**16th DOE NUCLEAR AIR CLEANING CONFERENCE**

CONF-801038--6

# INCINERATION OF CONTAMINATED ORGANIC SOLVENTS IN A FLUIDIZED-BED CALCINER

**MASTER**

R. E. Schindler
Exxon Nuclear Idaho Co., Inc.
Idaho Falls, Idaho

## Abstract

The reprocessing of expended reactor fuels at the Idaho Chemical Processing Plant (ICPP) generates contaminated organic solvents. An evaluation of potential management alternatives shows that several are suitable for management of contaminated solvents containing tri-butyl phosphate (TBP):

1) The solvent could be burned in a commercially-available burner which absorbs the phosphorus on a fluidized-bed of limestone leaving a solid product for burial.

2) The solvent could be burned in a small fluidized-bed calciner which solidifies non-radioactive feed by in-bed combustion of the contaminated solvent. The fluidized-bed absorbs the phosphate forming a solid product for burial.

3) The solvents could be solidified with a gel or sorbant for burial if the reprocessing system were modified to reduce the solvent volume.

4) The contaminated solvent could be burned in an existing fluidized-bed calciner designed for solidifying high-level aqueous wastes.

Burning the solvent in the existing calciner was selected for process verification because it provides an existing burner, off-gas system, and solids transfer and storage system. No additional wastes are generated.

A set of four pilot-plant tests verified the absence of adverse effects from the phosphorus in the fuel when calcining simulated ICPP aqueous wastes. Essentially all of the phosphorus remained in the calcined solids with only a neglegible quantity remaining in the scrubbed off-gas. Combustion efficiency was high (93-96%). There were no observable adverse effects on solids in the scrubbing system, corrosion rates, or solids flowability (for retrieval).

Conclusions of general applicability are: 1) alternative technologies are available for disposal of contaminated solvents, and 2) the use of an existing fuel-using facility, e. g., calciner or incinerator--designed for contaminated wastes will usually be cost effective.

## I. Introduction

The aqueous reprocessing of expended fuel elements at the Idaho Chemical Processing Plant (ICPP) leaves contaminated organic solvents requiring disposal or management. The solvents from a fuel reprocessing campaign are: 1) about 2 $m^3$ of extraction solvent consisting of 6% tri-butyl phosphate (TBP) in dodecane (30% TBP may be used in the future) contaminated with transuranics, fission products, and degradation products, and 2) 10 to 30 $m^3$ of washing solvent consisting of AMSCO (kerosene) contaminated with about 1% TBP and small concentrations of transuranics and fission products. Potential alternatives for disposal or management of the contaminated solvents were evaluated.

The difficulty with burning--the "obvious" first choice for a disposal method--is the formation of a fume when TBP is burned. The phosphorus forms an oxide, $P_4O_{10}$, which can exist in 3 forms[1] all of which can condense at elevated temperatures (up to about 500°C) forming a solid fume or (wall) deposit. The $P_4O_{10}$ will react with water vapor generated during combustion to form[1] meta phosphoric acid, $(HPO_3)_n$ which condenses at elevated temperatures[1] (depending on n) forming a glassy solid deposit or a fine fume that will plug filters. Hence, a solvent burning system requiring HEPA filters for radionuclide retention must remove the phosphoric acid and/or phosphorus oxide fume from the effluent before it reaches the filters.

## II. Alternatives for Management of Contaminated Solvents

An evaluation of potential alternatives for disposal of TBP-containing, contaminated solvents shows several alternatives of tested or potential suitability for ICPP solvents:

### A. Fluidized-Bed Burner

A fluidized-bed solvent burner has been developed by Gale[2] and is being patented by Energy Incorporated (EI). The solvent is burned at 800°C in a fluidized bed of limestone with which the phosphorus oxides react. A jet grinder removes reacted calcium and renews the surface of the bed particles. The calcium phosphate and limestone attrited from the bed are collected by a cyclone to form a solid by-product waste. The proposed[2] off-gas system contains a cyclone, a cooler, a sintered-metal filter, and a HEPA filter. A 146-mm diameter prototype with a simplified off-gas system was tested for 130 hr. The fluidized-bed burner basically converts the contaminated solvent to solid waste.

