated sludges are listed in Table 2.6.[11] Neat cement pastes receiving gamma radiation exposures during curing exhibit lower compressive strengths than normally cured samples. Strength of high-alumina cement containing simulated sludges is not affected by heat or irradiation during curing. The same effect of waste additions is seen for steam-cured samples, i.e., strength is decreased in neat pastes but unaffected by sludge additions. Specimens heated at 100°C for 3 months exhibit about 25% lower strengths than unheated samples of identical formulation. Gamma irradiation effects on the strength of cured samples are minimal. Sorbents alone tend to decrease strength; however, formulations with sludge plus sorbent exhibit

Table 2.6

Compressive Strength of Concrete Waste Forms

SRP Simulated Sludge Type	wt%	Compressive Strength (psi) Cement Types					
		I	II	III	V	I-P	HAC
	0	10 824	11 284	13 478	11 898	11 916	9 311
I	10	8 402	8 243	8 694	8 829	8 296	9 574
	25	4 588	4 630	6 180	5 620	4 472	5 792
	40	464	1 259	1 546	3 054	2 380	4 363
II	10	8 973	9 045	9 321	11 159	7 692	9 624
	25	5 779	6 412	7 230	7 158	5 855	7 158
	40	3 932	3 352	4 736	4 234	3 311	5 884
III	10	9 313	7 557	7 603	8 490	7 761	8 465
	25	5 171	4 627	5 817	4 732	4 930	6 658
	40	2 388	2 884	3 317	2 700	3 088	3 371

strengths that are higher than those of formulations with sludge or sorbent alone.[10] Compressive strength is a measure of the stress required to fracture or plastically deform a material. Since no correlation of strength and safety has been developed, workers at SRL have also conducted impact tests on solid waste forms. In the tests, samples are broken by impact of known energy and the particle size distribution of the sample is determined after impact. The results of this type of test are considered important because the creation of a large number of small particles increases surface area and the potential for leaching. The surface area, A, created by impact with energy input, E, may be a useful parameter in defining the safety of solid waste forms. Typical values of A/E for various waste forms are given in Table 2.7.[12] The particle size distribution resulting from impact is also an important consideration because the production of excessively small particles increases the potential for creating an airborne hazard.

The combined effects produced by cement curing exotherms, waste heat generation, and sorbed and free water within the cement matrix may result in extreme pressures in a closed container. Tests conducted to determine the pressure generated during heating of concrete waste forms show that preheating the waste form to 150°C for 5 to 6 hours prior to sealing the canisters can limit pressures generated by steam to about 345 kPa at a temperature of 240°C. With no preheating, canister pressures at 240°C may reach 3105 to 3450 kPa.[9]

Table 2.7

Relative Impact Resistance of Various Waste Forms

Waste Form	Surface Area Increase Per Joule Input[a] A/E, cm^2/J
Glass with 45% Sludge	9.5
Neat HAC	7.3
Neat I-P	10.3
HAC + 40% Sludge	28.9
I-P + 40% Sludge	19.4
Portland III + 40% Sludge	25.3

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[a] 8 kg-m input for glass; 9.6 kg-m input for concrete forms.

Leachability of alpha radioactivity from concrete waste forms containing actual SRP sludges was very small and near the limit of detection. Actual values ranged from about 10^{-5} g/cm^2-day initially to about 10^{-8} g/cm^2-day after 6 weeks with less than 10^{-3}% Pu leached after 6 weeks. Consistent with cesium and strontium leachability, alpha emitter leachability is a strong function of time; however, the data more closely follow a t^{-1} relationship (rather than $t^{-1/2}$), indicating that leachability is controlled by factors other than simply diffusion within the matrix. These results are similar to those obtained from concrete waste forms containing simulated SRP sludges. Plutonium leachabilities from samples containing 5 x 10^7 dis/min of Pu-239, which range from 10^{-5} g/cm^2-day initially to 10^{-8} g/cm^2-day after 12 weeks, are strong functions of time, and are relatively unaffected by cement type, sludge type, and sludge content.[11]

Leach rates for plutonium from simulated ILW cement products have been determined in four different leaching media.[13] Plutonium leachabilities in deionized water, 0.01 M NaCl solution, and 1 M NaCl solution are comparable and range from 2-11 x 10^{-7} g/cm^2 -day. In saturated carnallite solution the plutonium leach rate after 35 days is about 5 x 10[illegible] g/cm^2-day. Carnallite solution corresponds to an equilibrium solution from water-leached natural salt deposits; its composition includes 62.83 wt.% H_2O, 2.04% $MgSO_4$, 34.3% $MgCl_2$, 0.62% KCl, and 0.21% NaCl.

Gas generation problems associated with, and the consequences of, the α-radiolysis of concrete containing simulated process sludge or TRU incinerator ash will be discussed in Section 4.2.1.3 of this report. Also discussed are techniques and additions that help minimize the importances of gas generation for long term disposal of TRU waste in concrete.

2.2.3.2 FUETAP Concrete

Preliminary results have been published on the fixation of simulated waste sludge in concrete formed under elevated temperature and pressure (FUETAP).[14] Cementitious solids were formed under relatively mild conditions (generally 250°C and 4140 kPa). Generic information provided from scoping studies are presented below.

2.2.3.2.1 Physical and Chemical Properties

Concretes were made with four different compositions which are listed in Table 2.8.[15] The composition of the simulated sludge used in these studies is given in Table 2.9.[15] In these studies, the wet composites were autoclaved (250°C and 4140 kPa) for 1.5 hours. They were cured under these conditions for 22.5 hr and returned to ambient. Some physical property measurements have been made for samples prepared with portland type I cement (Table 2.10).[15] A maximum in the thermal conductivity and compressive strength was observed for a fly ash to cement ratio of 0.82 (Mix 4). In general, no significant changes were observed in the physical properties of FUETAP as a result of varying the curing time, temperature, and pressure.[15]

Table 2.8

FUETAP Mix Compositions

	Composition, wt%			
	Mix 1	Mix 2	Mix 3	Mix 4
Component				
Cement	37.54	38.94	23.24	27.55
Indian red clay	8.94	9.27	8.94	8.94
Fly ash	8.94	9.27	23.24	22.51
Simulated sludge	14.30	14.83	14.30	10.00
Quick-gel	0.41	0.42	0.41	0.40
$NaNO_3$	2.60	0	2.60	2.60
Water	27.27	27.27	27.27	28.00
Mix ratios				
Fly ash/cement	0.24	0.24	1.0	0.82
Water/fly ash + cement	0.59	0.59	0.59	0.56

Table 2.9

Simulated Waste Sludge

Oxide	wt%
Fe_2O_3	75.18
Al_2O_3	14.89
Cr_2O_3	4.94
NiO	4.78
SrO	0.14
$Ru(OH)_3$	0.03
CeO_2	0.04

Table 2.10

Effect of Mix Composition on FUETAP Concrete

Mix No.[a]	Compressive Strength,[b] psi	Thermal Conductivity, W/cm °K(x 10^3)	Porosity, %	Density, g/cm^3
1	14.2	4.4	47.6	1.56
2	13.1	4.6	51.4	1.54
3	18.6	4.9	39.4	1.75
4	29.3	5.1	40.1	1.76

[a] All mixes were made with type-I portland cement. Specimens were cured at 4140 kPa and 250°C, including the 1.5 hr required to reach curing conditions.

[b] Pressure required to crush a right-circular cylinder 4.8 cm diam. by 10.2 cm.

2.2.3.2.2 Stability

The measurement of the long term stability of FUETAP is still in its early stages. In general, concretes have long term structural stability to heat (up to 400°C) and to radiation. Evolution of water above 100°C is minimal because of a dewatering step in the production process. However, the remaining water does undergo radiolytic decomposition by alpha particles.[16] The hydrogen and oxygen produced by degradation were observed to undergo recombination in the presence of FUETAP at a rate $\geq$ ten times the rate observed for neat cement. The recombination reaction rate at ambient temperature in the presence of FUETAP is equivalent to the hydrogen production rate at the high dose rate of about 10^6 rad/hr (assuming a hydrogen yield of 0.5 molecules/100 ev). This suggests that if the hydrogen and oxygen remained in close proximity to the FUETAP, the recombination rate will exceed the production rate even for high dose rate.

Initial leach rate data indicate a value for ^{239}Pu in spring water of less than 10^{-8} g/cm^2-day.[17] Investigations are currently in progress to determine leach rates for FUETAP (dynamic and static procedures) using distilled water, local spring water, and simulated Sandia type B brine.[15]

2.2.3.3 Cold-Pressed Concrete (Mound Facility)

This final section on traditional forms deals with TRU incinerator ash encapsulation in concrete by a cold-pressing (173 MPa) technique. This should not be confused with the technique of hot-pressing concrete containing SRP sludge developed at Penn State University.[18] The cold-pressing technique at Mound Facility (MF)[19] involved compression of TRU incinerator ash incorporated into portland type-I cement or high-alumina cement. The waste form characterization studies included leachability, density, crush strength, mechanical strength, and waste loading.

MF incinerator ash is composed mainly of silicon, aluminum and calcium oxides. The pellets (1.2 cm O.D. x 1.2 cm) of cement-ash paste are compressed at 173 MPa and nominally contain less than 3% (w/w) of water compared to 30% (w/w) in cast concrete. The pellets can hold up to 70% (w/w) of ash without adversely affecting the compressive strength of the final product. The loading rate, defined as the grams of ash immobilized per cubic centimeter of the total matrix, is given in Table 2.11 for some typical pellet mixtures.[20] Waste loadings are some 20 to 30% lower for cast concrete than for pressed pellets.

Table 2.11

Cold Pressed Concrete Pellet Mixtures and Water Content

Mix	Cement (wt%)	Ash (wt%)	Pressed pellets Water/cement ratio	Ash/Matrix Loading in Pressed Pellets (g/cm^3)
A	70	30	0.10	0.62
B	60	40	0.12	0.85
C	50	50	0.16	1.00
D	40	60	0.19	1.17
E	30	70	0.29	1.32
F	20	80	0.70	1.50

Leach rates for pellets doped with Pu-238 were determined.[21] The pellets were placed in distilled water at ambient temperatures. Each week, samples of the leach solutions were analyzed for Pu-238 content. The total leach solution volume was changed weekly. Leach rates were of the order of 2.4×10^{-10} to 2.4×10^{-11} g/cm^2-day. However, it would appear that the leach rates were calculated from sample surface areas that had been experimentally determined by gas adsorption.[22] These surface areas, for a typical pellet, are some three orders of magnitude greater than calculated geometrical areas. The experimental areas most likely reflect the high porosity of the pressed pellets. The effective surface area contacted by the leachant is probably somewhat less than the experimental areas, thus the leach rates are certain to be higher than reported. The worst case limit for these pellet sizes would be about 10^{-7} to 10^{-8} g/cm^2-day.

At this stage, the assessment of concrete as a viable alternative waste form is inconclusive due to a lack of some pertinent information and to the limited time in which this evaluation was made. It would appear that most of the information on radwaste incorporation in concrete deals with HLW and the actinides are considered only by virtue of their contribution to HLW waste streams. The fixation of only actinides has been considered by way of TRU incinerator ash encapsulation in cold pressed pellets and in SRL concrete. The latter study was to determine the extent of gas generation due to α-radiolysis. No studies have been conducted at SRL on the long term stability or leachability of TRU ash/cement compositions.*

An important negative aspect of the concrete types and processing techniques discussed above is the information on leach rates. In the case of SRL, the data suffered from a fair amount of scatter and lack of reproducibility, insufficient data are available for FUETAP, and the values for cold-pressed concrete are in doubt because of how the leach rates were calculated.

The compressive strengths of these concretes are significantly lowered by addition of sludges. The comparative compressive strength of neat cold-pressed concrete was apparently not determined. Also, most concretes have moderate to poor impact resistance. These are important considerations related to transportation safety. The high water content of simple cast concrete would probably prevent this waste form from meeting several acceptance criteria. However, some techniques for reducing this free water content have met with success (see Section 4.2.1.3). Finally, concrete is generally inferior to other waste forms (e.g., glass) in terms of leachability of radionuclides, mechanical strength, radiation stability, maximum product temperatures, etc.

Until more information on FUETAP concrete is made available and the results for the hot-pressed concrete[18] are thoroughly reviewed, our judgment is that concrete cannot be ruled out as an acceptable waste form for TRU immobilization.

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*N. E. Bibler, Savannah River Laboratory, private communication to G. Bida, BNL, April 22, 1980.

2.3 Borosilicate Glass and Sintered Ceramics

2.3.1 Rocky Flats Plant (RFP) Borosilicate Glass

2.3.1.1 Properties

Rockwell International has developed a vitrification process for immobilization of TRU incinerator ash and other low-level residues.[23,24] The main objectives of the research program conducted at their Rocky Flats Plant, were volume and weight reduction. The waste streams were processed in a fluidized-bed incinerator.[25] Table 2.12 contains the chemical composition of the ash resulting from incineration of ordinary TRU combustible trash (e.g., paper, plastics, etc.), HEPA filters, and tributyl phosphate.[24] The incineration yielded a 97% volume and 83% weight reduction. The vitrification process involved blending the incinerator ash with small amounts of B_2O_3 (as H_3BO_3) and Na_2O (as Na_2CO_3) at 1050°C. Molten borosilicate glass was allowed to free fall onto a rotating disc where it solidified into a roughly hemispherical button 6 mm high by 10 mm in diameter. The desired size of the pellets dimensions and shape were reproducible to within ±5%. The shape was chosen for good reported mechanical strength, uniform product size, and ease of handling. The waste loading was about 70% (w/w), and the glass in monolithic form occupied only 16% of the volume of its dry constituents, including glass forming additives.[24]

Table 2.12

Chemical Composition of Simulated Waste Streams by wt%

Chemical compound	Ordinary waste ash, %	Tributyl phosphate ash, %	HEPA filter ash, %
NaCl	5.0		
Na_2CO_3	30.0	17.2	
Cr_2O_3	10.0	3.0	1.2
Al_2O_3	35.0	10.4	11.9
SiO_2	12.0		39.6
Na_2SO_4	5.0		1.2
C	3.0	0.5	3.8
Na_3PO_4		68.9	3.6
MgO			33.9
Fe_2O_3			2.6
CaO			2.2

2.3.1.2 Stability

Batches of the pellets were routinely subjected to quality control tests that evaluated properties such as impact resistance, compressive strength, resistance to extreme temperature changes, and abrasion and leach resistance. The results of the tests qualified the pellets for the designation of special form material (USDOT).[26] The hemispherical buttons were reported to have a leach rate on the order of 10^{-4} g/cm^2-day for dynamic testing (Soxhlet; ambient temperature assumed) in deionized water.[24] Leaching in brine produced no apparent weight change after a year. The estimated annual release (fractional weight loss per year) for a leach rate of 10^{-4} is one part in ten. Although the leach data are not of direct applicability to a real repository system due to differences in leach solutions, test temperatures and the nature of the test procedures, it does seem clear that the RFP TRU glass waste form is unlikely to meet the NRC release rate requirements of less than one part in 10^5 per year.

2.3.2 Pacific Northwest Laboratory (PNL) Program

A TRU Waste Immobilization Program has recently been initiated at PNL (beginning of CY 78). At the inception of the program, its scope was "...to determine the degree of immobilization that may be necessary for the acceptable disposal of transuranic waste residues, and to develop process technologies to provide such immobilization ."[27] The program organization was subdivided into five task areas: Program Management, Waste Containment Analysis, Source Term Definition, Waste Form Development, and Process Development and Demonstration. The emphasis in the area of Waste Form Development was put on using waste forms and processing technologies developed for HLW immobilization. The PNL program was later wholly focused on developing borosilicate glass formulations for the incorporation of TRU incinerator ash and feasibility studies on the use of sintered ceramic waste forms for these residues.

2.3.2.1 Borosilicate Glass

It had been anticipated that the glass immobilization effort would result in the accommodation of mixtures of transuranic ash residues of varying composition at high waste loadings. Initial scoping studies looked at eleven frit compositions and seven different waste residue compositions.[28] Glasses that met criteria for homogeneity, porosity, etc., were further characterized according to leach resistance, viscosity, and electrical resistivity. These studies resulted in the selection of two waste compositions and three frit compositions for additional modifications and improvements. In the next progress report, the investigation focused attention on the improvement of a glass composition specifically tailored for RFP incinerator ash. The compositions were improved with respect to leach resistance under moderately acidic conditions by decreasing the amount of Al_2O_3, B_2O_3, and Na_2O in the frit.[29] However, the frit had to again be modified because analysis of ash received from RFP showed the alumina content to be much higher than a previous residue composition.[28] Frit additive modification resulted in an acceptable composition except for pH 4 leach resistance. Several melts of this new composition were prepared in which the ash-to-frit ratio was varied. The leach resistance was found to be a function of the ash loading (Figure 2.1).[30] The leaching behavior is apparently due to the large quantities of alumina and silica in the ash. Further compositional changes resulted in a final formulation, designated 79-160.[30] The composition of this ash-glass is given in Table 2.13.[30] The characteristics of this particular composition are listed in Table 2.14.[30]

Table 2.13

Composition of RFP Bulk Ash Glass, 79-160 [TRU-RFP-1]

	wt% 79-160
TRU-RFP-1 Ash	30.0
SiO_2	26.0
B_2O_3	12.0
Na_2O	11.0
Li_2O	2.0
K_2O	4.0
CaO	7.0
TiO_2	4.0
ZnO	4.0

The fractional annual release rates based on the data of Table 2.14 are extremely large. Another objection to this waste form is the fact that incorporating TRU waste residues of variable composition is not compatible with a single frit composition or waste loading. It appears that undue processing complexity would result due to "tailor-making" the glasses. Other shortcomings of the PNL program are the lack of data for actual TRU incorporation into glasses and no assessment of their long-term radological stability. The initial results on ash incorporation into borosilicate glasses developed at PNL are discouraging and certainly unacceptable in terms of waste form acceptance criteria. It is not known at this time if further research in this area is being continued at PNL or if technological improvements have resulted or will result in an acceptable waste form.

