DELIVERABLE REPORT

Thermal treatment for radioactive waste minimisation and hazard reduction

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THERAMIN Project Partners

Andra	Agence nationale pour la gestion des déchets radioactifs – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
GSL	Galson Sciences Limited – UK
FZJ	Forschungszentrum Juelich GmbH – Germany
LEI	Lithuanian Energy Institute – Lithuania
NNL	National Nuclear Laboratory – UK
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
ORANO	Orano – France
SCK•CEN	The Belgian Nuclear Research Centre – Belgium
USFD	University of Sheffield – UK
VTT	Teknologian Tutkimuskeskus VTT Oy (VTT Technical Research Centre of Finland Ltd)
VUJE	VUJE a.s. – Slovakia

THERAMIN End User Group

Andra	Agence nationale pour la gestion des déchets radioactifs – France
AWE	The Atomic Weapons Establishment, UK
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
EDF	Electricité de France – France
Fortum	Fortum Oyj – Finland
IGD-TP	Implementing Geological Disposal of Radioactive Waste Technology Platform
INL	Idaho National Laboratory, USA
Nagra	Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle – Switzerland
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
RWM	Radioactive Waste Management Ltd – UK
Sellafield	Sellafied Ltd – UK
TVO	Teollisuuden Voima Oyj – Finland

Executive summary

VTT has developed, constructed and tested a thermal gasification based treatment method, especially for organic ion exchange resins (IXR). Technically the method can also be used for reduction of volume of low level operational waste containing organic matter but the waste has to be crushed before treatment. The technology has been designed for compact process, which can be operated at NPP site. The process has been designed primarily for reduction of volume of high organic matter containing radioactive waste.

The primary product from thermal gasification is fine dust collected by high temperature filter In addition to the filter dust the process produces some bottom ash, which consists mainly of bed material. Usually bed material is aluminium oxdide when targeting to treatment of spent ion exchange resins. Both filter dust and bottom ash are powders and thus the final residues have to be immobilised (cementation, vitrification, etc.) after waste processing before final disposal. VTT's thermal treatment process is based on thermal gasification, gas conditioning and flue gas cleaning and its principle is shown in Figure 1.

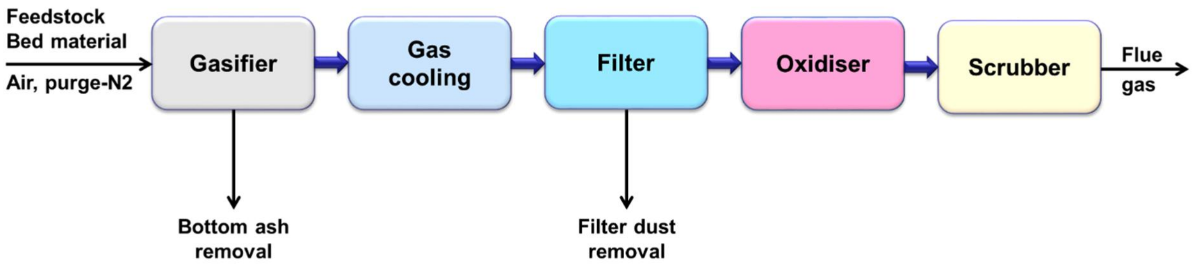

Figure 1. Principle of the gasification based thermal treatment facility (patented by VTT).

1 Introduction

VTT has developed already from 80's gasification and gas cleaning technologies for different applications and different feeds. The primary focus has been in production of fuel gas or synthesis gas from high quality fuels but later in 90's the development was focused also on different wastes containing harmful contaminants. The development of the thermal gasification technology for treatment of low and intermediate radioactive waste was based on this experience from gasification and gas cleaning of conventional waste fuels.

VTT's process is based on well-controlled thermal fluidised-bed gasification followed by an efficient gas cleaning, gas oxidation and wet scrubbing of the oxidised gas. The process was now verified to be a suitable thermal treatment method for organic IXR. Removal of organic matter by thermal gasification results in significant reduction of the volume of the IXR. Volume reduction of the original waste (IXR) was now demonstrated successfully. Filter dust is the final residue, which needs to be processed further (immobilised) in order to enable safe disposal. Immobilisation can be made for example by cementation. However, VTT has also developed an advanced immobilisation technology based on the use of geopolymers. This geopolymerisation will be used to immobilise the samples from demonstration test trials carried out in this project.

2 Description of the technology to be deployed

Thermal gasification is a technology used almost 200 years to produce energy from carbon containing fuels. Gasification can be seen as a partial oxidation so that only 20…30 % of oxygen, which is required to complete oxidation, is available. Thus the produced gaseous product contains still combustible components and the conditions in the gasification reactor are reducing. Some oxygen is needed to produce the heat requested for gasification reactions but gas atmosphere is reducing having an impact on inorganic chemistry in the reactor.

