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SECTION 9.0 TO STATUS REPORT ON THE DISPOSAL OF RADIOACTIVE WASTE

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Supplement I

Section 9.0 to

STATUS REPORT ON THE DISPOSAL OF RADIOACTIVE WASTES

Prepared by the

COMMITTEE ON DISPOSAL AND DISPERSAL
OF
RADIOACTIVE WASTES

For the

NATIONAL ACADEMY OF SCIENCES
NATIONAL RESEARCH COUNCIL

Date Issued

SEP 3 1957

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Operated by
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9.0 CHEMICAL PROCESSES FOR FISSION PRODUCT CONCENTRATION, REMOVAL OR FIXATION

9.1 Introduction

Several general observations serve to define the perspective in which all waste processes should be viewed.

It is a salient fact that no process for the concentration, fixation, isolation, or use of radioactive fission products is a means of permanent disposal or management of wastes, as is so frequently claimed in both the scientific literature and the general press. A chemical or physical technique cannot be more than one of a series of steps leading to ultimate disposal. The removal of cesium and strontium may simplify handling of gross wastes, but the isolated fission product concentrate, as well as the gross wastes, must still find a safe grave, one that receives perpetual care for a millennium. In fact, certain of the heavy elements such as plutonium, americium and curium demand attention, by virtue of their long half-lives, for periods of time that extend far beyond the millenary period. No processing method for radioactive waste is an end in itself.

This leads us to the statement of a self-evident truth: radioactive isotopes can be removed from nature only by their natural decay, except through artificial transmutation in a nuclear reactor or particle accelerator. These methods are economically impractical. A curie of Sr^{90} would require about 10^{-4} grams of neutrons to change it to Sr^{91}, which would decay through Y^{91} to stable Zr^{91}. The cost of these neutrons would be about two dollars. This is equivalent to about $40 per gallon of process waste, exclusive of all charges for separation and fabrication of Sr into form suitable for irradiation. All that can be accomplished by waste disposal techniques is to provide a relatively safe place and form in which radionuclides can decay. It follows that since many of the fission products have short half-lives, it is entirely feasible to allow them to disappear from nature by decay before any processing is undertaken. Storage to allow for decay before ultimate disposal must always be considered as a first step and constantly effective part of the processing complex.

The high-level aqueous raffinate streams, which will be the raw material for waste treatment, have always been regarded as difficult to process. The volumes of these streams are approximately the same as the feed streams containing fissionable and fertile material in the radiochemical processing plant. They are contaminated with reagents introduced in the chemical process. The fission products generate appreciable quantities of heat during decay, sufficient to cause boiling or to require external cooling for many years. This heat is sufficient to cause a cooling problem in the handling of any solids produced as a product of waste processing. Solids are more difficult to handle than any other form of radioactive material - in process, in isolation, and in packaging.

Problems of containment of wastes in any form must take into account long-term chemical effects such as gradual precipitation of components of liquid waste solutions, long-term corrosion, etc. From a philosophical point of view the processing of radioactive wastes will be inherently more difficult than recovery and decontamination of uranium, plutonium and thorium. The products of waste processing will become increasingly higher in specific activity rather than becoming less active as do the products of fissionable and fertile material separation.

One further restriction that will be a factor in determining the applicability of any waste process is that of economy. Most waste processing proposals appear, at first glance, to be relatively costly, possibly too high to permit the production of electricity at 8 mills per kwh, (see Section 10.0).

However, all of these pessimistic statements do not deny the necessity and desirability of studying processing methods. They serve to point out difficulties and do not define an impossibility.

9.2 Summary of Waste Processes

Processes for chemically or physically treating liquid wastes can be divided according to their purpose, as follows:

1. Processes for the recovery and isolation of fission products for use.

   The degree of recovery for this purpose is determined by recovery cost vs. sale price of fission product activity recovered.

2. Processes for the separation of fission products or heavy elements from water and inactive salts which make up most of the waste volume.

   Water and salts can be discharged to the environment if they are freed of radioactivity. (The definition of how "free" the discharge must be is a problem in itself.) To accomplish this, the degree of removal must be very high. It is necessary to remove specific radioactive nuclides such as Sr^{90}, Cs^{137}, Am^{241}, the several plutonium isotopes and Cm^{242} (in decreasing order of relative hazard, as defined in Section 5.0). Thus, the long-term hazard of the total waste stream can be reduced, making it safer to discharge these materials directly to the environment.

3. Processes for treating whole wastes that produce a product which is disposable to some isolated part of the environment.

   An example of this is a solid containing mixed fission products.

We have sorted chemical processes in the waste literature into the above categories in Figure 1. Many of the processes can be used in a variety of combinations with others. They can precede and be coupled with processes for ultimate disposal described in Section 8.0.

The Reference List at the end of this section should be used in conjunction with Figure 1. References are provided to the original work of a great number of investigators from which more specific information can be obtained.

9.3 Concept of a Multipurpose Waste Processing Facility

The variety of high level wastes, illustrated by the estimates made in Tables 7 and 8 of Section 3.3, may be discharged from each of the large chemical plants serving a nuclear power industry. Some wastes will more

FIGURE 1. PROCESSES FOR WASTE TREATMENT AND FP RECOVERY

PRELIMINARY TECHNIQUES

Comments: 1. Most wastes will use some or all of the steps below.

Decay Cooling
Basic Data in ORNL-2127
This report Figure 14, Section 4.0

Evaporation
1. With external heat (1–5)
2. Self-concentration

Neutralization of Acids

General Note: See Reference List at the end of Section 9.0 for source reports.

PROCESSES FOR RECOVERY OF USABLE FISSION PRODUCTS

Comments:
1. Fission product separation factor from bulk waste usually low, determined by economics.
2. Both fission product and bulk waste must be retained.
3. Isolated fission products must be disposed of after period of usefulness.
4. Most of these techniques can be extended for high separation factors.

Precipitation-Crystallization Methods
1. Ammonium alum co-crystallization for Cs
2. Hydroxide precipitation of rare earths
3. Sr^{90} by carbonate precipitation
4. Ruthenium by $Fe(OH)_2$ scavenge at pH 2.5, volatization of RuO_4
5. Ferrous sulfide, ferrous hydroxide, calcium phosphate precipitation of Cs, rare earths, Sr and Ru
6. Cs precipitation with silicotungstic acid
7. Ferrocyanide precipitation of Cs and Sr
8. MnO_2 precipitation of Ru
9. Precipitation of ceric pyro-phosphate
10. Tetraphenyl arsonium nitrate precipitation of technicium
11. Rare earth oxylate precipitation
12. Conc. HNO_3 crystallization for alkaline earths
13. 12N HCl crystallization of $BaCl_2$
14. MnO_2 precipitation for Zr-Nb
15. Phosphotungstic acid precipitation of Cs
16. Electrodeposition of Ru
17. Removal of Ba as $BaCrO_4$

Ion Exchange–Cation, Anion
1. Diban Process for Cs-Sr removal from alkaline wastes
2. Other separations possible
3. Cation exchange for Ba

Absorption or Adsorption on Inorganic Materials
1. Silica gel selective adsorption of Zr-Nb
2. Inorganic ion exchange using $ZrPO_4$, ZrO_2

Solvent Extraction for FP Removal
1. Tributyl phosphate extraction for Ce, Rare Earths, and Zr

PROCESSES FOR THE SEPARATION OF FISSION PRODUCTS AND INACTIVE CONSTITUENTS

Comments:
1. Fission products must be separated with factor of 10^5 to 10^6 from bulk wastes; determined by hazard
2. Objective usually to provide water or bulk wastes sufficiently free of activity for discharge into streams, pits, or relatively cheap storage
3. Some processes proposed to remove highly corrosive anions from waste
4. May be used in conjunction with processes of previous category

Removal of Inactive Salts, Concentration of FP Bearing Liquor
1. $Al(NO_3)_3$ crystallization with HNO_3
2. $Al(NO_3)_3$ removal through cation membrane in electrolytic cell

Evaporation and Calcination followed by Leaching
1. $Al(NO_3)_3$ screw calciner
2. Fluidized bed calcination of $Al(NO_3)_3$ wastes and leach

Solvent Extraction for Specific Fission and Heavy Element Removal

Ion Exchange for Specific FP Removal

Precipitation of Fission Products at Elevated Temperature and Pressure

PROCESSES FOR TREATING WHOLE WASTE TO OBTAIN A PRODUCT FORM SUITABLE FOR ULTIMATE DISPOSAL, PARTICULARLY SOLID PREPARATION

Comments:
1. These processes may use wastes directly from radiochemical plant; may start after period of decay; or may follow any of the preceding steps in the preceding categories.
2. Objective is usually to produce a fission product bearing solid in which radioactivity is chemically fixed or isolated physically.
3. If wastes can be discharged in dry strata, treatment could consist of removal of precipitate formers.

