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REVIEW OF EVALUATION TO DISPOSITION COMPONENTS OF K-BASIN FUEL SLUDGE

This document presents the currently available alternatives for the disposition of K-Basin sludges. Although most of the techniques indicated are technically sound, they may not be practicable. The first alternative is simple, reliable and can be done without involving complicated equipment. However, the use of $KMnO_4$ should be avoided since it introduces another metal into the system.

Alternative (6) doesn't seem to stand up, in terms of reaction rates, time available for necessary studies before actual treatment. Alternative (7) appears to be very promising since the acid dissolution, followed by peroxide oxidation, is very likely to oxidize all the organics (including PCBs).

I feel that the cost analysis may be inaccurate. Should we choose to use Na_2O_2, commercial grade Na_2O_2 can be purchased at a price which will be only a fraction of the retail price. I am quoting this out of my own experience. Hypochlorite oxidation is not desirable since it will saturate the solution with acid, and the evolution of chlorine is inevitable.

Further Na_2O_2 addition will elevate the pH of the reaction medium to a level comparable to the 105 AW contents. The hydroxide precipitation of TRUS can be accompanied simultaneously.

Technique (8) would certainly create a secondary waste, which may well be tainted with radwaste. After removing the PCBs, the waste should be incinerated at the site, since it may be impossible to find an incineration facility outside the Hanford site, that would accept the waste. Transportation of such a secondary waste will be an additional problem.

Alternative (9) is chemically sound. The storage of H_2O_2 (which spontaneously decomposes in sunlight) will be a major problem. The best available solution of H_2O_2 will be a 6% solution. This will result in substantial volume increase. The cost may be a negative factor.

We can effectively combine digestion with HNO_3, which will dissolve metals, metal hydrides, oxides, carbonates, etc. with Na_2O_2 oxidation, since this step would bring about several desired effects. The concept proof experiments to be conducted in my laboratory, will be able to answer all these important questions.

Evaluation to Disposition Components of K Basin Fuel Sludge

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U.S. Department of Energy Contract DE-AC06-96RL13200

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Key Words: K Basin, fuel, sludge

Abstract: The Spent Nuclear Fuels Program is in the process of planning activities to remove spent nuclear fuel and other materials from the 100 K Basins as a remediation effort for clean closure. The 105-K East Basin currently stores spent fuel, sludge, and debris. Sludge has accumulated in the 100 K East Basins as a result of fuel oxidation and a slight amount of general debris being deposited, by settling, in the basin water. The ultimate intent in removing the sludge and fuel is to eliminate the environmental risk posed by storing fuel at the K Basins. This report investigates options to disposition specific constituents of sludge (metallic fuel) and will supplement information used to make a final decision on K Basin remediation. Certain options, such as transfer of the sludge to the Tank Waste Remediation System, have been evaluated and screening criteria have revealed issues that need resolution. Resolution of the issues related to screening criteria is the main focus of this investigation.

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EVALUATION TO DISPOSITION COMPONENTS OF K BASIN FUEL SLUDGE

March 1997

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Prepared for
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Richland, Washington

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EXECUTIVE SUMMARY

Components of the K Basin sludge may require chemical treatment to meet acceptance requirements established by the Tank Waste Remediation System (TWRS). These requirements are based, in part, around chemical compatibility with existing TWRS inventory and the ability of sludge components to maintain the existing criticality envelope of tank 241-AW-105.

Eleven processing alternatives have been identified for treatment of the sludge components. These alternatives were selected from existing technology pertinent to sludge treatment requirements as presented by the TWRS organization. The alternatives were evaluated against the benefit they provided in meeting TWRS acceptance concerns and the overall cost of implementation. Of these eleven alternatives, five show promise to produce a final acceptable waste form based on a benefit-to-cost ratio. These alternatives include: dissolution of fuel with nitric acid followed by caustic precipitation, oxidation of fuel in a heated water bath, dissolution of fuel followed by precipitation with an oxidizing agent (e.g., hydrogen peroxide), washing of sludge with an organic solvent to remove polychlorinated biphenyls (PCBs), and the combined oxidation of PCBs and/or fuel with an oxidizing agent (e.g., hydrogen peroxide, sodium peroxide).

Three final technical issues (discussed in Section 12.0) need to be resolved in the laboratory before making a decision to select the final preferred process. These technical issues require investigation of reaction kinetics, chemical compatibilities, and partitioning

factors of PCB between the solvent and the final sludge solution. Laboratory results from the investigation of technical issues will be evaluated against the guidelines set forth in Section 12.0 and can be compared against the cost associated with each alternative in arriving at a final decision.

Alternative Comparison Summary

Alternative	*Benefit/[a] cost ($ x 1000) ratio*	*Schedule[b]*	*Safety*	*Combined impact*
1) Dissolution/ Precipitation	*490/1035*	*Able to meet throughput requirement*	• *Fully contained and shielded.* • *Remote operation* • *Contact maintenance* • *Batch process*	• *Very well suited for added PCB removal/destruction steps (Alt 8 and 9).* • *Chemically compatible with oxidizing agents (H_2O_2, Na_2O_2, $KMnO_4$).*
6) Heated H_2O Oxidation	*480/386*	*Oxidation rate not determined Needs further lab test*	• *Below 100°C, @ 1 atm* • *Shielded operation* • *Contact maintenance* • *Batch Process*	• *Very well suited for added PCB removal/destruction steps (Alt 8 and 9).* • *Chemically compatible with oxidizing agents.*
7) Dissolution/ peroxide precipitation	*410/1252*	*Meets throughput requirement*	• *Same as 1) above*	• *May be combined with peroxide destruction equipment to save cost.*
8) Organic washing for PCB removal	*100/250*	*Is not rate limiting*	• *Shielded operation* • *Contact maintenance* • *Batch process*	• *May be combined with oxidation steps for optimizing treatment.*
9) PCB destruction with Fenton's Reagent	*340/410*	*Meets throughput requirement*	• *Same as 1) above* • *Added iron may reduce criticality concerns*	• *May be added to Alternative 1) or 6) process equipment to save cost.*

[a]The benefit is the ability of an alternative to satisfy all the concerns towards TWRS disposal. A score of 600 is the highest achievable.

[b]Schedule to implement these alternatives is based on a 10 month time for sludge removal. The baseline feed rate to any of the processes is for a 70% total operating efficiency and a one shift per day cycle.

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LIST OF TERMS

AOV	Air operated valve
APEG	Alkali metal polyethylene glycolates
BCD	Base catalyzed decomposition
CSER	Critical Safety Evaluation Report
DOE	U.S. Department of Energy
DST	Double-shell tank
DWPF	Defense Waste Processing Facility
HWVP	Hanford Waste Vitrification Plant
IOSR	Interim Operational Safety Requirement
IWTS	Integrated Water Treatment System
KPEG	Potassium polyethylene glycol
LANL	Los Alamos National Laboratory
MOV	Motor-operated valve
NaPEG	Sodium polyethylene glycol
PCB	Polychlorinated biphenyls
PLC	Process Logic Controller
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium-uranium extraction
SNF	Spent Nuclear Fuel
TOE	Total operating efficiency
TRU	Transuranic
TSCA	Toxic Substances Control Act
TSR	Technical Safety Requirement
TWRS	Tank Waste Remediation System

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EVALUATION TO DISPOSITION COMPONENTS OF K BASIN FUEL SLUDGE

1.0 BACKGROUND

The Spent Nuclear Fuels Program is in the process of planning activities to remove spent nuclear fuel and other materials from the 100 K Basins as a remediation effort for clean closure. The 105 K East Basin currently stores spent fuel, sludge and debris. Sludge has accumulated in the 100 K East Basins as a result of fuel oxidation and a slight amount of general debris being deposited, by settling, in the basin water.

1.1 PROBLEM STATEMENT

The ultimate intent in removing the sludge and fuel is to eliminate the environmental risk posed by storing fuel at the K Basins. This report investigates options to disposition specific constituents of sludge (metallic fuel) and will supplement information used to make a final decision on K Basin remediation. Certain options, such as transfer of the sludge to the Tank Waste Remediation System (TWRS), have been evaluated and screening criteria have revealed issues that need resolution. Resolution of the issues related to screening criteria is the main focus of this investigation.

Sampling and analysis of the East Basin floor and weasel pit sludge has been conducted (Makenas et al. 1996) and results indicate the sludge contains significant amounts of iron and uranium as well as numerous minor constituents. The particle size analysis of the sludge revealed that most (about 90 percent) of the sludge on a volume basis was less than 100 μm in size. Some of the larger particles were attributed to ion exchange resins. It should be made clear that no analysis was performed to determine the presence of particles in the range of 700 μm to 6,350 μm. The sludge was found to be free of pyrophoric materials; however, the x-ray diffraction method used may not have revealed the presence of metallic or hydride components. Fuel handling activities are expected to generate metallic debris that will require dispositioning before disposal. Sludge samples have been observed to produce bubbles. These bubbles have been analyzed and identified as xenon, krypton, and hydrogen. It has been suggested that the formation of these gases is the result of metallic fuel corrosion or the result of hydride reactions (Omberg 1996). Generation of gases was observed in samples obtained from KE Basin canister sludge. Hydrogen generation in some cases is the result of radiolysis.

Particle size reduction of the sludge was presented as a consideration for transfer to TWRS. The Spent Nuclear Fuels (SNF) organization has indicated a desire to obtain a final particle size (resulting from treatment) to less than 177 μm. This size of particle should satisfy most disposal criteria (Higley 1997).

Other particle sizes have been identified as potentially acceptable. A 1,300 μm size has been identified by SNF in consideration of criticality issues relating to TWRS transfer. This particle size relates to fuel with a 0.95 percent enrichment only and only if this material is kept segregated. Previous TWRS correspondence (Higley 1996) on the particle size issue has revealed that particles over 0.635 cm (0.25 in.) will not be acceptable.

Polychlorinated biphenyls (PCBs) have been detected in isolated areas of the KE Basin sludge (Bacon 1996). These compounds impose Toxic Substances Control Act (TSCA) regulatory considerations when evaluating disposal alternatives. A secondary focus of this report will be to investigate treatment options for PCB compounds.

1.2 ORGANIZATION OF DOCUMENT

This document uses a weighted value approach to evaluating alternatives where each alternative is compared against criteria (Table 1) and concerns (Table 3) and assigned an effectiveness value. The value is compared to the cost associated with implementing the alternative. The throughput of the alternative is evaluated and a recommended alternative is suggested along with measures that might optimize the process.

The ultimate goal of the effort described in this document is to offer a product stream (through a recommended treatment process) that will meet the requirements for transfer to TWRS.

Section 2.0 provides a functional analysis of the overall sludge dispositioning task. This overall view of the sludge mission is highlighted on the specific function this study is intended to address. The figure provided (Figure 1) highlights the general philosophy developed for sludge dispositioning.

Additional information is provided in Attachment 12 and relates some of the solid waste issues that might be relevant to the disposal of solids from incineration or to the sludge issue as a whole (if evaluating the entire mass estimated at 70 m^3).

Section 3.0 includes an identification of the assumptions and requirements that are considered in defining the functions of each alternative. Assumptions pertain to the boundary conditions surrounding alternatives. The reader should understand that the alternatives are discussed from a higher level point of view. After the selection of a preferred course of action to be taken in remediating the sludge issue, the processing path will be further defined on a lower working level and discrete process components and stream definition will be developed.

Decision criteria are discussed in Section 4.0 and the intent of treatment alternatives is tabulated along with the basis for the criteria. This table (Table 1) reveals why the alternative is investigated.

The preliminary task of identifying alternatives is conducted in Section 5.0 as "Alternatives Generation." Alternatives are discussed along with a brief description of each.

Flowsheets and mass balances are discussed in Section 6.0. Actual flow sheets are developed for each alternative and a set of mass balances provided as appropriate. These mass balances give the reader a feel for relative product volumes associated with each option.

Section 7.0 reveals a process description of each alternative in more detail. Issues related to each alternative are discussed in this section.

The process of evaluating each alternative is presented in Section 8.0. The criteria for transfer to TWRS are tabulated and the benefits of each alternative are compared accordingly.

Cost impacts are addressed in Section 9.0 and accompanying cost estimates are provided in the attachments. Each alternative cost is based on two basic process flowsheets. These two basic flowsheets relate to an incineration option and a liquid oxidation option. Two processes, previously designed, were used as models for baselining the estimates. The remaining alternatives are then compared to these two processes and relative estimates, for each of the others, are derived accordingly.

Section 10.0, is used to make a final comparison of the alternatives based on cost and fulfillment of the criteria.

The last section (Section 11.0, Recommendation) discusses the recommended path of action in implementing remediation of the components addressed by this investigation.

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2.0 FUNCTIONAL ANALYSIS

Figure 1 represents the conceptual flow scheme identified for sludge disposition. The shaded block represents the portion of the overall conceptual flowpath that this investigation is intended to define.

The general concept of the flow diagram is to provide an overview of the various functional steps envisioned for handling the sludge and segregating the particle sizes for treatment and/or packaging for ultimate disposal.

Functional descriptions and requirements of the flow path illustrated in Figure 1. are contained in (Precechtel 1996, Packer 1996, WHC 1996) Functional Design Criteria documents. The sludge will be retrieved from various locations in the KE basin and pumped to temporary storage (i.e., weasel pit) by the Integrated Water Treatment System (IWTS). The Weasel Pit sludge is then removed by the K Basin Sludge Process and Loadout System. In the KW basin, only sludge in the North Loadout Pit is slated for removal (a potential exists to include canister sludge and other sources if deemed necessary).

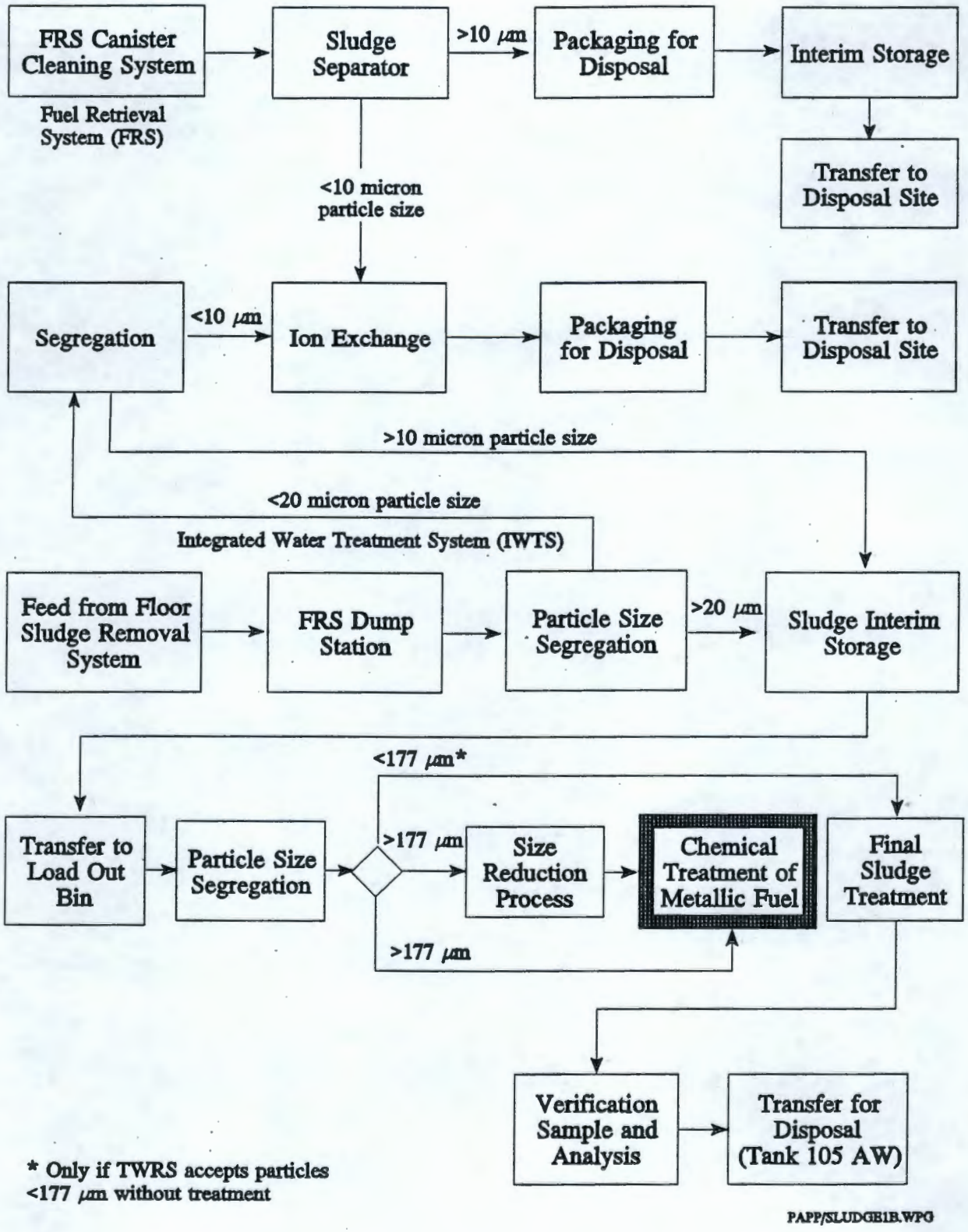
The block indicating the scope of this investigation is bypassed by a line indicating; less than 177 μm. This path will only be followed if TWRS accepts this size particle without treatment.

The K Basin Sludge Process and Loadout System will provide physical modifications at the K Basins necessary to enable direct transfer of sludge from an in-basin location into the Sludge Transportation System for shipment to TWRS. The Sludge Process and Loadout System will provide pumping capability and ancillary equipment to connect with the Sludge Transportation System.

The Sludge Process and Loadout System also provides for chemical storage, processing, and confinement as necessary to meet TWRS acceptance criteria. The Sludge Transportation System is designed to meet onsite shipping requirements while allowing for sampling and monitoring. The IWTS provides water suitable for flushing the K Basins Sludge Process and Loadout System and accepts water from dewatering and flushing operations.

Discussion of the block that identifies treatment of metallic fuel also addresses the disposition of PCBs which were identified as constituents of the basin sludge. The treatment and subsequent handling of PCBs is not anticipated to be a major influence on the preferred option for treating metallic fuel. The available technologies for removing/treating PCBs is well established and understood (some chemical compatibility issues are raised when existing technologies are applied to the spent fuel and sludge, these problems are discussed in Sections 7.0 and 10.0). This concept will become more apparent in Section 4.0, which addresses decision criteria. The issue will also be addressed in Section 10.0, which discusses a comparison of the alternatives against the decision criteria.

Figure 1. Conceptual Sludge Handling Functional Diagram.



3.0 REQUIREMENTS ANALYSIS

Requirements for the ultimate disposal of products resulting from the implementation of alternatives is restricted by the acceptance to TWRS. It is understood that options for disposal of products could also be expanded to include solid waste options (which do not result in subsequent processing). Interim storage measures that do not include transfer to TWRS are not investigated.

These additional issues may be included in separate investigations and incorporated into a higher level document that consolidates the benefit/cost for the added scope. After preparation of this higher level document, a different recommendation may be reached than the recommendation presented in this report.

4.0 DECISION CRITERIA

Functional identification of process steps in Figure 1 indicates a potential need to chemically treat pieces of metallic fuel to reduce particle size and render the fuel in a stable form conducive to final and permanent disposal. In addition to the metallic fuel issue there is a concern that PCBs may inhibit the options for disposal. The PCBs will be evaluated for possible treatment and/or segregation. Non-fuel components will be filtered and mechanically sized to meet TWRS requirements before transfer, or delivered to solid waste as appropriate.

Certain criteria have been requested by the SNF organization and is identified in Table 1. These listed criteria will be used in the final comparison of alternatives in Section 10.0.

Table 1 contains the identification of the material in question, a set of criteria to be applied for the materials final condition, and the basis for the criteria. It should be noted that additional consideration for deciding the final disposition of the material in question will also be based on factors related to cost, schedule, and safety. These considerations will be given a weighted value for alternative comparison in Section 10.0.

- **Cost.** Cost is evaluated with respect to project implementation and operating/life cycle costs.

- **Schedule.** Schedule will involve evaluating the ability to implement a process in a timely manner and achieve the overall final cleanup target date.

- **Safety.** Individual process implementation considers safety in relation to personnel exposure and minimizing the impact to the work environment. Evaluation of reactants and reaction products will identify areas of interest and concern.

- **Combined impact.** The cumulative effect of each of the above issues will be considered in the final decision analysis. For example, the ability of an individual process to meet all the criterion listed in Table 1 and achieve the most favorable rating with respect to the above bulleted items will be ranked with the highest value for recommendation.

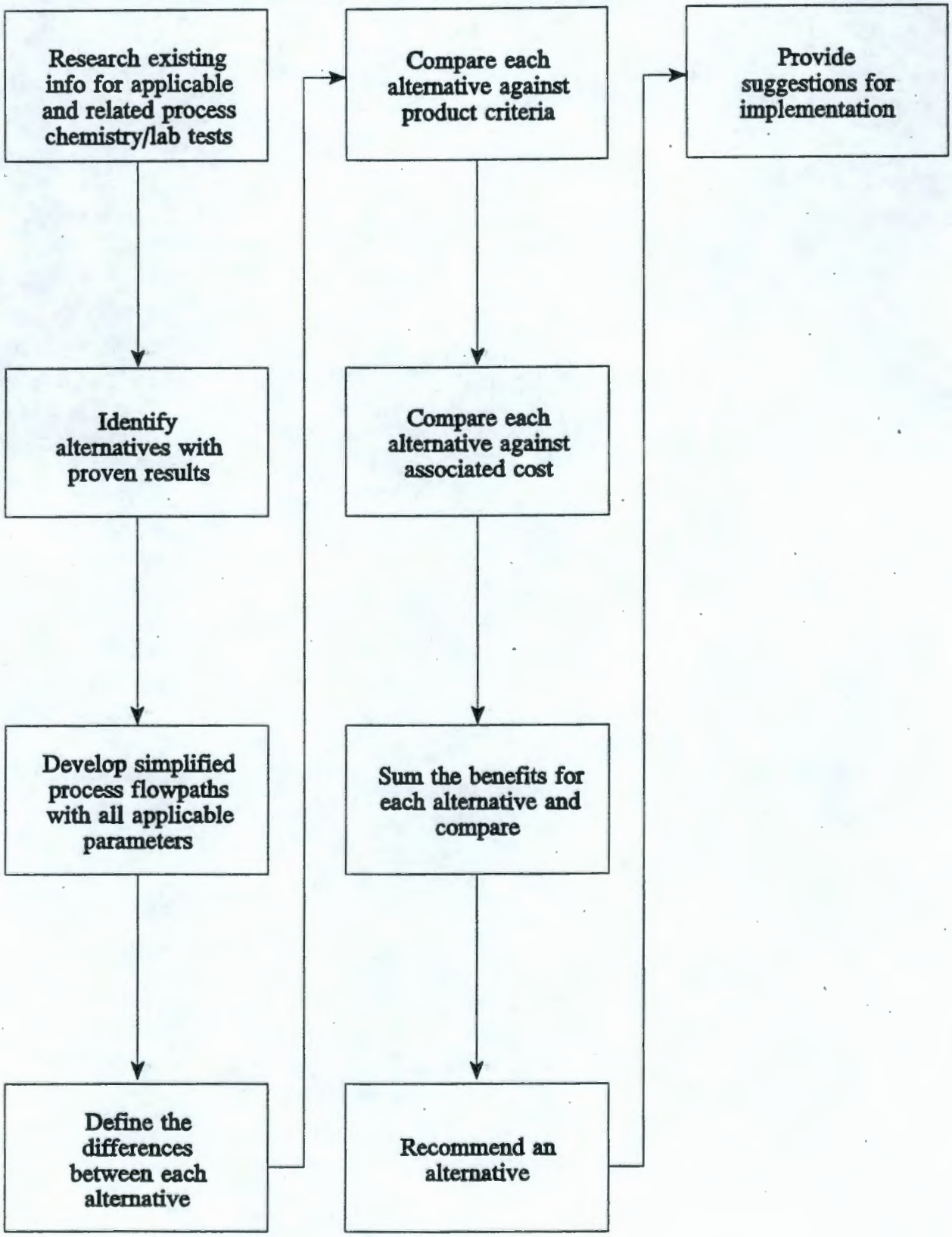
Figure 2 illustrates the methodology for identifying alternatives and arriving at an alternative suitable for implementation.

Table 1. Criteria for Material Disposition.

Material	Criterion	Basis
Metallic Fuel Components	Particle size less than 177 μm	Particle size has been determined to be a concern from three aspects. The first concern is potential damage to pumps and handling equipment. Transfer pumps, instrument ports, orifices, valves, etc. have the potential to become clogged, fouled or otherwise damaged if large materials are present in a given process. The nature of spent fuel is that it possess a relatively high hardness value. Particles greater than 177 μm were deemed unacceptable by the SNF group through discussions with various other Hanford organizations. The second concern arises from the subsequent ability to process waste at other Hanford facilities such as the vitrification plant. There are specific size limitations when accepting waste for vitrification. The design basis for feed to DWPF and HWVP is 177 μm. The third concern is based on criticality safety. It has been determined that particles of 0.95 percent enriched fuel less than 1,300 μm are unlikely to form into a reactive configuration.
	create an unreactive or otherwise stable condition	The chemical stability of the fuel is important in maintaining a safe condition for disposal. Continued chemical reactions would be undesirable with respect to generation of gas, heat, or chemically corrosive products.
PCB (poly chlorinated biphenyl. Arochlor 1254)	stabilized/ destroyed or removed for disposal	Disposal practices would necessitate the destruction of a compound as opposed to disposal or storage. Removing the compound for future remediation in a small quantity may be necessary if it alleviates larger concerns with mixing waste. Waste stored in underground tanks acceptable for sludge disposition are not necessarily conducive to accepting this type of organic.

DWPF = Defense Waste Processing Facility
HWVP = Hanford Waste Vitrification Plant.

Figure 2. Methodology Flow Path for Recommending an Alternative.



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5.0 ALTERNATIVES GENERATION

Alternatives have been collected and represented in this section as a result of searching library abstracts, personal interview, personal experience, and theoretical derivations.

This section of the document will not attempt to draw conclusions or weight alternatives. This section is only meant to be a compilation of information based on achieving the criterion mentioned in Section 4, Table 1.

The "do nothing" alternative is not included in the listing below. This report will only address the functional block identified in Figure 1 as the chemical treatment step. The do nothing alternative belongs to the broader functional requirements identification of the sludge as a whole. This broader functional identification and study would include, but not be limited to, the disposition of sludge by leaving it in its current state.

Each alternative identified below has been evaluated for its respective ability to meet the criteria in Table 1. It is understood that not all criteria will be satisfied by each alternative. How these alternatives can be used to meet the criteria is defined further in later parts of this document. Alternatives that were not deemed to provide fundamental treatment criteria were not considered as options.

