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CHEMICAL ENGINEERING DIVISION

WASTE MANAGEMENT PROGRAMS

QUARTERLY REPORT

October—December 1974

by

**M. J. Steindler, N. M. Levitz, W. J. Mecham,
W. B. Seefeldt, L. E. Trevorrow, I. O. Winsch,
T. F. Cannon, T. J. Gerding, B. J. Kullen,
D. S. Webster, and L. Burris**

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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March 1975

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ABSTRACT

In the study of the consolidation of Zircaloy hulls, emphasis was continued on the potential for pyrophoric reactions and the separation of zirconium from contaminants. Reaction of Zircaloy and zinc chloride yields volatile zirconium tetrachloride under moderate conditions. Uranium and ceric oxides added to the metal appeared unaffected by contacting with $ZnCl_2$. An attempted separation of zirconium tetrachloride from zinc chlorides by simple sublimation was not successful. Preliminary studies on compaction of simulated Zircaloy hulls by drop hammer and by hydraulic press revealed no unusual or hazardous consequences. A review of experiences with similar operations on a commercial scale is provided.

Recent progress in analyzing methods of disposing of tritium-bearing low-level aqueous waste is presented.

Work on the reliability of high-level waste canisters included a review of methodology appropriate to the retrievable surface storage facility. Data on a major mode of failure such as stress corrosion cracking of stainless steel is reviewed in detail, with particular emphasis on the role of metallurgical characteristics and impurities in the water. Stresses developed by contraction of the canister and glass during cooling from the filling temperature and stresses developed due to pressurization by water vapor and nitrate decomposition products are identified.

SUMMARY

Consolidation Techniques for Fuel-Cladding Hulls

A study is in progress to develop a long-term management scheme for the contaminated, Zircaloy-based cladding waste stream that is generated by the chop-leach processing of spent LWR fuel. This program explores and evaluates chemical and mechanical process steps that will consolidate the waste and circumvent any pyrophoric hazard. Means of reducing the alpha-waste volume include exploratory studies for separating the zirconium from the long-lived

alpha-emitters and other radionuclides. Initial work is with unirradiated Zircaloy tubing. Efforts to acquire irradiated hulls and tubing for later testing are continuing.

Two chemical methods selected for initial study provide separation of the zirconium as the volatile tetrachloride: 1) hydrochlorination with anhydrous HCl and 2) reaction with molten $ZnCl_2$.

Two experiments were carried out in which molten $ZnCl_2$ (m.p. 283°C) was reacted with 1-in.-long sections of Zircaloy tubing at 500°C after the tubing was oxidized; oxidation had been done at 350°C for 2 hr, giving a gunmetal-blue finish. The first experiment was conducted with a single piece of tubing contained in an alumina crucible heated in air for 4.5 hr. Successive washes with water and HCl solutions left a clean Zircaloy residue. Weighing showed that 91% of the metal had reacted.

The second experiment was carried out at 500°C for 6 hr under an argon atmosphere in a tungsten crucible heated in an induction-heated, tilt-pour furnace; five pieces of Zircaloy (29.8 g) and 300 g of $ZnCl_2$ along with uranium dioxide granules and CeO_2 added as a stand-in for PuO_2, were reacted in this experiment. The molten salt (~30 wt % $ZrCl_4$-$ZnCl_2$) and metal phases obtained were poured into a graphite crucible, and the residue in the tungsten crucible was given a water/acid wash treatment to remove residual salt and zinc. A weight determination of the remaining Zircaloy showed that the reaction was 91% complete. The residual Zircaloy was coated with a reasonably adherent coating of zinc, which was not the case in earlier experiments conducted at lower temperatures (ANL-8152, p. 7). Coating of the hulls with an inert material represents one option to allay concern over the possible pyrophoric hazard.

The UO_2 and CeO_2 appeared to be unaffected by the reaction system. Analyses of the various phases to confirm this are pending. An attempt to separate the $ZrCl_4$ from the remainder of the salt mixture by sublimation at 400°C resulted in cosublimation of both $ZrCl_4$ and $ZnCl_2$.

Exploratory mechanical compaction tests were made on single pieces of Zircaloy tubing, using a hydraulic press (2000 psig) and a drop hammer. Both oxidized and unoxidized samples were used: oxidation was done in 2 hr at 350°C, which gave a gunmetal-blue finish, or in 24 hr at 700°C, which resulted in about 85% conversion to the oxide. All but the highly oxidized sample remained intact except for cracks that appeared along the edges. The highly oxidized sample crumbled into powder and small compacted pieces. Little heatup of samples was noted, and no sparking was evident.

Discussions pertinent to an analysis of the pyrophoric hazard question were held during visits to two firms: Shock Hydrodynamics, which has extensive experience in ignition of metals, and Teledyne Wah Chang Albany (TWCA), a major producer of raw and wrought zirconium and nuclear-grade Zircaloy. The visit to TWCA, made with the cooperation of TWCA and General Electric Co., was also for the purpose of observing a special series of production-scale compaction tests on scrap Zircaloy tubing. The scrap fed to a large hydraulic press was produced by chopping tubing into several-inch lengths. Some fines were produced during chopping, estimated at less than 0.1 wt %, but no special care was taken in handling any of this scrap with

regard to possible ignition; it was handled in air and generally treated as ordinary metal scrap. Each compact formed was 11 in. (28 cm) in diameter by 5 in. (13 cm) high, weighing 80 lb (36 kg). The final density of the compacts was about 72% of the theoretical density; compaction pressure was about 52,500 lb/in.[2] Routine handling of other scrap forms, *i.e.*, saw fines and machining turnings, was also observed. Compaction of turnings (after cleaning) was also done routinely. Fines that have a tendency to ignite were handled carefully, avoiding sources of sparks. Scrap is stored in 55-gal drums.

If irradiated Zircaloy is physically similar to the tubing scrap, it appears that extrapolation of the experience at TWCA to actual hulls will be uncomplicated.

Storage and Disposal of Tritium

Recent activities are reviewed related to the evaluation of alternative schemes for management of waste tritium arising from the production of civilian power by light water reactors. These activities have included a preliminary evaluation of catalyzed hydrogen-water exchange to concentrate aqueous tritiated wastes; the arrangement, conduct, and distribution by us of the proceedings of a government-industry conference on tritium control; a survey of literature on deep-well injection of wastes; and the beginning of an evaluation of the application of deep-well injection for disposal of low-level aqueous wastes from fuel reprocessing plants. Efforts in the last-mentioned activity have included negotiations to obtain expert consultation in the development of this evaluation, construction of a detailed outline of scope and content of the work, and collection of data to characterize the composition of the low-level aqueous waste streams.

Reliability of High-Level Waste Container

The reliability of containers for high-level wastes in the glass and calcine form during 1) storage under water at a reprocessing plant, 2) transit to a Retrievable Surface Storage Facility (RSSF), and 3) storage at a RSSF is being examined. The several concepts of storage at a RSSF include cooling by air and by water.

Methods of establishing reliability have been reviewed with the objective of identifying a technique useful for this study.

Stress corrosion cracking (SCC) has been identified as one of the principal modes of failure when canisters are exposed to exterior environments. A review of the literature has been made to ascertain the sensitivity of 304L stainless steel to SCC as a function of stress levels in the metal, metallurgical state of the metal (sensitized or not sensitized), chloride and oxygen concentrations in cooling water, and temperature.

For application to the storage of waste in the glass form, the differential contraction of the canister and glass has been identified as a source of stress during cooling from temperatures associated with filling the canister with molten glass. Neglecting stress-relieving mechanisms, stresses developed in the metal were found to be about 20,000 psi for each 100°F of cooling. This stress level is sufficient to initiate SCC in stainless steel.

Internal pressurization of the canister due to decomposition of residual nitrates and volatilization of residual moisture present in waste in the calcine form is also a source of stresses in the canister. Calculations showed that nitrate and moisture concentration levels above 1000 ppm can develop internal pressures that result in high stress levels in the canister.

I. CONSOLIDATION TECHNIQUES FOR FUEL-CLADDING HULLS
(N. M. Levitz, I. O. Winsch, B. J. Kullen, T. F. Cannon)

A. Introduction

This program concerns the development of methods for the safe and economic long-term management of waste Zircaloy cladding* that is generated in the reprocessing of spent LWR fuel by the chop-leach process. The cladding is contaminated with long-lived alpha-emitters, fission products, and neutron-activation products. Current attention is being given to the potential of a pyrophoric hazard from Zircaloy, particularly finely divided metal. Consolidation processes that transform the waste so that it can be classified and treated as a compact, nonpyrophoric, non-alpha-bearing waste are being identified, tested, and evaluated. The processes should also provide for the collection of the alpha-emitters in a compact form, amenable to storage, disposal, or further processing. Identification of methods for salvaging the Zircaloy for reuse remains a secondary goal. The plan of work includes review and evaluation of the literature to assess the state of knowledge and technology, an experimental phase, and a flow sheet and concept design phase that will identify process options. Resolution of the pyrophoricity question will be emphasized in the work this fiscal year.

Experimental work continues to stress methods that provide a separation of the zirconium as the volatile tetrachloride, namely, hydrochlorination with anhydrous HCl (see ANL-8152, p. 5) or reaction with molten $ZnCl_2$. The apparatus for the HCl work was fully assembled and heat-tested, but actual startup of experimentation was delayed because of unexpected delay in the delivery of important components. Two additional scouting experiments involving molten $ZnCl_2$ and unirradiated Zircaloy tubing are summarized. Efforts were continued to obtain and develop information related to the potential ignition of Zircaloy hulls and to the mechanical compaction of hulls; highlights of a trip made to obtain this type of information are summarized.

Efforts also continued during the quarter to obtain some irradiated Zircaloy tubing. Negotiations are continuing with the Karlsruhe Laboratory in Germany to transfer some hulls (20-40 pieces) from their chop-leach operations. Some material that appears suitable has been located at HNL (ORNL), and preliminary arrangements for acquiring this material have been initiated.

