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HIGH-LEVEL WASTE CONCENTRATION AND STORAGE - AN OVERVIEW

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CONCENTRATION AND STORAGE OF HIGH-LEVEL RADIOACTIVE WASTES

Chemical reprocessing of irradiated nuclear fuels to recover and purify uranium and plutonium (and possibly other valuable constituents such as neptunium) produces waste streams which are highly radioactive, hence, extremely toxic to man. These wastes must be managed and disposed of by techniques which are safe and economically reasonable. Under current regulations in the United States, applicable to commercial fuel reprocessors, these wastes may be stored in liquid form for a period up to five years and then they must be converted to solids. Later these solids will be transferred to a federal repository for storage and/or ultimate disposal.

Nearly all nuclear fuel reprocessing plants in the world today, and those planned for the near future, use a version of the Purex solvent extraction process. Large volumes of aqueous high-level waste which are moderately concentrated in nitric acid are produced in these processes. As a precursor to solidifying the wastes, they are concentrated and stored for some interim period. Most of the nitric acid present is recovered for reuse

in the plant; some <sup>may be</sup> is destroyed to reduce the acidity of the concentrated waste during interim storage.

This paper is intended to be an overview of high-level waste concentration <sup>and storage</sup> operations and some of the problems involved in them.

Other papers in this session will discuss some of these problems in greater detail. Papers in other sessions of this meeting will discuss waste solidification operations and problems.

#### Composition of High-Level Wastes

First, we need to define, as well as we can, what we mean by high-level waste, i.e., what is it that is to be concentrated and stored. For this paper, I will discuss <sup>primarily</sup> the high-level waste produced in the reprocessing of commercial power reactor fuel. However, many of the operations and problems are also common to the processing of ERDA fuels as we shall see from other papers in this session.

As an example of a commercial power reactor fuel, consider fully irradiated fuel from the light water reactor, Diablo Canyon.

Reference (1) gives the fission product and actinide element content of fuel from this reactor based on 33,000 MWD/MT integrated exposure at 30 MW/MT. If we assume that (1) the fuel is reprocessed at 150 days out of the reactor, (2) all of the xenon and krypton and 50 percent of the iodine present are volatilized from the fuel prior to or during dissolution operations, (4) 0.5 percent of the uranium and plutonium is lost to the waste during the reprocessing and (5) essentially all of the remaining fuel constituents appear in the high-level waste, then the fission product and actinide element composition will be that shown in Table 1. Also shown are the Curie levels of the various constituents as well as the radioactive decay energy contributed by them. Thus, we see that the high-level waste will contain about  $3.5 \times 10^4$  g of fission products and actinide elements per tonne of fuel processed, that it will contain about  $5.4 \times 10^6$  Curies of radioactivity and that it will be generating about  $2 \times 10^4$  watts per tonne of fuel processed (at 150 days). While the Curie level and decay heat level of the

waste will decrease somewhat with time, the total mass of fission products and actinide elements will not decrease with time.

*Table II shows those elements which contribute one or more percent of the mass, radioactivity and decay heat.*

Defining the volume and nonradiochemical composition of the high-level waste that we are going to concentrate is complicated by the fact that different processing schemes may be used and that different <sup>combinations</sup> ~~continuations~~ of process wastes may be made to generate the high-level wastes. For example, in the Hanford Purex process, aqueous wastes from cycles beyond the first cycle are routed back for use as salting agent in the first cycle. (2)

Hence, chemicals present in such waste ultimately appear in the first cycle or high-level waste. This means of reducing the volume of high-level waste is advantageous in the overall waste management operation at Hanford. However, it may not be desirable for commercial reprocessors to combine process waste streams in this fashion because they must ultimately solidify the wastes.

Salts present in the backcycled wastes, particularly sodium salts, may complicate storage and solidification operations.

However, whether waste streams from later cycles are returned to the first cycle will not change greatly the volume and acidity of the first cycle waste since these are determined by the operating conditions for the first cycle. Hence, the volume and acidity of the Hanford Purex Process first cycle waste may be used as an example. The volume and nitric acid concentration of the waste are about 6250  $\ell$ /MTU and 3 M, respectively. Since 99%+ of the fission products 0.5% of the U and Pu and 99%+ of the remaining actinide elements present in the irradiated fuel should be in this waste stream, it will have <sup>basic</sup> the composition shown in Table 3.