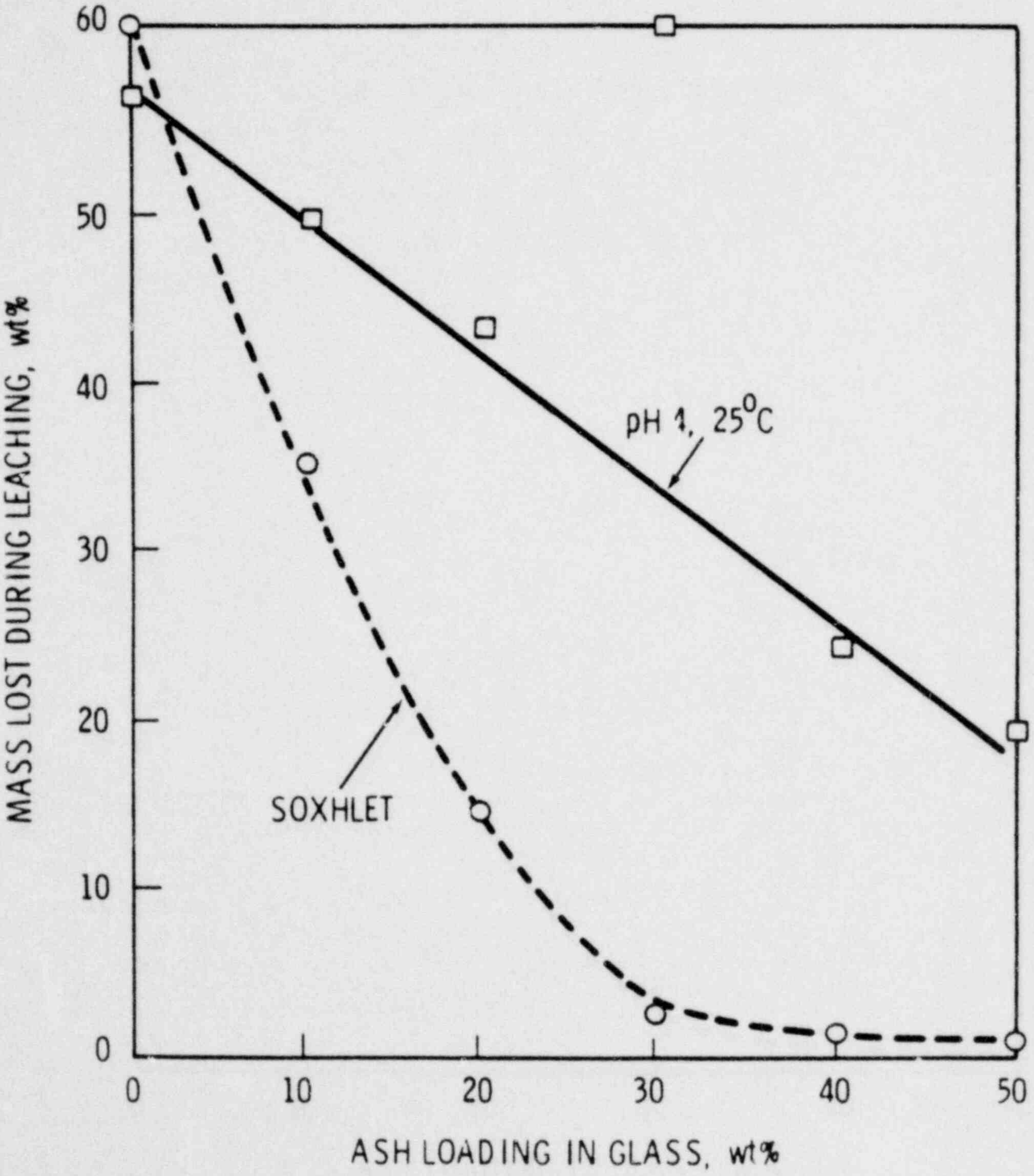

Figure 2.1. Leaching behavior of a typical PNL glass as a function of waste loading.

Table 2.14

Characteristics of Laboratory Glass 79-160

Viscosity, poise	
at 950°C	360
at 1050°C	110
at 1150°C	44
Bulk density, g/cm^3	2.68
Leaching rate, total wt	
Soxhlet (24-hr)	1.2
Buffered pH 4 (19-hr)	16
Buffered pH 9 (19-hr)	0
Melting time, hr[a]	1
Corrosion rate, 304L SS, 1050°C	
Flux line, m/day	8
Submerged, m/day	0

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[a] Time to melt 300-g batch in a 304L SS cylinder, 4.5 cm dia x 10 cm, at 1050°C.

From the above discussion, it can be seen that the scope of PNL's glass immobilization program, after about a year and a half, had severely narrowed from the initial objective of developing a formulation that was capable of high waste loadings and insensitive to variations in feed stream composition. In addition, a change in program philosophy was noted: the objective now was "... to conduct a comparative assessment of alternative immobilization systems for selected transuranic wastes, and recommend the most promising technology for development and demonstration."[30] This is certainly an important change from the proposed adaptation of existing HLW technologies to TRU immobilization.

2.3.2.2 Sintered Ceramics

Scoping studies at PNL on incorporation of TRU waste into sintered ceramic pellets has reportedly been completed;[30] however, few data have been published. The conclusion of the study was that the dispersibility of ashes, resins, and filter media can be significantly reduced by sintering at elevated temperatures. Two simulated RFP ash residues were chosen for the feasibility studies. The following mixtures were prepared: (a) neat waste (reference case), (b) waste plus commercial glass frit at 50 and 67 wt%, (c) waste plus silica at 50 and 67 wt%, (d) waste plus bentonite clay at 50 and 67 wt%. For each mixture, pellets were cold pressed at 140 MPa and sintered at temperatures from 700° to 1100°C.

A subset of promising samples was selected for characterization of density, distribution of particle size following impact event, leach resistance, and sinter behavior. The following qualitative observations were reported[30]:

- Additives generally produced pellets with more desirable characteristics. Silica and bentonite were better additives than the commercial frit, but required higher sintering temperatures.
- The results of "accelerated" static leach tests with deionized water indicated an increased leach resistance of pellets containing additives and fired at higher temperature.
- Pellets containing 67% (w/w) bentonite and fired above 900°C were rated superior.

Waste characterization is in an early stage for sintered ceramics. The lack of sufficient data does not allow us to make any meaningful evaluation at this time.

2.4 Mineral Phases

2.4.1 Monazite

It has been suggested by McCarthy et al. that synthetic monazite should be an ideal host for actinide wastes on the basis of the natural mineral's uranium and thorium content and its impressive stability under geologic conditions.[31] They cite the example of a deposit 10^9 years old which is believed to have survived severe hydrothermal conditions and two cycles of surface weathering with no loss of actinides from inside the crystals.

2.4.1.1 Properties

The nominal composition of monazite is $LnPO_4$, where Ln represents a rare earth element, or lanthanide, with Ce, La, Nd, and Y as the dominant lanthanides. The structure is monoclinic, space group $P2_{1/n}$ with 8-coordinated Ln and 4-coordinated P. Isolated irregular PO_4 tetrahedra are linked together by LnO_8 polyhedra to form a space filling network. In most natural monazites, the actinides Th and U substitute in part for Ln, with charge balance provided by accompanying substitutions of monovalent or divalent cations on the Ln sites and/or Si on the P sites. Huttonite, the high temperature polymorph of $ThSiO_4$, has the monazite structure, so there might be complete solid solution between $LnPO_4$ and $ThSiO_4$. Monazites are known with as much as 31 wt% of ThO_2[32] and 16 wt% UO_2.[33] Small percentages of Al_2O_3, Fe_2O_3 and CaO are commonly present. Thus incorporation of relatively large proportions of actinide waste into synthetic monazites should be feasible. The mineral has a specific gravity of 5.0-5.3 g/cm^3, similar to a number of oxide minerals and greater than silicate glasses.

2.4.1.2 Stability of Natural Monazite

The natural mineral can hold rather large quantities of helium. One sample from Norway[32] when dissolved in sulfuric acid, released >5 cc of helium/cc of monazite, which corresponds to some 3×10^{19} α-decays/cc of the mineral for a total dose of 3×10^{25} ev/g. Thus extensive gas build-up in the crystal can be tolerated, as can very large doses of α-radiation. Even though the dose rate in the mineral is very low because of the low specific activities of U and Th, resistance to such a high total dose indicates impressive radiation stability. Also, stability to hydrothermal conditions more severe than any likely to be encountered in a geologic repository can be documented.[31]

2.4.1.3 Preparation of Synthetic Monazites

McCarthy successfully prepared a number of synthetic monazites,[31] with and without Th and U, with a wide range of lanthanides, and with substitutions of Ca for lanthanides and Si for P up to a mole fraction of 0.2. With uranium only in the products, phase pure material was obtained for Ca-Ln substitution but not for Si-P substitution. The process used, involving firing of calcined pellets at 1050° and 1200°C, gave products with x-ray diffractograms closely resembling those of natural monazites after 4 hours heating. These results indicate that a suitable process could be developed for treating actual radioactive wastes by this general method.

2.4.1.4 Leach Test Results

No leach tests appear to have been reported for synthetic mineral samples containing actual waste. However, Boatner and Beal[34] have reported on leach tests carried out with natural monazites containing up to 6% Th and 1% U. In tests at room temperature and 100°C in both distilled water and 4M NaCl, their results indicated that the leach rate is approximately one thousand times less than the values reported in the literature for waste glasses. Insufficient information was published to permit calculation of release rates, but the results are obviously promising.

2.4.2 Supercalcine

The supercalcine waste form has been proposed for use with HLW and considerable effort has gone into its development. It is considered in the Task 1 topical report as a HLW form and will not be described in any detail here.

Supercalcine, or supercalcine-ceramic, as developed at Pennsylvania State University is a multi-phase synthetic mineral assemblage made directly from complex nuclear reprocessing waste liquids.[31] Two of the crystalline solid solution phases making up a typical supercalcine have the monazite and fluorite structures,[35] and both are hosts for lanthanides and actinides. Monazite has been discussed in the previous section (2.4.2.1). A number of oxides crystallize in the fluorite structure, and solid solutions of ThO_2, CeO_2, lanthanide oxides of formula Ln_2O_3, and U_3O_8, have been identified and studied in synthetic samples.[35]

We have seen no literature references to studies of ceramics of the supercalcine type done specifically with TRU wastes. However, there appears to be no reason why a supercalcine form for TRU waste would not be as suitable as those for HLWs. The two mineral phases, monazite and fluorite are excellent hosts for the actinides, and phases containing Fe, Ni, Cr, Al, and other elements likely to be present in TRU waste, are regularly present in HLW supercalcine.[36]

2.4.3 SYNROC

This ceramic waste form candidate, like supercalcine, has been proposed for fixation of HLW.[37] Since it is discussed at some length in the Task 1 topical report it will be considered here only with respect to its special applicability to TRU waste.

Like supercalcine, SYNROC is composed of several mineral phases. Unlike supercalcine, in which the nuclear waste oxides themselves make up most of the final product, the phases in SYNROC permit replacement of some of the host atoms by waste atoms. There are several SYNROC formulations, in which the principal phases are barium feldspar, hollandite, perovskite and baddeleyite. The first two minerals can host Sr, Cs and several other fission products. The baddeleyite can host tetravalent actinides in particular, while the perovskite will hold lanthanides and trivalent actinides and also a number of elements such as Fe, Cr and Al which could be constituents of TRU waste. Thus, a mixture of these last two minerals should be capable of incorporating TRU waste oxides in a simplified type of SYNROC. No studies on such a system appear to be under way.

2.5 Alternative Waste Forms

Alternative waste fixation immobilization procedures that could serve as back-up processes have been under development on a small scale, mostly at PNL. Among the waste forms they have studied in connection with incorporation into metal matrices are glass-coated supercalcine pellets, and supercalcine pellets coated with a layer of pyrolytic carbon and a layer of alumina.[36,38] A relatively new program is under way at Catholic University to investigate the porous glass waste form concept. Both this porous glass form and the coated ceramics are being considered in terms of HLW, but there is no reason why they could not be applied to TRU waste, since neither type is sensitive to the particular oxide or mixture of oxides which would be encapsulated.

2.6 Combined HLW-TRU Waste

Until recently it was widely accepted that TRU waste would be permitted to be placed in a repository after fairly simple immobilization treatment. For example, in the DOE document "Technology for Commercial Radioactive Waste Management" issued in May 1979, the reference treatment for failed equipment and non-combustible waste was to package it in either 55-gal drums, 1.2x1.8x1.8 m steel boxes, or stainless steel containers.[39] The reference treatment included decontamination and disassembly if required. Reference treatment for combustible waste consisted of incineration, followed by immobilization of the incinerator ash in steel drums.[39]

Since HLW treatment involved much more sophisticated and quite different processes than treatment of TRU waste, it was logical to have separate facilities for the relatively simple TRU waste processes. However, with the emphasis on waste form criteria, volume reduction of TRU waste and avoidance of metallic waste altogether, as described in Sections 2, 3, and 4, quite a different situation exists at the present time.

In the processing of both cladding hulls and failed equipment, almost all the decontaminated metal should be capable of being classed as non-TRU and either relegated to shallow land burial or even recycled. (Some cladding hulls might not be eligible for shallow land burial because of activation product contents causing too high a radiation field.) The removed radioactivity would be concentrated in relatively small volumes for immobilization treatment, and it should be feasible to arrange for a product compatible with the HLW stream, e.g., dry actinide oxides or an actinide-containing oxide sludge. Similarly, incinerator ash from treatment of combustible TRU waste could be made so as to be readily incorporated into the HLW stream. Combining TRU waste with the HLW stream at the stage of producing a final waste form should not complicate the process appreciably, since HLW already contains actinides. Some waste forms, such as supercalcine are sensitive to composition, as specified by the relative proportions of the various radioactive and inactive constituents. However, including additional TRU elements and inactive materials with those already present in the HLW should pose no problem, since the composition used for the final waste form will probably be checked for each batch in any case. Other waste forms, such as porous glass and coated ceramics, are not sensitive to the oxide composition used, so combining HLW and TRU waste in these forms is certainly feasible from that point of view.

The argument for combining the two waste streams before processing into a final waste form is largely one of simplification, though volume reduction is also an important factor. Combination would result in the following simplifications:

1. Only one type of waste package (i.e., a HLW package) would have to be handled at the geologic repository.

2. Immobilization facilities would not have to be duplicated.

Advantages associated with the smaller number of facilities include the savings in plant and equipment, and the decreased handling of the waste with resultant decrease in exposure risk.

In view of these advantages, it seems that combination of HLW and TRU waste, with elimination of a separate TRU waste form and waste package, should be evaluated as an alternative for handling the bulk of the TRU waste. This suggestion is particularly appropriate in view of the changing philosophy regarding geologic disposal of both HLW and TRU waste, with the shift to more stringent waste form criteria that is occurring, and the increasing emphasis on more advanced waste forms for HLW. We are not aware of an evaluation of this concept, and if, in fact, one has not been made recently, we feel strongly that it should be. The idea has merit, but may have significant disadvantages also when all the relevant factors are considered.

2.7 Conclusions and Recommendations

At the present stage of reviewing waste forms for TRU disposal it is not possible to recommend one which will "provide the lowest release rates reasonably achievable, but at most one part in 10^5 per year." Rather, from the information so far covered, it appears that most of the TRU waste forms being actively investigated are not capable of providing such release rates. However, borosilicate glasses and specifically treated concretes cannot be ruled out, and certain HLW candidate waste forms have obvious potential as TRU waste forms, including several mineral phases.

There are problems common to many of the traditional waste forms reviewed. These include the scarcity of release rate data, and the scatter of the data. Another is the fact that often experiments were carried out with samples derived from HLW which contained actinides, but the waste used was not specifically TRU waste. No extensive comparisons should be attempted, but those forms which are unlikely to be acceptable can be identified.

Clearly in this category are bitumen and urea-formaldehyde. Being organic, they are badly damaged by high doses of radiation. Radiolysis causes decomposition to yield gaseous products, which are undesirable in a repository. The decomposition and other damage done to the waste form allows radionuclides to become mobile and thereby capable of ready release.

Concretes in general contain water, which undergoes radiolysis to form hydrogen and oxygen, and because of generation of this potentially explosive mixture are not suitable for repository emplacement. However, specially prepared concretes such as FUETAP and ML cold-pressed concrete have low water contents and might be suitable from that point of view. Because of the problems mentioned earlier, leaching data are not particularly useful, but are in a range such that the material cannot be ruled out as a potentially suitable waste form.