### B. Fluidized-Bed Calciner

Aqueous radioactive wastes are solidified routinely[3,4] at the ICPP in a fluidized-bed calciner heated by in-bed combustion (at 500°C) of kerosene. Effluent clean-up technology is well established[5]. The concept could be reversed, with contaminated solvents burned while calcining a non-radioactive feed. Pilot-plant tests described later verified the retention of the phosphorus (from the TBP) in the solids. A calciner for burning contaminated solvent would be similar to a fluidized-bed burner in use of a fluidized bed, having roughly the same space requirement and likewise converting the liquid waste to a solid waste. Differences are formation of fresh bed surface by calcining feed rather than jet grinding and addition of fresh limestone, and different operating temperatures.

### C. Oil Burner with Off-Gas System

The addition of a filtration system on the off-gas duct from an ordinary oil burner is an apparent choice for solvent burning. However, development is needed on the off-gas system because of high concentrations of solids in the burner effluent. Effluent samples (cascade impactor) taken from an existing oil burner burning 20 L/hr of solvent containing 1 to 3% TBP contained about 1 $g/m^3$ of total solids of which 30 $mg/m^3$ were submicron. The 1- to 30+-micron-diameter particles were essentially all (carbonaceous) soot, but the submicron particles were mostly a phosphorus compound. A more efficient burner would undoubtably reduce the soot concentration but not the concentration of phosphoric acid (or oxide) fume. Hence, a filtration system with a HEPA filter for radionuclide retention would need a pre-filtration system with a collection efficiency of at least 90% for submicron particles (99+% if 30% TBP is burned) to prevent excessive clogging of the HEPA filters. In addition, deposition on surfaces would be troublesome.

### D. Solidification

A moderate volume of contaminated solvent could be solidified with a gel or sorbant and stored as a solid waste. A (feasible) process modification to eliminate the washing column would reduce the ICPP waste solvent volume to the 2 $m^3$/yr of extraction solvent which would solidify to 20 to 30 drums of solidified solvent. The solidified solvent could then be stored at an on-site solid-waste storage facility. Required would be: 1) the process modification to reduce the solvent volume, 2) some development on the solidification procedure, and 3) facilities in which to solidify the solvent. General application of this option would depend on access to a solid waste storage facility at which the solidified solvent could be accepted.

### E. Existing Calciner

The multiple use of an existing facility will often be cost effective. The ICPP has two existing fluidized-bed calciners designed to solidify aqueous HLW--the (soon to be shut down) Waste Calcining Facility (WCF) and the almost-complete New Waste Calcining Facility (NWCF). Figure 1 shows the flowsheet for the NWCF. In bed combustion of kerosene provides the process heat for fluidized-bed calcination of the aqueous wastes; the resulting solids are transported pneumatically to storage bins. If the contaminated solvent could be burned as part of the fuel in the NWCF, the NWCF would supply the burner (calciner), off-gas system, and solids storage systems. The required facility modification would be an upgrade of the fuel supply system to one (of four) fuel nozzle to allow the use of contaminated fuel.

The burning of the contaminated solvents in the NWCF is the alternative selected for process verification because:

1) No by-product waste streams are generated. Instead, two waste streams are combined for processing in one facility with the resulting solids stored in one existing storage facility.

2) Cost effective use is made of existing facilities designed for solidifying radioactive wastes.

## III. Test Program

Four pilot-plant tests were conducted to verify that the phosphate in the fuel had no adverse effect on calciner operation. the composition of the simulated plant wastes used in 3 of the tests are tabulated in Table I. Solid calcium nitrate is added to the feed before calcining to react with the fluoride during solidification. The Ca:F mole ratio is 0.55 for straight HLW and 0.7 for a blend of HLW and ILW.