Thermal gasification is used to produce fuel gas for direct combustion in power plants, industrial kilns and gas turbines etc. Gasification offers also an attractive opportunity to produce combustible gas from different wastes with minimal risk of corrosion and after efficient gas cleaning the produced gas can be combusted as a clean gas. This can be applied in utilisation of different waste streams in energy production but also in treatment of radioactive waste. Gas cleaning prior gas combustion plays a very essential role in the treatment of organic low and intermediate waste. When the gas cleaning is made in a correct way all solid material can be removed easily prior gas combustion. Gasification temperature is significantly lower than high temperature treatment by Joule heating or plasma and thus a very minor part of some metals is vaporised. However, these metals can be converted to solid form by cooling the gas below 450…500°C prior particulate removal and thus these metals can be removed together with other solids. In radioactive waste treatment the flue gases are also cleaned after gas oxidation (combustion) as a backup in order to guarantee complete gas cleaning.

Technically gasification can be realised in several different ways. For radioactive waste treatment the fluidised-bed technology is one of the best because of several reasons: e.g. very efficient mass and heat transfer, fuel flexibility, continuous operation and maturity of technology. Therefore fluidised-bed technology was selected by VTT for the technology to treat low and intermediate radioactive waste. VTT has designed, constructed and operated several fluidised-bed reactors during last 40 years and thus VTT has excellent know-how and expertise on this technology. VTT has also developed successfully product gas cleaning and ultra-cleaning already from 80’s for conventional as well as for very demanding applications.

The development of thermal gasification based treatment of low and intermediate radioactive waste has been based on so called bubbling fluidised-bed (BFB) gasification. In BFB gasifier bed material is fluidised by blowing gasification air or other gas from the bottom through the air distributor. Used fluidising gas velocity is restricted low enough in order to avoid elutriation of bed particles from the reactor. The other type of fluidised-bed reactor is so called circulating fluidised-bed (CFB) reactor, which uses significantly higher fluidising velocity. High fluidising velocity results in high circulation of the bed material from the reactor to the recycling cyclone, from where the bed material is returned back to the bottom of the reactor. High fluidising velocity enables high energy density and thermal capacity per cross-sectional area. Both reactor types can be applied for thermal gasification of LILW and are used in THERAMIN demonstration test trials.

Schematic diagrams of the VTT’s bench-scale Bubbling Fluidised-Bed (BFB) and pilot-scale Circulating Fluidised-Bed (CFB) gasifier are shown in Figures 2 and 3.

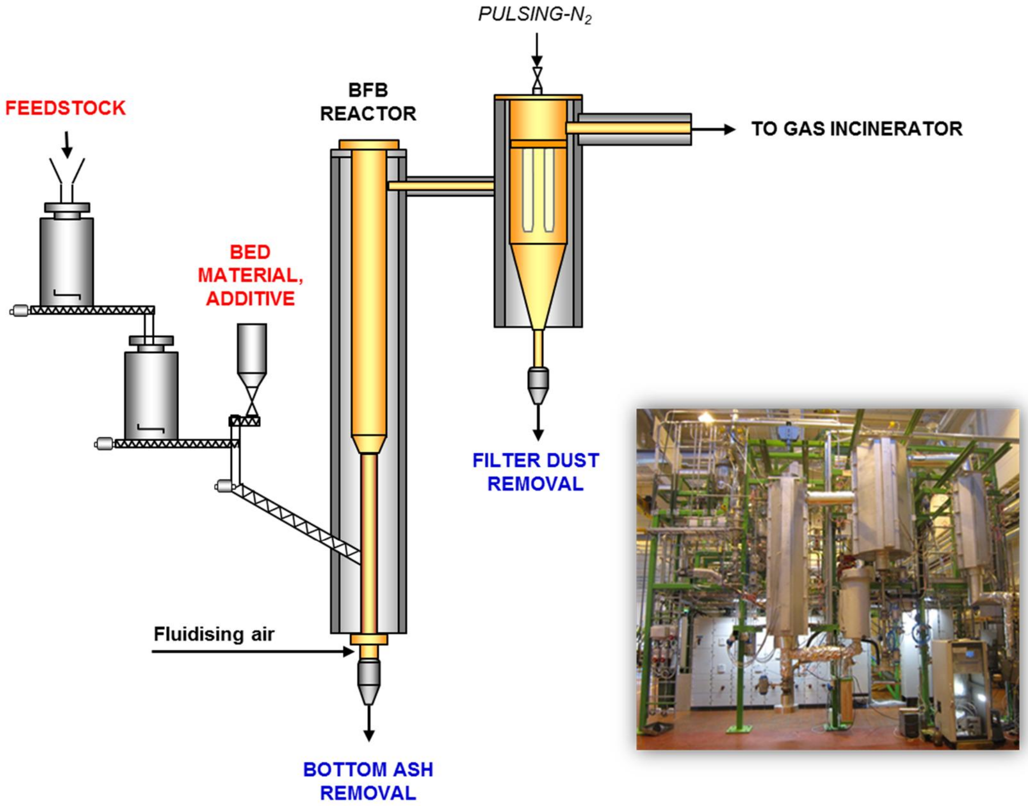

Figure 2. Bench-scale Bubbling Fluidised-Bed gasification test rig (BFB100).

