Pyrolysis of Spent Ion Exchange Resins – 12210

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ABSTRACT

Organic ion exchangers (IEX) play a major and increasing role in the reactor coolant and other water purification processes. During their operation time they receive significant amounts of radioactivity, making their disposal, together with their organic nature, as medium active waste challenging. Processes applied so far do not eliminate the organic matter, which is unwanted in disposal facilities, or, if high temperatures are applied, raise problems with volatile radionuclides. NUKEM Technologies offers their well introduces process for the destruction of spent solvent (TBP), the pebble bed pyrolysis, now for the treatment of spent IEX (and other problematic waste), with the following benefits: the pyrolysis product is free of organic matter, and the operation temperature with approx. 500°C keeps Cs radionuclides cpmpletely in the solid residue.

1. THE DISPOSAL QUESTION

Ion exchangers (IEX in international language) are used to remove radionuclides from the primary coolant in all nuclear power stations with a water cooling circuit. This is done by continuously removing a volume of coolant from the primary circuit and passing it through coolers, filters and the ion exchange beds. Cation and anion exchangers, in the form of coarse-grained resin beads in pressurized-water reactors and as finely ground powdered resins in boiling water reactors, are used.

The trend for new power stations is to exploit all the possibilities for avoiding the generation of contaminated liquids and then to clean, as far as possible, the solutions that are nevertheless generated using ion exchange for it to be possible to dispose of them as non-radioactive waste. This relieves the burden on evaporator facilities, or means that these can even be dispensed with entirely.

Regeneration is possible in principle, but little use is made of it.

Depending on the water regime, some 3 to 10 m^3 of spent ion exchange can be produced each year in a 1300 MW class unit.

When operating, the ion exchangers remove both cations and anions and after adequate decay delay, radioactivity is predominantly from Cs-134/137, Co-60, Sr-90. The specific activity levels can vary widely, with values around E5 to E6 and even E7 Bq/g expected in the future, these are classified as medium-level waste but can approach the limits for high-level radioactive waste, depending on national definitions.
Ion exchangers generally comprise cross-linked polystyrene (Fig. 1) to which functional groups are added for ion exchange purposes: these are trimethyl ammonium groups $–NMe_3OH$ for anion exchangers and sulfonyl groups $–SO_3H$ for cation exchangers:

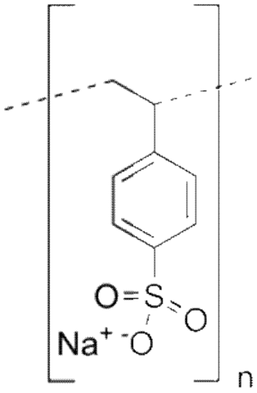

Fig. 1: Polystyrene with Sulfonyl Group (Na Form)

As the regeneration usual in conventional technologies is not employed in nuclear power stations, it is necessary to dispose of this material as radioactive waste, which brings with it the following problems:

- With a water content of over 50%, the spent IEX are too wet for direct ultimate disposal
- They comprise organic matter, and must therefore be assessed critically in respect of combustibility, resistance to fire and gas formation – caused radiolytically or chemically

On the international level, a great number of processes are offered that are intended to meet the relevant national regulations, and these will be discussed in brief below with their advantages and disadvantages:

- **Drying** and direct ultimate disposal leads to no reduction in volume and does not solve the majority of the problems referred to above.
- **Cementation** releases large quantities of amines, increases the volume for ultimate storage and the product has poor resistance to fire with radiolysis generating gases.
- **Embedding** in plastics such as PVC, PE, epoxy resins increases the volume and does not resolve the problems of combustibility and radiolysis.
- **Combustion** is technically complex because of the poor combustibility. Higher radioactivity levels make maintenance of the furnaces more difficult, in particular because of the contamination of the brick lining, and volatile nuclides such as Cs nuclides pass into the flue gas. The latter arguments also apply especially for plasma combustion.
- **Pyrohydrolysis** (thermal decomposition under steam, also known as steam reforming) solves all the problems with regard to suitability for ultimate storage, but requires complex facilities and works at 1000°C, temperatures at which Cs can begin to evaporate.

The aim is then to find a process which reduces the volume, yields an inert or mineralized product, works at temperatures of no more than approximately 600°C and can be run in a simple facility.

2. NUKEM PYROLYSIS: PRINCIPLES

Originally, the pyrolysis process was developed to treat liquid organic waste from reprocessing. A typical application is the decomposition of spent solvent (TBP, tributyl phosphate, mixed with kerosene).

