POSTER SESSION I

J. Blomeke, Chairman
R. Yoshimura, Co-Chairman

PERFORMANCE TEST OF A PYROLYSIS UNIT FOR THE VOLUME REDUCTION OF ORGANIC WASTES

G. Kemmler, Nukem
E. Schlich, Nukem
H. Vietzke, Nukem

Introduction

Nukem has developed a pyrolysis system to process and volume reduce spent solvent (TBP/kerosene) and spent resins. Treatment of sludges and evaporator bottoms in this system is planned as an item for further development.

Improved radwaste processing technology, principally volume reduction followed by solidification of the volume reduced waste form, is a major area of Nukem's research and development activities.

The pyrolysis system is characterized by low system operating temperatures, inert or substoichiometric atmospheres and low flow rates in the reactor vessel. Compared with combustion, pyrolysis or gasification has the disadvantages of an overall negative energy balance and lower specific combustion chamber performance. However, these disadvantages are not significant since the nuclear wastes to be pyrolyzed are relatively small amounts when compared with non-nuclear trash. The processing costs are more than offset by the considerably lower storage costs following volume reduction.

Important considerations in any nuclear waste volume reduction system and inherent in the pyrolysis equipment are high decontamination factors, low equipment costs, small amounts of secondary waste, ease of equipment decontamination, adaptability of the product to solidification and/or storage requirements and ease of final product handling.

This paper describes a concurrent flow agitated packed bed thermal treatment process for liquids and sludges.

Thermal treatment is:

- concentrating and drying of wet wastes such as evaporator bottom and resin slurries at 200-300°C.
- decomposition of spent solvent from reprocessing and formation of calcium phosphate in one step at 400-600°C
- cracking of spent resins and formation of inert carbon residue which does not have ion-exchange capability at 400-600°C

These are examples of the multiple purposes for which the Nukem agitated bed pyrolysis reactor could be used.

This type of reactor could in fact be used for substoichiometric destructive distillation. So far, the prototype system has been used for extended experimental runs in the decomposition of spent solvent and the pyrolysis of spent resin.

The concentration and drying of sludges and evaporator bottoms and also destructive distillation will be future R&D areas.

Feed Materials and Process Parameters

For a German reprocessing plant with a uranium throughput of 350 t/yr the amount of spent solvent will be about 50 m^3/yr. These are mainly used extractants (30% TBP/ 70% kerosene) as well as waste oils, lubricants, cleansers and solvents. For these wastes the pyrolysis system throughput should be 15-20 kg/h.

For U.S. nuclear power stations spent resin may amount to many thousands of cubic feet per year of which several hundred will be of high specific activity.

The pyrolysis system can be sized to any required throughput. Typical requirements would be between 4 and 40 gal/h of resin (wet). Laboratory tests have been performed to determine overall reaction equations and recovery yields from thermal decomposition of these feed materials.

Spent solvent (TBP/kerosene) is mixed with calcium hydroxide before being fed into the reactor vessel. The TBP is decomposed to phosphoric acid, butane and butanol, while the kerosene is evaporated without cracking. The phosphoric acid forms calcium phosphate from the alkaline admixture.

Spent resin swells in contact with water, e.g. during solidification in cement. This is one reason that the loading of resins into concrete can not be more than 10 percent. A second reason for this limitation is that resins contain a lot of hydrogen, which is able to come out of the concrete product by radiolysis. Due to these effects, it is desirable to destroy the chemical activity of the ion exchange material by thermal decomposition, and - at the same time - to keep the activity inside the solid residue which avoids a disadvantage of combustion. Laboratory experiments have shown that at temperatures between 400 and 600°C and under nitrogen atmosphere these results occur.

The solid residue of the process contains all heavy metals and can be solidified into concrete, asphalt or organic resins or can be stored as is in high integrity casks.

Plant Description

The Nukem pyrolysis plant to decompose TBP/kerosene and to treat resins has been in operation since 1980 as a non-radioactive full scale prototype. Based on annual throughput requirements, a pyrolysis system was built for 15 kg/h water equivalent evaporation. This capacity is able to process up to 30 kg/h spent solvent or spent resin.

