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PRELIMINARY PLAN FOR TREATING MIXED WASTE

by

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Chemical Technology Division

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ABSTRACT

A preliminary waste treatment plan was developed for disposing of radioactive inorganic liquid wastes that contain hazardous metals and/or hazardous acid concentrations at Argonne National Laboratory. This plan, which involves neutralization and sulfide precipitation followed by filtration, reduces the concentration of hazardous metals and the acidity so that the filtrate liquid is simply a low-level radioactive waste that can be fed to a low-level waste evaporator.

SUMMARY

A preliminary waste treatment plan was developed for disposing of aqueous mixed low-level radioactive wastes that are also corrosive (highly acidic or basic) and/or contain hazardous metals. This plan uses pH adjustment by calcium-hydroxide slurry addition followed by sodium-sulfide-solution addition to precipitate the hazardous metals as sulfide salts.* Additions will be monitored and controlled by titration using pH and sulfide-ion-selective electrodes. In general, radioactive components will be found in both the solution and the precipitate fractions. After the hazardous metals are removed by filtration, the filtrate can go to a low-level waste evaporator for concentration. The slurry of filtered metal salts will go directly into mixed-waste drums, which will be shipped to the Hanford site for disposal. Eventually, a mixed waste concentrator will be used to further concentrate the slurry of filtered solids before they are placed in the mixed-waste drums. By dividing these wastes into groups based on the hazardous metals that they contain, a standard treatment plan can be followed that should apply to more than 95% of the non-transuranic inorganic mixed wastes stored at ANL.

* Depending on the metal and its oxidation state, in a few cases additional treatment steps will be required.

I. INTRODUCTION

A preliminary waste treatment plan was developed to reduce the volume of ANL mixed waste stored on site and to convert it to a form acceptable for disposal at the DOE site in Hanford, Washington. The effort to reduce the volume of mixed waste is required by the Hanford Waste Acceptance Criteria [WILLIS] and will also result in a substantial lowering of the waste-disposal costs for ANL. The mixed wastes considered here are low-level radioactive wastes (henceforth referred to as LLWs) that are also hazardous wastes under the Resource Conservation and Recovery Act (RCRA). In particular, the mixed wastes are hazardous because they are corrosive liquids and/or contain toxic metals at concentrations greater than the RCRA limit.

The waste treatment plan focuses on converting the aqueous mixed waste to a low-level waste while concentrating the toxic metals as a solid. This is done principally by neutralizing the waste and removing the toxic metals using precipitation followed by filtration. The filtrate from this process, now a low level waste, can be fed to the existing LLW evaporator run by ANL's Waste Management Operations (WMO). A slurry of the solids retained on the filter can be loaded directly into mixed waste disposal drums with the appropriate volume of sorbent for water retention. These drums should be suitable for disposal at Hanford. In the future, when a mixed waste concentrator becomes available, a slurry of the retained solids will be fed to this unit, further reducing the volume of the mixed wastes.

The next three sections cover (1) an inventory of typical ANL wastes that were considered in developing the preliminary waste treatment plan, (2) compliance with the Hanford waste acceptance criteria, and (3) the treatment plan itself. Details of various aspects of this treatment plan are included in six appendices: (A) Technical Basis for the Precipitation Methods, (B) Mass and Energy Balance Calculations, (C) Preliminary Step-by-Step Operational Procedure, (D) Discussion of ES&H Concerns, (E) Description of the Filtration Skid, and (F) Suggestions for Future Work.

II. STORED WASTE INVENTORY

Over the years, ANL has generated a substantial volume of mixed wastes from its R&D activities. These wastes have been stored, awaiting treatment and/or an appropriate disposal site. Hanford has accepted responsibility for disposal of the low-level and mixed low-level wastes at ANL. To that end, Hanford has developed comprehensive waste acceptance criteria. This preliminary waste treatment plan was developed so that, following treatment, the wastes will be suitable for shipment and will be acceptable at Hanford for disposal.

Liquid radioactive wastes at ANL can be classified as shown in Fig. 1. This preliminary treatment plan addresses only the inorganic low-level wastes that are hazardous and considered non-transuranic, i.e., less than 100 nCi of alpha activity due to long-lived transuranic (TRU) elements per gram of waste. The non-hazardous portion of these wastes goes directly to the LLW evaporator. The hazardous portion is to be treated following the treatment plan given here. As shown in Fig. 1, the characteristics of these hazardous wastes that we addressed are their corrosivity, toxicity, and reactivity. The other hazardous characteristic, ignitability, can be ignored because these are aqueous wastes.

Fig. 1. Classification of Liquid Radioactive Waste

To provide a basis for the preliminary waste treatment plan, chemical waste disposal requisitions were reviewed for the current inventory of waste stored by WMO. From these wastes, we identified mixed wastes that are inorganic (aqueous) low-level radioactive liquids and have the hazardous characteristics of corrosivity or toxicity. In the treatment process itself, the hazardous characteristic of reactivity was also considered, but no LLWs were found at ANL with that characteristic. Because these are aqueous solutions, the hazardous characteristic of ignitability is not applicable. A list of typical wastes is given in Table 1. Based on this list, hydroxide, sulfide, and other precipitation methods were evaluated for hazardous metal removal.

Table 1. Typical Mixed Low-Level Inorganic Wastes Stored by WMO

Generator ^a	Chemical ^b	Conc., <u>M</u>	Amount			Total
			Vol., L	Vol. Fract.	Wt., g	Vol., L
NBL (RL-2600)	H ₂ SO ₄ Na ₂ Cr ₂ O ₇	c	0.85		72	0.9
CMT (RL-1845)	Cd(NO ₃) ₂ LiCl KCl HCl HNO ₃	 2 2		 0.06 0.09	50 50 50	3.8
CMT (RL-1884)	UO ₂ (NO ₃) ₂ Cu(NO ₃) ₂ HNO ₃	c 0.5 1	4 1 5			10
CMT (RL-1843)	Cu(NO ₃) ₂ HCl HNO ₃	 2 2		 0.06 0.09	200	3.8
CMT (RL-1810)	Cd(NO ₃) ₂ Cu(NO ₃) ₂ HNO ₃	 c		 0.999	150 5.0	0.9
CMT (RL-0558)	Arsenazo III ZrCl ₄ H ₂ SO ₄ HCl	 c c	 <0.001 1.258		0.12 <0.001	2
CMT (RL-1824)	Zn(NO ₃) ₂ HNO ₃	 1		 0.999	50	1
CMT (RL-1823)	Cd(NO ₃) ₂ HCl HNO ₃	 1 1		 1.0 ^d 1.0 ^d	250	23
CMT (RL-1806)	Hg(NO ₃) ₂ Cu(NO ₃) ₂ HNO ₃	 2		 1.0 ^d	1200 800	4
CMT (RL-1809)	Hg(NO ₃) ₂ Zn(NO ₃) ₂ HNO ₃	 2		 1.0 ^d	700 200	4
CMT (RL-1889)	Cd(NO ₃) ₂ LiCl KCl HCl HNO ₃	 2 2		 0.06 0.09	400 30 150	19
CMT (RL-1808)	Mg(NO ₃) ₂ Zn(NO ₃) ₂ HNO ₃	 2		 1.0 ^d	700 2000	3

^a Waste form numbers shown in parentheses; NBL indicates New Brunswick Laboratory, and CMT, Chemical Technology Division.

^b Radioisotopes not shown; in general, their presence or concentration will not affect the process.

^c Concentration not given.

^d Volume fraction assumed; none given on form.

III. COMPLIANCE WITH HANFORD WASTE ACCEPTANCE CRITERIA

All solid wastes (both low-level and mixed) generated by Argonne following the waste treatment plan discussed here are to be shipped to Hanford for storage and disposal. The Hanford waste acceptance criteria (WAC) were reviewed to ensure that these wastes will be acceptable to Hanford. We also discussed this plan with ANL-WMO personnel to get (1) their understanding of the Hanford WAC and (2) Illinois EPA requirements that must be followed as the waste treatment plan is carried out.

A. Hanford Requirements

The Hanford requirements are given by Willis and Triner [WILLIS]. This general document refers users to documents of the Washington State Department of Ecology [ECOLOGY] and the U.S. Environmental Protection Agency [EPA] for many of the details.

For this work, we have focused on the concentration of the eight metals listed in Table 2. The given regulatory levels determine if a waste exhibits the toxicity characteristic for a hazardous waste. The toxicity is determined by applying the toxicity characteristic leachate procedure (TCLP), as given in [EPA]. The 32 organic components, which are also part of the TCLP, are not listed here because only mixed wastes contaminated with toxic metals were considered. The Washington (State) Administrative Code classifies a toxic waste as a dangerous waste (DW) if the concentration of a metal in Table 2 exceeds the level shown there. However, if this metal concentration is 100 times the level shown, the waste is re-classified as an extremely hazardous waste (EHW). If more than one listed metal is present, the fractional concentration of each metal is calculated relative to its regulatory level. If the sum of these fractions is greater than 1.0, the waste exhibits the toxicity characteristic.