Calcination, Leaching, Packaging as Solid
1. Screw calciner
2. Fluidized bed calcination

Adsorption and Absorption on Naturally Occurring Minerals
1. Adsorption on Montmorillonite clay
2. Ion Exchange capacity of shale
3. Survey work on others

Fixation of Activity after Mixing Waste and Minerals
1. Nepheline syenite
2. Casting in concrete
3. Synthetic feldspars
4. Sintering (and self-sintering in shales)
5. Fixing in glasses

readily fit certain waste processing schemes than others; some may be best allowed to decay for an extended period of time; others may best go directly to ultimate disposal. It is reasonably certain that a single radiochemical plant must utilize chemical processes that will recover fuels from many reactors if reprocessing costs are to be kept low. The large central multipurpose reprocessing plant is probably an economic necessity.

This concept of a multipurpose fuel reprocessing plant can be extended to cover waste disposal processes. A multipurpose waste processing plant, in which most or all techniques shown in Figure 1 can be performed, will be a necessary companion to the multipurpose chemical plant. Although the chemistry differs in many of the listed processes, the equipment in which the chemistry is accomplished is simple, i.e., the unit operations are the same. Thus, a waste disposal unit for high level waste in any chemical plant could include provisions for any of the processes shown.

9.4 Details of Some of the Waste Processes

Some of the processes listed in the summary in Figure 1 have received more development than others. To supplement the general section, we include a summary of those processes on which we have found the most information.

9.41 Evaporation

If corrosion and solubilities permit, it is usually economic to evaporate waste prior to tank storage.

Since condensate decontamination factors of 10^8 - 10^{12} may be required in the evaporation of high level waste, a major design problem is limitation of the carry-over of activity into the condensate by entrainment, splashing and foaming. Caution must also be exercised to guard against volatilizing appreciable quantities of fission products.

Table 1 indicates the effect of boilup rate and percent freeboard on condensate decontamination.

If large volume reductions are desired, evaporation may have to be conducted with strong acid solutions or slurries, or both. Tables 2 and 3 show some performance data from four evaporator installations.

Table 1

WASTE EVAPORATOR TEST

(Simulated High Activity Waste, 10^5 β cts/min/ml in pot)

Boilup Rate in Pot lb/hr/ft^2	% Freeboard	Pot Decontamination Factor (L/V)
48	175	9.5×10^3
80-90	125	9.3×10^3
	175	7.8×10^3
	225	2.2×10^4
115-125	125	$\sim 7 \times 10^3$
	175	4.4×10^3
	225	1.7×10^4

Table 2

EVAPORATOR AND DEENTRAINER PERFORMANCE

Unit	Vapor-Filtration Vapor-Compression Cyclone Separator	Forced Circulation Flash-Type 4 Bubble-cap Trays	Double Effect with Reflux
Boilup, $lb/hr/ft^2$	87	-	20
Decontamination Factor (Pot to Condensate)	6×10^7	10^7	5.5×10^8
Volume Reduction Factor	33	350	-
Concentrate, % Solids	60	70	0.2

Table 3

INTERMEDIATE-LEVEL WASTE EVAPORATOR PERFORMANCE

Design

Throughput:	300 gph evaporated
Maintenance:	direct

Operation

Throughput:	250-600 gph evaporated
Feed:	$1 \times 10^5 \times 5 \times 10^5$ β c/m/ml
	pH 10-11
Concentration:	5-25 Fold to 50-75% solids
Condensate D.F.:	1000

Evaporation of waste is basically a technique of volume reduction performed for the purpose of decreasing the cost of succeeding treatment or disposal steps.

9.42 Precipitation Processes for Fission Product Recovery from High-Level Aqueous Systems

Removal of the fission products from radiochemical process effluents is desirable and/or necessary for both economic and safety reasons. The present discussion will deal primarily with removal of fission products from the high-level aqueous effluents.

A reduction of over-all waste storage and disposal costs represents the prime long-range objective for development of processes for fission product recovery and concentration. Removal and concentration prior to cooling of the aqueous effluents would be dedicated to the simplification of large-volume storage systems, and perhaps to the availability of short-lived, high-energy concentrates of fission product radiations. Subsequent to long periods (one to five years) of cooling, such removal and concentration would have the purpose of simplifying the ultimate disposal problems, and perhaps of providing useful long-lived radiation sources, e.g. Sr^{90} and Cs^{137}. In either case, it may be suggested that a prime objective would be the safe containment of the several hazardous fission product elements, in a physical state and volume most amenable to human surveillance and control.

Development efforts to-date in fission product separations processes have been directed mainly to specific problems facing existing radiochemical plants and sites where relatively simple reactor fuel elements of uranium and aluminum are being processed. Most of such chemistry and technology will be of invaluable assistance in finding the answers to problems of future radiochemical wastes. It is anticipated that the higher-burned fuels and more complicated fuel element compositions (stainless steels, zirconium, ceramincs, etc.) in power reactor systems will dictate quite severe new problems in both the fuel recovery and waste treatment. The choice of future

fission product recovery and concentration schemes will nevertheless probably include one or more of the general techniques described briefly in the following review of present processes.

Although attention has been given to chemical processes for many fission products, it will be noted that primary efforts have been directed to recovery of long-lived Cs^{137} and Sr^{90}, which are the most feared radioactive hazards, as well as the most desired products for commercial radiation sources.

1. FISSION PRODUCT RECOVERY AND ISOLATION: ORNL RADIOISOTOPES DEPARTMENT

Perhaps the most highly developed and production-tested separations processes to date are those attained by the Radioisotope Department of the Operations Division at Oak Ridge National Laboratory. Aqueous solutions providing feed to such processes are primarily: 1) alkaline, highly salted effluents from the diverse chemical processes employed in the research and development facilities, and 2) nitric acid waste effluents from fuel recovery operations closely simulating conditions of the Purex process.

CESIUM CO-CRYSTALLIZATION WITH AMMONIUM ALUM

Alkaline, highly salted supernatants remaining from the precipitation of sodium diuranate are neutralized with sulfuric acid and adjusted to a pH of approximately 4.5. Ammonium alum, $(NH_4)_2Al_2(SO_4)_4$, is added to its solubility limit at about 80°C, then cooled to room temperature to recrystallize the hydrated alum and to co-crystallize the traces of $Cs_2Al_2(SO_4)_4 \cdot 24\ H_2O$. Such a co-crystallization, capable of 99% Cs^{137} removal, is possible because the heavier alkali ions form decreasingly soluble alums. By virtue of this, crops of ammonium alum crystals may be redissolved and recrystallized in successive batches of the feeds to effect progressively higher concentrations of Cs^{137} in the final crystal beds. When losses to the decanted supernatant liquors become significant, the crystals are redissolved in water and transferred to smaller vessels. Successively

smaller batches of crystals are grown to get the cesium into progressively smaller volumes of liquid. If enough cesium is accumulated, pure cesium alum may be crystallized in a final step. By proper recycle of crystals, and countercurrent arrangements of the various recrystallization stages, highly efficient separations and concentrations may be accomplished in the two end-streams of a production operation. Procedures are readily adaptable to remote control and very large-scale operations.