Table 3 shows only  $\text{HNO}_3$  and those waste constituents which come from the irradiated fuel. Other chemicals may or will be present depending on the flowsheet and operating conditions used. Chemicals added for plutonium valence adjustment may be present if wastes are backcycled. Corrosion products derived from processing equipment will be present. Since austenitic stainless steels are generally used for process equipment, the



TABLE I. FISSION PRODUCT AND ACTINIDE ELEMENT CONTENT OF DIABLO CANYON REACTOR FUEL AGED 150 DAYS

	<u>g/MT</u>	<u>Curies/MT</u>	<u>Watts/MT</u>
Se	$5.2 \times 10^1$	$3.93 \times 10^{-1}$	$1.49 \times 10^{-4}$
Br	$1.5 \times 10^1$	---	---
Rb	$3.33 \times 10^2$	$1.85 \times 10^0$	$8.69 \times 10^{-3}$
Sr	$8.96 \times 10^2$	$1.73 \times 10^5$	$4.45 \times 10^2$
Y	$4.68 \times 10^2$	$2.35 \times 10^5$	$1.04 \times 10^3$
Zr	$3.66 \times 10^3$	$2.76 \times 10^5$	$1.45 \times 10^3$
Nb	$1.32 \times 10^1$	$5.24 \times 10^5$	$2.49 \times 10^3$
Mo	$3.44 \times 10^3$	$1.02 \times 10^{-10}$	$4.59 \times 10^{-13}$
Tc	$8.35 \times 10^2$	$1.42 \times 10^1$	$9.62 \times 10^{-3}$
Rw	$2.26 \times 10^3$	$4.99 \times 10^5$	$3.15 \times 10^2$
Rh	$3.89 \times 10^2$	$4.99 \times 10^5$	$3.98 \times 10^3$
Pd	$1.29 \times 10^3$	---	---
Ag	$6.01 \times 10^1$	$2.95 \times 10^2$	$4.46 \times 10^0$
Cd	$8.35 \times 10^1$	$4.41 \times 10^1$	$1.9 \times 10^{-1}$
In	$1.20 \times 10^0$	$3.15 \times 10^{-5}$	$9.50 \times 10^{-8}$
Sn	$5.15 \times 10^1$	$3.78 \times 10^2$	$1.26 \times 10^0$
Sb	$1.77 \times 10^1$	$8.82 \times 10^3$	$2.84 \times 10^1$
Tc	$5.65 \times 10^2$	$2.65 \times 10^4$	$4.50 \times 10^1$
I	$2.72 \times 10^2$	$2.21 \times 10^0$	$8.96 \times 10^{-3}$
Cs	$2.72 \times 10^3$	$3.20 \times 10^5$	$2.41 \times 10^3$
Ba	$1.39 \times 10^3$	$1.00 \times 10^5$	$3.92 \times 10^2$
La	$1.27 \times 10^3$	$4.95 \times 10^2$	$8.21 \times 10^0$
Ce	$2.88 \times 10^3$	$8.25 \times 10^5$	$7.87 \times 10^2$
Pv	$1.20 \times 10^3$	$7.71 \times 10^5$	$5.73 \times 10^3$
Nd	$3.91 \times 10^3$	$5.01 \times 10^1$	$1.43 \times 10^{-1}$
Pm	$1.07 \times 10^2$	$9.98 \times 10^4$	$5.65 \times 10^1$
Sm	$8.08 \times 10^2$	$1.15 \times 10^3$	$2.01 \times 10^0$
Eu	$1.82 \times 10^2$	$1.34 \times 10^4$	$7.17 \times 10^1$
Gd	$1.03 \times 10^2$	$1.89 \times 10^2$	$5.98 \times 10^{-1}$
Tb	$1.80 \times 10^0$	$4.66 \times 10^2$	$3.64 \times 10^0$

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Pc.

TABLE I. (continued)

	<u>g/MT</u>	<u>Curies/MT</u>	<u>Watts/MT</u>
Dy	$1.02 \times 10^0$	$5.39 \times 10^{-16}$	$4.57 \times 15^{19}$
Ho	$8.99 \times 10^{-2}$	$7.71 \times 10^{-5}$	$8.30 \times 10^{-7}$
<del>Ev</del> <sup>EN</sup>	$2.79 \times 10^{-2}$	---	---
<del>Th</del> <sup>Th</sup>	$2.65 \times 10^{-4}$	$9.89 \times 10^{-4}$	$3.24 \times 10^{-5}$
Pa	$2.05 \times 10^{-6}$	$3.49 \times 10^{-4}$	$8.88 \times 10^{-7}$
U	$4.87 \times 10^3$	$4.39 \times 10^{-3}$	$8.11 \times 10^{-5}$
Np	$7.6 \times 10^2$	$1.79 \times 10^1$	$5.16 \times 10^{-2}$
Pu	$4.69 \times 10^1$	$6.14 \times 10^2$	$1.33 \times 10^0$
Am	$1.44 \times 10^2$	$1.97 \times 10^2$	$6.30 \times 10^0$
Cm	$3.53 \times 10^1$	$1.74 \times 10^4$	$6.38 \times 10^2$
TOTAL:	$3.493 \times 10^4$	$5.4 \times 10^6$	$2.0 \times 10^4$