Table 2. Toxicity Characteristic List for Metals in Liquid and Soluble Solid Wastes

EPA Hazardous Waste Number	Contaminant	Chemical Abstracts Service Number	Regulatory Level, mg/L
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D006	Cadmium	7440-43-9	1.0
D007	Chromium	7440-47-3	5.0
D008	Lead	7439-92-1	5.0
D009	Mercury	7439-97-6	0.2
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0

Besides the toxicity for a hazardous waste, three other general characteristics must be considered: ignitability (D001), corrosivity (D002), and reactivity (D003). If a waste exhibits any of these four characteristics, it is said to be a RCRA waste. In addition, other hazardous (RCRA) wastes are often referred to as listed wastes, which are typically pure components or spent solvents; they are not considered here. Corrosivity is normally eliminated by neutralizing the aqueous waste so that its pH is between 2 and 12.5. The Hanford WAC requires that this be done. If this is not possible, special approval for disposal at Hanford must be obtained from Westinghouse Hanford's Solid Waste

Engineering (SWE). The ignitability characteristic may apply to the final solidified wastes from ANL-WMO treatment if they contain a significant amount of nitrate salts, which are oxidizing agents. The reactivity characteristic would apply to the concentrator solids if the RCRA metals were precipitated as sulfide salts. These solids could possibly generate a toxic gas (H_2S) if exposed to pH conditions between 2 and 12.5. In particular, since the pK_1 for H_2S is 6.97 [DEAN], the concentration of sulfide in the water as H_2S will become significant as the pH drops below 8. Kenneth Chui (WMO) reports that sulfide salts make a solid radioactive waste a mixed waste if the concentration of sulfide is above 500 mg/kg.

A further condition for the Hanford WAC is that the waste be a solid. For aqueous wastes, this means that an aqueous sorbent must be in direct contact with the liquid and have twice the absorbing capacity actually required for sorbing the free water present. Hyo No (WMO) has talked to people at Hanford, who told him that the 208-L (55-gal) waste drums should have each layer of the paste-like aqueous solids separated by a layer of aqueous sorbent.

A final condition for the Hanford WAC is that ANL must have a general program in place to reduce the amount of waste generated and to segregate low-level wastes appropriately before they are shipped to Hanford. This means that similar wastes will be packed together. In particular, all LLW shall be segregated as Category 1, Category 3, or greater than waste Category 3 (GTWC3) by using the concentration limits given in Table 3 [WILLIS]. Also, the radioactive component of all mixed wastes shall be classified according to this classification system. Waste shall then be segregated prior to shipment to the burial grounds. Radioactive waste is to be segregated into the highest category determined from the limits in Table 3. If this waste contains a mixture of the radionuclides listed in Table 3, the total concentration shall be determined by dividing the concentration of each radionuclide by its limit for the chosen waste category and summing the fractions. If this sum is less than 1.0, then the concentration falls within the chosen waste category.

Only radioisotopes with half-lives greater than 5 years will have Category 3 limits. If a radioactive waste contains radionuclides that have half-lives greater than 5 years and are not listed in the table, then Westinghouse Hanford SWE must be notified so that a waste classification limit can be determined for that nuclide. In addition, incompatible materials are not to be packed in the same waste drum. Oxidizing wastes, such as the nitrate wastes, are not to be packed with combustible wastes. For example, inorganic sorbents rather than organic sorbents should be employed for slurries containing nitrate salts. Reactive wastes are not to be packed with a chemical with which they could react. For example, the sulfide wastes are not to be packed with acid wastes.

In the near future, ANL personnel will review this preliminary waste treatment plan with appropriate Westinghouse Hanford personnel. In this way, we will assure that wastes generated by this treatment will be acceptable for disposal at Hanford. One point needing clarification is the concentration limit for nitrate salts in a solid waste below which it will be a non-hazardous waste. A related point is a discussion of acceptable sorbents for solidifying slurries of oxidizing agents such as nitrate salts.

B. Illinois Requirements

The Illinois regulatory requirement for the current low-level waste evaporator of ANL-WMO is that only non-hazardous liquid wastes, i.e., non-RCRA wastes, be fed to it. To meet the corrosivity characteristic, all wastes will be neutralized to a pH between 2.0 and 12.5 before they are sent to the evaporator. To meet the toxicity characteristic, any RCRA metals (Table 2) will be precipitated and removed by filtration before the liquid is sent to the evaporator. To meet the reactivity characteristic,

the sulfide concentration must be kept to less than 500 mg/kg. The ignitability characteristic is not applicable to aqueous wastes. Listed hazardous wastes will not be fed to the evaporator.

Chemical treatment operations must be done in a controlled-air space, e.g., a hood that can accommodate any H₂S that is generated during sulfide precipitation of the RCRA metals. If there is the possibility of additional H₂S release, operations in the ANL-WMO concentrator should also be contained in a controlled-air space. While H₂S release is not regulated under the EPA National Emission Standard for Hazardous Air Pollutants (NESHAP) or the Illinois Environmental Protection Agency (IEPA) implementation of NESHAP, it is regulated by the Occupational Safety and Health Administration (OSHA). The OSHA standards for H₂S are that its time-weighted average (TWA) in the work place be no more than 10 ppm (15 mg/m³), and its short-term exposure limit (STEL) be no more than 15 ppm (22 mg/m³) [LEWIS].

Table 3. Radionuclide Concentration Limits for Hanford WAC Categories

Radionuclide	Half-life, yr	Category 1, Ci/m ³	Category 3, Ci/m ³
³ H	1.2 E+01	5 E+00	a
¹⁴ C	5.7 E+03	6 E-04	8 E+00
¹⁴ C ^b	5.7 E+03	6 E-04	8 E+01
⁶⁰ Co	5.3 E+00	3 E+02	a
⁵⁹ Ni ^b	8.0 E+04	3 E+00	2.2 E+02
⁶³ Ni	9.2 E+01	2 E+00	7 E+02
⁶³ Ni ^b	9.2 E+01	2 E+01	7 E+03
⁹⁰ Sr	2.8 E+01	5 E-03	7 E+03
⁹⁴ Nb	2.0 E+04	8 E-04	2 E-01
⁹⁹ Tc	2.1 E+05	7 E-03	3 E+00
¹²⁹ I	1.2 E+07	1 E-03	8 E-02
¹³⁷ Cs	3.0 E+01	2 E-02	4.6 E+03
²⁴¹ Pu	1.3 E+01	5 E+01 ^c	3.5 E+03 ^c
²⁴² Cm	4.4 E+01	2 E+03 ^c	2 E+04 ^c
⁷⁹ Se	6.5 E+04	7 E-03	7 E-04
Alpha-emitting transuranic nuclides	>5	10 ^{c, d}	100 ^{c, d}

^a No values are provided.

^b In activated metal.

^c Expressed in units of nanocuries per gram of waste.

^d Number selected in accordance with already-established limits and definitions.

IV. WASTE TREATMENT PLAN

A. Introduction

A waste treatment plan was developed for mixed inorganic LLW stored and generated at ANL. That plan is described below.

1. Purpose

This preliminary waste treatment plan will separate the RCRA metals, leave a solution that can be concentrated in a liquid radioactive waste evaporator and will not be designated for treating as RCRA-listed waste, and produce wastes that can be shipped to and disposed of at the Hanford site.

The primary goal was to find one treatment applicable to 95% of the inorganic mixed wastes generated at ANL/NBL. Other goals for this process include (1) process safety and simplicity, (2) acceptability of the solid fraction for disposal at Hanford with little or no additional processing, (3) minimization of chemical additions to the waste, (4) minimization of the volume of mixed waste, and (5) minimization of disposal costs. The first wastes to be treated are mixed LLW, and the process was primarily designed with them in mind. However, the goal is that all aqueous wastes (including TRU mixed radioactive waste and hazardous wastes) will be treatable by this method.

2. Method of Choice

A precipitation/filtration method was selected because of its ability to separate the majority of the toxic metals in a simple and inexpensive manner. The preliminary waste-treatment plan developed to remove the toxic metals is described in more detail in Sec. IV.B.

3. Treatable Waste and Nontreatable Waste

The wastes to be treated by this method are mixed inorganic, aqueous, non-TRU wastes that (1) are corrosive due to their pH being outside the 2-12.5 range and/or (2) contain RCRA metals. Other wastes to be considered later are TRU and organic waste solutions. Waste solutions that are not treatable by the processes given in this report are those aqueous solutions containing complexants such as:

- Ethylenediaminetetraacetic acid (EDTA)
- Organoarsenic compounds
- Oxalic acid
- Cyanide
- Ammonia and alkylamines
- Citric acid
- Other organic complexants

Potential methods for handling such wastes are discussed briefly in Sec. IV.B.2, and in greater detail in Appendix A.

B. Treatment Plan

1. Overview

Radioactive liquid wastes can be broken down into two large categories: organic and inorganic. Organic liquids are defined as those that contain organic solutions and organic/inorganic mixtures. The inorganic wastes are further delineated into TRU and non-TRU categories, and the non-TRU category divided into hazardous and non-hazardous. An overall division of these wastes is shown in Fig. 1.

a. Waste Classification

As discussed in Sec. I, this preliminary treatment plan deals only with inorganic, non-TRU, hazardous waste solutions that contain toxic metals and/or are corrosive. These wastes are classified below based on treatment (see Fig. 2).

