

# Pyrolysis of Radioactive Spent Resins in the PRIME Installation

**J Hansen<sup>1</sup> and J Deckers<sup>2</sup>**

<sup>1</sup> Montair Process Technology B.V.

<sup>2</sup> Belgoprocess N.V.

Email: jurgen.hansen@belgoprocess.be

**Abstract.** Montair and Belgoprocess developed the pilot PRIME (Pyrolysis Resins In Mobile Electric) Installation for treatment of spent resins in one single reactor without pre-treatment and without intermixing of other waste, allowing for easy traceability and isotopic characterization of the end product. Both low level waste (LLW, < 2 mSv/h) and medium level waste (MLW, > 2 mSv/h) can be treated in the installation. The PRIME pilot installation is designed to treat 2 batches of 100 litre of saturated ion exchange resins over a period of 24 hours. The pyrolysis reactor contains a special design mechanical stirrer and can operate at a temperature of up to 600°C under inert conditions. As a result, the organic molecules will decompose at an accelerated rate until only carbon-rich and mineralised product free of hydrocarbons remains. Gases that are released during drying and pyrolysis are treated in a thermal oxidizer, which uses an innovative, electrically heated design instead of a traditional natural gas- or fuel oil secondary combustion chamber design. After passing through the thermal oxidizer, the gases are cooled down to saturation temperature and treated in the wet scrubbing system. An induced draft fan keeps the system under negative pressure to prevent the possibility of any off-gas leakage out of the system. The pyrolysing reactor and oxidiser are fully electrically powered which creates also a higher safety level. A series of tests were performed successfully with wet cationic resins, anionic resins and a mixture of both. The results of these tests are described in the presentation. For intellectual property protection, the system and process of pyrolysis of organic waste and the system of thermal oxidation of pyrolysis gases described in this paper are patent pending.

## 1. Introduction

Internationally, handling of the continuously generated waste stream of radioactively contaminated ion exchange resins remains a critical issue [1], [2]. While various treatment installations are operational, a true mineralization (conversion to unreactive inorganic products) of spent ion exchange resins is not obvious due to the resins' activity and isotopic composition. Mineralization is desirable however, since it reduces waste volume and eliminates the possibility for further decomposition of organic material during storage. Stored and untreated spent resins may provoke chemical reactions from or between the organic resin, the container/drum, filler material and concrete. A chemical reaction can affect the storage quality of the products and can compromise the container, resulting in leaking storage units. Treatment of such spent resins must therefore meet severe criteria for the organic waste content.



The problem with incineration is that it is an uncontrolled thermal process where the temperature in the waste can easily rise above 1.000°C. The high temperatures obtained during incineration will lead to carry-over of isotopes such as caesium, while the quick evolution of gasses will lead to carry-over of contaminated dust particles. An additional problem that occurs during incineration is that the resin beads will clog together when they are fed in packages, merging together into large chunks. Clearly, this clogging together of the resin beads negatively impacts the effectiveness of treatment, as it inhibits heat- and mass transfer.

Pyrolysis of organic waste under nitrogen atmosphere on the other hand is a controlled process. [3] The temperature in the waste can be limited, preventing carry-over of radioactive isotopes. The controlled conditions also prevent the undesired clogging together of individual resin beads. Currently, pyrolysis is already a “proven technology” for specific applications in the nuclear industry, such as for pyrolysis of tributyl phosphate (TBP)-containing liquids and/or plutonium-containing organic products. [4]

## **2. The Prime – Installation Working Principles**

The PRIME pilot installation is designed to treat 2 batches of 100 L of saturated ion exchange resins over a period of 24 hours. A dosing unit with screw feeder is used for the dosing of the saturated ion exchange resins to the pyrolysis reactor. The pyrolysis reactor contains a special design mechanical stirrer and can operate at a temperature of up to 600°C under inert conditions. As a result, the organic molecules will decompose at an accelerated rate until only the mineralized material remains. The lower temperature and the absence of oxygen also prevent the breakdown of ion exchange resins into (powdery) ash, which is a considerable advantage during further handling.