TABLE *D*. ELEMENTS CONTRIBUTING 1% OR MORE OF TOTAL MASS,  
RADIOACTIVITY AND DECAY HEAT

	<u>g/MT, %</u>	<u>Curies/MT, %</u>	<u>Watts/MT, %</u>
<del>Sn</del> <i>Sn</i>	2.51	3.20	2.23
Y	1.36	4.36	5.2
Zr	10.48	5.11	7.25
Nb	---	9.70	12.45
Mo	9.85	---	---
Tc	2.39	---	---
<del>Ru</del> <i>Ru</i>	6.47	9.24	1.58
Rh	1.11	9.24	19.90
Pd	3.69	---	---
Te	1.62	---	---
Cs	6.66	5.93	12.10
Ba	3.98	1.85	1.96
La	3.63	---	---
Ce	8.25	15.28	3.94
<del>Pu</del> <i>Pu</i>	3.44	14.27	28.65
Nd	11.19	---	---
Pm	---	1.85	---
Sm	2.31	---	---
U	13.94	---	---
Np	2.18	---	---
Cm	---	---	3.19
Others	4.96	19.97	1.55

major corrosion products present will be iron, chromium and nickel. Their concentration will depend on process conditions. Some degradation products of the solvent will be present; for TBP these will be di- and monobutyl phosphate and phosphate ion. If a soluble poison such as gadolinium or boron is used in the process, it too will appear in the high-level waste. The Hanford Purex process high-level waste contains also a small amount of sulfate and sodium ion from backcycled waste streams containing Pu and Np valence adjustment chemicals. It also contains some aluminum and fluoride which result from the fact that zirconium cladding is chemically dissolved in the headend operation. Wastes generated in processing commercial power reactor fuels will not have the aluminum and fluoride since a chop-leach headend is used instead of chemical decladding.

#### Waste Concentration Operations

Recovery of nitric acid from the dilute high-level waste is desirable for two reasons. The recovered nitric acid, though slightly contaminated with radioactive constituents, can be

TABLE 3. BASIC COMPOSITION OF FIRST CYCLE WASTE

	<u>g/l</u>	<u>M</u>
Sr	0.14	0.0016
Y	0.07	0.0008
Zr	0.59	0.0065
Mo	0.55	0.0057
Tc	0.13	0.0013
Ru	0.36	0.0036
Rh	0.06	0.0006
Pd	0.21	0.0021
Te	0.09	0.0007
Cs	0.44	0.0033
Ba	0.22	0.0016
La	0.20	0.0014
Ce	0.46	0.0033
Pr	0.19	0.0013
Nd	0.63	0.0044
Sm	0.13	0.0009
U	0.78	0.0033
Np	0.12	0.0009
Other Fission Products and Actinides	<0.06	<0.0008
H <sup>+</sup>		~3
NO <sub>3</sub> <sup>-</sup>		~3.1

recycled for use in the plant. Also, nitric acid recovered at this point reduces the amount which must be treated later to reduce the acidity to that desired for interim storage.

Recovery of nitric acid is accomplished with a concentrator and an absorber. Further concentration of the acid is done with an acid fractionator.

Major problems in these operations are corrosion, volatilization of some components and problems due to solids present in the waste. The bottoms of the waste concentrator are usually held at about 6-7M in  $\text{HNO}_3$ . The waste contains a wide variety of constituents, some of which can promote attack on the stainless steel commonly used for evaporator construction. Iron (III) and chromium (VI), if present, can promote intergranular attack on 304 stainless steel. Fluoride, if present and not complexed tightly, can accelerate corrosion. Heat transfer surfaces, because of their relatively high temperature, are

especially subject to attack. Stainless-steel equipment, sometimes utilizing titanium tube bundles in the evaporator, have given good service in ERDA installations. Since the waste from commercial power reactor fuel reprocessing will contain higher concentrations of fission products and actinides and since flow-sheets used may vary from plant to plant, evaluation of the corrosion potential and selection of optimum material for the evaporator will be needed on a plant by plant basis.

The possibility of volatilizing waste components during nitric acid recovery must be considered. Such volatilized components could appear in the recovered acid, in the acid fractionator overhead and in the offgas.