Following attainment of the cesium alum concentrate, the aluminum is removed as the granular hydroxide, by the ammonia gas technique, providing a highly concentrated filtrate which contains cesium and ammonium sulfates. The latter is then transferred to a source fabrication plant where the sulfate is removed on an anion exchange resin. An eluate of cesium hydroxide and ammonium hydroxide is treated for ammonia removal by distillation, then neutralized with HCl to form cesium chloride, which is finally taken to dryness at 460°C. A cesium chloride pellet is produced under hydraulic pressure at 20,000 psi in the preparation of a radiation source.

The above process can be readily adapted to Redox-type wastes, and even more efficiently to nitric acid waste concentrates from the Purex process. A multikilocurie fission product plant now nearing completion will employ such waste solutions as feeds to its cesium recovery units.

STRONTIUM AND RARE-EARTH REMOVAL

Processes for strontium and rare-earth removal may be adapted to follow the cesium-ammonium alum procedure. The main separation of the rare earths from the Sr^{90} is initially accomplished by ammonia gas precipitation of the rare-earths as hydroxides in a carbonate-free alkaline medium. Sr^{90} and other alkaline earths are subsequently removed as carbonates by bubbling carbon dioxide into the alkaline solution. The carbonates are then converted to sulfates, oxides or fluorides for source preparations, or for containment. Anhydrous strontium fluoride may be poured into a thin-walled nickel tube and fused at 1190°C into a glass-like mass, providing a suitable beta-radiation device. Rare-earth sources can be similarly prepared.

RUTHENIUM REMOVAL

Precipitation of iron hydroxides at about pH 2.5 to 4.0 was found to carry 80-95% of the ruthenium fission products (Ru^{103}, Ru^{106}) from the wastes. This method has been employed both as a method for removing iron and for concentrating the ruthenium. Isolation of the latter is then accomplished by oxidation to the tetroxide, RuO_4, a volatile compound which is readily distilled from acidic solutions of the iron carrier at about 100°C. The distilled product may then be collected and reduced to lower oxides, chlorides, or other salts as desired for radiation sources.

PROCESS FOR NEUTRALIZED PUREX WASTE

When Purex wastes, which do not contain coating solution waste (Al bearing) are processed, the following modified procedure is used:

1) The pH is adjusted to 3 resulting in the precipitation of Fe and most of the Ru.

2) Then NH_3 and Na_2CO_3 are added in steps and the pH adjusted to 8 to precipitate rare-earths and strontium. (This procedure and the purification steps which follow are similar to those given above for the general process.)

3) The Cs is removed last by crystallization with $(NH_4)_2Al_2(SO_4)_4$.

2. FISSION PRODUCT RECOVERY FROM HANFORD AQUEOUS WASTE SOLUTIONS

The following procedures or processes have been developed to permit recovery of cesium, strontium, and rare-earth fission products from Purex (and perhaps Redox) process aqueous effluents, i.e. primarily nitric acid concentrates from evaporation of wastes in the first cycle of the extraction process. A typical waste solution has a composition of approximately 7.6 M HNO_3, 0.05 M $Fe_2(SO_4)_3$, 0.02 M $UO_2(NO_3)_2$, 0.4 M $NaNO_3$, 0.05 M Na_2SO_4, and 3 g/l fission product salts. The cesium concentration would be about 0.0006 M. Processes have been developed through tracer-level scouting

studies and further tested for use with full activity-level plant waste solutions.

STRONTIUM, GROSS FISSION PRODUCT, AND URANIUM REMOVAL

The typical acidic feed solution may be neutralized with 50% sodium hydroxide and adjusted to pH 12 to precipitate the iron as ferric hydroxide. This precipitate carries about 5% of the cesium, 70% of the ruthenium, about 100% of the uranium as sodium diuranate, and about 100% of the remaining fission products. Centrifugation and water washing of the precipitate then provides a gross fission product concentrate for storage in a volume about 0.1 the initial feed volume. The supernatant is then treated by the ferrocyanide technique to remove the cesium in a relatively pure state.

An alternate process employs precipitations at controlled pH to separate fission product groups. Partial neutralization by slow addition of gaseous ammonia to pH 2-4 precipitates the iron, which carries most of the zirconium and niobium fission products. The supernatant is further neutralized with excess caustic to precipitate sodium diuranate, which carries the strontium and rare-earth fission products. Finally, this supernatant is then treated for cesium removal by ferrocyanide scavenging precipitation. The dissolved precipitates are then amenable to small-scale chemical operations for separation and isolation of the individual fission products.

CESIUM SCAVENGING BY FERROCYANIDES

Several metal ferri- and ferrocyanides have been investigated as co-precipitants for cesium (e.g. as $Cs_2Zn\ Fe(CN)_6$) from neutralized wastes. Metal ions such as Zn^{+2}, Ni^{+2}, Fe^{+3}, Co^{+2}, Cd^{+2}, Fe^{+2}, and Mn^{+2} were studied at concentrations of about 0.0001 M to 0.005 M in solutions ranging from $\geq$ 5 M HNO_3 to pH's $\geq$ 10. At pH 4, with a slight excess of ferrocyanide, it was found that 0.0002 M Zn^{+2} and 0.005 M Mn^{+2} provided equivalent (95% cesium recovery) product yields, indicating the former as most desirable on the basis of relative precipitate volumes and specific activity of the Cs^{137} product. Equivalent concentration requirements for other ions, in the order

listed above, were determined to be intermediate between the two. The Ni^{+2} ferrocyanide was almost equally effective in the wide acid range of pH 10 to 5 M HNO_3. The Zn^{+2} was most effective from pH 1 to pH 8. Oxalate and carbonate ions were determined as appreciable interferences. After addition of the ferrocyanide and the metal ions, the precipitates are formed during a digestion period of about one hour and then centrifuged. The precipitate volume is 0.01 to 0.001 that of the feed solution, permitting small-scale operations in subsequent cesium isolation processes.

Steps for cesium isolation and source preparations from the precipitated products have not been thoroughly demonstrated. It is desirable to convert the ferrocyanide to some simpler material, such as cesium chloride, to permit further steps of decontamination from impurities and of concentration for packaging as a source. Calcining in air at about 550°C, followed by water leaching, was found to permit separations from iron and zinc. The leach solution may then be acidified with hydrochloric acid and evaporated to yield relatively pure cesium chloride.

REMOVAL OF CESIUM AND STRONTIUM FROM WASTE SOLUTIONS

A process based on carrier precipitation has been developed at Hanford for the purpose of reducing the cesium and strontium content of intermediate- and low-level wastes to an extent sufficient to permit disposal to the ground. The process was developed as an economical method of treating large volumes of aqueous process wastes in existing mild steel equipment and utilizes nickel ferrocyanide and strontium phosphate as scavengers for cesium and radiostrontium, respectively.

The acidic wastes as produced are first made 0.005 molar in sodium ferrocyanide and 0.004 M in strontium nitrate. The waste is then made 0.005 M in nickel sulfate and the pH is adjusted to 9.5 ± 0.5 with sodium hydroxide. Phosphate, normally present in the waste, causes precipitation of strontium. Following a digestion period of about one hour the alkaline waste is transferred to large underground tanks where the precipitates are allowed to settle out. Under normal circumstances the concentrations of cesium and

strontium in the supernatant liquid will have been reduced from 20-100 microcuries per milliliter (μc/ml) to less than 0.1 μc/ml and can be discharged to the ground under carefully regulated conditions.