Borosilicate glasses are in much the same category. Leach data are again scattered. Although some of the glasses designed specifically for incorporation of TRU waste have shown rather high release rates, glass as a waste form cannot be eliminated out of hand, particularly since some glasses have performed very well with HLW.

The mineral and ceramic forms used for HLW which we have considered in this report (Section 2.4) are SYNROC and supercalcine. Synthetic monazite has been proposed specifically for TRU because, in natural occurrences, U and Th are incorporated into its crystal lattice. These mineral forms have not had sufficient work done with either real or simulated TRU waste (in some cases none at all) to enable valid comparisons to be made. However, in view of what is known about incorporation of actinides into these mineral phases, and their known refractory properties and extremely low aqueous solubilities, it seems reasonable to conclude that waste forms consisting of these mineral assemblages have considerable potential.

Significant effort should not be expended on waste forms which are unlikely to meet NRC criteria. It is recommended that effort be concentrated instead on those waste forms mentioned as having potential to meet the criteria. These include specially prepared concretes, borosilicate glasses, forms based on synthetic minerals and multibarrier waste forms. Although some of the initial results on special concretes, such as FUETAP, are encouraging, it is apparent that some areas require further research in order to provide and improve the data base necessary for evaluation of a candidate waste form. In some cases, the data are from results of scoping studies to determine the feasibility of these processes for concrete-waste solidification. Thus, although the assessment of the long term stability of some of these special concretes is now under way, additional research efforts should address whether the candidate waste form is capable of satisfying the strawman criteria and other criteria governing the thermal, chemical, and radiological stability of waste forms. To this end, the following points should be considered:

(1) Since the work with FUETAP and hot-pressed concretes has been done with simulated HLW process sludges, it should be determined whether they are capable of encapsulating TRU waste incinerator ash while maintaining long term stability.

(2) While hydrogen and oxygen are produced by radiolysis of water in FUETAP concrete, they recombine in the presence of the concrete at rates comparable to the rate of production. Research should be carried out to understand the recombination mechanism and the concrete's role. Without such an understanding, use of FUETAP concrete could lead to buildup of explosive atmospheres due to gas generation.

(3) The leach rate data for FUETAP are incomplete while those for the cold-pressed concrete are imcomplete, questionable, and in need of verification. An extensive research effort should be undertaken to determine their leaching behavior under anticipated repository conditions, such as expected temperatures, and realistic leach solutions.

Results on the incorporation of TRU incinerator ash in borosilicate glass are discouraging in terms of leach resistance. Also, based on results from PNL, the glass frit composition apparently has to be tailormade for a particular ash residue composition. Thus, it is not clear if the processing technologies and borosilicate glass composition developed for HLW immobilization are immediately applicable for TRU waste disposal. Additional research efforts are needed in this area and should include development of a frit composition that is flexible in terms of accommodation of various ash compositions, and demonstration of compliance with the release rate criterion by a thorough investigation of the glasses' leach resistance and long term radiological stability. This research effort should include leaching studies under realistic repository conditions, effect on leachability of radiation damage anticipated for realistic waste loaded glasses, and leach testing conducted on glass-TRU waste compositions and loadings that represent actual anticipated waste formulations.

Synthetic mineral waste forms show great promise, but until now no results of work with actual TRU have been reported. A relatively large effort should therefore be devoted to developing and characterizing a monazite waste form for TRU. Along with this development effort, a comprehensive program of leach testing should be carried out. No work is known to have been done on SYNROC as a TRU waste form. A simplified SYNROC based on the minerals perovskite and baddeleyite has potential to incorporate actual TRU waste in a very stable form, and a level of effort in characterizing and testing similar to that applied to monazite should be initiated. Both the monazite and SYNROC waste forms should be tested for stability to alpha radiation.

The other HLW waste forms, which BNL is suggesting should be given high priority as potentially excellent candidates, include porous glass and coated ceramics. Since these forms are not sensitive to the particular oxide composition of the waste, they would be just as suitable for TRU waste as for HLW. The coated ceramic, in fact, could almost be considered tailor made for TRU waste, since its technology has been highly developed in the preparation of UO_2 and ThO_2 fuels for the High Temperature Gas Cooled Reactor.[40,41]

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3. MANAGEMENT OF WASTES

3.1 Introduction

The purpose of this subtask is to evaluate alternative technologies for decontamination of selected TRU wastes, such as those generated when processing equipment fails or when whole facilities are decommissioned.

Decommissioning, or retiring a nuclear facility from active service, requires that its remaining radioactive material be either contained, or reduced to a low enough level that public health and safety are protected. There is a wide variation in size and type of the facilities to be dealt with, and therefore, in the difficulty and complexity of decommissioning them. However, in general, two principal ways of handling the job are applicable to almost any facility: dismantlement, or some form of on-site storage. Dismantlement will result in removal of all radioactive materials so that the site can be restored to unrestricted use. The radioactive materials must then be disposed of in some acceptable way. Decontamination will usually be a requirement prior to ultimate disposal, and in fact, in order to keep worker exposure low, partial decontamination will often be necessary before dismantlement can even be carried out. Thus it is of great importance to develop effective methods for decontaminating a variety of structures and mechanical equipment, made of different materials, both in situ and after dismantling and sectioning.

The importance of having these methods in hand is emphasized by the magnitude of the decommissioning effort which will be required in the next few years, merely to handle existing backlog and without considering facilities which will become due for decommissioning during that time. A recent DOE planning document for the Surplus Facilities Management Program[1] sets forth a 20-year plan to handle the backlog of 87 facilities at a cost of over $400 million, with the bulk of the effort to come in the next ten years.

The different classes of material to be decontaminated can be divided conveniently into two main types: cladding hulls, and failed or decommissioned equipment. They will be discussed under those headings in the review which follows.

3.2 Management of LWR Cladding Hull Waste

Although this subject is of relatively minor concern at present, cladding hulls must be considered as potentially making up a sizable fraction of the nuclear waste inventory. Because of present U. S. policy, light water reactor (LWR) spent fuel (classed as HLW) is being stored rather than chopped and chemically processed at a commercial fuel reprocessing plant (FRP). However, while the West Valley FRP of Nuclear Fuel Services, Inc., was in operation, some 218 metric tons of LWR fuel was processed,[2] generating a considerable quantity of cladding hulls. Also the present policy of not processing, largely because of proliferation considerations, cannot be relied on to continue since it is the result of a political policy decision rather than of a scientific or technological problem. There are pressures for change from sources other than the nuclear industry, which include the government itself. A Ford Foundation report[3] of September 1979 comments that ultimate recovery of plutonium and uranium from spent fuel (i.e. by chemical processing) must be considered now, since classing waste fuel as a waste form is not likely to be accepted by other countries, or or even by the U. S. Very recently, the Government Accounting Office (GAO) in a report to Congress[4] strongly criticized U. S. safeguards practices and policy. Pointing out the large amount of plutonium which will be produced outside North America in the near term, it urged the U. S. to reconsider its bias against reprocessing and throw its full weight behind the international plutonium management and storage regime proposed by the IAEA.

Contamination on the LWR cladding hulls consists of residual irradiated uranium not dissolved during the fuel dissolution stage of the fuel reprocessing. One method proposed for dealing with the hulls is simply to compact them before disposal. Extensive fuel reprocessing would lead to large volumes of this type of waste, which is well above the 10 nCi/g TRU limit. Decontamination to below the 10 nCi/g limit would be a distinct advantage (provided the secondary waste generated was kept manageable), since it would eliminate the hulls as TRU waste. Also, if the hulls could be sufficiently cleaned, the Zircaloy could be recycled, at least within the nuclear industry. Two decontamination methods have been under development in the U. S. - the chloride volatility process studied by Argonne National Laboratory (ANL), and a method based on treatment with a gaseous HF-Ar mixture at 600°C, developed by Pacific Northwest Labortory (PNL). Exploratory studies at ANL[5] aimed at development of a pyrochemical process using molten zinc did not show promise and were abandoned.

3.2.1 Chloride Volatility Process

3.2.1.1 $ZnCl_2$ Process

Results of experiments with molten $ZnCl_2$ are given in ANL progress reports.[5,6] In all experiments UO_2 was added to the melt as a stand-in for PuO_2. At 500°C for five hours with a large excess of $ZnCl_2$, less than half the Zr was converted to $ZrCl_4$; however, with near stoichiometric amounts over 80% conversion was obtained and most of the $ZrCl_4$ distilled out of the reaction zone. Less than 1% of the uranium was found in the $ZrCl_4$. Although these results showed promise for the $ZnCl_2$ process, it would certainly have to be tested with Pu contaminated Zircaloy, preferably with actual irradiated cladding hulls, before being seriously considered as a candidate for a large scale process.

3.2.1.2 Gaseous Chlorination

Preliminary work[7] showed that chlorination at 400°C with HCl gas would volatilize $ZrCl_4$ from the reaction zone and leave uranium behind. Because of the potential explosion hazard from the product gas mixtures containing hydrogen, it was decided to try gaseous Cl_2 as the chlorinating agent. This was done in a series of experiments[8] in which PuO_2 was also included with the Zircaloy tubing to be treated. Since it was known that chlorination of Pu at temperatures of 550°C and above forms volatile tetrachloride, the temperature in the experiments was held at 400°C. Even so, much greater amounts of Pu were found with the $ZrCl_4$ than when HCl was used. The amount was consistently near the 10 nCi/g level, which means that much of the material would still have to be classed as TRU waste unless the 10 nCi/g limit were relaxed. There is, for example, some indication that NRC will recommend an increase in this value.[9]

Two experiments, one with Cl_2 and one with HCl, were carried out with pieces of actual cladding hull which had been irradiated to 6600 MWD/MTU at

Dresden. Their purpose was to find how fission products and neutron activation products in the hull waste behaved during chlorination at 400°C. The temperature was difficult to control in the experiment with Cl_2, with the reaction zone running about 10°C hotter than desired. Occasional hot spots on the Zircaloy surface were also observed. In the experiment with HCl, virtually none of the fission and activation products were volatilized with the $ZrCl_4$, but in that with Cl_2 substantial fractions of many of the radionuclides followed the $ZrCl_4$.

This means that use of a strong chlorinating agent such as Cl_2 gas at a temperature sufficiently high to form and volatilize $ZrCl_4$ from cladding hulls will also volatilize appreciable amounts of the associated β,γ-activity. Thus, even if the process could be controlled to keep the $ZrCl_4$ product below the 10 nCi/g limit for TRU waste, it might require disposal as a highly radioactive material since it would be unattractive as salvaged material for reuse in the nuclear industry (the only place it could be used). Use of the mild chlorinating agent HCl, on the other hand, could lead to a salvaged product well below the TRU limit, and also acceptable for reuse from the point of view of β,γ-activity.

A comparison of the salient features of the two gaseous chlorination processes and the molten $ZnCl_2$ process is given in Table 3.1.

Table 3.1

Comparison of Chloride Volatilization Processes

	Gaseous Reagents		
	HCl	Cl_2	$ZnCl_2$ Process
Temperature (°C)	400	400	500
Temperature control	Good	Difficult to control	Good
Type of reagent	Corrosive gas	Corrosive gas	Solid
Hydrogen in off-gas	Yes	No	No
Transfer of fission and activation products with $ZrCl_4$	Trace only	Substantial fraction transferred	Process not tested with actual cladding hulls
Degree of TRU decontamination	Excellent	Difficult to achieve better than 10 nCi/g in final product	

3.2.2 HF-Argon Treatment

The objective of the PNL program in decontamination and densification of chop-leach cladding residues is described in PNL progress reports as follows:

"to develop methods for removal of long half-life transuranics from fuel cladding residues and to consolidate the decontaminated cladding into a dense, chemically unreactive form for storage or burial." Their studies have centered on surface treatment with hot gaseous HF-Ar mixtures to accomplish the first part of the objective, and melt densification producing ingots for achieving a satisfactorily dense, unreactive form.

The latter process concerns our task only insofar as any hull residue reaching that stage would still be classed as TRU waste, in which case it should be ascertained that the second objective above can be met. The induction melting process was tested with a number of heats of Zircaloy-4 using CaF_2 flux under an argon atmosphere.[10] The soundness and hardness of the ingots produced were both excellent, well within ASTM hardness specifications for nuclear grade Zircaloy and within acceptable chemical and corrosion resistance standards for Zircaloy-4. The second part of the objective can thus be considered met.

For meeting the decontamination objective, laboratory scale experiments were first carried out to demonstrate a method, then pilot scale equipment was designed, assembled and tested. The laboratory experiments to demonstrate satisfactory descaling with TRU removal ended up with the following process:[11] one-hour treatment of the cladding hulls with a 25% Ar - 75% HF mixture at one atmosphere and 600°C, followed by two half-hour rinses at 95°C with an aqueous solution 0.4 M in ammonium oxalate, 0.16 M in ammonium citrate, 0.1 M in ammonium fluoride and 0.3 M in hydrogen peroxide. This treatment removed all visible surface oxide from both BWR and PWR hulls, and achieved excellent decontamination from TRU elements (99.7% in a typical experiment).

The pilot scale plant, designed to process 2 kg/hr of cladding hulls, after a series of mechanical tests with inactive Zircaloy,[12,13] was tested to verify the chemical processing aspect of operation.[14-16] During this phase, several unexpected problems were encountered. Some of these involved mechanical equipment failure and were fairly easily corrected. A more serious problem whose cause was not determined for some time was an excessive temperature rise in the HF reactor which quickly halted experiments each time it occurred. The cause was finally found to be the highly exothermic reaction of zirconium with hydrogen, the latter formed by the reaction of HF with zirconium metal. This reaction occurs only with nearly pure HF, indicating that argon was not mixing properly with the HF before contact with the hulls. Further equipment modification was to be carried out in order to solve the problem.

It appears that the technical basis for the process is sound and that problems encountered in scale-up were due to design weaknesses. However, the importance of testing processes on a production scale before placing reliance on them as steps in an actual full scale waste handling system is well illustrated by PNL's experience in this situation.

3.2.3 Secondary Waste Streams

The secondary waste stream generated in the HF-Ar process comprises the aqueous rinse solutions. No mention is made in any of the PNL reports[10-16] of possible methods of treating them to immobilize the TRU content, although an independent review of the process recommended that bench scale studies of secondary waste stream treatment processes should be carried out.[11]

In the ANL volatilization processes, the secondary waste stream consists of the non-volatile residues, which are already solid, but not homogeneous. Since stainless steel and Inconel are not chlorinated significantly at 400°C, massive pieces associated with hull assemblies would remain with the residue and would have to be sorted out for separate disposal if a glass or similar waste form were chosen for the disposal of the residue. Also, many of the chlorides in the residue would be hygroscopic and could cause corrosion problems, so would preferably be converted to oxides regardless of the final method chosen for disposal.

3.2.4 Evaluation of Processes

The main characteristics of the chloride volatilization process and the HF-Ar treatment are compared in Table 3.2. Only the decontamination stage is considered in the table because of the difference in final form of recovered zirconium in the two cases, and because NRC has only minor interest in the recovered product if it does not require disposal. If disposal is required, the processes could probably be compared equitably on the basis of ingot production in the HF-Ar process and a final product of ZrO_2 in the volatilization process.

Table 3.2

Comparison of Cladding Hull Waste Management Methods

	HF-Ar Decontamination Process	Gaseous Chlorination Processes
Temperature (°C)	600	400
Reagent gas mixture	HF-Ar	HCl/N_2 or Cl_2/N_2.
H_2 content of off-gas	Small	None with Cl_2 use; appreciable with HCl use.
Extent of conversion required	Surface only.	Complete chemical conversion of hulls.
Form and type of secondary waste	Liquid -- Aqueous solution.	Heterogeneous solid. Ferrous metal chunks + actinide and FP chlorides.
Stage of development	Pilot scale equipment debugged and ready for final testing late 1979.	Proven on lab scale. No plans mentioned for scale-up.

In the decontamination stage, the volatilization process has the disadvantage that all the metal in the cladding hull has to be converted, and not just a surface layer as in the HF-Ar process. The latter is operated at somewhat higher temperature, but both temperatures are moderate. Both processes require handling very corrosive and dangerous gases. The volatilization process appears to be at a disadvantage when secondary waste streams are considered, at least partly because its waste residue is heterogeneous and would probably have to be sorted prior to disposal. However, since very little information is given on proposed treatment of either waste stream, valid comparison cannot be made. The volatilization process has been demonstrated only on the laboratory scale, whereas pilot-scale equipment for the HF-Ar process has been installed and made operational.

3.3 Decontamination of Facilities and Equipment

3.3.1 Electropolishing

The major U. S. effort in developing electropolishing methods has been at PNL. SRP has also been working in this area and has had several small units in routine use for some time for cleaning tools and small equipment for reuse.[17] They have designed a relatively large facility (TRU Solid Waste Facility, TSWF) for processing their TRU wastes. Because of the importance attached to volume reduction, a critical part of the TSWF is a line of automated electropolishing units.

3.3.1.1 Pretreatment

An obvious requirement for electropolishing is that the surfaces to be polished must be conductive. Such coverings as paint, rust, enamel, tape, grease, and epoxy resin prevent current flow and therefore must be removed before electropolishing can be carried out. While a specific chemical such as a commercial latex stripper will remove certain of the coatings,[15] none is generally applicable. Two methods developed at PNL, liquid honing[15] and vibratory finishing,[13] both use abrasive, and prepare metal surfaces for electropolishing by easily removing all types of coating. In fact, since they tend to remove some of the metal as well, they do a good job of decontaminating in their own right, as will be described in Section 3.3.3.