It must be noted that processing of metallic fuel components will yield a waste stream that meets the compatibility requirements for disposal to TWRS; however, there are constituents of sludge (not fuel) that will be acid insoluble or otherwise not oxidizable by any of the process alternatives identified in this investigation. An example of this type component would be sand and/or tiny pieces of rock. These components require separation from the process train by filtration. Disposition of these components would require handling and/or disposal by a separate evaluation other than what is included in this investigation.

Table 2, identification of alternatives, also offers a brief description of each alternative.

Table 2. Identification of Alternatives. (2 Sheets)

Alternative	Description
Dissolving fuel pieces with nitric acid followed by precipitation with sodium hydroxide. Alternative 1	Dissolution of fuel is well understood and processes have been developed for full scale processing. As part of the fuel processing flow path it has been required that actinides be precipitated for stabilization. This precipitation is a rapid reaction with the actinides in a nitrate form. Precipitation of Uranium Nitrate Hexahydrate at 400 g/l has been performed with 50 w/w % sodium hydroxide. The solids formation was immediate and was filterable with conventional filtration (i.e., bag filters, cartridges).
Dissolving fuel pieces with I_2 with 2-propanol under anaerobic conditions. Alternative 2	Dissolution of metallic uranium with I_2 in 2-propanol under anaerobic conditions results in complete dissolution of the metal in a matter of hours (metal fragments resulting from turning operations). This process results in a solution that will yield lavender colored crystals formulated as $UI_2(O\text{-}i\text{-}Pr)_2(HO\text{-}i\text{-}Pr)_2$ when the volume of the solution is reduced and cooled to -35°C. This reaction mechanism produces a small amount of heat and is applicable to other actinides and lanthanides; however, the full spectrum of metals is undetermined.
Isolation of TRU component by physical-chemical separation process to allow disposal as non-TRU waste. Alternative 3	The nitric acid dissolution of spent uranium fuel, in general, and basin sludge, specifically, has been well documented. After acid digestion, the insoluble sludge fraction is filtered off as a non-TRU solid waste (<100 nCl TRU/g) suitable for stabilization and disposal. The TRU in the digest liquor is selectively precipitated, filtered off, and packaged for storage in CSB or for disposal at WIPP. The digest liquor is then treated by ion-exchange to ensure that the final precipitate, obtained by neutralizing the acid liquor, is classified as a non-TRU solid waste suitable for stabilization and disposal. PCB's are selectively absorbed and deferred for thermal destruction in a permitted hazardous waste incinerator.
Direct Fired Incineration (Gas Phase Oxidation) Alternative 4	Uranium can be oxidized by incinerating the metal in air at a high temperature, 500-700°C. Some sites in the DOE complex have performed this process to stabilize reactive waste metals. Uranium is a pyrophoric metal (can ignite spontaneously) and presents special challenges to implementation of this technology.
High Temperature Oxidation (Gas Phase Oxidation) Alternative 4	Solids can be oxidized under an inert atmosphere and heated while slowly adding oxygen. This process maintains strict control over the amount of material oxidized by limiting the amount of excess reactant.
Steam Oxidation (Gas Phase Oxidation) Alternative 4	Metallic components are heated and contacted with steam. Some Hydrogen gas is generated.
Liquid Phase Oxidation of Fuel. Alternative 5 Alternative 6 Alternative 7	Investigations including laboratory scale and full scale processes have been developed that successfully oxidize uranium to produce an insoluble uranium dioxide. This process uses sodium hypochlorite as the oxidizing agent. This is basically a four step process. The first step is to oxidize the metal to uranyl hydroxide using an excess of bleach. In the second step, thiosulfate is used to convert the hydroxide form to uranium dioxide (which is less soluble). The third step is to add sodium thiosulfate to reduce the excess bleach to sodium chloride. And finally, excess sulfuric acid is neutralized with hydroxide if pH control is required. Oxide coatings present on the uranium in the form of UO_2 do not inhibit the reaction. This process has been effective in oxidizing 200 kilograms of uranium metal in about 8 hours using a solution of 12% sodium hypochlorite.

Table 2. Identification of Alternatives. (2 Sheets)

Alternative	Description
	Oxide formation can take place by exposing the metallic fuel in water. This process has been readily observed in the K East basin where the cladding has been breached and fuel components have formed a sludge in the bottom of the basins. Heating the water has revealed an acceleration of the rate of reaction.
	Uranyl salts at pH values from 0.5 to 3.5 can react with hydrogen peroxide to form ($UO_4 \bullet 2H_2O$). This reaction is carried out with uranyl compounds such as $UO_2(NO_3)_2$ in water to form ($UO_4 \bullet 2H_2O$) and $2HNO_3$ as products. It should be noted however that metallic uranium seems to require pretreatment to a salt. Reports from LANL indicate that metallic uranium is not readily reactive with hydrogen peroxide.
Destruction of PCBs (Arochlor 1254*) Alternative 9	Fenton's reagent and hydrogen peroxide have been tested for destruction of PCB capability. This solution has been tested on soil remediation and is proven to be effective in this application under laboratory conditions. The effective rate of reaction in this application is approximately 3-15 days and is dependent on peroxide concentration, pH, and iron concentration. The reaction is best carried out in acidic conditions. Proof of concept testing would be required for application to PCB destruction with K Basin sludge.
Alternative 8	PCBs are almost insoluble in water and tend to adhere to surfaces, particulates or dissolve in oils. In the case of K Basin sludge the disposal requirements must be identified before disposal if PCB contamination is a limiting factor. PCBs could be extracted from the sludge through a process of first dissolving sludge particles followed by solvent extraction. The dissolved sludge is then precipitated to a stable form and shipped for disposal.
Alternative 11	Batch Vacuum Thermal Desorption utilizes an indirect heated system that operates under vacuum (27" - 29" Hg) and temperatures up to 900° F to effectively desorb organics from a solid waste form.
Alternative 10	Base Catalyzed Decomposition (Dechlorination) has been developed to specifically treat halogenated organics. Alkali is added to the contaminated material (solid form) ranging from about 1 to 20 weight percent. A hydrogen donor compound is then added to complete the reaction of dehalogenation. The process runs between 200-400 °C.

DOE = U.S. Department of Energy
LANL = Los Alamos National Laboratory
PCB = Polychlorinated biphenyls
TRU = Transuranic
*Arochlor products are characterized by a four digit number. The first two digits represent the type of molecule; 12= chlorinated biphenyl. The second two numbers represent the weight percent of chlorine.

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6.0 FLOWSHEET AND MASS BALANCES

Each alternative identified in Table 2 of Section 5.0 is depicted in Attachments 1 through 11. A description of each alternative is described in this section. The flowsheets contained in Attachments 1 through 11 are considered simplified because components such as instrumentation and minor process equipment are not shown.

The intent of this section is to provide flowsheet depictions of processes envisioned for each alternative. Mass balances that relate unit values of specified points within the flow paths are provided in the attachments. Mass balance values are only represented for key constituents and are based on stoichiometric relationships as defined by balanced chemical equations. Also, a basis of one metric ton of uranium was assumed in all calculations. This basis was established for comparison of the alternatives against one another. It should be noted by the reader that each process will require specific inventory control and the basis of one metric ton of uranium will not apply in actual operations or design of the alternative.

Actual throughput volumes may be greater because of size requirements that accommodate tanks and pumps. Certain chemical reactions are important to control by adjusting the pH or dilution factor of a particular stream.

These mass or volumetric quantities (for a given constituent) offer the reviewer an appreciation for the efficiency of the alternative and the relative amount of product expected.

The unit values represented are based on available data (specific references are cited). No laboratory testing or pilot scale testing has been performed as proof of concept. Proof of concept testing will be required before implementation of the preferred alternative.

Physical parameters have been provided when available along with balanced chemical equations and stoichiometric calculations.

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7.0 PROCESS DESCRIPTIONS

7.1 ALTERNATIVE 1--DISSOLUTION WITH NITRIC ACID FOLLOWED BY CAUSTIC PRECIPITATION

Alternative 1 provides for the dissolution of metal components and associated oxides, in a nitric acid bath, for subsequent precipitation of solids with concentrated sodium hydroxide.

The purpose is to create a product that is compatible with current TWRS inventory and not produce a product that inhibits the processing of TWRS waste in future Hanford vitrification facilities.

Inventory control is the first step performed and is identified by the feed staging tank. The dissolution process will be conducted on a batch basis for regulation of products of reaction. These products include offgasses such as NO_x and some volatile radio isotopes.

A vessel ventilation system will collect all gas emissions for processing and recycling. Acid recovery is performed for both waste minimization as well as conservation of reagents thereby reducing overall costs. This system will also provide for the monitoring of radionuclides. The ultimate goal of the vessel vent system is to achieve minimum discharge of offgas to the environment. It is understood that some gas products are produced as a result of the process chemistry and the system cannot be completely closed.

This goal will be achieved through stepwise removal of offgas constituents for collection or return to downstream portions of the process. Nitric acid is recovered from a countercurrent scrubber that acts as a nitric acid absorber. This nitric acid is collected and returned to the process for reuse.

Volatile radionuclides are removed by specific means. Iodine removal may be accommodated by silver nitrate removal (as previously used in the Plutonium-Uranium Extraction [PUREX] facility (WHC 1989). Tritium releases from the PUREX facility were largely a result of tritiated water. Condensation of water vapor and scrubbing of the offgas will be attempted for maximum tritium recovery. This condensate will then be returned to the final disposal step before waste transfer for disposal. Krypton releases may be collected on fixed beds such as charcoal or silica gel (it is also noted that the halflife of Krypton-85 is 10.7 years, further evaluation of the effect from Krypton will need to be made before implementing this alternative). Carbon-14 releases from the dissolution process need to be evaluated for their expected concentration in the overheads stream.

Dissolution of the fuel is achieved with nitric acid in a 10*M* concentration. The dissolution process will require some temperature control. This will be provided by closed heating and cooling loops. The inventory charged to the dissolver is scaled so as not to allow concern for criticality. The dissolver solution is dumped on a batch wise basis for the purpose of inventory control.

Current criticality specifications call for a final transfer concentration of Pu to below 0.013 g/L (per CPS-T-149-00010). In addition, one gram of ^{233}U or ^{235}U in excess of 1 wt% enrichment shall be assumed equivalent to one gram of Pu, unless otherwise restricted by a specification. The amount of ^{235}U less than or equal to the equivalent of 1 wt% enrichment may be excluded in concentration and total mass calculations. A criticality feasibility report is being prepared and the final criticality criteria will be documented in the Technical Safety Requirements (TSRs).

Precipitation of the dissolver solution is achieved by introducing sodium hydroxide to the solution. Some initial adjustment may be made to the concentration of the dissolver solution before caustic addition.

Finally a last adjustment is made before transfer for disposal. The intent of this step is to create a solution suitable for transfer and disposal (meeting acceptance standards related to pH, particle size and concentration). Recycle solutions may be introduced in this step for final dilution of the product stream and thus maximizing the closed loop concept for operations.

Dissolution of the sludge constituents falling into the 0.635 cm (0.25 in.) or less category will result in two product streams. Those being; insoluble solids and a solution bearing hydroxides (as noted above) formed by the process system. Insoluble solids may include sand and pieces of rock, as well as small pieces of cladding. Very small pieces of fractured resin may also be present. These solids may be filtered out of the process before formation of the uranyl hydroxide final waste form (which will be transferred to TWRS). This process will also lend itself to resolving cladding issues. Chemical changes to the dissolution of fuel can be made to allow for dissolution of cladding. The quantity of cladding that will require dispositioning is not known at this time. For this reason the scope of this investigation will be focused on the fuel alone.

Cladding can be processed by means of dissolution in a solution of ammonium fluoride and ammonium nitrate. This cladding dissolution step would follow the fuel dissolution and therefore not likely result in Pu fluoride compounds. Removal of ammonia would be evaluated and can be performed by caustic addition to the dissolver solution. The offgas system will already be equipped with a scrubber suitable for removing ammonia in the offgas. Hydrogen gas generation in the cladding dissolution step would be controlled to below 6 percent by volume in the offgas. The control limit would be targeted to less than 4 percent for conservatism. Also, the water vapor in the offgas will be targeted for a process set point of greater than 10 percent during the caustic strike in the cladding dissolver solution.

7.2 ALTERNATIVE 2--DISSOLUTION OF FUEL USING I_2 IN 2-PROPANOL

This process yields an ultimate product precipitate of disodium diuranium heptoxide. The process begins when metal feed is contacted in a dissolver with a solution containing iodine and propanol. This solution causes the metal to be oxidized to produce uranium alkoxide. The intermediate reaction step is to produce a uranium halide alkoxide complex that is then separated from by product salts and excess halogen. This intermediate compound is subsequently hydrolyzed to uranium oxide.

There have been studies (Barnhart et al. 1995) to investigate the effectiveness of this process with Lanthanides (La, Ce, Nd). These investigations reveal that between 58 and 86 percent yields of product can be formed for specific elements.

The reaction rate is relatively slow (5 to 12 g taking 1 to 2 days to dissolve). The reaction rate is further reduced by the build up of oxide layers on the surface of the metal.

The complete products of this reaction process are not fully determined. This information was lacking in the available literature of the process. Specifically, treatability on other spent fuel components was not known, nor was there information on offgassing. For developing a conservative approach to process evaluation, it would have to be assumed that any volatile components in the fuel would not be complexed and held in solution. Therefore, the process would require ventilation equipment to handle a variety of constituents.

7.3 ALTERNATIVE 3--DISSOLUTION FOLLOWED BY SEPARATION OF TRANSURANIC/NONTRANSURANIC COMPONENTS

The Recovery Dynamics Corporation has proposed a process that involves the initial dissolution of the metallic/sludge components in a nitric acid bath then follows dissolution with a precipitation of TRU components. The solutions are run through progressive separations steps that take TRU components out and ultimately yield solids and liquid streams that can be slated for disposal and additional treatment respectively.

This process is similar to Alternative 1 as described above, with the exception that an added dissolution step, three additional separations steps, and ion exchange step and two precipitation steps are added to the process.

The flowsheet is depicted but mass balances are not provided. The Recovery Dynamics Corporation has not provided specific information that can be used to determine if this scheme is truly proprietary and unique. Also, there was no indication, with the information provided, as to the nature of the ion exchange resin, the precipitation reagents and the method of solids liquid separation.

Consideration must be given to many of the same concerns that affect Alternative 1 with respect to vessel ventilation. The process of dissolution will require treatment of the offgas constituents in a similar manner. There are some concerns over the use of precipitating agents. It must be known what type of agent is being proposed with relation to its selectivity for TRU compounds as indicated by the flow sheet provided.

Many ion exchange resins suffer from chemical shock if exposed to solutions greater than 8 wt% acid. It must be known what type of resin is being proposed to avoid the breakdown of resin and subsequent generation of solid waste. Also the effectiveness of the resin would be compromised if it was subject to chemical breakdown.

Comments that relate to the provided flowsheet would include the following:

- Questioning the need for separate dissolution tanks if the reagent in both is the same.

- The first TRU precipitation step would appear to be somewhat inefficient because of the need to provide another off the ion exchange backwash stream. This would also indicate that the resin is a cation type. No mention is made to loading from other cations contained in the spent fuel that are not TRU compounds.

- A description of what further liquid waste treatment would be required. It should be noted that the need for further treatment of this stream may be a significant factor in determining the cost to benefit breakdown of such a process.

- Dilution factors related to each of the product streams must be determined in order to measure the cost for disposal. The disposal costs will also be affected based on the precipitating agent used. For example if hydrogen peroxide is used, then typically, residual peroxide must be decomposed before entering the ion exchange column. Hydrogen peroxide can react with the functional groups of many resins causing degradation of the resin, which renders it ineffective and creates additional solid waste.

7.4 ALTERNATIVE 4--DRY OXIDATION OF FUEL

This alternative really encompasses three different scenarios. They involve heating the metal to a high temperature that initiates oxidation (or burning) of the fuel by the introduction of oxygen or steam. Only one process flow path has been laid out because the oxidizing unit can be accommodated to fit either of the three methods.

Oxidation reactions have been presented as balanced chemical equations along with the respective heats of reaction. The rate of oxidation will in part depend on the exposure of the metal surface to the oxidizing agent. For example, if the oxide product is allowed to build on the surface of the metal, then the rate of the penetration through the oxide layer would

become the rate limiting factor. For pure uranium this rate is well known and reported up to a temperature of 625 °C to be only 0.053 cm/h. Higher temperatures rates are not available nor is the rate for N fuel available. It is therefore important to note that the system must be kept agitated or the particle size of the metal must be kept to a minimum.

An investigation of the concept of burning N Fuel was performed by PNNL (Ryan 1991). In this report it was stated that after review of all pertinent chemical and physical data, burning of N fuel appeared to be a viable option for stabilization. Throughput can not be depicted at this point in time because the characteristics of burning irradiated fuel are not the same as burning uranium fines or turnings. The burning of Uranium produces 4.3×10^6 BTU per ton of uranium. Removal of this heat from the equipment places a limit on the rate that the uranium could be burned.

The ultimate product of the oxidation reaction of uranium would be U_3O_8. The process would begin as the feed material is staged and prescribed quantities are weighed. Weighing of the feed is required for inventory control. Only a specified amount of feed would be processed at any given time to allow for better monitoring and handling of the product streams. Also the heat of reaction is better controlled by this metered input and thus ensure a more uniform product quality.

Offgas is likely to contain tritiated water vapor, ^{129}I, ^{85}Kr, ^{99}Tc, ^{106}Ru (if not decayed completely by time), ^{137}Cs, and ^{14}C. Cesium, most of the Ru and Tc, and possibly some I, are expected to condense on particles in the offgas stream and be removable by filtration. Remaining iodine, krypton and carbon (as CO_2) can be removed by absorption processes. Krypton can possibly be removed by cryogenic absorption on activated carbon. Iodine removal can be achieved by a silver zeolite or other process, and $^{14}CO_2$ by absorption in a stripper with a basic solution, or cryogenically. Tritium could be removed as water in cold traps or by dry zeolites.

7.5 ALTERNATIVE 5--LIQUID PHASE OXIDATION USING SODIUM HYPOCHLORITE

The oxidation of fuel can be accomplished in the dry state as outlined above or it can be accomplished in a wet state by introduction of an oxidizing agent. In this alternative the use of sodium hypochlorite as the oxidizing agent will be investigated.

There has been quite a bit of work done on the oxidation of uranium with sodium hypochlorite (here after referred to as bleach because of its wide spread used as a laundry bleach). The Chemical and Environmental Research and Development group at Los Alamos National Labs (Burns and Sauer 1993) has performed several laboratory studies related to oxidation using bleach. Their investigation was primarily related to the oxidation of depleted uranium turnings that resulted from the machining processes. A scale treatment skid was constructed for the implementation of this process although it had never been placed into actual service.

The process begins by charging an oxidation reactor with a measured quantity of metal and/or oxide. A concentration of approximately 6 percent bleach is introduced to the reactor and the oxidation proceeds.

Heat is given off by the reaction and the solution temperature is controlled with cooling water. Nitrogen may be introduced as a cover gas if required.

Offgas is controlled in a similar fashion to the nitric acid dissolution steps; however, the oxidation with bleach process may produce chlorine gas. Chlorine is theoretically capable of being produced but was not monitored for in the laboratory tests. Chlorine emissions should be controllable with a scrubber if it does occur.

Some excess sodium chloride (above the stoichiometric ratio) is expected from the reduction of excess bleach with sodium thiosulfate. This process is expected to yield about 331 g (0.73 lb) of sodium chloride per 454 g (1 lb) of uranium feed.

7.6 ALTERNATIVE 6--OXIDATION OF SPENT FUEL BY EXPOSURE TO WATER

A flowsheet diagram was not developed for this alternative because of the relative simplicity of the process. Components of the sludge are simply exposed to water for a period of time and allowed to form oxides, thus reducing the particle to a size compatible with disposal criteria.

Information on the rate of oxide formation is available from literature. The Spent Nuclear Fuels program had previously released information that shows the rate to be a straight line function based on water temperature. The rate therefore increases with increasing water temperature. An example of this rate is given by observing the line depicting a water temperature of 150°C. The treatment criteria will require a particle to be reduced from 0.635 cm (0.25 in.) to less than 177 μm. The reaction at this temperature would reduce a particle in 9 days time.

Since water boils under 1 atmosphere at 100 °C a contained vessel would be required to raise the pressure of the system and allow higher temperature conditions to exist.

Another report of oxidation rates (Burns and Sauer 1993) indicates that 1.5 μm thickness of uranium per hour is oxidized at 100 °C. This translates to approximately 88 days for a 0.635-cm (0.25-in.) diameter particle to completely oxidize at 100 °C.

It is also reported (Burns and Sauer 1993) that below 150 °C UO_2 (at 260 Kcal/mole) is the primary product of oxidation. Above 150 °C U_3O_8 (at 860 Kcal/mole) is primarily formed.

7.7 ALTERNATIVE 7--LIQUID PHASE OXIDATION WITH HYDROGEN PEROXIDE

The conversion of a uranyl nitrate to a hydrated uranium oxide ($UO_4 \bullet XH_2O$) precipitate is accomplished by the introduction of hydrogen peroxide (oxidizing agent) to the nitrate solution. The reaction may somewhat be inhibited by the acidic conditions of the nitrate solution. Carbonate ion may be introduced in a pH adjustment step to allow for raising the pH (to compensate for the acidity of the solution) after dissolution.

The extent of the hydrate is not known at this time and some further tests would need to be accomplished for that determination.

The dissolution of metal is required to achieve a solution compatible with this process. The same flow path as alternative one would be followed with the added steps, outlined in this alterative, performed subsequently. The difference between the two is in the products formed from the different chemistries involved (uranyl hydroxide formed from alternative one and hydrated uranium oxide formed from this alternative).

7.8 ALTERNATIVE 8--PCB EXTRACTION WITH HEXANE

Identification of PCBs on the sludge have been observed and documented (Makenas et al. 1996) to be present at various areas within the sludge mass. The PCB concentration range from KE Basin floor/pit samples on an as-settled basis is 31 to 140 ppm. (Schmidt 1997). Removal of the PCBs can be accomplished through solvent extraction with hexane (Bloom et al. 1995).

The flowsheet depicts the receipt of sludge material and metal components from the load out bin of the floor sludge removal system (the sludge received could come from other retrieval sources as well). It would then be pumped to a contacting vessel. For the purpose of defining a process, a centrifuge was chosen because of the good contact washing capability achievable.

To achieve a good washing of the solids a water holding tank is utilized and contains separable volumes of hexane and water. Hexane being the lighter of the liquids would float on the water. If the water is being run out of the centrifuge then hexane would be valved in by opening a side tap on the holding tank that is above the interface line. If hexane is being run out of the centrifuge then water would be valved in by opening a bottom tap and monitoring the interface level. This operation keeps the sludge components immersed at all times.

When hexane from the hexane removal tank is introduced to wash the sludge components, the PCBs are extracted from the sludge by the more favorable non polar hexane and the process is repeated until all the sludge components have been processed.

After the washing cycle is finished, size segregation and subsequent treatment can follow.

7.9 ALTERNATIVE 9--PCB DESTRUCTION WITH HYDROGEN PEROXIDE

Destruction of organics (in general) with hydrogen peroxide is becoming more well known and understood than in the most recent past. Hydrogen peroxide is being accepted as the "oxidant of choice" because of its environmental friendly nature. This friendly nature results from the breakdown products of oxygen and water.

Peroxide destruction of organics, as applied, is most likely enhanced by the addition of energy in the form of UV light (around 240-260 nanometers, corresponding to the peak wavelength of mercury vapor) or by the addition of a catalyst such as Fenton's reagent Fe^{2+}. There are factors that will enhance the process of destruction such as the pH adjustment of the solution and limiting components in the solution, or the physical materials of construction, which cause degradation of the peroxide. Such degradation of peroxide into its breakdown products would occur if impurities were not filtered or removed before the destruction step.

There are several reactions that will compete with the peroxide destruction of organics. Some dissolved metals in solution tend to form oxide compounds (i.e., iron, copper). These metal oxide reactions scavenge peroxide radicals from the solution and rob the organic destruction reaction. Nitrates in a solution tend to compete with peroxide destruction. In a UV light/peroxide system laboratory tests have shown that the destruction process is significantly reduced at nitrate concentrations above 100 ppm (1996 PAPP). It is not known if the destruction of PCBs will be inhibited by the addition of peroxide to a nitrate solution that contains dissolved sludge.

There is reason to believe (as pointed out in Alternative 7) that peroxide will tend to react with sludge solution components such as the uranyl compound. However, adding excess peroxide to the solution may overcome the interference caused by the oxide formation. Adding the additional peroxide to the solution may require a destruction step to remove residual peroxide. Many applications destroy residual peroxide by utilizing an activated carbon bed. Some oxide compounds can also be used for this purpose such as MnO.

Some bench top laboratory work will be required to determine the full extent of the destruction process. This testing would require the preparation of a surrogate solution to simulate the sludge and/or dissolved sludge. This surrogate would then be subjected to conditions simulating the actual processing environment for PCB destruction and results would then be measured to determine the effectiveness of the reaction.

Part of this surrogate testing would also determine the combined impact, or lack of combined impact, related to the combination of Alternative 7 and this alternative.

7.10 ALTERNATIVE 10--BASE CATALYZED DECOMPOSITION

Halogenated compounds such as PCBs have been introduced to solid matrices (in several forms) and triggered solid waste disposal requirements that necessitated clean up measures.

PCBs are reacted with a formulation known as APEG (alkali metal polyethylene glycolates) that include potassium polyethylene glycol (KPEG) and sodium polyethylene glycol (NaPEG). The process begins with the combining of AOH (KOH or NaOH) with the PEG-400 (polyethylene glycol, average molecular weight=400). This mixture then forms an alkoxide (ROA, R being the organic chain) that in turn reacts with a chlorine atom on the aryl ring (of the PCB) to produce an ether and a chloride salt (ACl). Credit for destruction of the PCB is taken by replacement of the chlorine atom on the aryl ring with an ether linked PEG.

By review of the simplified flowsheet (attached) we can see that several process steps are employed to implement this mechanism. A mixing tank is employed to achieve the initial blend of AOH with PEG. Adjustment of this solution is made with water as a diluent.

The APEG solution is blended with the solid waste matrix and introduced to the reactor. Blending of the solid and APEG is achieved in the reactor by agitation (rotating) while steam is employed to raise the temperature of the reactants. The reactor is basically a rotary kiln capable of sustaining a temperature such that dehalogenation can take place. Steam can be substituted with burners in order to achieve higher reaction temperatures.

Following the reaction step is a neutralization step. Here the excess chemicals (basic in nature) are reacted with sulfuric acid to reduce the pH of the final waste product.