Fig. 2. Classifications of Mixed, Non-TRU, Inorganic Wastes Stored by WMO

(1) Toxic Metals

The plan for treating RCRA metals (scheme A) can be divided into three classes (Fig. 2) on the basis of the chemical treatments that are required to remove them from the waste streams. These classes are defined as follows:

Class 1: Contains metals that can be removed by an alkaline sulfide precipitation. These are Cd, Cr(II) and (III), Se(II) and (IV), Hg(I) and (II), Pb(II), and Ag(I).

Class 2: Contains those metals that require a simple pretreatment before they can be removed by the alkaline sulfide precipitation procedure. This class includes only one metal, Cr(VI)--i.e., chromate or dichromate.

Class 3: Contains those metals, oxidation states, or additional waste components that require special pretreatment and/or a different precipitation procedure than Class 1 metals. These include barium, arsenic, metals in solution with complexing agents, and rare oxidation states of some of the Class 1 metals.

(2) Corrosive Wastes

Corrosive wastes are those with pH less than 2 or greater than 12.5 and may contain a variety of non-hazardous components. They may be divided into two classes, based on pH:

Acidic: Those with pH less than 2 will be treated with $\text{Ca}(\text{OH})_2$ slurry or other basic reagents until the pH is approximately 8.

Basic: Those with pH greater than 12.5 will be treated with 8M HNO_3 until the pH is approximately 8.

(3) Reactive Wastes

Reactive waste treatment, referred to in Fig. 2 as scheme C, is outside the scope of this treatment plan, and is only shown for completeness.

b. Treatment Schemes

Three schemes are discussed below for treating the three types of hazardous waste. The three schemes are labeled scheme A (toxic metals), scheme B (corrosive), and scheme C (reactive). It is highly likely that separate treatment and filtration facilities will be used for Scheme A and B activities. Dashed lines are used in the figures describing these schemes for operations that are optional and/or under consideration.

(1) Scheme A

For scheme A (Fig. 3) waste solutions will undergo chemical treatment to precipitate the toxic metals. Under the toxic-metals category, the wastes are divided into three classes. Each of these three classes requires a different chemical treatment to precipitate the toxic metals. After chemical treatment, the solution will be fed to the filtration unit to separate the solids from the supernatant. When the mixed waste concentrator is in place and permitted, those solutions having a high solids content may be fed directly to it.

Filtration produces two radioactivity-containing streams, a non-hazardous liquid and a solid stream containing the hazardous metals. The solids can be divided into two groups: solids trapped on cartridge filters and solid suspensions created from filter back flushing. Cartridge filters will be classified as mixed waste and disposed of at Hanford with the appropriate amount of sorbent. Until the mixed waste concentrator is in place and permitted, the solid suspension will be disposed of like the cartridge filters. (Once the mixed waste concentrator is in place and permitted, the solid suspension will be fed to it. The distillate from the mixed waste concentrator will

be fed to the Acid Waste Tank, for eventual feed to the evaporator* and the solids will be disposed of the same way as the cartridge filters.)

^a Treatment for the three classes within scheme A will vary.

^b Organic sorbents may not be used for waste containing oxidizing materials (e.g., nitrates).

^c The TCLP test may be used at this point. If the waste passes, it will be categorized as LLW, not mixed LLW.

Fig. 3. Scheme A -- Treatment of Mixed Waste (MW) with Toxic Metal and, Possibly, Corrosive Hazard

* It is highly likely that operational knowledge will allow the treatment of the liquid streams from these operations in non-RCRA-applied evaporators; analysis should not be necessary.

The liquid stream from the filtration system will be sampled for radioactivity. If it meets alpha limits of 0.03 pCi/mL and beta/gamma limits of 1.0 pCi/mL [ANL], then it can be fed directly to the Lab Site Drain System. Liquid with radioactivity greater than the above limits will be fed to the Acid Waste Tank and eventually to the LLW evaporator.

The evaporator also produces two streams (evaporator distillate and evaporator concentrate). The evaporator distillate will be checked for radioactivity. If it meets the above radioactivity requirements, then it can also be disposed of directly to the Lab Site Drain System. If the distillate fails to meet the radioactivity limits, it will be recycled to the evaporator. The evaporator concentrate will be fed to the concentrator to reduce further the volume of waste bound for disposal.

The concentrator produces a solid/slurry stream and a concentrator distillate. Solids from the concentrator, like the cartridge filters, will be classified as mixed LLW and disposed of at Hanford. The TCLP test could be used at this point to classify the waste as LLW, rather than mixed LLW. The concentrator distillate will be recycled to the evaporator.

(2) Scheme B

Scheme B (Fig. 4) wastes will undergo a pH adjustment to remove the corrosivity characteristic (see Sec. IV.B.1.a.2). The pH adjustment could cause precipitation. After pH adjustment, solutions containing little or no solids will be fed to the filtration unit to separate the solids from the supernatant liquid. Solutions containing large amounts of solids will be fed directly to the existing LLW concentrator.

The filtration produces two streams (liquids and solids). The solids can be divided into two groups: solids trapped on cartridge filters and solid suspensions created from filter back flushing. Cartridge filters will be classified a LLW and disposed of at Hanford after absorption onto an appropriate media. The solid suspension will be fed to the existing LLW concentrator.

The liquid stream from the filtration system will be sampled for radioactivity. If it meets the alpha limits of 0.03 pCi/mL and beta/gamma limits of 1.0 pCi/mL, then it can be disposed of directly to the sewer. Liquid with radioactivity greater than the above limits will be fed to the LLW evaporator.

The evaporator also produces two streams (distillate and concentrate). The distillate will be checked for radioactivity. If it meets the above requirements, then it can also be disposed of directly to the Lab Site Drain System. If the distillate fails to meet the radioactivity limits, it will be recycled to the evaporator. The concentrate will be fed to the existing LLW concentrator to reduce disposal volume.

The concentrator produces a solid stream and a distillate stream. Solids from the concentrator, like the cartridge filters, will be classified LLW and disposed of at Hanford. The concentrator distillate will be recycled to the evaporator.

(3) Scheme C

Scheme C, which is for those wastes that have a reactive hazard, is yet to be defined. These wastes will require special treatment, and consultation with CMT is necessary before they can be treated.

^a Organic sorbents may not be used for waste containing oxidizing materials (e.g., nitrates).

Fig. 4. Scheme B -- Treatment of Mixed Wastes with the Corrosive Hazard

2. Chemical Treatment

The chemical treatment box shown in Fig. 3 is designed to be operated in controlled-area chemical hoods available to WMO (Bldg. 306). The process procedures will be straightforward and can be operated by current WMO personnel. A step-by-step procedure is given in Appendix C, and ES&H concerns are discussed in Appendix D. The following treatment process is applicable to waste solutions containing these corrosive acids and toxic metals:

Corrosive acids

- Hydrochloric acid
- Nitric acid
- Sulfuric acid

- Hydrofluoric acid
- Phosphoric acid
- Other inorganic acids

Toxic metals

- Cadmium(II)
- Chromium(II) and (III)*
- Selenium(II) and (IV)
- Silver(I)
- Mercury(I) and (II)
- Lead(II)

Acidic waste solutions will be treated with $\text{Ca}(\text{OH})_2$ slurry and Na_2S solution until the pH is about 9. A 10 wt % slurry of $\text{Ca}(\text{OH})_2$ will be added (pumped) slowly (with intermediate pauses to allow equilibration) with continuous stirring.** The rise in pH will be monitored during the additions with an on-line pH meter. When the waste solution is at pH 5 or higher,*** the saturated (1.97M) Na_2S solution will be slowly added, until the concentration of sulfide reaches 50 ppm. An ion-selective sulfide electrode will monitor the free sulfide concentration. If an excess of sulfide is inadvertently added, a 1M $\text{Cu}(\text{NO}_3)_2$ solution will be added to precipitate CuS until the free sulfide is lowered to 50 ppm. (Concentrations of sulfide of 500 ppm or higher are considered of RCRA concern.) The heat of neutralization may increase the temperature to an average of 35°C, which will be satisfactory (Appendix B). As a precaution, the temperature of the solution will be monitored. If the temperature exceeds 35°C, the feed pump should be shut off, and the solution should be allowed to cool before it is restarted. The vessel may require provisions for cooling.

The mixture will be stirred for 30 min, and if the sulfide concentration and pH remain constant, the precipitation will be considered complete. The waste slurry will then be pumped directly to a carboy and will be taken to the filter system.

3. Exceptions to Normal Treatment

Waste solutions that are basic or contain Cr(VI), As, Ba, or unusual oxidation states of the toxic metals will be treated by a modification of the process given in Sec. IV.B.2, or by another precipitation procedure using the same physical setup. These procedures are given below. Combinations of these metals with other RCRA metals must be looked at on a case-by-case basis.

a. Basic Solutions

In the absence of complexing agents, the only RCRA metals that can be present in basic solutions are Ba, Cr(VI), and As. The processing of these metals is described individually below. If the solution is classified as mixed waste due to being alkaline (pH greater than 12.5), it will be neutralized with 8M HNO_3 solution to a pH equal to 7 ± 3 . The temperature and pH will be monitored as described in the general procedure in Sec. IV.B.2.

