DESCRIPTION OF AN INCINERATOR FOR PHOSPHORUS-CONTAINING RADIOACTIVE SOLVENTS

L. G. GALE
Energy Incorporated
Idaho Falls, Idaho

ABSTRACT

This paper describes the design and development of an incinerator to process waste solvents containing phosphorus from nuclear fuel reprocessing facilities. A unique feature is a fluidized bed composed of limestone in which combustion occurs and, simultaneously, phosphorus combines with calcium to form a stable, solid product. Solid separators and adsorbers clean the exhaust gas before release to the atmosphere.

INTRODUCTION

Nuclear fuel reprocessing commonly uses a solvent extraction process to extract uranium and plutonium from an aqueous solution of fission products. The solvent is reused; however, a fraction of the solvent is degraded and must be disposed of. The solvent is combustible and in the past has been frequently disposed of by incineration. Two serious problems are inherent with incineration: (1) the solvent contains fission products and their uncontrolled release to the atmosphere is unacceptable; and (2) one of the constituents of certain solvents is tributyl phosphate (TBP) which forms a corrosive combustion product (phosphoric acid) when incinerated.

A satisfactory process for disposing of waste solvents has been developed which features the combustion of solvent in a fluidized bed of calcium oxide. The calcium oxide combines with the phosphorus released during the combustion of TBP forming a relatively inert solid. The radioactive products, ash, calcium phosphate, and excess calcium oxide are elutriated from the bed and are collected by gas cleaning equipment that make up the off-gas system.

This process has several important performance features which make it ideally suited for processing solvents containing tributyl phosphate.

1. The solvent is converted directly to a gaseous phase and a solid phase without forming a liquid waste stream. The radioactivity is in a solid form and is separated from the gas stream. The result is a single product stream of radioactive solids which can be safely stored or committed to permanent disposal.

Processes which employ a wet off-gas system to control phosphoric acid and scrub radioactive particulate from the exhaust gas can be effective. However, they have a major disadvantage in that an aqueous waste stream is formed which requires additional processing to convert it to a solid form suitable for permanent storage.

2. The fluidized bed-calcium oxide process simultaneously oxidizes the TBP and converts the phosphorus to an inert calcium phosphate. This precludes the formation of phosphoric acid anywhere in the incinerator system. By eliminating the corrosive effects of the phosphoric acid, it is possible to design an incinerator vessel with a long life and an off-gas cleanup system that will not corrode and will be effective in removing radioactive materials from the exhaust gas.

Combustion processes that rely on phosphoric
acid neutralization in an off-gas system external to the combustion zone experience rapid corrosion of the combustion chamber and have plugging problems from the formation of sticky-semiliquid phosphoric acid polymers.

PROCESS DESCRIPTION

The solvent incinerator is designed to burn radioactive solvents composed of TBP and a diluent. Combustion occurs in a fluidized bed of CaCO₃ and CaO. Phosphorus that is released from the combustion of TBP combines with calcium from the bed forming a solid calcium phosphate product. The solids are separated from the gas stream by a filter and a cyclone separator and are deposited in storage cans. Figure 1 is an outline of the process.

INCINERATOR

Solvent is pumped from a storage tank and is injected with air into the bottom of the fluid bed. The bed is composed of particles of CaO and CaCO₃ that are fluidized by air passing upward through the vessel. At the operating temperature of 1475 F (802 C), the TBP decomposes and oxidizes. The phosphorus combines with the calcium forming a calcium phosphate compound. The exact compound has not been identified, but it is believed to be either Ca₃(PO₄)₂ or Ca(PO₃)₂. The other combustion products are water and carbon dioxide. The solvent contains a relatively large amount of hydrogen; consequently, the water content or saturation temperature of the exhaust gas is relatively high. The solvent destruction efficiency approaches 100 percent as demonstrated by gas chromatograph analysis of the exhaust gas during pilot plant tests.

Limestone (CaCO₃) is injected into the vessel with a pneumatic conveyor. The CaCO₃ decomposes to CaO at the bed operating temperature and the CaO rather than CaCO₃ reacts with the phosphorus. Stoichiometric conditions are satisfied if the weight ratio of limestone to TBP is 0.57. However, experiments with a 5.76 in. (146 mm) diameter fluidized bed have demonstrated that a limestone to TBP ratio of about 3.2 is required. If insufficient limestone is injected, the bed becomes
coated with a sticky material (probably a phosphoric acid polymer) and defluidizes. It is believed that the relatively low utilization of the limestone grinder is used to remove reacted products from the surface of the bed particles. The grinder continually exposes unreacted calcium for reaction with the phosphorus. The product (calcium phosphate) is in the form of a particulate and is elutriated from the bed with the gas stream.

