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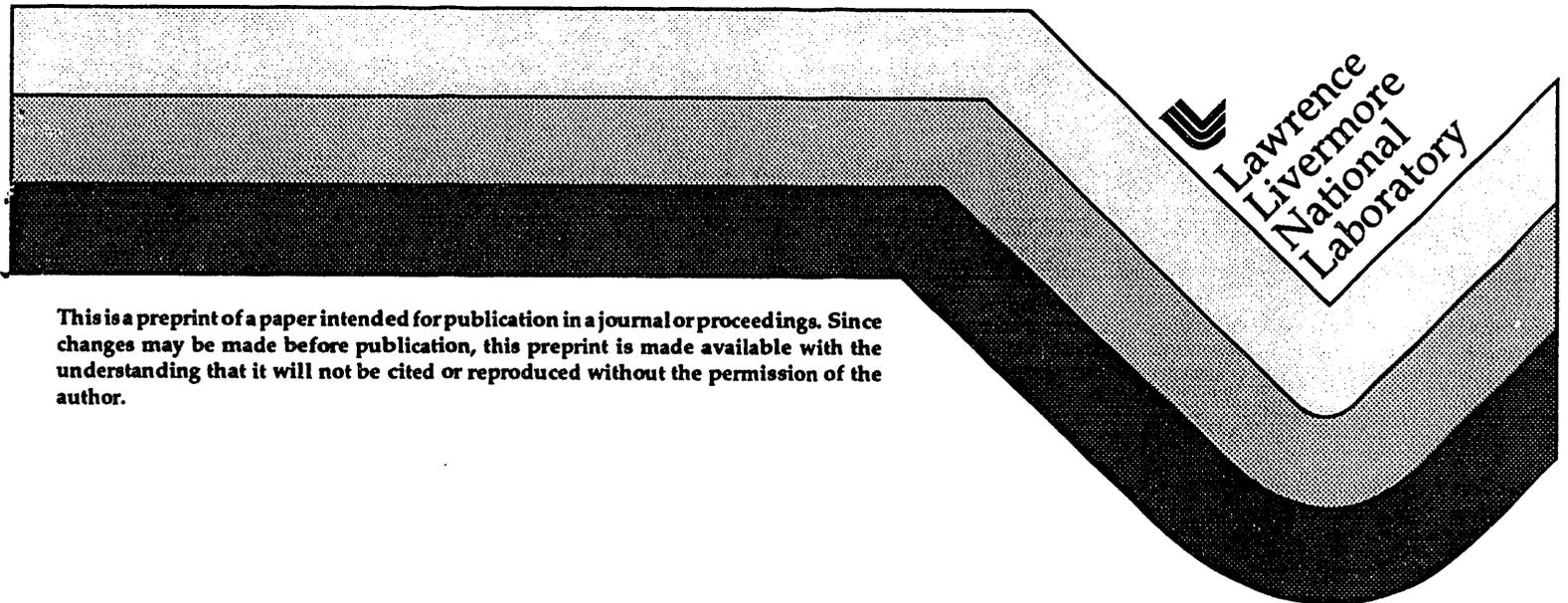
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MOLTEN SALT DESTRUCTION PROCESS FOR MIXED WASTES

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ABSTRACT. We are developing an advanced two-stage process for the treatment of mixed wastes, which contain both hazardous and radioactive components(1). The wastes, together with an oxidant gas, such as air, are injected into a bed of molten salt comprising a mixture of sodium-, potassium-, and lithium-carbonates, with a melting point of about 580°C. The organic constituents of the mixed waste are destroyed through the combined effect of pyrolysis and oxidation. Heteroatoms, such as chlorine, in the mixed waste form stable salts, such as sodium chloride, and are retained in the melt. The radioactive actinides in the mixed waste are also retained in the melt because of the combined action of wetting and partial dissolution. The original process, developed by Rockwell International, consists of a one-stage unit, operated at 900–1000°C. The advanced two-stage process has two stages, one for pyrolysis and one for oxidation. The pyrolysis stage is designed to operate at 700°C. The oxidation stage can be operated at a higher temperature, if necessary.