* Chromium(II) is unstable in aqueous solution and is rapidly oxidized to Cr(III) by oxygen or water. The other oxidation state of chromium in aqueous solutions, Cr(VI), is discussed in the next section.

** An alternative procedure of pumping the waste solution into the 10 wt % $\text{Ca}(\text{OH})_2$ slurry was suggested by John Herman, Deputy Manager, WMO. This is likely to be the better means of treatment.

*** Evolution of H_2S can be a problem at pH less than 8.

b. Chromium(VI) Option

Chromium(VI) exists as CrO_4^{2-} (chromate) or $\text{Cr}_2\text{O}_7^{2-}$ (dichromate) anions in aqueous solution, and Cr(VI) must be reduced to Cr(III) in order to precipitate as the hydroxide. The Cr(VI) reduction must be done under acidic conditions. If the solution is not acidic, the pH will be adjusted to 1 by the addition of 8M HNO_3 , and the temperature and pH will be monitored as described in the general procedure in Sec. IV.B.2. A 30% solution of hydrogen peroxide (H_2O_2) will be pumped into the waste solution until the color changes from yellow to blue-green, which is the color of Cr(III). The solution will then be stirred for 5-10 min, and, if the blue-green color remains, the reduction will be considered complete. An optional oxidation-reduction system for potential control may be used for peroxide addition. Then a 10% $\text{Ca}(\text{OH})_2$ slurry will be pumped into the solution until the pH is 7-10. In this pH range, precipitation of $\text{Cr}(\text{OH})_3$ is complete.* The slurry will be treated as described in Sec. IV.B.2. At pH values higher than 10, $\text{Cr}(\text{OH})_3$ will begin to redissolve.

c. Arsenic Option

Both As(III) and As(V) exist as H_3AsO_3 , and H_3AsO_4 in acidic aqueous solutions and as salts of these acids in basic solutions. Both oxidation states can be precipitated as sulfides under acidic conditions. If the solution is not acidic, 8M HNO_3 will be added to obtain pH 1. Then, saturated Na_2S solution will be added as described in Sec. IV.B.2 until the sulfide concentration is 50 ppm. At the same time, pH will be monitored and maintained at 1 with the addition of 8M HNO_3 . The temperature and pH will be monitored as described in the general procedure in Sec. IV.B.2. After the solution temperature and sulfide concentration have remained constant for an hour, the precipitation will be considered complete, and the slurry will be filtered. After filtration, the filtrate must be treated as a corrosive liquid mixed waste (Scheme B).

As an alternative, ferric hydroxide co-precipitation can be used when trace amounts of arsenic are present. For this process, 1M $\text{Fe}(\text{NO}_3)_3$ solution will be added to obtain a ferric ion concentration of 2 g/L, then 10% $\text{Ca}(\text{OH})_2$ slurry will be added to pH 7 to precipitate $\text{Fe}(\text{OH})_3$. The solution will be stirred for 30 min, and the slurry can be filtered as described in Sec. IV.B.2.

Arsenazo dyes, organic compounds containing As(V), can be destroyed by oxidizing agents (H_2O_2 , Cl_2 , Br_2) or strong reducing agents [$\text{Ti}(\text{III})$, $\text{Na}_2\text{S}_2\text{O}_3$] [SAVVIN]. Once the As(V) is released, the above treatment for arsenic precipitation can be used.

d. Barium Option

Barium will be found in the (II) oxidation state and will not precipitate in the procedure described in Sec. IV.B.2. Waste solutions containing Ba(II) will be adjusted to pH of 9 with saturated Na_2CO_3 solution to precipitate barium as BaCO_3 . The slurry will be filtered as described in Sec. IV.B.2.

e. Rare Oxidation States of Toxic Metals

Examples of rare oxidation states of the RCRA metals are Pb(IV), Se(VI), selenide, and arsenide. Waste solutions containing these species will be treated on a case-by-case

* Note, sulfide addition may still be needed if other RCRA metals (Class 1) are in the waste.

basis to determine if they must be oxidized or reduced before using the general treatment process described in Sec. IV.B.2.

4. Reagents Required for Treatment Process

The reagent solutions or slurries that are required for the treatment process described above are as follows:

- 10 wt % $\text{Ca}(\text{OH})_2^*$
- Saturated Na_2S
- 8M HNO_3
- 1M $\text{Cu}(\text{NO}_3)_3^{**}$
- 30 wt % H_2O_2
- Saturated Na_2CO_3
- 1M $\text{Fe}(\text{NO}_3)_3$

5. Equipment

a. Process Overview

The flow diagrams for the complete treatment process are given in Figs. 3 and 4. The process equipment for chemical treatment will be described in this section. The details for the filtration system are reported in Appendix E. The evaporator and concentrator are being developed in parallel with the treatment process and will be discussed elsewhere.

Based on the design and control considerations discussed below, the treatment vessel should appear as shown in Fig. 5. This equipment has been ordered and will be set up and in operation by September 1993.

b. Design Basis for Treatment Vessel

The treatment vessel should be circular with a liquid-height-to-diameter ratio of one so that a circular mixing pattern is generated. To promote flocculation/precipitation, the mixing impeller should have a high pumping capacity at a low shear rate. A 45° pitched blade turbine is ideally suited to this task. It has a low solidity ratio (i.e., ratio of the impeller projected area to the impeller swept area), which will allow a high flow mixing rate to be induced in the tank. When operated at a low speed (30 rpm), both solids suspension and blending should be readily accomplished. Since the tank is not baffled, the impeller shaft should be inserted at an angle of 15° off the center vertical axis of the tank. The impeller should be rotated so that flow leaving the impeller is pumped downward. This is the most efficient way to operate this impeller as a blending device [OLDSHUE].

* Consideration has been given to replacing the calcium hydroxide with magnesium hydroxide. The lower solubility of $\text{Mg}(\text{OH})_2$ will limit the maximum pH of the filtrate and decrease possible corrosion of the stainless steel evaporator. Magnesium hydroxide will precipitate the same metals with a lower final pH.

** This solution can be used as a scrub solution in the event of H_2S formation.

Fig. 5. Setup for Treatment Vessel

c. Treatment Process Equipment

Equipment needs for precipitating heavy metals are listed in Table 4, along with a potential supplier (with catalog number) and estimated unit costs.

d. Treatment Process Control

Process control will be provided by a variety of controllers and measuring electrodes. The existing pH control system at ANL may be adequate for the needs of this precipitation process. The pH controller is linked to a metering pump capable of delivering between 0.38 and 41.6 mL/min. The controller turns the pump on until the desired pH is attained and then turns the pump off. The rate of addition is controlled at the pump. For purposes of this precipitation, the rate of addition should be set low enough to allow for good flocculation. An additional benefit to slow addition of base is the dissipation of heat, as the neutralization process is exothermic.

One of the keys to this treatment is the use of sodium sulfide to precipitate metal sulfides. The sulfide control system is very similar to that of the pH system. The controller

turns a metering pump on until the desired free sulfide concentration is attained. The metering pump is the same kind used in the pH system. The sulfide concentration is measured using a sulfide-ion-selective electrode, and the potential controller must have a ± 0.1 mV resolution. Using this method, an excess of 0.5 mg/L of free sulfide can be maintained [FREEMAN].

The oxidation-reduction potential (ORP) control system is optional,* but it is similar to the other control systems. A chemical system's ability to oxidize or reduce is measured by its ORP. An ORP electrode connected to a potential controller can be used to control oxidation and reduction reactions. The resolution for this controller can be ± 5 mV. The controller will control the pump adding reductant. The pump is the same type used for the base and sulfide additions. Again, the rate should be set low enough that the reaction can be controlled.

Table 4. Equipment Needs for Treatment Vessel

Item	Supplier	Catalog Number	Estimated Unit Cost ^a
Tank, 20 gal cap.	Cole-Parmer	G-06738-12	\$25
Tank Cover	Cole-Parmer	G-06738-13	\$5
Agitator, 2-180 rpm	Cole-Parmer	G-50002-10	\$390
Speed Controller	Cole-Parmer	G-50002-00	\$175
Clamp	Cole-Parmer	G-04560-24	\$83
45° Pitched Blade Turbine (PBT)	Cole-Parmer	G-04370-18	\$26
Mixing Shaft	Cole-Parmer	G-04370-02	\$30
pH Electrode	Existing	---	---
Sulfide Electrode	Cole-Parmer	G-27502-41	\$280
ORP Electrode	TBD	---	---
pH Controller	Existing	---	---
Potential Controller (0.1 mV resolution)	TBD	---	---
ORP Controller	TBD	---	---
Peristaltic Pump	Existing	---	---
Metering Pump ^b	Serfilco	A74, 10-1741	\$440
Basic Plumbing Supplies	Any Supplier	---	\$200 ^c

^a Costs in 1993 dollars.

^b Two existing pumps.

^c Estimated.

* It may be useful for wastes containing Cr(VI) and Arsenazo III.