Fig. 1 shows the pyrolysis reactor for liquid organic wastes. This is a vertical cylindrical vessel with a diameter of approximately 0.5 m and a height of 1 m. The reactor is filled with a packed bed that is kept in motion by a specially designed agitator. The liquid that is to be decomposed is sprayed onto the packed bed from a number of jets with the aid of nitrogen. The solid residues are milled very smoothly by the slow motion of the packed

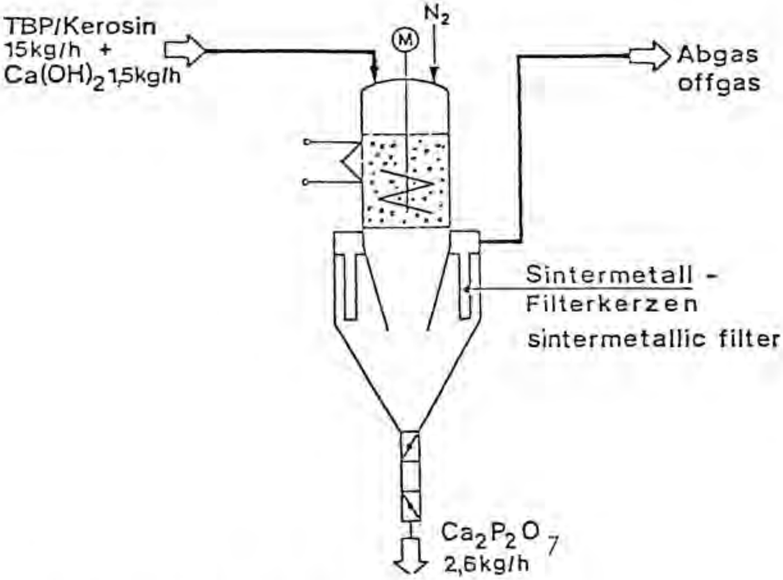

Fig. 1. Pyrolysis-Unit for Spent Solvent.

bed, which consists of aluminium oxide balls. The bed is agitated to keep the solid residue from caking and slagging and to increase the overall heat transfer from the outside electrical heaters to the inside chemical reaction. The packed bed can be removed through the bottom of the furnace.

The gaseous products leave the packed bed reactor through sintered metal filters to remove any dust contamination. The offgas treatment consists of a cyclone combustion afterburner with a supporting flame, a scrubber and hepa-filter equipment, as shown in Fig. 2.

The pyrolysis reactor itself and its operation was the item of research and development. The offgas treatment equipment depends on local emission limits.

The offgas treatment equipment the Nukem prototype system uses does not differ from the offgas treatment used by the pyrohydrolysis reactor (Fig. 3). This reactor was developed in a critical safe geometry to decompose solid TRU-contaminated feed under substoichiometric conditions.

Results

The experiments in the laboratory gave the same results obtained with the full scale prototype system. So far, 1000 kg of spent solvent and about 500 kg of spent resin have been processed. The overall volume reduction is as follows:

Feed Material	Volume Reduction
Spent solvent	1 : 20
Spent resin	1 : 7

The cementation of the calcium phosphate residue of spent solvent and of the decomposed resin shows very reasonable results with loadings of up to 45 weight percent (compared with 10% before). The pyrolysis residues have also been solidified in asphalt and organic binders with very good results because of the inert behaviour of the residues. The solidified product meets the waste form specifications for quality.

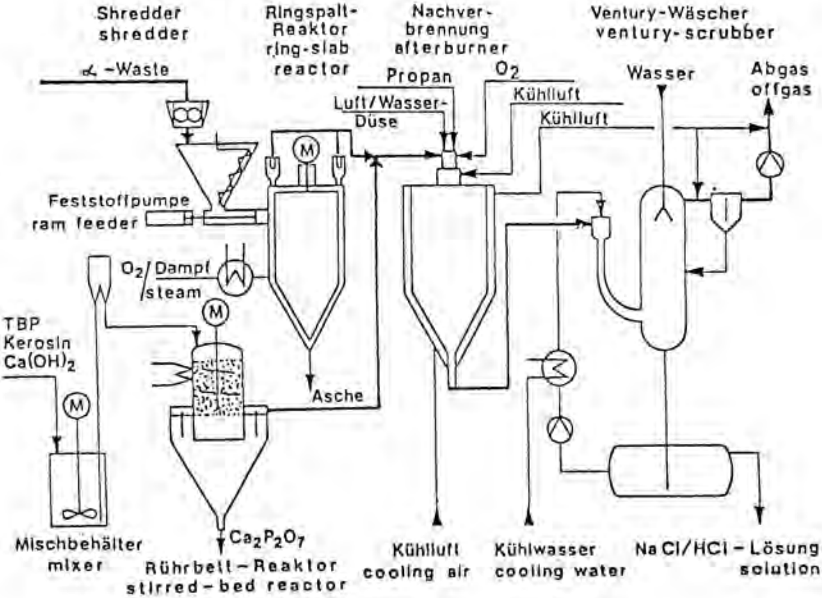

Fig. 2. Plant Flow-Sheet.