INTRODUCTION

Mixed wastes are hazardous wastes that are also radioactive. Acceptable methods for the treatment of mixed wastes are not currently available. The Molten Salt Destruction Process (MSD) is an alternative to, and offers several advantages over, incineration. MSD was originally developed by Rockwell International as a single stage process for coal gasification, and later used for treatment of hazardous wastes, such as PCB's(2). MSD differs from incineration in several ways: there is no open flame in MSD, the containment of actinides is accomplished by chemical means (wetting and dissolution), the operating temperature of MSD is much lower, thus lowering the volatilities of radioactive actinides, and no acid gases are generated in MSD. These differences provide the main reason for developing MSD as an alternative to incineration.

In MSD, mixed wastes are introduced into a bed of molten salt (typically alkali metal carbonate), together with air or oxygen. (See Fig. 1 for a conceptual flowsheet). The organic components of the mixed waste are converted into CO₂ and H₂O, heteroatoms such as chlorine form stable salts such as sodium chloride, and the actinides are retained in the melt through dissolution and wetting. The lower operating temperature of the process (700–900°C, compared to 1000–1200°C for incineration) keeps the actinide volatilities lower than what would be expected at higher temperatures. At the termination of a run, the salt can be drained out, and dissolved in water. The oxides and salts of actinides, being insoluble in the alkaline solution, precipitate and are filtered out. The dissolved salts are separated by crystallization. The carbonates are recycled back to the reactor, and the stable salts are disposed of as low level waste (LLW). The products of the MSD process are either benign gases (CO₂, H₂O), concentrated actinide oxides/salts, or low level waste, thus resulting in a large volume reduction from the original mixed waste. Treatable waste streams consist of organic liquids (including the ones containing chlorinated solvents and PCB's), greases, and combustible solids such as cellulosic matter, rubber and plastics.

TECHNICAL BASIS

The molten salts are typically mixtures of alkali or alkaline earth carbonates and halides. The salts provide excellent heat transfer and reaction medium, catalyze oxidation of organics, and prevent formation of acidic gases (e.g., HCl, SO₂, and P₂O₅) by forming instead solutions of their neutral (and stable) salts (e.g., NaCl, Na₂SO₄, and Na₃PO₄)(2,3). The relatively high thermal inertia of the melt tends to resist changes in temperature resulting from sudden changes in the feed or heat transfer. The melt avoids the formation of

potentially fugitive radioactive particulates and molecular species by a combination of particle wetting, encapsulation and dissolution with complex formation. Therefore, containment of the radioactive material is based on a physico-chemical process rather than on mechanical means alone, as is the case with incineration.

The melt must remain fluid for contacting of the waste with oxygen, wetting the particulates, and transfer of the melt. For wastes containing substantial quantities of inorganic oxides, (e.g., paper products containing kaolin), the "ash" builds up as either dissolved substances or to form a slurry, resulting in increase of viscosity and loss of fluidity. In this case, a fraction of the melt can be removed, and replaced by fresh salt. The withdrawn melt can be processed as shown in Fig. 1. If the salt accumulates high concentrations (20–30%) of alumina and silica while the process is operated under oxidizing conditions, the alumina and silica combine to form solid deposits on the vessel walls(1). This phenomenon is not observed during oxygen deficient conditions (i.e., in the pyrolysis mode), or in the presence of silica or alumina alone. This observation has led us to develop the advanced two-stage process wherein the first stage is operated under reducing conditions, and the second under oxidizing conditions. In this mode of operation, the main reaction undergone by the organic portion of the waste is pyrolysis, with partial oxidation of the pyrolysis products. The acid gases are, however, completely avoided by formation of their respective salts, and the actinides, along with the ash, are retained in the melt. The ash may now build up to higher levels than those that limit operation under oxidizing conditions, with no chance of a melt freeze-up. The products of pyrolysis from the first stage are completely oxidized in the second stage, which is operated with excess oxygen. The second stage also acts as a "polishing" step for cleaning up residual amounts of acid gases, and for retaining any entrained actinide particles; it operates without ash build-up under near optimal process conditions.