APPENDIX A. TECHNICAL BASIS FOR THE PRECIPITATION METHODS

1. Overview

Removal of the RCRA metals (As, Ba, Pb, Cd, Cr, Ag, Se, Hg) from mixed waste can be accomplished by precipitation [GORONSZY, GRULICH]. The metals are converted to an insoluble form and removed by filtration. Although there are other separation methods, precipitation was chosen because of its simplicity and cost effectiveness. A review of the current untreated liquid waste solutions stored by WMO revealed high concentrations of RCRA metals, as well as other metals, in some low-level radioactive wastes. The combination of radioactivity and hazardous chemicals is called mixed waste. Disposal of this waste is very expensive. The separation of the two types of waste would reclassify the liquid waste as low level, reducing the disposal cost by a factor of about four. The initial efforts center on converting aqueous mixed waste to LLW by selective precipitation of the toxic metals and then reducing the volume of the resulting LLW solution in an evaporator and/or concentrator. The following describes methods used elsewhere for removal of toxic metals.

A pilot-plant demonstration to remove Sr-85, Cs-137, Cd, Pb, U, Fe, Ca, benzene, and trichloroethylene from groundwater leachates was completed at Chalk River Laboratories [BUCKLEY]. Since groundwater was being treated, the high hardness required a modified lime-soda softening process to remove the hazardous components along with the calcium [HAMMER, REYNOLDS]. Zeolite was necessary to recover the Sr-85 and Cs-137 [GARAMSZEGHY]. An early version of the lime-soda softening process to remove radionuclides was operated at Oak Ridge National Laboratory during 1957-1975; clay was added as the ion-exchange agent for Sr-90 and Cs-137. Since 1975, the SPIX process (Scavenging Precipitation Ion Exchange) has been used. In this process, NaOH is added to precipitate CaCO_3 at pH 12. This results in about 50% removal of the strontium. In addition, ferrous sulfate (as a scavenging precipitate) and ion exchange are used to remove the remaining cesium and strontium.

It is well known that complexing agents can interfere with precipitation processes, and this is discussed in a recent review paper [GARAMSZEGHY]. For these precipitation processes to function, the complexing agent must be destroyed by ozone, peroxide, chlorine, or other oxidizers. At Los Alamos, a ferric flocculation process gave poorer performance if complexing agents were present, and the combination magnesium-hydroxide/ferric-flocculation process was effective in the presence of complexants such as EDTA. At the Savannah River Site, precipitation with iron and aluminum at pH 7 is used to prevent fouling of downstream reverse-osmosis units, and ion exchange is used to remove radionuclides from low-level streams.

However, none of these processes is directly applicable to the waste solutions in WMO, and none will remove all the RCRA metals. We have determined that a combined hydroxide/sulfide precipitation process is relatively simple and cost effective, and it is applicable to at least 95% of the aqueous waste solution at ANL.

2. Sulfide Precipitation

Sulfide salts are acceptable for disposal at Hanford as solid mixed waste, provided acids are not present (to prevent H_2S formation). Table A-1 summarizes the conditions under which the metals of interest would precipitate from solution as sulfide or hydroxide salts. The chemistry of the precipitation process is being designed to minimize any precipitation in the evaporator.

Table A-1. Precipitation Characteristics of the RCRA Metals

Metal	pH	Reagent	Interferences	Conc. in Filtrate, mg/L
Ag(I)	11.1	hydroxide	--	0.2
	11.5	lime	--	0.2
Ba(II)	10.5	carbonate lime	--	0.03
Hg(I, II)	11.5	ferric hydroxide	organics	0.0005-0.005
	8	sulfide		0.01-0.02
Cu(II) ^a	9-10.3	hydroxide	organic	0.02-0.07
	8.5-9.5	sulfide		0.01-0.02
As(III, V)	<7	sulfide	CN ⁻ , NH ₃	0.5
		Fe hydroxide coppt		
Cr(III)	8	lime		0.5
Cd(II)	10-11	hydroxide	CN ⁻ , NH ₃	0.05
	2.5-8.5	sulfide		0.008
Pb(II)	11.5	hydroxide	organic	0.019
	7.5-8.5	sulfide		
Se(II, IV)	6.6	sulfide		0.05

^a Important for use in an H₂S scrubber or to precipitate excess sulfide.

The advantages of the sulfides are that their salts are stable even under drastic changes of pH. Under suitable acid conditions, H₂S can be produced, and, if generated, a Cu(SO₄) or Cu(NO₃)₂ solution can be used to trap the hydrogen sulfide by CuS precipitation.

Table A-2 shows the behavior of the insoluble RCRA metal sulfides in acid solution. Of special interest are the arsenic sulfides, which precipitate best in strong acid solution and precipitate only slowly and incompletely in basic solution.

Table A-2. Characteristics of Sulfide Precipitates

Compound	HCl Conc.				Precipitate Color
	<u>6M</u>	<u>3M</u>	<u>0.5M</u>	<u>0.2M</u>	
As ₂ S ₅	P	S	S	S	yellow
As ₂ S ₃	P	P	P	P	yellow
As ₄ S ₄	**	**	**	**	red
HgS	P	P	P	P	red or black
CuS	P	P	P	P	black
PbS	-	I	P	P	black
CdS	-	-	P	P	yellow

S = slow but eventually complete precipitation.

P = complete precipitation.

I = incomplete precipitation.

- = no precipitation.

** = data not available.

The individual RCRA metals are discussed below.

a. Lead

Lead(II) precipitates as the sulfide in dilute acid as well as in basic solution.

b. Mercury

Mercury in either oxidation state, (I) or (II), will precipitate as the sulfide in acidic or basic solution. Concentration of 50 mg/L can be reduced to 10 µg/L using Na₂S. This reaction in combination with filtration, flocculation, or settling can achieve a high degree of separation [PATTERSON]. Some of the Hg(I) will precipitate as the metal.

c. Silver

Silver forms a highly insoluble sulfide in both acid and basic solution.

d. Selenium

Selenium (II and IV) will be reduced and precipitated as the metal by Na₂S. Selenium can be precipitated from wastewater at a pH of 6.6. Effluent levels of 0.05 mg/L are reported. Other oxidation states of selenium are rare and must be considered on a case-by-case basis.

e. Arsenic

Arsenic (III and V) will be precipitated as the sulfide by adding hydrogen sulfide or sodium sulfide in acid solution. The result of this precipitation can yield arsenic concentrations as low as 0.05 mg/L. In basic solutions, arsenic will redissolve as arsenites or arsenates. If the sulfide concentration is too high, soluble sulfide compounds will also form.

f. Chromium

In the alkaline sulfide environment, Cr(III) will precipitate as the hydroxide and not as the sulfide. Chromium(II) is very unstable in acid solution and will be oxidized to Cr(III).

g. Cadmium

Cadmium sulfide will precipitate from slightly acidic or alkaline solutions, leaving less than 0.01 mg/L of cadmium in solution.

3. Hydroxide and Other Precipitation

Hydroxide precipitates of heavy metals tend to be gelatinous, non-crystalline, and difficult to filter. The best results are obtained when the precipitation is made from a hot solution with slow addition of the precipitating agent, and the solution is digested before filtration. The behavior of each of the metal hydroxides of concern is discussed below.

a. Cadmium

The addition of a hydroxide, such as Ca(OH)₂, to an acidic cadmium solution produces a highly stable and insoluble metal hydroxide at basic pH. At pH 8, the cadmium in solution is about

1 mg/L; at pH 10-11, it is 0.05 mg/L. With ferric hydroxide coprecipitation at pH 6.5, the cadmium concentration is reduced to 0.008 mg/L. Complexants such as oxalic acid, ammonia, and cyanide will interfere with the cadmium precipitation and must be removed or destroyed before the $\text{Cd}(\text{OH})_2$ will precipitate. Cadmium precipitates with organic complexants, such as hydroxyquinoline and α -benzoinoxime. Other inorganic compounds that will precipitate cadmium are H_2SO_4 and $(\text{NH}_4)_2\text{MoO}_4$ [ECKENFELDER].

b. Mercury

The addition of hydroxide precipitates mercury (I and II) oxides at basic pH. Mercurous oxide is extremely insoluble in excess alkali but mercuric oxide is somewhat soluble (0.5 mg/L). Elemental mercury must be oxidized to the mercuric ion for precipitation methods.*

c. Lead

Precipitation with calcium hydroxide produces an insoluble metal hydroxide at alkaline pH. Concentrations of lead in solution of 0.019-0.2 mg/L at pH 11.5 to 9.5 are obtained. Other materials known to precipitate lead are H_2SO_4 , hydroxyquinoline, α -benzoinoxime, and $(\text{NH}_4)_2\text{MoO}_4$ [KING]. The addition of carbonates (soda ash) produces insoluble lead carbonates at basic pH; concentrations of lead in solution of 0.01-0.03 mg/L can be obtained at pH 9 to 9.5.

d. Silver

The addition of chloride to a silver solution precipitates insoluble silver chloride, and concentrations of silver in solution of 1.4 mg/L can be obtained. Under basic conditions, a dark brown precipitate of Ag_2O is obtained, with a residue concentration of 0.2 mg/L. Complexants such as cyanide and ammonia will interfere with the silver precipitation. Low concentrations of silver can be removed using activated carbon at pH 5.4 (up to 12% by weight) and at pH 2.1 (only 9% by weight) [PATTERSON].

e. Arsenic

Some of the waste solutions stored at ANL contain arsenic in the form of organic bound dyes, such as Arsenazo III. Arsenazo III, an organic compound derived from the As(V) acid form, can be destroyed by oxidizing agents (H_2O_2 , Cl_2 , Br_2) or strong reducing agents [$\text{Ti}(\text{III})$, $\text{Na}_2\text{S}_2\text{O}_3$] [SAVVIN]. Once the As(V) is released, the above treatment for arsenic precipitation can be used.