The final step employs a dryer for removing excess moisture before disposal of the decontaminated waste. The dryer is also heated with steam from a package boiler system.

Decontaminated solids are removed from the dryer and dispositioned appropriately. The offgas system collects PCB laden water vapor from the reactor and contacts this mixture in a scrubbing unit to collect contaminants before venting to the atmosphere. The liquid scrubber stream is collected and passed through a carbon filter for final PCB removal or returned to the process for reuse.

Cooling capability is required for the system but is not shown on the flowsheet. It is uncertain if a cooling system must be constructed or if single pass cooling water may be employed.

7.11 ALTERNATIVE 11--BATCH VACUUM THERMAL DESORPTION (THERMAL PHASE SEPARATION)

Applications of this technology have been investigated with application to soil remediation. Average PCB levels of 148 mg/kg (wet) have been reduced to an average of 0.058 mg/kg (wet) (as reported in HazTECH News Vol.10 No.13). This reference also indicates that wastes containing up to 11 percent polyaromatic hydrocarbons has been treated to meet regulatory limits (applying to the specific circumstances).

Feed is typically processed to less than 2.54 cm (1 in.) in diameter. Feed material is introduced to the process through an airlock and pushed by augers through a circular chamber that sits within a heated containment area. The feed is progressively heated, as it moves through this chamber to the respective boiling point of the contaminant(s) in question. The initial (first) heating zone primarily vaporizes water contained in the feed. Secondly, organics are volatilized and lastly, the final or high temperature zone accomplishes a sustained heat zone for final polishing. This heating process is conducted entirely within a vacuum for ease of removing the contaminants.

The extracted vapors are rapidly quenched to 55 °C by a water spray, and then further cooled to 10 °C in a gas chiller. The condensate (organic and water mix) is sent to an oil water separator. The water is recycled back to the quenching process and the organics that usually constitute less than 1 percent of the original waste volume is prepared for ultimate disposal.

Units that have been placed in operation have been designed to accommodate 6.36×10^3 kg (7 t) and 12.712×10^3 kg (14 t) of waste per hour.

8.0 LAYOUTS FOR LEADING ALTERNATIVES

Identification of the leading alternatives will follow the methodology as illustrated previously in Figure 2. The selection of alternatives resulting from a search of available literature has identified three applicable categories. These are metal/metal-oxide treatment by incineration or wet oxidation (in a liquid phase), and PCB treatment. The options resulting from the search are outlined in Figure 3.

Evaluation of the alternatives will be discussed with respect to the ability to dispose of waste products after implementation of the alternative. Issues related to disposal are identified in the following sections.

8.1 TRANSFER TO TANK WASTE REMEDIATION SYSTEM

A letter was previously issued (Bacon 1996) that addressed several concerns related to the transfer of sludge components to TWRS. This letter had addressed a specific request for more information related to the following issues:

- Sludge waste could contain some pyrophoric material.
- Fissile material concentration and total inventory may exceed current TWRS Authorization Basis limits for the receiver double-shell tank (DST).
- The sludge waste stream, as described in the Waste Stream Profile sheet (KBSN-96-01) does not meet DST corrosion specification limits.
- The specific gravity of the sludge may necessitate an evaluation of the potential for flammable gas accumulation in the receiver DST.
- Maximum cesium and strontium concentrations could exceed current DST Operating Specification Document limits.
- The presence of PCBs in the sludge make it necessary to gain a clear understanding of regulatory requirements that will be imposed on the treatment/disposal of the contaminated waste.
- Sludge waste stream particle size could prevent waste mobilization, damage pumping equipment or adversely impact high-level waste/transuranic waste vitrification.

Figure 3. Processing Alternatives.

Dry phase oxidation (Incineration/burning)	• Steam oxidation • Incineration • Oxygen induced at high temp with inert gas control	All are included in Alternative 4
Wet phase oxidation (Liquid phase oxidation)	• Dissolution with precipitation	Alternative 1
	• Sodium hypochlorite	Alternative 5
	• Hydrogen peroxide	Alternative 7
	• Iodine with 2-propanol	Alternative 2
	• Heated water	Alternative 6
	• Dissolution with selective precipitation	Alternative 3
PCB Treatment	• Solvent extraction	Alternative 8
	• Hydrogen peroxide destruction	Alternative 9
	• Base catalyzed destruction	Alternative 10
	• Thermal phase separation	Alternative 11

In addition to the above mentioned issues, the waste resulting from implementation of any alternative should be compatible with any existing tank waste. An example of this compatibility would relate to the fact that PUREX previously transferred the solutions resulting from cleanout of the E5 and D6 tanks to 241-AW-105.

Radionuclide inventories in the product stream resulting from a specific alternative will be evaluated against concentrations for ^{137}Cs, ^{90}Sr, and $^{239/240}Pu$ as a basis in meeting the DST requirements.

Currently the ^{137}Cs allowable level is 5.74×10^5 uCi/L for 241-AW. The ^{90}Sr allowable is 4.04×10^5 uCi/L for 241-AW (FDH 1997a). And the allowable concentration for $^{239/240}Pu$ transfers is 0.013 g/L (FDH 1997b). Final product concentrations may require adjustment to meet these respective values.

Some of the issues raised above are addressed by several of the options and can be discussed in general. Table 3 below addresses several of the all inclusive issues related to treatment alternatives. It should be understood that the concerns raised by the TWRS over receiving the sludge was applicable to the entire sludge volume. The discussion of the alternatives below only relates to the acceptance of the product stream resulting from the treatment of a specific portion of the overall sludge mass (namely the components that are deemed to be metallic fuel components larger than 177 μm in size). TWRS acceptance of metallic components less than 177 μm depends on additional safety issues as well as particle size criteria.

The table discusses the comments received from TWRS (Bacon 1996) and the response relating to the effectiveness of specific alternatives. The alternatives affected by the issue are reported in the right hand column.

Table 3. Comparison of general treatment issues related to disposal requirements. (4 Sheets)

Criteria/requirements and discussion	Applicable alternatives
COMMENT 1 - Verification sampling must be performed before transfer of the product stream. This will assure waste product specifications of the treated sludge. **RESPONSE** - This issue is related to the requirement to maintain inventory control in the TWRS. Proof of concept testing can offer some insight as the expected concentrations and the requirement for verification sampling can be initially adjusted, based on this evidence. It will then be adjusted further after actual samples are analyzed and shown to support earlier predictions. This requirement relates to all alternatives equally and will not be considered when determining the effectiveness of an alternative.	ALL

Table 3. Comparison of general treatment issues related to disposal requirements. (4 Sheets)

Criteria/requirements and discussion	Applicable alternatives
COMMENT 2 - Analytical results indicate that K Basin sludge waste will be both caustic and nitrite deficient. SNF will be responsible for the chemical adjustment of each transfer batch and for verification that applicable DST corrosion control and criticality safety pH criteria are met before waste acceptance. **RESPONSE** - The entire intent of sludge processing will be aimed at developing an acceptable waste form suitable for Tank Farm storage. The product streams resulting from alternates will be adjusted to achieve the desired chemical compatibility based on Tank Farm criteria. This will be accomplished by final pH and or chemical injection before transferring. Final concentrations will be based on mass balance equations and verified through sampling and analysis as indicated above.	ALL
COMMENT 3 - ETFTP will not accept PCB contaminated waste without clear understanding of the regulatory requirements that will be imposed on treatment and disposal of the PCB waste. Acceptance of waste containing PCBs may require a revision to the DST permit and/or required agency concurrence that planned tank sludge removal and processing will meet the regulatory requirements pertaining to land disposal of the combined K basin sludge waste and tank waste. **RESPONSE** - PCBs can either be removed or destroyed by the alternatives presented. The liquid phase alternatives can be applied in conjunction with one another. The two viable options for PCB treatment are destruction with peroxide or extraction with a solvent. The "solid" phase alternatives will result in destruction of the PCBs. In either case, the treatment product will have to be approved by the regulating agency as applicable treatment before delisting the product stream from PCB concerns. A brief discussion of disposal as a solid waste form is included in Attachment XX for information.	ALL
COMMENT 4 - A sludge mobilization evaluation must be performed before the acceptance of K Basin sludge in the DST system. Additional testing to address issues associated with the ability to remove the waste from the DST system for final disposal will be required. **RESPONSE** - The intent of each processing option is to create a particle size that is compatible with Tank Farm components (pumps, piping, etc.). Also the particle size has been identified as an issue related to subsequent processing at the Hanford vitrification plant. The optimum particle size has been determined to be <177 μm as denoted in the criteria analysis discussion of Table 1. The actual particle size that results from processing as defined in Alternative 1, 2,5,6,7 will result in a particle in the range of 5-20 μm in size. It is not determined what particle size dry oxidation will result in. Indications are (Ryan 1991) that most of the particles resulting from incineration are greater than 20 μm.	1,2,5,6,7

Table 3. Comparison of general treatment issues related to disposal requirements. (4 Sheets)

Criteria/requirements and discussion	Applicable alternatives
COMMENT 5 - A change in the TWRS Authorization Basis document must be approved and implemented to allow for the increase in the fissile material limit and concentration. **RESPONSE** - The product streams resulting from the identified alternatives will be able to meet the criticality specifications for the TWRS and will be in accordance with CPS-T-149-00010, Criticality Prevention Specification. The product streams will be capable of meeting OSD-T-151-00007, Operating Specifications, as well. It may be expected for the TWRS to review the 0.013 gPu/L transfer concentration in relation to the Pu content in the receiver tank (241-AW-105). The ability to increase this transfer quantity may result in a reduction of the overall volume produced by adjusting the concentration.	1,2,3,4,5,6,7
COMMENT 8 - A Criticality Safety Evaluation Report (CSER) addressing the issues associated with the addition of pyrophoric material into the DST system must be performed. **RESPONSE** - Pyrophoric material (resulting from the metallic fuel alone) would not be present in any of the product streams resulting from any of the alternatives discussed. However, Pyrophoric material may result from size segregation activity streams that do not feed the inlet to any of the alternatives. Also, it is noted that dissolution of fuel with nitric acid is not conducive to dissolution of cladding nor is the alcohol/I2, hydrogen peroxide, or sodium hypochlorite systems known to affect cladding. Cladding would require treatment as described in Section 7.1. Oxidation of fuel and cladding is observed with incineration. This requirement relates to all alternatives equally and will not be considered when determining the effectiveness of an alternative.	1,2,3,4,5,6,7
COMMENT 9 - Reactivity group numbers assigned to the waste must be verified. Verification can be performed as specified in EPA-600/2-84-057, "Design and Development of a Hazardous Waste Reactivity Testing Protocol," or by alternative methods as approved by Environmental Compliance and Support Services. **RESPONSE** - This requirement relates to all alternatives equally and will not be considered when determining the effectiveness of an alternative.	ALL
COMMENT 10 - Two mixing studies will be required before sludge waste acceptance into the DST system. A mixing study of K Basin sludge waste with both tank 241-AW-105 supernate and sludge is necessary. **RESPONSE** - The compatibility issue is reviewed in relation to all the product streams resulting from the various alternatives. By reviewing the constituent make up of the current AW-105 inventory it is noted that a direct similarity can be drawn between the product stream of Alternative 1. This is because the previous transfers made to the AW-105 tank were from the PUREX facility E5 and D6 tanks that maintained inventories of dissolved fuel almost identical to the product of dissolution defined by alternative 1.	ALL

Table 3. Comparison of general treatment issues related to disposal requirements. (4 Sheets)

Criteria/requirements and discussion	Applicable alternatives
COMMENT 11 - Disposal engineering will perform an evaluation assessing the impacts and limits for the planned vitrification of waste. **RESPONSE** - This issue can be two fold in nature. The first is due to the volume of waste generated and the impact to vitrification resulting from the added mass generated from each alternative (more solids in the product stream amount to more money spent on overall vitrification). The second issue relates to the compatibility of the product stream constituents with the vitrification process. It stands to reason that if the alternatives produce a product similar in nature to the existing tank waste, then any impact to vitrification is minimized. This compatibility includes the particle size and nature of chemical constituents.	ALL
COMMENT 12 - Chemical composition of the acid insoluble material is required. **RESPONSE** - It is the intent of these alternatives to reduce the particle size of metallic fuel components to less than 177 μm in size. By doing so, all components of the fuel that can be oxidized or dissolved and precipitated will be effected. There is undoubtedly some components of fuel that will not be oxidized or dissolved. If the dissolution step is chosen then cladding pieces quite possibly will not be affected by the dissolution process and remain in the dissolver solution as a solid. The cladding would be relatively easy to characterize and evaluated. Cladding can be treated using alternative 1 (the relative volume of cladding must first be identified). Resin often experiences chemical shock when subjected to strong acid solutions. It may then form smaller particles resulting from cracking of the beads. Particulates of resin should be looked for during composition analysis. Also, bits of gravel may remain as solids. If incineration is ultimately employed it can be suspected that concrete pieces or bits of gravel may be present and would fall into this category. The overall contribution of non dissolvable components are expected to be very small. This requirement relates to all alternatives equally and will not be considered when determining the effectiveness of an alternative.	ALL

The information in Attachment 19 evaluates the disposal criteria of the waste products from each alternative against the disposal concerns identified above. This comparison is used to derive a weighted value of the option. The weighted value is defined as a percentage of the effectiveness of the alternative in meeting the requirements/concerns.

A score of 100 is given to an alternative that satisfies the comment completely. A score of 70 is given to an alternative that satisfies the comment but adds additional loading to a tank system either mechanically (fluidization, pumping ability, mixing time) or chemically (requires more than three basic processing steps). A score of 50 means the alternative adds both mechanical and chemical loading for implementation. A score of 30 means the alternative meets either the mechanical or the chemical loading requirements but not both simultaneously. A score of 0 means that either the alternative does not meet either the mechanical or chemical requirements or its ability to meet the requirement cannot be

substantiated by the available information. Some intermediate values are suggested by the author based on professional judgement.

Table 4 is presented to sum the benefits of all the identified alternatives as noted in Attachment 19.

Table 4. Summary of Weighted Processing Values.

Comment	Alternatives										
	1	2	3	4	5	6	7	8	9	10	11
2	100	0	0	70	70	70	70	0	0	70	0
3	50	50	0	100	50	70	70	100	70	100	100
4	70	0	0	30	30	100	30	0	30	20	0
5	100	100	0	100	100	70	70	0	70	30	0
10	100	30	0	100	30	100	100	0	100	70	0
11	70	0	0	30	30	70	70	0	70	0	0
TOTALS	490	180	0	430	310	480	410	100	340	290	100

Note: The higher the total the more favorable the option for disposal to TWRS.

Alternatives 1 and 6 received ratings equal to or greater than 80 percent out of a possible 600 points. Alternative 1 rated approximately 82 percent. The next highest from these alternatives is Alternative 4 with a 72 percent rating.

Figure 4 is provided to illustrate a summary evaluation of alternatives.

Figure 4. Summary Evaluation of Alternatives.

Alternative 1
- Dissolution w/Precipitation

Remote operation, 2 shift cycles, extensive offgas treatment, rate limited by energy requirements

Alternative 2
- Dissolution w/iodine and alcohol

Introduction of new waste form (I), significant offgas treatment, remote operated, 2 shift cycle

Alternative 3
- Dissolution w/selective precipitation

Significant number of process steps, vessel same as 1), additional waste from ion exchange resin

Alternative 4
- Dry oxidation (incineration)

Remove operation, extensive decon (airborne contaminant), extensive vent system, significant building structural requirements

Alternative 5
- Wet oxidation w/bleach

Significant chloride waste from (NaC1), remote operation, 2 shift cycle, sulfate additions, rate limited by process parameters (energy requirements). Requirement for titanium

Alternative 6
- Wet oxidation w/warm water

Shielded operation, reduced ventilation and building requirements, inherently milder ion exchange, 1 shift operation, not rate limited

Alternative 7
- Wet oxidation w/hydrogen peroxide

Sludge component interference, extensive offgas system, additional process steps from 1), 2 shift cycle remote operation

Alternative 8
- PCB solvent extraction w/hexane

Shielded operations, 1 shift cycle, hexane waste to incineration, no offgas, one time chemical loading, PCB only

Alternative 9
- PCB destruction w/hydrogen peroxide

Generation of Fenton's solid (Fe), some added waste from H_2O_2 destruct, rate limited (unknown rate), PCB only

Alternative 10
- PCB Destruction w/Na(K) and glycol (PEG)

Remote operated, airborne potential, 2-shift cycle, extensive vent system, additional waste from (C, SO_4), PCB only

Alternative 11
- PCB removal w/thermal extraction

Extensive offgas, airborne potential, remote operations, PCB only

9.0 COST IMPACTS

Costs will be broken down into two categories for evaluation as operational (expense) costs and capital (construction) costs. These costs will be the basis of the cost comparison and additional costs (such as deactivation) will be discussed when significant effort is required. Equipment that can be reused will be given a credit toward deactivation costs.

9.1 EXPENSE COSTS

Expense costs are derived from the cost to staff the process depicted by the alternative and the cost to supply raw materials (e.g., chemical deliveries) to operate the process.

The weighting value associated with each alternative is based on the volume of chemicals used and the staffing requirements. The weighting values are based on Alternative one as the standard. This alternative will be rated as 50, on a scale of zero to one hundred. If the alternative requires less chemical usage or less staffing, but not both simultaneously, a value of 30 is assigned. If an alternative requires less chemicals and less staffing a value of 0 is assigned. If an alternative requires more chemicals or more staffing a value of 70 is assigned. If the alternative requires more staffing and chemical usage a value of 100 is assigned. Intermediate values are based on professional judgement as related to the variations in the requirements stated above. The alternatives with more loading are rated higher because this value, when added to capital costs, will produce a higher value in a benefits to cost ratio.

Utilities requirements are directly related to the amount of staffing and number of equipment components. This is evident by noting that the more components requiring electrical usage there is in an alternative the higher the electric bill will be. There is consideration given to equipment that operates by alternate energy sources such as propane fired heaters as opposed to electric, or air operated valves (AOVs) in contrast with motor operated. Since most of these components that use alternate sources of energy require additional equipment such as compressors (usually electric motors) and air delivery systems, these systems are more labor intensive to construct. There is more of a gain to be had, from these types of alternatives, in facilities that have comparatively longer operational lives. The schedule for the activities resulting in sludge remediation are scheduled to be completed within a one year time frame. The offset cost from saving capital money during construction activities as opposed to saving expense money during operations is considered.

9.1.1 Alternative 1 Expense Cost

Material usage for alternative 1 includes the following chemical reagents: Nitric acid (50 percent), sodium hydroxide (50 percent), hydrogen peroxide (50 percent).

Table 5 is the staffing level projected for this alternative.

Table 5. Alternative 1 Staffing Requirements.

Job description	Number of staff required
Operators (Operators would be required to staff the process during the entire dissolution sequence. This includes the initial charging of the dissolver until the solution has completely reacted and stabilized.) One operator would be required to monitor the dissolution process continuously, another would be required to monitor feed staging and offgas and conduct sampling, while a third would be required to monitor pH adjustment and product transfers (load out) as well as provide relief for lunch and breaks).	3 per shift on a two eight hour shift basis.
HPTs	1 per shift on a two eight hour shift basis.
Cognizant process engineers	1 per shift on a two eight hour shift basis.
Millwrights, pipefitters, electricians, and instrument techs would be called on from the 100 area plant forces as required.	
Management/secretarial support would be provided from the existing 100 area management structure.	
Safety and QA representatives would be provided from existing 100 area management support.	
Training, Procedure writers, document control, environmental compliance would all be absorbed by existing 100 Area personnel. It can be estimated that about 25 operating procedures would be required as POPs (plant operating procedures) and ARPs (Alarm Response procedures). About 15 maintenance procedures would be expected including PMs (preventive maintenance) and calibrations.	

9.1.2 Alternative 2 Expense Cost

The iodine process will be expected to have a bit more material handling than Alternative one. A vented hood is anticipated for material handling (based on availability). This fact would raise the requirement of operator action and thus lower the weighted value of this alternative.

There is no less requirement for staffing of operations or engineering. The reaction is expected to require monitoring from its initiation until completion. The reaction would not be expected to be complete in a one-shift cycle particularly if oxide buildup on the surface of the metal causes a reduction in the rate of reaction.

The full nature of the offgas stream is not well understood at this time therefore the equipment is deemed to be the same with every respect other than iodine removal. Iodine in

the offgas may be expected to increase slightly from Alternative 2 and loading on equipment may be greater than estimated.

The exposure to operators by the different nature of the chemicals involved in iodine handling would also make this alternative less favorable than the baseline (Alternative 1).

Chemical usage would be only slightly reduced but an additional Iodine waste stream would be generated. This additional waste would itself require investigation for remediation.

This alternative is rated as 100.

9.1.3 Alternative 3 Expense Cost

A significant number of operating steps are required by this system. At least one more operator would be required to run the process because of the added dissolver, ion exchange, two additional precipitation steps and increased solids handling. There is also added burden by the additional solids handling related to the certification of the waste. The process would require an additional person to act as a shipper (to certify the waste packaging).

Utility costs would be greater because of the added components. Chemical usage would be increased by the fact that there are two dissolvers and dissolver acid is not added in greater than stoichiometric quantities. This increase would cascade to the amount of caustic used for neutralization. The chemical and operational burden is increased if ion exchange columns are to be regenerated. The waste stream from regeneration would then require further processing as a liquid waste or transfer to TWRS for disposal.

This process is rated as 100.

9.1.4 Alternative 4 Expense Cost

The incineration process would require the same number of operators and process engineers even though the nature of the process is different. The Process control is slightly reduced but material handling requirements are increased along with the requirement to certify waste shipments for solid waste (if decided to package in drums as opposed to shipment to TWRS). The chemical usage is reduced in this alternative, but that is dramatically offset by the difficulties in dealing with airborne contamination problems.

There is also an additional decontamination cost placed on the removal of radioactive particulates from process equipment, as well as added cost for maintenance and operations (operators and craftspersons would require additional training and resources to accomplish work in an area that required activities "on mask and fully suited." Therefore, an added cost burden (order of magnitude) can be assumed for these alternatives.

This alternative is rated as 100.

9.1.5 Alternative 5 Expense Cost

Processing requirements related to this alternative are very near our baseline. No additional operations or engineering staffing would be anticipated. The process would be controlled in a similar fashion to the nitric dissolution process.

The key difference in this process is in the fact that additional waste forms that are not conducive to TWRS disposal are created. This fact would require some continued operational activities to disposition those wastes and create an added burden. The continued activities would be to separate the sodium chloride waste before disposal.

Chemical usage is very near to the baseline.

This alternative is rated as 70.

9.1.6 Alternative 6 Expense Cost

This alternative would require fewer numbers of operational and engineering personnel because the process would not have to be operated on a two shift basis (unless desired to implement an aggressive schedule). The reaction would not be such that the same degree of monitoring would be required as in the baseline case. This reaction would be an order of magnitude safer by inherent characteristics (e.g., heat of reaction, offgas produced).

Chemical usage is much reduced by this option in the fact that the reaction takes place in the transfer medium (water, no nitric acid). Control of the reaction is by a fail safe mechanism in that loss of power reduces the rate of the reaction.

The reaction rate is about the same as that with the baseline case for a given quantity of feed material (oxidation rate for 0.635-cm [0.25-in.] diameter particle as a basis); however, the feed quantity of this alternative could be increased to accommodate a faster overall production capability without significant equipment changes.

Energy consumption would be reduced by this option because of the reduced number of components and processing steps.

This alternative is rated 0

9.1.7 Alternative 7 Expense Cost

This alternative could add another two processing steps to the baseline case. It is not anticipated that more staffing would be required because the relative ease in implementing these two steps would not be deemed significant. Some chemical usage would be added and a slight amount of energy consumption.

The final waste stream would be very much like the baseline and no added handling requirements would be realized.

This alternative is rated 55.

9.1.8 Alternative 8 Expense Cost

Washing of the feed to remove PCBs requires much fewer steps than the baseline case. The number of staff required would be reduced to two operators and a part time engineer. This process can be conducted on a one-shift basis. The chemical usage is restricted to the initial charging of the system. No additional chemical purchases are anticipated during the entire operations life of the process.

There is no chemical reaction step that requires the degree of monitoring as in the baseline case.

Energy usage is much less reduced from the baseline and the amount of support from crafts and management is lessened overall.

There is a waste stream produced by the process that will require a one time load out at the conclusion of the process. The disposal of this waste (PCB laden hexane) will be incinerated by a regulatory accepted method.

This alternative is rated 30

9.1.9 Alternative 9 Expense Cost

The Fenton's reagent mechanism is accomplished with a fewer number of steps than the baseline case. Operations staffing is reduced as is engineering. The process is inherently safe and would not require the same degree of monitoring as in the baseline case.

The overall equipment requirement is greatly reduced and thus the energy consumption is lessened.

Some additional volume (Fenton's solid) is created as a slurry but handling is the same as in the baseline with the possible addition of a dilution requirement to ease transferring.

Chemical usage is lower than the baseline and the nature of the chemicals requires less of a risk to the operator (because concentrated nitric is not used).

This alternative is rated 40.

9.1.10 Alternative 10 Expense Cost

The Base Catalyzed Destruction process (or KPEG as depicted) does not lessen the amount of staffing from the baseline. The process is such that a lesser degree of monitoring may be required from the dissolution process; however, this process offers many more mechanical components to maintain. The product stream will require more material handling efforts and certification of waste will be necessary.

Chemical usage will be about the same except different chemicals will be employed. Energy costs are expected to be higher by the nature of the equipment and the high operating temperatures required to complete the processing steps.

There is a possibility that airborne contamination will be created by this process that creates an additional loading to operators.

This alternative is rated 90.

9.1.11 Alternative 11 Expense Cost

Phase separation would require less staffing than the baseline because the process is much simpler in nature. This process could be operated on a one-shift basis but through put would be reduced from equipment preparation (feed staging, warm up times for the dryer etc.). A solid waste stream would be generated and require some additional handling but this fact is not anticipated to be a significant factor.

Chemical usage is greatly reduced because the process does not employ the addition of reagents. Offgas is expected to be generated and the need for some ventilation equipment will be required but the extent is not known at this time. A factor is applied to this section to account for the possibility of airborne contamination to exist.

The system will require a amount of energy that may be slightly less than the baseline case because of the reduced number of electrical motors; however, the energy for the dryer will be significant since much of the input will go towards vaporizing water in the feed.

This alternative is rated 65.

9.1.12 Expense Cost Summary

Table 6 summarizes the weighted values assigned to each alternative with respect to expense costs.

Table 6. Summary of Alternative Expense Costs.

	Alternative										
	1	2	3	4	5	6	7	8	9	10	11
Weighted value	50	100	100	100	70	0	55	30	40	90	65

In summary, the lower the weighted value presented in Table 6 indicates the more favorable alternative.