Gases that are released during drying and pyrolysis are treated in a thermal oxidizer, which uses an innovative, electrically heated design instead of a traditional natural gas- or fuel oil secondary combustion chamber design. After passing through the thermal oxidizer, the gases are cooled down to saturation temperature and treated in the wet scrubbing system. An induced draft fan keeps the system under negative pressure to prevent the possibility of any off-gas leakage out of the system.

A series of tests were performed successfully with wet cationic resins, anionic resins and a mixture of both. The results of these tests are described in the presentation.

For intellectual property protection, the system and process of pyrolysis of organic waste and the system of thermal oxidation of pyrolysis gases described in this paper are patent pending.

## **3. Research and Development**

Montair and Belgoprocess conducted an R&D project to investigate the feasibility of mineralizing ion exchange resins through a single process of drying and pyrolysis – a simple and straightforward process. To reduce the installation size and simplify possible dismantling afterwards, the installation size has been designed on the footprint of a 20-foot container. This small footprint also makes the installation mobile. To reach these goals, an innovative compact electrically heated oxidizer for the off-gas was designed, built and tested.

The pilot plant was designed, constructed and functionally tested, see Figure 1. For experimental testing, the pilot plant is designed to treat 100 L wet cationic resins or anionic resins or a mixture of both. The goal of the testing was to investigate the effectiveness of treatment of the ion exchange resins, to characterize the end product and to verify that no clogging occurred during treatment. In addition, the functionality of the dosing unit with screw feeder and the electrically heated oxidizer were tested.

The results of this pilot plant will be used to realize a mobile commercial installation for the treatment of radioactive spent ion exchange resins from nuclear power plants.



**Figure 1.** PRIME Pilot Installation, dimensions 2.3 x 5.7 x 3.8 m (w x l x h).

### 3.1. Ion exchange resins

The PRIME pilot installation is designed to process ion exchange resins. Ion exchange resins consist of a cross-linked matrix consisting of a styrene and divinylbenzene co-polymer. The resins can bind ions using specific functional groups. The cationic ion exchange resins contain sulfonate groups ( $\text{R-SO}_3^-$ ), while the anionic ion exchange resins contain quaternary ammonium groups ( $\text{R-N}(\text{CH}_3)_3^+$ ).

- Cationic ion exchange resins  
Molecular formula:  $\text{C}_{25}\text{H}_{25}\text{S}_3\text{O}_9$
- Anionic ion exchange resins  
Molecular formula:  $\text{C}_{34}\text{H}_{52}\text{N}_3\text{O}_3$ .

## 4. The Prime Pilot Installation Design

The PRIME pilot installation is easy to operate with the support of the fully automated control system. The PRIME pilot installation was operated by one operator during all tests.

The PRIME pilot installation is based on the treatment of 100 L of saturated ion exchange resins over a period of 24 hours. A dosing unit with screw feeder is used for the dosing of the saturated ion exchange resins to the pyrolysis reactor. The pyrolysis reactor contains a special design mechanical stirrer and can operate at a temperature of up to  $600^\circ\text{C}$  under inert conditions. Gases that are released during drying and pyrolysis are treated in a thermal oxidizer which uses an innovative, electrically heated design instead of a traditional natural gas- or fuel oil secondary combustion chamber design. After passing through the thermal oxidizer, the gases are cooled down to saturation temperature and treated in the wet scrubbing system. An induced draft fan keeps the system under negative pressure to prevent the possibility of any off-gas leakage out of the system. The flow diagram of the pilot plant is shown in Figure 2 below.