In the development of the present process, the removal of cesium and strontium was studied separately in order to optimize operating conditions and establish the range of applicability. Nickel ferrocyanide as a carrier precipitate for cesium was found to perform satisfactorily only at pH less than 10. Above 10, there is an abrupt decrease in carrying. Of several metal ferrocyanides tested, nickel, ferrous and cobalt ferrocyanide gave equally good decontamination at pH up to 10. Nickel ferrocyanide was ultimately chosen because it possessed much greater chemical stability than ferrous ferrocyanide, and nickel salts are more readily available and less expensive than those of cobalt. The ferrocyanides have been found to be very specific for cesium. Under optimum conditions radiocesium concentrations of the order of 10^{-9} molar have been obtained in the presence of sodium concentrations as high as five molar. Decontamination factors for other fission products are usually less than 10.

As might be expected from its chemical properties, strontium was found to be much easier to scavenge than cesium. When the wastes are neutralized, the ferric iron and phosphates normally present precipitate and carry most of the strontium, particularly at pH greater than 11. Cesium is not carried at this pH, however, either by this precipitate or by any of the metal ferrocyanides. It was found that addition of inert strontium nitrate and subsequent precipitation of stronium phosphate supplied the additional decontamination required at pH of 8.5 to 10. Calcium phosphate was also found to be an efficient scavenger for strontium but was somewhat more sensitive to pH than was strontium phosphate.

The process as now employed is limited by the mild steel equipment in use to the pH range of from 7.5 to 10. Consequently, it is not applicable without modifications to wastes containing high concentrations of aluminum or other salts insoluble at this pH. Other cesium precipitants have been studied for their applicability to strongly alkaline wastes, and of these, sodium tetraphenyl boron has shown most promise. Scavenging with this compound is also being studied at Idaho. The effectiveness of the metal

ferrocyanides in separating cesium from acidic wastes have been studied with a view to preparing very pure cesium sources for purposes of commercial utilization with results as reported above.

3. BRITISH METHODS FOR FISSION PRODUCT SEPARATION

The high level liquid waste from chemical processing in Great Britain resembles the unneutralized Purex wastes in this country, being nitric acid solutions of fission products with iron, nickel and chromium present as corrosion products, and uranyl nitrate and tributyl phosphate as trace constituents. These wastes are routinely concentrated by evaporation to less than 1% of their original volume and stored in underground tanks. Volume reduction of acidic wastes by evaporation is normally limited by the appearance of ruthenium in the evaporator overheads. This behavior is attributable to nitric acid oxidation of ruthenium to the volatile tetroxide. It is avoided in this case by destruction of the nitrate through reaction with formaldehyde.

From the standpoint of commercial utilization of fission products, interest has centered primarily on methods of separating Sr^{90} and Cs^{137}. However, processes for removing gross mixtures of fission products from the wastes for purposes of disposal have also been studied.

Strontium is separated from the waste by precipitation as the nitrate from 68% nitric acid solution. It is then further purified by additional precipitation from 80% nitric acid to radiochemical purities of about 98%.

Cesium is recovered by phosphotungstate precipitation from waste 8 M nitric acid. The cesium phosphotungstate is then dissolved in dilute caustic and precipitated again, yielding ultimately a product with a radiochemical purity of 99.9%. The excess phosphotungstate remaining with the waste is removed by solvent extraction.

A process has recently been tested on a pilot plant scale for removal of gross fission products. Decontamination factors as great as 1,000 were obtained by this process which consists first of precipitation with trisodium phosphate and ferric chloride at a pH adjusted to 11.5 with sodium

hydroxide. A second precipitation is then carried out at the same pH using ferrous sulfate, sodium sulfide, and the effluent is then passed through a column of vermiculite.

Other methods of treating the waste solutions for purposes of fission product recovery or more economical storage includes studies of nitric acid destruction with formaldehyde and extraction with ether, fission product separation by solvent extraction, electrolytic precipitation, anion exchange precipitation, and precipitation with ammonia.

9.43 Fission Product Recovery by Ion Exchange

Ion exchange recovery processes for cesium, strontium, and rare-earth fission products have been developed for treating aqueous waste effluents. Systems based on either acidic or alkaline solutions have been devised for operations in the Higgins continuous ion exchange equipment which permits minimum radiation exposure and damage to organic resins. Such processes, adaptable to a great variety of present and anticipated waste effluents, have been tested on laboratory-scale at relatively low radiation levels. The "Diban" procedure discussed below was investigated as a tentative process for removal of fission products from complicated waste effluents of a conceptual multipurpose reprocessing plant (six tons uranium per day capacity). This plant would recover U^{238}, Th^{232}, U^{235}, Pu^{239}, and U^{233} from a complex variety of power reactor fuel elements. The alkaline procedure is being developed as a tentative process for treating neutralized aluminum nitrate and nitric acid wastes, such as effluents from present-day reprocessing plants.

FISSION PRODUCT RECOVERY
BY THE DIBAN-ION EXCHANGE PROCESS

The mixed high-level aqueous waste effluents from the multipurpose facility, at an estimated volume rate of about 2.3 million gallons per year, were calculated to have an average composition as follows: 3.6 $\underline{M}$ HNO_3, 0.35 $\underline{M}$ $Al(NO_3)_3$, 0.173 $\underline{M}$ F^-, 0.025 $\underline{M}$ Zr^{+4}, 0.06 $\underline{M}$ Fe-Cr-Ni nitrates, and

lesser concentrations of Hg^{++}, $SO_4^{=}$, etc. It was calculated that about 2.4 x 10^7 curies each of Sr^{90} and Cs^{137} would be contained in the yearly volume. Employing a two-stage evaporation, the nitric acid can be recovered from this solution to produce, in the first stage, an acid-deficient solution containing mono-basic $Al(NO_3)_2OH$, and in the second stage, a more acid-deficient solution containing dibasic $Al(NO_3)(OH)_2$. The latter substance has been called "diban", solutions of which have an acidic reaction, e.g. approximately pH 2. Centrifugation of solid residues, and MnO_2 precipitation techniques, are effective in the removal of many fission products such as zirconium, niobium and ruthenium. A final resin column feed solution can then be prepared at a concentration of about 1.6 M $Al(NO_3)(OH)_2$. Employing Dowex 50 cation exchange resin (ammonium form) in a Higgins-continuous sorption-elution system, it is possible to recover cesium, strontium and rare earth fission products from such a feed, achieving decontamination factors of $>10^4$ for each. Thus, the large volumes of effluent from the system can be freed of the most hazardous fission products, and the sorbed cesium, strontium and rare earths can be eluted in small volumes of a 2 to 3 M $(NH_4)_2CO_3$, 0.1 M $(NH_4)_3$-citrate solution, and subsequently, efficiently separated on small fixed resin beds at controlled pH.

FISSION PRODUCT RECOVERY FROM ALKALINE WASTES BY CONTINUTOUS ION EXCHANGE

Aqueous waste effluents from solvent extraction processes such as Redox, Thorex, and "25" contain considerable quantities of aluminum nitrate with smaller quantities of nitric acid, corrosion products, and process additives. These solutions may be neutralized with sodium hydroxide to form alkaline solutions of an approximate composition: 0.1 M $NaAlO_3$, 0.3 M $NaNO_3$, 0.1 M NaOH, 0.002 M Fe^{+3}. The iron is precipitated as ferric hydroxide and very effectively scavenges the strontium (99%), zirconium, niobium, ruthenium (~90% each), and rare earth (99.9%) fission products from the solution. The supernatant solution is fed to a continuous Higgins column containing a phenolic cation exchange resin, which has a very high sorptive

affinity for cesium, strontium and rare earths in alkaline solution. All of the Cs^{137}, and the remaining traces of Sr^{90} and rare earths, can thus be efficiently ($\sim 10^4$ DF) removed from the large volumes of alkaline solution. The products are then eluted from the resin with a solution of 6 M HCl, which can subsequently be removed by evaporation to provide very high concentrations of the fission product chlorides.