In this process TBP is pyrolysed together with calcium hydroxide in a fluidized bed facility at temperatures of around 500 °C, the calcium hydroxide reacts with the phosphate groups directly to form calcium pyrophosphate which contains all the radioactivity and is disposed of as medium level waste. The organic components pass into the pyrolysis gas which is burnt. The flue gas is further cleaned.

TBP pyrolysis facilities have been built in France (La Hague), Belgium (Mol) and in Japan (Rokkashomura). The Belgian plant has recently ceased operating as all the TBP arising from EUROCHEMIC operations had been successfully processed. The facility in Japan is in the commissioning stage.

Many experiments have been carried out at the existing facilities, and also in corresponding pilot plants including NUKEM's own, to extend the range of waste that can be processed.

3. PYROLYSIS OF ION EXCHANGERS

Initial tests have shown that IEX can be decomposed by pyrolysis with very good results, yielding an inert and chemically resistant product. No additives are necessary. The main constituent of the product, the pyrolysate or ash, is carbon. It has been discovered that the entire radioactive inventory remains in the pyrolysate during pyrolysis of the IEX. This is achieved by relatively low process temperatures that prevent highly volatile nuclides such as the caesium nuclides from passing into the gaseous phase. Sintered metal filters in pyrolysis plant ensure that even the radioactivity bonded to the dust remains in the pyrolysate.

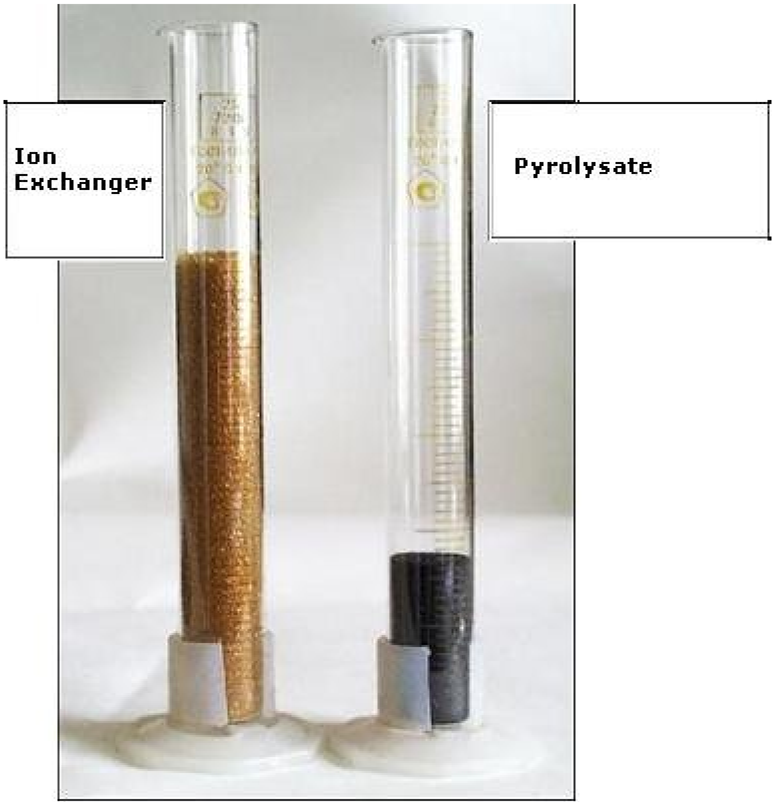

Fig. 2: Comparison of Ion Exchanger and Pyrolysate

In addition to the radionuclides, the main constituents of the residue are carbon from the original polystyrene matrix and sulphur from the functional groups. The pyrolysate occurs as a flowable solid material and not as a melt. It is thus easy to handle and can be compressed or cemented, depending on the requirements for interim and permanent storage.

Any further constituents such as inorganic filter materials or even other organic materials do not interfere with the process, they are dried, calcined or also pyrolysed.

Hydrocarbons such as methane or propene, steam and low volumes of ammonia are the products in gaseous form. The pyrolysis gas generated must be burnt in a burner and then passed to the emission control system and the HEPA filters.

Figure 3 shows a basic flow chart, figure 4 is a process flow chart including exhaust gas treatment.