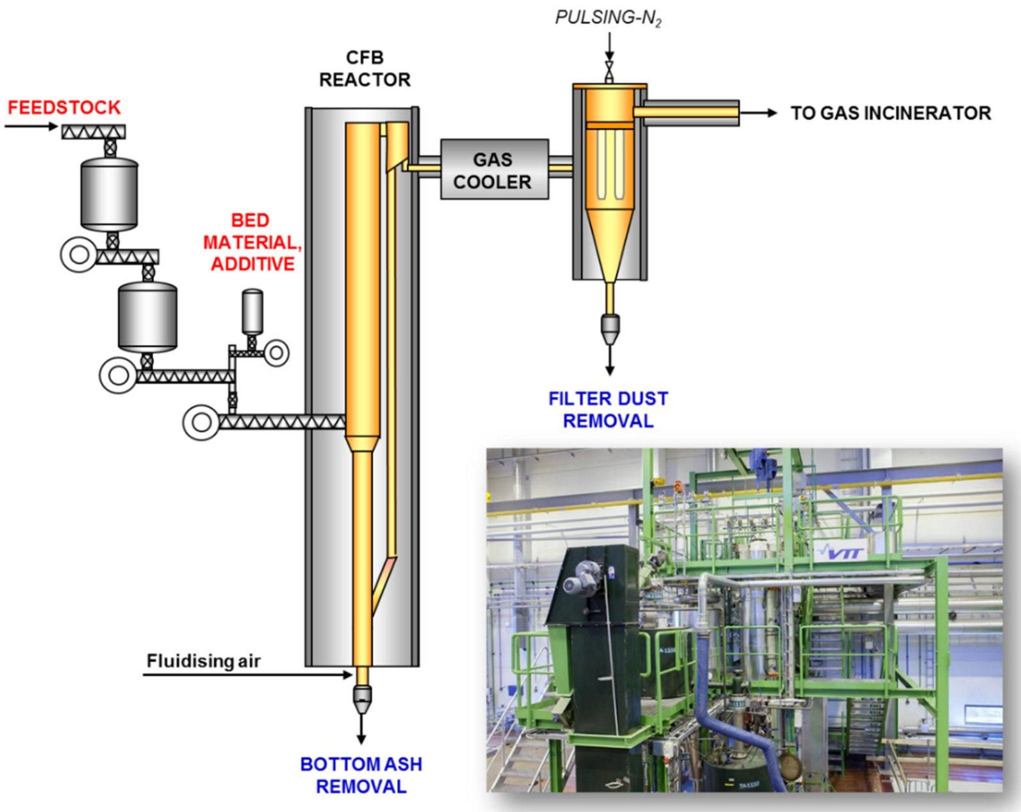

Figure 3. Pilot-scale Circulating Fluidised-Bed (CFB) gasification test rig.

The gasification test trials reported in this Deliverable were carried out with an atmospheric pressure pilot-scale Circulating Fluidised-Bed (CFB) gasification test rig at Bioruukki - VTT's Piloting Center. The bed diameter of the reactor is 102 mm and the freeboard diameter 150 mm. The height of the bed section is 1817 mm and freeboard 5510 mm, respectively. Electrical heaters were used around the reactor and gas pipes to compensate heat losses.

The test rig is equipped with versatile fuel feeders: e.g. feedstock hoppers of the live-bottom type, suitable for low-bulk-density fuels. In addition, the test rig is equipped with a separate feeder for a bed additive. The fuel feeding port locates above the dense bed (approximately 2.4 m above the air distributor). The particles from the recycling cyclone is introduced close to the air distributor.

Only air was used as a gasification agent in these test trials and it was electrically preheated.

The reactor, the recycling cyclone and the recycling line are electrically heated in order to minimise heat losses. The use of electrical heaters together with the rather high circulation rates makes it possible to maintain a uniform temperature distribution over the whole reactor.

The gasification product gas was cleaned in the recycling cyclone followed by a gas cooler and a high-temperature filter unit. The filter unit consists of 12 metal candle elements, which are about 60 mm in diameter and 1000 mm in length. The candle elements are located in four clusters and each of them is equipped with a pulse ejector and a pulse cleaning tube. Nitrogen was used as a filter pulsing gas (back pulse cleaning). The filter unit can be operated over a wide temperature range, the maximum temperature being 800-900°C. In these test trial the target filtration temperature varied 415-450°C.

The role of the filter unit is to remove particles from the product gas. The filter is operating practically as total filtration. Easily volatile compounds condensate to the particles when the gas is cooled and filtering temperature is low enough and harmful compounds (e.g. Cs in these test trials) are removed from the process with the filter dust.

The bottom ash removal frequency from the gasifier during operation is based on the pressure drop of the bed, which is targeted to maintain stable. IXR has so low ash content that bottom ash removal is normally not needed during the treatment process. No additional bed material is neither needed after the start-up. Minimised need for make-up bed material reduces the overall bottom ash waste, which has to be immobilised and disposed in a similar way as filter ash.

The test rig is equipped with an automatic data acquisition of temperatures and pressures measured at different locations. The flow rates of gasification agents and purging nitrogen are continuously measured and recorded. Nitrogen is used to purge fuel feeding system and the pressure drop measuring lines. The fuel feed rate is controlled on the basis of the screw calibration curve, and the rotation speed of the metering screw is continuously measured. In addition, feedstock (IXR) batches are always weighed when loading into the feeding hopper in order to check the actual feedstock consumption after the test trial.

