MASTER

CHEMICAL ASPECTS OF NUCLEAR WASTE TREATMENT

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ABSTRACT

The chemical aspects of the treatment of gaseous, liquid, and solid wastes
are discussed in overview. The role of chemistry and the chemical reactions in
waste treatment are emphasized. Waste treatment methods encompass the chemistry
of radioactive elements from every group of the periodic table. In most
streams, the radioactive elements are present in relatively low concentrations
and are often associated with moderately large amounts of process reagents,
or materials. In general, it is desirable that waste treatment methods are
based on chemistry that is selective for the concentration of radionuclides and
does not require the addition of reagents that contribute significantly to the
volume of the treated waste. Solvent extraction, ion exchange, and sorbent
chemistry play a major role in waste treatment because of the high selectivity
provided for many radionuclides. This paper deals with the chemistry of the on-
site treatment methods that is typically used at nuclear installations and is
not concerned with the chemistry of the various alternative materials proposed
for long-term storage of nuclear wastes. The chemical aspects are discussed
from a generic point of view in which the chemistry of important radionuclides
is emphasized.

INTRODUCTION

Nuclear waste treatment deals with a variety of gaseous, liquid, and solid
wastes streams. In addition to radionuclides, waste streams often contain
substantial amounts of chemical reagents which also influence the choice of the

chemical or physical methods of waste treatment. The objective in waste treatment is to reduce the volume of the waste using a chemical or physical process that yields a concentrated product of radionuclides which is suitable for temporary on-site storage or which is compatible with waste fixation processes for long-term waste management. This paper deals only with the chemical aspects of waste stream treatment methods. Fixation of wastes into their final forms have been reviewed in several publications.[1-4]

Wastes containing radionuclides are produced throughout nuclear industry. Gaseous wastes are usually described by their radioactivity per unit volume. Solids and liquids are generally categorized according to radioactivity and toxicity as low, intermediate, and high active waste. However, definitions of activity levels of these categories differ somewhat at the various nuclear installations throughout the world.[5] For the purpose of discussion of the chemical aspects of waste treatments, the author will avoid the difficulty of a rigorous definition and only point out how the category dictates the choice of chemical methods. Low active wastes are generally significantly higher in volume, require little or no shielding, and contain < 10 nCi/g of transuranium elements. The other two categories have in a relative sense considerably smaller volumes and require shielding. High active waste results from the first cycle solvent extraction raffinate in the reprocessing of sent fuel and treatment methods have to take into account radiation damage to process reagents. Quantities, compositions, and heat generation rates of the various types of wastes are described in detail by several publications.[2,6,7]

Waste compositions even in the same radioactivity classification and how they are treated vary at the different nuclear production and research sites

throughout the world. This is primarily due to differences in the types of chemical processing and nuclear reactor operations that generate the waste streams. Therefore, the chemical aspects of waste treatment are discussed generically in this paper primarily emphasizing the chemistry of the component radionuclides. Considerably more detail regarding specific waste treatment methods and processes used at various nuclear installations can be found in other publications. The chemistry of volatile or gaseous fission products has recently been reviewed by Toth and Mailen.[8] Chemical and physical methods for treating low active and high active liquid and various solid wastes have been treated comprehensively in numerous publications.[2,3,6,7,9-12] Guidelines for the permissable concentrations of radionuclides in process streams that may be released to the environment are given in the Federal Register.[13]

GASEOUS WASTE STREAMS

The volatile fission products iodine, kryton, tritium and ^{14}C (as CO_2) have received considerable attention in recent years because of their potential contributions to the long-term dose commitment to the general population. Xenon is also formed in fission but the relatively short half-life of ^{133}Xe ($t_{1/2}$ = 5 d) only requires short storage or hold-up periods for its decay. Krypton, tritium, and $^{14}CO_2$ are not presently removed from effluent streams but revisions in these standards may require[13] that the release be as low as reasonably achievable.

Gaseous Iodine

A number of chemical reactions and sorbent systems have been utilized for iodine removal. Recent reviews[8,14] gives a detailed description of iodine

removal processes. Although iodine is principally present in gas streams as molecular iodine, a significant fraction also exist as volatile organic iodides. Therefore removal systems must deal with both species.

Hyperazeotropic nitric acid (Iodox Process) and mercuric nitrate-nitric acid solutions have been shown to be effective scrubbing agents for both I_2 and organic iodides. In the Iodox process, the hyperazotropic (20-22 $\underline{M}$ HNO_3) nitric acid absorbs the iodine and ultimately converts it to HI_3O_8, a dehydrated form of iodic acid which can be converted to solid $Ba(IO_3)_2$. The reaction of I_2 takes place in at least two steps.

$$I_2 + 4HNO_3 + 2I^+ + 2NO_3^- + 2H_2O + N_2O_4 \tag{1}$$

$$I^+ + 3HNO_3 + NO_3^- \rightleftarrows HIO_3 + 2N_2O_4 + H_2O \tag{2}$$
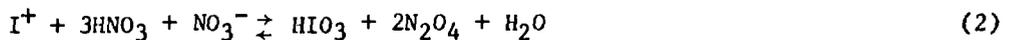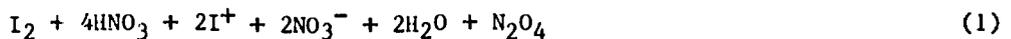
Oxidation of I_2 to I^+ proceeds rapidly, but the oxidation of I^+ is rather slow.

The initial reaction of organic iodides is a rapid nitrolysis.

$$CH_3I + 2HNO_3 \rightarrow CH_3NO_3 + 1/2\ I_2 + 1/2\ N_2O_4 + H_2 \tag{3}$$
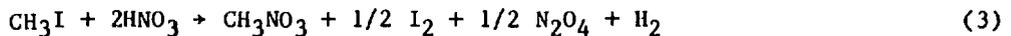
The I_2 produced then reacts with HNO_3 according to Eqns. 1 and 2.