3.3.1.2 Tank Electropolishing

This is the standard method for treating relatively large pieces which can be readily attached to racks for immersion in the polishing bath. The normal electrolyte used is 85% H_3PO_4 at room temperature. With the equipment in use at PNL,[11] decontamination has been consistently achieved to well below the 10nCi/g limit with electrolysis times of only a few minutes.[11,12]

3.3.1.3 In Situ Electropolishing

A contact type in situ device has been used at PNL[10,14] to decontaminate portions of large flat areas such as walls and floors of plutonium gloveboxes. Flat areas are necessary to permit gasketing of the electrolyte container to the work surface. A typical decontamination factor obtained was 5.5×10^3, which reduced the Pu contamination to below the TRU level.[14] The decontamination factor is defined as the ratio of activity in the original material to that in the final product.

3.3.1.4 Barrel Electropolishing

In order to avoid racking of small pieces, PNL has developed a method for polishing them in a slowly rotating barrel anode.[16] Although the same H_3PO_4 electrolyte can be used for the latter application as is used for the others, current tends to be excessive (200 to 300 A). By using a mixture of H_3PO_4 and H_2SO_4 much lower current is drawn. The rotating barrel was also successfully applied to the removal of uranium contamination from molybdenum pieces. In all the trials made with the different electropolishing techniques, decontamination to levels well below the 10 nCi/g limit for TRU wastes was achieved.

3.3.1.5 Alternative Electrolytes

For ferrous alloys, H_3PO_4 is the electrolyte of choice because it has good throwing power and can be used at reasonable current densities. For specific applications changes may have to be made, such as addition of H_2SO_4 for the barrel electropolishing. Also, other metals may require alteration of the electrolyte. For example, a mixture of H_3PO_4 and HCl was required for treating B-Cr-Ni alloys.[12]

Other solutions can of course be used as electrolytes. One such solution developed at Rocky Flats has been evaluated by PNL.[16] Apparently an important reason for its development was that its use could help reduce exposure in decontamination operations involving high activity levels, since the removed TRU contaminants precipitate out and become part of the sludge. This advantage of the process was borne out by PNL's evaluation, but there were a number of disadvantages such as:

1. Poor throwing power (1/6 that of H_3PO_4)
2. High current densities
3. High operating temperature (70-90°C)

While it could be applied to tank use, its poor throwing power would make the alkaline electrolyte unsuitable for in situ use and for barrel electropolishing. The secondary waste stream is small and should be easily treated since all the actinides are found in the hydroxide sludge which settles out of the electrolyte. No information was given on the degree of decontamination achieved.

3.3.2 High Temperature Processes

3.3.2.1 Fused Salt Decontamination

Work at PNL showed that contaminated stainless steel could be effectively decontaminated using oxidizing fused salts.[18] Decontamination factors of 10^6 or better were obtained using fused $NaNO_3$ at 800°C and several stages of salt-metal contact. The process generated a large amount of contaminated salt, however: a three to one salt-to-metal weight ratio (and even greater volume ratio) was required to achieve a decontamination factor of 10^6. The method therefore could not be considered as a large scale process unless the TRU content of the salt phase could be removed regularly in a small volume (e.g. as oxide precipitate) allowing recycle of the salt.

3.3.2.2 Melt-Slagging

Melt-slagging (melt-refining) of steels contaminated with plutonium has been suggested as a possible decontamination process which has the potential advantage of producing steel for reuse and at the same time simplifying analytical problems encountered in keeping track of the plutonium. Such a method was investigated in some exploratory work at PNL in 1973,[18] but partition of the radioactivity between molten stainless steel and a fused inorganic slag was found to favor the metal phase, so the process was not investigated further.

Some years later ANL began a program to test the use of various silicate slags for removal of plutonium from contaminated metal. A number of promising experiments were described in two 1977 progress reports[7,8] and a topical report was published last year[19] which covers the work described in the progress reports and, apparently, all the work done on the project. Sufficient experimental detail is given to evaluate the scientific aspects of the work as well as its usefulness as the basis for a full scale decontamination process. A comprehensive conceptual design for such a process is given in the topical report.[19]

In connection with the latter aspect, the relatively high temperature and long heating times used are of particular concern, namely 1500°C and one to two hours. In one experiment the melt was held at 1500°C for only one minute, however, with similar results to the other experiments indicating that times considerably shorter than an hour might well be feasible.

In terms of the scientific results, the method of setting up the experiments is of prime importance. In most of the experiments contaminated metal samples were simulated by placing PuO_2 in a hole drilled in a piece of stainless steel or nickel and inserting a stainless steel or nickel plug in order to restrict accessibility of the PuO_2 to the slag until the metal had melted. To conduct an experiment, pieces of slag were placed around the metal sample in a recrystallized alumina crucible, the crucible contents melted and held at 1500°C for one to two hours, then cooled so that the phases could be sampled. The interior of the molten metal and fused slag phases were not sampled to determine the concentration of plutonium, so these experiments could not yield true distribution coefficients. The distribution coefficient, K_d, is defined as

$$K_d = \frac{\text{Pu concentration in slag}}{\text{Pu concentration in metal}}.$$

A few experiments were carried out in which conditions approached those required for obtaining distribution coefficients. These involved (a) use of a metal sample from a previous experiment, in which the unextracted plutonium was at least partially distributed throughout the (solid) metal, and (b) contacting clean metal with contaminated slag to see how much plutonium partitioned to the metal phase. Too few of the latter two types of experiment were done to permit assessment of reproducibility.

Although true K_d values were not obtained, apparent values are of interest in comparing performance of different metals and slags. The apparent K_d values ranged from 2×10^6 to 8×10^6 for steel, being about a factor of two lower for diopsidic than for borosilicate slag. For nickel with borosilicate slag, apparent K_d was around 5 x 10^4. Presence of small amounts of copper and brass (up to 5%) had little effect.

This indicates a higher solubility of PuO_2 in nickel than in steels, and such a conclusion is supported by the distribution of plutonium in the different metal samples after slag contacting. Refined analytical methods, including autoradiographic techniques and fission track counting of neutron irradiated samples enabled the authors to map out thoroughly the relative distribution of the plutonium in different parts of the slag and the metals, e.g. near the phase boundary, near the crucible wall, or in the interior of the slag, and on the surface, in visible defects, or throughout the interior of the metal. This information is judged to be of considerable scientific value in contributing to chemical and metallurgical knowledge of the systems studied, even though it cannot enable distribution coefficients to be determined.

From the process point of view, it is unimportant whether or not the plutonium in these experiments was ever in the liquid metal phase. Only the extent of decontamination and ability to reproduce it are important. Decontamination factors from the data given appear to be of the order of 10^5 in a number of experiments, which should be adequate for a viable process. In fact, since most of the plutonium associated with the metals after contacting was on the surface and in visible defects and very little was in the interior, it may have been held in tiny pieces of slag adhering to or trapped in the surface of the metal, and actual decontamination therefore might be made even greater if a better way could be found to separate the slag from the metal.

The report suggests that, in a large scale process, a second extraction would be useful. Experiments were, in fact, done which showed that further decontamination was obtained in a second extraction. Even the first extraction was able to reduce the Pu concentration to below the 10 nCi/g limit in nickel as well as steel.

3.3.3 General Methods

It was pointed out in Section 3.3.1.1 that two pretreatment procedures developed at PNL can be considered as decontamination methods in their own right. These two, liquid honing and vibratory finishing, can often decontaminate material to below the TRU limit, and have the added importance that they are applicable to materials other than metal, such as rubber and plastics.

3.3.3.1 Liquid Honing

Liquid honing is used in the metal finishing industry to clean surfaces, remove burrs and machine marks, and relieve stress concentrations. It uses a jet of liquid containing abrasive particles directed at the work from hand held guns by a stream of high pressure air. The guns can be designed for specific applications, such as cleaning holes with a large depth-to-diameter ratio. About 0.1 mm thickness of metal is removed during a typical decontamination cycle.

PNL's evaluation of the method[15] showed that in three to five minutes it not only cleaned exterior metal surfaces, but also decontaminated threaded areas and deep into bolt holes as well as giving fair decontamination factors for rubber surfaces. However, blast from the jet tends to disperse the removed contamination, so that a high degree of operator care with a well designed system would be required to keep loose contamination under control. Since each piece of contaminated equipment has to be handled on an individual basis, there also would be no time advantage over methods which take longer but treat many pieces at a time (such as vibratory finishing).

3.3.3.2 Vibratory Finishing

Metal pieces for decontamination are often corroded or coated with paint, oil, epoxy resins, or other non-conductive material which has to be removed before electropolishing can be carried out. Chemical pretreatment using a commercial latex stripper at 150°F was developed at PNL[15] and successfully removed organics such as paint, tape and grease, but not epoxy. The treatment often removed most of the alpha contamination as well, but as just indicated is not applicable to all kinds of surface coverings. Vibratory finishing, on the other hand, was shown to have general application as a pretreatment, and was usually capable on its own of decontaminating not only metal, but also rubber and plastics, to below the 10 nCi/g level.[15] After vibratory finishing, electropolishing could be quickly and easily carried out to reduce alpha contamination to a barely detectable level, several orders of magnitude below 10 nCi/g.

The vibratory finishing machine developed by PNL used a commercial latex stripper with a fast cutting ceramic burnishing medium (unspecified). After the vibration treatment, contaminated ceramic medium was drained into a sludge tank which was monitored for Pu criticality,[16] and the pieces thoroughly rinsed. Besides typical Pu-contaminated metal pieces (sections of pipe, ducting, glovebox parts), the vibratory finisher cleaned pieces of plexiglass, rubber gloves and all other major components of plutonium gloveboxes to below the 10 nCi/g limit.[15]

3.3.4 Secondary Waste Streams

Descriptions of secondary waste streams and their treatment have not been found yet for a number of the processes described. For some others, information has been located, but has not yet been reviewed. In general, it appears that the volumes of the secondary waste streams can be kept to a reasonably small fraction of the original TRU contaminated waste. This conclusion is emphasized for example, in Table 3.4, reproduced from a PNL report.

3.3.5 Evaluation

Parameters and characteristics of the various methods for decontaminating facilities and equipment are summarized in Table 3.3. All the methods work at least adequately and produce secondary waste streams of smaller volume than the original contaminated material.

No one method is applicable to all materials and all situations although liquid honing and vibratory finishing can be applied to most, with activity levels below the TRU limit of 10 nCi/g usually achievable. Liquid honing's main disadvantage is that removed activity is too readily dispersed by the nature of the removal process. If a means of preventing this dispersal were developed, liquid honing could be very useful for in situ decontamination of large irregular surfaces which would be impractical to treat by in situ electropolishing.

Table 3.3

Evaluation of Methods for Decontaminating Equipment

	Electropolishing	Melt Slagging	Liquid Honing	Vibratory Finishing
Temperature (°C)	Ambient or a little above.	1500	Ambient	Ambient
Time required	Few minutes.	1-2 hours[a]	Few minutes.	<1 hour
Able to treat non-metals	No	No	To reasonable extent.	Yes
Adaptable to in situ use	Yes	No	Yes	No
Adverse factors		High temperature operation.	Difficulty of controlling dispersal of removed activity.	
Degree of decontamination and quality of product	Excellent decontamination to give highly polished surface.	High decontamination factor, but residual activity mostly on (the much smaller) surface.	Good decontamination, normally to <10 nCi/g. Surfaces cleaned of oxides and extraneous material but not polished.	
Stage of Development	Commercial	Demonstrated in lab.	Pieces treated singly and by hand.	Pilot scale.

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[a] One experiment indicated much shorter times (of a few minutes) might be sufficient.

Vibratory finishing cannot be adapted for in situ use, but otherwise it has no obvious disadvantages, and its advantage (and liquid honing's) over electropolishing is that it can be applied to plastic and rubber components of contaminated equipment as well as to metals.

Melt slagging uses a low ratio of slag/metal (0.1 to 0.15 on a weight basis) at each contact. If slag could be reused for several contacts with contaminated metal, the secondary waste stream would be kept very small. This advantage could be offset by the extra volume from used crucibles, unless their average service life was reasonably long. The principal disadvantages of the process are the high temperature required (1500°C) and the fact that the residual contamination, though slight, is concentrated on the surface of the recovered metal.

Electropolishing provides the most complete decontamination of the various methods, but of course is applicable only to metals with surfaces reasonably free from extraneous non-conducting materials. For metals, particularly ferrous alloys, it has the advantage that, with pretreatment such as vibratory finishing, pieces can often be cleaned to the point where activity is essentially undetectable. Thus, such material is not only no longer TRU waste, but could be either reused or recycled. It also should be noted that the electropolishing techniques developed by PNL were being used by two commercial firms as early as 1978 to provide decontamination services to nuclear facilities.[13]

3.4 Conclusions

Even as late as 1978 when the DOE report "Technology for Commercial Radioactive Waste Management"[20] was in preparation, densification by compaction and melting was seriously considered as the standard method of preparing contaminated metal wastes for disposal. It had been shown at PNL (then BNWL) that when contaminated metal was melted under an inert atmosphere the radioactivity could be dispersed and fixed in the solidified metal.[17] However, as pointed out in Section 3.1, even if the relatively large volumes of compacted or melted metals could be tolerated, partial decontamination will often be necessary so that dismantlement can be carried out. It seems worthwhile, then, to carry the process one step further and consider decontamination as a preferred disposal method.

In the case of cladding hulls the argument for decontamination was expressed in an ANL report[8] as follows:

"The TRU content of this residue plus that from activation of the 1 ppm of tramp uranium in Zircaloy cause the hull waste to exceed the proposed limit (FEDREG-1974B) of <10 nCi of TRU elements per gram of solid. Accordingly, this voluminous waste must be packaged in a retrievable manner and consigned to a Federal repository rather than to a commercial burial site. Considerable savings in packaging, interim storage, shipping, and burial costs can be realized if the volume can be reduced." This can be achieved, the report continues, by using the ANL chloride volatilization method.

The argument for decontaminating failed and decommissioned equipment is essentially the same. If its activity level can be reduced below 10 nCi/g, it will be non-TRU waste suitable for shallow land burial. In other words, the entire retrievable storage process with its attendant costs, hazards, and increased (rather than decreased) waste volume can be eliminated. That this should be achievable in most instances is supported by the examples, cited in previous sections of this chapter, of decontamination procedures which reduced TRU contamination to well below the 10 nCi/g limit, and often to a level undetectable by routine radioactivity survey methods. This latter degree of cleanliness would permit reuse of equipment, and, in the case of scrap, would allow recycle of metal within the nuclear industry.

The case for treating TRU contaminated material by decontamination, rather than by retrievable storage followed by later exhuming and processing for geologic disposal, is summarized in Table 3.4 as excerpted from a PNL report.[15]

Table 3.4

Comparison of TRU Waste Treatment by Decontamination
Versus Retrievable Storage/Geologic Disposal

Retrievable Storage/Geologic Disposal	Decontamination to Produce Non-TRU Waste
Remove contaminated component	Remove contaminated component
Load into storage box	Transport to decontamination facility
Transport storage box	Disassemble/section
Store/monitor for 20 years	Pretreat/decontaminate
Exhume box	
Transport to repackaging facility	Non-TRU waste - final disposal by convenient shallow land burial
Unpackage deteriorated waste	
Disassemble/section waste	
Process waste	
Repackage for geologic disposal ←	Prepare small amount of secondary waste for geologic disposal
Overpack for transport	
Transport to disposal site	
Final disposal	
Amount of TRU Waste for Disposal	Amount of TRU Waste for Disposal
At least double the initial amount	Small fraction of the initial amount

In our view, decontamination technology is in a well developed state in this country. A great deal of effort has been put into both research and development in the last few years, with very good results. The electropolishing method had even reached the stage of commercial use more than a year ago.[12] So far, work done in other countries has not been reviewed, but on the basis of the U. S. work evaluated, it appears that no major R&D effort is required for decontamination methods. However, one technique which could be important when extensive decommissioning efforts are required, is liquid honing since it has obvious application to in situ decontamination of large pieces of equipment, particularly those of irregular shape. The method presently decontaminates well, but gives poor control of removed activity. A reasonably large effort should be expended in this area in order to develop a means of recovering all the removed activity. On the basis of our review to date of the U. S. work, further efforts are required on treatment of secondary waste streams to ensure compatibility of end product with an accepted TRU waste form.

3.5 References

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4. U. S. Government Accounting Office, Report to Congress of March 18, 1980.

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15. Ibid, Jan-Mar 1979, PNL-3000-1, May 1979.[a]

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[a] Available for purchase from the National Technical Information Service, Springfield, Virginia, 22161.

[b] Available in public technical libraries.

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20. U. S. Department of Energy, "Technology for Commercial Radioactive Waste Management," DOE/ET-0028, Vol. 2, May 1979.[a]

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[a] Available for purchase from the National Technical Information Service, Springfield, Virginia, 22161.

[b] Available in public technical libraries.

4. GAS GENERATION

4.1 Introduction

A key responsibility of the NRC is the evaluation of all aspects of the geologic repository performance which could affect the public health and safety. In this context, an assessment of the performance of the waste package in a mined geologic repository is required. One important process that could affect the long term isolation behavior and safety of a repository is the potential evolution of toxic and/or explosive atmospheres within the waste package or emplacement room. Thus, it is the purpose of this section to discuss the results of recent and ongoing programs that are concerned with gas generation from TRU contaminated wastes and to show how and whether the information can be used to support proposed regulatory criteria.

