Characterisation and Evaluation of Wastes for Treatment in the Batch Pyrolysis Plant in Studsvik, Sweden – 13586

Maria Lindberg, Carl Österberg and Thomas Vernersson
Studsvik Nuclear AB, Studsvik Nuclear AB; 611 82 Nyköping, Sweden
maria.lindberg@studsvik.se

ABSTRACT

The new batch pyrolysis plant in Studsvik is built primarily for treatment of uranium containing dry active waste, “DAW”. Several other waste types have been identified that are considered or assumed suitable for treatment in the pyrolysis plant because of the possibility to carefully control the atmosphere and temperature of the thermal treatment. These waste types must be characterised and an evaluation must be made with a BAT perspective. Studsvik have performed or plan to perform lab scale pyrolysis tests on a number of different waste types. These include

- Pyrophoric materials (uranium shavings)
- Uranium chemicals that must be oxidised prior to being deposited in repository
- Sludges and oil soaks (this category includes NORM-materials)
- Ion exchange resins (both “free” and solidified/stabilised)
- Bitumen solidified waste

Methodology and assessment criteria for various waste types, together with results obtained for the lab scale tests that have been performed, are described.

INTRODUCTION

During 2012, Studsvik Nuclear´s incineration facility was expanded with the building and commissioning of a pyrolysis facility. The 2 m^3 batch fed pyrolysis unit is primarily intended for treatment of uranium contaminated waste, for example from fuel factories. However, the facility has been designed in order to offer versatility and enable, facilitate or improve treatment of a number of other identified waste fractions. The preliminary assessment of a waste fraction’s suitability for treatment in the batch fed pyrolysis unit must be verified with a more comprehensive analysis constituting material characterisation, evaluation and lab scale tests. Material characterisation encompasses physical and chemical analysis, as well as radiological measurements.

DESCRIPTION (METHOD)

The general principle for assessment of a waste fraction's suitability for treatment in the batch pyrolysis unit follows the process below.

Feasibility study

The feasibility study always includes an initial theoretical assessment of the waste type of interest. The evaluation is based on known characteristic of the waste, such as

- physical form
- density
- chemical composition
- reactivity
- pyrophoric properties
- dose rate
- nuclide content etc.
- waste handling

Pre-trial planning

Pre-trial planning, takes into account constraints or demands from for example a customer or repository regulations. These constraints can take on a number of forms, such as achieving a desired (maximum or minimum) volume or weight reduction; reducing or completely eliminating the content of a specific compound (for example carbon or chelating agents); achieving a certain chemical composition, *i.e.* complete oxidation of waste material. Depending on these constraints and/or the outcome of step one above, the treatment could require certain conditions, for example a controlled oxygen level in the atmosphere as in the case of treatment of uranium chemicals or addition of steam during treatment of organic DAW. The pre-trial planning includes the following steps:

- Initial process parameters such as temperature, treatment time, atmosphere/additives

- Determination of suitable inactive materials or surrogate materials to be used in inactive trials. As an example, other, inactive, pyrophoric materials than uranium can be used in initial trials, for example magnesium and cerium.

- When the waste is comprised of several fractions an evaluation is made of in which order these fractions should be processed, starting with the fraction that is "easiest" to determine process parameters for, and gradually increasing the difficulty of process prediction.

- Adjustment of experimental equipment

- Determination of analyses, chemical and radiological, of the waste material and the secondary waste

Lab-scale trials

Lab-scale trials are performed in a 2 dm^3 vessel placed in a muffle furnace equipped with temperature regulation. The lab-scale heat-treatment equipment layout is shown in Figure 1.

The material to be treated is placed in a beaker inside the vessel. Gases (nitrogen, N_2, oxygen, O_2) and water is added via mass-flow-controllers. It is then led into a steam-generator located inside the furnace. The gases produced in the pyrolysis vessel are led into an after-burner where air is added in order to oxidise the gases from the organic material in the pyrolysis vessel. The off-gases are then cooled and led through a mechanical filter and a wet-scrubber. Finally the off-gases are released into the ventilation system. In case of a sudden increase of pressure the gases from the pyrolysis-vessel will be led through a separate tube to an emergency quench with the purpose of rapidly cooling these pyrolysis-gases.