In mercuric nitrate-nitric acid scrubber systems, and aqueous solution of $Hg(NO_3)_2$ in subazetropic acid is used to trap the iodine as the mercuric iodide complex, HgI_4^{2-}. Unless NO_x is present in the gas stream which produces nitrous acid in the scrubber solution, the following reaction takes place

$$6I_2 + 6Hg(NO_3)_2 + 6H_2O \rightarrow 5HgI_2 + Hg(IO_3)_2 + 12HNO_3 \tag{4}$$
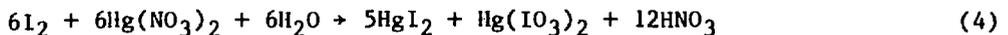
Mercuric iodate has a low solubility but fortunately the presence of nitrous acid presents its formation. The reactions of CH_3I have not been studied. It may be either of the following reactions.

$$CH_3I + 1/2 \ Hg(NO_3)_2 \rightarrow 1/2 \ HgI_2 + CH_3 \ NO_3 \tag{5}$$

$$CH_3I + 1/2 \ Hg(NO_3)_2 \rightarrow 1/2 \ HgI_2 + CH_3OH + HNO_3 \tag{6}$$
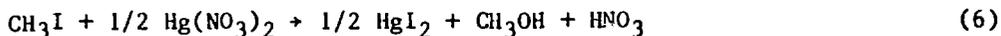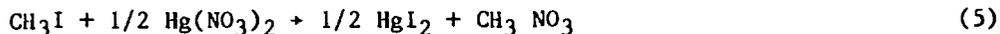
The kinetics of the CH_3I reaction[8] have been determined to be first power dependent on mercuric ion concentration (Fig. 1). The HNO_3 dependence is more complex, the reaction proceeds in the absence of HNO_3 but increases linearly with HNO_3 concentration. The reaction of I_2 is very fast and has not been measured. Caustic scrubbers perform well in removing I_2 but are not effective in removing organic iodides.

$$3I_2 + 6KOH \rightarrow 5KI + KIO_3 + 3H_2O$$

The presence of organic impurities in the caustic can lead to production of volatile organic iodides.

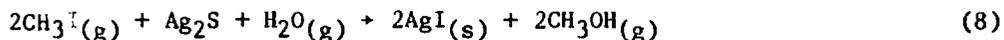Impregnated activated charcoal and metal-ion-impregnated inorganic solids have been the most effective sorbents for volatile iodine compounds. Charcoal or silicia impregnated with $AgNO_3$ and silver zeolites have been studied extensively. The silver zeolite sorbents are the most recent development and appear to have many advantages. The silver ions are assumed to be bonded to oxygen in the zeolite structure. Reactions of I_2 and CH_3I with the silver zeolite may be depicted as:

$$I_{2(g)} + Ag_2O_{(s)} \rightarrow 2AgI_{(s)} + 1/2 \ O_{2(g)} \tag{7}$$

$$2CH_3I_{(g)} + Ag_2S + H_2O_{(g)} \rightarrow 2AgI_{(s)} + 2CH_3OH_{(g)} \tag{8}$$
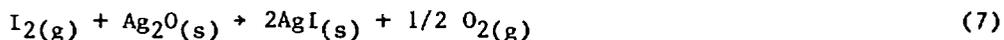
Krypton and Xenon

Removal of krypton and xenon are based on physical sorption on solids or solubility in liquids since they are not chemically reactive in the ordinary sense. Sorption on active carbons or zeolites or solubility in fluorocarbons
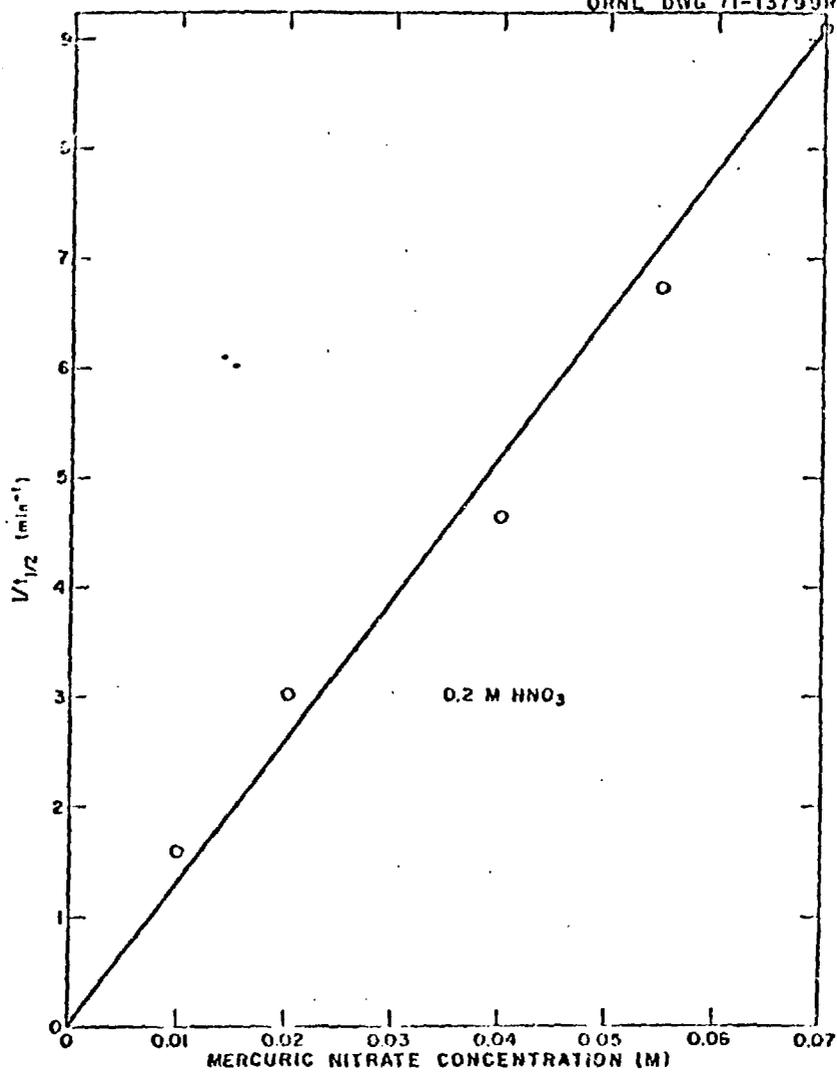
are the most extensively studied methods for removal of Kr and Xe. Since the
phenomena involved in trapping these rare gases are physiciochemical in nature,
this paper which is principally, concerned with purely chemical aspects will not
further consider Kr and Xe. Excellent reviews are available elsewhere.[8,15]