The main gas components CO, CO_2, H_2, CH_4 and also O_2 are monitored by on-line analysers. In addition, besides the main gas components nitrogen and hydrocarbon components (C_2-C_5H_y), are automatically analysed by micro gas chromatograph.

All mass streams were measured except product gas, which is calculated based on the other mass streams and product gas composition. All solid residues (bottom ash and filter dust) were collected, and filter dust was also analysed for the CHNS and ash content.

3 Waste feed

CFB gasification test trials were carried out with the unspent organic ion exchange resin IXR (Figure 4), which was impregnated with CsCl in order to simulate Cs content in a real spent IXR. Pure IXR was at first slightly dried from moisture content of 50 wt-% to about 40 wt-% with a Lödige vacuum dryer (Figure 5). The initial weight of IXR batch to be impregnated was about 260 kg. Then a measured amount of CsCl-water solution was added to the pre-dried batch of IXR and this mixture was stirred 1-2 hours before it was dried again to have a final moisture of about 30 wt-%. Cs content was targeted to be 4 ppm-wt in dry matter.

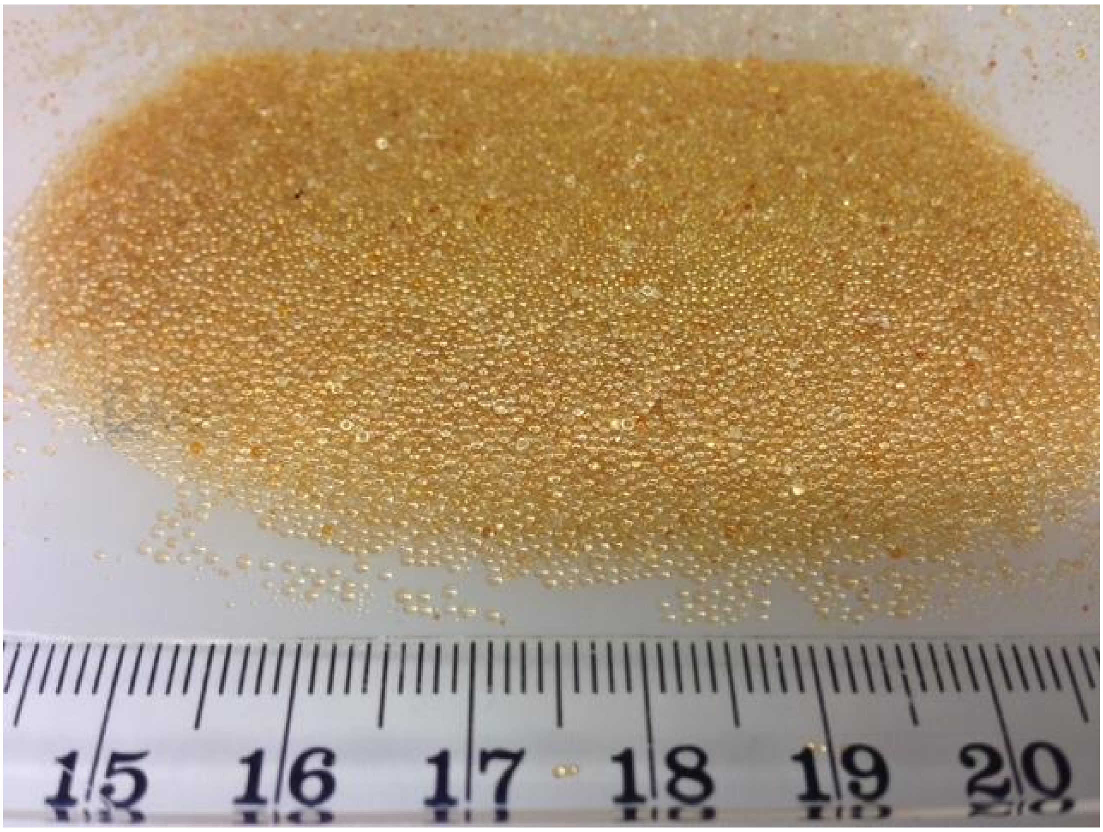

Figure 4. IXR used in CFB gasification test trials (scale is in cm).

Figure 5. Lödige VTA600 vacuum dryer.

Different kind of IXR was studied to be chosen for the test trials, but it was decided to use the very same IXR which VTT has used in previous test trials. Its composition has been analysed several times, because feedstocks are always analysed when gasified in order to determine the variation of their quality (in different batches). The elemental and ash analyses are needed in order to calculate the fuel feeding rate for the gasification process, and mass balances of the main elements. Variation of the analysed IXR compositions is presented in Table 1.

Table 1. Variation of IXR composition.