B. Pyrochemical Studies

Numerous pyrochemical (molten metal/molten salt) process flow sheets appear to be applicable to the processing of Zircaloy hulls, with process selection being dependent on program objectives.[1] Processes under initial consideration are intended 1) to transform the Zircaloy into a form that no longer represents a potential pyrophoric hazard, and 2) to effect a separation and concentration of the long-lived alpha-emitting radionuclides. By

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*Cladding in this context comprises the short Zircaloy tube segments referred to as hulls, as well as extraneous fuel element hardware such as Inconel grids and nozzles. Zircaloy is a zirconium-based alloy containing tin, iron, chromium and sometimes nickel.

maximizing the recycle of process reagents, a reduction in overall volume of alpha-bearing waste is achieved.

Current studies continued with the use of $ZnCl_2$ as an oxidizing agent, the main reaction being $Zr + 2\ ZnCl_2 \rightarrow ZrCl_4 + 2\ Zn$. A temperature of 500°C was selected, based on earlier scouting studies.[1] This scheme separates the bulk constituent, zirconium, as the volatile tetrachloride for possible salvage, while retaining and concentrating the plutonium and other radio-nuclides in the residual metal and salt layers. Experiments were carried out on 1-in.-long by 0.5-in.-OD by 0.0312-in.-wall Zircaloy-2 tubing sections that had a gunmetal-blue surface finish produced by air oxidation for 2 hr at 350°C; the weight gain during this oxidation period was negligible. A single piece of tubing was used in a scouting experiment; five pieces (29.8 g) were used in the second experiment. Both UO_2 and CeO_2 (as a stand-in for PuO_2) were added in the second experiment to determine their distribution after the reaction. Neither experiment involved any stirring.

The single piece of Zircaloy was reacted with 250 g $ZnCl_2$ for 4.5 hr at 500°C in an alumina crucible open to the air. The salt phase was separated from the residue by dissolution of the salt in water and decanting of the solution from the metallic residue of unreacted Zircaloy and zinc. The zinc appeared to form an adhering coat on the residual Zircaloy under these conditions (500°C). The zinc was dissolved in HCl, and the residual Zircaloy section was weighed. A weight loss of 91% indicated that reaction with the $ZnCl_2$ had essentially been complete.

For the larger-scale experiment, the reaction equipment consisted of a tungsten crucible in an induction-heated tilt-pour furnace; 300 g of $ZnCl_2$ was used. An argon atmosphere of 10 psig was maintained in the furnace during the experiment. Reaction time was 6 hr at 500°C. Attempts to take filtered salt samples during the run using tantalum frits were not successful, possibly because of the fine grade of the frits. A relatively coarse grade of porous graphite may be tried for subsequent experiments.

After the reaction period, the melt was poured into a graphite receiver; 200 g of salt and 21.8 g of zinc were recovered. Samples of the salt will be analyzed for zirconium, zinc, uranium, and cerium. A white powder that coated the inside walls of the tilt-pour furnace was recovered, leached with water, and sampled for analysis. The tungsten crucible heel was water-washed and was found to contain unreacted UO_2, CeO_2, salt, and zinc-coated tubing remnants. The UO_2 and CeO_2 appeared to be unaffected by the $ZnCl_2$. The zinc-coated metal heel was leached with hydrochloric acid. Weighing of the residual metal indicated that about 91.5% of the Zircaloy had been reacted.

The zinc coating had not been observed in earlier experiments at lower temperature (ANL-8152, p. 7). It is of some interest since coating of hulls with an inert material represents one option for circumventing the possible pyrophoric hazard.

An attempt was made to separate and recover the $ZrCl_4$ from the salt phase by sublimation. The salt (≈30% $ZrCl_4$) was sublimed at 400°C under vacuum from an alumina tube furnace. After a sublimation period of 24 hr, it was found that about 85% of the salt charge had sublimed; a dark gray residue

remained in the boat equivalent to about 15% of the charge. An analysis of the residue will be made, but apparently, very little separation of the $ZrCl_4$ from the $ZnCl_2$ occurred.

The work to date has established that the oxidation reaction between $ZnCl_2$ and Zircaloy is feasible at a practical temperature, 500°C. Uranium dioxide and CeO_2 (a stand-in for PuO_2) appear to be unaffected during this reaction. A change in the $ZnCl_2$-$ZrCl_4$ ratio in the final salt appears to be needed to effect separation of the $ZrCl_4$ by sublimation.

Another experiment is planned in which less than the stoichiometric quantity of $ZnCl_2$ to oxidize the Zircaloy will be used. If all of the $ZnCl_2$ is reacted, removal of the $ZrCl_4$ by sublimation should be easy. Any unreacted Zircaloy would be reacted with a subsequent charge of Zircaloy. The $ZnCl_2$ for reacting the next batch of hulls would be regenerated by reacting the zinc with chlorine. This latter reaction needs to be examined to establish the behavior of the radionuclides in the zinc phase; any volatilization of these radionuclides would be undesirable. Options for treatment of the plutonium-containing material will be proposed for evaluation, as this work progresses.

Further treatment of the $ZrCl_4$ will depend on the extent of separation from the radionuclides and on the nature of the contaminants in this stream; possibilities include storage as a non-alpha-bearing waste as 1) the chloride, 2) the more stable oxide (at a much reduced cost), or 3) metal. The metal might be salvaged for reuse. The results of the current program should provide some direction for further experimentation and flow sheet development.

To facilitate future pyrochemical studies, a high-temperature (2000°C) inductively heated furnace with a tilt-pour capability is being reactivated; this equipment will be used jointly for both this study and the program on Salvage of Alpha-Contaminated Metal.[1] Experiments will include larger scale $ZnCl_2$ oxidations; these tests will also be used 1) to establish the distribution of the minor constituents (contaminants) in the system and 2) to determine whether oxide coatings on the Zircaloy inhibit or interfere with the reaction. Other pyrochemical scouting tests will examine the feasibility of 1) precipitating zirconium from a zinc solution when the concentration is above the normal solubility level (*e.g.*, solubility at 850°C is about 12 wt %); the distribution of the contaminants between the metal phase and a salt cover (*e.g.*, $MgCl_2$-NaCl-KCl) will be examined; the salt cover also reduces the loss of metal by vaporization, 2) separating zirconium as the nitride from a zinc-zirconium melt, and 3) slagging the contaminants in Zircaloy; this requires a system near 2000°C since the melting point of zirconium is about 1850°C. Work with plutonium-contaminated tubing will commence if results of the next set of scouting studies are definitive. Irradiated materials are being acquired for later studies.

C.   Compaction of Zircaloy-2 Tube Sections

Compaction is being studied as a means of consolidating waste Zircaloy hulls. The objectives include an evaluation of the pyrophoricity hazard during compaction and reduction in volume.

Three sections of Zircaloy-2 tubing (0.0312-in. wall x 0.5-in. OD x 1 in. long), one piece unoxidized, one section oxidized at 350°C for two hours

(gunmetal-blue finish), and one section oxidized at 700°C for 24 hours (tan ceramic appearance), were compacted with a slow-action hydraulic press under a pressure of 2000 psig. The unoxidized and slightly oxidized sections were compressed to a thickness of 0.0685 in. (0.1740 cm). Longitudinal cracks developed along each edge of the compressed sections but the pieces remained totally intact (no slivers or small particles were formed). The third section, which has been oxidized at 700°C and was primarily oxide, crumbled into a powder and small compacted pieces. In none of the experiments did the tubing sections appear to be warm because of compaction.

Two Zircaloy-2 tube sections that had been oxidized in air at 350°C for two hours were subjected to single and double blows, respectively, from a Vulcan drop hammer.* A single blow compacted the first tube section to a thickness of 0.076 in. (0.193 cm) and double blows to the second tube compacted the tube section to a thickness of 0.067 in. (0.170 cm). As in the tests with the hydraulic press, longitudinal cracks in the tube sections developed. It was also noted that the tube sections subjected to the force of the drop-hammer were warm to the touch. There was no evidence of sparking in any of the tests.

Sections of Zircaloy tubing held in a muffle furnace at 700°C for about 65 hr oxidized completely, producing zirconia powder and oxides of the other Zircaloy components. Oxidation could be another method that might be used for reducing the volume of the hulls. If no decontamination were required, the resulting powder could be incorporated directly into a glass for subsequent storage or burial.[2]

D.   Industrial Visits

Visit to Shock Hydrodynamics and Teledyne Wah Chang Albany (TWCA)

Discussions were held with Shock Hydrodynamics personnel to explore possibilities for applying their expertise in the areas of ignition and combustion of metals and explosives (largely ordnance-related) to our problem of examining the potential of Zircaloy hulls as a pyrophoric hazard. This firm has recently done development work for TWCA on the standardizing of ignition tests for selected zirconium materials (mainly sponge). A major discussion point was consideration of tests that can provide high energy input to, for example, a mass of hulls in bulk or compacted form, and for which a correlation can be developed for establishing the sample temperature. Physical changes in the sample during and after such tests would be examined. Additional consulting regarding this topic is planned. A preliminary conclusion was offered that hulls alone under ordinary conditions (*e.g.*, during shipment) do not represent a pyrophoric hazard; this may not be true for the fines fraction. Furthermore, the fraction of fines in hulls, estimated at only 0.1 wt %, would not be expected to ignite the hulls even if the fines burned.

TWCA is a major U. S. producer of raw and wrought zirconium and nuclear-grade Zircaloy, and has significant experience in areas of interest to this program. Through the cooperation of the General Electric Co. and TWCA, we were invited to observe a series of compaction tests on scrap Zircaloy tubing

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*Product of S and S Machinery Co., Brooklyn, N. Y.

conducted in one of TWCA's large hydraulic presses; this operation is routine at TWCA. The compacts are normally made into electrodes and recycled to the metal fabrication process to make new ingots. The visit to TWCA offered opportunities for:

1) Observation of production-level mechanical operations involving scrap tubing (chopping, washing, compaction). Other scrap forms (saw fines, machining turnings) were also involved in some of the work.