EXPERIMENTAL PROGRAM

We have built a two-stage experimental unit to investigate the applicability of the molten salt destruction process to the treatment of mixed wastes. Figure 2 shows a schematic of the current configuration, while Figure 3 shows an isometric sketch of the unit.

The two crucibles, physically identical, are made of stainless steel. (Stainless steel is stable in the presence of alkali carbonates, but susceptible to stress corrosion in the presence of chlorides. The crucibles can be

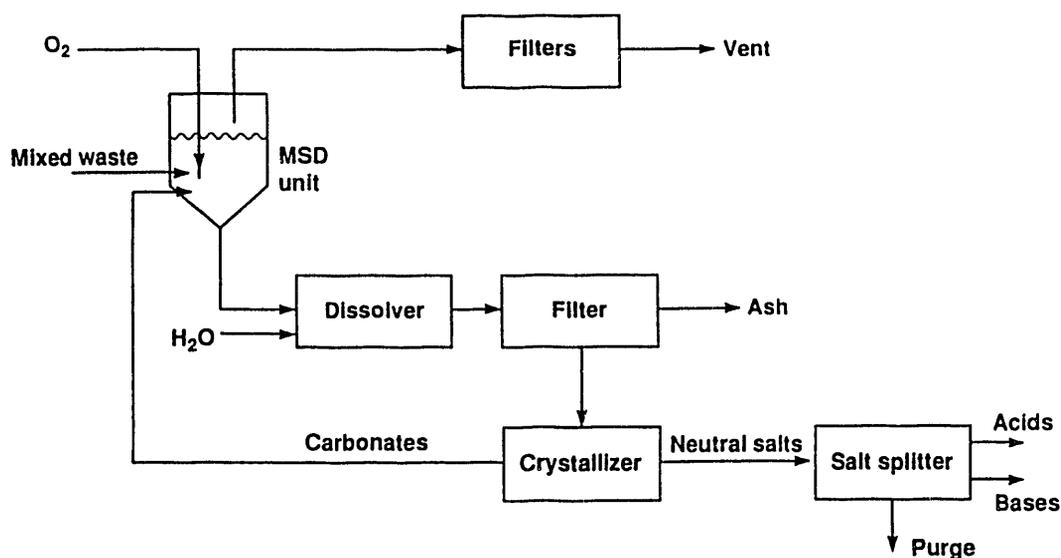


Figure 1. Mixed waste flow sheet using molten salt.