**Figure 2.** Flow diagram of the pilot plant based on a 20 ft container footprint.

#### 4.1. Safe design principle

The PRIME pilot installation is designed with only electric heating as heating source, even thermal oils are excluded. As no flammable fuel sources such as oil or natural gas are used, there is no need for storage tanks and piping to the system. For a mobile system this is a huge advantage, as it allows the system to be placed at many more locations. No specific safety studies for storage tanks and transfer for fuel to the facility are needed.

The thermal oxidizer is designed to heat up using electrical power and control the internal temperature at the minimum 850°C, assuring the minimum 2s residence time of the off-gases in the presence of at least 6% oxygen by volume as in a conventional thermal oxidizer to ensure good oxidation of the pyrolysis gases.

Since no extra fuel is introduced for heating the off-gases by means of a burner, another big advantage is that no additional combustion gases are introduced by operating the burner. As a result, the new concept for the electrical oxidizer and the design of the other off-gas systems can be significantly smaller due to the reduced off-gas volume.

In the event of electrical power failure, the complete installation heating will be shut-down. The pyrolysis process in the reactor will stop automatically and the remaining pyrolysis gases will be oxidized in the oxidizer due to the accumulated residential heat of the bricks and excess of oxygen. Off-gas extraction fans (one e.g. as standby) as well as the pre- and HEPA filters can be operated in parallel as common practice for nuclear process installations.

#### 4.2. Pyrolysis reactor

The PRIME pilot installation pyrolysis reactor has a useful volume of 100 L, with a design temperature of 600°C and is equipped with a special design mechanical stirrer on a central axis, see Figure 3. A resin inlet on the top connects the reactor to the dosing unit and a pyrolysis gases discharge connection at the top of the reactor connects the reactor to the thermal oxidizer. A discharge connection at the bottom of the reactor is connected to a receiver drum for the resins after treatment. Connections on the bottom and the top allow for nitrogen blanketing, ensuring an inert atmosphere. The inlet and discharge for the resins can be closed with pneumatically actuated slide valves. The pyrolysis reactor is heated by ceramic heating elements around the conical part of the reactor.

Although the installation does not make use of external flammable fuels, the pyrolysis gases themselves must also be considered as a flammable mixture when oxygen is introduced at high temperature. The pyrolysis gases cannot leak out of the installation, since the installation is kept at negative pressure by the extraction fans.

To prevent air leaking into the reactor section, before the thermal oxidizer, all possible leakages are sealed and/or flushed with nitrogen. On top of this, before start-up a leakage test is performed to ensure leak tightness.



**Figure 3.** Dosing unit (top left) and pyrolysis reactor (front). Dimensions approximately 1 x 0.1 x 1.3 m (w x l x h).

#### 4.3. Dosing unit

Loading of the ion exchange resins into the reactor is controlled by a dosing unit with screw feeder, see Figure 3. The dosing unit contains a hopper to hold the ion exchange resins. This hopper can either be filled by using a pump or by manual loading. The saturated ion exchange resins are typically handled in 20- 40% free water, since the wet resins will not transfer well. The bottom of the hopper is fitted with a sieve to recover this free water, also known as transport water. A connection for nitrogen allows the oxygen to be purged from the ion exchange resins before loading into the reactor.

The loading of the ion exchange resins into the reactor is done with the screw feeder. The dosing can be set at a high rate, to quickly fill the reactor for batch operation, or at a low rate, for treatment of the ion exchange resins in a continuous process.

#### 4.4. Thermal oxidizer

In the thermal oxidizer, the pyrolysis gases released during treatment of the ion exchange resins are heated electrically to 850°C at a minimum residence time of 2s, in the presence of at least 6% volume of oxygen. This ensures that over 99.9% of all volatile organic compounds (VOC's) are combusted. Traditionally, a natural gas or fuel oil burner is used for heating the thermal oxidizer (afterburner). However, the combustion products that are generated by the burner increase the size of the system considerably. Also, the burner flame prohibits a design for the thermal oxidizer that is not straight, making a compact design difficult to realize.