2) Acquisition of a variety of Zircaloy materials for small-scale tests at ANL.

3) Discussions with process development staff, covering possible ignition tests and suggestions for working with pyrochemical systems.

Feed for the compaction tests was provided by a manually fed chopper that was briefly seen in operation. The feed of mainly off-specification Zircaloy tubing was chopped, one tube or several tubes at one time. The ends of most cut sections were pillowed, but were generally clean-cut. Few fines were produced (estimated at less than 0.1 wt %). The chopped scrap was collected in 55-gal drums and was moved to the compactor, which is housed in a separate building.

Drum contents were dumped into a large, shallow rectangular tray; this was followed by manual loading into 5-gal buckets, weighing, and manual feeding to the press cavity. The material was mainly tubing having a wall thickness of 0.025-0.035 in., but occasional short sections of heavier tubing (*i.e.*, 0.125-in. wall thickness) were also seen. Machining turnings, after a washing operation in a large tumbler vessel to remove cutting oil, are also compacted routinely and without difficulty.

Eighty pounds of scrap was pressed at a time, making a compact 11 in. in diameter and 5 in. high. The compacts were only slightly warm to the touch as they came from the press at intervals of a few minutes; actual pressing required only about one minute. The starting density of the material was approximately 1 g/cc; the final density, using 2500-ton pressure (equivalent to about 52,500 lb/in.^{2}) was about 4.7 g/cc or about 72% of the theoretical density.

In a separate compaction trial, Zircaloy fuel element spacers, sheetmetal-like structures, were compacted with no difficulty. A test compaction of fuel element end fittings, which have sections greater than 1/2 in. in thickness, was deferred. It was suggested that these should be cut up before feeding to this particular press. A larger machine may accept these sections directly. Alternatively, these end fittings may be handled completely apart from the hulls since they are massive, represent no pyrophoric hazard, and may have only minimal contamination.

It was noted that no special care is taken in handling cut tubing, which can be considered as resembling hulls, and chopper fines. All operations are done in air. An air hose is even used to clean the metal fines away from the area around the press cavity. Provisions for safety rely on avoiding the

accumulation of fines. In the present case, the fines are compacted with the tubing sections. If irradiated Zircaloy is physically similar to this cut tubing, extrapolation of this experience to actual hulls apparently will be uncomplicated.

The TWCA operating personnel indicated that no particular problem arises when "clean, high-quality" metal scrap becomes alternately wet and dry. Such exposure can be a problem with zirconium sponge. In addition, unexplained ignitions have occurred in the past under such conditions, but the scrap form has not been clearly described in these cases. Scrap, including saw fines and machining turnings, is normally stored in covered, 55-gal drums. The saw fines are usually segregated because they often contain oxygen and nitrogen in excess of that allowed for normal recycle. Fines were singled out as requiring special care to avoid ignition; spark sources are avoided, but if ignition occurs, the fire is allowed to burn out.

II. STORAGE AND DISPOSAL OF TRITIUM
(L. E. Trevorrow)

A. **Introduction**

The general, long-range objective of this project is to evaluate alternatives in the management of tritium in waste arising from the production of power by nuclear reactors. In the near term, electric power will be produced predominantly by light-water reactors. If tritium is not removed from the fuel (*e.g.*, by the Voloxidation Process) before dissolution in aqueous acid (an early step in Purex reprocessing flow sheets), a major portion of the tritium formed by ternary fission in light water reactors is expected to appear in the low-level aqueous waste (LLAW) stream of the plants reprocessing the spent fuel from LWRs. Presently accepted schemes for managing this waste stream include dispersal as a vapor to the atmosphere or as a liquid to surface streams; this waste stream is diluted with air or water to concentrations less than those specified by radiation concentration guidelines. Such dispersal schemes, however, have met some objection by groups and agencies who believe that the radiological risks associated with these schemes are excessive. In preparation for the possibility that these objections might ultimately result in more restrictive regulations on disposal, alternative disposal techniques have been proposed by several organizations involved in nuclear energy development. The evaluation of such proposals constitutes the main effort in this project.

Proposals for retention of the tritium contained in low-level aqueous waste have generally fallen into two categories: those that do and those that do not involve concentration (*i.e.*, isotope separation).

Schemes involving concentration employ some separations operation that would convert the LLAW stream into 1) a tritium-enriched stream of sufficiently small volume that it could be stored economically and 2) a tritium-depleted stream of large volume, but of concentration sufficiently low that it could be recycled as makeup water to the reprocessing operations or dispersed to the biosphere in accordance with future regulatory specifications, however restrictive. Schemes both with and without concentration of tritium are being evaluated in the course of this project.

B. **Review of Recent Activities**

Activities in this project during recent months have included a preliminary evaluation of the use of the catalyzed hydrogen-water exchange reaction to concentrate aqueous tritium-bearing wastes; the arrangement, conduct, and distribution by us of the proceedings of the government-industry conference on tritium control that was held in conjunction with the 13th AEC Air Cleaning Conference; a survey of literature on deep-well injection of wastes; and the beginning of an evaluation of the application of deep-well injection to disposing of low-level aqueous wastes.

1. **Evaluation of Concentration of Tritiated Water by Catalyzed Hydrogen-Water Exchange**

In evaluating the potential application of catalyzed hydrogen-water exchange to the concentration of aqueous tritium wastes, the scope was limited

to a concept employing recent developments at the Institute for Stable Isotopes, Cluj, Romania, in catalyst efficiency and design of an exchange column.[3,4] Conclusions on the technical and economic feasibility of adapting these developments to retention of tritium from the LLAW of a fuel-reprocessing plant were offered in the preceding report in this series.[1] It was noted that information on which to base the concept was limited, and that the demonstration of the new developments has been on a small laboratory scale with feed that is not representative of LLAW.

In general, the technical feasibility of separating or concentrating hydrogen isotopes by the catalyzed exchange between hydrogen and water is unquestionable, since it has been employed on a large scale to produce heavy water.[5,6,7] No demonstrations have been reported, however, of separation of tritium for the particular concentrations of feed (LLAW) waste, and product of interest in the decontamination of LLAW. It may be significant, for example, that in this particular application, the concentrations, in feed and depleted streams, of the heavy isotope of interest are much lower than in heavy-water production processes. Thus, the technical feasibility of the present application has apparently never been actually demonstrated on the isotope at the concentrations of interest.

In the course of our study, perhaps the two most serious questions that became evident regarding the technical feasibility of applying the Cluj column to the decontamination of LLAW, are 1) whether the throughput limitations mentioned[3] but not clearly defined by the designer are too low for practicable application to treatment of the volumes of low-level waste to be expected from a fuel reprocessing plant, and 2) whether the catalyst efficiency would be significantly lowered by exposure to the trace residues of iodine, metallic ions, nitrogen oxides, solvents, and solvent-degradation products remaining in LLAW from fuel reprocessing operations.

With regard to economic feasibility, it was noted that the process once used at the well-known plant at Trail, B. C.,[5,6,7] based on the catalyzed hydrogen-water exchange reaction, is not practiced today by any of the world's heavy-water producers since it is not economically competitive with other processes. The exchange reaction was reconsidered for the present application, however, because of advantages claimed for recent developments in catalyst efficiency and design. Limitations on the information available about Cluj developments preclude estimation of the capital cost of the column, but the simplicity of its design compared to that of the Trail plant promises substantial reductions in capital costs attributed to column construction. Costs associated with materials flow and phase reversal, assumed to represent a major portion of operational costs, were calculated for two flow schemes:

1) For a scheme involving reduction of tritium in LLAW to 3×10^{-3} μCi/ml (the radiation concentration guideline for nonoccupational exposure)[8] and environmental dispersal of the depleted stream, the annual costs were 1.1×10^{-2} mills/kWh or \$0.66/Ci retained.

2) For a scheme involving reduction of tritium concentration in LLAW to 2 μCi/ml and recycle of the depleted stream as aqueous makeup to the reprocessing plant, the annual costs were 9.7×10^{-3} mills/kWh or \$0.53/Ci retained.

The waste stream from such separations processes would contain the bulk of the tritium and would be stored. The volume of HTO was arbitrarily assumed to be 0.015% of the feed volume. Hence, for a reprocessing plant of 300 MTU/yr capacity, an annual storage of about 1700 liters of H_2O containing 1.5×10^5 Ci tritium is implied in these calculations for the Disperse mode. The same volume of water containing slightly less tritium (1.3×10^5 Ci) is obtained as waste for the Recycle mode. No cost data were included for isolation, handling, and storage of this stream.

2. Government-Industry Conference on Tritium Control

Recent efforts in this project were devoted to the arrangement, conduct, and distribution of proceedings of the government-industry conference on tritium control, which was held in conjunction with the 13th AEC Air Cleaning Conference. These activities were consistent with one goal of this project, *i.e.*, to maintain a surveillance of recent developments related to tritium control. Discussions of such developments by 44 attendees from a number of government and industrial organizations of the U. S. and other countries were recorded and transcribed into a manuscript. The correction of comments by those participating in the discussion is nearly finished, and plans are being made to distribute the proceedings to attendees and several other requestors around the first of March, 1975.

3. Survey of Deep-Well Injection of Wastes

A survey was made of literature describing deep-well injection of industrial wastes of all types to determine what topics should be addressed in an evaluation of the application of the technique specifically to LLAW. This survey was initiated through a computerized search of abstracts of articles published in the fields of geology, chemistry, nuclear science, and engineering using GEOREF, Nuclear Science Abstracts, Engineering Index, National Technical Information Service, and Chemical Abstracts. Subject to amendment pending the receipt of additional literature information and the advice of USGS personnel and private consultants, the survey resulted in the conclusions that the most important topics to be addressed in a feasibility study include the composition of LLAW and the required pre-injection treatment, costs, clarification of legal and regulatory constraints, details of geologically suitable siting, and environmental risks. These topics are described in added detail below.