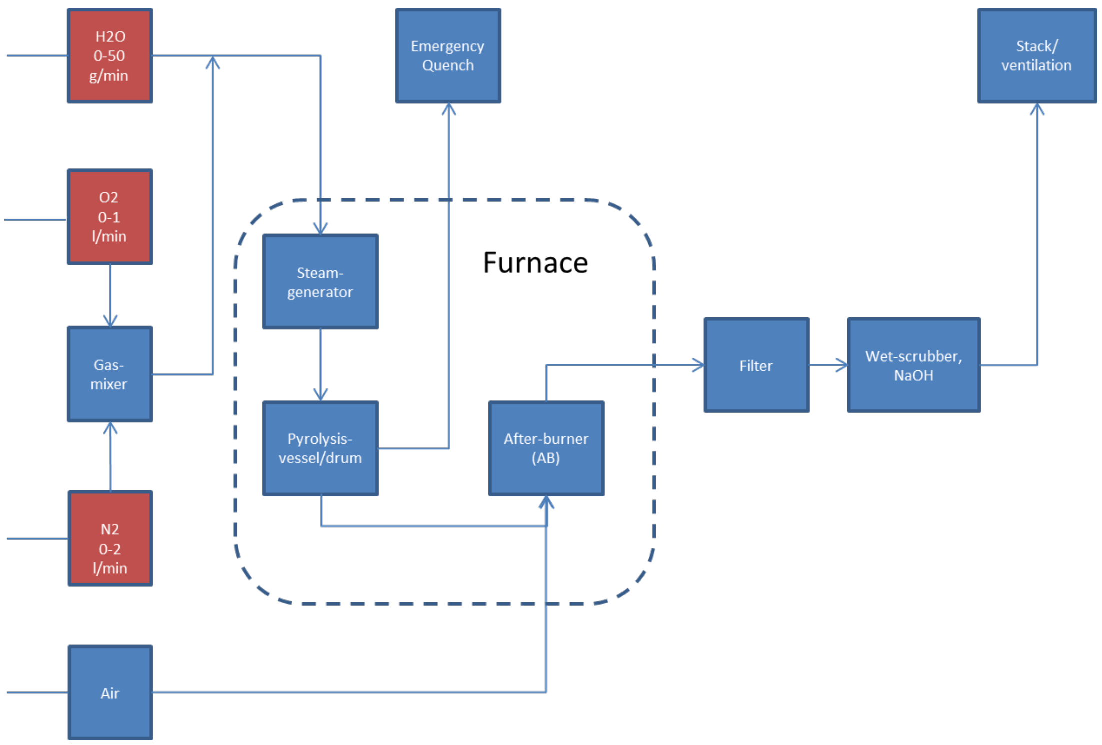

Fig. 1 Schematic description of lab scale heat treatment equipment.

The lab-scale trials are performed using the initial process parameters determined under pre-trial planning, above. Analysis results, chemical and radiological as determined during pre-trial planning, from the initial inactive tests can be used to modify the process parameters. Repeated trials are carried out to gather data and verify the process. The lab-scale trials are carried out in a series of steps, adjusting process parameters based on analysis results and exchanging inactive representative material or surrogate material for actual representative waste. The final step of the lab-scale trials is made using active representative waste material, and repeated to ensure reproducibility.

Analysis on the secondary waste is also carried out in order to evaluate fulfillment of constraints and to determine activity distribution between the different fractions of secondary waste (ashes, filters, scrubber fluid).

Based on the outcome of the repeated trials the scale-up feasibility can be assessed. This can also be accomplished by performing pilot scale trials.

Full-scale test planning

If considered necessary full-scale testing can be carried out using the same representative material or surrogate material as in the lab-scale trials. The planning of the full scale tests obviously takes into consideration the same constraints as the lab scale trials, and is based on the results obtained during the lab scale trials, and/or pilot scale tests.

Full-scale testing

The full scale batch pyrolysis plant has, from left to right, a pyrolysis vessel where the waste is treated with under stoichiometric amounts of oxygen, an afterburner (EBK) where the pyrolysis gases are burnt and oxidised fully to carbon dioxide and water, the off-gas treatment system is a dust filter, followed by a wet scrubber and an activated charcoal filter before the off-gases are released to the atmosphere. Before the dust filter the gases are cooled to suitable temperature and the heat is recovered and partly used to produce steam to the process, before the activated charcoal filter the off-gases are re-heated to prevent condensation in the charcoal and before the release to atmosphere the off-gases are sampled for activity and environmental analyses in parallel to the on-line measuring system.