The pilot-plant tests were conducted in two different pilot-plant calciners. The 30-cm calciner has a 30-cm square fluidized bed with one fuel nozzle and one feed nozzle. It normally burns about 6 L/hr of fuel. The off-gas system, shown in Figure 2, contains a cyclone for fines collection and a recirculating scrubbing system with a quench (cooling) tower and a venturi scrubber. The 15-cm calciner has a 15-cm fluidized-bed in which about 2 L/hr of fuel is burned solidifying about 7 L/hr of feed. The off-gas system contains a cyclone and an abbreviated scrubbing system that cools and scrubs with a venturi scrubber.

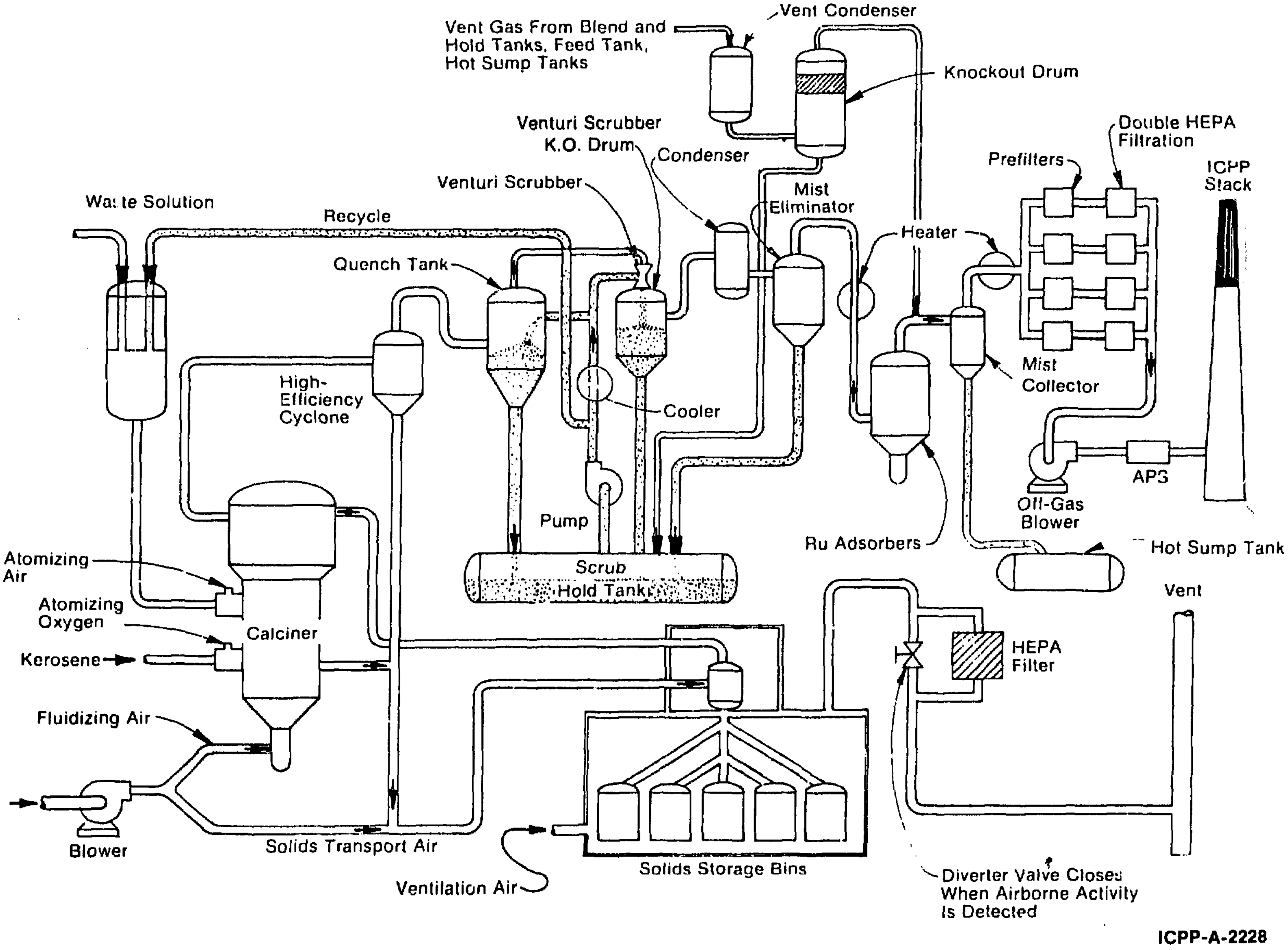

Figure 1: NWCF Flowsheet

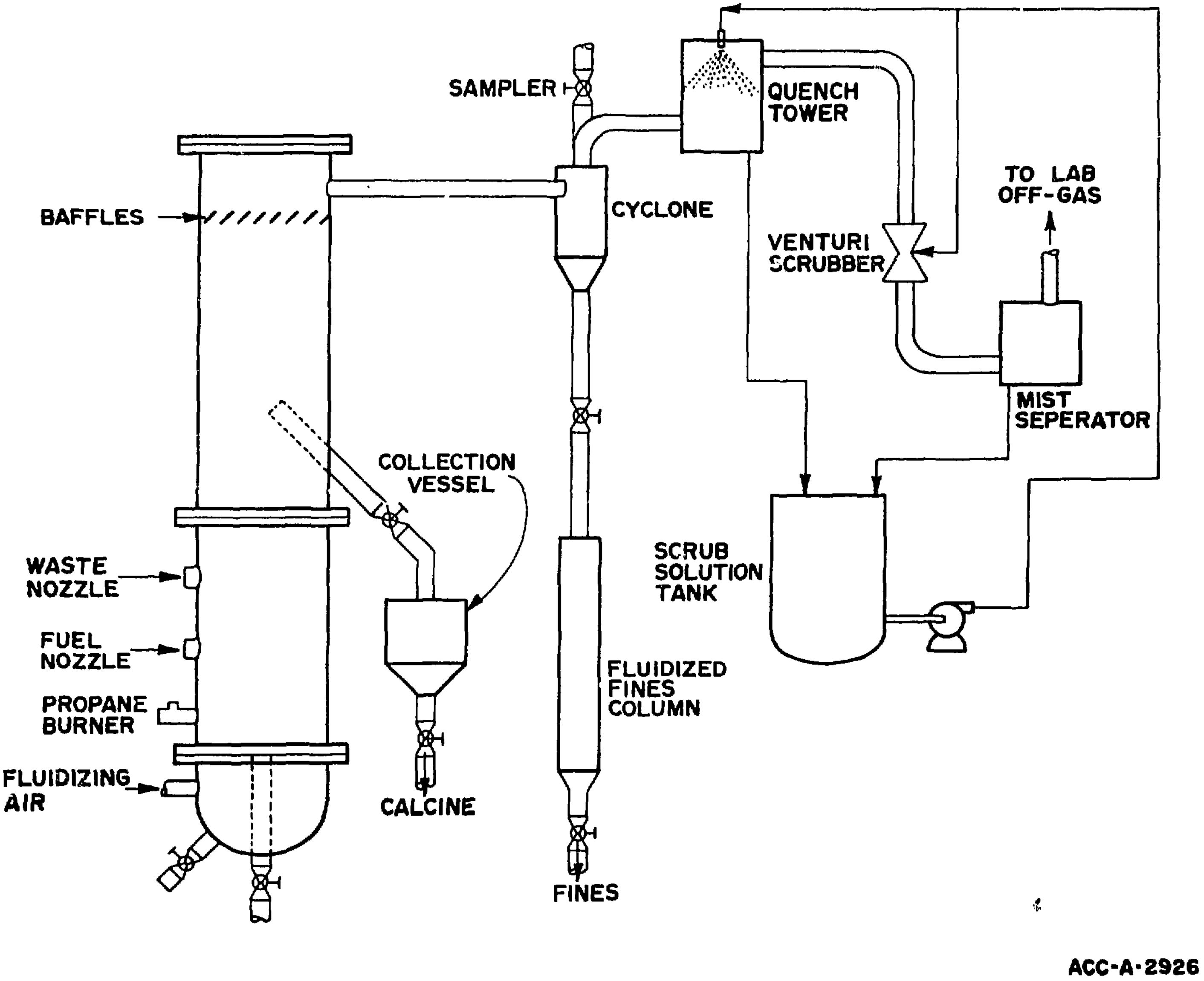

Figure 2: Pilot-Plant 30-cm Calciner

The four pilot-plant tests are described below:

Table I

Composition of Simulated Wastes

| Component | Composition (M) | | |
|---|---|---|---|
| | Normal HLW | Dilute HLW | ILW |
| Al | 0.66 | 0.45 | 0.52 |
| B | 0.2 | 0.12 | 0.011 |
| Cr | - | 0.012 | -- |
| Cl | - | 0.01 | 0.057 |
| F | 3.25 | 1.64 | 0.027 |