A substantial effort was devoted to the evaluation of deep-well injection of high-level aqueous wastes and to identifying areas of the U. S. that are suitable for deep-well injection of liquid wastes; this was done by the U. S. Geological Survey and the American Association of Petroleum Geologists in the 1950s.[9] These efforts resulted in the outlining of broad areas known to be sedimentary basins. The disposal site must be geologically suitable, but preferably remote from population centers. Perhaps the best arrangement would be colocation of the fuel reprocessing plant and disposal site. It was suggested that further work incorporating recent data obtained in geologic, demographic, and economic surveys is needed to define in additional detail areas of the U. S. that are suitable for deep-well disposal.

The environmental risks involved in the practice of deep-well disposal of LLAW need to be estimated. Risks would also be dependent on definition of the composition of LLAW, including expected concentrations not only of tritium, but also of other fission products and actinides. It was suggested that various possible failures be anticipated and that population doses resulting from each be calculated.

The legal and regulatory constraints on the application of deep-well disposal promise to become an increasingly important factor in determining the feasibility of its application to LLAW.[10],[11] State governments are the primary regulators of deep-well injection operations. At present, however, state laws regarding liquid wastes are not uniform and, in many cases, their application to deep-well disposal is not clear. Federal water-pollution control regulations apparently affect deep-well disposal only indirectly through recommendations to states via the National Pollutant Discharge Elimination System, and through a recent policy statement by the Environmental Protection Agency,[12] both of which resulted from the Federal Water Pollution Control Act. Other legal constraints on deep-well injection include the rights of owners of private property adjacent to disposal sites. Also, the practice of deep-well injection of LLAW by commercial fuel reprocessors has not been tested in environmental impact review procedures. It was therefore suggested that a complete assessment of the feasibility of deep-well injection of LLAW would require that all currently foreseeable legal and regulatory constraints on the practice be collected, summarized, and clarified.

The composition of LLAW will determine the extent of pre-injection treatment that may be necessary to prevent plugging of pores in the receiving geological strata. Such plugging may be caused by suspended solids present in the fluid, either before injection or after injection as a result of reaction between waste and rock, and also by pH effects not involving suspended solids that may cause swelling of the strata. The concentration of actinides in LLAW may also have an important bearing on the environmental impact of this technique and its acceptability. Although a reference composition of high-level waste from fuel reprocessing has been defined, no such reference for LLAW is available. Estimates of the composition should be derived, if possible, from reprocessing experience at AEC sites and at Nuclear Fuel Services Company, or from calculations in which expected decontamination factors from evaporative operations are applied to the concentrations defined for a reference high-level waste.

The cost of deep-well injection of LLAW would be important in determining its economic acceptability to commercial reprocessors and power consumers. Cost estimates for deep-well injection of other industrial liquid wastes are available and can be taken as a rough estimate of the costs of application to LLAW. Calculations based on the assumption that past estimates of cost per volume[13] injected for other wastes can be applied directly to LLAW resulted in cost estimates of 8-16¢/Ci of ^{3}H or $1-3 \times 10^{-4}$ mills/kWh of nuclear power. Costs need to be developed, however, that represent recent costs of labor and materials and that apply in particular to the characteristics of LLAW.

4. Current Progress

The recommendations derived from the survey and listed above are to serve as guidelines in developing a study of applying deep-well injection to disposal of LLAW. Current progress in this project has been concentrated mainly on initiating this study, which is intended to aid decisions on the applicability of deep-well injection if regulations on the release of tritium to the environment were to become more restrictive in the future. The study will result in a report that would serve as a useful reference to organizations engaged in such activities as reprocessing, licensing, regulation, and waste management and who, at some future time, may need to assess the applicability of this technique against other disposal options.

The proposal for this study included obtaining consultation in the field of deep-well injection wastes. Recent activities have therefore included negotiations to obtain consulting help. Consultants would contribute to decisions on the contents and scope of the evaluation, writing some sections of the evaluation, and reviewing all sections of the evaluation. A detailed outline of the evaluation has been constructed.

A necessary initial step in the evaluation is characterizing the composition of the fluid to be injected. Information on the composition of the fluid is important because it is a determinant of the equipment and operating conditions used in the injection, therefore ultimately affecting such factors as costs, environmental impact, and the legal and regulatory restrictions that must be observed in the operation. Since in most Purex fuel-reprocessing flow sheets, the low-level waste is the product of at least two evaporative stages, the concentration of most dissolved and suspended solids is likely to be extremely low. Entrainment, however, will probably cause the presence of even nonvolatile species in the evaporator overheads. Although the tritium concentrations are readily estimated from burnup and the water balances of the fuel-reprocessing flow sheets, information on a number of other compositional characteristics is desired but not readily available. These characteristics include pH and concentrations of organics, concentrations of all radioactive species, total suspended solids, total dissolved solids, and dissolved gases. Predictions of some properties, mainly the concentrations of radioactive species of most concern, are available from the environmental statements of the commercial reprocessing plants. Other properties, however, which have not warranted environmental concern but which may determine the procedures to be used in a deep-well injection operation are not available from these statements.

Current effort has therefore also involved developing a reference composition for LLAW. Several information sources on which to base a reference composition for LLAW are being considered. First, reports of reprocessing by AEC contractors and the Nuclear Fuel Services Plant are being searched for discussion on reprocessing stream compositions. Second, since the LLAW stream results from operations on the high-level aqueous waste stream, for which reference compositions have been developed, the composition of LLAW may have been predicted by personnel of the three U. S. companies that have reached the construction phase in their fuel-reprocessing ventures; communications with representatives of the three companies have been initiated in order to determine whether predictions are available.

Several difficulties in trying to arrive at a reference list of constituent concentrations are recognized: 1) Information based on experience with commercial fuels is limited to a few campaigns of one company (NFS). 2) Information on the composition of waste streams recorded for past AEC reprocessing activities at the Hanford, Idaho, and Savannah River plants is not representative of the composition of waste streams that will emerge from future commercial reprocessing of LWR fuels. 3) Some constituents, *e.g.*, suspended solids, that would have a bearing on deep-well injection have no significance in present methods of disposal of low-level aqueous waste and therefore may have been ignored by those planning commercial reprocessing operations. In view of these considerations, it is anticipated that a reference composition of LLAW, constructed at this time, will be largely predictive in nature.

C.   Conclusions

Deep-well injection for disposal of low-level aqueous wastes warrants detailed evaluation as a possible option that might be considered if future waste-disposal regulations become more restrictive. A preliminary survey of the applicability of the technique to industrial wastes in general has indicated that an evaluation of application of the technique to low-level aqueous waste should include discussions of pre-injection treatment, costs, legal regulation, siting, and environmental impact. Current progress includes negotiations to obtain consulting help in the development of this evaluation, preparation of a detailed outline of the evaluation, and collection of data related to the expected composition of LLAW streams. Compositional characterization is very important to the development of this disposal concept, ultimately affecting such factors as treatment, costs, applicable laws, and environmental impact. Since experience to typify commercial reprocessing of civilian fuels from LWRs is scant, a reference composition for LLAW must be based largely on prediction rather than observation.

III. RELIABILITY OF HIGH-LEVEL WASTE CONTAINERS
(W. Seefeldt, W. Mecham)

A. Purpose and Scope

The purpose of the container reliability studies is to identify as quantitatively as possible the reliability against failure and leakage of the canisters used to contain high-level wastes in a glass or calcine form.

Container degradation due to internal metallurgical characteristics, thermal and mechanical events occurring during transport and handling (but not major events such as earthquakes and tornadoes), and interactions with internal and external environments will be considered.

Environments to be included are interim storage of solidified wastes at a reprocessing plant, transport from a reprocessing plant to a Retrievable Surface Storage Facility (RSSF), interim storage at the RSSF, and transport to the ultimate disposal site.

The study requires the establishment of reference systems prior to the determination of canister reliability. Three storage concepts have been developed by ARHCO for application to an RSSF. These concepts will be part of the reference system. In addition, waste compositions, canister material and fabrication methods, coolant compositions, and mechanical and thermal events should be selected for the reference system.

The three concepts of interim storage at the RSSF are:

1) the Water Basin Concept, in which canisters are stored bare in a water pool,

2) the Air-cooled Basin Concept, in which canisters are overpacked in mild steel and stored and cooled in air moving by thermal convection, and

3) the Sealed Storage Cask Concept, in which canisters are overpacked in mild steel, encased in a freestanding concrete shield placed outdoors on a concrete pad, and cooled by thermal convection.

The sequence of events to be considered for reference was 10 years of interim storage under water at a reprocessing plant, followed by 100 years of interim storage at an RSSF, together with transfer from both facilities. In addition, 40 years of interim storage under water at the reprocessing plant followed by shipment to the ultimate disposal site is also included.

Initially, the two waste forms to be considered for incorporation into the reference systems were calcine and glass, but no specific compositions were established for reference purposes. Through discussions with DWMT, two modes of heat transfer for the calcine form were established: with and without internal fins. This was later reduced to one of the two modes, with no specific selection made.

B.   Current Work

Work is proceeding on several parallel paths.

The literature is being examined to identify alternative methods for establishing reliability. A review is also being made of the stress corrosion cracking behavior of austenitic stainless steels in water environments, similar to those expected in the Water Basin Concept of the RSSF.

Efforts have been made to identify and examine principal sources of stress in the stainless steel canisters. For application to the storage of waste in the glass form, the widely different coefficients of expansion for stainless steel and glass have been identified as a source of stress during the cooling of waste-containing canisters after filling. Calculations have been made to determine the magnitude of the stress levels if stress-relieving mechanisms such as creep are ignored.