The limestone injection rate is proportioned to the TBP injection rate. During normal operation, both the limestone and the solvent rates are controlled at single predetermined rates. The bed depth is controlled by adjusting the grinding rate of the jet grinders.

The bed temperature can be controlled either by adjusting the excess air or by transfer of heat directly from the bed to a secondary coolant. Generally, for smaller facilities, excess air would be used to control temperature. However, for larger facilities, it is more economical to transfer heat directly to a secondary coolant, thereby reducing the physical size of the fluidized bed vessel and gas cleanup equipment.

Startup is accomplished by preheating the bed to approximately 1475 F (802 C) before injecting solvent into the bed. An oil fired startup burner is positioned to discharge hot exhaust gas directly into the side of the bed. The startup burner is operated until the bed temperature is high enough — 1300 F (704 C) — for reliable in-bed combustion of fuel oil. Then fuel oil is injected into the bed through the solvent injectors to complete the heatup to 1475 F (802 C).

Shutdown is affected by switching from solvent injection to fuel oil injection and operating a short time period for the solvent to burn out of the bed. Then, the bed feed, jet grinders, fuel oil, fluidizing air, and bed cooler are shut down in that order. If it is desired to cool the system before shutdown, the fuel injection is stopped and fluidizing air is allowed to flow through the bed until the desired bed temperature is reached.

OFF-GAS SYSTEM

The exhaust from the incinerator vessel is composed of gaseous combustion products (\( \text{CO}_2, \text{H}_2\text{O}, \text{O}_2, \text{N}_2 \)) and suspended particulate \([\text{Ca}_3(\text{PO}_4)_2, \text{CaO}, \text{ash}, \text{and solid radioactive isotopes}]\). None of the constituents, with the exception of the radioactive isotopes, is considered hazardous. The primary purpose of the off-gas system is to remove the particulate, which contains most of the radioactivity, from the gas stream before it is exhausted to the atmosphere.

The first component in the off-gas system is a hot cyclone. A cyclone separator has the ability to handle gas streams with high particulate loadings \([~219 \text{ grains/ft}^3(44 \text{ g/m}^3)]\). Approximately 90 percent of the particulate will be captured by the cyclone and will drop by gravity into a product container located below the cyclone. The product container is sealed and operates at the same pressure as the cyclone.

Following the cyclone is a gas cooler which reduces the temperature of the gas to a value consistent with temperature tolerance of the downstream exhaust gas equipment. However, it is necessary to maintain the gas temperature above the saturation temperature to eliminate plugging problems that would occur if moisture were to condense on housing surfaces or filter faces. Therefore, the heat exchanger is of special design which has multiple cooling regions in series. This design allows coolant flow to the downstream coolant regions to be throttled to affect temperature control of the gas without exposing uncooled surfaces to high temperature gas.

Next, the exhaust gas passes through a filter which is designed to remove 99 percent of the particulate from the gas stream entering the filter. This filter is a special design using commercially available sintered metal elements in a special housing. A blowback system using high pressure air alternately cleans banks of filter elements. The particulate collected by the filter drops by gravity into a sealed product container. A filter was specified for this function to achieve a high particulate removal efficiency. However, the gas stream still contains a relatively high concentration of particulate — 1.9 grains/ft\(^3\) (4.4 g/m\(^3\)) — and frequent filter cleaning is necessary. Sintered metal was selected because of its durability, low maintenance, and configuration that allows frequent cleaning by blowback with high pressure air.

Optional gas cleaning can be incorporated in the system if necessary to control high concentrations of certain radioisotopes. For example: silica gel bed for volatile ruthenium, silver zeolite or charcoal for volatile iodine, and HEPA filters for
solids such as plutonium. Due to the wide variation in radionuclide concentration of solvents, the optional gas cleaning equipment is specific for each application.

The induced draft fan is sized to handle the entire exhaust gas volume while drawing enough vacuum to maintain a zero or negative gauge pressure in the incinerator and the off-gas system. A negative pressure will ensure that any minor leakage will result in air leaking into the system rather than the leakage of radioactive gases into the building.