Tritium

Since tritium readily exchanges with H_2O, tritium in gas streams exists as
the species HTO. To avoid tritium contamination of process liquids in fuel
reprocessing, the tritium in spent fuel may be oxidized to HTO by air oxidation
at 400-500°C and captured on molecular sieves (or other drying agents) from the
off-gas prior to aqueous dissolution of the fuel.[8] Some of the tritium produced
at nuclear power station finds its way to coolant water as HTO.[7] To remove this
HTO from coolant water would require an isotope separation method.

$^{14}CO_2$

The ^{14}C released from nuclear power stations and that released from spent
fuel reprocessing is principally[16] in the chemical form, CO_2. Hence removal
methods are based on chemical reactions and properties of CO_2. Any small
amounts of ^{14}C in hydrocarbon gases can readily be converted to CO_2 prior to
CO_2 trapping. Methods proposed and studied for trapping ^{14}C as CO_2 include phy-
sical adsorption on molecular sieves and chemical reaction with alkaline solu-
tions or slurries. One of the more promising methods developed by Haag[16] is the
trapping of CO_2 as $BaCO_3$ which is accomplished by the reaction of CO_2 with
barium hydroxide octahydrate.

$$CO_{2(g)} + Ba(OH)_2 \cdot 8H_2O_{(s)} \rightarrow BaCO_{3(s)} + 9H_2O_{(g)} \quad \Delta H = 364 \text{ kJ/mol} \quad (9)$$
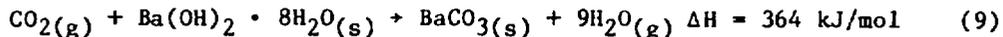
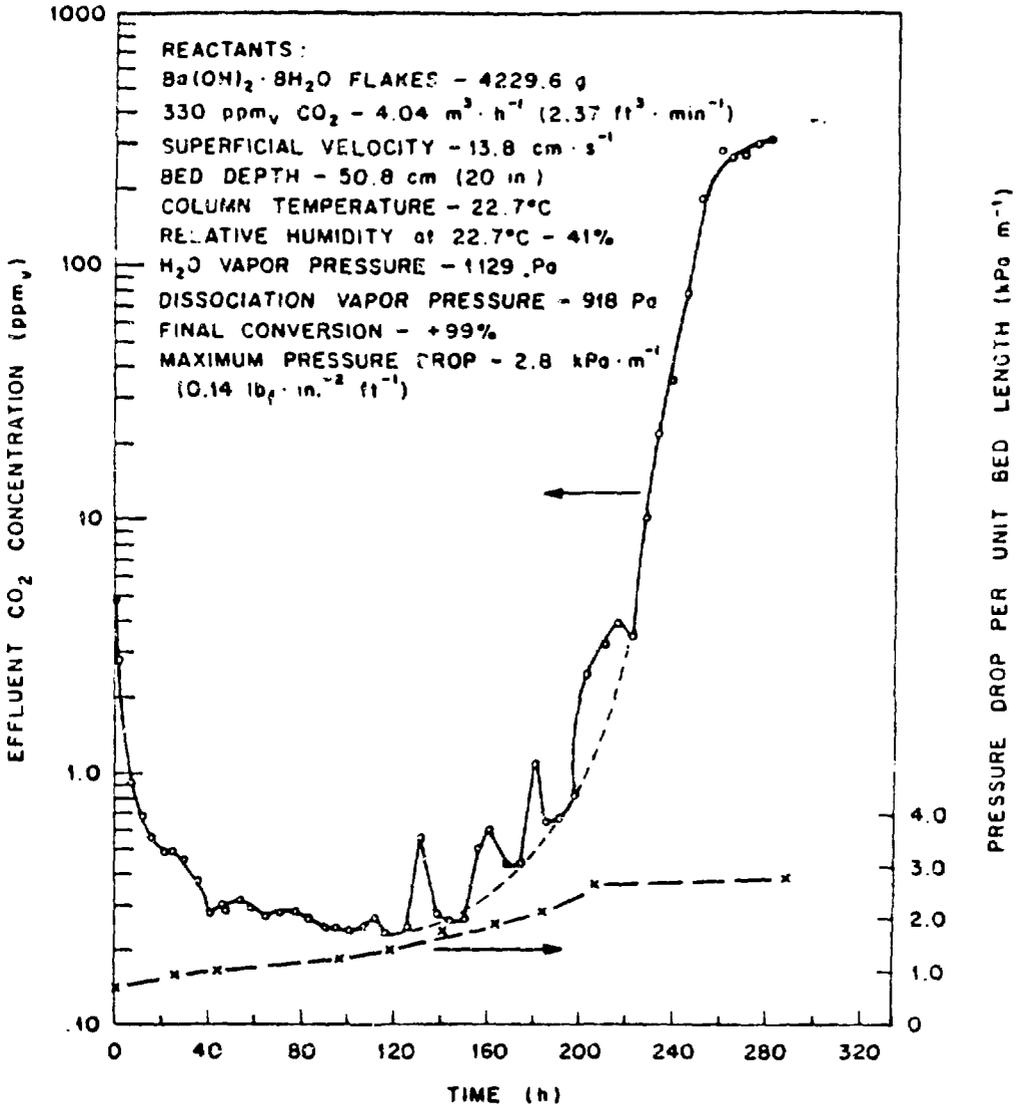The $^{14}CO_2$ is directly trapped on a dry solid which is thermally stable. The

performance of a packed bed of flaked particles of $Ba(OH)_2 \cdot 8H_2O$ is shown in Fig. 2 for the removal of CO_2 from air. The CO_2 removal efficiency initially undergoes a dramatic increase, then gives an essentially constant removal and finally CO_2 breakthrough of the bed. Best performance is attained by using water saturation values in the gas stream that are somewhat greater than the 918 Pa (6.9 mm Hg) dissociation pressure of the octahydrate.