For application to the storage of waste in the calcine form, the internal generation of pressure due to decomposition or volatilization of impurities was also identified as a source of stress. Calculations were made for residual nitrates and residual moisture.

    1.   Methodology

A review has been made to identify various methods by which the reliability of canisters can be established. It is assumed that for these purposes the reference system has been adequately described by others--*i.e.*, that the time span of interest, the method of storage and transportation, the processes for producing the solid to be stored, composition of such solids, composition of canisters, thermal histories including heat treatments, etc., have been defined. Where a range of options or lack of detail exists in the reference design, reasonable specifications will be made and identified for purposes of reliability analysis.

The second step is the identification of failure paths. This may be done by careful listing of failure paths based on the best judgments available. This technique, if performed by competent and knowledgeable individuals, has a high probability of identifying all significant pathways if the overall system under examination is not too complex. A systematic method for identifying failure paths in complex systems is the development of a fault tree which is initiated by identifying the final failure type, then working backwards in a logical fashion to identify all mechanisms leading to that failure type. A simple example, illustrated in Fig. 1, shows how the level of detail is expanded at each succeeding lower level. The formalism provides greater assurance that all potential steps leading to a failure are identified.

If the final result of reliability is to be expressed quantitatively as a probability of failure, each of the steps at the lowest levels in the fault tree is examined in detail for the establishment of probability for that particular step. This determination may be simple if considerable experience is already available for the step in question, and may be complicated if there is no experience or if considerable extrapolation is required from known experiences. With probabilities of individual steps thus established, an

appropriate mathematical combination of them which includes considerations of interactions can be made, to yield the desired quantitative value.
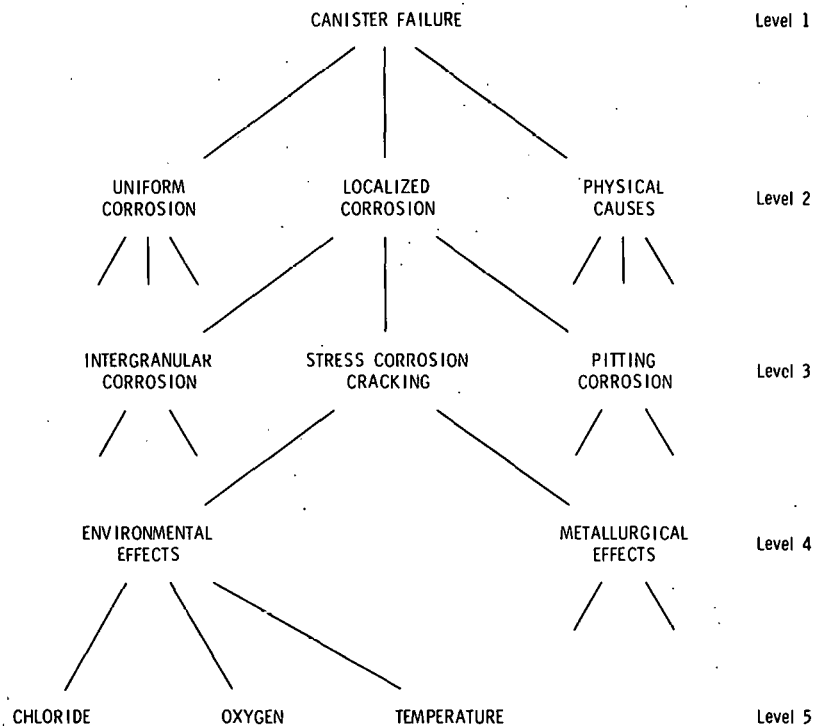

Fig. 1. Simplified Example of Fault Tree for
Identifying Canister Reliability

In addition to establishing an overall probability measure, the reliability analysis is expected to have use, in the identification of those steps leading to high failure rates, and to lead to recommendations to modify the reference system to ameliorate the high rates.

2. Review of Localized Corrosion Behavior of Stainless Steel
    in Water Environments

An effort has been made to identify the behavior of austenitic stainless steels—with emphasis on types 304 and 304L—when exposed to environments and conditions comparable to those expected in the storage of solidified high-level waste in a Retrievable Surface Storage Facility (RSSF). Type 304L is the reference material of construction for the waste canisters.

In general, austenitic stainless steels of the 18-8 type (18% chromium and 8% nickel) have excellent surface corrosion properties in both water and aggressive oxidizing environments. However, under some conditions, these steels are also subject to severe localized attack that leads to early failure. The reliability of the use of austenitic stainless steel as canister materials is determined by such localized attack.

The following forms of localized attack have been identified:

1) Stress corrosion cracking,

2) Intergranular attack, and

3) Pitting.

It is necessary to ascertain as well as possible the envelope of conditions within which there exists a significant potential for local corrosion phenomena, to determine whether the reference conditions of storage in the RSSF infringe on that envelope, and, if so, to determine the reliability.

Localized attack phenomena are strongly dependent on the thermal history of austenitic stainless steels. In normal use for corrosive service, these steels are heat treated at temperatures (usually greater than 1000°C or 1830°F) at which their constituents are solubilized. The solid solution austenitic phase thus formed is forcefully retained by rapid cooling. The non-equilibrium alloy is then subject to changes when it is exposed to temperatures where atom mobility is increased. These changes, in turn, may have an effect on local corrosion behavior.

Carbon is almost always present as an impurity in austenitic stainless steels, and special efforts are usually made to keep its content low in order to reduce what are known to be adverse effects. For example, the specification for carbon content of type 304 stainless steel is a maximum of 0.08 percent, and the specification for type 304L is a maximum of 0.02 percent. Though reliable data for carbon solubility as a function of temperature is lacking, some general observations can be made. Carbon solubility decreases markedly with decreasing temperatures, and it is known that at temperatures of 550 to 850°C (1020-1560°F), the solubility is greatly exceeded in normal grades of stainless steel (e.g., type 304), and is even exceeded in the low-carbon grades (e.g., type 304L). It is generally agreed that carbon tends to form a precipitate with the chromium contained in the alloy ($Cr_{23}C_6$), and that it does so preferentially along grain boundaries. Such alloys are said to be sensitized, and the process by which it occurs is sensitization. The sensitization phenomenon is significant because experience has shown that it adversely affects the corrosion-resisting properties of stainless steels in many environments and frequently contributes to accelerated local attack.

Stress Corrosion Cracking

Emphasis in this review has been placed on stress corrosion cracking of stainless steels in water environments. The severity of this phenomenon is dependent on many factors, including temperature, stress level, oxygen and chloride concentrations and the state (sensitized or unsensitized) of the stainless steel.

It was anticipated that a review would allow definition of the limits of the various parameters, below which it can be assumed with high probability that stress cracking does not occur. This objective may be somewhat elusive, as was stated by Latanision and Staehle in a paper presented at the 1967 conference on the Fundamental Aspects of Stress Corrosion

Cracking: ". . .there is great difficulty in defining a minimum chloride concentration below which cracking will not occur because of effects of the concentrating processes such as drying or boiling."[14]

A great deal of work has been done in water environments at temperatures characteristic of those in light water reactors, *i.e.*, 200 to 300°C (390-570°F). Far less work has been done at the lower temperatures of interest for the RSSF, namely, 60 to 90°C (140-190°F), though some efforts have been made to determine the effect of temperature on cracking behavior.

At 200°C (390°F), stress cracking of type 304 stainless steel has been observed in water environments with chloride concentrations as low as 2 ppm in the essential absence of oxygen (0.78 ppm).[15] The specimens tested consisted of fully annealed, 0.015-in.-dia wires, and were stressed at a level of 90 percent (about 32,000 psi) of the yield stress. Failure times ranged from 480 to 938 min. At higher chloride (100 ppm NaCl) and oxygen (10 to 15 ppm) concentrations, time to cracking was reduced to about 50 min for all stress levels tested between 60 and 100 percent of the yield stress (21,000 to 35,000 psi), and to 300 min for 40 percent of yield stress (14,000 psi). No tests were conducted at lower stress levels that might have enabled the determination of a threshold stress. Increasing the temperature to 260°C also resulted in short cracking times (∿70 min) at 100 percent of yield, but cracking tendencies were reduced considerably with reduction in stress. The data suggests that the threshold stress is higher at 260°C (500°F) than at 200°C (390°F).[16]

Figure 2 shows a compilation of data relating chloride and oxygen concentrations to cracking time.[14,17] The data is for type 304 stainless steel stressed at a level of 21,000 psi (∿60 percent of the yield stress) at 260°C (500°F). When sodium chloride concentrations are high--about 2000 ppm-- cracking times are nearly independent of oxygen concentration, but at low concentration, the effect of oxygen in causing stress cracking is much more pronounced.

Though these types of tests with specimens consisting of wires are severe in using specimens with a high surface to volume ratio, they nonetheless are indicative of those conditions that favor adverse behavior. Specimens consisting of thick sections of metal do not fail as rapidly as thin wire.

Sensitized stainless steel is more prone to stress cracking than is annealed material. The mode of cracking changes from transgranular in annealed material to intergranular in sensitized steel. Further, in sensitized material, the presence of chloride ions is not a prerequisite to initiate cracking; the presence of oxygen is sufficient.

Sensitized specimens in the forms of plates and internally pressurized cylinders at a temperature of 288°C were exposed to water containing various amounts of oxygen and no chloride at three different stress levels.[18] The alloys used were types 304 and 316 stainless steel, and the stress levels were about 27,000, 54,000, and 81,000 psi. These levels compare to a yield stress of about 32,000 psi at 288°C (545°F). No failures were observed in periods ranging up to 450 days if oxygen levels were held at

10 ppm or lower if stresses were 54,000 psi or less. At the highest stress level (81,000 psi), failure was observed at 14 days for type 304 stainless steel and at 10 days for type 316. At oxygen concentrations of 100 ppm, type 304 stainless steel failed rapidly at all stress levels (mill-annealed material does not fail under these conditions).

