

EXPERIENCE ON RESIN PYROLYSIS

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ABSTRACT

The Swedish State Power Board has together with Nukem, Hanau, West-Germany carried out pyrolysis of powder resins in a pilot plant with a capacity of about 30 kg/hr. The pyrolysis reactor with its afterburner and offgas scrubber system has been operated under steady state condition. About 2200 kg resins have been pyrolysed under Nov-Dec 1983 and the decontamination factor for Cs has been measured. Solidification of the residues from the pyrolysis reactor and scrubber water solutions has been carried out and various recipes with cement have been tested. The pyrolysis process has high decontamination factors and no offgas problems as the operating temperature of the reactor is low. The residues from the reactor are chemically dead and can not cause swelling problems. Compared with a normal cementation process the final waste volume will be reduced with a factor of 4 if also the scrubber water after neutralization is solidified. The reduction factor will be 5 if the scrubber water after neutralization is evaporated to a dry salt.

BACKGROUND

In Sweden two different techniques are used for treatment and solidification of ion-exchange resins and filter material. The two solidification matrixes are cement and bitumen. The cement solidification process is used at Oskarshamn and Ringhals nuclear power stations. At Barsebäck and Forsmark nuclear power plants bitumen is used but with different bitumen solidification processes. At present all the waste treated at the power plants is stored in intermediate stores at each nuclear site.

In July 1983 the Swedish government granted a licence to start construction work for a central repository for low and medium level waste. The construction work is now in progress at Forsmark and the final repository will be in operation 1988.

However, in the safety evaluation of the repository the Swedish authorities have expressed some concern about the disposal of bituminized ion-exchange resins due to the risk of swelling.

The Swedish State Power Board has therefore started an investigation for alternative processes which will give products that are acceptable in the final repository and have a volume smaller than normal cement solidification. The pyrolysis process developed by NUKEM, Hanau, West-Germany appeared very promising. Up to that time only bead resins had been processed and consequently an extensive test program was started on the pyrolysis of powder resins and solidification of the residues in cement.

This report will give a short description of the work done and the results obtained with the pyrolysis of resins and the solidification of the residues with cement.

PYROLYSIS PLANT

The pyrolysis plant was developed to decompose TBP/Kerosene and to pyrolyze spent resins. It has been in operation since 1980 as a non-radioactive full scale prototype.

In early 1983 the plant was modified for operation with radioactive tracers by a complete off-gas treatment line, an interlock system to comply with the safety requirements and a reduced pressure equipment.

Figure 1 shows the main components of the pyrolysis plant.

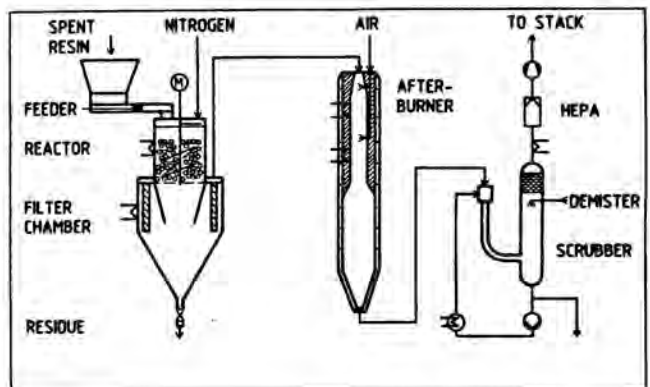


Fig. 1. Pyrolysis Test Plant For Spent Resins

The pyrolysis reactor is filled with a bed of Al_2O_3 -balls, which are kept in slow motion by a helical agitator. The waste is distributed on the bed surface by a distributor disc mounted on the agitator. The solid residues pass through the bed slowly, supported by the motion of the balls.

Formation of crusts or slags is prevented by the motion of the balls and the overall heat transfer is increased.

The gaseous products leave the reactor through metallic hot gas filter candles, which hold back any entrained dust.

The off-gas treatment consists of an electrically heated cyclon afterburner, a scrubber system, filters and an exhaust fan.