LOW ACTIVE AQUEOUS LIQUID WASTE

The choice of chemistry for decontamination of low active liquid wastes depends on (1) the particular radionuclides, their chemical forms and concentrations and (2) the other nonradioactive chemical species present and their concentrations. In cases where decontamination factors of 10 to 100 are needed only a precipitation or flocculation step may be necessary. However, when a greater decontamination factor is required, ion exchange methods or precipitation steps coupled with ion exchange may be necessary. Because of the different type operations that are carried out at various nuclear installations throughout the world and the quality of process water used, precipitation or ion exchange processes take into account the specific chemical compositions of the solutions at each site. Distillation is sometimes a viable alternative to chemical treatment methods when modest volumes or low dissolved solids contents are involved. Reverse osmosis and ultrafiltration are being evaluated as alternatives to distillation or ion exchange. Excellent reviews of chemical and physical processes carried out at various nuclear sites have been published.[9,10,17-20] Since the same type chemical methods are usually employed in treating the medium

EFFLUENT CO_2 CONCENTRATION (ppm$_v$)

PRESSURE DROP PER UNIT BED LENGTH (kPa m^{-1})

REACTANTS :

$Ba(OH)_2 \cdot 8H_2O$ FLAKES − 4229.6 g

330 ppm$_v$ CO_2 − 4.04 m$^3 \cdot$ h^{-1} (2.37 ft$^3 \cdot$ min^{-1})

SUPERFICIAL VELOCITY − 13.8 cm $\cdot$ s^{-1}

BED DEPTH − 50.8 cm (20 in)

COLUMN TEMPERATURE − 22.7°C

RELATIVE HUMIDITY at 22.7°C − 41%

H_2O VAPOR PRESSURE − 1129 Pa

DISSOCIATION VAPOR PRESSURE − 918 Pa

FINAL CONVERSION − +99%

MAXIMUM PRESSURE DROP − 2.8 kPa $\cdot$ m^{-1}

(0.14 lb$_f \cdot$ in.$^{-2}$ ft^{-1})

1000
100
10
1.0
.10

4.0
3.0
2.0
1.0
0

0   40   80   120   160   200   240   280   320

TIME (h)

active wastes, they are not discussed in this paper. Strontium-90 ($t_{1/2}$ = 28 yr) and ^{137}Cs ($t_{1/2}$ = 30 yr) are the radionuclides of major concern in low active waste treatment because of their relatively long half lives, high solubility in water, and high fission yields.

Precipitation

Some precipitates found useful for removing radionuclides are listed in Table 1. All of the mechanisms for the "carrying" of radionuclides are not always known in applications to waste streams but may involve one or all of the following: (1) coprecipitation, (2) adsorption and (3) ion exchange at solid surfaces. Coprecipitation can involve two types of distribution of the microcomponent within the crystal, homogeneous, or heterogeneous distribution. Laws governing these two types of distributions are well known. Adsorption processes may obey either the Gibbs, Freundlich, or Langmuir type isotherms. Zeta potential measurements are found most useful in determining the best flocculation or settling characteristics of precipitates. Zeta potential determinations on raw and treated wastes allows the measurement of the effectiveness of colloid removal.

The type of chemical treatment often depends on the composition of raw water used to supply the various facilities at a nuclear installation. The total hardness of the water may be a governing factor. For this reason, precipitation based on adaptations of water-softening steps are often utilized to either fully or partially decontaminate the water from radionuclides and to also remove the unwanted ions which may affect subsequent operations such as ion exchange. In cases where high quality water is used, such as certain coolant waters at nuclear reactors, the precipitation step may be omitted and ion exchange is

Table 1. Typical precipitates used in removing radionuclides from
liquid waste streams

Type precipitates	Compounds commonly used	Radionuclides
Hydroxides	Fe, Al	Sr, rare earths, actinides
Carbonates	Ca	Sr, rare earths
Sulfates	Ca, Ba	Sr, Ra
Phosphates	Ca	Sr, Ra, rare earths, actinides
Ferrocyanides	Fe, Co, Ni	Cs
Sulfides	FeS_2	Ru

directly applied. Depending on the nature of the raw waste water, either the lime-soda, alum, or phosphate processes (Table 2) may be used as the initial treatment step. In some cases where only decontamination factors of 2 to 100 are required, the water softening treatment may be sufficient for certain radioelements such as those of Sr and the rare earths. However, water softening is not effective for the radioelements such as Cs, Ru, I, and Co, and further treatment is required for these elements. Ruthenium is one of the more difficult elements to remove since it may be present in cationic, anionic, or colloidal forms. Other than ion exchange methods, the best removals of ruthenium have been obtained with ferrous sulfide precipitation at pH values above 8. The removal of cesium is ineffective by water softening and often strontium removal is inefficient. The presence of clay (natural ion exchanger) during precipitation has been found helpful at Oak Ridge. Strontium removal may require considerable excesses of reagents. In the soda-lime treatment, Morton and Straub[21] have shown that a considerable excess of reagent is required to significantly increase the strontium removal above the 75% value at stoichiometric amounts (Table 3). In water softening precipitations, maximum removal efficiency of particular radionuclides may often occur at certain optimum pH values.