#### 4.5. Wet scrubbing system

The hot off-gases from the thermal oxidizer are passed through an injector-venturi scrubber for further treatment, see Figure 4. In the injector-venturi, water is injected into the off-gases at high pressure. The off-gases are then forced through the narrow venturi throat section, greatly increasing flow velocity and atomizing the water to create a finely dispersed mist. At these conditions, particles and pollutants are quickly captured by the water droplets. In addition, the evaporating water cools down the hot off-gases till saturation temperature. After treatment, the cleaned off-gases are released into the atmosphere by use of an induced draft fan.



**Figure 4.** Thermal Oxidizer (left) and Wet Scrubbing System (front). Dimensions approximately 2 x 3.4 x 3 m (w x l x h).

Important note: for R&D purposes, a much-simplified design for the off-gas treatment system is used to save costs. Treatment of contaminated off-gases is a core business for Montair and will be designed when required.

### 5. Discussion of Experimental Results

The reactor was loaded with 100 L cationic saturated ion exchange resins with 6.8 % free water, containing 97.5 kg of wet resins. The resins were treated over 10 hours, at a maximum temperature of 550°C and under inert nitrogen atmosphere.

After drying and pyrolysis treatment, 13.2 kg of ashes were recovered from the 97.5 kg of wet cationic resins loaded into the reactor, a mass reduction of 7.4. A volume of 14.7 L of ashes was recovered from the 89.8 L of wet cationic resins loaded into the reactor. The volume reduction factor obtained was 6.1. A comparison by volume of the wet resins, dry resins and treated resins are shown in Figure 5. The wet resins are dark brown compared to the light brown colour of the dry resins. The

wet resin beads are larger in size than the dry resin beads due to the absorbed water. The resins treated by pyrolysis are grey coloured and are smaller than the dry resins.



**Figure 5.** Wet ion exchange resins in water (left), dry ion exchange resins (middle) and residue after pyrolysis treatment (right).

The general mass balance for the pyrolysis process is shown in Table 1. The estimate of the total amount of gas released is 52.6 kg.

**Table 1.** General mass balance.

Wet resins with free water ( <i>loaded</i> )	104.6	kg
- <i>Free water</i>	7.1	kg
Wet resins	97.5	kg
- <i>Absorbed water (calculated estimate)</i>	31.7	kg
Dry resins	65.8	kg
- <i>Residue recovered</i>	13.2	kg
Gas released over 4.5 hours	52.6	kg
Average mass flow	11.7	kg/h
Average gas flow after oxidation	18.0	Nm <sup>3</sup> /h*

\*Nm<sup>3</sup>: standard volume for gases at a pressure of 1 atmosphere and at a temperature of 0°C)

### 5.1. Pyrolysis residue volume increase in water

Taking a sample of 100 g pyrolysed resins with a volume of 110 ml, water was added up to a total volume of 400 ml. After 48 hours, no noticeable increase in the volume of the resins could be observed. Evolution of nitrogen gas from the sample was observed and after 48 hours the total volume had been reduced to 370 ml. A likely explanation is that nitrogen was present in the pores of the pyrolysed resins and was replaced by water. The pH of the water after these 48 hours was 9.2, indicating the presence of soluble species in the pyrolysed resins.

### 5.2. Ignition residue determination

After heating the pyrolysed resins to 550°C for 4 hours in air, 26.5% residue remained. After heating the pyrolysed resins to 900°C for 3 hours in an oxygen atmosphere, 1.36% residue remained. The pyrolysed resins were found to have a sulphate content of 20 ppm and a moisture content of less than 0.05 wt%.

### 5.3. Results with anionic resins

A test with anionic resins was done with 50 L resins. Although further testing and sample analysis will be required, the initial results with anionic resins are similar to the results with the cationic resins. A clear volume reduction was observed for the anionic resins. The residue recovered after the test resembled the residue from the cationic resins, with no undesired aggregation of the beads into large chunks.