Methods for removal of the aluminum and sodium from the effluent have also been developed, in case it appears desirable or valuable in the final disposal of these low-level radioactive wastes.

It will be noted that similar, and more highly efficient, operations may be readily developed for neutralized concentrates of nitric acid wastes from the Purex process.

VITRO STUDIES OF COPRECIPITATION AND INORGANIC EXCHANGERS

Vitro has investigated possible procedures for removing strontium from waste solutions at elevated temperatures by utilizing carrier techniques. Along with this study, the use of certain minerals as ion exchangers or adsorbers of cesium from acid and basic waste solutions were also studied.

Decontamination factors of 3440 and 4050 have been obtained by coprecipitating strontium with a barium sulfate carrier at 334° and 350°C, respectively, from a 5 M HNO_3 solution that initially contained 0.005 g of $SrSO_4$/liter and 2 g of $BaSO_4$/liter. At higher initial strontium concentrations with 2 and 6 g of $BaSO_4$/liter, the factors were considerably less. These experiments showed that higher decontamination factors are obtained by: 1) increasing the temperature, barium concentration and barium-to-strontium ratio, and 2) decreasing the initial strontium concentration.

Further study of minerals as exchangers or adsorbers of cesium from strong nitric acid solutions indicated that none of the sixteen minerals tested are particularly good for this application. Those minerals which were tested are: monazite, andradite, hessonite, wernerite, illmenite, pyroxene, wollastonite, bytownite, rhodonite, garnet, barton sand, epidote, variscite, sphere, diopside, lead fluorspar. In 5 M HNO_3 solution, only

variscite, wernerite, wollastonite, and lead fluorspar showed any exchange after one day contact time. Variscite, wernerite and wollastonite had distribution coefficients* of 0.49 whereas the coefficient for lead fluorspar was 0.97. In preliminary tests of the same minerals at pH 12, variscite, which is principally aluminum phosphate, had a distribution coefficient of 61.5 after 24 hours contact time between one gram of mineral and 20 milliliters of a cesium nitrate solution (pH 12) containing 0.409 g of cesium/liter. After 3 days the factor increased to 66.7. Under the conditions of 1 day contact time, 77% of the cesium was removed from the solution and the cesium loading on the mineral equalled 6.3 g of cesium/kg of mineral.

9.44 Fission Product Recovery by Solvent Extraction

Considerable knowledge of fission product extraction by organic solvents has been attained during research and development efforts connected with processes now employed for recovery of fissionable and fertile materials. Variables affecting their chemistry and their organic-aqueous distribution coefficients were rather thoroughly scouted to establish conditions for their optimum separation from uranium, thorium, and plutonium. In most of the processes it was found that alkali metals (e.g. Cs^{137}) and alkaline earths (e.g Sr^{90}) were among the least organic-extractable chemical species, whereas certain fractions of the rare earths, ruthenium, zirconium and niobium were somewhat extractable and difficult to separate from process products. Thus, it may be judged that, in general, present process solvents such as tributylphosphate (TBP) or hexone will not be particularly effective extractants for the hazardous Cs^{137} or Sr^{90} products. However, it has evolved that modified systems employing TBP may prove quite effective and adaptable processes for the removal of rare earths from the waste effluents. Similarly, by chemical conversion of ruthenium and niobium to extractable species, they may also be removed by TBP.

*Distribution coefficient = $\frac{\text{mg Cs/gm mineral}}{\text{mg Cs/ml solution}}$

Several other organic solvents have been investigated as potential fission product extractants. Some of these will also be discussed.

EXTRACTION OF FISSION PRODUCTS FROM AQUEOUS EFFLUENTS BY TBP

In the absence of significant quantities of TBP-extractables, such as uranium or thorium nitrates, which create TBP-saturation (and/or strong back-salting effects on less extractable species), the cerium and rare-earths are readily extracted by tributylphosphate. In cases where nitric acid is the only aqueous salting agent, relatively strong concentrations of acid (e.g. 8-16 M) are required to provide usefully high rare earth distribution coefficients* (D.C.) because the TBP-extractable nitric acid may effectively back-salt the rare earth nitrates. However, such systems have been effectively employed in the extraction and separation of the naturally occurring rare earth elements. In aqueous systems containing aluminum nitrate, either acid-deficient or with relatively low acidities, fairly low salt-strengths provide usable distribution coefficients for the cerium and yttrium rare earths. The concentration of TBP in the organic extractant has been studied both at 1) full-strength and 2) various dilutions (30-45%) in inert solvents.

In tracer studies employing 1.0 volume of a synthetic solution (1.6 M $Al(NO_3)_3$, 0.16 M HNO_3, 0.02 M $SO_4^{=}$) with 0.2 volume of 100% TBP, it was found that a combination of chemical treatments of the aqueous waste provided a system for extraction of the cerium, yttrium, zirconium, niobium and ruthenium fission products. Greater than 99% of the rare earths were extractable without treatment. The addition of cupferron was employed to attain about 89% removal of zirconium-niobium; and reduction (metal addition to aqueous phase) was employed to attain approximately 90% removal of the ruthenium.

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*concentration in organic phase/concentration in aqueous phase

In other studies actual wastes from the Thorex process were employed. Evaporator waste concentrates of nitrate solutions at 2.74 M Al^{+3}, 0.87 M HNO_3-deficiency, 0.11 M $SO_4^{=}$, were treated for fission product removal by 1) extraction with 42% TBP for cerium rare earths; 2) $PbSO_4$ precipitation for strontium, barium and lanthanum; and 3) ferrous ferrocyanide precipitation for cesium. Employing a batch counter-current extraction and stripping system, it was possible to completely extract and concentrate the cerium rare earths. Extraction distribution coefficients for the latter were observed to be greater than 10^4, making it possible to employ efficiently small organic volumes for the extraction process.

INVESTIGATION OF OTHER ORGANIC EXTRACTANTS

Studies of various solvents (aqueous phase 1.6 M $Al(NO_3)_3$, 0.16 M HNO_3) revealed possible extractants for rare earth groups, zirconium-niobium, and strontium; however, none of those studies were effective for the cesium. Some examples are given below.

0.9 M Tridecyl Phosphine oxide was highly effective (distribution coefficients of 115 to 190) for Ce^{+3} and yttrium, and zirconium-niobium (D.C. of about 20). 1.3 M tri-n-octylamine was effective for Ce^{+4} (D.C. of 61) and for Ce^{+3} (D.D. of 3 to 4). 1.3 M Di-2-ethylhexyl phosphoric acid was effective for yttrium (D.C. of 104) and Ce^{+3} (D.C. of 2), and for zirconium-niobium (D.C. of about 25). 0.5 M thenoyl triflouracetone (TTA) in benzene was effective for zirconium-niobium (D.C. about 10).

9.45 Brookhaven Screw Calciner

In order to reduce the hazards and costs involved in storing highly radioactive wastes, Manowitz et al have proposed that the wastes be dewatered and fused to compact salt. After dehydration the wastes would be in the form of insolubles and dried salts which can be fused upon further heating. Any solids which do not dissolve in the fused salt can be occluded or fluxed by having an adequate amount of fusible salt present in the waste.

Present neutralized aqueous wastes, which are stored as 20 to 30% salt solutions, contain large quantities of sodium nitrate. Because of its low melting point (308°C), sodium nitrate can serve as a fluxing agent for the other solids including the fission products in the waste stream. In waste streams where there is no fluxing agent present, other low-melting salts can be added to serve as fluxing agents for the dehydrated concentrates. The fluxing constituent is necessary because it gives mobility to the concentrated product and serves as a heat transfer medium for the removal of the radioactive decay heat. The conversion to a fused salt reduces the volume of wastes to be stored, and because the fused salt can be stored as a solid in the final container, the potential hazard is decreased.