Because of the different chemical properties of the various radionuclides that may be present in wastes, double or multiple stages are often used combining any of the precipitation processes previously discussed. Combinations that have been used are discussed elsewhere.[9,10] Typically multistage precipitations utilize specific precipitation steps for the removal of ruthenium (paraperiodate or FeS_2) and for cesium (nickel ferrocyanide) ahead of soda-lime softening.[10]

Table 2. Water softening processes which have been adapted for precipitation/flocculation of radionuclides

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Lime-Soda Process

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

$$Mg(HCO_{32} + Ca(OH)_2 \rightarrow CaCO_3 + 2Mg(OH)_2 + 2H_2O$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

Alum Process

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4$$

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3 + 3CaSO_4$$

Phosphate Process

$$2Na_3PO_4 + 4CaSO_4 + 2NaOH \rightarrow Ca_3(PO_4)_2 + Ca(OH)_2 + 4Na_2SO_4$$

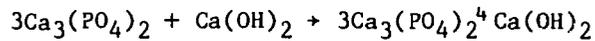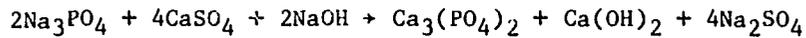$$3Ca_3(PO_4)_2 + Ca(OH)_2 \rightarrow 3Ca_3(PO_4)_2^4 Ca(OH)_2$$
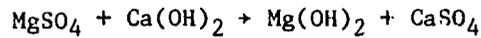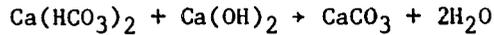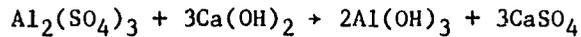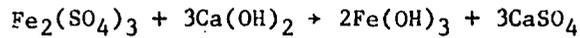
Table 3. Effect of precipitant excess in the removal of
          strontium using the lime-soda treatment[a]

Excess lime-soda ash $(mg\ell^{-1})$	% removal
0	75.0
20	77.0
50	80.1
100	85.3
150	97.3
200	99.4
300	99.7

[a]Adapted from Ref. 21.

Natural radionuclides such as radium which are present in liquid wastes from the milling of uranium ores can be treated by barium sulfate precipitation or by baryte columns. In many liquors, simple neutralization is all that is required since barium and sulfate ions are already present in the acidic liquors.

Numerous additives that have been utilized in conventional water treatment plants have been tested to aid in the coagulation of precipitates. However, apart from clays, inorganic minerals have found only limited use. In certain particular wastes, it may be found that organic polyelectrolyte coagulants are beneficial. Organic polyelectrolytes can best be described as a material that is both a polymer and an electrolyte (e.g. polyacrylamides). Many polyelectrolytes are available commercially and often can be effective as concentration ranges in the 0.5 to 4 ppm range.[10]

Ion Exchange

The high selectivity of ion exchange materials make them near ideal for removals of low concentrations of radionuclides. Ion exchangers that are used in nuclear applications include both inorganic and organic materials. The main disadvantage of inorganic exchangers are their lower exchange capacities and slower kinetics. The choice of ion exchange materials depends on the particular applications. Natural minerals, of the aluminosilicate class (which include the clays: vermiculite, montmorillonite, etc.) are used to treat laboratory and general plant wastes.[20] Natural minerals have the advantage of being much cheaper than synthetic resins and do not make regeneration mandatory. The minerals may be suitable for incorporation in some final waste forms or in other cases, they may be suitable for storage after calcination. Zeolites of both

natural (clinoptilolite and mordenite) and synthetic (chabazite) are particularly effective for the sorption of cesium and also perhaps its final fixation. A disadvantage of zeolites to general waste treatment is their reactions with acids.

Synthetic organic ion exchangers have found many applications in nuclear waste treatment because of the diversity of the ion exchange materials available. A variety of functional groups for both cation and anion exchange are provided. The high selectivity exhibited by these organic resins, on the basis of ionic charge permits separations of radionuclides into various groupings when that is desired. Although the organic exchangers are relatively expensive, the resins can be regenerated. Proper selection of reagents for regeneration permits good volume reduction factors of liquid wastes to be attained, although it is sometimes necessary to concentrate the regenerant effluent by evaporation.

Ion exchange is used extensively to treat laboratory wastes, general plant wastes, and coolant waters at nuclear power stations. Phenolic or phenolic-sulfonic resins are particularly useful in removing Cs and Sr from alkaline supernates after water softening or precipitation scavenging steps. Typical distribution coefficients[22] for Cs are illustrated in Fig. 3. Excellent decontamination factors are achieved using this ion exchanger when combined with a previous precipitation-scavenging step (Table 4).[23] Numerous examples of the use of ion exchange for treatment of laboratory and general plant wastes have been reported.[10,17,20]