9.2 CAPITAL COSTS

Capital costs are broken down by major equipment components required to build the process depicted in each alternative flow diagram. These costs are extracted from current cost data generated by Hanford Site estimators, private vendors, other government agencies or other DOE sites (references are given when applicable).

The review of the economic discard limit for components of spent fuel (e.g., Pu) is not within the scope of this investigation.

Each alternative is broken down by major component and discussed in some detail in Attachment 14. Costs are assigned for each of the components described and totals are summed for comparison to other alternatives.

All capital costs are defined on the basis that components are skid mounted and installed by fixed price contractors. In some cases as much as 75 percent contingency is attached because a conservative safety classification was assigned for the purpose of preparing this cost comparison.

None of the costs reflect the installation of utilities (e.g., electrical power, sanitary, raw water) unless the utility is required specifically for the process described (e.g., cooling tower, package boiler).

The cost of constructing a structure to house any of the alternatives is factored into the following descriptions. This cost will be determined during a conceptual design phase when developing a line item project to ultimately implement a preferred alternative. The costs in

this evaluation are purely designed to act as comparisons in identifying a recommended alternative for development.

Factors accounted for in the installation of tanks and vessels include labor for the site preparation, form work, concrete placement, and piping. Not included in the cost are clean up, AI services, superintendent, laggers, painters (and special protective coatings), general labor, and management. A cost for field engineering is presented as an individual line item.

References used in preparing these cost figures are (Kim et al. 1990), (Rosson 1997a, b), (FDNW 1996b), (Papp 1997a, b).

9.2.1 Capital Cost Summary

The following table summarizes the capital cost assigned to each alternative in 1997 U.S. dollars.

Table 7. Summary of Alternative Capital Costs.

	Alternative $ x 1,000										
	1	2	3	4	5	6	7	8	9	10	11
Capital value	1,035	1,800	1,963	1,600	1,471	386	1,252	250	410	1,116	593

The building structure was not evaluated in the capital cost breakdown. There are three main types of structures to be considered in this evaluation. These are based on the requirement for containment and shielding. The most stringent requirement is for a structure to provide shielding and control of airborne contaminants. Alternatives 4, 10, and 11 fall into this category. The cost to provide an additional barrier of protection in the form of ventilation control is required on these structures over what is required for the remaining alternatives.

The second type of structure requires remote operation but no airborne contamination is expected. All process vessels and components provide containment of the process solutions at all phases of the process train. Remote operation is performed by Process Logic Controller (PLC) and/or reach rods (valve operators). A minimum amount of equipment is actually in the remote operations section of the process. This remote section is anticipated to be contained in a housing similar to a CONEX box (the type of container usually used for transportation by sea). This box would be provided with internal catch pans and be placed within an operations building that has additional shielding. A mean cost factor would be applied to alternatives requiring this type of building containment. Alternatives 1, 2, 3, 5, and 7 fall into this category.

The cost for each of the above (first and second types of structures) is based on $21,500/m^2$ ($2,000/ft^2$) (professional judgement estimate by DESH estimating). The cost of the first type structure (Gas Phase Oxidation) would have an added burden of cost due to the separation of air spaces required to control airborne particulates. The baseline requirement for the second type structure would be equipped with process ventilation that maintained a negative pressure boundary between the process and the environment. The first type structure would be required to have an additional barrier that separated the process area from the environment with an additional air space maintained by a separate ventilation system. The baseline cost for a building 15.2-m (50-ft) wide by 30.48-m (100-ft) long is $10 million. This cost might be minimized by housing the structure in the CONEX type housings mentioned above.

The third type of structure would provide the less stringent requirement. This structure minimizes exposure by means of a labyrinth entrance to the process area. The processes contained within, would pose no threat to airborne contamination or require the type of remote operation (based on the reaction chemistry) that necessitate hands off control. Operator and crafts protection would be provided by the time distance and shielding concept. System components could be sized for chemistry and geometry to minimize exposure and would pose minimum risk from operations. Shielding walls are expected to be constructed of cement or cinderblock (grouted), or other appropriate means. This structure would have the lowest cost factor applied. The alternatives falling into this category are 6, 8,. and 9. This type of structure is valued at $74/m^2$ ($800/ft^2$) (estimate based on IWTS annex to K Basin cost). The cost for this type structure [15.2-m (50-ft) wide by 30.48-m (100-ft) long] is valued at $4 million.

9.3 DEACTIVATION COSTS

Each of the alternatives has been identified according to the building structure requirements as stated above. Only those components that are in direct contact with radioactive and or hazardous waste solutions will be the main focus of deactivation activities (this would include dissolvers, oxidation vessels, precipitation tanks, etc.). Secondary consideration is then given to components that do not come into direct contact with radioactive or hazardous waste streams (chemical storage tanks, chemical feed pumps, utility equipment).

All components in contact with the main process stream will be designed with the concept of deactivation. This means maintaining complete self draining capability or be provided with the capability to be flushed and cleaned. Flushing may be accomplished with chemical solutions such as acid and then followed with water. These features will not only aid in deactivation but will also allow for contact maintenance that will be an assumption in the final design of a preferred process flow path.

Those alternatives that do not lend themselves to flushing (alternatives 4, 10, and 11 because they produce a dry product that is subject to airborne particulates) are the most

costly in relation to maintenance and decommissioning. All the other alternatives can make the accommodation for flush solutions and complete draining.

Alternatives 1, 2, 3, 5, and 7 can be designed such that the main processing components are housed in a CONEX box that also serves as a transport container for final deactivation.

Equipment will be minimized by only installing components in the main process area if absolutely necessary. Redundant equipment requirements can be evaluated and if possible additional ports can be installed to accommodate redundancy at a later date. For example if a pH meter is installed with some 1.27-cm (0.5-in.) tubing and this meter is suspect of failure within the year time frame. The redundant component can be stored outside the process area until its need becomes required by failure of the initial component. This concept will allow minimum entry into the process area for calibration or repairs and it will also minimize the number of components requiring decommissioning if they are not installed.

Flushing capability of the process area should also be provided in case a component develops a leak.

Equipment sizing is to be minimized whenever possible so decommissioning activities are minimized. This concept also cascades to minimizing the amount of final waste being produced.

Final decommissioning solutions should be run through any pertinent steps of the process train for ultimate disposal.

Cost for final deactivation is on the same order of magnitude for alternatives 4, 10, and 11. These three alternative represent the greatest cost for deactivation because they produce a powder product that can easily become airborne and result in a spread of contamination over all the process equipment. Alternatives 1, 2, 3, 5, and 7 represent the middle range cost and are all on the same order of magnitude. This cost is associated with flushing operations. No airborne contamination is expected with these alternatives but there is a limited amount of removable contamination expected in the vessel ventilation system.

Alternatives 6, 8, and 9 represent the least cost for decontamination because the flushes can be accomplished with very dilute streams of chemicals (dilute acids and caustics or water).

Cost for decommissioning as outlined in this section fall in line with the previous cost evaluation as compared to expense and capital cost for the respective alternative. Final cost determination is therefore not effected by the lack of an actual dollar value for decommissioning when comparing one alternative against another. The final cost for decommissioning is important to know when the preferred process is evaluated for conceptual cost.

10.0 FORMAL ALTERNATIVES COMPARISON AGAINST DECISION CRITERIA

10.1 REVIEW OF ALTERNATIVE EVALUATIONS

Final evaluation of the alternatives will not only be conducted by summary review of analysis contained in the previous sections but, it will also include evaluation of their combined impact (of all alternatives) and the ability to achieve the highest benefit/cost ratio in accomplishing the remediation goal.

In doing so we begin the evaluation with a review of the previous analysis related to efficiency of the alternatives technical capability to meet acceptance criteria as summarized by Table 4, the review of expense related cost associated with each alternative and summarized in Table 6, and finally a review of the capital related costs as summarized in Table 7.

The following table is prepared to conduct a final tally of the value each option offers (relative to treatment and cost).

Table 8. Summary of Alternatives Benefits and Cost.

	Alternative										
	1	2	3	4	5	6	7	8	9	10	11
Table 4 Value	490	180	0	430	310	480	410	100	340	290	100
Expense Cost	50	100	100	100	70	0	55	30	40	90	65
Capital Cost	1,035	1,800	1,963	1,600	1,471	386	1,252	250	410	1,116	593
Total *	.45	.09	0	0.25	0.2	1.2	0.31	0.36	0.75	0.14	0.15

*The total is a ratio of the Table 4 process benefits per the sum of cost. The higher the total the more attractive the alternative.

By matrixing all the alternatives (related to the certain benefits identified in Table 4) the ratings of all alternatives in combination with each other are revealed (see attachment 13 for matrix). Review of the matrix shows that combining the following alternatives will produce a rating of 200 (200 being the highest): 1/4, 1/8, 1/10, 1/11, 4/4, 4/8, 4/10, 4/11, 6/4, 6/8, 6/10/, 6/11, 7/4, 7/8, 7/10, 7/11, 9/4, 9/8, 9/10, 9/11.

Of the combinations producing a rating of 200 or greater a selection of alternatives from Table 8 (that achieve a benefit to cost ration higher than 30 percent) is made (>30 percent was decided as the cutoff point because this corresponds to the alternatives that presented the least safety risk and chemical incompatibility issues). The alternatives that fall out of this evaluation as being more favorable are now identified as individual alternatives (or combinations of) 1, 6, 7, 8, and 9.

Alternatives 4, 10, and 11 do not prove to be cost efficient from the capital, expense, and decommissioning cost, and have an additional burden of cost placed on them from the building structural requirements. Alternative 3 is not cost effective because of the relatively large number of processing steps required to achieve the final product. Also, the final products of this alternative are not well suited for the scope of this investigation. Alternatives 2 and 5 have a lower benefits to cost value mostly because they produce a low benefit to achieving a final waste compatible to existing TWRS waste and represent added expense costs to implement.

10.2 REVIEW OF DECISION CRITERIA

The decision criteria discussed in Section 4.0 are again reviewed with relation to Table 8. The four items identified in Section 4.0 were cost, schedule, safety, and combined impact.

10.2.1 Cost

Each alternative has been evaluated according to the cost to implement. This evaluation has shown that expense costs related to material usage, staffing requirements, utility usage, and product disposal contribute to the expense burden. Material usage was evaluated with respect to the number of chemical reagents required. Each of the processes use commercial grade reagents that are all readily available (with the possible exception of iodine). Expense costs due to staffing requirements will reflect the burden associated not only with payroll but also by the incidental cost associated with each individual. These incidental costs associate with habitability issues and fundamental human requirements (i.e., sanitary, work supplies, etc.).

Capital costs were evaluated against the individual breakdown cost for processing components and against the cost for the building structure. The alternatives were separable in relation to the specific requirements needed to house the processes they represent. It is anticipated that building costs for alternatives 4, 10, 11 will be in excess of $10 million. The building cost for alternatives 1, 2, 3, 5 and 7 is closer to $10 million and the cost for alternatives 6, 8, and 9 is approximately $4 million.

10.2.2 Schedule

The schedule required for processing is defined by the requirement to meet pace with the overall sludge remediation effort. The scheduled for sludge removal activities is based on a one year duration (starting in September 2000 and ending in September 2001). To ensure the sludge removal schedule was not impacted by implementation of the alternatives a 10 month duration was set as the base line for operations. Also, to account for scheduled maintenance a 70 percent total operating efficiency (TOE) was established as the basis for all alternatives. This TOE was chosen on the basis of professional judgement with respect to the types of components required for processing (types include slurry pumps, motor-operated valves (MOV), specific instrumentation, etc.). The amount of material to be processed was baselined at 6.5 m^3 (230 ft^3) of irradiated fuel. A one-shift operation was used to keep pace with sludge removal activities outside the scope of this investigation.

Calculations provided with Flowsheet 1 (Attachment 15) reveal the instantaneous throughput requirements for each of the alternatives. The capital cost associated with each process (Section 9.0) considered this throughput requirement when identification of equipment sizes was made.

10.2.3 Safety

Safety concerns were identified by review of the following manuals:

Standard Operating Procedures, WHC-CM-1-5

Safety Manual, WHC-CM-1-10
Industrial Hygiene Manual, WHC-CM-1-11
Industrial Hygiene Manual, WHC-CM-4-10
Safety Analysis Manual, WHC-CM-4-46
Nuclear Criticality Safety Manual, WHC-CM-4-29

Although safety concerns are not limited to the information contained in these manuals. It is understood that each alternative maintains the general concept of ALARA with respect to exposure by either radiation or chemicals. Aspects of the alternatives that are evidence of these considerations can be found in evaluation of building structure requirements, staffing levels, process component sizing, and operational requirements (remote operations rather than direct interface). Each individual alternative was also evaluated for specific safety related components such as equipment redundancy, cost for implementing safety classifications, specific material handling (e.g., offgas).

It must be noted that the specific flow balances, as related to process efficiency and kinetics will be established during definitive design. The information contained in this investigation is only meant to outline the processing alternatives that have established technical background and can be used as a basis for recommending a path forward.

10.2.4 Combined Impact

This final consideration is evaluated and depicted in Flowsheets 1-4 (Attachments 15 through 18). It is evident that not every alternative is capable of achieving 100 percent of the defined remediation goal and be cost effective. Therefore, combinations of alternatives are evaluated by these flowsheets and the particular process flowpath is further defined according to equipment components. These flowsheet depictions are only intended to be recommendations for further study of both process chemistry and equipment requirements. The options for combining alternatives is evident by the continuation arrows that reference the other flowsheets. Also, notation is made to the possibility of combining more that one alternatives process equipment to reduce cost.

The cost of housing an individual flowsheet process will be based on the building evaluation made in Section 9.0. The overall goal should be to provide the shielding required to the component in question based on that components function. This concept will reduce building costs as well as ancillary equipment such as H&V and remote operated components.

One facet of the benefit to cost evaluation is directed at satisfying concerns related to TWRS comments 3 and 8 from Table 3 above. Although other comments from Table 3 are equally important (as related to criticality and particle size etc.) creating a waste stream that is as near identical to waste previously accepted to TWRS should encompass many of the additional concerns. Attachment 13 contains a matrix evaluation of the comment 3 and 8 weighted values for a summation of combinations of alternatives that produce the greatest benefit.

11.0 CONCLUSION

Alternatives 1, 6, 7, 8, and 9 provide the technology and cost benefits to achieve the ultimate goal established as the criteria in this investigation. Flowsheets 1 through 4 (Attachments 15 through 18) are used to represent these alternatives singularly or in combination. The flowsheets are identified with continuation arrows (labeled as OPTIONS) or notes to indicate the combination possibilities.

These flowsheets are intended to provide a more detailed scope of processing equipment, which was established by Alternatives 1 through 11.

An appreciation for the limitations of each process can be gained by evaluation of the chemical equations included in Attachments 1 through 11. The only processes that provided satisfaction of all requirements is Alternative 4. Alternative 4 was ruled out on the basis of capital cost to implement and the cost burden it reflected to maintaining safety in operability and decommissioning. Alternative 7 was very close in achieving full satisfaction of requirements but some uncertainties with the process chemistry add doubt to the degree of effectiveness. These uncertainties are geared around the compatibility between peroxide and spent fuel components.

Alternative 1 provides a great degree of flexibility in fulfilling the required criteria. Alternative 1 will not, by itself relieve PCB concerns. Alternative 6 is identified as a very strong candidate, but some considerable discrepancies exist in the available information to support the rates of oxidation. These discrepancies are two orders of magnitude in disagreement and as with Alternative 1, this alternative does not relieve PCB concerns.

Alternative 7 is identified as satisfying most of the TWRS disposal criteria although more costly than a combination of Alternatives 6 and 8. As mentioned above, Alternative 7 does reflect a degree of uncertainty with respect to the compatibility of hydrogen peroxide and spent fuel components. It is expected that competition will exist between the PCBs and the spent fuel components for peroxide (spent fuel components may have a peroxide destruction effect). Failure of this alternative would result if peroxide was destroyed rather than being made available for PCB destruction.

Alternative 9 may be a likely candidate for achieving many of the TWRS criteria as well as reducing criticality concerns. This alternative is very similar to Alternative 7 and a combination of Alternatives 7 and 9 may produce good results.

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12.0 RECOMMENDATION

Attachments 15 to 18 are provided to illustrate the most likely alternatives to achieving satisfaction of all disposal criteria. These attachments illustrate how each of the likely alternatives can be combined or implemented directly to achieve the criteria as indicated in Table 1.

Two basic steps should be followed in selecting a final treatment process. The first step is to perform surrogate testing as a proof of concept test. The second step is to define the process design based on the proof of concept tests.

The simplified path in selecting a final preferred treatment process should proceed as follows.

- Prepare a work plan for laboratory proof of concept testing based on the chemistry required by the 4 flowsheets.
- Conduct laboratory testing on surrogate solutions to determine basic reaction compatibilities and kinetics.
- Consolidate the information gained in the surrogate testing to support a single preferred process.
- Develop a functional and conceptual design for this preferred process and obtain estimates. These estimates can be evaluated against funding forecasts and a schedule developed for implementing a new line item project.
- Continued proof of concept testing should now be performed on actual sludge and spent fuel components to test each phase of the process flowsheet. This testing is required to verify reaction mechanisms, kinetics, energy requirements, and waste forms.
- A definitive design can now be initiated for final funding validation and construction.

Initial surrogate testing should include the following investigation.

- Determine the reaction rate for oxidation of spent fuel in heated water. Also, investigate reaction rate enhancing agents.

- Determine the compatibility of hydrogen peroxide and spent fuel components. This investigation should look at alternate peroxides such as sodium peroxide and the effect of varying the solution conditions (e.g., oxygen concentrations, pH, temperature, catalysts, and interference from other solution components such as organics).

- Determine the effectiveness of washing sludge with a solvent such as hexane.

- Determine the effectiveness of a Fenton's reagent in the sludge system.

Once the surrogate testing, described above, is completed A final decision can be made as to the preferred process. Technical data and a conceptual estimate will be used to support the final decision.

12.1 CRITERIA FOR SELECTING A FINAL PROCESS

The laboratory testing will provide certain technical information related to heats of reaction, reaction kinetics, chemical to sludge compatibilities, and required reagent concentrations. This information is then to be used to select the process train that is most beneficial. The following criteria are to be used for that final determination.

Required Processing Rate:

The instantaneous flow rate of the process was identified as 7.6×10^{-4} m^3/min (0.2 gal/min). This value was based on a need to process 6.5 m^3 (230 ft^3) of fuel in 10 months. The schedule for K basin sludge activities is on a 12-month cycle but 10 months was chosen to avoid bottlenecking the retrieval activities. The operating efficiency is based on 70 percent total (TOE). A one shift per day cycle was selected in accordance with retrieval activities. The final process selection will have to meet this rate. Dissolution with nitric acid is expected to accomplish this rate but reservations are extended to the oxidation in heated water alternative.

Solvent Washing Effectiveness:

Washing the sludge with a solvent can be very cost effective as shown in the previous analysis. Evaluation of this process will reveal the compatibility of the solvent to the sludge and reveal the partitioning of the PCB from the sludge to the solvent. This partitioning must result in a final PCB to sludge concentration that is acceptable under the current TWRS regulatory restrictions.

Peroxide compatibility and optimization:

The compatibility of hydrogen peroxide with components of sludge should be evaluated and the effectiveness of this reagent verified. Compatibility will be based on the

effectiveness to decompose PCBs. By review of the chemical equations depicted as Fenton's reagent reactions (Alternative 9) with hydrogen peroxide, and the concentration of PCBs in the sludge (using 200 ppm as a max concentration), a value of the required peroxide concentration can be determined. This comparison indicates that using more than 400 ppm of peroxide plus a 35 percent margin (as excess reagent) in the solution may result in excess chemical use. An evaluation of the chemical cost associated with the process would be required if this excess usage requirement was shown to be true. The chemical cost associated with this process is the driver for selecting this option.

Alternative reagents should be investigated as well as hydrogen peroxide. Sodium peroxide has been suggested as a possible alternative. Selection of this reagent would be dependent on cost factors associated with material procurement and associated costs of material handling. The safety considerations surrounding operator exposure need to be evaluated and the total expense burden used as a comparison. This reagent is not expected to produce waste constituents that cause a concern to the TWRS compatibility issues.

Potassium permanganate has also been suggested as an alternative. The same type of cost evaluation for this reagent would be required as with the sodium peroxide.

Once the three pieces of information as outlined above are known, then the comparison can be made against flowsheets 1 through 4. The process that meets the requirements stated above, and is the most cost effective (as based on the costs previously established) should be pursued as the preferred process.

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13.0 REFERENCES

Bacon, R. F., 1996, *Preliminary Acceptance Recommendation for KE Floor Sludge Waste,* Internal Memo to J. C. Fulton (June 26), Westinghouse Hanford Company, Richland, Washington.

Barnhart, D. M., et al., 1995, *Dissolution of Lanthanide and Actinide Metals Using Iodine and 2-Propanol, Synthesis and X-ray Crystal Structure of LnI3(HO-i-Pr)4(Ln=La,Ce) and Th2I4(O-i-Pr)4(HO-i-Pr)2*, LANL, Chemical and Technology (CST) Division, Inorg. Chem. 1995, 34, 4862-4867.

Bloom, G. A., et al., 1995, *PCB Extraction from ORNL Tank WC-14 Using a Unique Solvent*, ORNL/TM-13078 Chemical Technology Division, Lockheed Martin Energy Systems Inc.

Burn, C. J., and N. N. Sauer, 1993, *Novel Chemical Methodologies for Uranium Metal/Alloy Oxidative Dissolution*, white paper report, Chemical and Environmental Research & Development Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

DOE, 1994, *Disposal Requirements for PCB Waste*, EH-231-056/1294, U.S. Department of Energy, TSCA Information Brief, Office of Environmental Guidance.

FDH, 1997a, *Operating Specifications*, OSD-T-151-00007, Fluor Daniel Hanford, Richland, Washington.

FDH, 1997b, *Criticality Prevention Specification*, CPS-T-149-00010, Fluor Daniel Hanford, Richland, Washington.

FDNW, 1997, *Working Construction Estimate, ETF Piping Enhancements Phase II*, file number YA32CAB1, Job number E29277 (January 13), Fluor Daniel Northwest, Richland, Washington.

Higley, B. A., 1996, *Comments for Inclusion in the TWRS Letter on Requirements for Acceptance of K Basin Sludge into the DST System*, DSI 96-067, to K. G. Carothers, (June 7), Westinghouse Hanford Company, Richland, Washington.

Higley, B. A., 1997, Particle Size Acceptance Criteria, Correspondence to F. G. Hudson, DESH, 9750522 DPO-97, Lockheed Martin Hanford Corporation, Richland, Washington.

Kim, B. C., et al., 1990, Conceptual Design, Cost Estimate and Preliminary Plans for the kpeg Process for Guam, Contract No. DAAL03-86-0001/ Delivery order 1368, Pacific Northwest National Laboratory, Richland, Washington.

Makenas, B. J., et al., 1996, WHC-SP-1182, *Analysis of Sludge from Hanford K East Basin Floor and Weasel Pit*, Westinghouse Hanford Company, Richland, Washington.

Omberg, R. P., 1996, *Highlight Report: Accelerated Examinations of K East Basin Canister Sludge*, DESH-9655840 (November 21), DE&S Hanford, Inc., Richland, Washington.

Packer, M. J., 1996, *Functional Design Criteria for the K Basin Sludge Retrieval System*, WHC-SD-SNF-FDC-005, Westinghouse Hanford Company, Richland, Washington.

Papp, I. G., 1997a, Personal communication between I.G. Papp and D.R. Shannon Co. 23407 Pacific Hwy So, Des Moines, WA 98198 (206) 824-3308.

Papp, I. G., 1997b, Personal communication between I.G. Papp and Mitchel Lewis and Staver Co. E. 2502 Trent Avenue, Spokane, WA 99202, (509) 534-0343.

Precechtel, D. R., 1996, *Functional Design Criteria for the K Basin Sludge Removal System*, WHC-SD-SNF-FDC-004, Westinghouse Hanford Company, Richland, Washington.

Prelburg, J., 1996, Letter Report of Laboratory Studies Conducted, Letter to I. G. Papp (WHC), Vulcan Peroxidation Systems, Tucson, AZ.

Rosson, L., 1997a, *Engineering Study Estimate*, File #YA68SAB1, Fluor Daniel Northwest, Richland, Washington.

Rosson, L., 1997b, *Engineering Study Estimate*, File #YA68SAA1, Fluor Daniel Northwest, Richland, Washington.

Ryan, J. L., 1991, *Review of Information Pertinent to the Oxidation (Burning) of Irradiated N Reactor Fuel*, Letter report (December 1991), Pacific Northwest National Laboratory, Richland, Washington.

Schmidt, A. J., 1997, *Evaluation of Polychlorinated Biphenyls (PCB) Data from K East Basin Sludge Samples*, letter to R. P. Omberg (DESH) (January 7), Pacific Northwest National Laboratory, Richland, Washington.

WHC, 1989, *PUREX Technical Manual*, WHC-SP-0479, Westinghouse Hanford Company, Richland, Washington.

WHC, 1996, *Functional Design Criteria for the K Basin Sludge Process and Loadout System*, WHC-SD-SNF-FDC-006, Westinghouse Hanford Company, Richland, Washington.

WIPP, 1996, *Waste Acceptance Criteria for the Waste Isolation Pilot Plant*, DOE/WIPP-069, Waste Isolation Pilot Plant, Carlsbad, NM.