The apparatus proposed for this process was a screw calciner since this equipment possessed the following desirable features:

1) It is mechanically simple.
2) The entire concentration sequence can take place in one piece of equipment.
3) It can operate continuously.
4) A minimum amount of manual process operations is involved.

The fused salt calcination process has been demonstrated at BNL using a pilot plant model calciner. The salt solution was fed continuously from the feed tank to the calciner by means of a centrifugal pump. The rate of flow was controlled by means of throttling valves and was measured by a flowrator. The feed entered the calciner body at the cold end (200°F) where the solution was dehydrated, and as the auger moved the dried salts toward the discharge end the temperature of the salt was raised until it fused. The fused salt was then discharged continuously to a heated sump for transfer to a final container. The water vapor and oxides of nitrogen which were given off during the calcination pass through an entrainment separator to a condenser where all the water vapor was condensed and received in a condensate receiver. Any oxides of nitrogen which do not dissolve in the condensate passed on through a scrubber where they were removed by reaction with 25 per cent sodium hydroxide.

A half section of 4-in. Schedule Type 347 stainless steel pipe, 6 ft. long, served as the trough of the calciner. A rectangular-shaped vapor dome was welded to the trough. Standard pipe flanges served as inspection ports and connections for the feed and vent lines. The entrainment separator contained a wire basket, 8 in. by 12 in. high, packed with stainless steel mesh. The U-shaped cross section of the calciner body made it possible to observe the operation of the equipment through the observation ports and offered a large free volume above the process stream, but it also resulted in the heating of the calciner body and poor utilization of heat input.

The greater part of the process heat for the calciner was provided by the U-shaped strip heaters located uniformly along the bottom half of the calciner body.

During operation, the liquid height in the calciner was kept at about 1 or 2 in. Therefore, a portion of the heat did not have direct access to the process liquid. This resulted in the maximum calciner body temperature occurring in the middle and upper sections, and limited the production capacity and thermal efficiency of the unit.

The lower section ran between 200°F at inlet and 700°F at outlet, while the upper sections ran at much higher temperatures (900°F). During operation the heating circuits were controlled in three section of equal length. The first section of the calciner operated at 100 to 200°C, the second section at 200 to 300°C, and the third section at 300 to 350°C. It was planned to dewater in the first section, dry in the second section, and fuse in the third section of the calciner. In the initial runs it was anticipated that a 30 wt % sodium nitrate solution could be fed to the unit at such a rate that anhydrous fused sodium nitrate would be discharged continuously from the hot end of the calciner with the temperature gradient across the unit maintained at the prescribed levels. After a period of epxerimentation, which included variation of the auger speed, calciner pitch, and heat inputs, the desired operating procedure was attained.

9.46 Fluidized Bed Calcination

A promising method of inexpensively treating and storing first cycle waste streams containing aluminum or zirconium is calcining to a free-flowing non-corrosive granular solid in a fluidized bed. By this method the corrosive nature of the waste is reduced and the volume to be stored is considerably decreased. This means that a calcined waste can be stored in smaller and less expensive containers.

Another significant feature of a granular solid waste obtained from a fluidized bed calciner is that it can be readily leached with water or mild acid; thus, a valuable source of fission products is potentially available.

The process under investigation by Jonke at Argonne National Laboratory and by Grimmett at the Idaho Chemical Processing Plant consists of evaporation and calcination of waste solutions to the oxides of the constituents in a fluidized bed. The calciner consists of a cylindrical vessel containing a porous, conical, sintered stainless steel plate. Operation of the fluidized bed calciner is relatively simple. Enough solid material between -20 and +65 mesh, is charged to the vessel to cover the top spray nozzle when the bed is quiescent. After the solids are charged the bed is fluidized. Between one and three feet per second superficial velocity of the fluidizing medium is used depending on the particle size. The bed temperature is brought to the required value by manual control. Preheated air (present studies indicate super-heated steam may be used as the fluidization medium) is passed through the plate to fluidize the bed, the entire mass behaving much like a vigorously boiling liquid. Waste solution is injected into the bed through pneumatic spray nozzles spaced on the periphery of the calciner in a single horizontal plane. The fluidized bed is operated at temperatures ranging from 400-500°C by means of electric bayonet heaters mounted internally. External heating has been used but found inoperable because of burnout.

A number of methods for supplying heat to a fluidized bed calciner have been studied, but for one reason or another the systems have been narrowed to two. One method is that of supplying heat to the fluidized bed by means of high temperature heat transfer surfaces buried in the bed. The other

method consists of passing hot burner gases through the bed as the fluidizing medium, and using the sensible heat of these gases as the heat source. A comparison of these two methods indicates that heat transfer surfaces in the bed would require smaller equipment for a given calciner capacity and at the same time the volume of off-gas would be much smaller.

A 12-in. diameter settling and filter section is mounted above the bed section. The filter is made from eight 18-in. x 1-1/2 in. 1-1/8 in. bayonet-type, porous stainless steel filter elements. Two off-gas manifolds are provided, with four filter elements venting into each manifold. Valves are provided so that while one manifold is filtering the off-gas, the filter elements in the second manifold can be individually cleaned by blow-back air.

The calciner is run under vacuum of 0.5-5 in. mercury, supplied by means of a steam jet exhauster, through the multiple banks of porous, sintered, stainless steel filters. These filters are capable of removing entrained oxide particles of 2-3 μ. Particulate removal may also be accomplished by cyclone separation with return of collected fines to the calciner. The granular product is removed to storage containers by means of a bottom outlet or by means of an overflow pipe.

Of prime importance to the waste calcination program is the type of solid produced by the calcining equipment. The solid product should have as high a bulk as possible. This depends upon the physical structure of each solid particle as well as the size distribution of the particles making up the bulk of the waste. The solid waste should be as closely sized as possible, and of such particle diameters as to simplify transportation and leaching. The particle size distribution of the waste will have an effect on its heat transfer characteristics, and this will influence the design of a burial vault as well as the calcining equipment.

Results of exploratory runs indicated that the following operating variables may affect the size and bulk of the calciner product: 1) calcination temperature, 2) liquid waste feed rate, 3) liquid waste feed composition, 4) fluidizing air rate, 5) feed spray nozzle air rate-to-feed ratio, 6) product draw-off air rate.

A hot pilot plant for the purpose of evaluating the fluidized bed techniques has been constructed at the Argonne National Laboratory. Demonstrations at intermediate levels of radioactivity are presently underway.

9.47 The Nepheline Syenite Waste Disposal Process

The Nepheline Syenite method of disposal as proposed by AECL* is to be used for concentrated fission-product solutions. However, it is presently being studied only on laboratory-scale of operation.

There are three sources of aqueous fission product solution from the Canadian recycle schemes which will be disposed by this method: 1) nitric acid solution from the first contactor of the uranium process, 2) aluminum nitrate solution from the first and fourth contactors of the plutonium process, and 3) ferrous sulfamate solution from the anion exchange columns used in the uranium process. The first two of these wastes can be economically combined and evaporated until the aluminum crystallization point is approached. Ferrous sulfamate is converted by evaporation (using a volume reduction of 10 fold) in the presence of nitric acid to ferric sulfate. If the ferrous sulfamate solution were added to the aluminum nitrate solution the formation of sulfate ion would cause precipitation of some fission products. Therefore, this evaporation must be done separately.