The formidable amount of TRU waste in the U. S.[1] has been mentioned in Section 1. It includes the 2,000,000 ft^3 retrievably stored at the Idaho National Engineering Laboratory (INEL) and Hanford, but mostly at INEL. Some of the characteristics of TRU waste at INEL and Los Alamos Scientific Laboratory (LASL) have been evaluated.[2,3]

Approximately 20 to 25% of the waste by volume in retrievable storage at INEL is combustible. In addition, as will be discussed below, a sizable fraction of the organic, combustible TRU waste is susceptible to production of gas by various degradation mechanisms. The combustibility and potential dispersibility of the waste is an important factor during the operational phase of the repository while the tendency to produce gas is important in terms of long term repository behavior. However, in spite of these considerations, retrieval and shipment without processing has been entertained as a TRU waste management alternative.[4,5] The acceptability of this non-processed waste, in terms of its potential for gas generation and the consequences thereof, is the major focus of this section.

The evaluation of possible gas generation situations within a repository requires careful consideration of several areas. An assessment of existing DOE programs has been in progress and will constitute the major portion of this section. Also, a thorough computer literature search into programs that may be under way in the academic and industrial sectors has been initiated. International programs will be included in the literature review. The Department of Energy (DOE) has been conducting research in the area of TRU waste management through its Waste Isolation Pilot Plant (WIPP) program. The purpose of the activities of that program is to provide technical support for the development of waste acceptance criteria for the deep geologic terminal isolation of transuranic wastes. The scope of this review and evaluation of the available information on gas generation from the WIPP program includes the mechanisms responsible for gas generation and how they are affected by various parameters, quantities and identification of gases produced, consequences of gas generation, conclusions drawn from the results, how the information supports proposed regulatory criteria, and a recommendation to NRC based on the evaluation.

4.2 DOE/WIPP Assessment

The most extensive effort regarding the potential for gas generation from TRU wastes for which experimental information is available is the Waste Isolation Pilot Plant (WIPP) Transuranic Waste Experimental Characterization Program conducted by Sandia Laboratories (Albuquerque) and sponsored by the Department of Energy. The results of this program have recently been reported.[6-8] A comprehensive review of all applicable waste degradation-gas generation data for TRU wastes was the subject of two of these reports.[6,7] The reports provide a summary and interpretation of these data from research over the past several years. The information in these two reports and the references therein are discussed below. Topics discussed included gas generation rates from several TRU waste forms, degradation mechanisms, synergistic effects between mechanisms, composition of the gases produced, methods for reducing gas production rates, and comparisons of the modes of gas generation.

Mechanisms which result in gas generation from the degradation of existing and potential forms of defense related TRU waste matrices and containers along with the primary participants in the Sandia program are given in Table 4.1.

Table 4.1

Waste Degradation Mechanisms and WIPP Program Participants

Mechanism	Investigating Laboratory
1. Radiolysis	Los Alamos (LASL) Savannah River Laboratory (SRL) Rocky Flats Plant (RFP)
2. Thermal and Catalyzed Thermal	LASL, SRL
3. Chemical Corrosion	Sandia (SLA)
4. Bacterial	LASL University of New Mexico (UNM)

The conditions under which some of the experiments were conducted are environmental conditions anticipated to be present at the WIPP TRU waste storage horizon in the repository. Two of the more important parameters (and ranges of interest) that may affect gas generation rates in the repository are (1) temperature (20° to 100°C) and (2) pressure (0.1 to 15 MPa). Other factors considered for their influence on degradation and production rates were aerobic versus anaerobic conditions and the geochemical environment. The TRU waste matrices of primary interest for the WIPP program are cellulosics (paper, cotton, cloth, wood, etc.) plastics (polyethylene, polyvinyl chloride), rubbers (neoprene, Hypalon), a composite of the above organic matrices, concrete-TRU ash, process sludges, and asphalt. For purposes of assessment and intercomparison of gas generation rate versus degradation mechanism, representative TRU waste characteristics were defined to approximate the waste in temporary storage at INEL.[2] These characteristics are summarized in Table 4.2.

Table 4.2

Assumed Characteristics of Standard Drum (210 Liter, Mild Steel) Content
(Data taken from Table 2 of Reference 7)

Waste Material	Matrix Weight (kg)	Contamination (g wgPu)[a]
Cellulosics	51.4	0.5(0.039 Ci)[b]
Plastics	51.4	0.5
Rubbers	51.4	0.5
Organic composite	51.4	0.5
Organic setups (solidified oils)	190	0.5
Process sludges (first stage)	190	(89)(6.9 Ci)
Polyethylene liner	8.6	
Mild steel drum	25	
Concrete-TRU ash	300	200(15.4 Ci)
Asphalt	135	100(7.7 Ci)

[a] wgPu = weapons grade plutonium.
[b] Specific activity of Pu-239 = 0.062 Ci/g.

The pertinent data from the available information on gas generation from various waste matrices are summarized in Table 4.3. G values (defined as the number of gas molecules formed/100 eV of absorbed radiation) are a measure of the efficiency of radiation induced processes. Here, they refer to the total number of gas molecules formed according to the drum characteristics listed in Table 4.2. In the calculation of gas generation rates (as moles/yr/drum), pressure, temperature, and dose rate effects were not considered. Also, all the alpha decay energy was assumed to be deposited in the waste matrix.

4.2.1 Radiolytic Gas Generation

4.2.1.1 Cellulosics

Combustible cellulosics are a sizable component of the existing TRU inventory. This, plus the fact that cellulosics, polyethylene,[5] and polyvinyl chloride (PVC)[9] evolve more gas than other existing waste types, has resulted in much experimental information on the radiolytic degradation of this organic matrix. At the same time, significant uncertainties and discrepancies have arisen in the experimental results. The most extensive research effort in the areas of radiolytic and thermal degradation of cellulosics has been carried out at LASL, with additional work having been conducted at SRL and RFP. The variables investigated at LASL for their effect on gas generation were:

Table 4.3

Radiolytic Degradation Data Summary for TRU Waste Contaminated Matrices[a]

	Matrix[b]	G(Total Gas)	Moles/Yr/Drum
LASL	Cellulosics	2.9-1.3[c]	0.011-0.0050
	PVC (70°)	8.0-11	0.031-0.042
	Asphalt	0.20-1.0	0.15-0.76
	Cellulosics, Dry	1.6	0.0062
	Cellulosics, Wet	1.5	0.0058
	Composite	1.4	0.0054
	Polyethylene	1.9	0.0073
	Pump Oil	1.3-1.8	0.0050-0.0069
SRL	Cellulosics (22°)	1.9	0.0073
	Pump Oil	2.7	0.010
	Octane	4.5	0.017
	Concrete-TRU Ash	0.00030-0.60	0.00050-0.91
RFP	Cellulosics, Dry	0.63	0.0024
	Cellulosics, Wet	0.31	0.0012
	Polyethylene	0.73	0.0028
	PVC	0.43-0.96	0.0017-0.0037
	Plexiglas	1.9	0.0073
	Rubbers	0.37	0.0014
	Oil	3.1	0.012
	Ion Exchange Resins	0.11	0.00042
He Generation (From Alpha Decay)	(0.5 g ^{wg}Pu)		3.7×10^{-8}
	(200 g ^{wg}Pu)		1.5×10^{-5}

[a] Unless otherwise noted, temperature conditions were:
20° (LASL)
23° (SRL)
STP (RFP)

[b] Average content of weapons grade Pu per drum listed in Table 4.2.

[c] G values for a dose rate range of 80×10^5 nCi/g of waste to 640×10^5 nCi/g of waste.

(a) Waste matrix (see Table 4.3)
(b) Dose rate (expressed as contamination level/drum) - 0.1X to 160X (X = 200 g of weapons grade Pu/drum)
(c) Temperature - 20°, 40°, 70°, and 100°C
(d) Time - up to 480 days and >4 years
(e) Pressure - 101 to 1.45×10^5 kPa.

The important results for the radiolytic gas generation studies involving cellulosic waste matrices are given below:

(1) It should be first noted that the G values from LASL and SRP for cellulosics and pump oil are in fair agreement with each other while those from RFP do not agree. Possible explanations for the discrepancy are discussed below.

(2) G(gas) from alpha radiolysis is dependent on the quantity of contaminant radionuclide present. In other words, the G values are a function of the dose rate, whereas it has been assumed that G values for gas formation are independent of dose rate. Data from LASL[9] suggest that the validity of linearly extrapolating high dose rate data and short observation times to realistic low dose rate situations (i.e., existing TRU wastes) and long times is questionable. In the case of cellulosics, G°(gas) (the G value for gas formation at t=0) is 2.9 for dose rates ≤40X and 1.3 for dose rates of 80X and 160X.[9] The tentative explanation for this apparent anomaly is that there may be a sharp, rapid decrease in G(gas) at the higher dose rates that was not observed during the periodic sampling. This hypothesis awaits verification.* Based on results from SRL,[10] the opposite conclusion has been reached concerning the dose rate dependence of cellulose degradation. (It would appear from the SRL data that such is not the case. The G° value for alpha radiolysis of cellulosics was a factor of about 1.4 lower for an <u>increase</u> in dose rate of about 4.)

(3) G(gas) decreased with increasing total dose for dose rates (Pu loadings) that ranged over a factor of 1600. Also, G(gas) decreased more slowly for lower dose rate experiments than for higher dose rate experiments. This is an important observation in that actual TRU waste contamination levels are low. Thus, the wastes will be at their maximum gas generation potential. The decrease in G(gas) with time is attributed to localized matrix depletion, i.e., the short range of alpha particles results in material depletion in the immediate area of the radionuclide contaminant. Similar behavior in G(gas) was observed at SRL.[10] The effect in this case was claimed to be due to formation of products that produce less gas as the radiation exposure progressed. What the nature of these products (other than H_2, CO, or CO_2) might be and how they could "produce" less gas was not discussed. The results from RFP have shown that, in agreement with LASL and SRL, gas generation rates decreased as a function of elapsed time.[11]

(4) Compositions of radiolytically generated gas were determined by mass spectrometry. Hydrogen was found to be the major product (~60 mol %) with CO_2 and CO (order of decreasing contribution) being produced at the expense of oxygen present initially in the test cylinder.

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*Recent results from LASL on the alpha radiolysis of cellulosics at 40X and 80X conducted in an inert argon atmosphere yielded G° values of 1.9. Their conclusion is that, for their experimental conditions, G° is independent of dose rate (S. T. Kosiewicz, Los Alamos Scientific Laboratory, personal communication to G. Bida, BNL, March 28,1980).

At this point, a discussion of some of the results and discrepancies in these results for cellulosics is in order. The LASL data would seem to indicate that the initial G values for cellulosics are the same regardless of whether the material is wet or dry.[5] Water does undergo alpha radiolytic decomposition,[12] so this would suggest that water sorbed by the cellulose would affect gas production. The value of G° = 1.6 (LASL, Table 4.3) is for a dose rate of about 50X while that of 1.5 is for a dose rate of about 25X. Thus, the rates of gas production are similar for a difference of two in contaminant loading. In addition, along with the increased rate of gas generation for wet cellulosics, the fraction of H_2 produced increased from 50 to 80%. The G values (not G° in this case) obtained at RFP are lower than those from LASL and SRL but, more importantly, the gas yields for wet cellulosics are lower than for dry for dose rates comparable to those at LASL.[11] Although the cellulose-water system may not be completely understood under these conditions, the RFP results are surprising in view of the large amount of water reportedly present in the RFP samples and the effect of dose rate in aqueous systems.[12,13]

Possible explanations for the lower G values from RFP have been offered.[7] The G values reported by Kazanjian (RFP)[11] were determined from the slopes of graphs of the gas produced versus time after the oxygen had been depleted. Thus, they are not G° values and may be a measure of the rates after significant matrix depletion had occurred. However, the variability in the conditions under which these experiments were performed necessitates that the intercomparisons made among the three laboratories be viewed cautiously. The rate at which the total gas pressure changes during degradation depends on several variables, including the rate at which oxygen, in this case, is consumed. If oxygen is consumed at a rate that is negligible compared to the hydrogen production rate, for example, then the G values measured from the initial rate of production are truly G° values. This is not the case as the oxygen depletion rate becomes comparable to the production rate. In the case of the SRL results,[10] G° values were measured from experiments that were not conducted for more than 100 hours. The extent and rate of oxygen depletion after such a short observation time was not evaluated. The LASL G° values were determined by extrapolating G(gas) versus total dose curves to t=0. For the lower dose rates ($\leq$40X), the extrapolations were through regions where little or no data were collected due to the small gas production rates at these waste loadings. As mentioned in (2) above, the dependence of G(gas) on dose rate is anomalous, possibly due to the fact that G(gas) decreases rapidly in the region where no data exist.

Another concern is the depletion of the waste matrix. For particles of high linear energy transfer such as alphas, the rates of gas production from degradation are dependent on the amount of energy absorbed by the material. The greater the range of the alphas in the material, the greater the extent of degradation. Kazanjian recognized this fact but stated it in contradictory terms.[11] He concluded that for contaminant particles larger than 30 μm (PuO_2 in this case), the depletion times would be on the order of a few months, and for particles on the order of atomic dimensions, the material would never be depleted. As the PuO_2 particles increase in size, more of the alpha energy is absorbed by the contaminant and less is available for gas generation. This implies that depletion times should be longer, not shorter as suggested by Kazanjian, for larger particle sizes. Experimental results on TRU contaminated concretes from SRL are in contrast to those from RFP as regards particle size,[14] i.e., $G(H_2)$ from the alpha radiolysis of water decreased as the size of the PuO_2 particles increased. Some points regarding the reliability of data and interpretations based on matrix depletion were made by Kazanjian.[11] If the rates depend on depletion of material, then movement of contaminant particles can increase or decrease the rates.[5,11] A non-uniform dispersion of particles throughout the matrix can result in similar behavior due to increased alpha flux within a given volume. It has been stated that gas volumes generated by alpha radiolysis depend on contaminant particle size and distribution.[5] However, no corroborating evidence is apparent in support of this conclusion except for a comment on the possible dispersion of Pu-238 contaminant in a drum that was generating significant amounts of hydrogen. Other disconcerting results from RFP involved an anomalous dose effect. Wastes loaded with Pu-238 had a dosage about 200 times greater than the same wastes loaded with Pu-239. As Kazanjian noted, under similar experimental conditions, the Pu-238 should have been more effective in gas generation but the results did not strongly support the predicted behavior.

(5) A synergistic enhancement of gas generation was found with increased temperature. Upon going from 20° to 55°C, the production rate increased by 43%. For an increase from 20° to 70°C, rates increased by about 70%, diminished to 30% after 70 days and stabilized. The higher temperature experiments produced more gas even at long exposure times. The synergistic effect decreased with time but apparently did not disappear completely.[15] The observed decrease at elevated temperatures could be due to a matrix depletion phenomenon.

(6) In experiments designed to assess the effect of pressure on gas generation rates at LASL,[15] highly doped organic matrices (cellulosics and polyethylene) were allowed to self-pressurize. The experiments were compared to those in which the pressure was relieved at 100 kPa over ambient. The indication was that the generation rates decreased as the pressure increased. These data are in agreement with results from Zerwekh[5] conducted along the same lines. Cylinders of Pu-238 contaminated cellulosics were allowed to self-pressurize to 690 kPa,

sampled, depressurized, allowed to pressurize, etc. When compared to experiments in which the maximum pressurization allowed was 101 kPa, the rate of gas formation was less in the more highly pressurized cylinder. In addition, water formation from cellulosics was observed in cylinders that self-pressurized to 690 kPa but not for the 101 kPa pressurization. A suggested explanation is the recombination of H_2 and O_2 at the higher pressures although this has not been experimentally proven. This is interesting in that the oxygen initially present is depleted in about 3 to 4 weeks,[11] and initial sampling of the high pressure cylinder occurred after 285 days of reaction. SRL results showed no change in the rate of pressurization up to 1380 kPa for the alpha radiolysis of concrete and TRU contaminated sludge simulant. Pressurization of cylinders of highly doped cellulosic and polyethylene matrices to 10.4 MPa with deuterium suppressed the rate of hydrogen formation by 50 to 60%. The decrease appears to be the result of (a) recombination of D_2 with the matrix while H_2 is still being generated, or (b) very small leaks from the pressurized cylinders.[15]

4.2.1.2 Other Organic Waste Matrices (Polyethylenes, Pump Oil, Polyvinyl Chloride, Composite, and Asphalt)

This section will summarize the important results found for the above mentioned waste forms.

(1) According to LASL results, low density polyethylene (G° listed in Table 4.3) behaved in a similar manner to the cellulosics,[5] with some notable differences. The only major product from irradiation of thin (0.05 mm thick), low density polyethylene was hydrogen. $G(H_2)$ decreased as a function of total dose.[5,11] After 1318 days, no gas generation (LASL) was observed from alpha radiolysis of 100% cross linked high density polyethylene (2.3 mm thick) contaminated with Pu-238 to about 50X.[5] In contrast to these results, a value of G(gas) (listed in Table 4.3; note this is not G°) of 0.73 (Pu loading of about 100X) was found at RFP for 0.08 mm thick polyethylene after 270 days of exposure.[11] The reasons for the discrepancies were not addressed.