ATTACHMENT 1

ALTERNATIVE 1 SIMPLIFIED FLOW SHEET

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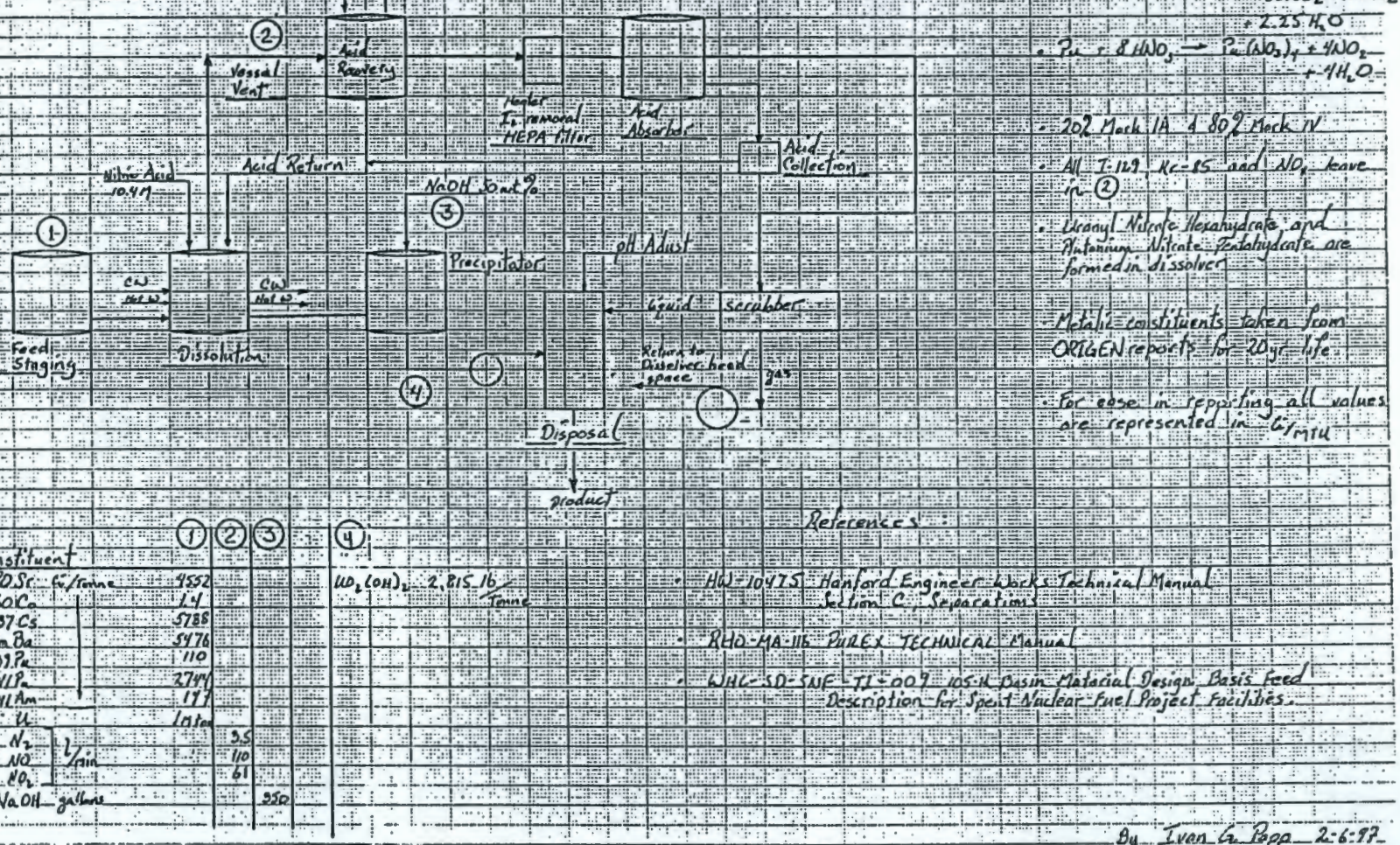
Alternative 1

— Dissolution followed by precipitation —



constituent	①	②	③	④
^{90}Sr Ci/tonne	4552			$UO_2(OH)_2$ 2,815 lb/tonne
^{60}Co	14			
^{137}Cs	5788			
^{137m}Ba	5476			
^{239}Pu	110			
^{241}Pu	2744			
^{241}Am	177			
U	1 Mton			
N_2 l/min		3.5		
NO l/min		110		
NO_2 l/min		61		
NaOH gallons			350	

Assumptions:

- No cladding particles require processing
- $U + 4.5\,HNO_3 \rightarrow UO_2(NO_3)_2 + .55\,NO + .85\,NO_2 + .05\,N_2 + 2.25\,H_2O$
- $Pu + 8\,HNO_3 \rightarrow Pu(NO_3)_4 + 4\,NO_2 + 4\,H_2O$
- 20% Mark IA & 80% Mark IV
- All I-129, Kr-85 and NO_x leave in ②
- Uranyl Nitrate Hexahydrate and Plutonium Nitrate Pentahydrate are formed in dissolver
- Metallic constituents taken from ORIGEN reports for 20 yr life.
- For ease in reporting all values are represented in Ci/mtu

References:

- HW-10475 Hanford Engineer Works Technical Manual Section C: Separations
- RHO-MA-115 PUREX TECHNICAL Manual
- WHC-SD-SNF-TI-007 105-K Basin Material Design Basis Feed Description for Spent Nuclear Fuel Project Facilities.

By Ivan G. Popp 2-6-98

ANALYSIS

For	Alternative 1	Page	1
Location	HNO_3	Job No.	
Subject	Dissolution of Fuel w/ precipitation	Date	2-6-97
		By	I. G. Papp
		Checked By	Karl Pool 3/6/97

* $U + 4.5\,HNO_3 \rightarrow UO_2(NO_3)_2 + 1.55\,NO + .85\,NO_2 + .05\,N_2 + 2.25\,H_2O$

$Pu + 8\,HNO_3 \rightarrow Pu(NO_3)_4 + 4\,NO_2 + 4\,H_2O$

* for dissolution @ Nitric acid > 8 M

$6\,NaOH + Pu(NO_3)_4 + UO_2(NO_3)_2 \rightarrow Pu(OH)_4 + UO_2(OH)_2 + 6\,NaNO_3$

for 1 Mton of U we need:

$$\left(\frac{2204.6\ lb}{Mton}\right)(1\,Mton)\left(\frac{lb\,mol\,U}{238\ lb\,U}\right)\left(\frac{6\,lb\,mol\,OH}{1\,lb\,mol\,U}\right)\left(\frac{40\ lb\,NaOH}{lb\,mol}\right)\left(\frac{lb\ 50\%}{.5\ lb}\right) = 4446\ lb\ 50\%\ NaOH$$

$$(4{,}446\ lb\ 50\%\ NaOH)\left(\frac{gal}{12.76\ lb\ 50\%}\right) = \underline{\underline{350\ gal\ 50\,wt\%\ NaOH}}$$

Off gas: Relative amounts of NO & NO_2 evolved follow:

$$3\,NO_2 + H_2O \rightleftharpoons NO + 2\,HNO_3$$

Since acid is recovered ① the consumption goes down from 4.5 to 3 mol acid / mol uranium:

① $2\,NO + O_2 \rightarrow 2\,NO_2$ see Note

$2\,NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

Stoichiometric Air requirements are about 7→12 scf/lb U dissolved when acid to uranium mole ratio is ~3.

Uranium dissolution increases with increased initial nitric acid concentration (about 50% HNO_3 [10.4 M])

SpG of dissolver solution should rise at min of .02 units/hr.

Note
Recovery of acid as depicted in ① above may be rate limited and require some rate enhancing agent.

ANALYSIS

Page 2
Job No.
Date 2-6-97
By I.G. Papp
Checked By Karl Pool 3/6/97

For Alternative 1
Location HNO_3
Subject Dissolution of Fuel w/ precipitation

$$\left(\frac{10.4 \text{ moles } HNO_3}{\text{lit}}\right)\left(\frac{63 \text{ lb}}{\text{lbmol}}\right)\left(\frac{\text{lbmol}}{454 \text{ gmol}}\right) = \frac{1.4 \text{ lb}}{\text{lit}}$$

Acid requirement: $10.4\ \underline{M} = 50\%$ wt HNO_3

SpG ~ 1.3

HNO_3

H — 1 x 1 = 1
N — 1 x 14 = 14
O — 3 x 16 = 48
63

$$\left(\frac{9.26 \text{ lbmol } U}{\text{tonne } U}\right)\left(\frac{4.5 \text{ lbmol } HNO_3}{1 \text{ lbmol } U}\right)\left(\frac{63 \text{ lb } HNO_3}{\text{lbmol}}\right)\left(\frac{1 \text{ lb } 50\% \text{ soln}}{.5 \text{ lb } HNO_3}\right)\left(\frac{1 \text{ lb } H_2O}{1.3 \text{ lb } 50\%}\right)\left(\frac{\text{gal}}{8.345 \text{ lb}}\right) = \frac{484 \text{ gal } HNO_3\ 50 \text{ wt\%}}{\text{tonne } U}$$

for 1 tonne U we have a final mass of $UO_2(OH)_2$ as:

$UO_2(OH)_2$

U ⇒ 238 x 1 = 238
O ⇒ 16 x 4 = 64
H ⇒ 1 x 2 = 2
304

$$\left(\frac{9.26 \text{ lbmol } U}{\text{tonne}}\right)\left(\frac{1 \text{ lbmol } UO_2(OH)_2}{1 \text{ lbmol } U}\right)\left(\frac{304 \text{ lb } UO_2(OH)_2}{1 \text{ lbmol } UO_2(OH)_2}\right) = 2,815 \text{ lb } UO_2(OH)_2$$

54-7400-276 (2 88)

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ATTACHMENT 2

ALTERNATIVE 2 SIMPLIFIED FLOW SHEET

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Alternative 2

Dissolving Fuel w/ I_2 with 2-propanol under anaerobic conditions

1. Light purple solution formed with some hydrogen evolution. Formation of a lavender solid is achieved by cooling to -35°C. This solid crystal is then dried in a vacuum to produce a light green solid as depicted in equation 1.
2. The dried green solid is contacted with a caustic solution to be hydrolyzed to uranium oxide.
3. Precipitate is formed by caustic addition. I_2 remains as NaI.

Possible reactions which accompany precipitate formation

A) $2UI_2(O\text{-}i\text{-}Pr) + 6NaOH + H_2O \rightarrow Na_2U_2O_7\downarrow + 4(OH\text{-}i\text{-}Pr) + 2H_2\uparrow + 4NaI$

or B.) Excess I_2 could serve as oxidizing agent to convert $U^{4+} \rightarrow U^{6+}$ and no H_2 would be involved.
An example is: $2UI_2(O\text{-}i\text{-}pr)_2 + 2I_2 + 10NaOH \rightarrow Na_2U_2O_7\downarrow + 4(iprOH) + 3H_2O + 8NaI$

Assumptions:

- $U + 2I_2 + 2HO\text{-}i\text{-}Pr \xrightarrow{HO\text{-}i\text{-}Pr} UI_2(O\text{-}i\text{-}Pr)_2(HO\text{-}i\text{-}Pr)_2 + H_2$ ①
  HO-i-Pr = 2 propanol
- The above compound is moderately soluble in 2-Propanol but readily turns green in noncoordinating solvents like Toluene.
- $2UI_2(O\text{-}i\text{-}Pr)_2(HO\text{-}i\text{-}Pr)_2 \xrightarrow[HO\text{-}i\text{-}Pr]{-2HO\text{-}i\text{-}Pr} U_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$ ②
- Iodine remains in final solution as NaI.
- Complete oxidation of 5-12 g batches of U metal turnings by a stoichiometric quantity of Iodine typically takes 1-2 days.
- Additional info ③ reveals $Ln + 3/2\,I_2 \xrightarrow{HO\text{-}i\text{-}Pr} LnI_3(HO\text{-}i\text{-}Pr)_4$ where Ln = La, Ce, Nd @ 86, 85, 58% yields (slightly exothermic)
- Reaction offgassing is not known.
- U must be relatively free of oxides.
- heat of reaction for dissolution is 20 Kcal/mol

References:

- ① Dissolution of Uranium Metal Using Iodine and 2-Propanol. Synthesis and X-Ray Crystal Structure of [Tetraiodotetraisopropoxybis (2-propanol) diuranium]
  Inorg. Chem., 1992, 31, 1316-1318
  J.C. Huffman et al
- ② Dissolution of Lanthanide & Actinide Metals Using Iodine and 2-Propanol. Synthesis and X-ray Crystal Structure of $LnI_3(HO\text{-}i\text{-}Pr)_4$ (Ln = La, Ce) and $Th_2I_4(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_2$
  Inorg. Chem., 1995, 34, 4862-4867
  David M. Barnhart et al
- ③ Novel Chemical Methodologies for Uranium Metal/Alloy Oxidative Dissolution. LANL, N.N. Sauer et al. Sept 30, 1993.

By I.G. Papp Feb. 1997

1

ANALYSIS

For	Alternative 2	Page	1
Location		Job No.	
Subject	Dissolution using I_2 with 2-propanol	Date	2-10-97
		By	I.G. Papp
		Checked By	Carl Poll 3/6/97

Reactants:

For 1 tonne of U as a basis:

$$(2204.6\ \text{lbs U})\left(\frac{1\ \text{lbmol U}}{238\ \text{lb}}\right)\left(\frac{\geq 1\ \text{lbmol}\ I_2}{1\ \text{lbmol U}}\right)\left(\frac{127\ \text{lbs I}}{\text{lbmol I}}\right)\left(\frac{2\ \text{lbmol I}}{1\ \text{lbmol}\ I_2}\right) \geq 2{,}352\ \text{lbs I or}\ I_2$$

per tonne U

2-Propanol $\cdot\dot{C}\cdot\overset{OH}{\dot{C}}\cdot\dot{C}\cdot$ C 3-12 = 36, H 8-1 = 8, O 1-16 = 16 } 60 SpG = .78505

Also: $$(9.26\ \text{lbmol U})\left(\frac{2\ \text{lbmol 2-Prop}}{1\ \text{lbmol U}}\right)\left(\frac{60\ \text{lb 2-Prop}}{\text{lbmol 2-Prop}}\right)\left(\frac{\text{gal}}{6.55\ \text{lb}}\right) = 169.6\ \text{gal 2-propanol}$$

required per tonne U

Products:

$$(9.26\ \text{lbmol U})\left(\frac{1\ \text{lbmol}\ Na_2U_2O_7}{2\ \text{lbmol U}}\right)\left(\frac{634\ \text{lb}\ Na_2U_2O_7}{\text{lbmol}}\right) = 2{,}935\ \text{lb}\ Na_2U_2O_7\ \text{per tonne of U}$$

Na - 2 · 23 = 46
U - 2 · 238 = 476
O - 16 · 7 = 112
634

NaOH required:

$$(9.26\ \text{lbmol U})\left(\frac{1\ \text{lbmol}\ Na_2U_2O_7}{2\ \text{lbmol U}}\right)\left(\frac{2\ \text{lbmol Na}}{1\ \text{lbmol}\ Na_2U_2O_7}\right)\left(\frac{1\ \text{lbmol NaOH}}{1\ \text{lbmol Na}}\right)\left(\frac{40\ \text{lb NaOH}}{1\ \text{lbmol NaOH}}\right)\left(\frac{1\ \text{lb 50\% soln}}{.5\ \text{lb NaOH}}\right)\left(\frac{1\ \text{lb}\ H_2O/\text{gal}}{1.5\ \text{lb 50\%/gal}}\right)$$

$$\left(\frac{\text{gallon}}{8.345\ \text{lb}\ H_2O}\right) = 59\ \text{gallons of 50 wt\% NaOH required for 1 tonne U.}$$

* see page 2 of this calc.

Hydrogen gas:

$$(9.26\ \text{lbmol U})\left(\frac{1\ \text{lbmol}\ H_2}{2\ \text{lbmol U}}\right)\left(\frac{2\ \text{lbs}\ H_2}{1\ \text{lbmol}}\right) = \frac{9.26\ \text{lbs}\ H_2}{\text{tonne U}}\quad \text{from:}$$

$$2U + \geq 2I_2 + 2HO\text{-}i\text{-}Pr \longrightarrow UI_2(O\text{-}i\text{-}Pr)_2\,(HO\text{-}i\text{-}Pr)_2 + H_2\uparrow$$

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For Alternative 2
Location
Subject Dissolution using I_2 w/ 2-propanol

NaOH requirement:

For possible side reactions.

$$(9.26\ \text{lbmol U})\left(\frac{6\ \text{lbmol NaOH}}{1\ \text{lbmol U}}\right)\left(\frac{40\ \text{lb NaOH}}{1\ \text{lbmol NaOH}}\right)\left(\frac{1\ \text{lb 50\% Soln}}{.5\ \text{lb NaOH}}\right)\left(\frac{1.1\ \text{lb}\ H_2O/\text{gal}}{1.51\ \text{lb 50\%/gal}}\right)\left(\frac{\text{gallon}}{8.315\ \text{lb}}\right) = 355\ \text{gal 50wt\% NaOH}$$

∴ we may want to assume an additional 355 gal of 50wt% NaOH based on this possible reaction.

The total 50wt% NaOH would then come to

355 gal + 59 gal = 414 gal

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ATTACHMENT 3

ALTERNATIVE 3 SIMPLIFIED FLOW SHEET

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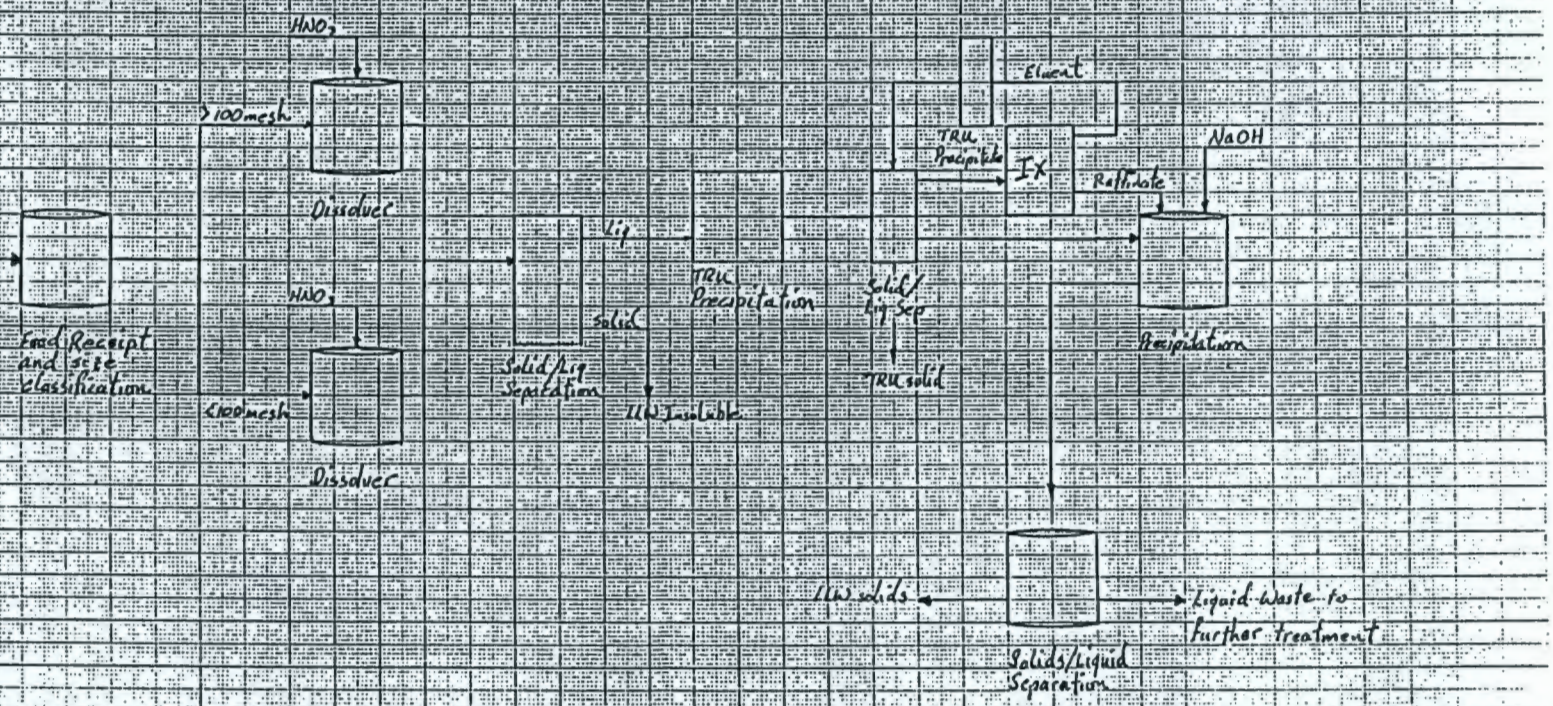
Alternative 3

— Dissolution followed by separation, IX, and precipitation —



By I.G. Papp Feb 1997

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ATTACHMENT 4

ALTERNATIVE 4 SIMPLIFIED FLOW SHEET

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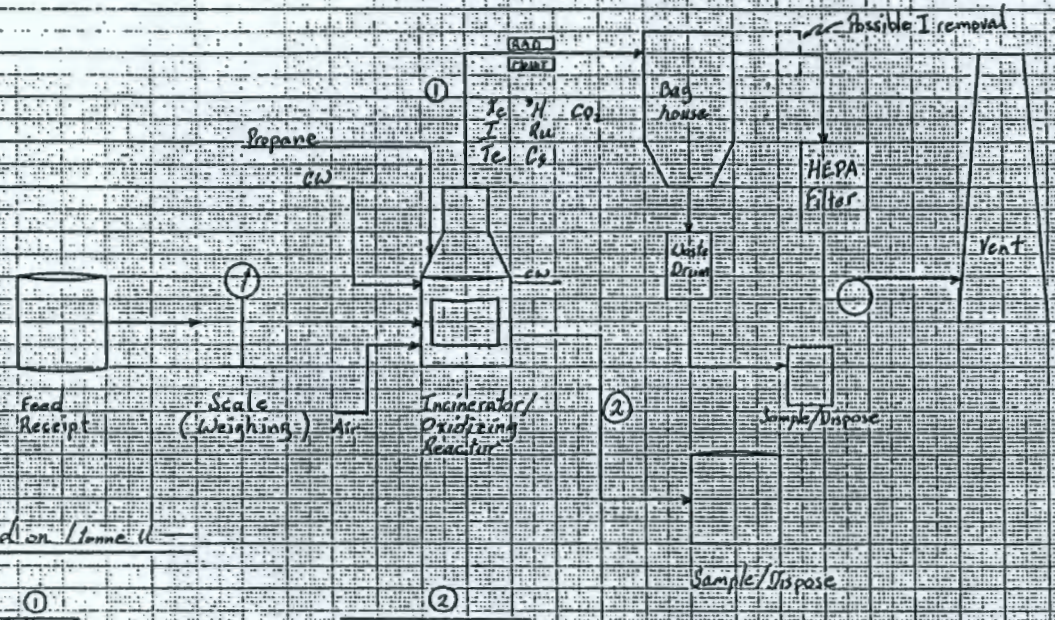
Alternative 4

– Roasting of Fuel (Burning) –



– Based on 1 tonne U –

① CO_2 expected as a product of n-C_3H_8 burning

^3H expected as water vapor (HTO)

^{131}I ~ .00027 Ci

^{137}Cs ~ 2,315 Ci

^{90}Sr ~ 2,504 Ci

Xe, Te, Ru are expected but values not available

② U_3O_8 – 2,600 lb

17,280 ft^3 Air @ 70°F to provide Stoichiometric ratio of O_2 for burning.

Assumptions:

- Measured amount of metal or sludge is oxidized by exposure to heat and oxygen.
- The following reactions apply:

	ΔH Kcal/mol
$U + O_2 \rightarrow UO_2$	-260
$U + 1/3\,O_2 \rightarrow 1/3\,U_3O_8$	-284
$UO_2 + 1/3\,O_2 \rightarrow 1/3\,U_3O_8$	-25
$U + 1/2\,N_2 \rightarrow UN$	-70
$U + 3/4\,N_2 \rightarrow 1/2\,U_2N_3$	-88
$1/2\,U_2N_3 + O_2 \rightarrow UO_2 + 3/4\,N_2$	-171
$U + 2H_2O_{(l)} \rightarrow UO_2 + 2H_2$	-144
$U + 3/2\,H_2 \rightarrow UH_3$	-30
$UH_3 + 7/4\,O_2 \rightarrow UO_2 + 3/2\,H_2O$	-316
$Zr + O_2 \rightarrow ZrO_2$	-262
$U + 2CO_2 \rightarrow UO_2 + 2CO$	-124
$U + 2CO \rightarrow UO_2 + 2C$	-206
$U + CO \rightarrow 1/2\,UO_2 + 1/2\,UC_2$	-113
$U + 1/3\,CO \rightarrow 1/3\,UO_2 + 1/3\,UC$	-84

- Ignition temperature of spent fuel is lower than that of pure uranium.
- Product of oxidation is U_3O_8 when taken to completion. Oxidation by O_2 >> than CO_2.
- Metal must be agitated to prevent passivation from oxide formation.

References:

– Review of Information Pertinent to the oxidation (Burning) of Irradiated N-Reactor Fuel, J.L. Ryan – PNL, Dec 1991.

– RHO-MA-116 PUREX TECHNICAL MANUAL

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Average releases of oxidation process as volatile fission products ①

The following values were actually released during oxidation in air: ②

10% ^{131}I ③

20% ^{134}Te

40% $^{136-137}Cs$

40% ^{95}Zr

50% ^{140}Ba

55% $^{89-90}Sr$

85% ^{103}Ru

Passing the furnace off-gas stream through and "absolute" filter rated at 99.95% for 0.3μm removed 50-99% of fission products excluding Tc

Some work on burning investigated particle size. ① Although most oxides were well over 20 micron in size (<4% was <20 micron) at any temperature from 400°C to 1200°C, some submicron particles were produced.

Burning has produced about 4.3×10^6 BTU/ton U.

Tritium is expected as tritiated water vapor (HTO) ④

④ RHO-MA-116 PUREX TECH Manual 1982

③ ^{131}I is not expected in appreciable quantities because of short half life (8.07 days)

② Hilliard, R.K. 1958. "Oxidation of Uranium in Air at High Temperatures. HW-58022 Hanford Atomic Products Operation, General Electric Co., Richland, WA.

① Review of Information Pertinent to the oxidation (Burning) of Irradiated N-Reactor Fuel, J.L. Ryan, PNL, Dec 1994

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From ORIGEN II reports for N-fuel.

^{129}I is assumed to be released in the same release fraction as ^{131}I.