$K_D \left(\dfrac{\text{c/s Cs-137 a 1c resin}}{\text{c/s Cs-137 ml solution}} \right)$
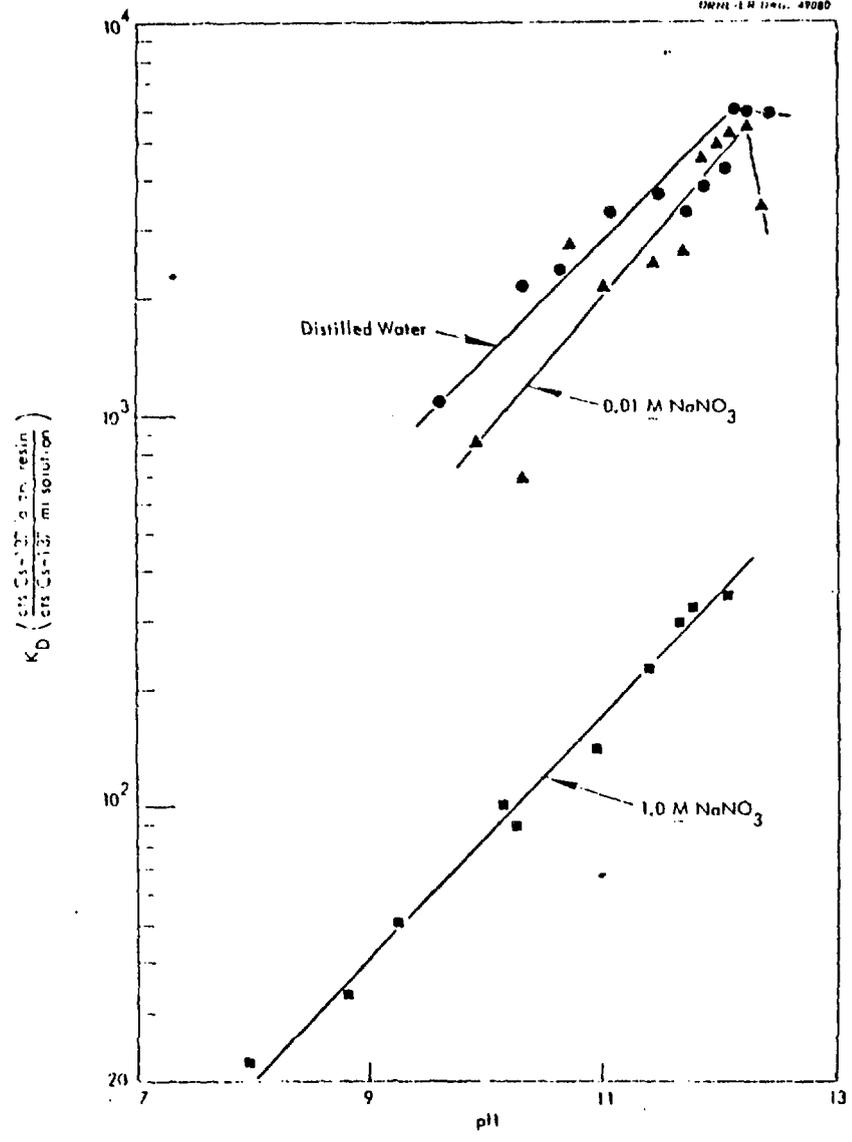
Distilled Water

0.01 M NaNO$_3$

1.0 M NaNO$_3$

pH

Table 4. Decontamination factors achieved using the
scavenging-precipitation ion-exchange method

Nuclides	Decontamination factor
^{137}Cs	1200
$^{89-90}Sr$	1400
Rare earths	580

Organic ion exchangers are used at nuclear power stations and research reactors to remove a variety of fission, activation and corrosion products coolant waters (Table 5). The quality of water must be very high to prevent corrosion and to reduce neutron activation products. Ion exchangers are ideally suited to this application because of their high affinities for ionic species. Cation and anion resins may be employed in series as separate beds or as a mixed-resin bed. Cation resin is of the strong acid, sulfonic type and anion resin is of the strong base, quaternary amine type. Ion exchange is usually preceded by filtration to remove suspended particulate matter. However, sometimes a mixed beds (-325 mesh) are used in a series of filter cartridges which permits the resin to serve both as a filter and an ion exchanger.[24]

LIQUID HIGH ACTIVE WASTE TREATMENT

High active wastes from present and past reprocessing of spent fuels are stored on site. Except at Idaho Nuclear Engineering Laboratory (INEL), the waste treatment consists of neutralization of the waste with caustic and storing the sludge of metal hydroxides along with its supernatant liquid in tanks. At

Table 5. Principal radioactive elements in low active
liquids collected for processing at a typical
pressurized water reactor[a]

Activation elements	Fission elements
^{51}Cr	^{89}Sr, ^{90}Sr, ^{91}Sr
^{56}Mn	^{90}Y, ^{91}Y, ^{92}Y
^{59}Fe	^{95}Zr, ^{97}Zr
^{58}Co	^{95}Nb
^{60}Co	^{131}I, ^{133}I, ^{135}I
^{95}Nb	^{134}Cs, ^{136}Cs, ^{137}Cs
^{95}Zr	^{140}Ba
	^{140}La
	^{144}Ce

[a]Adapted from Ref. 7.

INEL, the acidic liquid waste is treated in a fluidized bed at 400-500°C to pro-
duce a waste calcine (Table 6).[25] The calciner takes advantage of the relative
ease of the thermal decomposition of metal nitrates salts into metal oxides and
nitrogen oxide gases. Most of the metal nitrate content of the waste is due to
aluminum and zirconium nitrates which are readily decomposed in the 100-500°C
range. Alkali metal nitrates do not readily decompose rapidly except at tem-
peratures of 800 to 1000°C[26] and this method is not suitable for liquid wastes
of high contents of sodium salts.

To convert neutralized liquid waste to calcines or dried waste oxides it is
first necessary to separate the sludge and then recover the radionuclides
(principally Cs) from the supernatant liquid.[27,28] The separations from the
supernate are incomplete and the liquid raffinate is evaporated to solid salt
and which is to be managed as a low-active solid. Although the concentrations
of sodium salts in the supernate[28] are quite high (Table 7), it is possible to
remove cesium using a phenol-sulfonic cation resin. Elution of the Cs is
accomplished with 1.7 $\underline{M}$ $(NH_4)_2CO_3$ - 0.6 $\underline{M}$ NH_4OH. These ammonium compounds are
decomposed to gaseous NH_3 and CO_2 which are collected for regeneration and
recycle of the elution reagent. The synthetic zeolite (chabazite) may be used
to sorb cesium from the concentrate solution so that it is left in a solid form
for direct on-site storge or for incorporation into other solids matrices for
ultimate disposal.

Studies on waste management alternates for commercial wastes have shown that
it is technically feasible to significantly reduce the quantities of the long-
lived actinides (U, Np, Pu, Am, and Cm) from high-level and other fuel cycle

Table 6. Typical compounds in waste calcines from
INEL fluid-bed calciner[a]

| Compound | weight percentage | |
	Al waste	Zr waste
Al_2O_3	88–89	22
CaF_2	–	54
ZrO_2	–	21
Na_2O	1.3–2.0	–
HgO	2.9	–
N_2O_5	2.9–4.1	1.9

[a]Adapted from Ref. 25.