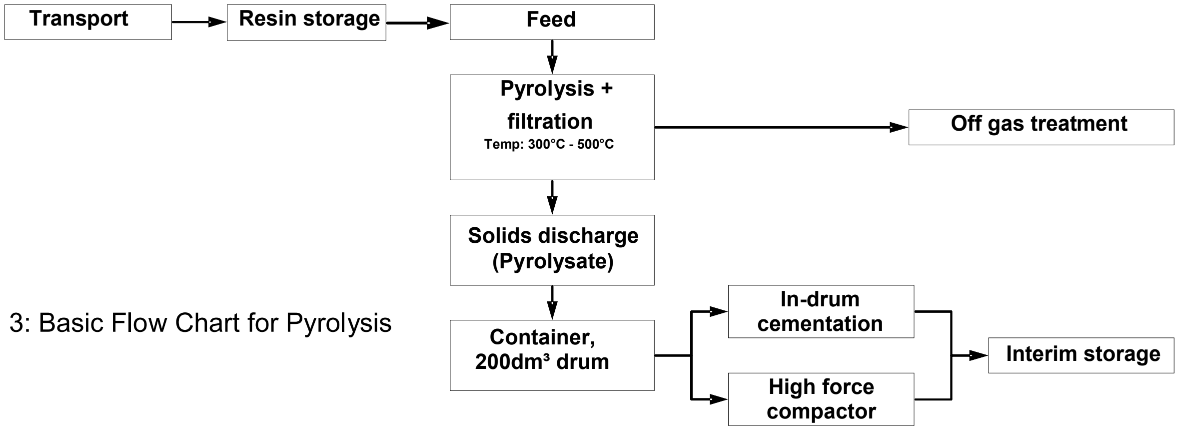

Fig. 3: Basic Flow Chart for Pyrolysis

The process is explained with the help of the process flow diagram (figure 4).

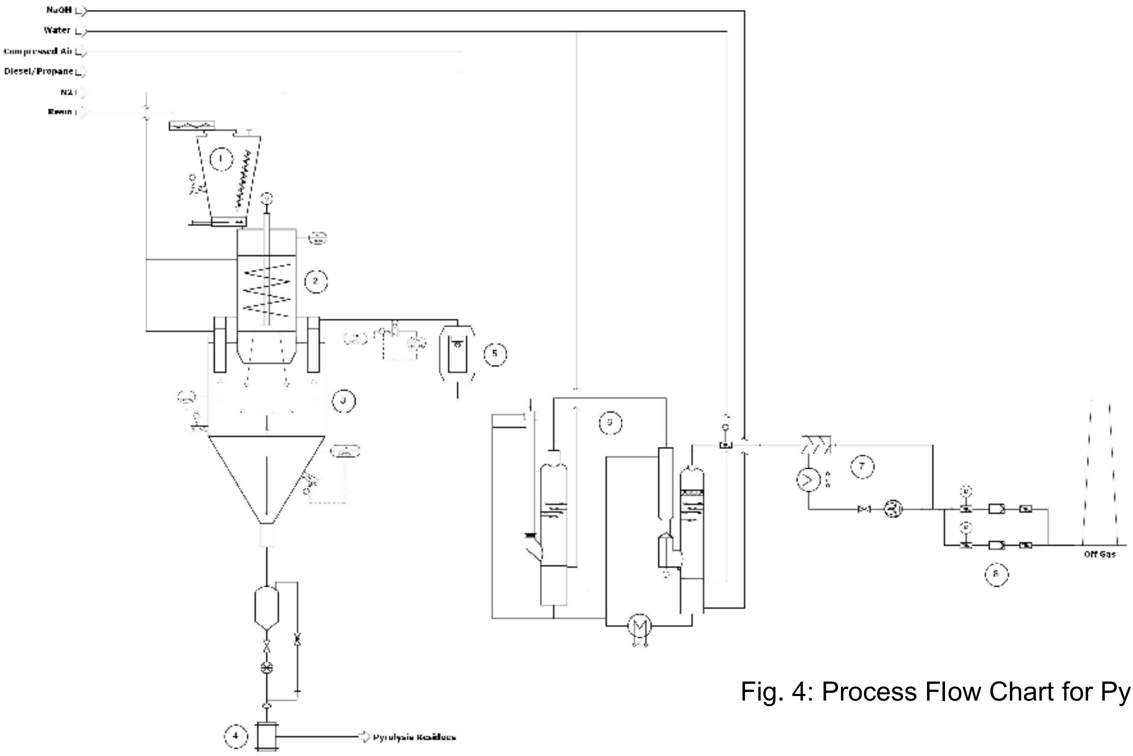

Fig. 4: Process Flow Chart for Pyrolysis

- Pebble bed reactor

Pyrolysis itself takes place in a pyrolysis reactor (2). This essentially comprises an externally heated pebble bed which is agitated to keep the temperature distribution in the reaction chamber as uniform as possible. The reactor is made from high-temperature resistant Inconel 600 to resist chemical and mechanical stresses. The hot gas filter (3), comprising a tapered container with sintered metal filter candles, is connected directly to the reactor. The solid matter is removed beneath the container (4), the off gases are passed from the top over the sintered metal filter candles with the best degrees of filtration to the combustion chamber (5).

The off gas is advantageously passed to an incineration facility should one be available at the location.