The waste solutions with a nitric acid concentration of approximately 6 M are mixed with an equal weight of nepheline syenite** powder in fire clay crucibles. The slurry gels rapidly and the gel is then dried at increasing temperatures up to 800°C. Drying removes water, nitric acid, and decomposes metallic nitrates. The nitric acid solution is condensed and the oxides of nitrogen are reconverted to nitric acid with oxygen in a packed reflux condenser. These acids are then concentrated for recycle in fuel processing. The major problem in this step is the distillation of RuO_4 which "plates out" on the first available surface. This raises the level of activity in the furnace as well as the operating cell itself.

**The empirical formula calculated from the gravimetric analysis is as follows: $(0.75\ Na_2O,\ 0.25\ K_2O)\cdot 1.1\ Al_2O_3\cdot 4.5\ SiO_2$.

*Chalk River, Canada

The dry powder of nepheline syenite and fission products is sintered at 1300°C after drying and decomposition is complete. The resulting glassy mass contained in fire clay crucibles is then annealed at 700°C, cooled and removed by conveyor to an underground water-proof and earthquake-proof storage vault.

Since the crucibles will contain fission products in a very concentrated form, forced convection cooling of the vault would be necessary. The limiting capacity of the crucible is determined by the rate of cooling possible. This capacity has been tentatively set at one gallon of concentrated fission product solution containing approximately 2×10^4 curies or 36 grams of mixed fission products.

9.48 Brookhaven National Laboratory Calcination and Clay Fixation Process

The clay fixation work of Hatch at Brookhaven National Laboratory is based on the assumption that by chemically compounding the fission elements into solid substances already known to be highly stable in the environment, a much more secure method of containment would be obtained. "Since the fission products, with the exception of ruthenium fractions, are largely cationic in aqueous solution, and since it is well-knon that some of the natural clays have good capacity for chemical exchange of cations, the investigation at Brookhaven National Laboratory has centered on the use of clays of the montmorillonite group. Three results of the investigation stand out thus far:

1) The capacity for cation exchange is found to be 1.2 milliequivalents per gram of clay
2) Ruthenium, possibly as an anion, is not effectively exchanged on the clay
3) The exchange capacity is reduced essentially to zero by heating the clay to about 1000°C

"By this last device the cations on the clay are firmly fixed and it is in this sense that the quality of permanence in disposal is to be determined." That is, the fission products fixed on the clay would not be

dispersed into natural waterways and would be highly restricted from ever finding their way into biological cycles. As long as the fired clay was confined, a major step would have been taken in securing safe disposal of the fission products without any significant reliance on the use of tanks or similar containers.

A pilot plant has been operated at Brookhaven National Laboratory to demonstrate the feasibility of adsorption on clay. "Briefly, the plant comprises a series of four columns of clay mounted in a vertical line with suitable mechanical manipulators so that the columns can be moved individually in a direction counter-current to the flow of fluid. Containers made of refractory materials are enclosed in stainless steel jackets joined at the mid-section by means of demountable, quick-opening bands." Loaded columns of clay are then fired in a high temperature kiln to approximately 1000°C.

Since the mechanism of incorporating the fission products into the clay is ion exchange, it is fundamental for most efficient use of the clay that the concentrations of extraneous cations, which may be present in the wastes as a result of the fuel process itself, be at a practical minimum. Aluminum and zirconium, for example, would be present in wastes from processing solid fuel elements containing these as alloying agents. There are two principal objectives in all of the clay adsorption work: 1) a pretreatment of the raw waste solutions designed to reduce or prevent the admission of extraneous ions, and 2) direct adsorption of radioactive ions on the clay.

It has been found that removal of nitric acid by volatilization and by electrolysis using ion-selective membranes are highly desirable over neutralization with caustic. A reduction of nitric acid concentration to less than 0.08 M with satisfactory electric current consumption has been demonstrated in a membrane unit. It appears evident that a combination of initial removal of nitric acid by volatilization and final reduction by use of membranes will prove most economical.

The separation of aluminum and zirconium from the fission products by first converting to the oxides on heating and then leaching with water or dilute acid, showns much promise. Not all of the fission products are

leached away in this manner. However, by this method it appears that the aluminum or zirconium, with whatever fission products remain after leaching, are converted into a stable form suitable for ultimate disposal; the leached fission products would then be fixed on the clay.

It is proposed to calcine aluminum or zirconium bearing wastes in a ball kiln calciner. A unit has been designed and cost-estimated by Blaw-Knox. In this process wastes are continuously fed from a feed tank through a preheater to the first section of the kiln. The ball kiln unit consists of one rotary ball kiln operating at 662°F for evaporating the solution to dryness and denitrating the resulting powder, and a second rotary kiln operating at 1300°F for hydrolyzing the fluorides of aluminum and zirconium to produce the oxides of these metals. Metal balls are used in the low temperature kiln to prevent agglomeration and to produce a free-flowing powder. A powder transfer unit is provided for collection of the low-temperature kiln product and transfer of this product to the high temperature kiln.

The off-gases from the low temperature kiln pass through a cyclone dust separator for removal of entrained powder. The recovered powder is returned to the powder transfer unit. The off-gases are then removed in a nitric acid absorption column.

The product from the high temperature kiln is cooled before discharge to the primary leach tank. The off-gases from the high temperature kiln are removed in a hydrofluoric acid condenser.

9.49 Fixation by Self-Sintering at Elevated Temperatures

A process for disposal of high level chemical processing wastes by mixing with ceramic ingredients and allowing the fission product heat to fix the activity in the form of a refractory cake sintered at 600 to 900°C is under study by Struxness and co-workers at Oak Ridge National Laboratory. It is anticipated that such cakes could be formed in relatively inexpensive pits, possibly adjacent to the chemical processing plant. The chief advantages claimed for this method are the somewhat lower temperatures required for fixation and the relative simplicity of the process in terms

of procedure and equipment. An important limitation appears to lie in its application to only the most concentrated, short-decayed wastes where the fission product heat evolution is at least several watts per gallon.

The present process entails mixing acidic aluminum wastes with limestone, soda ash, and locally occurring Conasauga shale in the proportions: 1 gal. waste, 1 lb. limestone, 1 lb. soda ash, 3.3 lb. shale. This mixture would then be allowed to stand in a well-insulated pit of large dimensions while the fission product decay energy evaporated the mixture to dryness, decomposed the aluminum, fission product and other salts present, and elevated the temperature of the resulting cake to the level required for sintering and fixation. The off-gas from the pit would be treated by condensation and the particulate matter separated by passage through a sand and charcoal filter.

The leachability of the sintered cakes have been investigated in a qualitative fashion by immersing samples tagged with strontium, cesium, cerium, ruthenium and mixed fission product activities in water for periods of time as long as one year. Analyses of the water have indicated that only cesium showed a tendency to be leached and this to only a minor extent. More detailed and systematic leaching studies are currently in progress.

Heat requirements have been investigated in a series of small, well-insulated laboratory-scale experiments of different surface-to-volume ratios. When the heat was added by means of electrical calrod heaters at rates decreasing in an exponential fashion similar to the decay of very short-decayed wastes, it was found that requirements could be maintained very near the theoretical minimum and the process completed within one week. On the other hand, it is yet to be demonstrated whether present-day aluminum wastes aged 90 days or more would contain sufficient radioactivity to self-sinter within a reasonable period of time.

Some of the engineering aspects of the process have been investigated in a field-scale experiment consisting of a pit six feet in diameter filled with 720 gallons of synthetic waste and the equivalent amounts of limestone, soda ash, and shale. Heat was added by means of calrod heaters and thermal requirements were found to be consistent with predictions based on

laboratory studies. A second experiment of this type is now imminent, where large-scale mixing equipment and off-gas facilities will be tested in the presence of tracer levels of radioactivity.