Moisture content of the feed, wt-%	22.5-39.7
Ultimate analysis, wt-% (dry basis)	
C	56.5-65.1
H	5.5-7.1
N	1.6-3.0
S	5.9-12.3
Ash	0.1-0.8
Cs in dry matter, ppm-wt	4.3

4 Trial information

Organic IXR was treated in total of 325 kg during three test trial days (9.-11.10.2018). After the first and second test trial days the gasifier was inertised by nitrogen and the electrical heaters of the reactor were adjusted lower to 600°C. In the next morning the gasifier was heated up back to the target temperature, the fluidising gas was changed from nitrogen to air and the IXR feed was started. Test trials were aimed to be carried out each day at the same operation conditions, but there came up some small variation in the process. Total duration of the trials was 26.5 hours of which a steady-state period was measured during 12.5 hours. Average gasification temperature was 885-915°C, and the filtering temperature varied 415-450°C. A total of 18 kg inert Al_2O_3 (particle size of 0.18-0.25 mm) was used as a bed material of the CFB gasification reactor.

The operating temperatures, main gas compositions, pressure drops, fluidising air and purge-N_2 feed rates during the second test trial day (on 10.10.2018) are presented in Figure 6-9 as an example. The targeted reactor temperature was 850…890°C but in the end of the test trial on 10.10.2018 the actual temperature was a little bit higher. This was because the feeding rate of IXR was slightly decreased in order to increase the equivalent air ratio. Small diluting dips in CO_2 content of the gas composition in Figure 7 are due to pulse cleaning of high temperature filters, which is done by pressurised nitrogen pulses. These nitrogen pulses are clearly seen in purge-N_2 mass stream in Figure 8. Each four candle filter cluster was cleaned by pulsing with nitrogen once in an hour. Figure 9 shows that the pressure drop in the bed (Bed-bottom) was rather stable during the whole test trial day without any bed material addition. Filter dust removal by nitrogen pulsing is seen also in filter pressure drops.

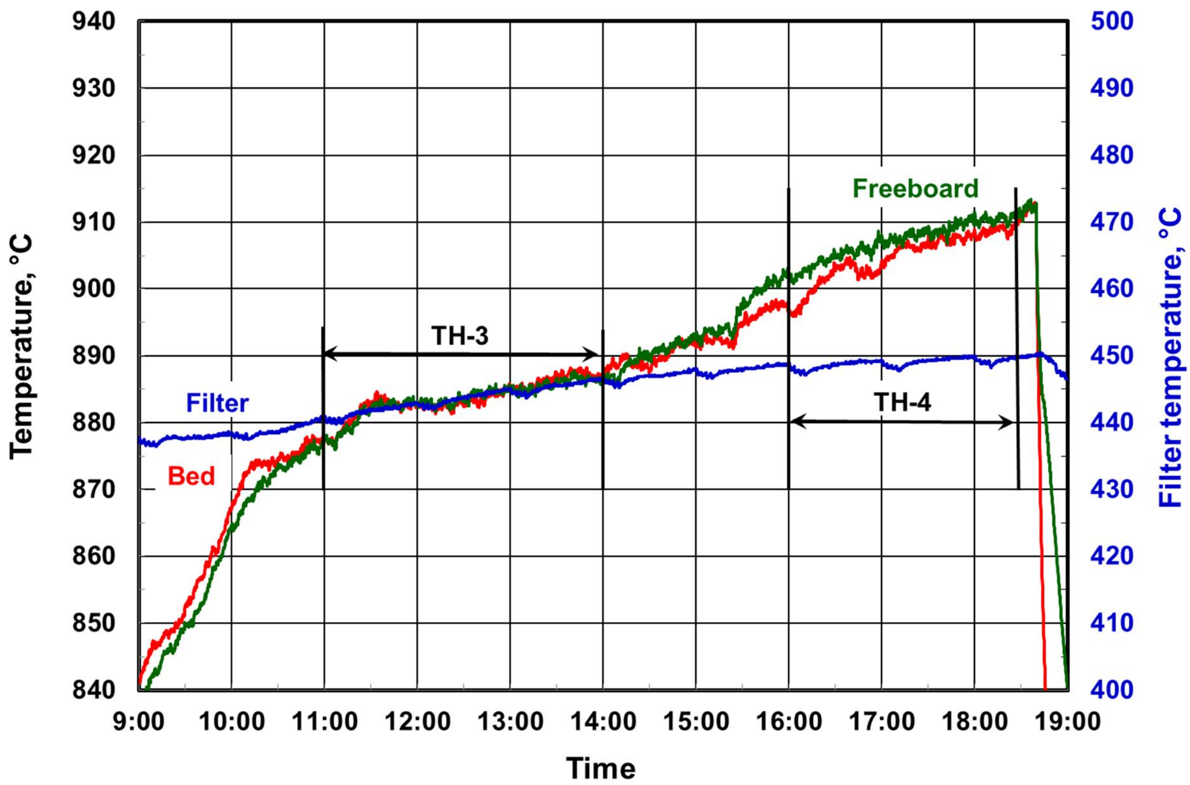

Figure 6. Gasification and filtering temperatures during 10.10.2018.