(2) A composite organic matrix consisting of 35% cellulose, 23% polyethylene, 12% polyvinyl chloride, 15% neoprene and 15% Hypalon (representative of typical LASL TRU waste) yielded mainly H_2 and CO_2.[5] Waste material typical of that from Mound Laboratory did not undergo degradation from alpha radiolysis after 400 days exposure.[5] This is quite surprising since the contaminant loadings and composition of the matrices were very similar in both sets of experiments.

(3) Some confusing results have been reported for the radiolysis of polyvinyl chloride (PVC). In experiments conducted at LASL, PVC exposed to a dose rate of 1X had an induction period of 8 to 10 weeks.[15] G(gas, 70°) was estimated to be 8 to 11 or greater, the largest G

value observed for any matrix studied and the only one whose G(gas) increased with increasing total dose. Thermal degradation was ruled out by control experiments. The gas was composed mainly of hydrogen, no chlorine species were detected by mass spectrometry although HCl has been reported to be a radiolysis product.[16,17] In an additional report from LASL,[5] Pu-238 contaminated PVC (1X dose rate) produced only 10 cm^3 of gas after 335 days, leading the author to conclude that insignificant quantities of gas are generated by alpha radiolysis of this material. In alpha radiolysis experiments conducted at RFP, PVC was contaminated with Pu-238 (28X) and Pu-239 (4X).[11] A higher G(gas) was found in the case of the Pu-239, an anomalous result in terms of dosage and matrix depletion. For other matrices, the G(gas) obtained by RFP was much lower than LASL's.

(4) Concerning results on the radiolysis of pump or machine oil from LASL, SRL, and RFP, there is general agreement that hydrogen is the main product and that CO and CO_2 are produced at the expense of O_2.[5,10,11] The values for G(total gas) listed in Table 4.3 for pump oil are G°(H_2) from SRL, G°(gas) from LASL, and G(gas) from RFP. The G values from SRL and RFP have been corrected for energy absorption by the chemical absorbent used in these experiments. The contaminant loading was about 280X for SRL, the lower limit for RFP was about 4X. In the case of the LASL experiments, the production of gas for a contaminant loading of 25X was approximately the same as that for a loading of 50X. Regardless of the differences in experimental conditions among the various laboratories, G(H_2) is significant for hydrocarbon oil as substrate.

(5) Bitumenization processing is used extensively in Germany for radwaste immobilization.[18] However, not much work has been done on the alpha radiolysis of this organic material. The major gaseous product formed from degradation is hydrogen, with some methane also reported.[15,*] Preliminary results from LASL indicate that the gas generation rate for bitumen is smaller than for cellulosics (dose rate = 160X).[16] A G°(gas) of 1.4 has recently been found.*

4.2.1.3 Concrete

Waste acceptance criteria extend beyond organic combustible wastes to other potential gas producers that might be placed in a repository. One waste form that has potential as a candidate material for solidification of TRU contaminated incinerator ash and process sludges is concrete. Experimental studies of gas evolution from the alpha radiolysis of concrete have been conducted at SRL as part of the WIPP project. The objectives of the SRL program are to determine (a) the relative gas generation capacities of concretes versus organic matrices, and (b) techniques and additives that could significantly reduce the gas generation rates of concrete.

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*S. T. Kosiewicz, Los Alamos Scientific Laboratory, private communication to G. Bida, BNL, March 28, 1980.

In the studies on process sludge incorporation, samples of simulated Savannah River Plant wastes were mixed with a high alumina cement to make concretes.[19] The cement composition used was (by wt. %) Al_2O_3, 41; CaO, 37; SiO_2, 9; Fe_2O_3, 6; and MgO, 2, plus some other oxides. Alpha radiolysis experiments were performed with concrete containing 40% (w/w, dry) SRP simulated wastes plus a known amount of Cm-244. The simulated waste was composed of equimolar mixtures of Fe(III) and Al(III) hydroxides or of Fe(III) and Mn(IV) hydroxides. The significant results for the alpha radiolysis of concrete plus simulated SRP sludge are:

(1) Both oxygen and hydrogen were produced in a O_2/H_2 ratio that varied from 0.2 to 0.5.

(2) For a dose rate of 2.8×10^{20} eV/hr (about 75X), the total gas pressure increased nearly linearly up to the maximum tested pressure of 1380 kPa. For gamma radiolysis under similar experimental conditions, a maximum steady state pressure of about 345 kPa is attained.[19]

(3) The G values reported were $G(H_2) = 0.21$ and $G(O_2) = 0.10$. $G(H_2)$ appeared to be independent of dose rate over the range studied (1.6 to 2.8×10^{20} eV/hr).

(4) An estimate of the long term pressurization of a sealed canister, typically 2 feet (I.D.) x 10 feet tall (10% free volume), containing concrete plus SRP wastes was made. The conceptual waste composition included Sr-90, Cs-137, Pu-238, and Pu-239. For the waste container and other assumed conditions (e.g., volume, weight of waste, dose, etc.), a final pressure of 2100 psig (14.5 MPa) after 10^5 years was calculated.

Cement types investigated at SRL were high alumina cement (HAC), Portland Type-I cement (I), and Portland-Pozzolanic cement (I-P). The compositions of these cements are given in Table 4.4. Concrete samples were prepared by mixing

Table 4.4

Composition of Various Cements
(From Table 1 of Reference 20)

	Composition, wt %						
Cement Type	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3^a	Other
High Alumina	36.5	8.5	40.5	5.5	1.0	0.2	7.8
Portland Type-I	63.1	21.3	5.8	2.6	2.9	1.8	2.5
Portland-Pozzolanic	50.5	37.0	4.7	2.1	2.3	1.5	1.9

[a] Present as sulfate.

30% (dry weight) ash in the dry mix with a Pu-238 solution or by adding PuO_2 particles to the mix. After evaporation at 20° to 23°C, the concrete consisted of 60 to 70% (w/w) water. The ash was obtained from incineration and calcination (at 800°C) of typical SRL TRU laboratory wastes. The samples were then placed in steel cylinders equipped with pressure transducers. The G values for these experiments were calculated from the rate of pressure change and also from the final gas composition and total dose. If oxygen is depleted by radiolysis, the G(gas) value calculated from the rate of pressurization will be less than that calculated for $G(H_2)$ from the final composition. The results obtained for the alpha radiolysis of concretes are summarized in Tables 4.5 and 4.6 and discussed below.

(1) The gas composition after radiolysis is apparently a function of the material in which the concrete was cast during curing. If the concrete was prepared as a monolith by using a removable mold, no oxygen was produced. A possible explanation is reaction of oxygen precursors with something that might have leached from the plastic mold. If the concrete was cast and cured in a steel cylinder, oxygen was produced.[21] In experiments where oxygen formation was observed, less than a stoichiometric amount was generated. This was also observed for the incorporation of SRP sludges into concrete.[19] This is an indication of some other oxidation product being generated, consistent with the observed behavior for the alpha radiolysis of water.

(2) For HAC, I, and I-P contaminated concretes cast in plastic molds, hydrogen was the only gas produced, oxygen was depleted and nitrogen was unaffected. The depletion of O_2 accounts for the fact that, in some cases, $G(gas) < G(H_2)$. $G(H_2)$ increased in the presence of added ash due to its water content. I-P concrete was eliminated from further study after these experiments. Control experiments conducted with non-radioactive samples of HAC and ash at three different temperatures confirmed that both hydrogen production and pressurization resulted from radiolysis.

(3) $G(H_2)$ was found to be independent of both temperature (up to 100°) and dose rate over the range 10^{16} to 10^{17} eV/min/g. For a mechanism that postulates H_2 formation from recombination of H atoms produced by the radiolysis of water, a lack of dose rate effect seems surprising.

(4) $G(H_2)$ is independent of the pH (0.6 to 7) of the water used in mixing the cement and ash. Previous experiments had used Pu-238 dissolved in 0.2 M H_2SO_4 solution. Actual waste will be added to the cement as a solid and the concrete will be made with neutral water. Thus, it was important to determine the pH dependence of $G(H_2)$.

(5) When Pu-238 was added as solid PuO_2 particles rather than being dissolved in the water used to make concrete, the G(gas) dropped from 0.51 (Pu, L) to 0.21 (Pu, S) for HAC and from 0.55 (Pu, L) to 0.27 (Pu, S) for Type-I concrete. The decrease in G is due to the absorp-

Table 4.5

Radiolysis Data of High Alumina Concrete-TRU Ash Samples
(Data obtained from Table 4a of Reference 7)

Cast as Monoliths (5 cm x 1.7 cm O.D.), Removable Mold

Test Condition		T°C (±2°C)	$G(H_2)$	G(Total Gas)
Without ash, Pu(L),	hdr	23	0.42	0.33
With ash, Pu(L),	hdr	23	0.55	0.51
With ash, Pu(L),	ldr	23	0.48	0.24
With ash, Pu(L),	hdr	70 sh	0.24	0.14
		70 hs	0.15	0.17
		100 hs	0.13	0.15
With ash, Pu(S)	hdr			
Non-heated (36% water)		23	0.21 ± 0.01	0.21 ± 0.03
Heated at 200° (17% water)		23	$0.02\overline{2}$	$0.01\overline{6}$
With ash, EDTA, Pu(L),	hdr	23	0.32	0.15
		70 sh	0.19	---
		70 hs	0.06	0.04
With ash, 0.01 M $Fe(NO_3)_3$, Pu(L)		23	0.30	0.25
With ash, 1 M $Fe(NO_3)_3$, Pu(L)		23	0.08	0.43
With ash, 2 M $Fe(NO_3)_3$, Pu(L)		23	0.03	0.43
With ash, 0.3 M $NaNO_2$, Pu(S)		23	0.15	0.14
With ash, 1 M $NaNO_2$, Pu(S)		23	0.079	0.087
With ash, 3 M $NaNO_2$, Pu(S)				
Non-heated (36% water)		23	0.084	0.03
Heated at 200° (27% water)		23	0.031	0.023

Cast in Steel Canister (10 cm x 2 cm I.D.)

Test Condition		T°C (±2°C)	$G(H_2)$	G(Total Gas)
With ash, Pu(S),	hdr	23	0.28 ± 0.04	0.31 ± 0.01
No[illegible]lated ash,	ldr	23	0.29^{-}	0.30^{-}
Heated at 90°C (22% water)		23	0.074	0.10
Heated at 200° (14% water)		23	0.0005	N.M.

Notes:
Pu(L) = Pu-238 in 0.2 M H_2SO_4
Pu(S) = particulate Pu-238-O_2
hdr = high dose rate, 10^{17} eV/min/g
ldr = low dose rate, 10^{16} eV/min/g
sh = sealed, then heated
hs = heated, then sealed
N.M. = not measurable

Table 4.6

Radiolysis Data of Portland Type-I Concrete-TRU Ash Samples
(Data taken from Table 4b of Reference 7)

Cast as Monoliths (5 cm x 1.7 cm O.D.), Removable Mold

Test Condition	T°C ($\pm$2°C)	$G(H_2)$	G(Total Gas)
Without ash, Pu(L), hdr	23	0.43	0.48
With ash, Pu(L), hdr	23	0.65	0.55
With ash, Pu(L), ldr	23	0.63	0.61
With ash, Pu(S), hdr	23	0.28	0.27
With ash, Pu(L), hdr	70 sh	0.48	0.46
	70 hs	0.15	0.17
	100 hs	0.11	0.05
With ash, EDTA, Pu(L), hdr	23	0.35	0.05
	70 sh	0.31	0.29
	70 hs	0.08	0.07
	100 hs	0.05	0.03
With ash, 0.01 M $Fe(NO_3)_3$, Pu(L)	23	0.34	0.31
With ash, 1 M $Fe(NO_3)_3$, Pu(L)	23	0.08	0.43
With ash, 2 M $Fe(NO_3)_3$, Pu(L)	23	0.03	0.16

Cast in Steel Canister (10 cm x 2 cm I.D.)

Test Condition	T°C ($\pm$2°C)	$G(H_2)$	G(Total Gas)
With ash, Pu(S), hdr			
Non-heated (30% water)	23	0.32	0.49
Heated at 90° (28% water)	23	0.20	0.30
Heated at 100° (8.2% water)	23	0.009	N.M.
Heated at 200° (7.4% water)	23	0.00029	N.M.

tion of some of the alpha energy by the larger PuO_2 particles. No major difference was observed whether the Pu-238 was added as PuO_2 or as ash from incinerated combustible trash.

(6) G(gas) values were significantly decreased by addition of scavenging agents such as nitrate and nitrite ions that reacted with H atoms and solvated electrons (hydrogen precursors). Addition of NO_3^- (as ferric nitrate) decreased $G(H_2)$ from 0.55 to 0.08 (1 M NO_3^-) or 0.03 (2 M NO_3^-) for HAC. For Type-I, $G(H_2)$ decreased from 0.65 to 0.08 or 0.03. However, oxygen production was significant. NO_2^- was added to the cement/ash mix in which PuO_2 particles had been incorporated. Acid solution could not be used because of the instability of NO_2^- ions at low pH. For 3 M $NaNO_2$, $G(H_2)$ changed from 0.22 to 0.084. Also, oxygen was consumed in the presence of NO_2^-, possibly due to oxidation of NO_2^-.

(7) Another approach used to reduce gas yields was lowering the water content by heating the concrete to remove free water. Most of the water in concrete was removed by heating (200°C) for several hours. This reportedly does not severely affect the strength of the concrete.[22] As can be seen from the results in Tables 4.5 and 4.6, $G(H_2)$ was greatly reduced for HAC and Type-I concrete. Heating had no effect on $G(H_2)$ for an HAC sample that contained NO_2^-.[7] The tremendous decrease in gas yields due to removal of free water indicates that the water involved in the hydration reactions is not very susceptible to radiolysis, possibly because of the ability of the water of hydration to transfer absorbed energy.

(8) Preliminary results on gas generation from pressed concrete pellets are promising.[21] The pellets, containing TRU incinerator ash, are compressed at 173 MPa. They contained about 3% (w/w) water and can accommodate up to 70% (w/w) ash. Results from some of these experiments are summarized in Table 4.7 for Portland Type-I cement containing three different simulated waste compositions.

Table 4.7

Pressed Concrete Pellet Results
(Data Taken From Table 5 of Reference 7)

Simulated Waste	$G(H_2)$
SRL Ash (primarily Ca, Ti)	0.005
ML Ash (primarily Si, Ca)	0.009
Bone Char[a] (primarily Ca, C)	0.003

Pellet Weight Composition:
65% ash (dry), 35% Portland Type I cement (dry), 3% water.

[a] Commercial absorbent, used to sorb Pu.

(9) Rewetting both the pressed concrete and the dehydrated (200°C) samples resulted in significant increases in $G(H_2)$. This emphasizes the importance of maintaining a water free environment in the case of this waste form.

The rate of hydrogen gas generation from TRU ash incorporation in concrete has been calculated for an assumed scenario:[7,14] (a) the concrete/TRU ash was contained in a 210 liter drum with a 10% void volume plus an assumed 10% porosity for the concrete; (b) waste contained 200 grams of weapons grade Pu-239; (c) all the alpha decay energy was absorbed by the waste form. The pressure increase as a function of storage time for various waste treatments or additives is shown in Figure 4.1.[7] Since the drums are not capable of holding pressure (see below), the void volume and pressure buildup can be considered as possible scenario conditions in an emplacement room.

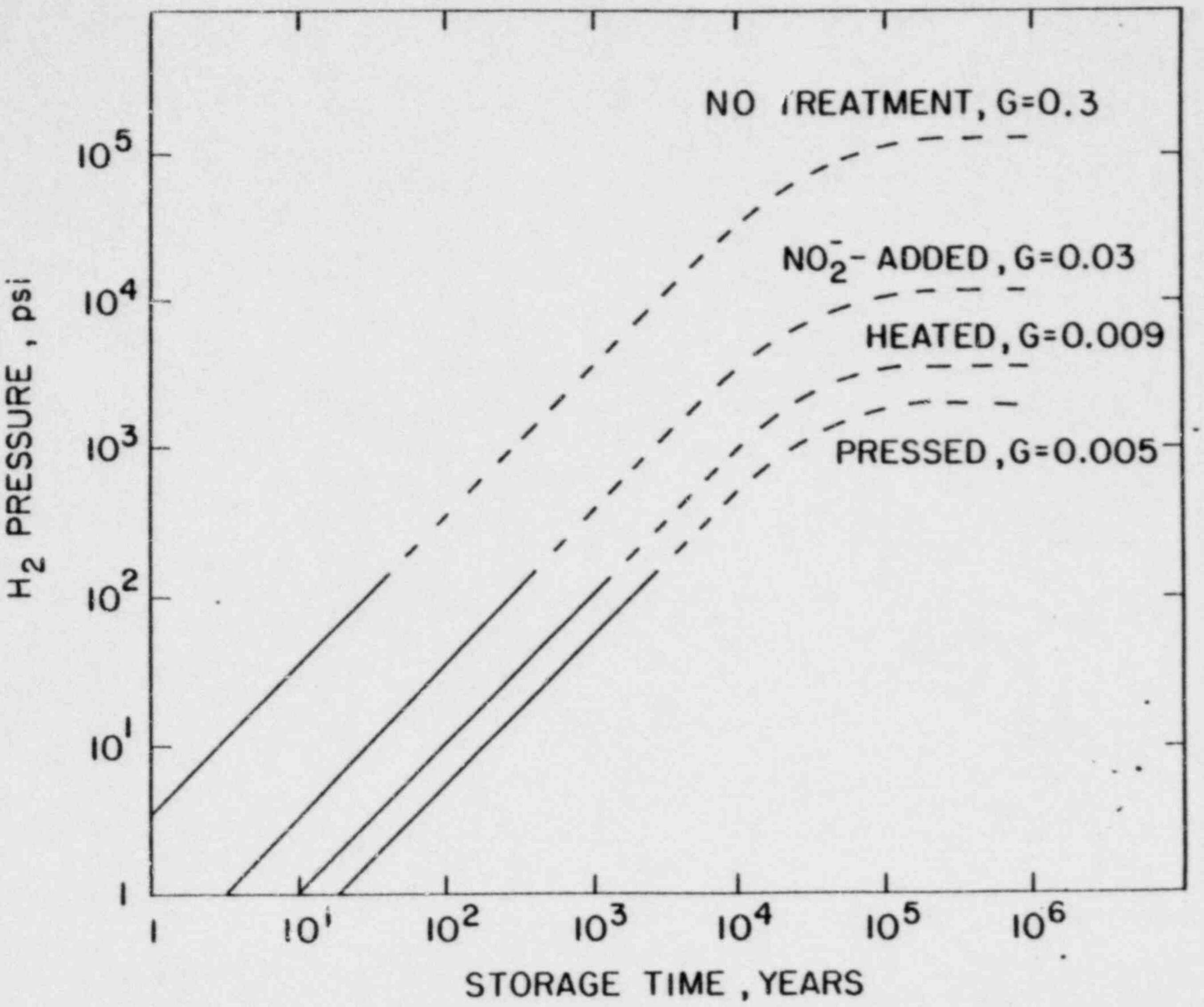

Figure 4.1. Long term pressurization for concrete-TRU ash matrix.