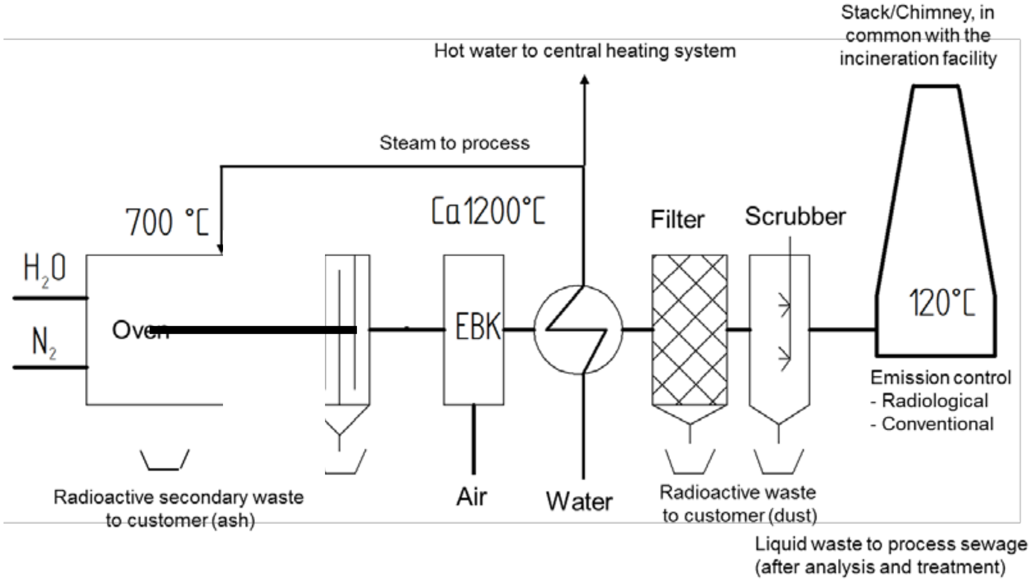

Fig. 2. Schematic description of the pyrolysis unit.

The full scale tests are performed, in the full scale production pyrolysis unit, using the process parameters determined during the lab scale trials, taking into account the adjustments found necessary in the scale up assessment. During full scale tests the process performance, *i.e.* the response to temperature increase, is continuously monitored. The secondary waste is analysed in order to evaluate fulfillment of the relevant constraints, as mentioned in pre-trial planning.

The end result of the full scale tests is a conclusion whether or not the waste fraction is suitable for full scale production in the pyrolysis unit.

RESULTS

The process described above has been applied to its full extent for uranium contaminated DAW [1]. The constraints for this type of waste include achieving sufficiently low carbon content in the ashes to facilitate uranium leaching. As the batch pyrolysis plant has recently (end of January 2013) received the approval for verification operation for treatment of active waste the final step of the full scale testing will start imminently. This includes verifying such things as mapping any spread of contamination in the afterburner and verifying all the parameters on real waste. The most positive thing about this process is that the plant is brand new and clean so any contamination is easily detected and no cross contamination has yet occurred.

The evaluation process has also been applied partly to uranium chemicals (non-nuclear waste), pyrophoric waste and ion exchange resins.

The uranium chemicals originated mainly from schools and universities but research institutes and some industries has also contributed to the inventory. Studsvik receive these chemical as part of an “amnesty” instigated by the authority in order to remove unwanted chemical in a controlled manner. The uranium chemicals are both oxides and other salts such as oxalates, nitrates and sulphates. For oxides in which uranium has an oxidation number higher than 2, i.e. oxides other than UO_2, the repository owner would like a chemical conversion to UO_2. The other salts also have to be treated so that they are converted to an oxide, preferably UO_2.

Tests were performed on uranyl nitrate as that was the most common chemical received. The salt was heat treated under several different conditions, varying as earlier described, time temperature and atmosphere.

Fig. 3 Uranyl nitrate from untreated to pyrolysed under different conditions

The conclusions from the trial are that the different salts, other than oxides, are easily destroyed but oxides higher than UO_2 are formed, which is exactly as expected. However, adding hydrogen gas is not an option so the next step is the discussion with the authorities and the repository owner on what has to be achieved.

Pyrophoric or hydrogen producing materials are another type of wastes that are not directly suitable for disposal. This can be both metallic uranium and other types of metals such as magnesium alloys.

In order to convert these to a disposable form or a form that can be treated further batch pyrolysis can be suitable since the amount of oxygen can be controlled and the system purged fast if the reaction rate is high.

In order to evaluate the process a surrogate in the form of cerium metal was used. Cerium is often used as surrogate for both uranium and plutonium in many different processes so the choice was obvious. Cerium was used both as a powder and in an ingot form, in figure 4 below the Ce-ingot in oil before heat treatment and after treatment is shown. The cerium is after treatment a salt, most likely CeO_2 but no chemical analyses were performed.