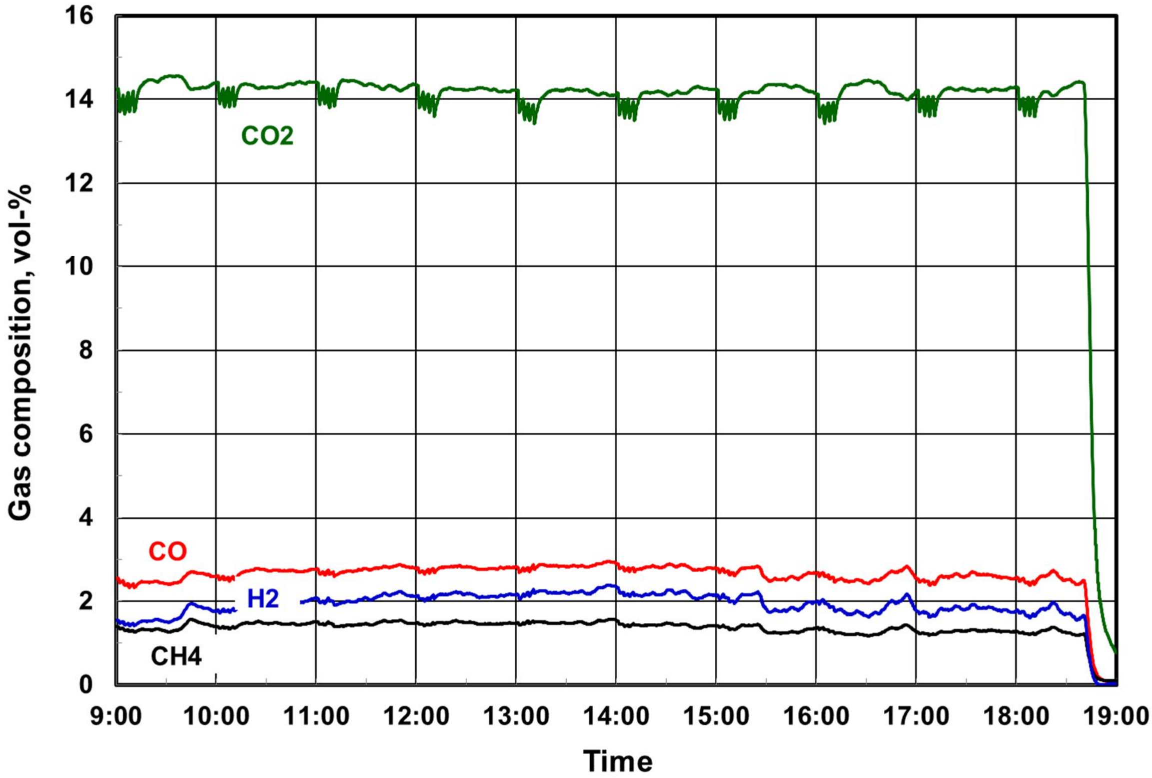

Figure 7. Main gas composition during 10.10.2018 (the main gas component is nitrogen, which is not shown in the figure).

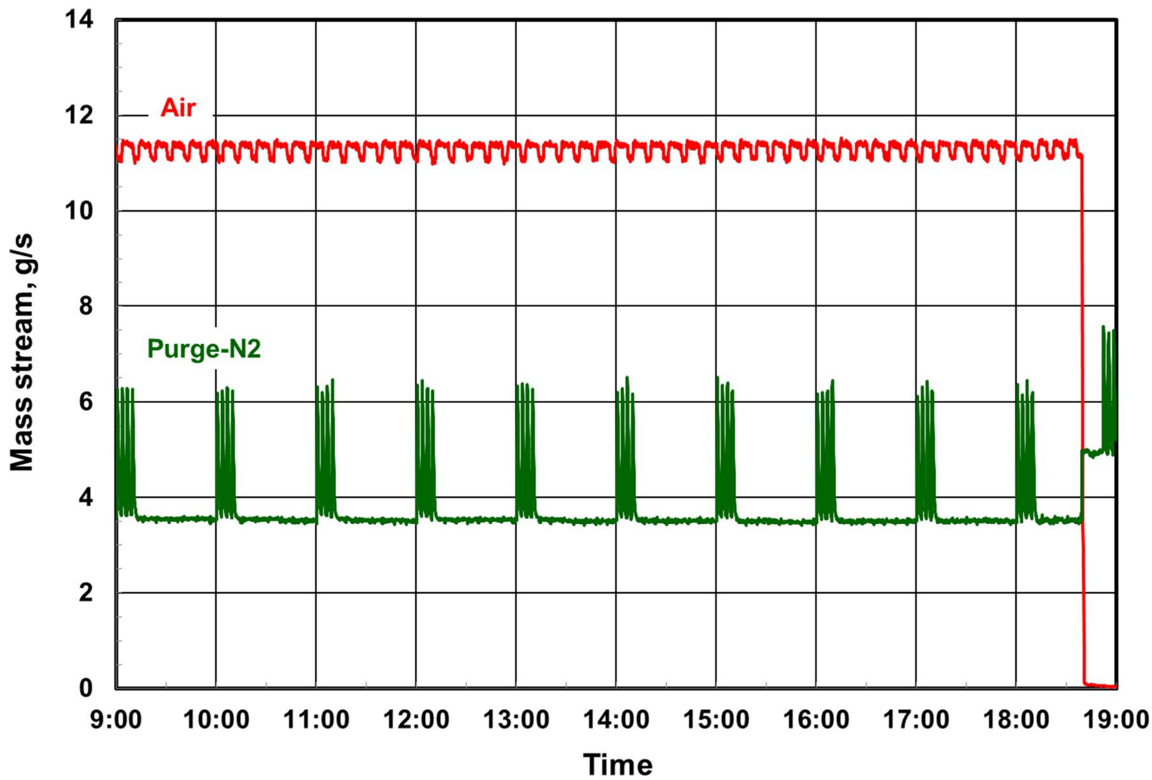

Figure 8. Air and purge-N_2 feed rates during 10.10.2018.