4.2.1.4 Field Studies

Some important data have been collected at LASL,[5] SRL, and RFP on gas generation in drums of production wastes.[7] The experiments were conducted on drums either in the field, brought back to the laboratory, or under field conditions simulated in the laboratory. At LASL, 115 liter drums of Pu-238 contaminated or 210 liter drums of Pu-239 contaminated organic wastes were periodically monitored for their gaseous content and, in the case of Pu-238, temperature and pressure. The amount of contaminant in the drums ranged from about 3×10^3 to 3×10^5 nCi/g of waste for Pu-239 and approximately 10^7 nCi/g for Pu-238. In addition to these experiments, gas mixtures from some of the drums contaminated with Pu-238 and from the cylinders containing hydrogenous wastes were evaluated for their explosive potential. The results from these and other tests are as follows:

(1) No significant pressurization above 1 atmosphere was observed due to gaseous diffusion through the drum sealing gaskets.

(2) Little evidence for gas generation from Pu-239 alpha radiolysis was seen, due mainly to diffusion of gas into and out of the drums. This does not imply that an explosive mixture is not possible in these waste containers, especially if the sealing were improved.

(3) Drums containing Pu-238 contaminated wastes generated gases, most notably H_2. Again, amounts could not be determined because of diffusion. Some of the gas mixtures in the drums were found to be explosive. After a period of time, some of the mixtures reached combustible compositions. Hydrogen concentrations increased with time and the oxygen was depleted due to CO and CO_2 formation.

(4) Tests conducted to establish the explosive limits of gas mixtures from radiolytic degradation of the organic wastes indicated that mixtures with $H_2 \leq 6$ mol % are probably not explosive. Pu contaminated wastes buried (5 years) in culverts at SRL resulted in hydrogen concentrations that exceeded minimum explosive limits.[7]

(5) Similar results were obtained for drums containing typical SRP wastes.[23] Hydrogen concentrations as high as 25% (v/v) were detected.

4.2.2 Thermal Gas Generation

The thermal degradation of waste matrices such as paper, cotton, composite and polyethylene at temperatures of 20°, 40°, 70°, and 100°C has been studied at LASL. The maximum temperature range anticipated in the proposed WIPP facility is 40° to 70°C.[15] Thermal degradation was monitored via thermogravimetric analysis to determine threshold decomposition temperatures and gas generation rates. The following observations concerning thermal degradation of organic matrices have been made:

(1) Materials such as rags, paper, polyethylene, PVC, latex, butasol and neosol did not decompose in air up to 150°C. At 200°C, all test specimens began to char and decompose. Thermal decomposition temperatures in air ranged from 175°C to 205°C for cellulosics, 150°C to 210°C for plastics, and 165°C to 195°C for rubber materials. Asphalt began to decompose at 275°C.

(2) Some studies were conducted under anaerobic conditions since oxygen was shown to be consumed in previous experiments.[15] Threshold decomposition temperatures under anaerobic conditions did not vary significantly from those found in air.

(3) The potential effects on decomposition temperature were investigated for catalysts found or formed by storing drums of TRU waste in a salt repository. Catalysts included NaCl, Fe_2O_3, $FeCl_2$, and Fe powder (2 to 38% w/w loading). These catalysts showed only minor changes in threshold temperatures (± 30°C from no catalyst situation). It should be noted that all of the measured decomposition temperatures are much higher than those anticipated at the WIPP TRU horizon.

(4) Due to the fact that degradation rates are relatively small, the gas generation experiments are long term studies. Thus, the results should be considered preliminary. At this time, the inconsistencies in the available data allow only qualitative statements to be made. Some gas generation has been observed at 70° and 100°C but not at 40°C. However, since the rates are so small, the possibility exists that generation due to bacterial degradation is occurring simultaneously,[15] thereby masking trends from thermal degradation. In partial support of this hypothesis, the gas generation rate measured at 70°C (LASL) is about five orders of magnitude greater than that predicted by previously available data,[24] thus indicating that some other degradation mechanism is operative.

(5) The gases generated by thermal degradation were composed mainly of CO_2 in the case of cellulosics and composite and O_2 in the case of cotton and polyethylene.

(6) Rates of dewatering LASL process sludge (25° to 100°C) were determined for conditions chosen to represent the WIPP environment. The time required for complete dewatering at a particular temperature, compared to the time required at 100°C, closely approximated the ratio of the vapor pressure of water at the temperature of dewatering to that at 100°C.[15] The conclusion from these experiments was that in the event of breach the sludge water will be rapidly (on a geological time scale) absorbed by the WIPP salt.

(7) Cement paste, used to immobilize certain LASL TRU waste, was found to be much more difficult to dewater than process sludge. For example,

only 3.3% (w/w) of water was evolved from the paste (containing no less than 10% (w/w) water) at 100°C. Some possible effects of thermal dewatering are:
(a) Dissolution of salt to yield brine pools or lenses.
(b) High humidity in a mine, pumped out via ventilation system during working phase of facility.
(c) Potential enhanced corrosion of metallic waste canisters, instrumentation, and mining-engineering equipment.
(d) Hydrolysis and hydration of minerals (anhydrite, clays, etc.) with consequent potential swelling effects.
(e) Leaching or dissolution of waste materials resulting in the potential water/brine mobilization of radionuclides as true solutions, colloidal dispersions, or entrained particulate material.

4.2.3 Microbial Gas Generation

At this time, all the relevant information and data pertinent to this area has not been received or thoroughly reviewed. However, the material presented in two technical reports dealing with this subject, and discussed in Reference 7, will be summarized below. The existing TRU contaminated waste may contain sufficient quantities and types of bacteria and fungi to cause microbial degradation. One important consequence of the degradation is the generation of potentially explosive gas mixtures produced by various metabolic processes.[25] The status of the results from studies conducted at LASL and UNM on the bacterial degradation of organic TRU waste is presented below. The waste matrices investigated included composite, sawdust, asphalt, composite without the cellulosic content, and carboxymethyl cellulose. The sawdust is representative of the plywood used in fiberglass reinforced polyester plywood boxes (FRP) that are used for waste disposal, and the carboxymethyl cellulose is used as a medium for bacterial detection. Parameters studied for their effect on gas production rates were incubation temperature, aerobic versus anaerobic conditions, solution content (e.g., de-ionized water, buffer, etc.), solution to waste ratio, and microbial inoculant. Control samples were utilized to correct for any gas generation of thermal origin.

(1) The only gas produced in significant quantity was CO_2. Methane, although expected, was not observed. It was felt that this was due to a lack of appropriate methanogenic conditions. Studies have indicated that methane would be substituted for CO_2 on a mole for mole basis.[26]

(2) The more recent results do not clearly indicate any effects of temperature on gas generation.[27] Previous results indicated that the rate of CO_2 evolution, under aerobic or anaerobic conditions, depended on temperature with the rate reaching a maximum at 50°C.[28] This may be due to the difference in water to waste ratios for the two studies.

(3) More CO_2 is generated under anaerobic conditions.

(4) For aerobic or anaerobic conditions, less gas is generated when the waste is dry (1% H_2O) than when it is saturated. Also, brine did not significantly affect the rates.

(5) Of the waste matrices studied, the largest quantities of CO_2 produced (moles/year/waste container) were for sawdust. When the results for the 100% sawdust were recalculated in terms of the weight percent of cellulose in the composite matrix, the generation rates agreed fairly well with those observed for the actual composite matrix. This suggests that the cellulosic component of the composite is the predominant substrate in microbial CO_2 production. Actual gas generation rates for FRP boxes are not expected to be as great because of the polyethylene liner used and for surface area reasons.

(6) The results for gas generation from biodegradation of composite and asphalt are comparable under aerobic and anaerobic conditions (25°C). Gas generation was greater for anaerobic conditions with a dry (1% H_2O) waste composition, but was greater under aerobic conditions for saturated and brine solution systems. No explanations were offered for this behavior.

4.2.4 Gas Generation From Chemical Degradation

A detailed treatment of the topic of gas generation from the corrosion of mild steel drums will be reserved for future reports. Briefly, the preliminary data[7] indicate that hydrogen will be generated by a corrosion mechanism only in a moist, anaerobic environment. In a moist air environment, oxygen is consumed. Under expected WIPP repository conditions, the corrosion of steel is not expected to yield significant quantities of gas. Studies are currently under way to assess the usefulness of anti-corrosion coatings.[6]

4.2.5 Comparison of Degradation Mechanisms

For the purposes of this Interim Report, this completes the discussion of the DOE/WIPP program as regards gas generation. The ranges of gas generation rates from degradation of some of the organic waste matrices by the various operative mechanisms are summarized in Table 4.8. These rates neglect factors that may tend to decrease the rates, e.g., pressure, matrix depletion, unfavorable conditions, etc.

The concern about gas generation stems from the possible consequences for the performance objectives of the repository, namely, safety during the operational phase and radionuclide containment during the long term isolation phase. Among the consequences of gas generation that are important in view of the results discussed above are pressurization of the waste container and the combustion/explosion hazards of the gases produced. In 1970, the AEC issued a directive dealing with the continued burial of TRU wastes.[29] The directive also called for packaging and storing conditions that would allow retrieval for a period of twenty years. Thus, much of the work on gas generation via degradation of TRU wastes is concerned with the behavior of the waste presently buried and stored in steel drums or FRP boxes. It is also for this reason that Molecke[7]

Table 4.8

Observed Ranges of Initial Gas Generation Rates
(Data Taken From Table 13 of Reference 7)

Mechanism	Matrix	Total Gas Rate (moles/year/container)		Comments
Radiolysis	Cellulosics	0.0050-0.011		LASL, SRL
	Polyethylene	0.0073		LASL
	PVC	0.031-0.042		LASL
	Composite	0.0054		LASL
	Process Sludge	0.70		6.9 Ci
	Concrete-TRU Ash	0.046-0.91		poured, 15 Ci (SRL)
	Concrete-TRU Ash	0.00050-0.035		heated, 15 Ci (SRL)
	Asphalt	0.15-0.76		7.7 Ci
Thermal	Paper	1.3		70°C
	Polyethylene	1.9		70°C
	Composite	0.02-0.20		40°C, calc.
		Aerobic	Anaerobic	
Bacterial	Composite, Test 1	0.9	1.2	25°C
		12	32	50°C
	Composite, Test 2	0-1.6	0.3-4.2	25°C
		1.3-5.5	0.6-7.8	40°, 70°C
	Plywood Box	0-14	11-26	25°C
		2.8-19	6.8-23	40°, 70°C
	Asphalt	0.1-2.6	0-4.8	25°C
		0-8.4	0-1.9	40°, 70°C
Corrosion	Mild Steel	2.0		wet, deaerated
Alpha Decay	He Generation	3.7×10^{-8}		0.039 Ci
		1.5×10^{-5}		15 Ci

Table 4.9

Comparative Gas Generation Rates
(Data taken from Table 14 of Reference 7)

Mechanism	Matrix	Gas Limits (moles/year/drum)[a]
Bacterial	Composite, Aerobic	0-(0.9-5.5)-12[b]
	Composite, Anaerobic	0-(1.2-4.2)-32
	Plywood Box,[a] Aerobic	0-(0.44-2.2)-3.0
	Plywood Box,[a] Anaerobic	0-(1.1-3.7)-4.1
	(Plywood Box, Aerobic, 3.2 m^3)	0-(2.8-14)-19
	(Plywood Box, Anaerobic, 3.2 m^3)	0-(6.8-23)-26
	Asphalt, Aerobic	0-(0.1-2.6)-8.4
	Asphalt, Anaerobic	0-(0-1.9)-4.8
Thermal	Composite (40°C)	0-(0.02-0.2)-0.4
	Paper (70°C)	0.5-(1.3)-2
Radiolysis	Cellulosics	0.002-(0.005-0.011)-0.012
	Polyethylene	0.003-(0.007)-0.008
	PVC	0.01-(0.03-0.042)-0.08
	Composite	0.002-(0.005)-0.006
	Asphalt (7.7 Ci)	0.1-(0.15-0.76)-1.0
	Concrete-TRU Ash (poured, 15 Ci)	0.03-(0.045-0.93)-1.0
	Concrete-TRU Ash (heated, 15 Ci)	0.0002-(0.0005-0.035)-0.05
Corrosion	Mild Steel	0-(0)-2.0
Alpha Decay	He Generation	0.00002

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[a] drum volume = 0.21 m^3

[b] lower limit - (most probable range) - upper limits; the upper and lower limits reportedly reflect the estimated uncertainty in the data used to calculate the values in this column.[7]

chose to express gas generation rates in terms of characteristics that are typical of existing TRU wastes. In the absence of waste form and canister requirements for this waste, the characteristics listed in Table 4.2 plus the parameters described above provide a convenient reference scenario for the estimation of probable gas generation ranges. Based on some of the experimental data presented, the total amounts of gas generated per year per drum of existing and developmental TRU waste matrices have been estimated for each degradation mechanism considered.[7] These estimates, summarized in Table 4.9, represent the most probable ranges anticipated along with upper and lower limits that reflect the uncertainties in the measured data. From this Table it can be seen that the total quantity of gas generated by microbial degradation under WIPP environmental conditions is more significant than that from any other mechanism. Thermal degradation is of secondary importance followed by radiolytic degradation. It should be emphasized that the final total pressure in a waste container depends very much on the size of the container and its void volume (see Section 4.2.1.3). Since it is difficult to maintain a gas tight seal on the storage drums in use, the effect of gas generated in the repository has to be assessed in terms of gas accumulation/dissipation, fracture propagation resulting from stress due to pressure buildup, etc. These topics have been addressed,[8] and will be included in future reports. The other consequence of importance, i.e., the combustion/explosion hazard of the gases was treated in Section 4.2.1.4. Thus, the assessment of the acceptability of existing organic combustible TRU wastes for repository disposal must be made in terms of the proposed criteria that deal with the short term considerations.

4.3 Conclusions and Support for Proposed Criteria

The immediately applicable proposed criteria and guidelines governing the allowability of combustible organic TRU wastes in a repository,[30] as given in 10 CFR 60, are as follows:

(1) The physical waste form and its associated packaging shall be considered as the primary barrier to the release of radionuclides, and shall take into account the leachability, solubility, and other potential physical and chemical interactions between the physical waste forms, packaging, emplacement media and the surrounding groundwater, so as to minimize the potential for release, dispersion and migration of the radionuclides.

(2) The waste form and its associated packaging, and the emplacement methods and schemes shall be such that emplacement in the host medium for the purposes of disposal shall not result in physical, thermal or chemical changes which compromise the ability of the repository to isolate the radionuclides from the biosphere and shall preclude accidental criticality.

(3) All solid or solidified radioactive waste classified as combustible shall be incinerated or otherwise reduced to a non-combustible ash which shall be fixed in a solidification matrix, or the original combustible wastes and their associated packaging shall be such that a fire and/or explosion involving a single package cannot migrate to involve other packages.

(4) There shall be no known explosive or pyrophoric materials or conditions existing in the radioactive waste, nor shall there be any gross quantities of highly toxic chemical wastes.

In what follows, several arguments and conclusions from the available data are listed that have been considered with respect to these criteria.