Other investigators have found that stress levels above yield, an increase of oxygen level from 0.2 to 5 ppm (also at 288°C or 545°F) results in sensitized type 304 stainless steel changing from a no-cracking region to a cracking region.[19]
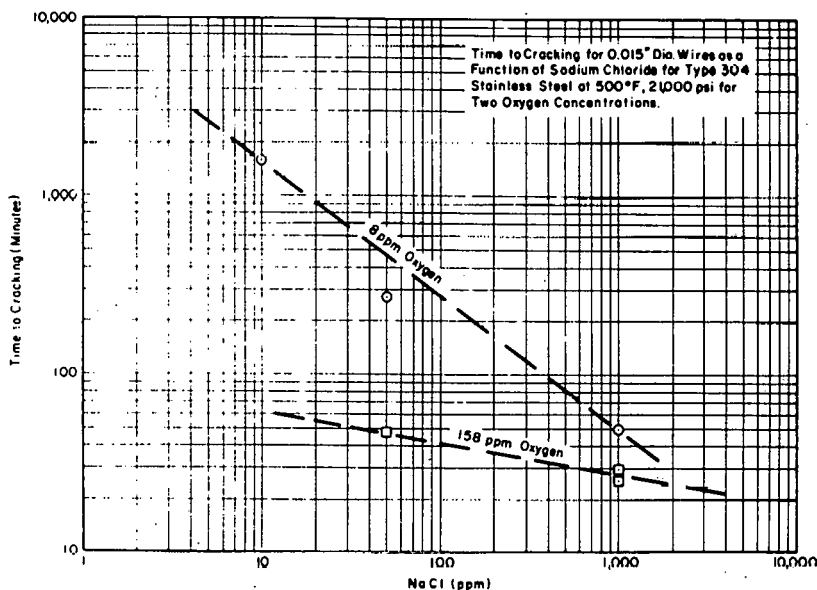

Fig. 2. Effect of Chloride and Oxygen on Time to Cracking of Type 304 Wire Held at Constant Load in Single-Phase Aqueous Environment.[14]

Figures 3 and 4 show the pronounced effects of dissolved oxygen and stress levels on time to cracking for sensitized type 304 stainless steel.

Stress corrosion cracking can also be induced in annealed types 304 and 347 stainless steels when they are exposed to chloride-containing water in a temperature range of 60 to 90°C (140-190°F). Highly stressed U-bend specimens were exposed to water containing 5 to 550 ppm sodium chloride in equilibrium with ambient air.[20] Oxygen concentrations ranged from 2.75 ppm at the lower temperatures to 0.88 ppm at the upper temperatures. During test periods of 48 hr in water containing 10 ppm sodium chloride, 10 percent of annealed type 304 specimens cracked at 60°C (140°F), while 90 percent cracked at 85°C (185°F). When specimens were sensitized, comparable cracking figures were 60 and 100 percent. In one series of tests in which oxygen was bubbled through the water, cracking failure rates did not increase significantly.

The above data establish that stress cracking can occur in type 304 stainless steel at the temperatures of interest for the RSSF, even under conditions in which no mechanisms are available for local concentration of chloride. It is recognized that these tests were conducted only at high stress levels well beyond the yield stress, and that they shed little light on the effect of various stress levels below yield stress on cracking tendencies or the existence of a threshold stress level below which cracking does not occur.
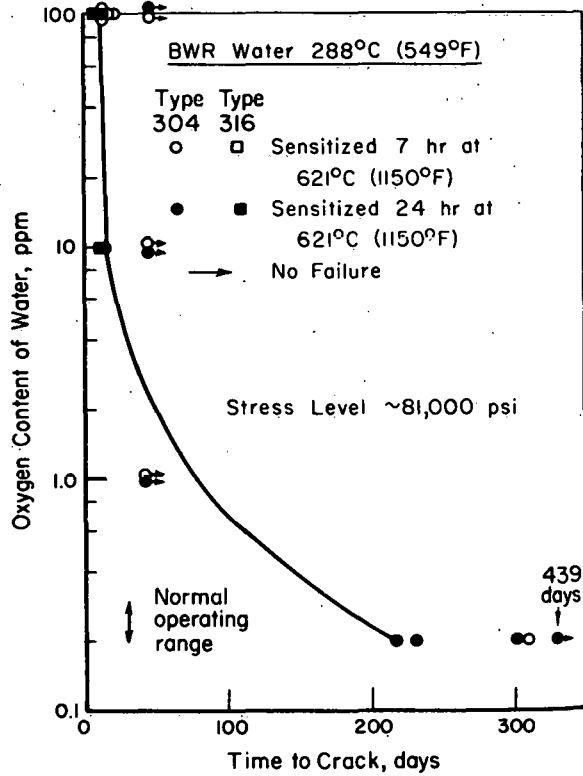

Fig. 3

Effect of Dissolved Oxygen Level on Time to Cracking of Stressed Sensitized Stainless Steel Specimens in Water at 288°C (545°F).18
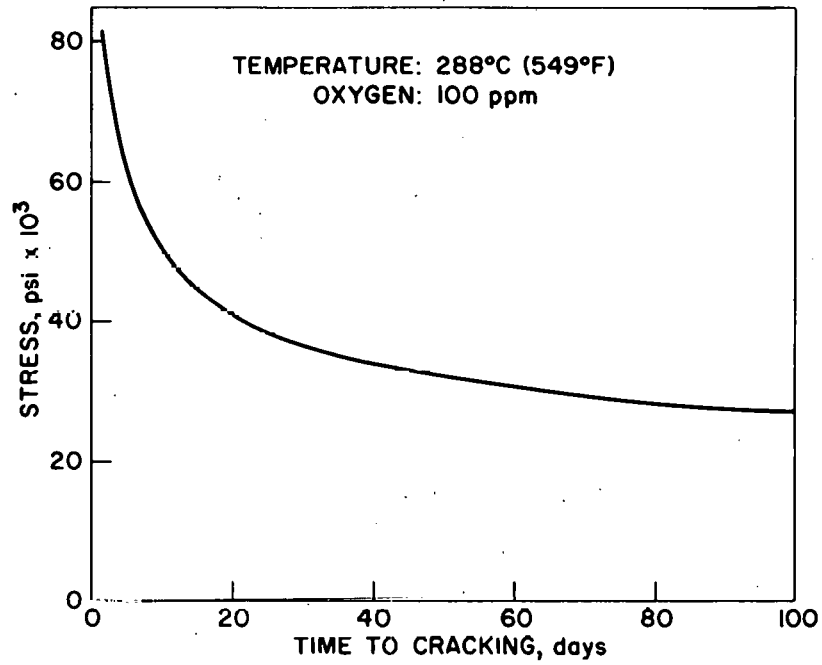
Fig. 4. Effect of Stress Level on Time to
Cracking of Sensitized Types 304 and 316
Stainless Steel in Water.[18]

A summary of data from a variety of sources relating cracking time to temperature of exposure is shown in Fig. 5.[21] Included is data obtained for a number of stainless steels generally regarded as the 18-8 type in solutions containing 25 ppm or more of chloride. Stress levels are not stated but in general are those associated with U-bend tensile specimens stressed beyond the yield stress. The pronounced effect of temperature is evident.

Several efforts have been made at establishing threshold conditions for the initiation of cracking. Figure 6 relates suggested oxygen and chloride levels for annealed type 347 stainless steel exposed to water at 260°C (500°F).[22] The authors pooled all data available to them, neglected all parameters except oxygen and chloride, and considered only whether specimens had failed or not.

Results of one of the few efforts to establish threshold stresses for annealed stainless steels are shown in Fig. 7.[14,23] The figure was constructed from data obtained using boiling solutions of concentrated magnesium chloride (42%) and indicates a threshold stress of about 10,000 psi. Though this environment is regarded as being highly aggressive, it is recognized that effects associated with it are sometimes different from those obtained with other chloride salts. Its applicability to the RSSF environments is uncertain. More data on threshold stresses are needed to more fully evaluate the behavior of type 304 stainless steel at the conditions of interest.

Most of the studies on stress corrosion cracking provide values of parameters that ensure that cracking will occur in water environments. Stresses above the yield stress, temperatures about 175°C (345°F), and chloride and oxygen levels above 5 ppm are highly conducive to promoting cracking. Extrapolation of existing data strongly suggests that at low stress levels and low temperature, cracking can be avoided. Data supporting this observation are generally lacking, however.

In the following sections, several sources of stress in waste canisters are identified. Calculations of the magnitude of developed stresses are presented.

3. Temperature-Induced Stress in Stainless Steel Canisters Containing Solid Glass

In order to minimize the potential failure of waste canisters in a water environment, the stress in stainless steel canisters must be restricted to low levels. No design threshold stress level has been established, but a reasonable strategy is to hold the stresses as low as practicable.