$(.0027\ Ci/tonne\ U)(1\ tonne\ U)(.10) = .00027\ Ci\ ^{129}I$

^{137}Cs

$(5788\ Ci/tonne\ U)(.4) = 2{,}315\ Ci\ ^{137}Cs$

^{90}Sr

$(4552\ Ci/tonne\ U)(.55) = 2{,}504\ Ci\ ^{90}Sr$

U_3O_8 U → 3×238 = 714
O 8×16 = 128
842

Solids generation calculated from:

$$\left.\begin{array}{l} U + O_2 \rightarrow UO_2 \\ UO_2 + \frac{1}{3}O_2 \rightarrow \frac{1}{3}U_3O_8 \end{array}\right\} \text{add}\quad U + O_2 + \cancel{UO_2} + \frac{1}{3}O_2 \rightarrow \cancel{UO_2} + \frac{1}{3}U_3O_8$$

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{\frac{1}{3}\ lbmol\ U_3O_8}{lbmol\ U}\right)\left(\frac{842\ lb\ U_3O_8}{lbmol}\right) = \frac{2{,}599\ lb\ U_3O_8}{tonne\ U}$$

$32\ \frac{lb\ O_2}{lbmol}$

Air Requirement:

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{1\ lbmol\ O_2}{lbmol\ U}\right)\left(\frac{1\ lbmol\ Air}{.21\ lbmol\ O_2}\right)\left(\frac{29\ lb\ Air}{lbmol\ Air}\right)\left(\frac{ft^3\ Air}{.074\ lb}\right) = 17{,}280\ \frac{ft^3\ Air}{tonne\ U}$$ to support burning

$$\left(\frac{28\ lit}{ft^3}\right)\left(\frac{12\times10^{-4}\ g\ Air\ @\ 70°F}{milliliter}\right)\left(\frac{1000\ ml}{lit}\right) = \frac{33\ g}{ft^3}$$

$$\left(\frac{33\ g}{ft^3}\right)\left(\frac{lb}{454\ g}\right) = \frac{.074\ lb}{ft^3}$$

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ATTACHMENT 5

ALTERNATIVE 5 SIMPLIFIED FLOW SHEET

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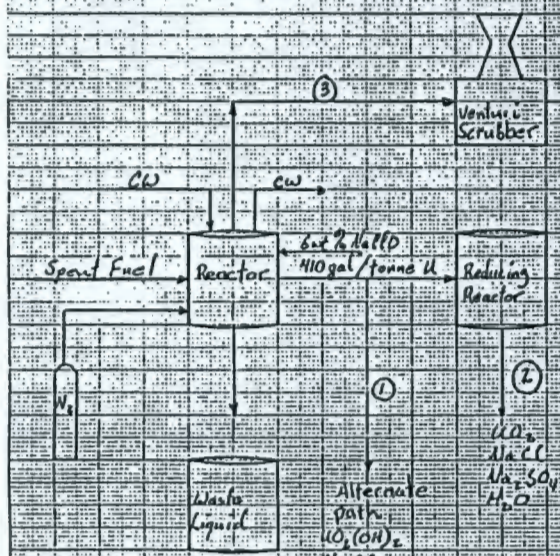
Alternative 5

— Liquid Phase Oxidation —

Sodium Hypochlorite



Heat of Reaction is ~250 kcal/mol U

Based on 1 tonne of U we have:

①		②		③
$UO_2(OH)_2$	2,315 lb	UO_2	2,500 lb	375 L/min Air
NaCl	1,611 lb	NaCl	1,611 lb #	<.5% H_2 (only if originally present in shipping container)
H_2O	410 gal *	Na_2SO_4	640 lb	Cl_2 could theoretically be produced but production has not been verified on bench scale.
		H_2O	410 gal	

* H_2O volume is based on stoichiometric balance between 6wt% NaClO and U. Actual volume will be based on receiving container with fuel

\# Some excess NaCl is expected but not much more. 20% more is a reasonable guess due to the 4:1 ratio of NaClO to NaCl in treating excess Bleach.

Assumptions:

- $U + 3NaClO + H_2O \rightarrow UO_2(OH)_2 + 3NaCl$
  Uranium oxidation using sodium hypochlorite
- $4UO_2(OH)_2 + Na_2S_2O_3 \rightarrow 4UO_2 + H_2SO_4 + Na_2SO_4 + 3H_2O$
  Uranyl Hydroxide reduced to uranium dioxide using thiosulfate
- $4NaClO + Na_2S_2O_3 + H_2O \rightarrow H_2SO_4 + Na_2SO_4 + 4NaCl$
  Excess Sodium Hypochlorite reduction using Thiosulfate
- $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
  Neutralize Sulfuric Acid with Sodium Hydroxide
- Some Chlorine gas is generated
- Some hydrogen gas may be present in Spent Fuel containers
- N_2 is supplied as a cover gas not for reaction
- Liquid waste may not be generated. This is dependent on what the fuel is packaged in.
- A stoichiometric balance would limit the ratio of Uranium to 1.3 kilograms/30 gallons or any ratio in this proportion.

— References —

- Depleted Uranium Oxidation Process, LANL Contract #9-XX2-Y9590-1 Work Release #04 - Rev 1, Oct 13, 93.
- Telephone conversation between N. Sauer and Ivan Papp Subject: Oxidation of Uranium w/ Sodium Hypochlorite. Feb. 3, 1997
- Novel Chemical Methodologies for Uranium Metal/Alloy Oxidative Dissolution, Carol J. Burns et al., CST-18, Los Alamos Nat Labs, Chemical & Environmental R&D Group. Sept 30, 1993
- US Patent # 5,098,677, Nancy Sauer for US, Date, Mar 24, 92

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ANALYSIS

For: Alternative 5
Location: Sodium Hypochlorite
Subject: Liquid Phase Oxidation

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By: Ivan G. Papp
Checked By: Karl Pool 3/6/97

① $U + 3NaClO + H_2O \rightarrow UO_2(OH)_2 + 3NaCl$

② $4UO_2(OH)_2 + Na_2S_2O_3 \rightarrow 4UO_2 + H_2SO_4 + Na_2SO_4 + 3H_2O$

③ $4NaClO + Na_2S_2O_3 + H_2O \rightarrow H_2SO_4 + Na_2SO_4 + 4NaCl$

④ $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Based on 1 tonne Uranium:

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{3\ lbmol\ NaClO}{1\ lbmol\ U}\right)\left(\frac{74\ lb\ NaClO}{lbmol}\right)\left(\frac{1\ lb\ 6\%\ Soln}{.06\ lb\ NaClO}\right)\left(\frac{gallon}{8.345\ lb}\right) = \frac{4100\ gallons\ 6\ wt\%\ NaClO\ solution}{tonne\ U}$$

NaClO
Na 1 × 23 = 23
Cl 1 × 35 = 35
O 1 × 16 = 16
74

@ 6% concentration density is close to H_2O

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{3\ lbmol\ NaCl}{1\ lbmol\ U}\right)\left(\frac{58\ lb\ NaCl}{lbmol}\right) = \frac{1,611\ lb\ NaCl}{tonne\ U}$$

$UO_2(OH)_2$
U ⇒ 1 × 238 = 238
O ⇒ 4 × 16 = 64
H ⇒ 2 × 1 = 2
304

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{1\ lbmol\ UO_2(OH)_2}{1\ lbmol\ U}\right)\left(\frac{304\ lb\ UO_2(OH)_2}{lbmol\ UO_2(OH)_2}\right) = \frac{2,815\ lb\ UO_2(OH)_2}{tonne\ U}$$

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{1\ lbmol\ UO_2}{1\ lbmol\ U}\right)\left(\frac{270\ lb\ UO_2}{lbmol\ UO_2}\right) = \frac{2,500\ lb\ UO_2}{tonne\ U}$$

Na_2SO_4
Na → 23 × 2 = 46
S → 32 × 1 = 32
O → 16 × 4 = 64
142

Assuming 200 Kgrams is stored in a 30 gal drum:

$$(200,000\ g)\left(\frac{lb}{454\ g}\right)\left(\frac{lbmol\ U}{238\ lb\ U}\right)\left(\frac{3\ lbmol\ NaClO}{1\ lbmol\ U}\right)\left(\frac{74\ lb\ NaClO}{lbmol}\right)\left(\frac{1\ lb\ 6\%\ Soln}{.06\ lb\ NaClO}\right)\left(\frac{gallon}{8.345\ lb}\right) = 820\ gal$$

$\frac{820}{30} = 27$ $\qquad \frac{200,000\ g}{27} = 7311$ g of U can be processed in 30 gal at a given batch.

Assume → Na_2SO_4 = 1.2 × mass of NaCl originally produced due to some excess added.

$$\left(\frac{9.26\ lbmol\ U}{tonne}\right)\left(\frac{3\ lbmol\ NaCl}{lbmol\ U}\right)(1.2)\left(\frac{142\ lb\ Na_2SO_4}{lbmol\ Na_2SO_4}\right) = \frac{4,734\ lb\ Na_2SO_4}{tonne\ U}$$

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ATTACHMENT 6

ALTERNATIVE 6 SIMPLIFIED FLOW SHEET

A flowsheet diagram was not developed for this alternative because of the relative simplicity of the process. See Section 7.6 for a description of the alternative.

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ATTACHMENT 7

ALTERNATIVE 7 SIMPLIFIED FLOW SHEET

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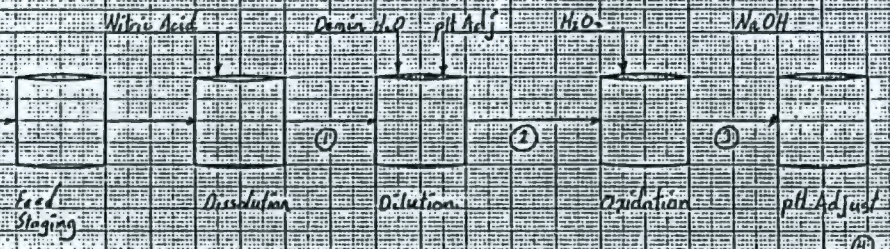
Alternative 7

Liquid Phase Oxidation
— Hydrogen Peroxide —



①	②	③	④
$UO_2(NO_3)_2$ 484 gal Soln (stoichiometric) (actual will be based on solubility & temp.) U / tonne	Demin H_2O addition is not deemed absolutely necessary. Only for adjustment of U concentration.	H_2O_2 63 gallons 50 wt % soln.	1 gal NaOH
H_2O_2 484 gal	.026 gal 50 wt % NaOH for pH Adj	Solution gains H^+ by oxidation	~ 2000 lit stoichiometric volume
			at least 2,800 lb $UO_4 \cdot XH_2O$ / tonne U
			(additional weight due to hydrate should be expected, but as yet undetermined)

Assumptions:

- $UO_2^{++} + H_2O_2 + XH_2O \rightarrow UO_4 \cdot XH_2O + 2H^+$
- The reference cited indicates a pH of 3.5 is required to ensure precipitation of UO_4, however no information was found on the effect of raising pH. The assumption is made that U remains as UO_2, since that would favor the right hand side of the above reaction.
- Dissolution was previously outlined in the dissolution of fuel w/ precipitation.

References:

- US Patent 4,298,578 Leach Method including means to Protect ion exchange resins, Tsoung-yuan Yan et al, Mobil Oil Corporation New York, N.Y.
- HW-10475 Hanford Engineer Works Technical Manual Section C, Separations
- RHO-MA-116 PUREX TECHNICAL Manual

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Job No.	
Date	2-12-97
By	I.G. Papp
Checked By	Earl Pool 3/6/97

For: Alternative 7
Location: Liquid Phase Oxidation
Subject: Hydrogen Peroxide

$$UO_2^{2+} + H_2O_2 + xH_2O \rightarrow UO_4 \cdot xH_2O + 2H^+$$

Based on 1 tonne of U dissolved in HNO_3

$$\left(\frac{9.26\ \text{lbmol}\ UO_2}{\text{tonne}}\right)\left(\frac{1\ \text{lbmol}\ H_2O_2}{1\ \text{lbmol}\ UO_2}\right)\left(\frac{34\ \text{lb}\ H_2O_2}{1\ \text{lbmol}\ H_2O_2}\right)\left(\frac{1\ \text{lb 50\% soln}}{.5\ \text{lb}\ H_2O_2}\right)\left(\frac{\text{lb}\ H_2O}{1.2\ \text{lb 50\% soln}}\right)\left(\frac{\text{gal}}{8.345\ \text{lb}}\right) = 62.9\ \text{gallons 50wt\% } H_2O_2$$

484 gallons of HNO_3 is required for dissolution *

* 484 gallons is a stoichiometric ratio, actual volume would be greater.

$$\left(\frac{2204.6\ \text{lb U}}{\text{tonne}}\right)\left(\frac{\text{lbmol U}}{238\ \text{lbU}}\right)\left(\frac{1\ \text{lbmol}\ UO_2}{1\ \text{lbmol U}}\right)\left(\frac{1\ \text{lbmol}\ UO_4}{1\ \text{lbmol}\ UO_2}\right)\left(\frac{302\ \text{lb}\ UO_4}{\text{lbmol}\ UO_4}\right) = 2{,}797.0\ \text{lb}\ UO_4$$

see NOTE

UO_4: U ⇒ 238×1 = 238; O ⇒ 16×4 = 64; 302

NOTE: The hydrated form will contribute to additional weight but the extent of hydration is not known at this time.

based on a stoichiometric balance of $U + 4.5HNO_3 \rightarrow UO_2(NO_3)_2 + 1.55NO + .85NO_2 + .05N_2 + 2.25H_2O$

there is no free H^+ so the minimum volume of caustic to raise the solution by 2 pH units is calculated as:

$$(500\ \text{gallons})\left(\frac{3.785\ \text{L}}{\text{gal}}\right)\left[\left(\frac{10^{-3}\ \text{moles}\ H^+}{\text{lit}}\right) - \left(\frac{10^{-5}\ \text{moles}\ H^+}{\text{lit}}\right)\right]\left(\frac{1\ \text{mol NaOH}}{1\ \text{mol}\ H^+}\right)\left(\frac{40\ \text{g NaOH}}{\text{mol}}\right)\left(\frac{1\ \text{g 50\% soln}}{.5\ \text{g NaOH}}\right)\left(\frac{\text{g}\ H_2O}{1.5\ \text{g 50\%}}\right)$$

$$\left(\frac{\text{lit}}{1000\ \text{g}}\right)\left(\frac{\text{gal}}{3.785\ \text{lit}}\right) = .026\ \text{gal 50wt\% NaOH}$$

$$\left(\frac{9.26\ \text{lbmol}\ UO_2}{\text{tonne}}\right)\left(\frac{2\ \text{lbmol}\ H^+}{\text{lbmol}\ UO_2}\right)\left(\frac{454\ \text{g mol}}{\text{lbmol}}\right)\left[\text{assuming 500 gal or 1900 L}\right] \text{ then } \left(\frac{8{,}408\ \text{mol}\ H^+}{1900\ \text{L}}\right)\left(\frac{1\ \text{mol NaOH}}{1\ \text{mol}\ H^+}\right)\left(\frac{.014\ \text{gal 50wt\% NaOH}}{\text{mol NaOH}}\right)$$

$$= .06\ \frac{\text{gal 50wt\% NaOH}}{\text{tonne}}$$ to neutralize H^+ resulting from oxidation

[This calculation indicates the requirement for 50wt% NaOH is probably not very high but likely more than represented here.]

then to raise pH to 14

$$(2{,}000\ \text{mol NaOH})\left(\frac{.014\ \text{gal 50wt\% NaOH}}{\text{mol NaOH}}\right) = 28\ \text{gal 50wt\% NaOH}$$

ATTACHMENT 8

ALTERNATIVE 8 SIMPLIFIED FLOW SHEET

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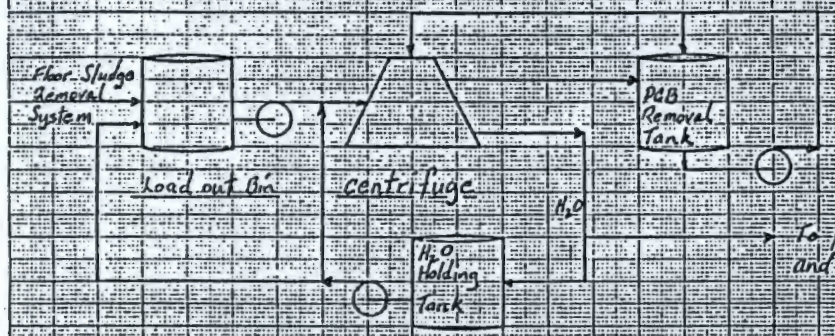
Alternative 8

Solvent Extraction of PCBs



Assumptions:

- PCB removal follows the trend for extraction in a like solvent. Hexane is a very likely candidate
- Partitioning of the PCBs favors the organic solvent rather than the more polar H_2O.
- Solubility of PCBs in Hexane is such that make-up of C_6H_{14} is not required
- Hexane is recirculated through centrifuge. Volume of PCB removal tank is sufficient to wash entire volume of sludge.
- Hexane does not favor extraction of radionuclides because it lacks a carrier such as TBP. No radionuclides are expected to be carried over.
- Concentration of PCBs in solvent may be limited with respect to disposal requirements. ≤ 25 ppm

References:

- "PCB extraction from ORNL tank WC-14 using a unique solvent" G.A. Bloom et al., Sept. 1995. ORNL/TM-13078. Chemical Technology Division, Lockheed Martin Energy Systems Inc

By: Ivan G. Papp 1997

ANALYSIS

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Location		Job No.	
Subject	Solvent Extraction of PCBs	Date	Feb 20, 1997
		By	I.G. Papp
		Checked By	Karl Pool 3/6/97

By referencing Fig 1. of this document we find the sludge is to be retrieved from the floor sludge removal system segregated and identified for possible treatment prior to tank farms disposal. This sludge has been found to contain PCBs.

A simple solvent system has been identified for washing the sludge and removing organic contaminants which inhibit or limit disposal options.

ATTACHMENT 9

ALTERNATIVE 9 SIMPLIFIED FLOW SHEET

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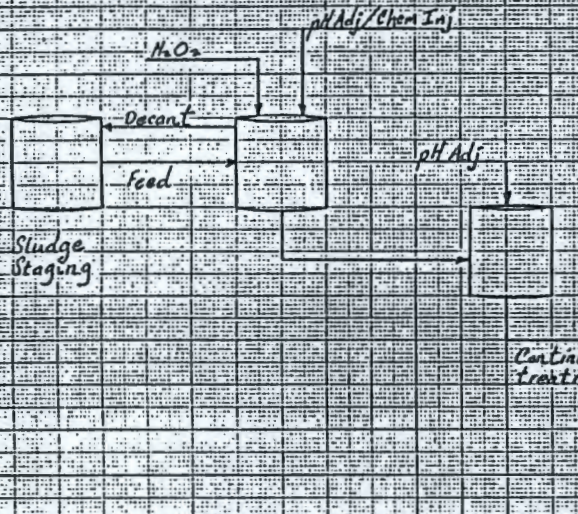
Alternative 9

Destruction of Organics



Assumptions :

- Primary reagent for organic destruction is H_2O_2 and follows the equation:
- Fentons reagent as :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^-$$
$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2\cdot + H^+$$

may be used to enhance destruction.

- The rate of H_2O_2 destruction is not determined. Several components of spent fuel may compete with organic destruction by causing H_2O_2 break down as:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

- Laboratory testing is required to determine efficiency of this method.

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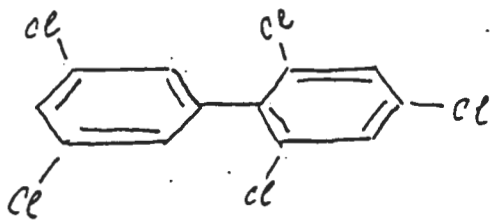
ANALYSIS

For	Alternative 9	Page	1
Location		Job No.	
Subject	Organic Destruction w/ H_2O_2	Date	Feb 20, 1997
		By	I.G. Papp
		Checked By	Karl Pool 3/6/97

General Equation

$$H_2O_2 + C_zH_yX_i \longrightarrow CO_2 + H_2O + X^-$$

where z, y, i denote the number of atoms in the compound.
X represents a halogen (for PCBs X = Cl)



Arochlor 1254 has a greater % of chlorination than many other PCBs. 54% chlorine.

Fentons reagent :

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\cdot + OH^-$$

$$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + HO_2\cdot + H^+$$

for organic reaction

$$RH + OH\cdot \longrightarrow R\cdot + H_2O$$

$$R\cdot + OH\cdot \longrightarrow ROH$$

Balancing the equation for PCBs is difficult because of the number of products that can be introduced such as:
chloroethane is used as an example for simplification.

$$3C_2H_5Cl + 4H_2O_2 \longrightarrow 2C_2H_5OH + 2CO_2\uparrow + 2H_2O + 3Cl^- + 8H^+$$

Then it must be noted that ethanol is not necessarily the final product which results in complete oxidation of the organic.

Water, carbon dioxide and chloride would be products of a complete reaction, there are several intermediate possibilities.

ATTACHMENT 10

ALTERNATIVE 10 SIMPLIFIED FLOW SHEET

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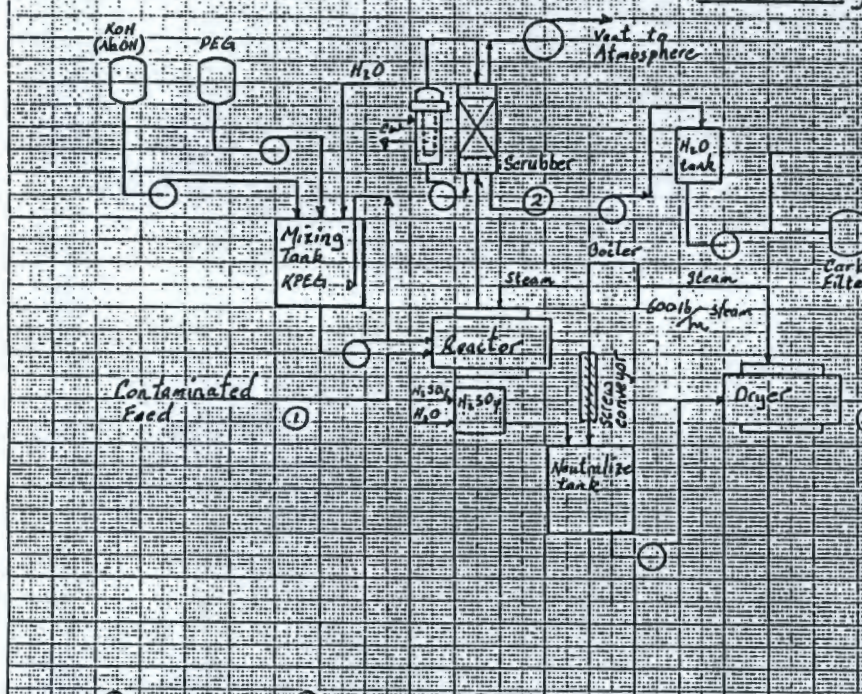
Alternative 10

Base Catalysed Destruction (BCD)

(KPEG depicted)



1	2	3
3400 lb solids	13.8 ppm PCB	15.87 ppm PCB
3778 ppm PCBs		

mixed in ~500 gal Reactor

see calculation page

Assumptions:

- Potassium Hydroxide (KOH) in conjunction with Polyethylene glycol (PEG) form a polymeric alkoxide referred to as KPEG (some applications use NaOH)
- Chemical equations in general terms:

$$KOH + AOH \rightarrow ROA + HO$$

$$ROA + ArCl_n \rightarrow ArCl_{n-1}OR + ACl$$

ROH – Polyethylene glycol
AOH – Potassium Hydroxide

ROA – KPEG ACl – KCl
$ArCl_n$ – PCB

- Batch Process
- Sulfuric Acid used to neutralize excess KOH

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$

- Cooling water cooling tower (not shown)

References:

- Conceptual Design & Estimate, Task # 89-C11A012 "Conceptual Design, cost estimation and Preliminary Plans for KPEG Process for Guam", B.C. Kim et al. Contract # DAAL03-86-D-001 Delivery Order 1368 Scientific Services Program.
- Base Catalysed Dechlorination http://kaos.erin.gov.au/portfolio/epa/environet/swtt/base.html

by Ivan G. Papp

ANALYSIS

For	Alternative 10	Page	1
Location		Job No.	
Subject	Base Catalysed Destruction (BCD)	Date	3-5-97
		By	I. G. Papp
		Checked By	Lal Poor 3/6/97

Relative mass and volume required for process.

from "Results of a field scale test of an APEG reactor for chemically degrading PCBs in contaminated soil" John Wentz et al, Naval Civil Engineering Lab, Port Hueneme, CA, 1989

$$(3400\ \text{lb soil})\left(\frac{3778\ \text{lb PCB}}{10^6\ \text{lb soil}}\right) = \underline{\underline{12.8\ \text{lb PCB}}}$$ (3778 ppm) originally contained in soil.

For each 1.5 yd³ of soil ~ 50 gal of condensate was collected.

13.8 ppm PCBs were discovered in condensate.

45 wt % KOH was used.

3400 lb of soil @ 3778 ppm PCB
1555 lb of PEG-400 — 400 avg mol wt.
285 lb of KOH

Lowest PCB destruction noted was 99.58%

Operational cost were reported @ $1700 – 1800/ton of PCB contaminated soil

$$(12.8\ \text{lb PCB})\left(\frac{\text{lbmol PCB}}{326\ \text{lb}}\right)\left(\frac{\text{lbmol KOH}}{\text{lbmol ROA}}\right)\left(\frac{56\ \text{lb KOH}}{\text{lbmol}}\right) = 2.1\ \text{lb KOH}$$ stoichiometric value for 1 Cl⁻ replacement (x S = 10.5)

S = # of Cl on molecule.

Aroclor 1254 →

$$(12.8\ \text{lb PCB})\left(\frac{\text{lbmol PCB}}{326\ \text{lb}}\right)\left(\frac{\text{lbmol ROH}}{\text{lbmol ROA}}\right)\left(\frac{400\ \text{lb}}{\text{lbmol}}\right) = 15.7\ \text{lb}$$ Poluethylene glycol stoichiometric for 1 Cl⁻ replacement (x S = 79)

Assuming an excess of 200 lb KOH:

H	1×1	1
S	1×32	32
O	4×16	64
		97

$$(200\ \text{lb KOH})\left(\frac{\text{lbmol KOH}}{56\ \text{lb KOH}}\right)\left(\frac{\text{lbmol } H_2SO_4}{2\ \text{lbmol KOH}}\right)\left(\frac{97\ \text{lb } H_2SO_4}{\text{lbmol}}\right)\left(\frac{\text{lb } 93\%}{.93\ \text{lb } H_2SO_4}\right)\left(\frac{\text{ft}^3}{114\ \text{lb}}\right)\left(\frac{7.48\ \text{gal}}{\text{ft}^3}\right) = \underline{\underline{12.2\ \text{gal } 93\%\ H_2SO_4}}$$

density of 93% @ 60°F

ATTACHMENT 11

ALTERNATIVE 11 SIMPLIFIED FLOW SHEET

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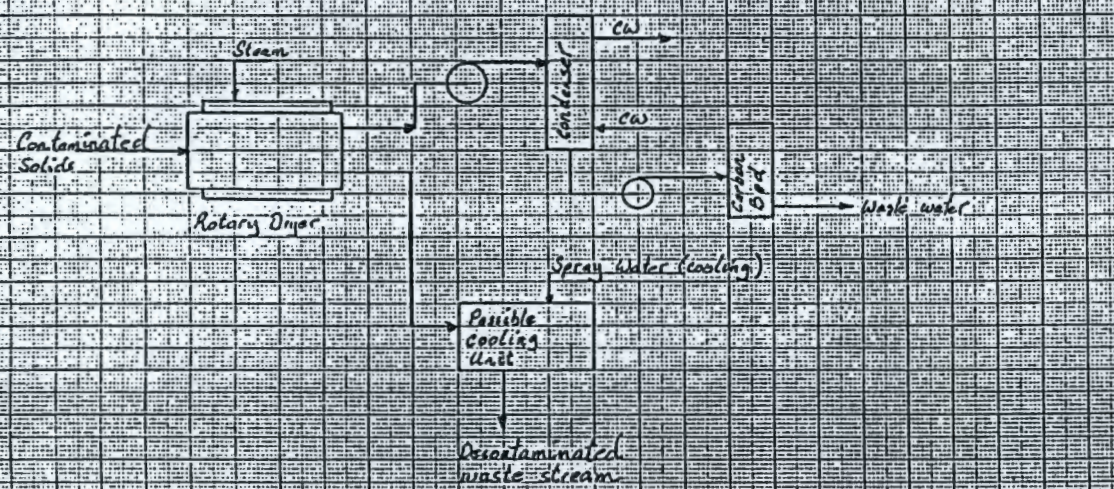
Alternative 11

Thermal Phase Separation



Assumptions:

- No destruction occurs
- Pressure & temp adjusted to facilitate vaporization
- Slight vacuum initiated in treatment vessel
- Batch operation

References:

- HazTech News Vol. 10 No. 13 "Thermal Process Employed to Remove PCBs & other contaminants from Solids"

by Ivan G. Papp

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ATTACHMENT 12

POLYCHLORINATED BIPHENYLS REGULATORY DISCUSSION

Polychlorinated biphenyls (PCBs) are a class of organic chemicals that had become widely used in industrial applications due to their practical physical and chemical properties. Historic uses of PCBs include dielectric fluids, hydraulic fluids, and other applications requiring stable, fire-retardant materials. Due to findings that PCBs may cause adverse health effects and due to their persistence and accumulation in the environment, the Toxic Substance Control Act (TSCA), enacted on October 11, 1976, banned the manufacture of PCBs after 1978 [section 6(e)]. The first PCB regulations include requirements specifying disposal methods and marking (labeling) procedures, and controlling PCB use. To assist the Department of Energy (DOE) in its efforts to comply with the TSCA statute and implementing regulations, the Office of Environmental Guidance has prepared the document "Guidance on the Management of Polychlorinated Biphenyls (PCBs)." That document explains the requirements specified in the statute and regulations for managing PCBs including PCB use, storage, transport, and disposal (1994 EH).