**MATERIAL BALANCE**

A material balance summary is presented in Fig. 1. This summary is based on a system with a nominal capacity of 7.9 gal/hr (30 l/h) of 30 percent TBP using direct heat exchange from the bed to the coolant (2.5 percent excess air). The input of radioactive solvent through line #2 is 54 lb/hr (24.5 kg/h) or 1.06 ft³/hr (0.03 m³/h). The output of solid radioactive material (line #7 plus #10) is 34 lb/hr (15.4 kg/h) or 0.78 ft³/hr (0.022 m³/h). This represents a volume reduction of 26 percent. The volume of waste generated is primarily a function of the phosphorus content of the solvent. For example, if the solvent contained 5 percent TBP rather than 30 percent, the volume reduction would approach 90 percent.

The solvent in this example was assumed to contain no significant contaminants such as water. If the solvent contains a large fraction of water such that the heating value was significantly reduced, it would be necessary to supply supplementary fuel in the form of fuel oil.

**BEHAVIOR OF RADIOACTIVE ISOTOPES**

The majority of the radioactive isotopes introduced to the system will be converted to a solid oxide at the incinerator operating temperatures 1475 F (802 C). The solid radionuclides will be separated from the gas stream either by the cyclone or the filter. These two components result in a decontamination factor (DF) of ~1000, which would satisfy the radioactive release regulations when incinerating many solvents. If necessary, additional filters can be added to obtain much higher decontamination factors.

Cesium oxides are liquid at incineration temperatures which may effect the cyclone performance slightly. However, the cesium would be solid after passing through the gas cooler and filtration would be effective.

A fraction of the ruthenium will volatilize and not be controllable by use of gas/solid separators. However, the ruthenium fraction volatilized during incineration is small (<1 percent) and should not require control. Silica gel absorbers can be added to the off-gas system to control volatile ruthenium.

A DF of ~1000 for volatile ruthenium is achievable.

Iodine in the solvent is expected to be converted to a volatile form and if the quantity is significant, control equipment would be required. Charcoal or silver zeolite adsorbers could be used for this purpose.

Each incinerator application involves solvents with differing activities and in some cases different radioactive release requirements; therefore, it is necessary to design the gas cleaning equipment to meet the requirements unique to each application.

The basic gas cleanup equipment consisting of a cyclone and sintered metal filter will easily meet the federal requirements of 10CFR20 when incinerating typical solvents that have been in storage for several years.

**EQUIPMENT LAYOUT**

Incinerators can be designed for almost any capacity and material-energy balances have been prepared for systems ranging from 0.4 gal/hr (1.5 l/h) to 30 gal/hr (114 l/h). Figure 2 is an example of an equipment layout for a typical system with a capacity of 7.9 gal/hr (30 l/h). The incinerator vessel and exhaust gas equipment are located in a cell measuring approximately 25 ft x 8 ft x 17 ft (7.6 m x 2.4 m x 5.2 m) high. Product containers are located in another cell immediately below the cyclone and filter. The radioactive field generated by the product containers is weak and relatively little shielding is required for transfer and handling of the containers. An equipment room containing non-radioactive equipment, such as the fluidizing blower and the bed feeder, is located adjacent to the incinerator cell. A small control room would also be required. This equipment layout does not include optional exhaust gas cleaning equipment.

**OPERATION AND MAINTENANCE**

The solvent incinerator instrumentation and control system is designed to monitor and control
all process variables using fail safe logic. This minimizes the duties of the operating personnel with the major tasks being startup and shutdown sequences, charging limestone to storage hoppers and preparation of radioactive product for transfer. It is estimated that one operator would be able to handle these tasks easily. The system has no special maintenance requirements. Routine maintenance on standard equipment such as blowers, motors, and instruments is expected to be minimal.

The basic operating and maintenance costs are predicted to be relatively low. However, the radioactive materials impose monitoring and recording tasks which could contribute significantly to the cost of operation. Operating materials such as limestone and fuel oil are a small cost item.

**DEVELOPMENT PROGRAM**

The development program was conducted in two phases. First, the basic technical feasibility was established during a series of short (≤4 hr) demonstration tests using a 5.76 in. (146 mm) diameter fluidized bed. The major conclusions from these tests were: (1) organic solvents typical of those used in nuclear fuel reprocessing can be efficiently incinerated in a fluidized bed; and (2) the chemically active bed of CaO is effective in converting phosphorus to a stable solid.