A calculational model for canister stresses has been developed along standard methods.[24] The reference case is borosilicate glass cast directly into a canister of type 304L stainless steel having an ID of 12.0 in. and a wall thickness of 0.375 in. The glass assumes a rigid solid form at a temperature well above the storage temperature of the canister. Because the thermal expansion of stainless steel is greater than that for glass, cooling the canister results in the development of circumferential tensile stresses in the canister.
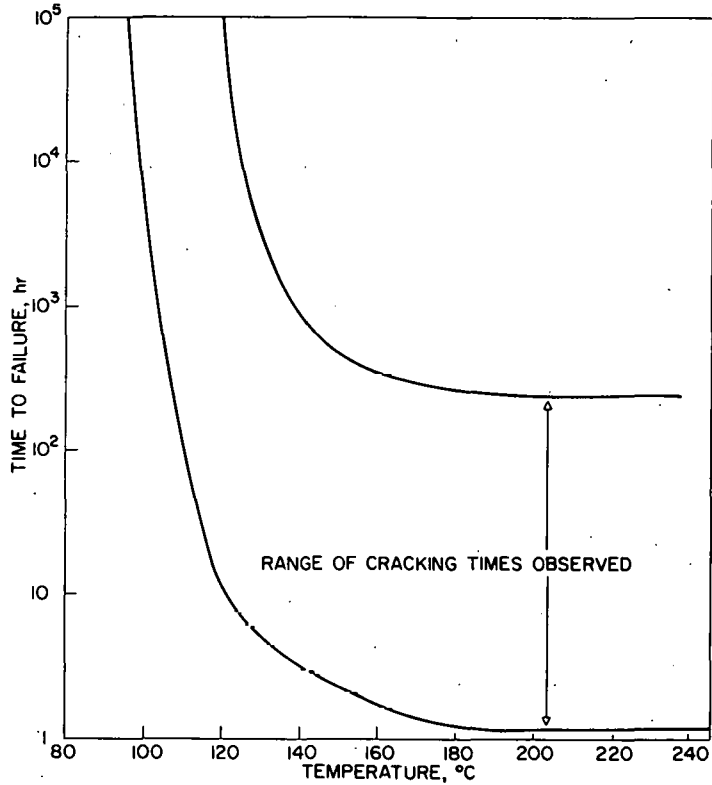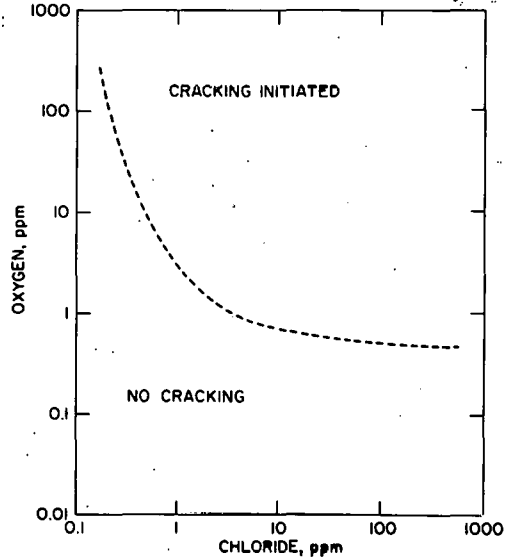
Fig. 5.

Time to Failure vs Test Temperature for 18-8 Stainless Steels.[21]

Fig. 6.

Proposed Threshold Levels for Cracking Related to Oxygen and Chloride Content of Water at 500°F (260°C), Applied to Type 347 Stainless Steel at High Stress Levels.[22]

Using a simple model, stresses have been calculated and compared with stress levels known to be conducive to the initiation of stress-corrosion cracking in oxygenated water containing chlorides. The mechanical properties of type 304 stainless steel and Pyrex (commercial grade borosilicate glass) were used and the model developed so that the effect of variables is evident by parametric analysis. The model assumes that the materials are only subject to strains within the elastic limit and that no "creep" phenomena are involved.
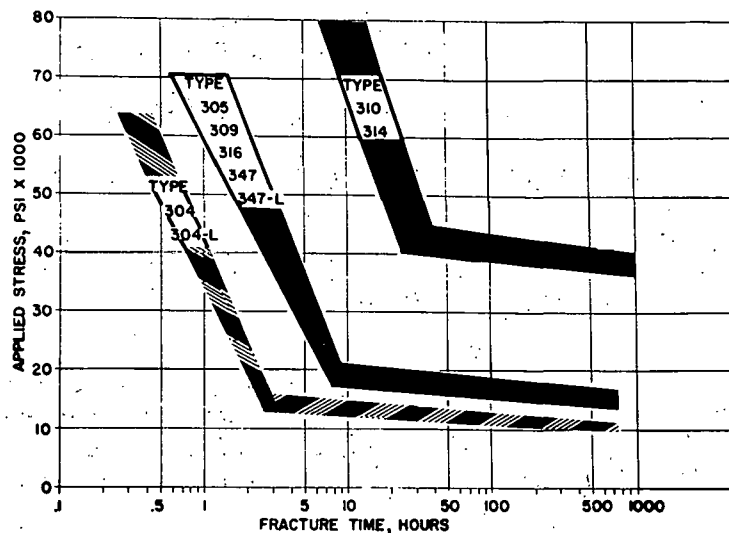
Fig. 7. Composite Curves Illustrating
the Relative Stress Corrosion Cracking
Resistance for Commercial Stainless
Steels in Boiling 42% Magnesium
Chloride (309°F or 155°C).[14,23]

The stresses in the stainless steel canister can be treated as those in a thin-wall cylinder, where the tensile stress is closely approximated by the following:

$$S_s = E_s \left(\frac{\Delta r_s}{r}\right) = \frac{P_s r}{t} \tag{1}$$

where S_s = circumferential tensile stress, psi

E_s = modulus of elasticity of stainless steel, psi

r = inside radius of canister, in.

Δr_s = absolute deformation (increase) in radius of steel within the elastic limit, in.

$\dfrac{\Delta r_s}{r}$ = relative elastic deformation, or strain

t = thickness of canister wall, in.

P_s = radial pressure acting on the inside wall of the canister, psi

For the solid cylinder under external pressure, the deformation is given by the following:

$$\frac{\Delta r_g}{r} = \frac{P_g \left(1 - \mu_g\right)}{E_g} \tag{2}$$

where p_g = the external (radial) pressure applied, psi

      r = radius of the glass (same as r above)

    Δr_g = absolute deformation (decrease in radius) of glass, in.

    E_g = modulus of elasticity for Pyrex, psi

    μ_g = Poisson's ratio for Pyrex.

At some high temperature below which glass is considered rigid, it is assumed that the internal diameter of the canister, and the external diameter of the glass cylinder are identical and that no stresses exist in either material. The decreases in diameter with cooling, assuming no restraint, are for stainless steel:

$$2r \cdot c_s \cdot \Delta T \tag{3}$$

and for glass:

$$2r \cdot c_g \cdot \Delta T \tag{4}$$

where c_s = coefficient of thermal expansion of canister, °F^{-1}

    c_g = coefficient of thermal expansion of the cylinder, °F^{-1}

    ΔT = temperature decrease from initial high temperature at which glass is considered rigid, °F

Consolidating the above information and using the proper sign to show increase or decrease in radii, one obtains

Change in radius of glass:

    due to cooling (from Eq. 4): $-rc_g\Delta T$

    due to external stress (from Eq. 2): $\dfrac{-p_g\left(1-\mu_g\right)r}{E_g}$

Change in radius of stainless steel:

    due to cooling (from Eq. 3): $-rc_s\Delta T$

    due to elastic strain (from Eq. 1): $\dfrac{+p_s r^2}{tE_s}$

In the final stressed condition, the algebraic sum of the changes in radius of stainless steel must equal the sum of the changes in radius of the glass

$$\frac{p_s r^2}{t E_s} - r c_s \Delta T = -r c_g \Delta T - \frac{p_g \left(1-\mu_g\right) r}{E_g} \tag{5}$$

Further, the external stress on the glass (p_g) is equal to the inwardly directed stress due to elastic strain of the stainless steel (p_s) which in turn is equal to $\frac{S_s t}{r}$ (from Eq. 1). Substituting $\frac{S_s t}{r}$ and multiplying by $\frac{E_s}{r}$, one obtains

$$S_s - E_s c_s \Delta t = -S_s \frac{t}{r} \frac{E_s}{E_g} \left(1-\mu_g\right) - E_s c_g \Delta T \tag{6}$$

which yields

$$S_s = \frac{E_s \Delta T \left(c_s - c_g\right)}{1 + \frac{t}{r} \frac{E_s}{E_g} \left(1-\mu_g\right)} \tag{7}$$

For the properties in Table 1 and for a cylinder diameter of 1.0 ft, the stress S_s in psi is given by

$$S_s = 214 \, \Delta T \tag{8}$$

This indicates a tensile stress of 21,400 psi developed in the steel for every 100°F of cooling. Since the softening point of Pyrex is about 1500°F (815°C) and the reference temperature of the canister in water-basin storage is about 140°F (60°C), the ΔT may be 1000°F (540°C) or higher.

These calculations (which neglect stress-relieving mechanisms such as creep) show that large circumferential tensile stresses may develop in the stainless steel canister on cooling that may lead to stress corrosion cracking, deformation, or rupture. The phenomenon of stress relief is being examined further because of its importance to the reliability of canisters during interim storage of high level wastes.

4. Development of Canister Stresses Due to Pressurization from Decomposition of Residual Nitrates and Volatilization of Residual Water in Calcine

High-level radioactive waste emerges from the Purex processing of spent reactor fuel as a nitric acid solution. Primary solidification of this high-level waste is accomplished by evaporation and calcination to form a dry solid product, consisting mainly of fission product oxides. Pure oxides are believed to be quite stable and unreactive to stainless steel at temperatures

of concern. However, residual nitrate and water, which may be present to the extent of 0.5% by weight[25] after primary calcination, may have effects that are adverse to stainless steel. At temperatures higher than those encountered during calcination, nitrate and water may form gaseous products by decomposition and desorption that could result in high internal pressures that are expected to produce stresses in the sealed containers.

A simple model has been developed to calculate pressure from decomposition of nitrate and from desorption of water. Some recent experimental results at PNL are cited in interpreting the results of the calculations.

TABLE 1. Pertinent Physical Properties of Stainless Steel and Glass

	Stainless Steel Type 304L	Borosilicate Glass
Coefficient of Thermal Expansion, °F^{-1}	10.4 x 10^{-6}	1.8 x 10^{-6}
Modulus of Elasticity	28 x 10^6	9.5 x 10^6
Theoretical Density, g/cc	8.0	2.23
Softening Point, °F	------	1500

a. Basis of Calculation

1) All residual nitrate in the primary calcine product is assumed to decompose as follows:

$$M(NO_3)_2 \text{ (solid)} \rightarrow MO \text{ (solid)} + N_2 \text{ (gas)} + \frac{5}{2} O_2 \text{ (gas)}$$
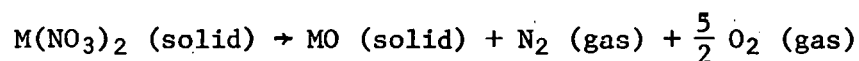
A divalent metal has been selected to establish basic proportions. The above decomposition yields 7/4 mol of gas per mol of nitrate.