- Emission control

If no incineration facility with an emissions treatment system is available, the off gas will have to be burnt (5) and then cleaned of hazardous materials such as SO_2 and HCl. An alkaline wet gas scrubber (6) is used to bind the soluble substances to the water. Finally, the off gas is passed through an HEPA filter structure (8) after reheating (7) to ensure that it passes all radiological permissible emission limits.

- Conditioning

There are a number of conditioning approaches aimed at meeting the wide variety of interim storage conditions. It is possible to compact the pyrolysate from low-activity IEX, while with medium activity IEX, it is advisable to cement the pyrolysate. The current project is using in-drum cementation, which guarantees a homogeneous distribution of the pyrolysate in the cement matrix and at the same time ensures that the material is highly resistant to leaching and is mechanically strong.

The greatest volume reduction factors (theoretically up to 10 times) are achieved with the super-compaction of pyrolysate; if in-drum cementation is used, the volume reduction achieved increases by a factor of 3 to around 2 which is, however, significantly above the conventional methods which, as a rule, do not reduce the volume at all, and may even increase it.

4. NUKEM PYROLYSIS: TECHNICAL DATA:

The technical data for the NUKEM Standard facility is listed below; smaller facilities can be built without problem.

I. Technical Data

Waste composition	Pre-dried ion exchanger resins, in beads or as powder (typical water content approximately 50 % by weight)
Permissible radioactivity	E13 Bq/m³
Throughput	Up to 50 kg/h (including residual water)
Volume reduction	Between 3 and 10 depending on the ratio of cation exchanger to anion exchanger
Output weight	Approximately 0.25 to 0.30 kg/kg dry resin
Operating conditions	Continuous, 24 h/d, 5 d/w
Decontamination factor	No radioactivity in the pyrolysis gas

Figure 5 shows an assembled pebble bed reactor

As the facility can be built to be very compact, particularly the off gas line, modular construction is possible so that the facility can be mobile for use at different locations.

Fig. 5: Assembled Pebble Bed Reactor

Figure 6 shows the open reactor, figure 7 shows the complete facility.

Fig. 6: Pebble Bed Reactor, opened

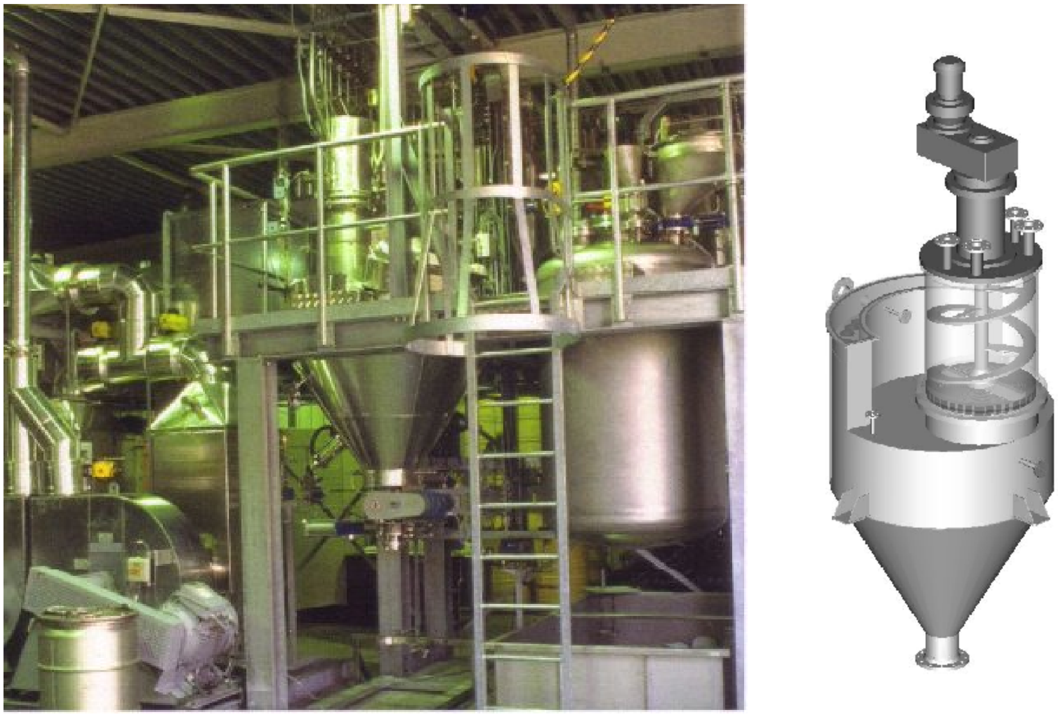

Fig. 7: Complete Facility