Ruthenium is perhaps of greatest concern. Significant volatilization of ruthenium can occur if the acidity of the evaporator bottoms is maintained too high ( $>6M$ ). One measure to prevent ruthenium volatilization while maximizing the amount of  $HNO_3$  which can be recovered is to add water to the system

and recycle it to the evaporator to keep the evaporator bottoms acidity low. Another is to add a reducing agent to the evaporator to generate oxides of nitrogen and reduce ruthenium volatilization. Sucrose is used for this purpose in the Hanford Purex plant.

Iodine, if present at this point, may be volatilized and may distribute among the recovered acid, the fractionator overhead and the offgas. This has not been a significant problem with ERDA fuels due to aging before processing for I-131 decay and the small amount of I-129 present. It may be a problem with commercial power reactor fuels because of the much larger I-129 content.

Tritium present in the high-level waste will distribute among the various streams (concentrated waste, recovered acid, fractionator overhead and offgas) in relation to the water present in them.

The concentrated waste will contain some solids. How much solids and their physical characteristics will depend on the



fuel being processed, the chemical flowsheet used (process additives present) and processing conditions (e.g., potential for degradation of solvent). They may be crystalline salts or they may be gelatinous materials. Their precise nature and their potential for causing problems should be determined for each waste evaporated. They may simply coat heat transfer surfaces and thus reduce evaporator capacity. They have been known to completely fill the spaces between tubes in a vertical heat transfer tube bundle. In commercial power reactor fuel wastes, the solids may have a high radioactive content, hence, a high decay heat output. They could create hot spots in equipment if allowed to accumulate.

The volume and acidity of the high-level waste following nitric acid recovery will, of course, depend on the waste composition and the operating conditions for any given installation. In one mode of operating the Hanford Purex plant system, a volume reduction of about 8 is achieved (to Ca.

770g/MT fuel) and the residual  $\text{HNO}_3$  concentration is 2.8M.

This is still a relatively large volume and ~~would~~ <sup>could</sup> be an undesirably high acidity for acid side storage. Further concentration and further reduction in acidity is desirable.

One used technique for reducing the  $\text{HNO}_3$  is simply to destroy it by adding a reducing agent to produce volatile oxides of nitrogen. Formaldehyde <sup>3</sup>/<sub>(4)</sub> and sugar <sup>4</sup>/<sub>(5)</sub> are the two reagents most studied and used for this purpose. Both are effective.

Formaldehyde has an induction period before reaction starts and process conditions must be controlled to avoid a runaway reaction.

The sugar reaction is slower and requires no special controls.

Oxalate is among the decomposition products of sugar. Some fission product and actinide element oxalates are sparingly soluble in the waste and may add to the amount of solids present. While either reagent can be used to produce an acid deficient waste, the terminal acidity normally sought is <sup>usually</sup> 0.5 - 1M.

Further reduction in volume might be done in an evaporator or by allowing the wastes to self-concentrate by boiling in a storage tank. The latter has been done at Hanford after the waste was made alkaline and stored in large (500,000 or 1,000,000 gal) mild steel underground tanks. Problems involved in allowing stored wastes to boil will be discussed under Waste Storage.

The problems involved in concentrating the denitrated waste in an evaporator are essentially the same as those discussed <sup>above</sup> under ~~above~~ nitric acid recovery.

The degree to which the high-level waste is concentrated prior to or during interim storage will depend on the fuel being processed, the particular flowsheet being used, the interim storage period involved and the design of the interim storage tank. Table IV shows the concentration of fission products and actinide elements which would be present in waste from processing fully irradiated Diablo Canyon Reactor fuel and concentrating the waste to 378ℓ (100 gal) per tonne of fuel processed.

TABLE IV. COMPOSITION OF DIABLO CANYON FUEL WASTE AT 378 g/MT

<u>Constituent</u>	<u>g/l</u>	<u>M</u>	
Sr	2.31	0.03	0.060
Y	1.16	0.013	0.039
Zr	9.75	0.11	0.22
Mo	9.09	0.09	
Tc	2.15	0.02	
Ru	5.95	0.06	0.12
Rh	0.99	0.01	0.02
Pd	3.47	0.03	0.06
Te	1.49	0.01	
Cs	7.27	0.05	0.05
Ba	3.64	0.03	0.06
La	3.31	0.02	0.06
Ce	7.60	0.05	0.15
Pr	3.14	0.02	0.06
Nd	10.41	0.07	0.21
Sm	2.15	0.01	0.03
U	12.89	0.05	0.10
Np	1.98	0.01	0.02
Other Fission Products and Actinides	<1	0.01	<del>1.26</del> NO

~~Total~~

~~92~~

~~$1.43 \times 10^4$  Ci/l~~

~~53 W/l~~

The concentrations given in Table III are based on the assumption that all constituents are in solution. In fact this will not be the case. High-level waste concentrated to this degree can be expected to contain a significant amount of solids and these solids can be expected to contain a significant fraction of the radioactive constituents present. This is an important consideration in storage of the waste.