PCB materials that are no longer in use and have been declared waste must be disposed of according to the requirements found at 40 CFR 761.60. These requirements establish disposal options for a multitude of PCB materials including soil and debris, liquid PCBs, sludges and slurries, containers, transformers, capacitors, hydraulic machines, and other electrical equipment.

Wastes containing less than 50 ppm PCB must be disposed of in a responsible manner; that is, they may be disposed of in a municipal waste landfill or equivalent. When disposing of any PCB waste material, potential Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) liability should be a consideration.

The disposal of industrial sludges and slurries containing PCBs at concentrations less than 500 ppm should be disposed of in a TSCA incinerator or TSCA chemical waste landfill, or by an alternate EPA approved method.

In considering the above guidance, review of the WIPP WAC listed above, and by further review of the Hanford Site Solid Waste Acceptance Criteria (WHC-EP-0063) we can evaluate the disposal criteria for solid waste resulting from the concerns raised by Comment 3 in Table 3.

Criteria	Requirements/limit	Discussion of Compliance
Contact Dose Rate	<= 200 mrem/hr	
Thermal Power	Report if greater >0.1 watts/ft³	
Tru Alpha Activity	> 100nCi/gram waste matrix	
Pyrophoric materials	< 1% radionuclide pyrophorics or no nonrad pyrophorics	
Mixed waste	Characterize per QAPP and Table 3.4.2.3 WIPP WAC Limited to EPA Waste Codes listed in Table 3.4.2.3-2 WIPP WAC	
Chemical Compatibility	All Chemicals must be allowable per the CH-TRAMPAC	
Hazardous Constituents	Target analytes and TICs to be reported per the QAPP	
Explosives, Corrosives and Compressed Gases	No compressed gases No ignitable, reactive or corrosive wastes	
PCB Concentration	< 50 ppm	

ATTACHMENT 13

BENEFIT COMPARISON OF SPECIFIC DISPOSAL CRITERIA

Tabulation of combined benefits comparing Comments 3 and 10 from Table 4.

Evaluation of combined alternatives benefit

		Benefit associated with comment 3 from Table 5 -->										
	#3	1	2	3	4	5	6	7	8	9	10	11
#10		50	50	0	100	50	70	70	100	70	100	100
1	100	150	150	100	200	150	170	170	200	170	200	200
2	30	80	80	30	130	80	100	100	130	100	130	130
3	0	50	50	0	100	50	70	70	100	70	100	100
4	100	150	150	100	200	150	170	170	200	170	200	200
5	30	80	80	30	130	80	100	100	130	100	130	130
6	100	150	150	100	200	150	170	170	200	170	200	200
7	100	150	150	100	200	150	170	170	200	170	200	200
8	0	50	50	0	100	50	70	70	100	70	100	100
9	100	150	150	100	200	150	170	170	200	170	200	200
10	70	120	120	70	170	120	140	140	170	140	170	170
11	0	50	50	0	100	50	70	70	100	70	100	100

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ATTACHMENT 14

CAPITAL COST PER ITEM BREAKDOWN

Alternative 1 Capital Costs

Table 14-1. Alternative 1, Major Equipment. (2 Sheets)

Description	Cost (in thousands of U.S. 1997 Dollars)
Dissolver (250 gallon, SS)	45
Precipitation tank (800 gal, Stainless Steel [SS])	40
Rework tank (Optional equipment, rework might be accomplished with the precipitator) (500 gal, SS)	[30] Optional
Acid recovery tank w/ cooling coils etc. (400 gal, SS)	8
HEPA filter and preheater	40
Acid Absorber	50
Acid collection tank (100 gal, SS)	8
Scrubber	50
ventilation fan	18
fluid pumps (5)	150
Caustic tank (2500 gal, HDPE)	18
cooling tower	30
Instrumentation allowance	65
hot water heater (250 gallon)	2
silver reactor (silver nitrate, packed for off gas)	50
alpha monitor	45
area rad monitors	25
Sample sink	15
metering pumps (3)	3
Nitric acid storage tank (5,000 gal, SS)	60
Hydrogen peroxide Storage tank (2,500 gallon, HDPE)	18
Total	770

Table 14-1. Alternative 1, Major Equipment. (2 Sheets)

Description	Cost (in thousands of U.S. 1997 Dollars)
Definitive Design (engineering)	100
Construction -O/C	100
Project integration	40
ventilation ducting allowance	25
	1,035

Alternative 2 Capital Costs

Table 14-2. Alternative 2, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Reactor vessel (250 gal, Titanium)	400
Weighing table (for mixing chemicals) [vent and hood]	15
Propanol feed tank (5,000 gal polypropylene)	25
Cooling tower	30
vacuum pump (ventilation)	75
Condenser (vacuum system)	45
alpha monitor	45
area radiation equipment	25
Instrumentation allowance (process control)	60
Vacuum tank (250 gal, Titanium)	300
fluid pumps (3)	200
ventilation piping (vacuum)	15
caustic tank (2,500 gal, HDPE)	18
caustic metering pump (2)	2
Rework tank (Optional equipment, rework might be performed from precipitate tank) (1,000 gal, SS)	40
Allowance for titanium piping	90

Table 14-2. Alternative 2, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Sample sink	15
Silver Reactor	50
HEPA Filter	40
Scrubber	50
Hot Water heater	2
Ventilation fan	18
Total	1,560
Definitive Design (engineering)	100
Construction - O/C (site engineering etc)	100
Project Integration	40
Total	1,800

Alternative 3 Capital Costs

Table 14-3. Alternative 3, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Feed Staging Vessel (500 gal, SS)	30
Backwashable filter (for size segregation)	150
Dissolver vessel (2) (250 gal, SS)	90
Settling tank (1,000 gal, SS)	40
Slurry pump (4)	80
Precipitation vessel (TRU) (1,000 gal, SS)	40
Settling tank (1,000 gal, SS)	40
IX columns (2) with additional rad monitoring	20
TRU precipitation tank (500 gal, SS)	30
Final precipitation tank (1,000 gal, SS)	40
Caustic tank (2,500 gal, HDPE)	18

Table 14-3. Alternative 3, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Nitric acid tank (2,000 gal, SS)	60
Final settling tank (1,000 gal, SS)	40
Liquid waste staging tank (1,000 gal, SS)	40
LLW solids drum loading system (conveyor system)	100
Rework Tank (Optional equipment possibly performed from final pH Adj tank) (1,000 gal, SS)	40
Acid recovery tank (400 gal, SS)	35
HEPA filter and preheater	40
Acid Absorber	50
Acid collection tank (200 gal, SS)	20
Scrubber	50
ventilation fan	18
Instrument allowance	100
Hot water heater (250)	2
silver reactor	50
alpha monitor	45
area rad monitors	25
Sample sink	15
Metering pumps (5)	5
Fluid pumps (11) (with redundancy factored in)	330
Cooling tower	30
Total	1,673
Definitive design (engineering)	150
Construction -O/C	100
Project Integration	40
Total	1,963

Alternative 4 Capital Costs

Alternative 4 is comprised of a few varying scenarios. These all result in basically the same product but slight differences in the application of the technology are noted. The scenarios are defined previously in Table 2. These are roasting, steam oxidation, and dry oxidation. In each case the reaction is carried out in an oxidation vessel (or incinerator).

The steam oxidation system will take place in the same basic incinerator design as is used to accommodate the propane incineration system. Steam will be provided from a package boiler system that could produce about 650 pounds per hour of 150 psi steam. The inert cover gas provided to the dry oxidation process is not considered to be an added expense in design or construction from the roasting option because they both are equipped with nitrogen purge.

Table 14-4. Alternative 4, Major Equipment. (2 Sheets)

Description Descriptions are for major components (dollar values include labor to install)	Cost (in U.S. 1997 dollars) x 1,000
Material handling equipment in the form of a screw feeder. (2 @ 60K each)	120
Weighing equipment to determine feed mass.	67
Feed staging tank. (800 gal, SS)	90
Nitrogen purge system.	53
Propane delivery system.	75
Incinerator (steam oxidizer/dry roaster)	130
Ventilation fan	18
Product staging tank (800 gal, SS)	90
Pump for cooling water	12
Instrumentation allowance (process control not rad)	53
HEPA filter (2 @ 35 plus 5K additional installation allowance)	75
area rad monitors	25
Vacuum pumps for H&V system	75
Cooling Tower for closed loop cooling system	30
Baghouse for ventilation system (special containment equipment for particulate control)	200
Ventilation duct work	25

Table 14-4. Alternative 4, Major Equipment. (2 Sheets)

liquid transfer pump (cooling water)	30
Forklift (drum handling)	20
Sample prep table	50
Scrubber for off gas system	50
Alpha monitor	45
TOTAL	1,333
Definitive design (engineering)	100
Construction -O/C (site engineering etc)	100
Project Integration	40
TOTAL	1,573
Additional cost for dry oxidation system include resistance heaters for air introduction system	45 K + 1,573= 1,618
Additional cost for steam oxidation system includes package boiler	70 K + 1,573= 1,643

Alternative 5 Capital Costs

Table 14-5. Alternative 5, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars)
Reactor (250 gallon, titanium)	400
Air driven mixer	24
Settler/decanter (500 gal, SS)	41
Scrubber	50
HEPA filters	110
Demister	14
Air operated scrubber pump	11
Chemical injection pumps (2)	2
Cooling Water Pump	20
Cooling Tower	30
Ventilation monitoring System (chlorine, hydrogen, beta/gamma, alpha etc)	60

Table 14-5. Alternative 5, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars)
Expansion tank	3
Plate and Frame exchanger (700 BTU/min)	10
Recirculation pump	20
Instrumentation allowance (process control)	75
Ventilation ducting allowance	25
Area rad monitors	25
Sodium Hypochlorite storage tank (2,500 gal, HDPE)	18
Sodium Thiosulfate storage tank (2,500 gal, Aluminum)	30
Sulfuric Acid Storage tank (2,500 gal, HDPE)	18
Caustic Storage Tank (2,500 gal, HDPE)	18
chemical transfer pumps (4, SS)	120
Alpha Monitor	45
Sample sink	15
Hot water heater (250 gal)	2
Slurry Pump	20
Rework Tank (1,000 gal, SS)	40
Total	1,246
Definitive Design	100
Construction -O/C	100
Project Integration	25
Total	1,471

Alternative 6 Capital Costs

Table 14-6. Alternative 6, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000
Receiving/Reaction tank (3- 2,000 gal, SS)	180
CALROD Jacket heaters	6

Table 14-6. Alternative 6, Major Equipment. (2 Sheets)

Slurry transfer pumps	20
Instrumentation allowance	10
Shell and tube heat exchanger w/vacuum breaker	25
Cooling tower	30
Area rad monitors	25
Chemical storage tank (2,500 gal, HDPE)	18
Metering pump	1
Basket filter	3
Total	318
Definitive design (engineering)	40
Construction -O/C	20
Project Integration	8
Total	

Alternative 7 Capital Costs

Table 14-7. Alternative 7, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Dissolver (250 gal) (SS)	45
Acid recovery tank (100 gal, SS)	8
HEPA filter and preheater	40
Acid Absorber	50
Acid collection tank (100 gal, SS)	8
Scrubber	50
ventilation fan	18
Vacuum pump	75
Ventilation ducting	25
fluid pumps (4)	120

Table 14-7. Alternative 7, Major Equipment. (2 Sheets)

Caustic tank (2,500 gal HDPE)	18
Cooling tower	30
Instrumentation allowance	65
Hot Water Heater (250 gal)	2
Silver reactor (off gas)	50
alpha monitor	45
area rad monitors	25
Sample sink	15
metering pumps (4)	4
Caustic solution tank (50 gal HDPE)	1
Hydrogen peroxide tank (2,500 gal HDPE)	18
Dilution tank (1,000 gal, SS)	40
Oxidation tank (800 gal, SS)	40
pH Adjustment / optional rework tank (1,000 gal, SS)	40
Fluid pumps (4) (redundancy factored in)	120
Nitric Acid Storage tank (2,500 gal, SS)	60
Total	1,012
Definitive Design (engineering)	100
Construction -O/C	100
Project Integration	40
Total	1,252

Alternative 8 Capital Costs

Table 14-8. Alternative 8, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Centrifuge	50
Fluid Pumps (3) (redundancy factored in)	90
Hexane tank (600 gallon, polypropylene or aluminum)	8

Table 14-8. Alternative 8, Major Equipment. (2 Sheets)

Solution tank (1,000 gal, SS)	40
Instrumentation allowance	17
Area radiation monitors	25
Total	225
Definitive design	15
Construction -O/C	3
Project Integration	2
Total	245

Alternative 9 Capital Costs

Table 14-9. Alternative 9, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Sludge Staging Vessel (500 gal, SS)	30
Peroxide injection tank (2,500 gal, HDPE)	18
Chemical Injection tank (2, 2,500 gal, HDPE)	36
Metering pump (3)	3
Lay up peroxide destruction vessel (optional) (1000 gal SS)	40
Slurry pumps (3)	60
ventilation piping allowance	10
Vent blower	18
HEPA filter	30
area radiation monitors	25
alpha stack monitor	45
Total	315
Definitive Design	45
Construction -O/C	30
Project Integration	20
Total	410

Alternative 10 Capital Costs

Table 14-10. Alternative 10, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
Mixing Tank (feed tank) (1,000 gal, SS)	40
PEG tank (2,500 gal, HDPE)	18
KOH/NaOH tank (2,500 gal, HDPE)	18
Reactor	200
Screw conveyor (6 ft)	20
Neutralization tank (optional) (1,000 gal, SS)	40
Dryer (optional)	85
Slurry pump on Neutralization tank (optional)	20
Package boiler	70
Ventilation fan	18
Duct work allowance	20
instrumentation allowance	45
Heat exchanger (off gas system) (SS)	20
Cooling tower	30
Scrubber (off gas) (SS)	50
Fluid pumps (4)	120
Slurry pump for mixing tank	20
Sulfuric Acid Tank (optional) (1000 gal, HDPE for 30wt% H2SO4)	12
Water condensate tank (600 gal, HDPE)	10
GAC Vessel (600 gal, HDPE)	10
Area radiation monitors	25
Alpha monitor	45
Sample sink	15
HEPA filter (off gas)	30

Table 14-10. Alternative 10, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars x 1,000)
GAC handling system (pressurized air and vacuum system)	5
Total	986
Definitive design (engineering)	60
Construction -O/C	45
Project integration	25
	1,116

Alternative 11 Capital Costs

Table 14-11. Alternative 11, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars)
Rotary drier	75
Screw conveyor (6 ft)	20
Cooling unit (possible) (slurry mixing tank) (800 gal, SS)	40
Ventilation piping Allowance	10
alpha monitor	45
ventilation condenser	45
Ventilation fan	18
Cooling tower	30
fluid pump	30
Granular Activated Carbon (GAC) bed (600 gallon, HDPE)	10
Instrumentation allowance	35
Area radiation monitors	25
GAC Handling system (pressurized air and vacuum system)	5
Package boiler	70
Duct work allowance	20

Table 14-11. Alternative 11, Major Equipment. (2 Sheets)

Description	Cost (in U.S. 1997 dollars)
Scrubber (off gas) (SS)	50
HEPA Filter (off gas)	30
Total	558
Definitive Design (engineering)	20
Construction -O/C	10
Project Integration	5
Total	593

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ATTACHMENT 15

FLOWSHEET 1

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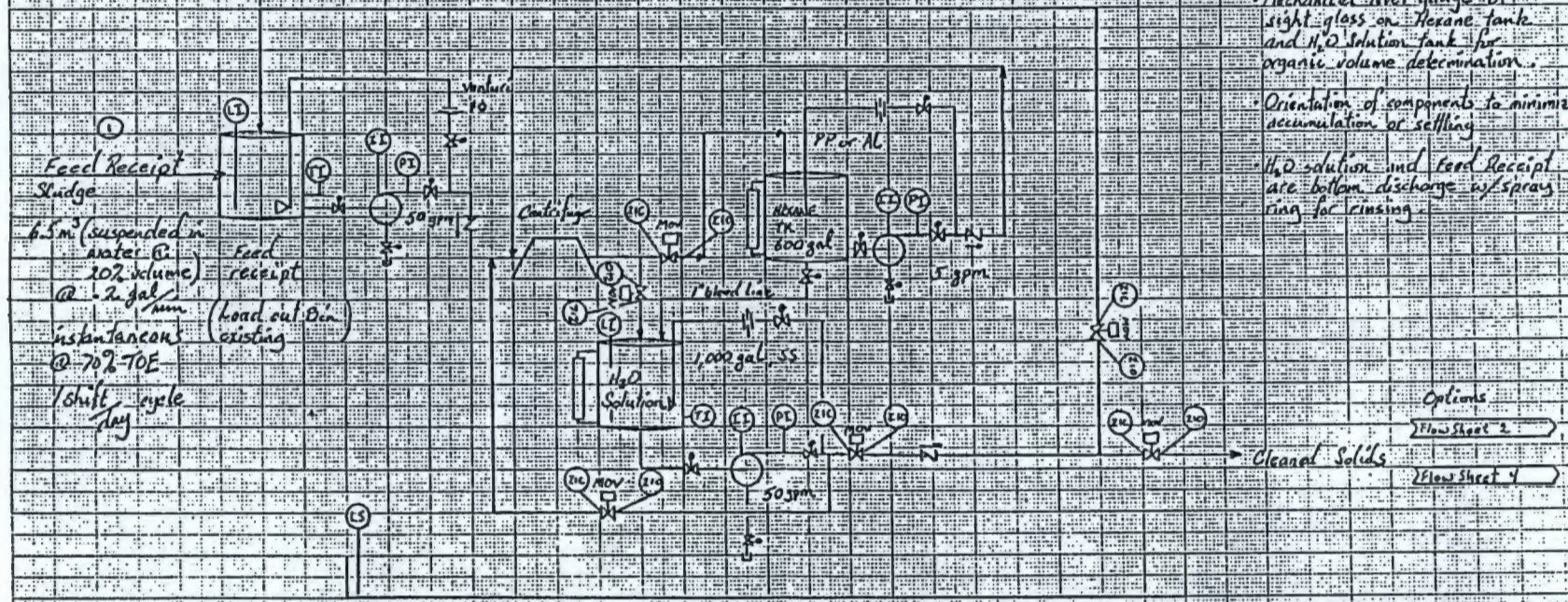
Flow Sheet 1.

PCB Washing



Assumptions:

- All transfer lines are 1 in diameter.
- Pumps are sized for max velocity in 1" line.
- H_2O Solution tank sized to allow retention of organic carry over.
- Mechanical level gauge or sight glass on Hexane tank and H_2O Solution tank for organic volume determination.
- Orientation of components to minimize accumulation or settling.
- H_2O solution and feed receipt are bottom discharge w/ spray ring for rinsing.

by Ivan G. Papp 3-13-97

47 1510

IGP Ivan G. Papp
Chemical Engineer

ANALYSIS

Page	1
Job No.	
Date	3-14-97
By	I.G. Papp
Checked By	K.H. Pool 3/19/97

For: Flow Sheet 1
Location:
Subject: Sludge Washing w/ Hexane

Feedstream ①

$$\frac{(6.5\,m^3)\left(\frac{gal}{.003785\,m^3}\right)\left(\frac{m^3\ solution}{.2\,m^3\ Sludge}\right)}{(7\,months)\left(\frac{22\,day}{1\,month}\right)\left(\frac{5\,hr}{1\,day}\right)\left(\frac{60\,min}{1\,hr}\right)} = .2\ \frac{gal}{min}$$

instantaneous feed rate

.13 gal/min Avg.

Assuming a 70% TOE over a 10 month cyle = 7 months, instantaneous

5 hrs / day in 1 shift cycle

calculation dilution of waste

$$^{239}Pu = \left(110\ \frac{Ci}{tonne}\right)\left(\frac{g}{6.2\times10^{-2}\,Ci}\right) = 1{,}774\ \frac{g}{tonne}\ ^{239}Pu$$

$$^{241}Pu = \left(2744\ \frac{Ci}{tonne}\right)\left(\frac{g}{103.0\,Ci}\right) = 26.6\ \frac{g}{tonne}\ ^{241}Pu.$$

$$1{,}800\ \frac{g}{tonne}\ Pu$$

$$^{137}Cs = \left(5788\ \frac{Ci}{tonne}\right)\left(\frac{g}{86.6\ Ci}\right) = 66.8\ \frac{g}{tonne}\ ^{137}Cs$$

$$^{90}Sr = \left(4552\ \frac{Ci}{tonne}\right)\left(\frac{g}{139\ Ci}\right) = 32.8\ \frac{g}{tonne}\ ^{90}Sr.$$

$$U = 19.05\ SpG \qquad (19.05)\left(\frac{62.4\ lb}{ft^3}\right)\left(\frac{35.3\ ft^3}{m^3}\right) = \frac{41{,}962\ lb\ U}{m^3}$$

$$\left(\frac{41{,}962\ lb}{m^3}\right)\left(\frac{tonne}{2204.6\ lb}\right) \cong \frac{19\ tonnes\ U}{m^3}$$

$$(6.5\,m^3)\left(\frac{19\ tonnes\ U}{m^3}\right) = 124\ tonnes\ U$$

$$(124\ tonnes)\left(\frac{1{,}777\ g\ Pu}{tonne}\right) = 220{,}348\ g\ Pu\ total.$$

54-7400-276 (2/88)

IGP Ivan G. Papp
Chemical Engineer

ANALYSIS

Page 2
Job No.
Date 3-14-97
By I. G. Papp
Checked By K. H. Pool 3/19/97

For Flow Sheet 1
Location
Subject Sludge Washing w/ Hexane

@ $(220{,}348\ g\ Pu)\left(\frac{gal}{.05\ g}\right) = 4.4 \times 10^6$ gal to transfer $6.5\ m^3$ of (initial volume metalic fuel. (as worst case if all $6.5\ m^3$ were metalic fuel)

Volume produced from processing:

Assuming transfers are made into washing mechanism with 20% metalic components on a volume % basis.

$$(6.5\ m^3)\left(\frac{gal}{.003785\ m^3}\right)\left(\frac{m^3\ solution}{.2\ m^3}\right) = 8{,}587 \text{ gal transfer vol.}$$

416 galons of Nitric used for 1 tonne of Fuel

on a $\underbrace{1.4\ lbs\ Fuel}_{liter\ HNO_3\ 10\ M}$ basis as $\left(\frac{1\ liter\ Nitric}{1.4\ lbs}\right)\left(\frac{2204.6\ lb}{tonne\ U}\right)\left(\frac{gal}{3.785\ lit}\right) = 416$ gal $10.4M\ HNO_3$

Ref: PUREX TECH MANUAL WHC-SP-0479

$$(6.5\ m^3)\left(\frac{19\ tonnes}{m^3}\right)\left(\frac{416\ gals\ HNO_3}{tonne}\right) = \underline{51{,}381\ gal\ HNO_3} \text{ for 124 tonnes of Fuel}$$

from Alternative 1: 350 gal 50wt% NaOH needed per tonne

$$(124 \text{ tonnes of Fuel})\left(\frac{350\ gal\ 50wt\%\ NaOH}{tonne}\right) = 43{,}400 \text{ gal } 50\%\ NaOH$$

$$(43{,}400\ gal) + (51{,}381\ gal) \approx \underline{95{,}000\ gal} \text{ Volume from processing}$$

This plus another 10,000 transfer feed volume (105,000 gal total) is still well below the 4.4×10^6 ~~gals~~ for .013 g/lit Criticality limits

SA-7400-276 (2 88)

IGP Ivan G. Papp
Chemical Engineer

ANALYSIS

For: Flow Sheet 1
Location:
Subject: Sludge Washing w/ Hexane

Page: 3
Job No.:
Date: 3-14-97
By: I. G. Papp
Checked By: K. H. Pool 3/19/97

For $70 m^3$* of total sludge material a flow rate would be calculated as:

* Estimated total sludge volume

$$\frac{(70 m^3)\left(\frac{gal}{.003785 m^3}\right)\left(\frac{m^3 \text{ solution}}{.2 m^3 \text{ Sludge}}\right)}{(7 \text{ months})\left(\frac{22 \text{ day}}{\text{month}}\right)\left(\frac{5 hr}{day}\right)\left(\frac{60 min}{hr}\right)} = 2.0 \frac{gal}{min} \text{ Instantaneous}$$

$1.4 \frac{gal}{min}$ Average

based on 70% TBE over 10 month cycle and $\frac{5 hr}{day}$ in 1 shift.

20% volume basis was chosen to correspond with transfer volume of transport cask. This value may have to be adjusted to compensate equipment.