| Fe | - | 0.01 | 0.057 |
| $H^+$ | 1.28 | 1.6 | 1.64 |
| Hg | 0.002 | - | 0.01 |
| K | - | 0.006 | 0.21 |
| Mg | - | 0.008 | - |
| Mn | - | 0.0008 | 0.016 |
| Na | - | 0.08 | 1.30 |
| Ni | - | 0.002 | 0.004 |
| $NO_3$ | 2.2 | 1.29 | 5.15 |
| Pb | - | - | 0.003 |
| $PO_4$ | - | - | 0.02 |
| $SO_4$ | - | 0.05 | 0.06 |
| Zr | 0.37 | 0.23 | 0.05 |

1. Blended Waste in the 30-cm Calciner

The 30-cm calciner calcined a 7:1 blend of dilute HLW and ILW for 100 hr. The test demonstrated: 1) efficient combustion with 5% TBP in AMSCO, 1% TBP in AMSCO, and 5% TBP in tetradecane, 2) absorption of the phosphate in the fluidized bed, and 3) the absence of phosphoric acid fume in the scrubbed off-gas. There was a tendency of the solids to cake that was determined later to be a result of the feed properties rather than the phosphate.

2. Normal HLW in the 30-cm Calciner

The 30-cm calciner calcined normal HLW (with simulated fission products added) at a higher-than-normal feed rate to produce solids for other development programs. The fuel was 5% TBP in kerosene. Samples of the solids were used to verify the absence of adverse effects of the phosphate on the flowability of the calcine.

3. Blended Waste in the 15-cm Calciner

The 15-cm calciner was operated for 96 hr with a 7:1 blend of "normal" HLW and ILW to generate solids for solids flowability evaluation. The calciner operated for 40 hr burning normal kerosene to generate baseline (phosphate-free) calcine samples, then for 56 hr burning 5% TBP in kerosene to generate a phosphate-containing calcine from the same feed. The absence of an adverse effect of the phosphate on the retrievability of blended-waste calcine (7:1) was verified by comparison of the solids flowability of the calcine samples.

### 4. Aluminum Nitrate in the 15-cm Calciner

A 1.7 M aluminum nitrate solution (with 0.02 M $H_3BO_3$) was solidified in the 15-cm calciner to simulate part of the WCF-NWCF start-up procedure. The calciner burned 5% TBP in kerosene for 24 hr, 12% TBP in kerosene for 24 hr, and 30% TBP in kerosene for 44 hr. The feed for the last 20 hr was 1.5 M $Al(NO_3)_3$, 0.25 M $Ca(NO_3)_2$, and 0.02 M $H_3BO_3$.