The second development phase was designed to produce information and data necessary for the design of a solvent processing facility. A number of investigations were conducted including combustion efficiency, bed chemical behavior, bed removal process, corrosion rates, equipment performance, and other aspects of the process.

**PILOT PLANT DESCRIPTION**

All process and equipment testing was conducted in a 5.76 in. (146 mm) diameter fluidized bed. The schematic of this system is shown in Fig. 3. The vessel is 6 ft (1.83 m) high and is constructed from Type 347 stainless steel. Several off-gas system configurations were used during the tests, but the majority of the tests and the final process demonstration were performed using the system described in Fig. 3. This arrangement simulates the design proposed for the final system.

**TEST SUMMARY**

Tests were performed to evaluate the various
configurations for solvent injection equipment. The goal of the solvent injection technique was to complete the combustion within the bed (no above bed burning) and to achieve 100 percent combustion efficiency. The solvent injection technique ultimately developed produced an occasionally visible flame above the bed and no detectable unoxidized matter in the exhaust gas indicating near 100 percent destruction of the solvent. The flue gas analysis was performed using a gas chromatograph.

Oxides and carbonates of various alkali and alkaline earths were researched to determine if they would be suitable for capture of phosphorus during incineration of TBP. Chemical and physical properties along with cost and availability were the major factors considered in the selection. Limestone met the performance requirements and is particularly attractive from cost and availability standpoints. A number of TBP combustion tests were performed with a limestone bed and with a chemically inert bed for comparison. Limestone addition rates were experimentally determined which resulted in effective control of the phosphorus.

Removal of spent material from the bed is accomplished by grinding material from the surface of the bed particles. This fine material is then elutriated from the vessel and collected by the off-gas equipment. Tests showed that the normal grinding rate in a fluidized bed does not equal the desired bed addition rate. In order to increase the grinding rate, a jet grinder was developed that could be controlled to achieve the desired grinding rate. The most effective grinder studied was an orifice which introduced a high velocity jet of air into the side of the bed.

The volatility of ruthenium during incineration is a primary factor in establishing the exhaust gas cleanup system design. Published test data is applicable to processes with major differences in operating conditions when compared to the solvent incinerator. Therefore, a series of tests was performed to measure the volatility. A nonradioactive
isotope of ruthenium was used to simulate radioactive ruthenium (Ru-106) requiring that chemical analyses be used to trace the ruthenium behavior. This necessitated using considerably higher concentrations of ruthenium than would be expected in contaminated solvent. Three separate tests in the fluidized bed were performed and in each case, the ruthenium volatility was determined to be approximately 1 percent.

A corrosion test was performed to provide data for the selection of construction materials. Twelve test coupons were installed in the bed and the vapor space of the pilot facility. The test included 130 hr during which TBP was incinerated. Seven alloys were identified which appear to give acceptable performance in the fluidized bed:

1. Rolled Alloy 333
2. Inconel Alloy 625
3. Haynes Alloy 188
4. Hastelloy Alloy C4
5. Hastelloy Alloy S
6. Hastelloy Alloy X
7. Hastelloy Alloy G

Visual inspection of the fluidized bed vessel showed it to perform in a generally acceptable manner with minor pitting the only visible effect. The vessel is constructed from Type 347 stainless steel.

A longer term demonstration test was performed to identify problems that would occur only after many hours of operation, such as plugging due to scale formation. No such problems were noted during the test. The demonstration test included about 130 hr of operation at design conditions.

The pilot plant tests have demonstrated that the process and the basic equipment perform as intended. The length of the demonstration was sufficient to identify any problems with the possible exception of corrosion. Although no corrosion problems are anticipated, a longer test period is required to verify this. The scale up factor to commercial systems is on the order of 2 to 6. Considering the extensive body of information on fluidized beds, it is believed that the scale up could be accomplished without additional testing.

**CONCLUSION**

The concept of using a fluidized bed composed of CaO in which incineration takes place while phosphorus is simultaneously neutralized by calcium has been developed through the preliminary design stage. The incinerator design was verified in a pilot scale fluidized bed incinerator.

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**Key Words**

Fluidized Bed
Hazardous Incinerator
Phosphorus