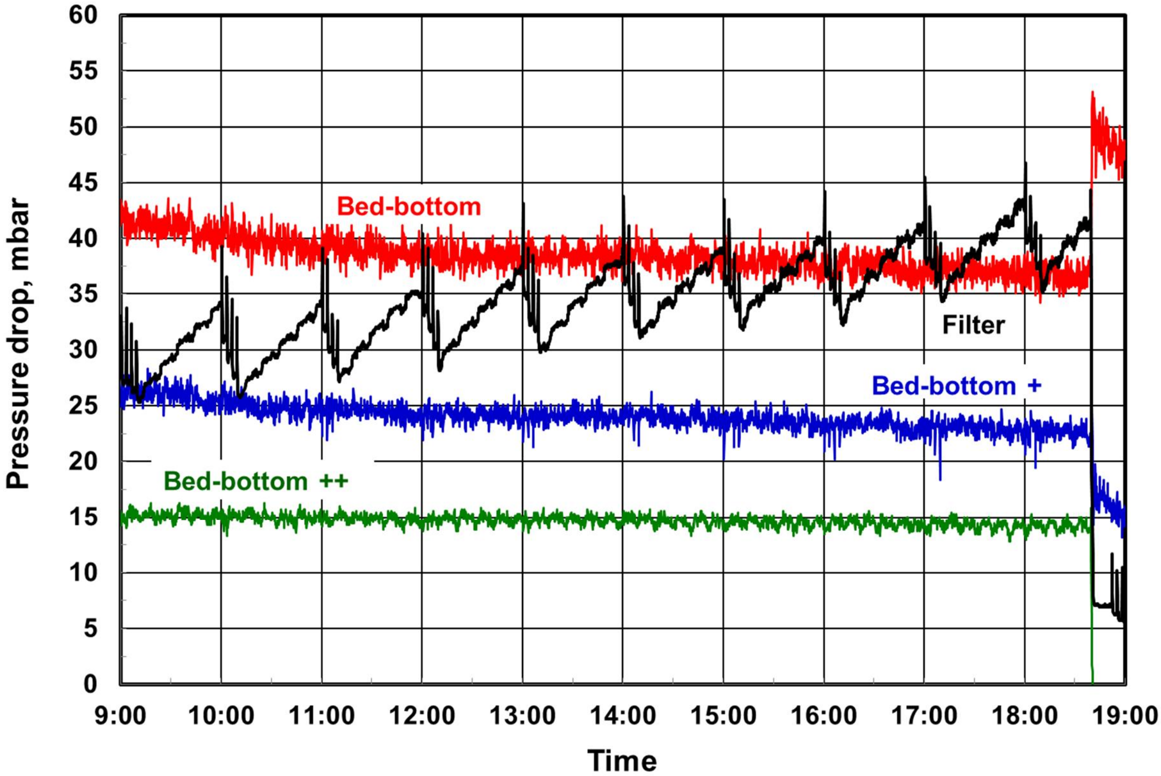

Figure 9. Pressure drops during 10.10.2018.

The primary assessment of the success of the test trial is done by determining mass balances for the main elements. The mass balances for the steady-state periods of the test trials were calculated based on the average values of the measured data (including ash and ultimate analysis of the IXR and filter dust as well as tar content in dry product gas). The hydrogen balance was used to calculate the water vapour content of the gas, and the nitrogen balance was used to calculate the dry product gas flow rate.

Calculation of the carbon conversion is based on the carbon mass balances and it describes how efficiently input carbon is converted to gas. The carbon conversion has been calculated as conversion of feedstock carbon into the gaseous carbon compounds and tars in the product gas. The carbon conversion to gas and tars was 92-96 wt-%, which means that the removal of the organic material from the IXR succeeded very well.

Gasification product gas was dilute because the equivalence air ratio λ was kept deliberately rather high (0.49-0.54) since the main target was to remove the organic matter from the feedstock (IXR), not energy production.

Summary of the operation conditions and process measurements of the steady-state periods are presented in Table 2.

Table 2. Summary of the average operation conditions and process measurements in different test trials (all gas measurement after thermal gasification but before gas oxidation and wet scrubbing).