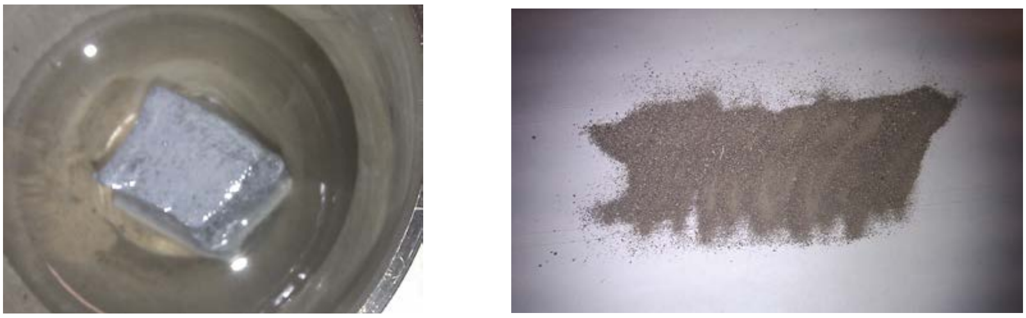

Fig. 4 Cerium metal before (ingot) and after heat treatment

Control of the process turned out to be a rapid process on lab-scale, i.e. purging the reaction in the vessel was almost instant, since the volume is only 2 liters. The temperature curve from the cerium ingot trial is shown in figure 5 below. It can be clearly seen that the process is under control during the whole trial as the temperature has not exceeded the want temperature, that was set to 600°C.

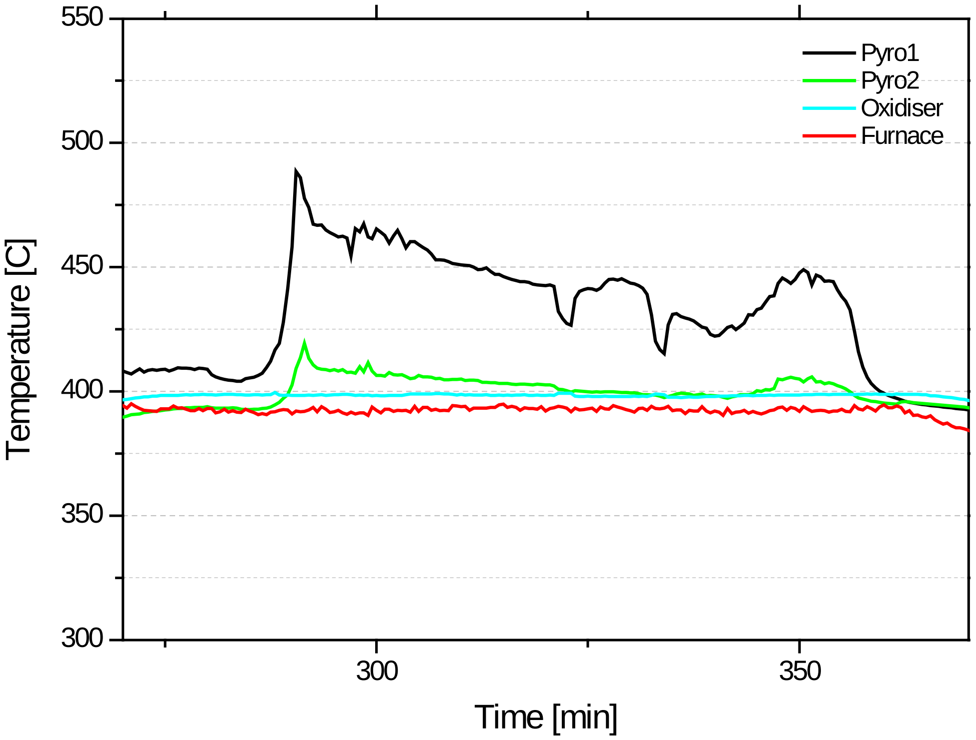

Fig. 5 Temperature curves from Cerium ingot trial

Similar trial has also been done with magnesium band in oil, with similar results, see figure 6 below.

Fig 6. Magnesium metal before and after heat treatment

Ion exchange resins, both solidified and raw, has also been tested as part of the uranium waste described in [1].

DISCUSSION

As the batch pyrolysis unit has now got its permit for active verification operation the full scale tests are possible to perform on other waste forms than the uranium contaminated DAW.

The final step of the process including lab-scale trials followed by small scale trials, either in a smaller facility or in the full scale facility, are now being concluded for the uranium contaminated DAW, as the verification operation starts.

The results from the inactive verification trials on simulant DAW together with the lab-scale tests on the above described waste forms give us confidence that we can proceed to the next phase, the full-scale trials on these wastes as well. As any trials the full scale trial has to start with smaller amount of waste, in particular if they are very reactive.

REFERENCES

[1] M. Lindberg, C. Österberg and T. Vernersson, The building and commissioning of a batch pyrolysis plant in Studsvik, Sweden, Paper 12447, WM2012, 2012, Phoenix, AZ