### 5.4. Additional tests

During the first quarter of 2020, Montair and Belgoprocess will perform additional tests on the carry over of non-radioactive Co- and Cs-doped anionic and cationic resins, as well as tests with organic absorbents for sludge or liquids.

## 6. Waste Form

The ashes are a carbon-rich, inert product similar to graphite, free from hydrocarbons and are ideally embedded in cement resulting in an end product ready for disposal. Tests performed on homogeneous cementation of the ashes were successful.

Alternatively, it is also possible to supercompact the drums with the ashes and embed the resulting pucks in cement in a drum. For this latter scenario, the activity levels of the end product need to be watched.

The ashes residue after pyrolysis a VRF of 7 to 8 is measured while test performed with homogeneous cementation an overall VRF from 4 is realised.

## 7. Conclusions

Montair and Belgoprocess designed, constructed and tested the PRIME pilot installation for treatment of spent resins. This compact installation is transportable in a 20-foot container, which makes the installation mobile and simplifies possible dismantling afterwards. The simple and straightforward process combines the drying of the wet spent resins and pyrolysis in one single reactor without pre-treatment and without intermixing of other waste.

The main features of the installation are a dosing unit with screw feeder which is used for the dosing of the saturated ion exchange resins to the pyrolysis reactor, the pyrolysis reactor itself to treat the resins, an electrically heated thermal oxidizer to treat the gases that are released during drying and pyrolysis, and a wet scrubbing system to scrub the gasses.

The goal of the tests was to investigate the effectiveness of treatment of ion exchange resins, to characterize the end product and to verify that no clogging of individual resin beads occurred during treatment.

The PRIME pilot installation test runs with both cationic and anionic resins were very successful and did not reveal any major issues. Montair and Belgoprocess successfully tested the viability of the installation for the combined drying and pyrolysis process for the resins, the performance of the innovative electrically heated thermal oxidizer and the dosing of the resins using the dosing unit with screw feeder.

The test with cationic resins was performed with 100 L wet resins, which were treated over 10 hours at a maximum temperature of 550°C and under inert nitrogen atmosphere. During pyrolysis, the minimum release of gases was estimated at 81 Nm<sup>3</sup> over a period of 4.5 hours, or 18 Nm<sup>3</sup>/h. The residue recovered after treatment consisted of dry, ash-coloured beads with almost no agglomeration of resin beads. A volume reduction of 6.1 was obtained over the wet resins. Analysis of the ashes after pyrolysis treatment indicated that the ashes were highly inert, indicating the pyrolysis treatment was successful. A test with 50 L wet anionic resins gave similarly promising results, although further testing and analysis will be required.

Additional tests on the carry over of non-radioactive Co- and Cs-doped anionic and cationic resins, as well as tests with organic absorbents for sludge or liquids are scheduled for the first quarter of 2020.



The results of this pilot plant will be used to realize a mobile commercial installation for the treatment of radioactive spent ion exchange resins from nuclear power plants.

### Acknowledgements

This project has received funding from the Euratom research and training programme 2014–2018 under grant agreement No. 755480. This paper reflects only the authors' views, and the European Commission is not responsible for any use that may be made of it.

### References

- [1] International Atomic Energy Agency 2002 Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers *Vienna*
- [2] Deckers J and Mols L 2007 Thermal Treatment of Historical Radioactive Solid and Liquid Waste into the Cilva Incinerator *ICEM Conference, Bruges, Belgium* pp. 1–6.
- [3] Dubois M A, Dozol J F, Nicotra C, Serosé J, and Massiani C 1995 Pyrolysis and incineration of cationic and anionic ion-exchange resins - Identification of volatile degradation compounds *J. Anal. Appl. Pyrolysis*, vol. 31, pp. 129–140
- [4] Luyckx P, Meeus A, Goetschalckx R, and Hansen J 1999 Pebble Bed Pyrolysis for the Processing of Alpha Contaminated Organic Effluents *WM Symposium*, 1999, Tucson, AZ