Note also that the concentrated waste has a radioactivity level of about 14,000 Ci/l which results in a decay heat evolution rate of about 50 W/l (180 BTU/hr - l). The latter is also of great significance to interim storage of waste.

#### Interim High-Level Waste Storage

Problem involved in interim storage of high-level waste are due to the decay heat evolved by the waste, the solids present in the waste, the corrosiveness of the waste (particularly if stored acidic), radiolysis effects due to its high radioactivity and, to a much less extent, to the potential for volatilization of constituents from it.

Concentrated and stored high-level radioactive wastes will boil due to the radioactive decay heat generated in them. This gives rise to several problems which must be accounted for in the design and operation of the waste storage system. For one thing, the wastes are more corrosive in both the liquid and the vapor phase if allowed to boil than if maintained below the boiling point. If the management decision is to cool the wastes to prevent boiling and to reduce the corrosiveness, an adequate cooling system must be incorporated. Backup provisions to maintain cooling are needed in case the primary system fails.

The stored waste may be allowed to boil either to provide some in-storage concentration or simply as a means of removing the decay heat. In either case, if the boiling waste is acidic, provisions must be made for condensing the offgas and either returning the condensate to the storage tank or disposing of it. Tritium, if present in the waste, will be present in the condensate.

Solids present in the stored wastes have a high decay heat generation rate. If these solids are allowed to settle, they may compact, form a barrier to heat transfer by convection, and become dry. The temperature of the solids could then rise to levels much above the boiling point of the liquid waste, perhaps high enough to threaten the integrity of the tank liner. Means such as air sparging or air lift circulators may be used to keep the solids suspended and prevent the formation of deposited solids which could produce hot spots.

A phenomenon called "bumping" was observed in stored alkaline wastes at Hanford. <sup>5</sup><sub>(7)</sub> These wastes were stored in large underground tanks which had no provision for keeping solids suspended. Solids settled to a layer on the bottom of the tanks. Since the solids generated decay heat more rapidly than the liquid, the liquid developed a temperature gradient. As the bulk liquid approached the boiling point, liquid near the solids was superheated. Once boiling started, liquid convection was rapid and the superheat was released rapidly as steam. A

momentary pressurization, amounting in cases to a few tens of inches of water, occurred. Installation of air lift circulators to keep the liquid agitated and the solids suspended stopped the bumping action.

Radiolysis in the stored waste will generate hydrogen. If the storage tank does not have an adequate flow of air (or other diluting gas) through it, the potential for developing an explosive offgas could exist. Air supplied <sup>for</sup> ~~to~~ sparging or air lift circulators, or simply air inleakage, is adequate to provide the needed dilution.

Stored high-level wastes have the capability of evaporating themselves to dryness if all means of maintaining the liquid phase should fail. The dried wastes could then become quite hot. Calcination and perhaps melting could occur. Volatilization of radioactive constituents could occur and the tank integrity could be threatened. Obviously, tank design, operation and backup facilities must be adequate to ensure the tank contents cannot concentrate to dryness.



Summary

This overview has cited recognized problems in the concentration and storage of high-level radioactive waste. The discussion was intentionally kept general since each fuel reprocessing site will have its own spectrum of fuels to process, its own reprocessing flowsheet and its own sequence of waste concentration and storage. The Hanford Purex plant and associated waste storage system was used as an example since the waste concentration and storage operations are similar to those in commercial plants except that the waste is made alkaline before storage.

Designs and procedures have been developed to cope effectively with these problems and to make the operations safe and reliable.

1. J. A. Blomcke, W. C. McKee and J. P. Nichols, Projections of Radioactive Wastes to be Generated by the U. S. Nuclear Power Industry, USAEC Report, ORNL-TM-3695, February 1974.
2. Separations Process Engineering Staff, Purex Chemical Flowsheet for Processing N-Reactor Fuels, USAEC Report ARH-2362, June 1972.
3. R. C. Forsman, G. C. Oberg, Formaldehyde Treatment of Purex Radioactive Wastes, USAEC Report, HW-79622, October 1963.
4. L. A. Bray, Denitration of Purex Waste With Sugar, USAEC Report HW-76973 Rev., April 1973.
5. R. E. Tomlinson, B. F. Campbell, E. Doud, "Management of High-Level Wastes - Current Practice," HW-SA-2478, February 1962.