2) The pressure in the canister is assumed to be that exerted by the above decomposition gas according to the ideal gas law.

3) Definitions:

V_o is the total canister volume, cm^3

y is the void volume of the canister, when filled with calcine, as fraction of V_o

x is the weight fraction of nitrate in the solid calcine

ρ_o is the theoretical density of calcine, g cm^{-3}.

b.   Calculation of Pressure from Nitrate

The mols of gas produced by decomposition of all residual nitrate (=n) is:

$$n = V_o \rho_o (1-y)(x) \frac{\left(\frac{7}{4}\right)}{(62)} = 0.02823 \ (x) \ (1-y) V_o \rho_o$$

where the molecular weight of nitrate is 62.

The pressure of gas in the void volume is given by:

$$P = \frac{nRT}{V} = \frac{0.02823 \ (x) \ (1-y) V_o \rho_o \ RT}{V_o y}$$

Letting $\rho_o = 4.0$ g $\cdot$ cm^{-3} (density of Al$_2$O$_3$), T = 825°C (1090°K or 1505°F), and using the appropriate R = 82.06 atm cm^3 (g mol)$^{-1}$ °K^{-1}

$$P(atm) = 10,173 \left(\frac{1-y}{y}\right) x$$

The temperature of 825°C (1515°F) selected is reasonably consistent with a temperature excursion and the assumption of complete decomposition of nitrates and desorption of moisture. The pressure at 825°C is plotted in Fig. 8 against x for various values of y.
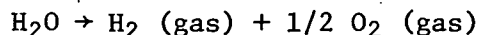
The general interpretation of this result is that loss of cooling presents the hazard of high pressure unless residual nitrate is reduced to $\sim$0.1 wt % (1000 ppm) in the calcine product or unless some pressure relief is provided.

c.   Calculation of Pressure from Desorption of Water

On the basis of the thermal decomposition of tightly bound water of hydration in solid calcine into water vapor:

$$MO \cdot H_2O \text{ (solid)} \rightarrow MO \text{(solid)} + H_2O \text{ (gas)}$$
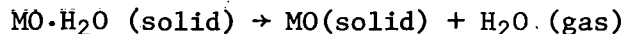
and, if radiolytic decomposition occurs:

$$H_2O \rightarrow H_2 \text{ (gas)} + 1/2 \ O_2 \text{ (gas)}$$

By thermal decomposition alone, 1 mol of gas is produced by 1 mol of residual moisture. By radiolytic decomposition, 3/2 mol of gas is produced per mol of residual moisture. On the assumption that net radiolytic decomposition is only a few percent, this avenue of pressurization will not be considered here, although it may be important from other considerations. Analogously to the calculation model for residual nitrate, a model has been constructed relating generated pressure to moisture content. The mols of water vapor present (n) are given by

$$n = \frac{V_o \rho_o \ (1-y)x}{18}$$

Using this relation for n, a calcine theoretical density (ρ_o) of 4.0 g · cm^{-3}, a temperature of 825°C (1098°K), and R = 82.06 cm^3 atm (g mol)$^{-1}$ °K^{-1}

$$P = \frac{nRT}{V}$$

$$= \frac{V_o \ (4.0) \ (1-y) \ (x)}{18} \cdot \frac{(82.06) \ (1098)}{V_o y}$$

$$= 20,027\left(\frac{1-y}{y}\right)x$$

When the pressure from water vapor is compared with that from decomposition of nitrate, it is seen that for equal x and y, the pressure of water is about twice that from nitrate decomposition. However, at calcination temperatures in the range of 400 to 600°C (750-1110°F), the concentration of residual water is typically an order of magnitude lower than that for residual nitrate.

The calculated increases in pressure due to desorption of moisture assumes that condensation does not occur at cool spots on the canister wall. This mechanism of limiting pressure increases is not operative in the case of decomposition of nitrates.

C. Discussion

The development of internal pressures in canisters from decomposition of nitrates and desorption of moisture can have adverse effects on canister reliability. The calculations indicate that such effects could develop if the concentrations of residual nitrate and moisture are each greater than 1000 ppm.

The above calculations estimate the development of pressures based on complete decomposition. Actual decompositions may be lower due to equilibrium stability, slow kinetics, recombination, or other effects. For example, the effect of temperature gradients in which centerline temperatures of calcine may be very high while those at the wall are low have not been taken into account. Small-scale experiments with synthetic calcines have been made by W. A. Ross at PNL, where pressurization was 1080 psi (73.5 atm) at 800°C (1470°F) for PW-4b product.[26] This high pressure point is indicated on Fig. 8 to show the consistency of these results with the model. The PNL decomposition data indicates that nitrate was fairly stable below 700°C (1290°F). The canister loading of 1.2 g · cm^{-3} indicates a void fraction of approximately 0.70. The pressures observed correspond to the complete decomposition of the nitrate present (two wt % or higher). Fluid-bed evaporation, calcination, and denitration of uranyl nitrate solutions has been studied in connection with the feed-materials program.[27] Some of the results obtained are shown in

Fig. 9. These fluid-bed runs showed that residual moisture was about 0.1 wt % at 500°C (930°F) while residual nitrate was about 0.5%. An extrapolation of the nitrate line indicates that a bed temperature of at least 800°C (1470°F) would be required to reduce nitrate to 0.1%. In the production of UO_2, treatment of the calcine with H_2 at 1100°C (2010°F) completely eliminates nitrate and water.

TEMPERATURE
825°C (1517°F)

VOID FRACTION, y

0.5
0.67
0.8

73.5 atm

POTENTIAL PRESSURE, atm

10^4
10^3
10^2
10
1
10^{-1}
10^{-2}

10^{-4} 10^{-3} 10^{-2} 10^{-1} 1

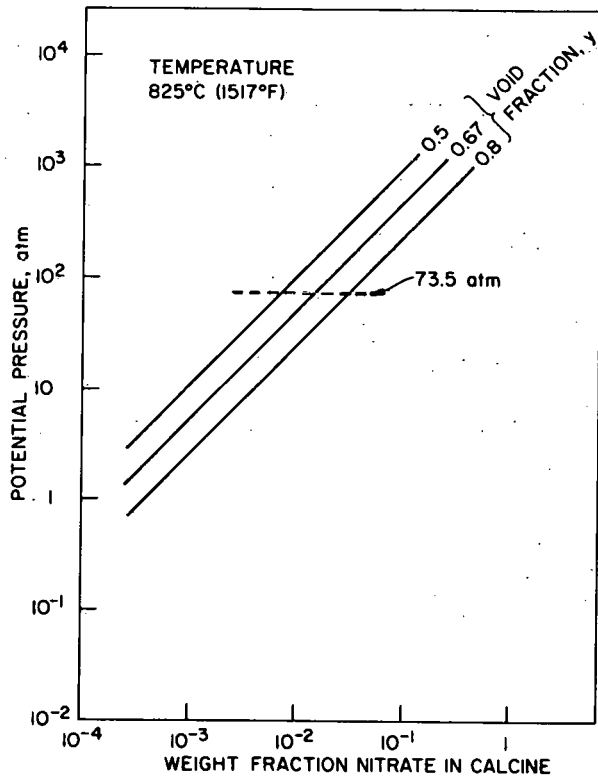WEIGHT FRACTION NITRATE IN CALCINE

Fig. 8.

Pressure at 825°C (1515°F) from Complete Decomposition of Residual Nitrate in Calcine.
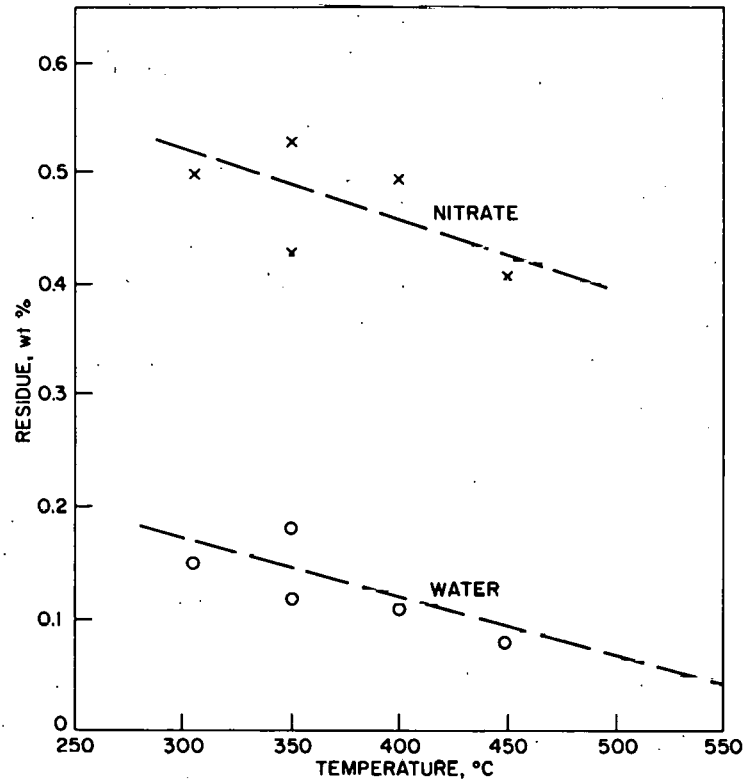
Fig. 9. Effect of Fluid-Bed Temperature
on the Residual Nitrate and Water Content
of the Product of Fluid-Bed Denitration
of Uranyl Nitrate Solutions.[27]

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