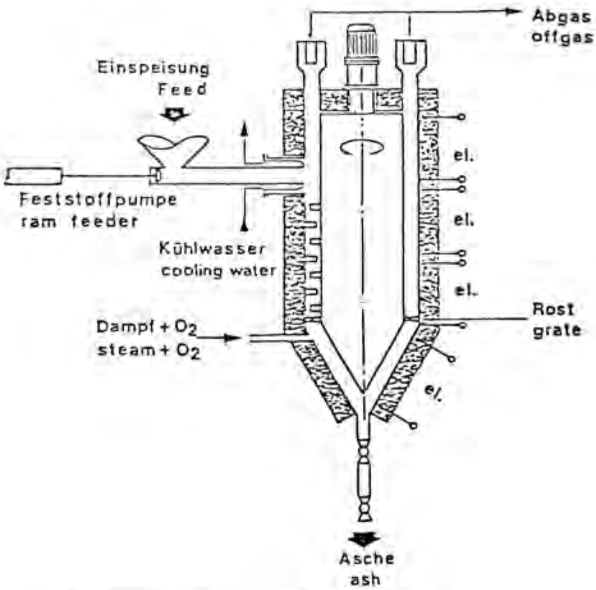

Fig. 3. Pyrohydrolysis-Unit for α-Waste.

Considering the amount of cemented drums produced by direct cementation and by cementation after Nukem-Pyrolysis, there is a factor of 4 fewer drums because of the volume reduction during the pyrolysis process and an additional factor of 4.5 fewer drums because of the higher waste loading per drum.

In all, a nuclear power station will have only 55 drums instead of 1000 drums which meet the U.S. requirements for quality cemented waste.

The decontamination factor has been measured with U and with Cs and is between 1000 and 100,000 for only the reactor itself. The offgas treatment provides another factor of 100 to 10,000.

The amount of secondary waste generated is very low since it has been found that the scrub solution can be used for a very long time without changing. The Hepa-filters also have long lifetimes. The whole system should have a very long operating life since there is no corrosive attack on the material and no high temperature conditions.

Because of the high decontamination factor of the pyrolysis reactor, all of the offgas equipment can be maintained by hands-on procedures.

The packed bed can be removed to prepare the reactor vessel for maintenance operations. The vessel components are easily decontaminated since all equipment is metal.

Conclusions

The advantages of pyrolysis as a volume reduction process when compared to combustion have been investigated by the Nukem R&D department during pyrolysis of spent solvent and spent resin in an extensive full scale prototype operation. The pyrolysis of resin demonstrates that these important considerations are part of this volume reduction system:

-low temperature in the reaction zone
-no problems with the equipment material lifetimes

-simple offgas treatment with high system decontamination factors
-all metal equipment for ease of decontamination
-small, easy to shield equipment for low cost

and

-suitability of the inert waste for successful solidification and product handling.

The disadvantage of lower volume reduction factors compared with combustion is offset by the higher specific activity of the combustion residue which would limit the waste loading in the solidified product. The pyrolysis process solid residues have been solidified in concrete, asphalt and organic binders. Considering both the volume reduction and the higher waste loadings in concrete after pyrolysis the amount of drums will be reduced by a factor of 20.

While incineration plants process low active trash at a high throughput, the pyrolysis system has been developed for high active wastes at low throughputs as with resins. R&D activities were started because the spent solvent cannot be incinerated due to the emission of phosphoric acid.

The future work at Nukem will be the adaption of the agitated bed reactor to sludges and evaporator bottoms.

At the Karlsruhe Nuclear Research Center (KfK) a hot prototype plant will be built and operated in the near future to demonstrate hot operation for a German nuclear reprocessing facility.