TEST TRIAL	**TH-2**	**TH-3**	**TH-4**	**TH-5**
Date	9.10.2018	10.10.2018		11.10.2018
Moisture content, wt-%	28.3	28.3	28.3	28.3
Fuel feed rate, g/s	3.6	4.0	3.6	3.8
Primary air feed, g/s	11.3	11.3	11.3	11.3
Air ratio λ	0.54	0.49	0.54	0.51
Bed temperature, °C	915	885	905	890
Freeboard temperature, °C	920	885	905	890
Filter temperature, °C	450	445	450	415
Dry gas composition, vol-% (before oxidation and wet scrubbing)				
CO	2.6	2.8	2.6	2.6
CO_2	14.3	14.3	14.3	14.3
H_2	2.0	2.1	1.8	1.7
CH_4	1.3	1.5	1.3	1.2
C_2H_2	0.02	0.02	0.02	0.02
C_2H_4	0.23	0.26	0.18	0.15
H_2S	0.80	0.95	0.90	0.90
N_2	78.7	78.1	78.9	79.0
Tar + benzene in dry gas, g/m^{3}n (before oxidation and wet scrubbing)	17.4	22.0	17.3	19.9
Dry gas flow rate, m^{3}n/h	45.5	46.0	45.5	45.3
Wet gas flow rate, m^{3}n/h	52.8	53.9	52.9	53.2
C balance closure (out/in)	0.97	0.94	0.96	0.94
C conversion to gas + tars, wt-%				
* 100 % - Carbon losses in filter dust	99.1	98.6	98.9	98.4
* from gas and tar yields	96.4	92.5	95.1	91.5
* corrected C conversion[1)]	99.2	98.4	98.8	98.3

[1)] C conversion calculated from gas and tar yields corrected (divided) by the carbon balance closure (out/in).

Demonstration test trials were carried out in order to verify the gasification process to be a suitable thermal treatment method for organic IXR.

One target of the demonstration trials was also to produce treated waste (solid residue) for further characterisation tests. The produced thermal gasification residues are powders and therefore an immobilisation is requested in order to enable final disposal. The solid residue can be immobilised by applying different technologies. In THERAMIN project VTT will apply geopolymerisation for immobilisation of the residues. The receipt and methodology has been developed in previous projects of VTT and until now the results have been significantly better than for example normal cementation.

Organic IXR was gasified during three test trials in total 325 kg, and filter dust was produced during the whole feedstock feeding time 3.3 kg, which is only 1 wt-% of the amount of fed IXR.

5 Post trial activities

After the test trials the test rig is always inspected in details. The reactor is opened and residual bed material removed and reactor walls inspected in order to identify possible deposits. Recycling cyclone is also opened and possible residual bed material and ash is removed. Filter is cleaned by pulsing the filter and collecting possible residual filter ash from the bottom of filter vessel (ash discharge valves).

Until now all test trials have been done using simulated non-radioactive feed materials. The most essential component of the whole process is thermal gasification and primary recovery of solid residues by hot gas filter. When treating hot radioactive feed material the cleaned gas from gasification has to be oxidised immediately after solids removal and flue gas is cleaned further by wet scrubbing followed by high efficiency particulate removal as a backup cleaning. In test trials with simulated feeds the oxidation is done using existing gas fired boiler and flue gases are wet scrubbed by existing flue gas scrubber. From environmental emission point of view the only significant emissions are those, which have been measured after the boiler and wet scrubbing but from technical development and assessment point of view the gas cleaning in the first phase prior the gas oxidation is an essential information. Emission measurements for cesium were not carried out for the flue gas after the wet scrubber because in VTT's Piloting Center Bioruukki the gas pipeline between the gasifier and the gas fired boiler is approximately 25 meters, which is not relevant for industrial facility. In addition, the existing gas fired boiler is designed for 1 MW fuel capacity, which is significantly more than the capacity of the used CFB gasifier.

The solid products from the thermal gasification are filter ash and also some bottom ash. Both mass streams are powdered and they should be immobilised in order to enable safe long-term storage. VTT has developed already several years geopolymerisation of dangerous waste materials and this technology has been planned to be applied also for the ash samples from the THERAMIN test trials. When the THERAMIN project was started it was not yet sure if the geopolymerisation technology is ready to be used in the project and therefore it was not promised to be included in the work plan but cementation was as a backup option. However, the geopolymerisation process development has progressed very well and the characterisation of the produced immobilised samples has resulted in very good results. Therefore it has been decided that instead of cementation the ash samples from the THERAMIN test trials will be immobilised by geopolymerisation. This will be done during the Spring 2019 and the final product will be characterised.

6 Conclusions

Gasification based thermal treatment test trials were carried out successfully and the produced treated samples are now ready for immobilisation and after that characterisation of immobilised test specimens. The results from characterisation of these test specimen will be used in WP4 to carry out assessment of immobilised products for long-term storage safety point of view.

More test trials will be carried out in 2019 in order to optimise further the treatment process and also to produce more treated material for immobilisation tests.

Test trials were carried out using VTT's Circulating Fluidised-Bed (CFB) gasification pilot plant. Results proved that CFB reactor is very efficient in removal of organic matter from ion exchange resin. The advantages of CFB compared to bubbling fluidised-bed (BFB) reactor are related to treatment capacity per cross-sectional area of the reactor. In addition, the heat and mass transfer are also better in CFB. However, in certain conditions CFB may have disadvantages related to deposit formation and agglomeration of the bed but in most cases these can be controlled and avoided by clever operation and selection of the bed material.