Table 7. Concentrations of major chemical in
Savannah River Plant alkaline supernates[a]

Chemical compound	Ave. conc. ($\underline{M}$)
$NaNO_3$	2.2
$NaNO_2$	1.1
$NaAlO_2$	0.8
NaOH	0.5
Na_2CO_3	0.3
Na_2SO_4	0.3

[a]Adapted from Ref.

wastes. The recovered actinides would then be converted to short-lived fission products by recycling them back to the reactors. Decisions regarding this alternative[29] are yet to be made. Demonstration of the chemical and technical feasibility was an essential part of the overall assessment. Removal of actinides from high active waste presented the most difficult challenge to chemists. Many chemical separations techniques were examined[30-32] and solvent extraction chemistry proved to be the method of choice for most separations steps. Modification of the tributyl phosphate extraction process which is already used (Purex Process) in fuel reprocessing was utilized to remove additional plutonium and uranium and also to remove neptunium. The extractant Dihexyl,N-diethylcarbamoylmethylphosphonate (DHDECMP) is employed to coextract the lanthanides and actinides from the waste solution. The lanthanides are subsequently separated from the actinides using di-2-ethylhexyl phosphoric (HDEHP) acid as an extractant or by cation exchange chromatography. The separations using HDEHP or cation exchange also depend on the greater stability constants of the aqueous diethylenetriaminepentaacetic (DTPA) complexes of actinide elements.

DHDECMP is an ideal type neutral extractant for the extraction from high-level waste solutions, since these trivalent elements can be extracted at high acidity and yet back-extracted at low acidity. Distribution coefficients of actinide elements as a function of aqueous HNO_3 concentration[33] are shown in Fig. 4. Extractions at high acidity (2-3 $\underline{M}$) avoids hydrolytic precipitation of fission products such as zirconium. Horowitz[34] has shown that this property is due to the presence of the amide grouping. Protonation of the amide group buffers against the effects of nitric acid on the phosphonate grouping. No significant chelation occurs and DHDECMP acts as a monodentate extract according to Eqn. 10.

$$Am^{3+} + 3NO_3^- + \overline{3DHDECMP} \rightleftarrows \overline{Am(NO_3)_3(DHDECMP)_3} \tag{10}$$
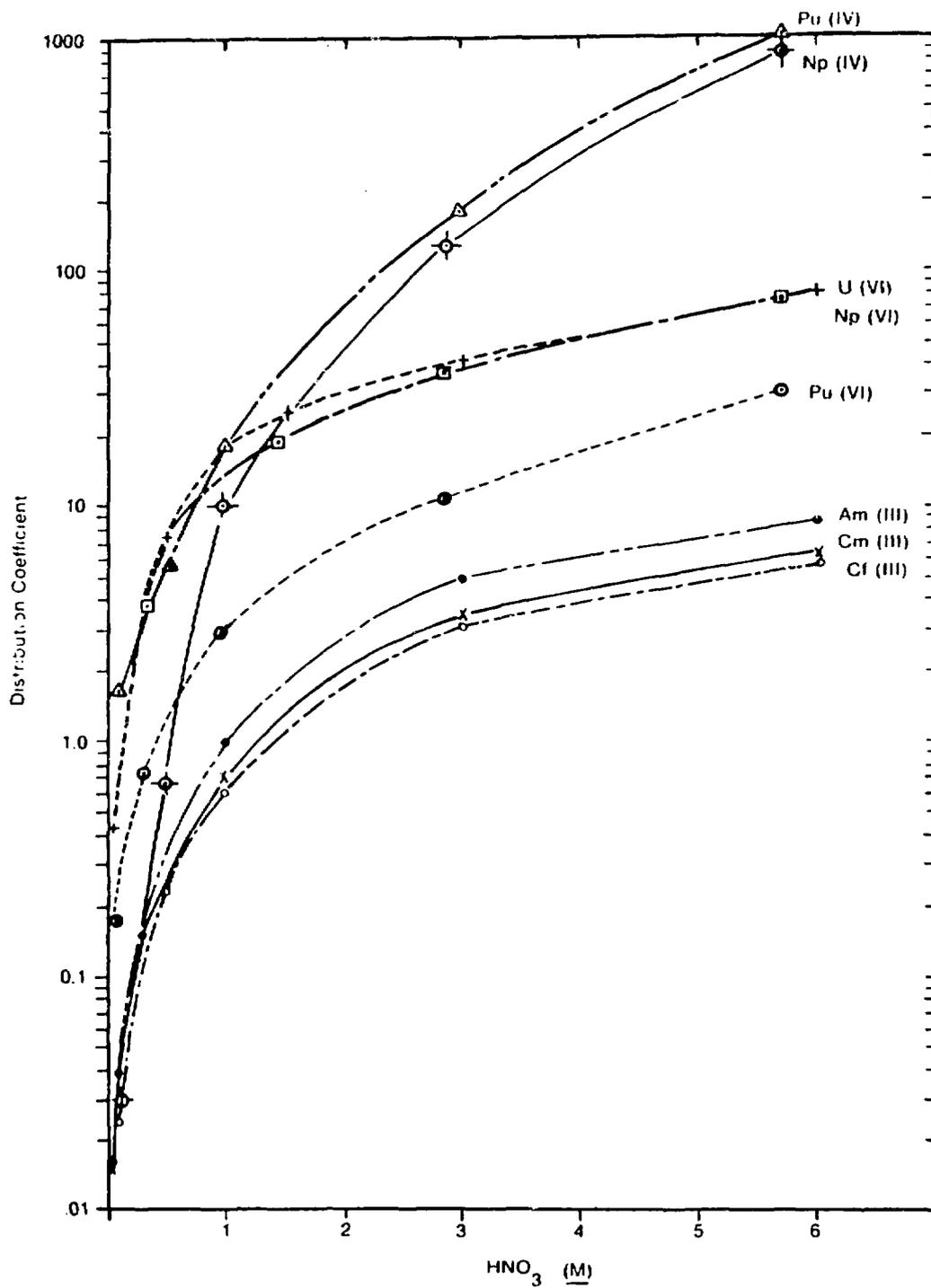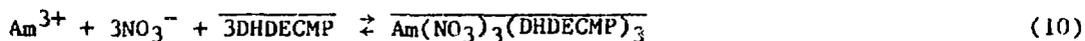
where the bar denotes the organic phase.