PROCESS DESCRIPTION

The pyrolysis system is characterized by low operating temperature, inert or substoichiometric atmosphere and low flow rates in the reactor vessel.

Pretreatment and Feeding of Resins

During the pilot plant operation the powder resin was pretreated in a batch type dryer. The remaining water content of the resin fed into the reactor was about 50% by weight.

The feeding into the reactor was done with a ram feeder. The main component of the ram feeder is a hydraulic agitated piston and a guiding cylinder. The predried resins were transported to the resin feed vessel bolted to the ram feeder as shown in Fig. 1.

The feed rate depends on the adjustable speed of the piston. The slow feeding movement of the piston ensures a nearly constant feed rate.

For a full scale commercial pyrolysis plant installed in a nuclear power station we expect that the pretreatment and feeding would be done in a continuous thermal dryer mounted directly on top of the pyrolysis reactor.

Pyrolysis reactor

The resins fall first on to a steel disc in the upper part of the reactor vessel and lose some water by evaporation. The resins are then slowly distributed to the surface of the ball bed.

Aided by the movement of the balls the resins absorb heat from the balls, lose the remaining water and get pyrolysed when passing downwards through the bed of spheres.

The thermal degradation of sulfur and nitrogen compounds begins at about 200 °C and is nearly completed at about 350 °C.

The balls take up their heat from the electrically heated walls of the vessel. The stirrer helix moves the spheres theoretically in a vertical circle: upwards along the wall of the vessel to get heated, then downwards- inwards to the centre of the vessel and finally outwards to the wall again to complete the circle.

The pyrolysed particles leave the ball bed through a steel grate and fall to the bottom of the filter chamber. This vessel is heated to maintain the operating temperature.

During the pilot test operation we maintained the following parameters:

- Resin feed rate	25 kg/hour
- Nitrogen feed	5 kg/hour
- Reactor wall temperature	ca 600°C
- Average ball temperature	ca 500°C
- Average residence time	> 20 sec

Under these conditions the resins are heated to 300-350 °C and the weight reduction is about 90% based on 65% water content of the starting material. The residues or ash from the reactor consist mainly of carbon, the analysis data are:

- Carbon	86.0%
- Sulfur	2.9%
- Nitrogen	0.7%
- Hydrocarbons, others	Rest

These residues are chemically inert and do not swell in water. The product flows freely like dry sand.

Because of the high heat capacity of the ball bed the product quality is not affected by moderate fluctuations in the feeding or the water content of the feed provided that the average feed rate for one hour is held constant.

The gaseous pyrolysis products (S- and N-containing organic compounds) and water plus nitrogen leave the filter chamber through the metallic filter candles.

Due to the low temperature of the pyrolysis process the radioactive components remain in the residue from the reactor. The decontamination factor for this process is therefore very good.

Afterburner

The afterburner consist of a conical upper section and two cylindric sections with steel walls lined with ceramics. Both cylinders are electrically heated.

After the high temperature combustion chamber there is a low temperature combustion chamber where the combustion is completed.

The pyrolysis gas flows into the conical part of the afterburner and is mixed with air which is introduced tangential. Liquid fuel can be added, if the caloric value of the pyrolysis gas is too low. During the test we added 2 kg of liquid fuel per hour.

At the top of the afterburner, only 50-70% of the necessary air for a stoichiometric reaction is blown in. The gas mixture sets fire in the first cylindric part of the combustion chamber and burns out to some extent.

In the second part of the combustion chamber more air is added so that the total amount of air increases to about 150% of the stoichiometric quantity.

The temperature in the combustion chambers is about 1200 °C.

At the end of the high temperature combustion chamber there is a low temperature zone in which the combustion is completed. The temperature in this part of the afterburner is held at only 600 to 900 °C as the walls of this chamber are air cooled. This part is not lined with ceramics.

The supporting electrical heating has the advantage that even when the pyrolysis gas has a low content of organic material a good combustion is guaranteed.

Furthermore, the electrical heating guarantees security of setting fire even when the interlock system stops the reactor feed or the feed rate is not constant. An electrically heated afterburner also produces about 40% less offgases compared with a propene flame supported afterburner.