## IV. Results

The test results verified the technical feasibility of burning TBP-containing solvents in the NWCF by showing the absence of observable adverse effects from the phosphorus in the fuel. Coincidentally, the test results also showed the feasibility of burning contaminated solvents in a dedicated fluidized-bed calciner. Specific concerns that were addressed are given below:

### 1. Combustion

Combustion of the fuels containing TBP was good. The only observable effect of the TBP was a decrease in the heat value of the fuel observed as an increase in the fuel needed for a given feed rate. Combustion efficiencies in the 30-cm calciner were between 93 and 96%, which are normal for the 30-cm calciner. No soot was observed in the off-gas of the 30-cm calciner. Some soot was observed in the off-gas of the 15-cm calciner when burning 5% and 12% TBP, but none was observed burning 30% TBP.

### 2. Phosphorus Behavior

Most of the phosphorus was found in the bed solids (not all the phosphorus was found). Table II shows the material balance for the 30-cm calciner run with blended feed. Except for the 5% of the phosphorus in the fines, very little phosphorus was found outside the bed.

Table II

Material Balance on Phosphorus
30-cm Run with Blended Feed

| Phase | | % of P from Fuel |
|---|---|---|
| Bed Solids | | 40-90 |
| Fines | | 5 |
| Scrubbing Solution | Liquid | 0.5 |
| | Solids | 0.1 |
| Off-Gas Solids | | 0.01 |

### 3. Solids in the Off-Gas

The test results show that the phosphorus in the (scrubbed) off-gas will have no appreciable effect on filter plugging because of the low concentration of phosphorus in the off-gas. The solids in the off-gas of the 30-cm calciner run with blended feed contained only 0.1 to 0.5% phosphorus which was 0.01% of the phosphorus from the fuel. Similar results were obtained from the aluminum nitrate run. (The other runs weren't sampled.)

### 4. Solids in the Scrubbing Solution

The test data show that the increase in undissolved-solids concentration in the scrubbing solution as a result of the phosphorus will be negligible. The data of Table II show only 0.6% of the phosphorus in the scrubbing solution. The resulting increment in undissolved solids concentration would be less than 1 g/L.

### 5. Deposition

There was no observable deposition of a phosphorus scale on corrosion coupons or vessel walls.

### 6. Corrosion

The phosphate had no observed effect on corrosion rates in the calciners. Corrosion rates on corrosion coupons in the scrubbing solution were in the normal range--less than one mil per month--for the pilot-plant tests.

### 7. Solids Flowability

Solids flowability is needed to allow future retrieval from the ICPP storage facilities. The phosphate from the fuel had no adverse effect on the flowability of the calcined solids; in the case of the solids formed calcining the blended waste, the phosphate improved their flowability.

## V. Conclusions of General Applicability

Some of the conclusions from this study are of general application:

A. A burner for TBP-containing contaminated solvents must remove or prevent the formation of a sub-micron phosphoric acid (or oxide) fume before a HEPA filter can be used.

B. Technologies are available for burning TBP-containing, contaminated solvents to a residual ash:

  1. A fluidized-bed burner absorbs the phosphate on a fluidized bed of limestone.

  2. A fluidized-bed calciner heated by in-bed combustion absorbs the phosphate on the fluidized-bed of calcined solids.

C. The use of an existing fuel-using disposal facility--e.g., incinerator or calciner--designed for radioactive materials will often be cost effective.

## VI. References

1. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol III. Longmans, Green, & Co., London, 1947, p 738, 744, 977-981.

2. L. G. Gale, Description of an Incinerator for Phosphorus-Containing Radioactive Solvents, paper presented at ASME National Waste Processing Conference, Washington, D.C., 1980.

3. J. A. Weilang, The Fourth Processing Campaign in the Waste Calcining Facility, FY-1971, ICPP-1004, 1972.

4. J. A. Weilang and W. A. Freeby, The Fifth Processing Campaign in the Waste Calcining Facility, FY-1972, ICP-1021, 1973.

5. R. E. Schindler, Removal of Particulate Solids from the Off-Gas of the WCF and NWCF, ICP-1157, 1978.