There is a coprecipitation method that employs ferric hydroxide to remove the arsenic. This method can result with solutions of 0.005 mg/L of arsenic. For very low concentrations of arsenic, activated carbon filters can be used to obtain 0.06 mg/L of arsenic in solution [ECKENFELDER]. Other reagents that can precipitate arsenic are KBrO_3 and KBr .

f. Chromium

Chromium in the (VI) oxidation state will not precipitate as a hydroxide. According to the generators, chromium is in some wastes as either dichromate, chromate, or chromium(III).

* This is important since an additional 15 lb (6.8 kg) of the mercury waste stored at ANL is in the form of liquid metal.

Chromium(III) can be precipitated as the hydroxide, but redissolves in concentrated hydroxide solution. The optimum pH to precipitate Cr(III) as a hydroxide is 8.0 to 9.9. Chromium(VI) can be reduced to Cr(III) by a variety of reducing agents, including hydrogen peroxide, sodium sulfite, sodium metabisulfite, and hydroxylamine. Chromates form insoluble precipitates with Ba^{2+} , Pb^{2+} , and Ag^+ in dilute acid.

g. Barium

Barium does not form a highly insoluble hydroxide or sulfide. It can, however, be precipitated from solution by the addition of sulfate (in neutral to basic solution) or carbonate (in basic solution).

4. Heat of Reaction

Neutralization of acid waste will produce heat from the exothermic acid/base reaction. This heat can result in a substantial temperature rise and can cause emission of volatile material. A few ways to control the temperature are (1) changing the reagent feed rates, (2) cooling the reaction vessel externally (maximum operating temperature of a polyethylene tank is 65°C), (3) adding of lime slurry prior to adding acid waste, (4) providing adequate ventilation of emissions, and (5) providing large surface area for neutralization. (See Appendix B.)

5. Solubility Product Constants

The solubility products (K_{sp}) of selected sulfide, sulfate, and hydroxide metal salts are given in Table A-3. In the hydroxide/sulfide system the relative amount of sulfide and hydroxide of each metal will depend on the relative solubility product.

Table A-3. Solubility Products for
Selected Metal Salts
[SISLER, ZUMDAHL]

Component	K_{sp}
CdS	7×10^{-27}
ZnS	7×10^{-24}
PbS	7×10^{-29}
NiS	3×10^{-21}
HgS	1.6×10^{-54}
PbSO ₄	1.3×10^{-8}
BaSO ₄	1.5×10^{-9}
Ba(OH) ₂	5.0×10^{-3}
Sr(OH) ₂	3.2×10^{-4}
Ca(OH) ₂	1.3×10^{-6}
AgOH	2.0×10^{-8}
Mg(OH) ₂	8.9×10^{-12}
Mn(OH) ₂	2.0×10^{-13}
Cd(OH) ₂	5.9×10^{-15}
Pb(OH) ₂	1.2×10^{-15}
Fe(OH) ₂	1.8×10^{-15}
Ni(OH) ₂	1.6×10^{-16}
Zn(OH) ₂	4.5×10^{-17}
Cu(OH) ₂	1.6×10^{-19}
Hg(OH) ₂	3×10^{-26}
Cr(OH) ₃	6.7×10^{-31}
Al(OH) ₃	2×10^{-32}

6. Conclusions

The simplest and most practicable chemical treatment for toxic metals is precipitation by sodium sulfide and calcium hydroxide. This treatment will precipitate all RCRA metals except Ba, As, and Cr(VI). If this simple one-step precipitation does not produce a filterable precipitate and a filtrate that contains less than the regulatory limits of toxic metals, the treatment can be modified. An analytical procedure is needed during the testing phase to determine small amounts of these metals in the filtrate; ICP-AES is satisfactory for determination of all the metals.

A first step in proceeding with the actual work is to prepare a synthetic mixture of a typical waste solution and go through the process to evaluate its behavior on a laboratory scale. The accuracy of the sulfide electrode must be evaluated under the conditions of the precipitations. Alternative treatment methods may involve those mentioned earlier, e.g., additional treatment of the filtrate with carriers present [Fe(III), PO_4^{3-}] to coprecipitate traces of remaining toxic metals.

All steps in the process must take into account the amphoteric properties of some of the metals. Arsenic sulfides and chromium(III) hydroxide dissolve in excess base, and cadmium hydroxide precipitated with ammonia will redissolve in excess ammonia due to complex formation.

Some of the RCRA elements can be separated by other means, but this requires a step-wise separation scheme and several filtrations. For example, barium and lead will precipitate as sulfates from acid solution, leaving the other metals in solution. Barium, cadmium, chromium(III), lead, mercury, and silver will precipitate with sodium carbonate from alkaline solution, leaving arsenic and selenium. With excess carbonate, chromium will redissolve.

Another precipitation process, termed homogeneous precipitation, for the sulfides, hydroxides, and other compounds produces more crystalline and more filterable precipitates than the method described above. In this process, a compound is added to the original solution and heated to decompose it to an anion that precipitates the metal molecule by molecule. This allows the precipitate to form relatively large crystals. For example, urea is used to precipitate hydroxides of Fe(III) and aluminum by hydrolyzing urea to form ammonia and carbon dioxide on heating to 90°C. In a similar manner, thioacetamide can be used to precipitate metallic sulfide.

APPENDIX B. MASS AND ENERGY BALANCE CALCULATIONS

1. Introduction

Mass and energy balance calculations were performed for the precipitation using the 72 L of waste that will be used for treatment-process testing and demonstration (see Table 1 in main text). This waste, excluding the waste containing Arsenazo III, is contained in 11 different containers. These containers will be run through the process based on the compositions of their contents. These calculations determine the chemical additions needed and heat released during the process for each of these 11 wastes. The energy balances determined that the adiabatic temperature rise was not large enough to warrant cooling. Mass balances showed that the supernatant would be non-hazardous and were used to determine the mass of precipitated solids and the quantities of reagents required for the precipitation.

2. Mass Balance Calculations

Mass balance calculations were performed for a combination of hydroxide pH adjustment and sulfide precipitation. Sulfide reacts with the RCRA metals, according to the following reactions:

Thus, it is a simple matter to determine the amount of sulfide required to precipitate the RCRA metals. Sulfide reacts with each metal ion in the stoichiometry shown in Eqs. B-1 through B-5. To calculate the volume addition, simply divide the number of moles of sulfide required to precipitate the metals by the molar concentration of the sulfide addition. For example, 2 L of waste containing 1M $Cd(NO_3)_2$ would require 2 mol of sulfide (or 2 L of a 1M Na_2S solution) to precipitate the cadmium.

The concentration of each RCRA metal left in solution after sulfide precipitation can be determined from the K_{sp} . If no excess sulfide is added, $[M^{2+}] = [S^{2-}]$; then, the concentration of metal left in solution is given by $[M^{2+}] = \sqrt{K_{sp}}$. Otherwise, using the measured sulfide concentration, the metal concentration can be determined from Eqs. B-1 through B-5.

Neutralization of acid occurs by the reaction*:

* Strictly speaking, K_w (and pH) is defined in terms of H^+ and OH^- activities and not concentrations. This difference is not important for this discussion.

From this reaction, one mole of hydrogen ion requires one mole of hydroxide ion. Thus, it is a simple matter to determine the moles of base necessary to neutralize the acid present; $[H^+] = [OH^-] = 10^{-7} \text{ M}$ (pH = 7). Calcium hydroxide, which will be used for pH adjustment, has 2 equivalents of base per mole of calcium hydroxide. To calculate the volume of calcium hydroxide slurry necessary to neutralize the acid, simply divide the equivalents of acid present by half the molar concentration of calcium hydroxide. For example, 2 L of waste containing 1 M HCl would require 2 equivalents of OH^- , or 4 L of a $Ca(OH)_2$ slurry equivalent to 0.5 M Ca^{2+} .

To calculate the base necessary to raise the pH to 9, assume that the sum of the volumes of the acid solution and the $Ca(OH)_2$ slurry is equal to the volume of the neutralized solution, i.e., $\Delta V_{\text{mix}} = 0$. To raise the pH to 9, the necessary free $[OH^-]$ is equivalent to 10^{-5} M . This concentration is readily obtainable from Eq. B-6 and the definition of pH:

$$\text{pH} = -\log [H^+] \quad (\text{B-7})$$

It is necessary to add enough OH^- to obtain the desired free $[OH^-]$ concentration ($[OH^-] = 10^{-5} \text{ M}$ for pH=9). The addition can be determined by:

$$V_b = (V_i + V_s + V_a) \frac{C_{OH}}{C_b} \quad (\text{B-8})$$

where V_b = Volume of base necessary to raise pH from 7 to 9
 V_i = Volume of the waste initially
 V_s = Volume of sulfide solution added to precipitate RCRA metals
 V_a = Volume of base necessary to raise pH to 7
 C_{OH} = Concentration of base required for correct pH ($C_{OH} = 10^{-5} \text{ M}$ for pH = 9)
 C_b = Concentration of OH^- being added

The following assumptions were used in deriving Eq. B-8:

$$\begin{aligned} C_{OH} &\ll C_b \\ [OH^-] &= 10^{-7} \text{ M at pH} = 7 \ll C_{OH} \\ \Delta V_{\text{mix}} &= 0 \end{aligned}$$

The total amount of base necessary to raise the pH of the waste to 9 is then $V_a + V_b$.