PCB mass @ 200 ppm is:

$$\left(\frac{200 \text{ lb PCB}}{10^6 \text{ lb Sludge}}\right)\left(\frac{3,744 \text{ lb Sludge}}{m^3}\right)(70 m^3 \text{ sludge}) = 52.4 \text{ lb PCB}$$

for $6.5 m^3$

$$\frac{52.4}{70}(6.5) = 4.9 \text{ lb PCB}$$

for 600 gallons of Hexane: PCB concentration is:

SpG = .66 $\Rightarrow (.66)(8.34 \frac{lb}{gal}) = 5.5 \frac{lb \text{ Hexane}}{gal}$

$$(600 gal)\left(\frac{5.5 \text{ lb Hexane}}{gal}\right) = 3,300 \text{ lb}$$

for $70 m^3$: $\frac{52.4 \text{ lb PCB}}{3,300 \text{ lb}} \approx 16,000 \text{ ppm}$

For $6.5 m^3$: $\frac{4.9}{3,300} \approx 1,480 \text{ ppm}$

ATTACHMENT 16

FLOWSHEET 2

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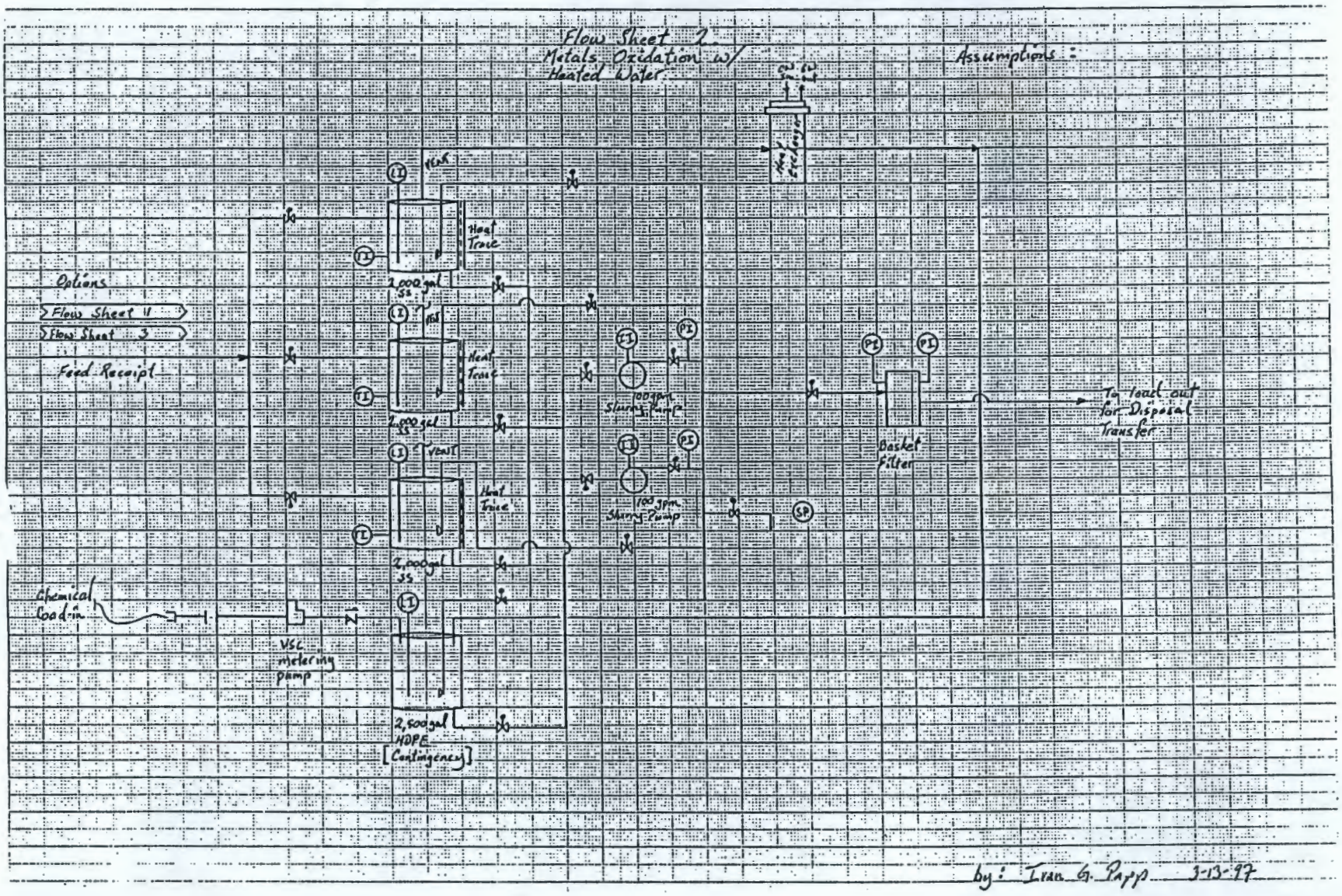
Flow Sheet 2
Metals Oxidation w/
Heated Water
Assumptions:
Options
Flow Sheet 1
Flow Sheet 3
Feed Receipt
Heat Trace
2,000 gal SS
VENT
2,000 gal SS
100 gpm Slurry Pump
Basket Filter
To load out for Disposal Transfer
Chemical Cond-in
VSC metering pump
2,500 gal HDPE [Contingency]
by: Ivan G. Papp 3-13-97

IGP Ivan G. Papp
Chemical Engineer

ANALYSIS

For: Flow sheet 2
Location:
Subject: Metal Oxidation w/ heated water

Page: 1
Job No.:
Date: 3-14-97
By: I.G. Papp
Checked By: K.H. Pool 3/19/97

Particle size in feed basis is ≈ ¼ inch. A particle of ¼ in in diameter (⅛ in radius) is observed to oxidize at 1.5 microns in 1 hour @ 100°C (1993a LANL).

⅛" = .125"

$$(.125\text{ in})\left(\frac{25{,}400\text{ micr}}{1\text{ in}}\right)\left(\frac{\text{hr}}{1.5\text{ micr}}\right)\left(\frac{\text{day}}{24\text{ hr}}\right) = 88\text{ days} \approx 3\text{ months}$$

LANL

@ 50°C $\frac{.035\text{ microns}}{\text{hr}}$ observed (1993a LANL)

$$(.125\text{ in})\left(\frac{25{,}400\text{ micr}}{1\text{ in}}\right)\left(\frac{\text{hr}}{.035\text{ micr}}\right)\left(\frac{\text{day}}{24\text{ hr}}\right)\left(\frac{\text{month}}{30\text{ day}}\right)\left(\frac{\text{yr}}{12\text{ month}}\right) = 10.5\text{ yrs}$$

SNF

@ 50°C $\left(\frac{1.39\times10^{-5}\text{ cm}}{\text{day}}\ \frac{\text{in}}{2.54\text{ cm}}\right) = \frac{5.46\times10^{-6}\text{ in}}{\text{day}}$ SNF data

$$(.125\text{ in})\left(\frac{\text{day}}{5.46\times10^{-6}\text{ in}}\right)\left(\frac{\text{month}}{30\text{ day}}\right)\left(\frac{\text{yr}}{12\text{ month}}\right) = 63.5\text{ yrs.}$$

@ 100°C $\left(\frac{3.125\times10^{-5}\text{ cm}}{\text{day}}\right)\left(\frac{\text{in}}{2.54\text{ cm}}\right) = \frac{1.23\times10^{-5}\text{ in}}{\text{day}} = \frac{.013\text{ microns}}{\text{hr}}$

$$(.125)\left(\frac{\text{day}}{1.23\times10^{-5}}\right)\left(\frac{\text{months}}{30\text{ day}}\right)\left(\frac{\text{yr}}{12\text{ months}}\right) = 28\text{ yrs.}$$

It is noted that a significant difference (2 orders of magnitude) is indicated between SNF data and LANL data. Verification of this data should be conducted for application to this process.

54-7400-276 (2/88)

ATTACHMENT 17

FLOWSHEET 3

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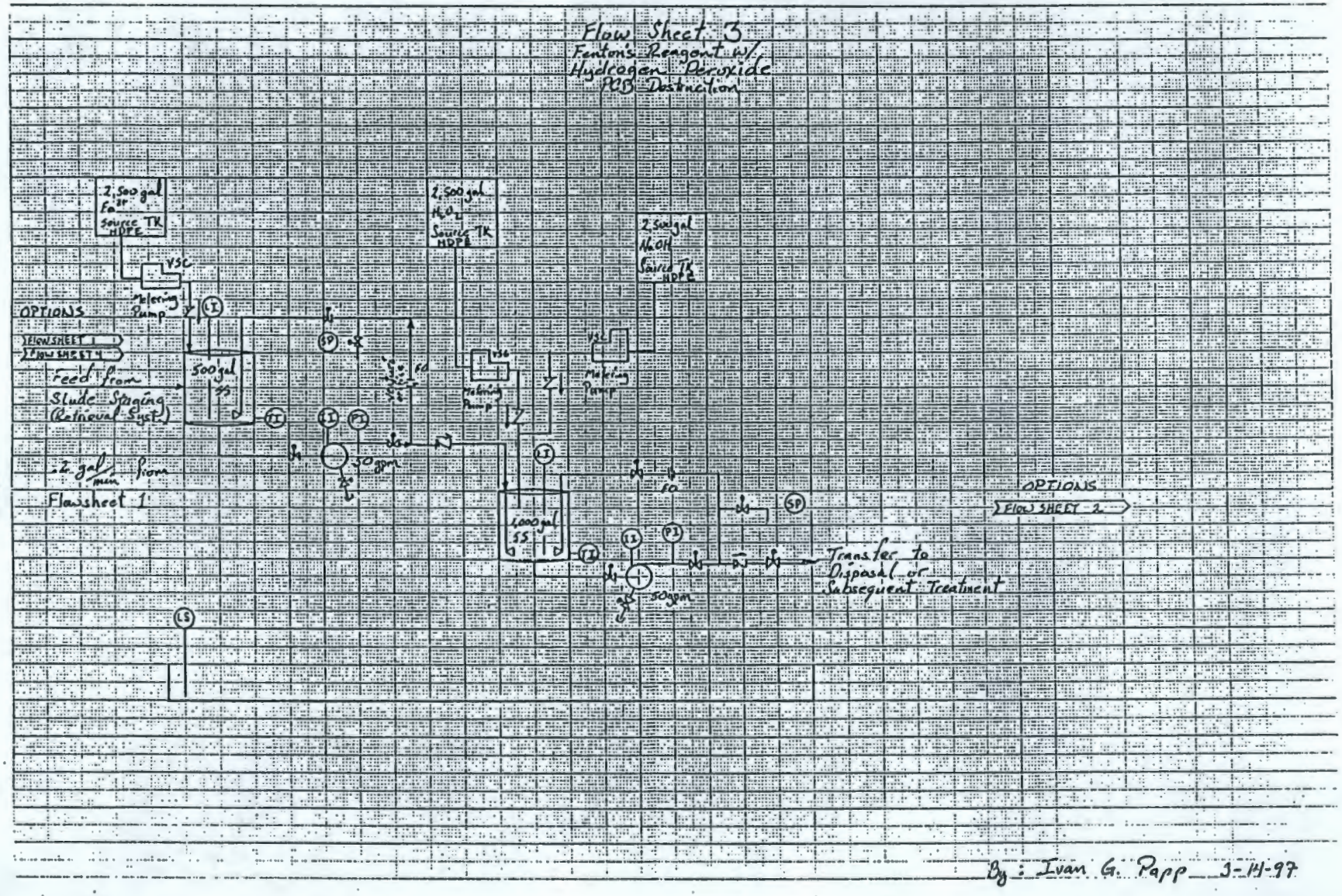
Flow Sheet 3
Fenton's Reagent w/
Hydrogen Peroxide
PCB Destruction
2,500 gal
Fe 2+
Source TK
HDPE
VSC
Metering Pump
OPTIONS
FLOWSHEET 1
FLOWSHEET 4
Feed from
Slude Staging
(Retrieval System)
2 gal/min from
Flowsheet 1
500 gal
SS
50 gpm
2,500 gal
H2O2
Source TK
HDPE
VSC
Metering Pump
2,500 gal
NaOH
Source TK
HDPE
VSC
Metering Pump
1,000 gal
SS
50 gpm
OPTIONS
FLOW SHEET 2
Transfer to
Disposal or
Subsequent Treatment
By: Ivan G. Papp 3-14-97

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ATTACHMENT 18

FLOWSHEET 4

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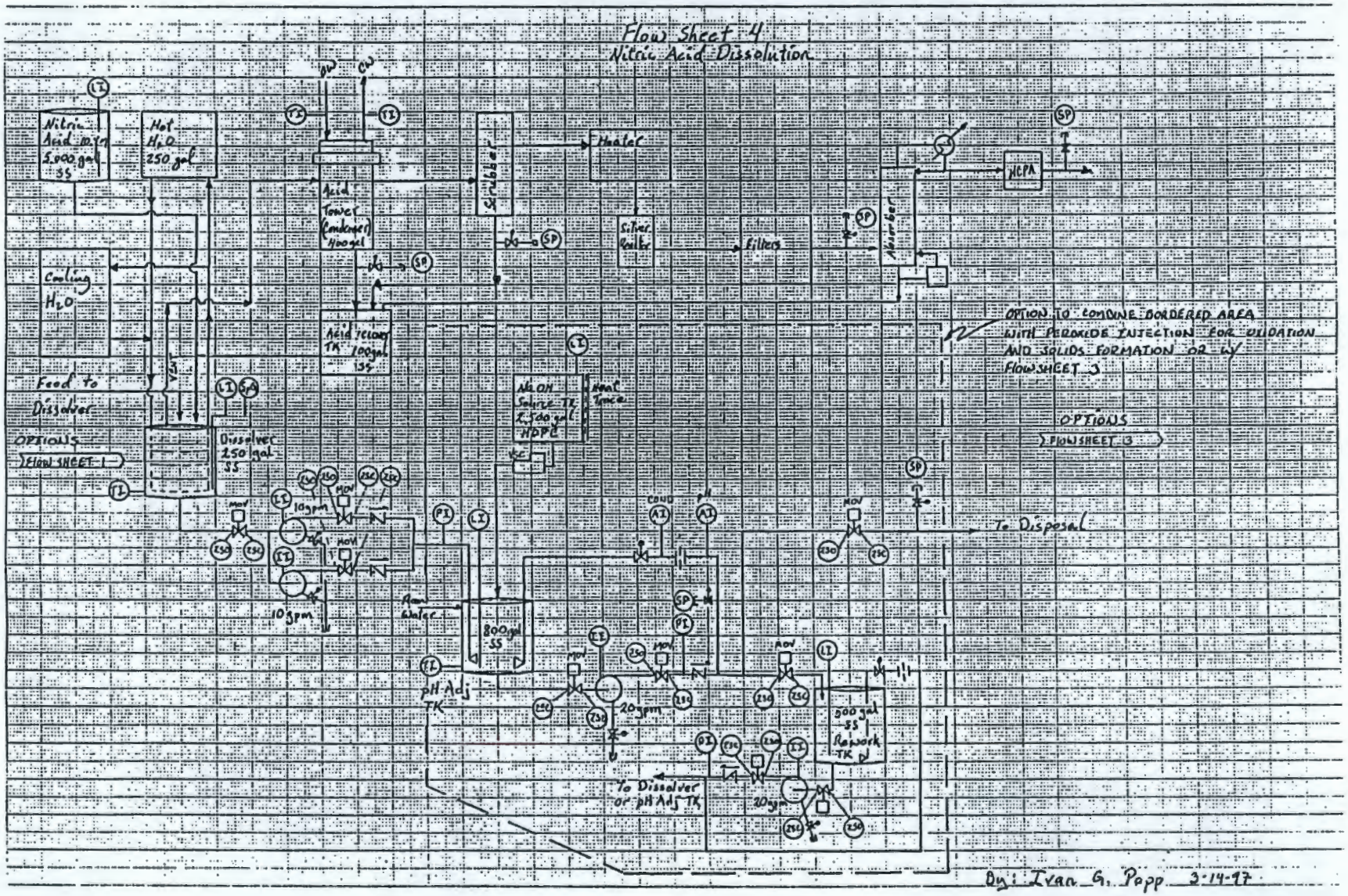
Flow Sheet 4
Nitric Acid Dissolution
Nitric Acid 10 M 5,000 gal SS
Hot H2O 250 gal
Cooling H2O
Feed to Dissolver
OPTIONS
FLOW SHEET 1
Dissolver 250 gal SS
Acid Tower (Condenser) 1000 gal
Acid Tower TK 1000 gal SS
Scrubber
Heater
Silver Reactor
Filters
Absorber
HEPA
NaOH Solution TK 2,500 gal HDPE
Heat Trace
10 gpm
Raw Water
800 gal SS
pH Adj TK
20 gpm
To Dissolver or pH Adj TK
900 gal SS Rework TK
OPTION TO COMBINE BORDERED AREA WITH PEROXIDE INJECTION FOR OXIDATION AND SOLIDS FORMATION OR W/ FLOWSHEET 3
OPTIONS
FLOWSHEET 3
To Disposal
By: Ivan G. Papp 3-14-97

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ATTACHMENT 19

TANK WASTE REMEDIATION SYSTEM COMMENT RESOLUTION

NOTE - Alternative 3 is not evaluated in this table partly because there was not enough vendor information available to perform an evaluation. The relative result from that process would yield a product similar to alternative 1 but with more steps required. The final waste form from that alternative is more suited for solid waste disposal similar to Alternative 4, again with additional steps required.

Table 19-1. Evaluation of Chemical Processes. (5 Sheets)

Alternative	Comparison against TWRS Comments.	Weighted value (%)
1) Nitric Dissolution w/ caustic precip	Comment 2. This alternative lends itself very well to the adjustment of the final product stream. Chemical adjustment to raise the pH will be performed to cause precipitation of solids and ensure the required particle size.	100
	Comment 3. No treatment for PCBs is taken credit for in the dissolution process. The process itself does; however, lend itself (by chemical compatibility) to PCB treatment as a follow up step or a pretreatment option.	50
	Comment 4. Mobilization of solids will be compatible with existing AW-105 waste. Particles currently in the tank will be of the same characteristics for fluidization as the particles resulting from this alternative. Since the drag forces on the particles in the tank currently are expected to be the same as those resulting from this alternative the ability to suspend the particles in solution should not change. This alternative will add more solids to the tank and thus increase the overall loading of solids requiring a need to evaluate mixing times and transfer velocities.	70
	Comment 5. The final product stream can be adjusted to account for the requirements based on the referenced documents. This adjustment does not create an additional processing step because of the allowance for final product adjustment. It is noted that a review to increase the limits for transfer will be requested to minimize the total volume of product.	100
	Comment 10. The compatibility of the product stream will be evaluated for compatibility; however, the nature of the process is very similar to processes which have discharge to the AW-105 tank in the past.	100
	Comment 11. This alternative produces a particle size and constituents compatible with existing tank waste. It does add to the current inventory of solids.	70

Table 19-1. Evaluation of Chemical Processes. (5 Sheets)

Alternative	Comparison against TWRS Comments.	Weighted value (%)
2) Dissolution with I2 and alcohol	Comment 2. The final product solution can be adjusted with caustic but nitrites are not present. The chemistry of interactions with the tank farm requirements is not clear. The particle size of the product stream is also not determined.	0
	Comment 3. Washing of the particulates is anticipated to be a viable option in treating the PCBs. The product form should lend itself to PCB treatment with hexane. The dissolution steps; however are not credited with treatment of PCBs.	50
	Comment 4. The product particle size is not determined from available info nor are the particle characteristics.	0
	Comment 5. The product stream will be adjusted in the final step of the proposed process. No additional steps will be required.	100
	Comment 10. It is not known what affect the supernatant will have on the existing TWRS inventory based on available info. The precipitate compatibility should not adversely impact the existing waste chemically.	30
	Comment 11. The impact of vitrifying the product stream is not known at this time based on the available info.	0
4) Dry oxidation or incineration	Comment 2. Transfer of the product resulting from the incineration options to TWRS would require an additional step which provides final adjustment of the product to meet the requirement of this comment.	70
	Comment 3. PCB contamination would be eliminated from the feed material during the incineration process which has been a technically and regulatory accepted method of destroying PCBs.	100
	Comment 4. The information relating to this comment indicates the particle size will be greater than 20 microns but the size range is not determinable with the available information.	30
	Comment 5. The TWRS criteria for fissionable material will not be exceeded by this alternative. Product streams will be adjusted to maintain inventory control.	100
	Comment 10. The product stream resulting from this alternative should not pose any chemical compatibility issues with the solids formed as oxides.	100
	Comment 11. Vitrification impacts are not known at this time based on the available particle size information and particle characteristics.	30

Table 19-1. Evaluation of Chemical Processes. (5 Sheets)

Alternative	Comparison against TWRS Comments.	Weighted value (%)
5) Wet oxidation w/ Bleach	Comment 2. The product streams can be adjusted in the final step to accommodate the concerns raised by this comment. It is noted; however, that there are more than one product streams resulting from this option. This fact results in an increase of the overall volume of waste transferred.	70
	Comment 3. Treatment of PCBs can be accommodated by this alternative even though the process itself is not likely to treat PCBs.	50
	Comment 4. Mobilization will require further evaluation due to the amount of sodium chloride produced by the reaction. It is understood that a number of salts are present within the TWRS inventory but the effect of this product stream is not know based on the available information.	30
	Comment 5. The product stream from this alternative can be adjusted to meet the radionuclide limits imposed on fissile material and other radionuclides. No additional steps are required.	100
	Comment 10. The compatibility of the supernatant with existing tank waste is not known based on the available information. No adverse compatibility is expected from the solids.	30
	Comment 11. The impacts related to the vitrification process are undetermined at this time based on available information. Particle size is within the acceptable range.	30
6) Wet oxidation contact w/ water	Comment 2. The final waste form will require adjustment to meet the requirements identified by this comment.	70
	Comment 3. The final solids can be treated for PCB contamination by a pretreatment step or a final treatment step.	70
	Comment 4. Mobilization of particles is expected to be the same as the existing sludge. These particles have been analyzed and observed in the 20 micron size range. The requirement is that the particles be less than 177 microns in size.	100
	Comment 5. Adjustment of the final product stream can be made to account for fissile material concerns. The loading of other radionuclides can also be accounted for in the overall inventory calculation.	70
	Comment 10. Compatibility is expected to be favorable with the oxides formed. The compatibility of the supernatant is also expected to be favorable.	100
	Comment 11. Impacts to vitrification should be minimal based on the oxide formation. No other constituents outside the current inventory of the TWRS is expected.	70

Table 19-1. Evaluation of Chemical Processes. (5 Sheets)

Alternative	Comparison against TWRS Comments.	Weighted value (%)
7) Dissolution w/ hydrogen peroxide oxidation	Comment 2. Oxidation with peroxide should result in a final product stream which is compatible with the requirements of this comment. This alternative is performed in conjunction with dissolution as prescribed by Alternative 1.	70
	Comment 3. There is a possibility that peroxide in this solution will affect the PCB concentration. The total effect is not known at this time based on the available information. Additional PCB treatment can be added to provide supplementary destruction. More chemical loading may be required by the addition of a catalyst.	70
	Comment 4. The characteristics of the hydrate formed by this alternative are not completely understood at this time based on the available information.	30
	Comment 5. The final product stream can be adjusted to meet radionuclide loading restrictions.	70
	Comment 10. Compatibility of the product stream is not expected to have adverse impacts on the current tank waste.	100
	Comment 11. Chemical compatibility with the vitrification plants is deemed acceptable.	70
8) Solvent extraction of PCBs w/ hexane	Comment 2. This alternative has no effect with respect to this comment.	0
	Comment 3. PCBs should be effectively removed from the sludge components by this method.	100
	Comment 4. This alternative has no effect with respect to this comment.	0
	Comment 5. This alternative has no effect with respect to this comment.	0
	Comment 10. This alternative has no effect with respect to this comment.	0
	Comment 11. This alternative has no effect with respect to this comment.	0
9) Treatment of PCBs with peroxide.	Comment 2. Oxidation with peroxide should result in a final product stream which is compatible with the requirements of this comment. The kinetics of this reaction are not fully understood with respect to the impact on metalic components.	0
	Comment 3. It is expected that peroxide in this solution will affect the PCB concentration. The total effect is not known at this time based on the available information. Additional PCB treatment can be added to provide supplementary destruction. More chemical loading is required by addition of Fenton's reagent.	70
	Comment 4. The characteristics of the product formed by this alternative are not completely understood at this time based on the available information. Addition of iron ions may be advantageous from a criticality perspective.	30
	Comment 5. The final product stream can be adjusted to meet radionuclide loading restrictions.	70
	Comment 10. Compatibility of the product stream is not expected to have adverse impacts on the current tank waste.	100
	Comment 11. Chemical compatibility with the vitrification plants is deemed acceptable.	70

Table 19-1. Evaluation of Chemical Processes. (5 Sheets)

Alternative	Comparison against TWRS Comments.	Weighted value (%)
10) Base Catalyzed Destruction	Comment 2. Transfer of the product resulting from the BCD option to TWRS would require an additional step (to deal with resulting organics) which provides final adjustment of the product to meet the requirement of this comment. This also introduces an additional waste stream.	60
	Comment 3. PCB contamination would be eliminated from the feed material during the BCD process and this process has been a technically and regulatory accepted method of destroying PCBs; however, applicable references did not necessarily deal with the small concentrations of PCB found in the sludge.	100
	Comment 4. The particle size relating to this comment is not determinable with the available information. It may be expected that some metal oxidation product could be produced but the extent is not yet verifiable.	20
	Comment 5. The TWRS criteria for fissionable material will not be exceeded by this alternative. Product streams will be adjusted to maintain inventory control. Additional loading is expected by the final adjustment of the waste stream.	30
	Comment 10. The product stream resulting from this alternative should not pose any chemical compatibility issues with the solids formed as oxides or hydroxides. There may be some consideration given for final determination to identify residual organics in the product stream.	70
	Comment 11. Vitrification impacts are not known at this time based on the available particle size information and particle characteristics.	0
11) Thermal Phase Separation	Comment 2. This alternative has no effect with respect to this comment.	0
	Comment 3. PCBs should be effectively removed from the sludge components by this method.	100
	Comment 4. This alternative has no effect with respect to this comment.	0
	Comment 5. This alternative has no effect with respect to this comment.	0
	Comment 10. This alternative has no effect with respect to this comment.	0
	Comment 11. This alternative has no effect with respect to this comment.	0

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DISTRIBUTION SHEET

To	From	Page 1 of 1
Distribution	I. G. Papp, Numatec Hanford Corporation	Date 4/3/97
Project Title/Work Order		EDT No. 617610
Evaluation to Disposition Components of K Basin Fuel Sludge, HNF-SD-SNF-ES-024, Rev. 0		ECN No. --

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
Central Files	A3-88	X			
DOE Reading Room	H2-53	X			
SNF Project Files	X3-85	X			
<u>DE&S Hanford, Inc.</u>					
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<u>Pacific Northwest National Laboratory</u>					
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