Within the next year, it is planned to perform a small-scale adiabatic self-sintering experiment. In this experiment, 30 gal. or less of high level waste will be used to produce a sintered cake without the addition of external heat. Peripheral electric heaters will be used, but only to balance the thermal losses during sintering. Such an experiment can be expected to establish over-all feasibility as well as to furnish information on thermal requirements and off-gas characteristics. In addition, it should provide a final product which can be tested most realistically from the standpoint of its leachability.

A further phase of the present work on this process is concerned with improving the basic recipe of the mix so as to reduce the volume of constituents to be added and further concentrate the heat source. Effort is also underway to extend the applicability of the process to other types of wastes such as Purex and those containing dissolved stainless steels and zirconium.

9.50 Use of Soils for Fixation of Radioactive Wastes

A very versatile ceramic process for fixing radioactive wastes in solids is under laboratory-scale development by Amphlett and co-workers at Harwell, England. It has been determined that when wastes, either as solutions, slurries, or granular solids, are mixed with Lower Greensand, a naturally occurring aluminosilicate-base soil, and fused at 1000°C in the presence of a flux such as sodium carbonate or sodium nitrate, a dense glass is produced which retains the active species in highly unleachable form. It is proposed that the solid products so formed could then be disposed at shallow depths without undue hazard or used in certain cases as radiation sources.

Although the Lower Greensand soil has an ion exchange capacity of about 0.2 milliquivalents per gram (meq/g), one of the advantages claimed for this process is that loadings many times in excess of this amount can be attained through combination of the fission product cations within the

aluminosilicate structure of the soil. Furthermore, the presence of gross amounts of inactive constituents within the waste such as aluminum and zirconium do not interfere with fixation. Loadings as high as 2 meq/g have been achieved where the ratio of impurities to fission product cations was 60 to 1. It is predicted that significantly greater loadings can be attained with further process development and that under the most favorable conditions a volume reduction factor of 2 could be realized in the treatment of a saturated aluminum-base waste.

Leachability of the final melts was investigated by exposing both powdered and intact specimens containing tracer levels of cesium, cerium, and mixed fission product activity to distilled water and synthetic sea water with agitation for several weeks. At the end of the tests, the solution was monitored for leached activity. Under these conditions it was found that decontamination factors of 10^4 to 10^5 could be attained.

Investigations of the off-gas during heating showed that ruthenium was the only fission product that tended to volatilize to a troublesome extent. When heating was performed in the presence of significant nitric acid concentrations, appreciable losses occurred by RuO_4 volatilization. However, under carefully chosen conditions where the nitric acid had been neutralized or destroyed chemically beforehand, the ruthenium losses were limited to 3%. It is believed that losses could be reduced still further by precipitating the ruthenium as the hydroxide and firing in an inert atmosphere, although there is little difficulty anticipated in filtering or trapping the ruthenium from the off-gas should such prove to be desirable.

Consideration has been given to the possibility of using the energy of fission product decay to achieve fixation without the addition of external heat. Calculations indicated that the feasibility of self-fixation depended on the presence of short and medium half-life fission products in the waste and was probably not practical if only the longer-lived isotopes were available as heat sources.

At the present time, emphasis is being placed on the investigation of other combinations of soils, fluxes, and wastes in an effort to achieve maximum loadings under optimum conditions of mixing and firing. Future effort

will lie in equipment development and pilot plant demonstration of the process at significant activity levels.

9.51 Fixation of Radioactive Nuclides as Synthetic Feldspars

A method of fixing radioisotopes as synthetic feldspars has been proposed by W. A. Patrick of The Johns Hopkins University. This process, for use with aluminum or zirconium type wastes, is designed to take advantage of the fact that the feldspar combination represents the most insoluble form of the alkali or alkaline earth elements and would, therefore, fix both cesium and strontium in a very permanent form suitable for underground or sea disposal.

In the case of aluminum, the wastes are initially evaporated to dryness and the aluminum and fission product nitrates are decomposed to their oxides, possibly by use of a fluidized bed calciner similar to the one under development at Argonne National Laboratory and Idaho Chemical Processing Plant. The aluminum oxide calcination product is dissolved in caustic to form sodium aluminate, which is then mixed with a solution of sodium silicate (water glass) until a transparent hydrogel if formed. This hydrogel is dried at 100°C without entrainment problems to the gel form, undergoing a shrinkage to 1/10 of its original volume as the hydrogel. When the gel is fired at 1000°C a crystalline compound is produced possessing a feldspar structure of the type, $M_2O \cdot Al_2O_3 \cdot 4SiO_2$. An additional 30-40% volume reduction is achieved during firing. It has been suggested that in treating short-decayed wastes the heat of fission product decay might be utilized to effect either the drying or the firing or both.

In order that a crystalline, non-leachable mineral be obtained, it was found necessary to reduce the amount of sodium present during formation of the hydrogel. This was accomplished by dissolving the aluminum oxide in about 80% of the stoichiometric amount of NaOH required for the formation of sodium aluminate and by removing up to 80% of the sodium from the water glass by means of ion exchange.

If zirconium type wastes are to be treated, the wastes as nitric acid solutions are mixed with a solution of colloidal silica to form a gel. When dried and fired at temperatures near 1000°C, a crystalline compound having a structure similar to that of zircon, $ZrSiO_4$, is produced. It has not been revealed whether zirconium when in solution as the fluoride or the sulfate, as is most often the case in current wastes, will react in the same manner as when it is present as the nitrate.

At the present time, this process has been investigated only on a laboratory-scale and in the absence of radioactivity. Future laboratory work will be concerned with testing at tracer and higher levels of activity. Such tests should give better indication of operational problems to be encountered as well as conclusive evidence of the non-leachability of the final product. The later phase of engineering development should be greatly simplified if the operability of the fluidized bed calciner has in the meantime been demonstrated. An additional question to be resolved is the limits of adaptability of the process with respect to other types of wastes, in particular to those containing dissolved stainless steels.

9.52 Treatment of Radioactive Effluents with Sawdust

The use of sawdust to adsorb activity from large volumes of intermediate and low-level aqueous wastes has been reported by de Jonghe and d'Hont of Belgium, It is expected to serve as a final step of waste treatment at Mol. Sawdust has been found to possess an adsorption capacity comparable to that of clay and, besides being an item of low economic value, its use offers the additional advantage of a high rate of liquid throughput and a large volume reduction factor. Following a chemical precipitation which removes 85% of the fission products together with the inactive constituents present, the supernatant is passed through columns containing sawdust which adsorb more than 99% of the remaining isotopes. A further concentration can be obtained by either burning the sawdust or allowing it to undergo natural deterioration.

Laboratory studies performed in small columns with tracer level activities established that poplar is the most suitable species of wood for this purpose. At flow rates of 0.5 ml/sec/cm^2, more than 99% of Sr, Cs, U, Zr and Ce were removed at pH values between 2 and 10. The adsorption capacity of the sawdust was found to be about 0.2 meq/g when contacted with neutral solution and somewhat greater under alkaline conditions. Sodium ions did not interfere with the adsorption of cesium and strontium but the presence of divalent and trivalent ions in the waste even at concentrations as low as 100 ppm noticeably interferred with separation.

Pretreatment of the sawdust with dilute chlorine water is required in order to prevent discoloration of the waste by soluble organic matter. This pretreatment is performed before packing the columns in order to limit more effectively the contact time between the sawdust and chlorine and thus avoiding excessive chemical attack.

The results of one experiment carried out with aqueous waste have been reported. In this case, a sample of waste solution supplied by AERE at Harwell was treated with sawdust following a chemical precipitation. By passage of untreated waste through a column 8 cm in diameter and 40 cm high at a flow rate of 15 liters/hr., 97% of the radioactivity was eliminated. After pretreatment by chemical precipitation with trisodium phosphate and calcium oxide, passage through a column 40 cm long removed 98%, and passage through a column length of 80 cm removed 99%.

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