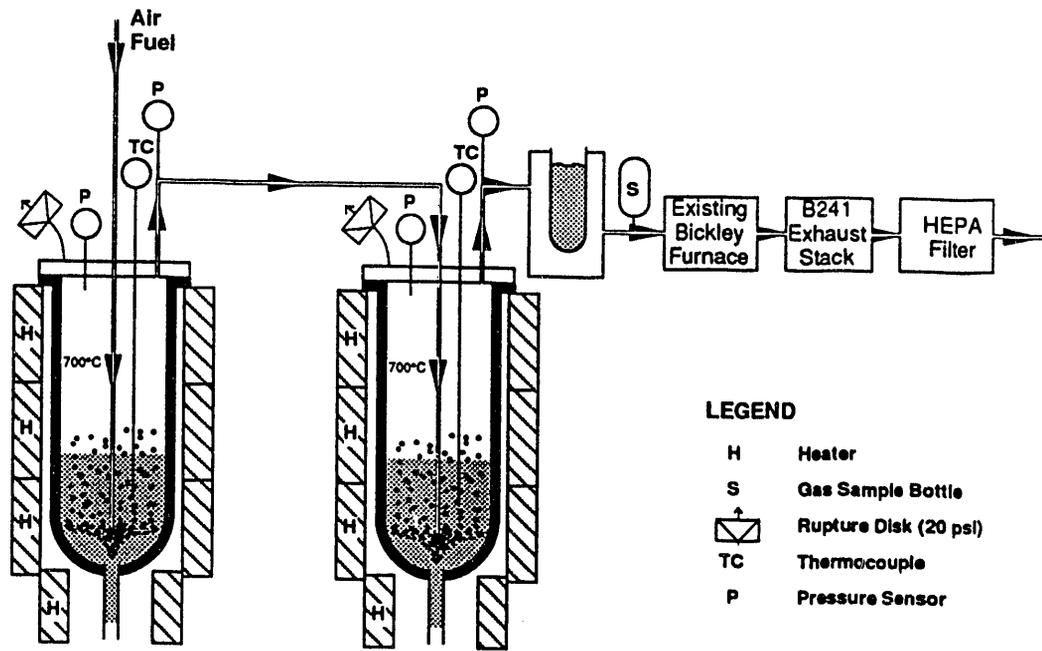


Figure 2. Schematic of the two-stage experimental unit.

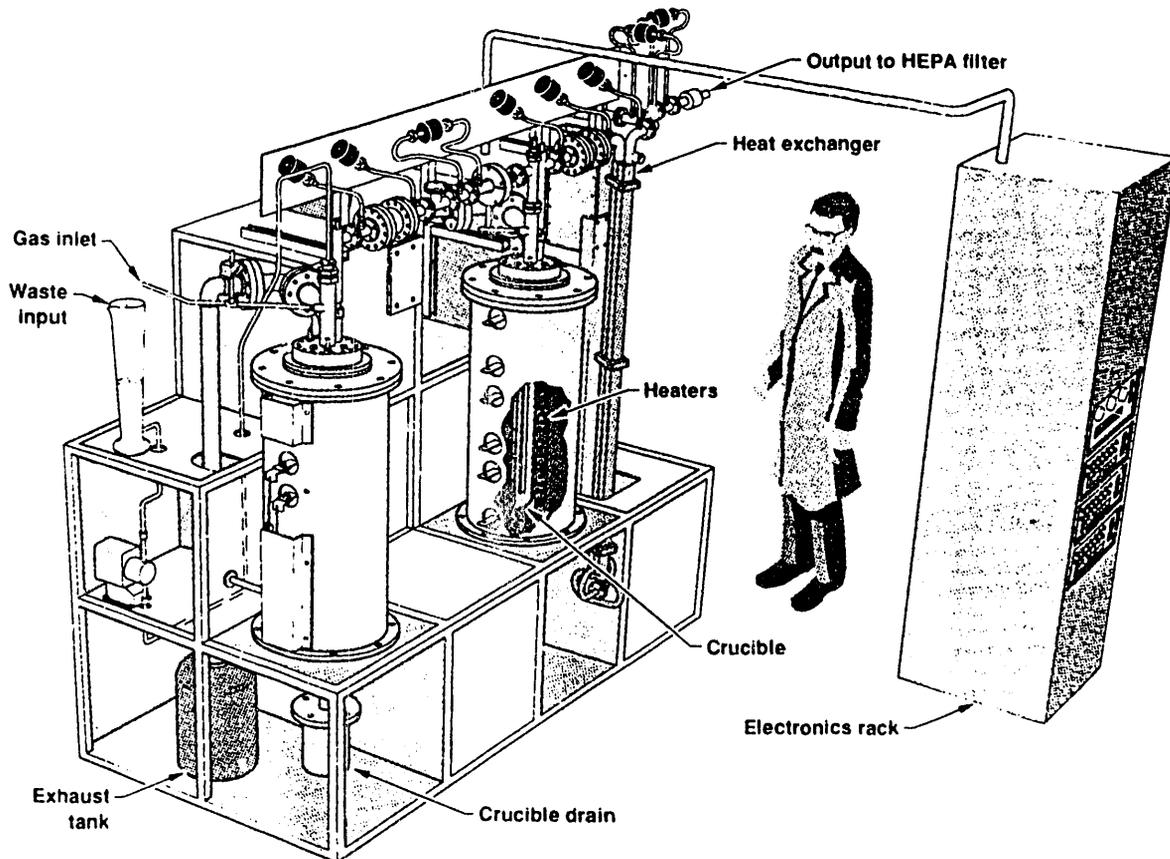


Figure 3. Isometric sketch of the two-stage experimental unit.