3. Energy Balance Calculations

In general, acid-base neutralization reactions are exothermic, and heat generation can be a problem. Excessive heat generation could soften the precipitation vessel; polyethylene has a maximum operating temperature of 65°C . Energy balances were completed to determine the heat generated by the pH adjustment and the precipitation. The amount of heat liberated or absorbed by a reaction is given by:

$$\Delta H_{\text{rxn}} = \Delta H_f (\text{products}) - \Delta H_f (\text{reactants}) \quad (\text{B-9})$$

To determine the heat liberated or absorbed, simply determine the specific free heats of formation (ΔH_f) from any standard reference text (e.g., *CRC Handbook of Chemistry & Physics*). Then, multiply the specific free heats by the moles of products and reactants, respectively; subtract the

results to determine the total heat. To calculate the adiabatic temperature rise caused by the reaction use:

$$\Delta T = \frac{\Delta H}{V\rho C_p} \quad (\text{B-10})$$

where

ΔH = heat calculated from Eq. B-9 in calories

V = Total volume of the waste after addition of base and sulfide in liters

ρ = Density of the solution (estimated to be 1300 g/L)

C_p = Heat capacity of the solution (estimated as 3 cal/g·°C)*

ΔT = The calculated temperature difference in degrees centigrade

Figure B-1 is an example of the use of the above mass and energy balance equations for the waste composition reported on form RL-1845 (see Table 1 in text). A summary of the mass and energy balance calculations for the 72 L of demonstration waste is shown in Table B-1.

Fig. B-1. Heat and Energy Balance Calculations for Waste Reported on RL-1845 (see Table 1 in text)

* Pure water has a heat capacity of 1 cal/g·°C. If temperature rise becomes of greater concern, we will need to investigate heat capacity data for concentrated salt solutions.

Table B-1. Mass/Energy Balance Summary for 72 L of Demonstration Waste

Solution	Waste Vol., L	Saturated Na ₂ S Required, L	10 Wt% Ca(OH) ₂ Required, L	Total Vol., L	Metal Sulfide Ppt., g	Final Temp., ^a °C
RL-01845	3.79	0.11	4.99	8.89	20	46°C
RL-01884 ^b	10.00	--c--	3.30	>13.30	--c--	--c--
RL-01847	3.79	0.42	4.99	9.20	79	49°C
RL-01810	0.90	0.33	0.59	1.82	63	49°C
RL-01824	1.00	0.10	0.33	1.43	20	40°C
RL-01823	22.74	0.54	14.97	38.25	101	40°C
RL-01806	4.00	3.50	9.22	16.72	1,153	61°C
RL-01809	4.00	5.23	2.64	11.86	1,289	106°C
RL-01472	0.02	0.31	0.00	0.33	144	--c--
RL-01889	18.95	0.86	24.95	44.76	162	46°C
RL-01808	3.00	5.23	8.76	16.99	1,289	55°C
Total:	72.19	16.63	74.74	>163.55	4,320	

^a Assuming initial temperature of 25°C.^b Contains unspecified amount of uranium.^c Insufficient information to predict.

APPENDIX C.

PRELIMINARY STEP-BY-STEP OPERATION PROCEDURE

This process is designed to treat liquid radwastes that meet the following criteria:

1. The waste does not contain any dissolved organic contaminants or complexants, and it is an aqueous solution containing one or more of the following metal ions: Cd, Pb, Hg, and Ag (metal-organic compounds are unacceptable). This procedure does not apply to the other RCRA metals: Cr, Ba, As, or Se. Other non-RCRA metals, such as Mg, Fe, and Al, do not interfere with the process.
2. The acid concentration is due to one or more of the following mineral acids: nitric, sulfuric, hydrochloric, hydrofluoric, and phosphoric. Other acids, such as oxalic acid, are unacceptable because they complex the RCRA metals and interfere with the precipitation.

The apparatus for this chemical treatment operation has been previously described (see Sec. IV.B.5). The steps describing the precipitation procedure are listed below. During all operations, appropriate safety apparel should be worn, and proper radioactive-hood working procedures must be followed.

1. Ensure that the waste meets the treatment criteria listed above. If it is acceptable, prepare the waste carboy by wrapping it in a plastic bag. The opening of the plastic bag should be loosely bunched at the handles of the carboy, and the lid should be left on the carboy. Set the carboy in the hood.
2. With a gloved hand remove the lid from the carboy and place it in a separate plastic bag. Close this bag, and place it in the hood off to the side.
3. Wrap the opening of the plastic bag around the mouth of the carboy, and seal-tape it in place so that no liquid will be allowed to drip onto the exterior of the carboy.
4. Carefully insert the filling tube into the carboy, and turn on the transfer pump. Fill the 20-gal (80-L) precipitation tank to a maximum of 25% full.
5. Prepare the feed solutions [10% $\text{Ca}(\text{OH})_2$ and saturated Na_2S]. Ensure that the feed pumps are working properly.
6. The pH and sulfide meters will need periodic calibration with standard solutions (purchased buffers for pH, standard sulfide solutions for the ion-selective electrode). If calibration is necessary, it should be done at this time. Manufacturers' literature will specify the calibration procedures and intervals. The thermocouple connected to the pH electrode may be factory calibrated and, in such case, would not need calibration by the user.
7. Install the pH and sulfide electrodes in the precipitation tank.
8. Turn on the mixer and set the rotation speed to 30 rpm. This will ensure good flocculation.

9. Turn on the Ca(OH)_2 pump; it will slowly add this feed until the pH equals 5, as determined by the pH electrode.
10. When the pH reaches 5, allow the Ca(OH)_2 to continue running, and turn on the Na_2S pump. The pump will slowly add this feed until the free sulfide reaches 50 ppm, as determined by the ion-selective electrode. Allow the sulfide controller to stabilize the sulfide concentration. This will take at least 1/2 h. The pH should continue to rise to 9. This is the target pH required for feed to the evaporator. If the pH is higher, the process will still work.
11. Using the transfer pump in the hood, pump the slurry (typically 1 g/L total suspended solids) from the precipitation tank to the transfer carboy. Because of the volume increase due to the treatment, more transport carboys may be needed. As each carboy is filled, it should be removed from the hood as outlined in steps 13-16, below.
12. After all liquid is removed from the precipitation tank, turn off the mixer.
13. Carefully dismantle the filling line from the transfer carboy.
14. Remove the tape from the mouth of the carboy and peel the plastic bag down toward the base, being careful not to spread contamination to the outside of the carboy.
15. Open the plastic bag containing the carboy lid. With a clean gloved hand, take the lid from the bag and secure it on the carboy.
16. Lift the carboy out of the hood, leaving the plastic bag wrapper inside the hood. Immediately have a Health Physics technician check the outside of the carboy for contamination. If it is clean, put the carboy in the secondary container. If the carboy is contaminated, decontaminate the surface as specified by the health physics personnel, recheck for contamination, and repeat this process until the carboy is clean. Then, put the carboy in the secondary container.
17. Put the pH electrode and ion-selective electrode in the standby mode. This may require dismantling the electrodes and submerging them in some type of manufacturer-specified solutions.
18. Clean up the work area in the hood, putting all waste in the solid radioactive waste receptacle.
19. Appropriate documentation should precede and follow this operation.

After this last step is completed, the other treatment steps, such as filtration and evaporation, can proceed. Whenever the waste carboys are moved, the carboy must be sealed and carried inside a secondary container. The precipitation tank is ready for reuse at any time, and rinsing the tank should not be necessary.

APPENDIX D. DISCUSSION OF ES&H CONCERNS

1. Overview

The health and safety of the employees involved in this work are of primary concern. No actual hands-on work shall be performed until all employees involved are adequately trained and understand all potential hazards. Also important but of secondary concern are the security and safety of ANL property.

Safety (and health) is a responsibility extending from the Laboratory Director to and through all supervisory personnel to the hands-on worker. Thus, safety is everyone's responsibility.

The governing document on health and safety issues is the *Environment, Safety, and Health Manual* (ANL-East) issued by the ES&H Division [ANL]. This manual should be consulted when any ES&H questions or problems arise. In addition, the names and phone numbers of the following individuals and Sections shall be prominently posted in the workplace:

The Divisional Safety Officer
The Divisional Environmental Compliance Officer
The Area Health Physics Technicians and Health Physicist
The Industrial Hygiene Section of the ES&H Division
The Health Physics Section Manager, and
The Emergency Safety Officer in ES&H Division.