(1) It has been stated[5] that drums containing the average amount of Pu-239 contaminated organic wastes do not generate measurable quantities of gas and, indeed, data accumulated over a two year period for drums with low Pu-239 loadings support this conclusion. However, this is not to say, given sufficient accumulation of total dose, presence of oxygen, and the uncertainty in some of the data, that explosive mixtures of hydrogen and oxygen are unattainable in some of the drums. If the generation of gas is independent of dose rate and decreases slowly with time at low Pu loadings, then measurable quantities of gas could indeed be generated in due time. It should be noted that an estimate of the amount of H_2 produced (extrapolated to 20 years) from radiolysis of Pu-239 contaminated combustible organic material[11] would exceed explosive limits in air in a closed storage facility.[5]

(2) The enhancement of radiolytic generation rates by increased temperatures will serve to generate explosive gas mixtures over relatively shorter time periods. This synergistic effect[15] will persist for some time since the repository temperature will rise fairly rapidly (to about 50°C; higher if emplacement is in close proximity to HLW) and then return to ambient very slowly.

(3) An argument has been made concerning the benefit, for underground disposal, of the decrease in gas formation as the canister pressure increases. The fact that the steel drums presently in temporary storage leak at pressures in slight excess of one atmosphere precludes any potential benefit of pressurization.

(4) One of the most important observations of the degradation of cellulosic material was the presence of a tan powder in the test cylinders that were opened after termination of the radiolysis experiments.[5] This powder was found to contain about 50% of the TRU contaminant originally added. It was also highly combustible and easily dispersible.

(5) Radiolysis can and does produce combustible and explosive gas mixtures in drums of trench stored, highly Pu-238 contaminated TRU wastes. Caution has been suggested in attempts to recover or reprocess temporarily stored Pu-238 contaminated wastes due to the potentially explosive atmospheres within these drums. This same warning was issued for the Pu-239 contaminated wastes that have been in storage the longest.

(6) The amount of combustible TRU contaminated waste in retrievable storage at LASL, for example, is about 20% (v/v) of the total inventory. However, only a few items, combustible and non-combustible,

do not have the potential to be gas generators. In a study aimed at establishing parameters for predicting explosiveness under a variety of conditions, 50% of the organic waste matrices studied generated explosive atmospheres. The initial gas samples were collected after only 94 days of storage.

(7) Although much useful information has been accumulated, large uncertainties and discrepancies in some of the experimental work necessitate viewing the results with caution. These discrepancies for the thermal and radiolytic degradation of organic wastes have been identified in Sections 4.2.1.1, 4.2.1.2, and 4.2.2 above, and elsewhere.[31] As concerns bacterial degradation, the status of this information is only preliminary. However, it appears that this mechanism has the potential to generate the largest amount of combustible gas under methanogenic conditions. Additional important information is lacking in this area, e.g., gas generation as a function of time (for both rate and quantities of gas produced), effect of pressure on generation rates, and effects of actinide contaminants. Finally, the potential for gas generation depends on the proper type and quantity of bacteria and how well they will flourish in a repository environment. This behavior will be very difficult, if not impossible, to predict.

(8) Processing of combustible organic TRU wastes followed by immobilization could lead to the elimination or substantial reduction of gas production by bacterial, thermal, and radiolytic processes. Results on immobilization of TRU incinerator ash in concrete (SRL and MF) are encouraging. Also, results on alpha radiolysis of borosilicate glass have found no gaseous products.[324] The benefits of processing also include volume reduction plus greater acceptability for purposes of handling, transportation, and mine emplacement.

4.4 Recommendation

Based on the presently available information on proposed repository waste acceptance criteria, it is strongly recommended that combustible organic TRU wastes be processed (by incineration, slagging, etc.) and the ash immobilized in an inert, durable waste form for the purpose of long term repository isolation. The key reasons for suggesting this recommendation are:

(1) Elimination of the potential for fire or explosion (with subsequent dispersion of radionuclides) in a handling, transportation, or emplacement accident due to combustion of the organic waste itself, the FRP plywood boxes, or due to combustion or explosion of the gases accumulated in the waste containers.

(2) Elimination or reduction of gas generation via the degradation mechanisms discussed.

(3) The volume reduction accomplished at the same time.

(4) Ease of conforming with existing regulatory guidelines.

It is interesting to note in DOE's most recent strategy document for the TRU waste management program[33] that they emphasize the decontamination of metal waste and the development of four types of incinerator for treatment of all combustible wastes. This indicates a realization by DOE that relatively sophisticated processing will normally be necessary to meet requirements for repository disposal, and that such processing has the advantage of volume reduction, a primary goal of the DOE TRU program.

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5. CONCLUSIONS AND RECOMMENDATIONS

The task on Alternative TRU Technologies addresses several areas of concern which are inherent in NRC's "strawman criteria." Certain conclusions have been drawn and recommendations made in the body of the report. These are assembled in this section along with a discussion of other points specified in the current task. It should be recognized that the conclusions and recommendations are based on the effort to date and may be modified as additional data become available.

5.1 Allowability of Combustible Waste in the Repository

The recommendation has been made (Section 4.4) that combustible organic TRU waste not be allowed in geologic repositories. Since incineration techniques are well established, we feel the position should be taken that all organic TRU waste must be incinerated and the incinerator ash immobilized in a suitable waste form before emplacement. Further support of this position is obtained from volume reduction considerations, covered in the next Section (5.2.1). It is our feeling that proposed requirements (including the release rate criterion) regarding incineration plus solidification in an appropriate matrix can more easily be met in this way than by attempting to prove that the thermal, chemical, and radiological stability of the combustible trash (and its associated packaging) (1) will not affect radionuclide containment and/or migration, and (2) will not affect (or be affected by) the emplacement medium.

Based on the argument of public health and safety, NRC will have to establish confirmatory testing procedures for whatever waste forms are proposed in order to ensure that the 10 CFR 60 requirements are met. These requirements include the strawman criteria and other pertinent requirements such as that excluding explosive and/or toxic substances. In the area of gas generation, items which require development of suitable tests include determination of the amounts and kind of gas formed and measurement of production rates.

Should the decision be made not to accept the recommendation concerning incineration and immobilization or if it is decided to extend the storage period of TRU combustible waste for a significant length of time, then the discrepancies in some of the existing data on gas generation must be rectified, uncertainties should be reduced and, in certain cases, the results should be confirmed by conducting replicate investigations. Some areas in which additional research is required, independent verification of the licensee's technical data base is deemed necessary, or evidence of compliance with proposed criteria should be given, have been listed below.

(1) Bacterial degradation has the potential to produce the largest amounts of gas, combustible or otherwise. However, much information is lacking. The lack of a thorough understanding of this process does not allow an assessment of long term repository behavior. Research in this area should include (a) duplication and verification of the original results concerning gas metabolism, (b) from a safety point of view, a thorough investigation of what conditions, if any, could lead to production of methane, or other combustible or explosive mixtures, and (c) a study of how the production rates are affected by various parameters (e.g., temperature, pressure, actinide contaminants).

(2) The dependence of G° values on dose rate should be reinvestigated. The conflicting data available on this subject, important to the prediction of long term stability and repository performance, necessitate that discrepancies be rectified and the uncertainties reduced.

(3) G(gas) decreases with increasing total dose, and this has been attributed to localized matrix depletion. However, some of the results are in question due to experimental procedures. With regard to the last two recommendations, the lack of reliable results can be due, in part, to the lack of similar experimental conditions. NRC should consider defining the appropriate testing conditions in these areas that it feels will provide the necessary information for a licensing decision.

(4) In experiments on radiolytic degradation of cellulose, formation of a tan powder was observed. These results should be verified. Since the tan powder was found to be highly contaminated, combustible, and easily dispersible, the onus would be on an applicant to show compliance with existing criteria governing" finely divided waste forms".

5.2 Waste Volume Reduction

5.2.1 Combustible Wastes

The recommendation has already been made (Sections 4.4 and 5.1) that combustible TRU wastes not be allowed in repositories because of the problems associated with gas generation. Even if it were permissible, there is still an important radiological incentive to keep the volume of waste to a minimum so as to decrease both handling and transportation requirements and thereby reduce risk to the public. The volume reduction would be achieved by incineration and immobilization of the incinerator ash in a suitable waste form. The additional advantages of the process are that the potential for gas generation would be minimized and radionuclide release rate would be decreased.

5.2.2 Contaminated Metal

A large fraction of the total TRU waste comes from contaminated metal. Ferrous metals from failed and decommissioned equipment make up the bulk of this waste at the present time, but Zircaloy cladding hulls will contribute substantially if processing of LWR fuel becomes a standard part of the fuel cycle. As described in Section 3.4, methods for decontaminating both classes of metallic waste on a pilot scale are well in hand and could presumably be developed to commercial scale in a short time. Reduction of contamination levels to well below the TRU limit of 10nCi/g is routinely achieved. The philosophy behind these decontamination programs, to reduce markedly the amount of TRU waste for geologic disposal, is appropriate and laudable. Providing secondary waste streams are a small fraction of the original contaminated metal, as they appear to be in most, if not all, cases, it is apparent that methods to obtain such a reduction have been developed. In view of this, we recommend that removal of TRU contamination from metals be seriously considered as the standard procedure for treatment of metallic TRU waste.

5.3 Emplacement of TRU Waste and HLW in the Same Repository

When WIPP was planned as the principal (perhaps only) U.S. repository for TRU waste, the suggestion was made that HLW also be emplaced on an experimental basis and perhaps permanently. This brings up the question of compatibility of TRU waste and HLW in the same repository. The matter can be considered from two points of view, namely that of how TRU waste could affect emplaced HLW and/or the repository, and that of possible effects of HLW on emplaced TRU waste.

5.3.1 Possible Problems Caused by TRU Waste

The most obvious problem which could arise from TRU waste is that of gas generation from combustible waste and certain waste forms. Release of toxic, combustible, or explosive gases would constitute a hazard to personnel, and possibly to waste packages, during repository operations. After the repository closure, combustible or explosive gases could cause damage to the repository and waste packages. Such problems would cease to exist if waste forms generating gases were excluded from the repository.

A possibility also exists of generating hydrogen and oxygen from α-radiolysis of water if TRU waste containers were breached and actinides leached out of the TRU waste form into ground water in the repository. However, if ground water were in the repository, it would be subject to intense gamma radiolysis from the HLW waste packages. Thus, for hundreds of years gas generation from this source would be considerably greater than that from α-radiolysis even if all the TRU activity were released from the TRU waste packages, so that the contribution to this problem from TRU waste would be small.

5.3.2 Effects of HLW on TRU Waste

The principal way in which HLW would affect TRU waste emplaced in the same repository is through the increase in temperature which would occur over the first hundred years or so. The precaution to be observed would simply be to require that the TRU waste package as well as the HLW package, be made to withstand the elevated tempertaure projected to be developed in the repository.

Another way in which HLW could cause a problem with TRU waste packages is via enhanced corrosion of containers caused by gamma radiolysis of the TRU waste package and its environs, probably only if these were aqueous, and particularly brines. This matter is considered in the Task 1 Report where it is concluded that under conditions which are expected to occur in bedded salt repositories, the problems could be appreciable. The obvious precaution for avoiding potential problems would be to require container quality similar to that of the HLW containers in that repository.

5.4 Research and Development Needed for Decontamination

As described in Section 3.4, methods for decontaminating the two main classes of metallic TRU waste, cladding hulls and failed equipment, have been developed at least to the pilot plant stage. Work is being done on methods of treating the secondary waste streams from the decontamination processes. Research and development should continue in this area to ensure that the secondary waste generated is compatible with acceptable waste forms, and that volumes for ultimate disposal are a small fraction of the volumes of initial contaminated material. As indicated in Section 3.4, development work on liquid honing should be carried out in order to solve the problem of dispersal of removed contamination so that a satisfactory alternative method will be available for in situ decontamination, and handling of large pieces of equipment.

5.5 Combination of HLW and TRU Waste

In Section 2.6 we considered the proposal of combining TRU waste with the HLW stream before production of the waste form. The idea has merit in terms of process simplification and decreased risk to the public because of decreased handling and transportation. We have seen no information indicating that it would not be applicable to disposal of this country's nuclear waste in geologic repositories. In fact, in view of the general tightening of criteria and regulations governing ultimate disposal of both HLW and TRU waste, we feel it is appropriate to recommend a thorough evaluation of the concept as the basis for a possible alternative disposal method for TRU waste.

5.6 Meeting NRC Waste Form Requirements

Section 111(c) of 10 CFR 60 which sets forth the release rate requirements for waste packages contains the sentence:

"To demonstrate that the waste package meets this as low as reasonably achieveable provision, a number of candidate waste forms and combinations of packaging should be selected for complete comparative evaluation and characterization."

So far this demonstration has not been accomplished, in large part, apparently, because HLW disposal was considered the paramount problem, whereas TRU waste disposal was thought to be of much less concern and easily handled. Thus, TRU waste form development was concentrated on several simple concepts, which have not proved adequate for NRC's requirements, instead of adopting the approach suggested above of selecting a number of candidate waste forms for complete comparative evaluation and characterization using the NRC criteria as guides.

- Of the waste forms considered in this report, bitumen and urea-formaldehyde are basically unacceptable because, like all organics, they are extensively damaged by high radiation doses. Decomposition from the radiolysis yields undesirable gaseous products as well as allowing incorporated radionuclides to become mobile and be released. Cast concretes are undesirable because of gas formation from water radiolysis and problems associated with dewatering. However, specially treated concretes such as FUETAP and cold-pressed concrete do not exhibit this problem. Leach rate data are too sparse to evaluate these concretes properly, but at this stage they cannot be ruled out as viable waste forms. The same is true for borosilicate glasses. Waste forms based on mineral phases appear promising from what little work and testing have been done, and the multibarrier forms have great potential for TRU waste as well as HLW.

- It seems ill-advised to continue work on waste forms which are unlikely to meet NRC criteria. It is recommended that effort be concentrated instead on those waste forms mentioned as having potential to meet the criteria. These include specially prepared concretes, borosilicate glasses, forms based on synthetic minerals and multibarrier waste forms.

- Although some of the initial results on special concretes, such as FUETAP, are encouraging, it is apparent that some areas require further research in order to provide and improve the data base necessary for evaluation of a candidate waste form. In some cases, the data are from results of scoping studies to determine the feasibility of these processes for concrete-waste solidification. Thus, although the assessment of the long term stability of some of these special concretes is now under way, additional research efforts should address whether the candidate waste form is capable of satisfying the strawman criteria and other criteria governing the thermal, chemical, and radiological stability of waste forms. To this end, the following points should be considered:

(1) Since the work with FUETAP and hot-pressed concretes has been done with simulated HLW process sludges, it should be determined whether they are capable of encapsulating TRU waste incinerator ash while maintaining long term stability.

(2) While hydrogen and oxygen are produced by radiolysis of water in FUETAP concrete, they recombine in the presence of the concrete at rates comparable to the rate of production. Research should be carried out to understand the recombination mechanism and the concrete's role. Without such an understanding, use of FUETAP concrete could lead to buildup of explosive atmospheres due to gas generation.

(3) The leach rate data for FUETAP are incomplete while those for the cold-pressed concrete are incomplete, questionable, and in need of verification. An extensive research effort should be undertaken to determine their leaching behavior under anticipated repository conditions, such as expected temperatures, and realistic leach solutions.

- Results on the incorporation of TRU incinerator ash in borosilicate glass are discouraging in terms of leach resistance. Also, based on results from PNL, the glass frit composition apparently has to be tailormade for a particular ash residue composition. Thus, it is not clear if the processing technologies and borosilicate glass composition developed for HLW immobilization are immediately applicable for TRU waste disposal. Additional research efforts are needed in this area and should include development of a frit composition that is flexible in terms of accommodation of various ash compositions, and demonstration of compliance with the release rate criterion by a thorough investigation of the glasses' leach resistance and long term radiological stability. This research effort should include leaching studies under realistic repository conditions, effect on leachability of radiation damage anticipated for realistic waste loaded glasses, and leach testing conducted on glass-TRU waste compositions and loadings that represent actual anticipated waste formulations.

- Synthetic mineral waste forms show great promise, but up until now no results of work with actual TRU have been reported. A relatively large effort should therefore be devoted to developing and characterizing a monazite waste form for TRU. Along with this development effort, a comprehensive program of leach testing should be carried out. No work is known to have been done on SYNROC as a TRU waste form. A simplified SYNROC based on the minerals perovskite and baddeleyite has potential to incorporate actual TRU waste in a very stable form, and a level of effort in characterizing and testing similar to that applied to monazite should be initiated. Both the monazite and SYNROC waste forms should be tested for stability to alpha radiation.

- The other HLW waste forms which BNL is suggesting should be given high priority as potentially excellent candidates, include porous glass and coated ceramics. Since these forms are not sensitive to the particular oxide composition of the waste, they would be just as suitable for TRU waste as for HLW, and, of course, for mixed HLW-TRU waste if a decision to combine the wastes were ever made. The coated ceramic could almost be considered "tailor made" for TRU waste, since its technology has been highly developed in the preparation of actinide (UO_2 and ThO_2) fuels for the High Temperature Gas Cooled Reactor.

- It should be noted that the second part of the strawman criterion -- radionuclide release rate of at most one part in 10^5 per year after 1000 years - is designed to protect the public from risks due to TRU isotopes remaining in HLW forms after the hazardous fission products Cs-137 and Sr-90 have decayed to safe activity levels. It is thus clear that research and development efforts on TRU waste forms based on HLW forms can be an adjunct to research on the HLW forms in addressing the strawman criterion, as well as serving their primary purpose of developing a satisfactory TRU waste form. This simply recognizes the fact that HLW forms become essentially TRU waste forms after a time of the order of 10^3 years.