Offgas Treatment

The offgases are cooled down in an air cooler, washed in a scrubber, filtered in a glass fibre demister and afterwards heated in an electrical heater before finally passing a HEPA filter on their way to the stack. An offgas fan produces the required underpressure in the whole pyrolysis plant and blows the offgases up through the stack.

In the air cooler the gas temperature is reduced from about 600 °C to 450 °C. The scrubber will then cool the gases down to 60 °C and clean them of their acid components.

A pump will recycle the acid scrubber water and the scrubber water tank is cooled.

In the glass fibre demister the aerosols can be separated from the offgases and the demister is washed with fresh water.

The offgas has now a temperature of about 45 °C and is saturated with water. To avoid condensation in the outlet the offgas is heated to 80 °C with an electrical heater before passing through the HEPA filter.

The absorption efficiency for SO_x and NO_x can be increased to more than 90% by adjusting the pH-value of the scrubber solution to 5-7 or by feeding a hydrogen peroxide solution to the demister instead of fresh water.

The activity level in the scrubber solution will be very low due to the pyrolysis process in itself but also because the metallic filter candles are capable of removing more than 99.9% of the dust.

FLOW SHEET OF THE PYROLYSIS PROCESS

The flow sheet of the pyrolysis process is given in Fig. 2. Per hour 25 kg resins with 50 weight percent water were reduced to 3.6 kg of residues plus the scrubber water.

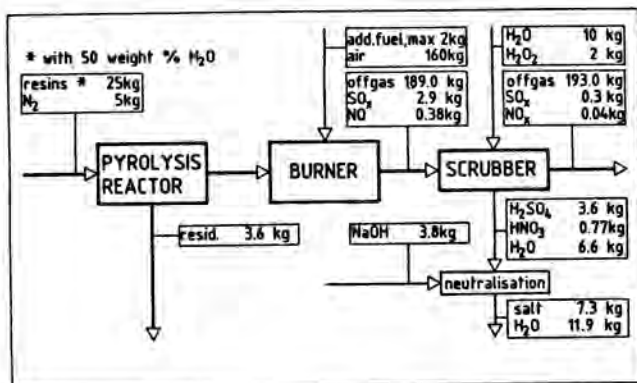


Fig. 2. Flow sheet of pyrolysis of powder resins.

DECONTAMINATION FACTORS

The decontamination factors of the reactor including filter candles for various radioactive elements are very high. The reason is mainly the low operating temperature of the pyrolysis process and the use of metallic filter candles. The filter efficiency is significantly improved by a dust layer on the candles.

During the pilot tests the resins were traced with non-active Cs but also Fe-, Co- and Ni-oxides were added.

The decontamination factors for Cs and Co across the filter candles are:

DF for Cs	10 ⁵
DF for Co	≥ 2.3 × 10 ³
	(detection limit)

The DF's for Fe and Ni must lie in the same range, but could not be exactly determined because of the (inactive) contamination of the plant with these elements.

SOLIDIFICATION OF RESIDUES AND SCRUBBER WATER

The spent resins in a nuclear power plant contain corrosion products, mainly Fe-compounds. In order to simulate spent resins we added these elements as oxides to the residues from the pyrolysis reactor.

The aim was to solidify the spent resin residues together with the scrubber solution from the off-gas system. In order to simulate the expected scrubber water additional salts were dissolved.

For solidification experiments we used standard portland cement and the same additives as now used in Ringhals. Three recipes were developed using lab pyrolysis products.

The intention was to solidify the resin residues with the scrubber water produced in order to obtain only one single waste form. The following recipe meets this requirement:

Water/Cement ratio	0.59
Pyrolyzed resins	12.3 weight-% of final product
Salt content	19.0 weight-% of final product

Plus additives

The mixture was well stirrable and thixotropic. The hardening time lay within 24 hours and there was no free water. The average density of the product is about 1.6 g/cm³ and the compressive strength after 28 days curing time is about 20 N/mm².

If it is preferred to treat the scrubber water separately from the pyrolysis residues, other recipes could be used.