2. Training

The Project Supervisor shall maintain a written, auditable record of the training received by each worker. The Divisional Safety Officer shall verify that the training is satisfactory before work begins.

3. Specific Areas of Concern

Respiratory protection will be required if toxic or irritating fumes or gases are generated. The Industrial Hygiene Section will provide the appropriate devices.

Skin protection shall be provided when working with waste solutions and chemicals. The Industrial Hygiene Section can provide information on the appropriate gloves if there is any uncertainty on this matter.

Protective clothing provided by ANL shall be used for all work.

Hazardous chemicals will be present in the waste solution (both chemical and radioactive) and may be generated during the treatment process. Some examples are:

- a. Sodium sulfide in acid solution will generate hydrogen sulfide, a toxic gas.
- b. Calcium hydroxide is caustic and corrosive to the skin and lungs.

c. Alkaline waste solutions containing cyanide ion will generate hydrogen cyanide, a toxic gas, if the solution is acidified.

Spill control measures for such toxic and corrosive substances shall be in place before work begins.

Material Safety Data Sheets (MSDSs) shall be available in the work areas for all chemicals (reagents) used and for the potentially hazardous products described above. Such sheets are available from vendors of the reagents. The Industrial Hygiene Section maintains a large data base of MSDSs and should be contacted for those of the potentially hazardous products.

Criticality

If WMO has a current Criticality Hazard Control Statement (CHCS), it should be examined by the Divisional Safety Officer to determine if any changes are needed for this project. If a CHCS does not exist, the Divisional Safety Officer and Project Manager shall determine if one is necessary. (This will be important when TRU wastes are treated.)

Radioactive or Mixed Waste Disposal Requisition Forms

Proper documentation on these forms by the generator becomes very important for the treatment of these wastes. These forms should be reviewed, with treatment of wastes taken into account. Also, a data base should be developed for use by WMO to classify wastes by content.

APPENDIX E. DESCRIPTION OF THE FILTRATION SKID

The hollow-fiber filter (HFF) skid, purchased by WMO from the Braidwood Station of Commonwealth Edison, was manufactured by HPD, Inc., in 1987. The skid contains a $0.1\ \mu\text{m}$ (nominal size) polyethylene HFF rated for 5 gpm (0.3 L/s) and 100 psi (0.7 MPa). Plumbing, instrumentation, and an air-flushing system for the filter are included to make the existing skid a stand-alone module. Instrumentation includes a number of pressure gauges, a differential pressure (dP) cell connected across the filter, a feed-temperature gauge, and an effluent rotameter (flow indicator). The air-flushing system includes two rotameters (for backwash and scrubbing air), pressure gauges and regulators, a hollow-fiber air filter, and plumbing connections.

This skid is to be modified to allow its use for filtering a wide variety of mixed waste streams. A number of liquid mixed waste volumes stockpiled around ANL-East will be the first items filtered through the modified skid. Laboratory filtration studies completed on some of these volumes have shown that filtration will drop the concentrations of toxic metals below RCRA concerns. The filtration system will then be used to filter the treated mixed waste that has been processed using the treatment plan.

A versatile filtration system, incorporating a number of modules, has been designed, as shown in Fig. E-1. The modular design allows the filtration scheme to be varied for research purposes and

Fig. E-1. Schematic of Filtration System

for treatment of a variety of influents. As seen in Fig. E-1, most modules can either be included in, or isolated from, the flow scheme as desired. All major components have been ordered, and fabrication is scheduled to begin in late January 1994. A sketch showing the filtration skid and the approximate location of the major components is given in Fig. E-2.

Fig. E-2. Sketch of Filtration Skid Showing Approximate Location of Major Components

The bag filter, with filter elements in the 20-50 μm range, will trap the bulk of the solids. A bag filter combines the advantages of high solids capacity and low disposable-cartridge volume, making this a valuable front-end addition. Plumbing connections in parallel with the bag filter will allow the later addition of a filter press or other pre-treatment option if studies show that it is needed.

Two prefilters in parallel have been included to protect the HFF from solids loading. One of the prefilter options will be a polypropylene mesh filter; the other will be a sintered-metal, back-flushable filter. The metal element is easily flushed with liquid by reversing the flow through it. If the nature or size of the particles trapped by the filter makes flushing inefficient, the sintered-metal cartridge can be easily replaced by a polypropylene cartridge. Both prefilters will be in the pore size range of 5-10 μm .

The open connection between the pre-filters and the HFF has been included to allow the addition of a carbon filter to adsorb dissolved organics from the aqueous stream. This addition may be necessary if streams containing dissolved organics are to be processed, since such organics would wet the pores of the HFF and plug it. A carbon filter has not been included in the current design for two reasons: (1) present plans do not include processing aqueous streams containing dissolved organics, and (2) the size of a suitable carbon filter would be too large for incorporation into the filter skid.

To adsorb volatile organic compounds (VOCs) dissolved in an aqueous liquid, reducing concentrations from the ppm range to the ppb range, the superficial loading should be 2 gpm/ft^2 ($1.4 \text{ L}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$) [REYNOLDS]. The depth of the filter will depend on the initial concentration of the VOCs and the desired life of the carbon bed. Information regarding suitable carbon filters is being gathered from vendors.

The after-filter in parallel with the HFF will be used mainly as a backup for the HFF, for streams which cannot be run through the HFF (e.g., streams containing undissolved organics, which cannot be absorbed by the carbon filter). Pore sizes for the after-filter will range from 1.0 to 0.1 μm .

All housings accept industry-wide standard cartridges, allowing the use of cartridges in a wide variety of pore sizes available from many manufacturers. Filter elements made with polypropylene will receive the most use. Each filter housing will have pressure gauges upstream and downstream and a sampling valve directly downstream to aid filtration studies. All housings are made of Type 316 stainless steel and have pressure ratings of at least 150 psi ($\sim 1 \text{ MPa}$).

The feed will be pumped through the system by an electrically driven, variable-speed, positive-displacement diaphragm pump, with a current draw of 25 A at 220 V and a rated output of 5 gpm (0.3 L/s) at 150 psi ($\sim 1 \text{ MPa}$). The diaphragm pump was chosen mainly because it is seal-less and self-priming. It also provides trouble-free pumping of slurries (up to 400 μm particle size) and the capability of running the pump dry without damage. The pump will include a relief valve to ensure that the design pressure of 100 psi (0.7 MPa) is not exceeded. A pulsation dampener will smooth out the flow pulses generated by the pump, leaving a maximum pressure fluctuation of about $\pm 1 \text{ psi}$ ($\pm 7 \text{ kPa}$). A flex hose on the suction side of the pump will allow for easy adjustment to a variety of feed-vessel sizes. The pump has a suction-lift capacity of at least 10 ft (3 m).

Total liquid holdup in the complete system will be about 14 gal (53 L). The maximum pressure drop across the system will be about 95 psi (0.65 MPa). This maximum accounts for plumbing losses as well as pressure drop across filters and will only be encountered when all filters, simultaneously, are in need of replacement or backflushing.

APPENDIX F. SUGGESTIONS FOR FUTURE WORK

This preliminary waste treatment plan has been developed completely from a literature survey. Before the treatment plan is ready for implementation, CMT and WMO personnel must get hands-on experience with the proposed chemical treatment. Further, the monitoring and control system must be developed and tested to the point that the reliability of the treatment process and equipment for producing consistent precipitation of all toxic metals to non-RCRA concern is verified. Also, all documentation must be written and approved before this treatment plan becomes a standard WMO procedure.

A Statement of Work for reaching this objective will be written in the near future. The following is a brief discussion of the tasks that will lead to implementation.

1. Procure Equipment and Supplies

Procurement orders will be written in cooperation with WMO personnel for the equipment and supplies needed for the development and demonstration phase of this effort.

2. Test Applicability of Sulfide-Selective Electrode

Using simulants of the high ionic-strength solutions typical of the mixed waste in Building 306 at ANL, we will precipitate toxic-metal sulfides using saturated Na_2S solution and measure the responsiveness of the electrode and the accuracy of its measured sulfide concentration. Testing destruction of the Arsenazo III dye should also be accomplished in a laboratory setting. These results will be repeated using actual waste solutions, initially in the laboratory and then in the actual equipment set up in Building 306.

3. Write Safety and Other Needed Documents

We will assist WMO in writing and submitting documentation necessary for testing, demonstrating, and implementing this treatment plan, including getting EPA approvals necessary.

4. Set Up, Test, and Break in New Process and Equipment

We will work in Building 306 to set up, test, and break in the mixed LLW treatment facility. Running the equipment will lead to the knowledge of the equipment and process steps needed to write operational procedures and train WMO personnel.

5. Write Procedures and Training Documents

We will write these documents in cooperation with WMO.

6. Assist in Training of WMO Technicians

We will provide assistance in training and provide on-hand advice as required by WMO.

7. Extend Applicability of Waste Treatment Plan to Mixed TRU Wastes

Based on successful implementation of this treatment for mixed low-level wastes, we will address additional concerns of treating mixed TRU waste. Small-scale laboratory experiments will be performed in Building 205 using actual waste samples before this treatment is demonstrated in Building 306.

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