Combustible Wastes

The dominant treatment method for the volume reduction of combustible wastes consists of burning these waste in air to produce an ash or a slag. A variety of materials comprise the combustible waste category and includes general trash (paper, rubber, plastics, wood, etc.) as well as spent process reagents such as organic ion exchange resins or solvent. Because burning requires a considerable air flow, off-gas treatment for removal of air-borne particulates, volatile radionuclides, and acidic or basic gases (HCl, NO_x, and SO_3) which may be generated from the wastes on burning. Depending on the age and source of waste, iodine removal may also be required. Since there are differences in composition of wastes, various nuclear installations generally utilize different type incinerators ranging from kilns to fluidized beds. Several authors[9,11,18] have described the different modes of incineration.

To trap the volatile radioanuclides and acidic gases various approaches are utilized. Most systems treat the off-gas by scrubbing with an aqueous solution of sodium carbonate to remove acid gases. However, in some cases the acidic gases are removed in situ by carrying out the combustion in the presence of sodium carbonate granules in a fluid bed or in a molten sodium carbonate phase. Incineration may utilize high temperatures (800-1400°C) to produce a slag rather than an ash product. Spent liquid scrubber solutions may require further treatment such as evaporation to slurries or evaporation-crystallization.

Reaction or combustion of waste in an acid digestion process[35] with $HNO_3-H_2SO_4$ at 250°C is particularly attractive when recovery of plutonium is required as in scrap recycle. The organic materials are principally converted to CO_2 and H_2O. The acid reaction end products are SO_x and NO_x and other volatile gases products (e.g. HCl from PVC) which are removed with an aqueous alkaline scrubber. Since any plutonium that is present in the waste is converted to soluble plutonium sulfate, the plutonium can easily be recovered from the digester precipitate. There are still safety related tests being carried out to determine if acid digestion can be applied to spent resins and solvents.[9]

Studies on pressurized aqueous combustion[36] indicate that this method may have potential merit in treating certain combustible wastes. Although it has found non-nuclear commerical application in sewage sludge and paper mill waste treatment,[37] it is not yet employed in nuclear applications. All organic materials soluble or insoluble undergo flameless combustion at elevated temperatures and pressures in the presence of air and liquid water. Using this principle, Clark and Ulrich[36] have shown that aqueous slurries of simulated combustible wastes typical of Pu glove box operations can be reacted at temperatures of 250-300°C at acceptable reaction rates. Maintaining the pH of the liquid water phase at values greater than 10 was effective in trapping HCl. Volume reduction factors for the waste were the same as for conventional air incinerators.

NON-COMBUSTIBLE WASTE TREATMENT

Treatment of these solid wastes (chiefly materials of construction and equipment) depends on the characteristics of the individual materials. When

radioanuclides are only deposited on the surface, fairly simple physical methods or chemical methods may be effective. In cases where radionuclides are distributed throughout the entire structure as is the case with neutron activated materials fairly complex operations would have to be employed. Non-combustible solid waste at present represent a relatively small fraction of all low active waste generated but will become much more significant as present day nuclear facilities and power reactors are decommissioned.[9]

At present no further treatment is given to solids after surface decontamination. However, there are research efforts being carried out to determine if materials such as metals can be further decontaminated by methods such as melting and slaging. Physical methods for removing surface contamination include sand blasting and agitated water washing. Chemical methods involve leaching with solutions of mineral acids and of chelating or complexing agents.[38] After physical and/or chemical treatment the materials are managed as low active solids. The solutions generated in decontaminating the materials are sent to liquid waste treatment facilities.

RECOVERY OF PLUTONIUM FROM WASTES

At plutonium metal or oxide production facilities, recovery of the plutonium may be included as a part of the waste treatment. The plutonium can be recovered from solutions obtained from the acid digestion of combustible wastes by ion exchange or by solvent extraction using tributylphosphate. Dibutyl-butylphosphonate or DHECMP[39] may also be used as extractants to remove americium if substantial amounts of daughter ^{241}Am are present.

ROLE OF CHEMISTRY IN THE FUTURE

Although chemical methods now employed are generally satisfactory for treatment of nuclear process effluents, chemists will continue to play a vital role in the future. A greater understanding of the chemical phenomena in current methods may possibly lead to improvements. New or improved inorganic ion exchangers or sorbents such as described in recent work[40] on $H(Ti_2O_5H)$, $H(Zr_2O_5H)$, $H(Nb_2O_6H)$, and $Ca_{10}(PO_4)_6(OH)_2$ may prove to be beneficial in processes removing trace actinides and fission products. Extraction chromatographic columns generally perform the same function as ion exchange resins and have the potential for providing a much wider variety in functional groupings; yet this technique has not been applied to waste treatment. Recent work by Horowitz[41] and coworkers, show that columns are highly efficient when the extractant is immobilized or sorbed on high porosity silica microspheres. Pressurized aqueous combustion is yet to find applications although it appears suitable to pretreat aqueous streams to remove dissolved or entrained organics and to treat solvents, resins, or other combustible materials. Better understanding of surface properties of contaminated metals and chemical reactions at these surfaces could contribute to the methods that will be needed for decontamination in the future decommissioning of nuclear facilities. Photochemical reactions may perhaps become of import in waste treatment as that knowledge is advanced. Toth, Bell, and Friedman,[42] have demonstrated photochemical methods for control of the valence of actinides. Perhaps this approach could be extended to other troublesome elements such as ruthenium. The potential merits of continuing research on the radiofrequency decomposition and on biodegradation of organic liquids have been discussed by Kibbey and Godbee.[9]

ACKNOWLEDGMENTS

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