The salt concentration in the scrubber solution depends also on the permitted discharge of SO_x and NO_x from the pyrolysis plant.

If the activity level of the scrubber water is very low it may be acceptable to simply discharge the scrubber water into the cooling water outlet of the power station as normal waste water. Another alternative can be to solidify the scrubber water separately.

MASS BALANCES

The final mass balance of the pyrolysis process depends on the permissible discharge of SO_x and NO_x and the selected treatment of the scrubber water.

We have therefore considered various mass balances for the pyrolysis plant. All balances are based on the annual powder resin consumption at Ringhals 1, 15 000 kg with 100% dry substance (D.S.). That amount of resins will also contain about 650 kg of corrosion products.

With the cement solidification process now used at Ringhals about 100 m³ of waste, excluding shielding, will be produced per year. All that waste would require shielded containers.

The following mass balances are calculated for the pyrolysis plant and shown in Table I:

- The scrubber water can be neutralized with NaOH, diluted and pumped to the waste treatment plant. Assuming that it can be released to the waste water outlet from the reactor site without further treatment, about 11 m³ final waste volume, excluding shielding, will be produced per year.
- The scrubber water can be neutralized with NaOH and after that complete drying of the salt sludge. The dry salt could then be stored in non-shielded containers. The salt volume would be about 8 m³. The total resulting waste volume will then be about 19 m³ final waste volume.
- If the scrubber water has to be solidified after neutralization the dilution of salts would be minimized. The limiting factors for volume reduction are the maximum acid concentration in the scrubber water and the pumpability of the neutralized salt sludge. The scrubber water (40 wgt-% acid) would be neutralized with NaOH to a salt sludge with 44-22 wgt-% solids content. This would result in 25 to 46 m³ final waste volume per year.

CONCLUSIONS

After having accomplished the operational tests with the pyrolysis plant and solidification of the residues we consider the results as encouraging. The average weight reduction amounts to 90%, related to resin containing 65 weight-% water. The residues from the pyrolysis reactor are chemically inert without any swelling tendency.

The throughput of the pilot plant reactor itself can be increased without any problem to 30 kg spent resin per hour with a water content of 50 weight percent. However, the afterburner must be scaled up if the feed rate is to be increased over 20-25 kg/hr. The outside dimensions would not change very much by a scale up corresponding to 30-40 kg/hr feed.

TABLE I. Mass balances of pyrolysis plant and solidification

RAW WASTE	15000 kg POWDER RESIN (100% D.S.) 650 kg CORR. PRODUCTS 60000 kg WATER			
REACTOR RESIDUE	4290 kg ASH, 650 kg CORR. PRODUCTS			
SCRUBBER SOLUTION	8230 kg SALTS (Na ₂ SO ₄ , NaNO ₃), 10380 kg H ₂ O			
TREATMENT	DILUTION, CEMENTATION	CEMENTATION	EVAPORATION (DRY SALT)	DIRECT RELEASE
- WASTE IN SHIELDED CONTAINER	11 m ³	11 m ³	11 m ³	11 m ³
- SALT-PRODUCT IN NON-SHIELDED CONTAINER	35 m ³	14 m ³	8 m ³	-
TOTAL WASTE VOLUME	46 m ³	25 m ³	19 m ³	11 m ³
VOLUME REDUCTION	22	4	5	9

The high decontamination factors of the reactor including the filter candles guarantee a very slight radioactive contamination of the scrubber water.

The solidification tests with simulated waste materials and standard portland cement have resulted in good product qualities with an ash content up to 30 weight percent of the final product. However, the water/cement ratio must be increased with higher ash content. Products with high contents of both ash and salt have also been mixed without any problems as regards workability and hardening.

The final waste volume is depending on the treatment of the scrubber water as could be seen in Table I.

A reduction of the waste volume with a factor around 4 compared with a normal cementation process would be possible to obtain.

Based on the test results it will be possible to design a commercial pyrolysis plant for bead and powder resins.

However, design studies must be carried out to get a suitable pretreatment and feeding system for the pyrolysis reactor. A cement solidification station must also be added to the plant.