subjected to a maximum of 47 thermal cycles based on a safety analysis of the welds. This limit is considerably lower than that imposed by chloride corrosion.) They have the dimensions 5.76" ID, 6.63" OD, and 37.75" length. They are fitted with a drain pipe at the bottom and a flange on the top. The drain pipe leads to a drain bucket, large enough to contain the molten salt inventory, which is placed under each crucible. The waste to be treated and the oxidant gases are introduced through a feed tube near the center of the crucibles. The gaseous product of the first crucible is sent to the second crucible for complete oxidation. The oxidant gas for the second crucible is introduced separately into the second feed tube. The off-gas from the second crucible passes through a cold trap, cooled by a central water tube, to capture entrained liquid droplets. Three cylindrical electrical heaters, each rated at 3 kW, are placed outside each crucible. A smaller fourth heater is located under each crucible, concentric with the drain pipe. A blower is placed under the crucibles to blow air through the annular space between the crucibles and the heaters. The heaters are needed for starting up the process, whereas the blower is needed to remove the heat generated by oxidation of wastes. The off-gas from the cold trap is passed through a Bickley furnace to ensure complete oxidation of any trace contaminants, and then through HEPA filters before being vented.

A number of thermocouples are placed at various locations, both inside and outside the crucibles, to keep track of temperatures. The pressures within the crucibles, and the differential pressures around the filters are continuously monitored, as are the feed rates of the waste and the oxidant gases. A residual gas analyzer is used to monitor the gas compositions. Gas samples can be taken through a number of sampling ports for a more accurate off-line analysis. We use a data logger/controller program to continuously save the data and to control the operation of the unit.

We have completed construction of the unit as described above. The shakedown runs have been completed. The unit is currently operating on waste simulants, such as dodecane and ethylene glycol.

In addition to the main program, we have several smaller supporting programs underway. We have built a plexiglass model of the crucible, which is dimensionally identical to the stainless steel crucibles, to conduct fluid flow experiments. This allows us to measure the variation of the froth height with respect to the gas flow rate, liquid height, liquid surface tension and viscosity, and inlet nozzle configuration. We have developed sensors to monitor the froth height on-line. Another experimental system is being used to study the effect of melt composition and ash loading on the melt viscosity. Finally, we have a number of corrosion studies underway to study the effect of the melt composition on different crucible materials.

RESULTS AND DISCUSSION

We have developed correlations for gas hold-up as a function of gas velocity, liquid height, and nozzle height based on our experiments on air-water and air-oil systems in the plexiglass model. These correlations have been extended to liquids with surface tensions significantly different from that of water. These correlations allow us to predict the froth height in the actual system for any configuration. In addition, our studies using color tracers have demonstrated a thorough mixing of the contents of the liquid phase for gas flow rates significantly less than those anticipated in real operation.

Krikorian has performed thermodynamic studies on the volatilities of radionuclides and toxic elements in the molten salt destruction process(4), and on the selection of salt mixtures(5). His analyses show significantly lower (orders of magnitude) volatilities for actinides at the molten salt temperatures compared to the temperatures of typical incinerators.

CONCLUSIONS AND FUTURE WORK

The process analyses conducted by Rockwell International(6) demonstrate that the molten salt destruction process is a viable option for the treatment of mixed wastes. A number of critical uncertainties, however, must be resolved:

- The effect of ash on melt stability under a variety of operating conditions.
- Processing of the spent salt under the limiting conditions of the build-up of ash and stable salts (such as sodium chloride).
- Retention of particulates in the molten salt bed.
- Tolerance to upsets under a variety of operating conditions.

The experimental program currently underway is designed to address these issues and to obtain sufficient process engineering data to design a pilot-scale unit. A more detailed description of the planned facility to house the pilot scale experiments is being presented at this conference by Brummond and Celeste from the Lawrence Livermore National Laboratory.

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