From Non-Disposable to Disposable, Treatment of Pyrophoric or Gas Forming Waste Forms for Disposal – 14155

Carl Österberg *, Maria Lindberg *
* Studsvik Nuclear AB

ABSTRACT

In order to dispose of waste in either a deep geological disposal or in a shallower repository there are several demands that the waste and its package must fulfil, one is that it is not to react with oxygen or the waste package or backfill in the repository, i.e. concrete or grout. The waste forms that do not fulfil this particular criterion must be treated in some way to render the waste non-reactive. One of these waste streams is metallic uranium. Metallic uranium is not only an issue originating from the nuclear industry, as fuel, it is also present in, for example, transport flasks and as samples used in schools, which all has to be disposed of sooner or later.

Another waste that arises is magnesium doped with thorium, originating from the aviation, aerospace and missile industry. These magnesium-thorium (Mg-Th) alloys are now being replaced with others without thorium so they are in need of handling and possibly treatment before disposal. Magnesium metal is also pyrophoric, in particular in molten or powder form.

In order to evaluate thermally treating these metals in a very controlled environment, such as a pyrolysis vessel, experimental work has been performed. The aim of the thermal treatment is to oxidise the metals and obtain an oxide with low leachability. Inactive trials were performed, first using small amount of magnesium tape followed by using Cerium (Ce) as a surrogate for uranium, to check the ability of controlling the process. Oxidation is obtained by adding steam or oxygen. Both cerium powder and blocks were used

After the process had been deemed safe the next step was to test the process first with metallic uranium and thereafter with magnesium thorium alloy.

INTRODUCTION

Lab-scale trials are performed in a 2 dm^3 vessel placed in a muffle furnace equipped with temperature regulation. The lab-scale thermal-treatment equipment layout is shown in Figure 1. The material to be treated is placed in a metal crucible inside the vessel. Gases (nitrogen, N_2 and oxygen, O_2) and water is added via mass-flow-controllers. The gas mixture is led through a steam-generator, located inside the furnace, into the pyrolysis vessel. The gases produced in the pyrolysis vessel, from organic material in the primary waste, are led into an after-burn chamber (ABC) where air is added in order to fully oxidise the gases. The off-gases are thereafter 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.
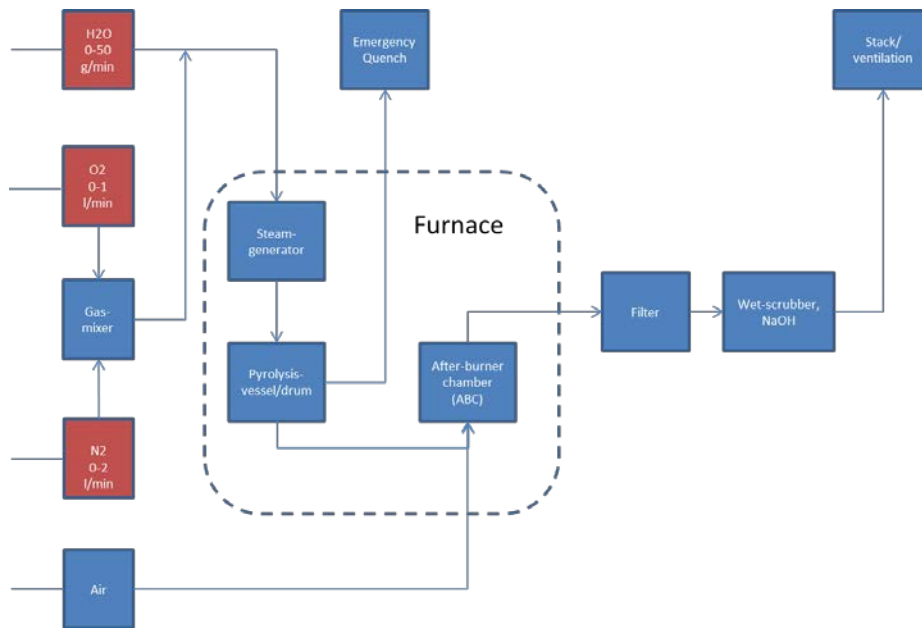
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Fig.1. Schematic description of lab scale thermal treatment equipment.

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 fulfilment of repository 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.

EXPERIMENTAL – INACTIVE MATERIALS

The first series of trials were performed with metallic magnesium shavings. These trials were executed to get fundamental understanding of the potential of system and the possibilities of varying the atmosphere. Different mixtures with metal-shavings, oil and sawdust were examined. Also different techniques for oxidation were used such as oxygen/nitrogen mixture and steam. As a continuation of these trials cerium was used as a surrogate for uranium. Both cerium powder and solid blocks were used. Also here, different mixtures containing metal, oil and sawdust were examined. This mixture was chosen based on knowledge of existing waste streams.

Trials with cerium as uranium surrogate

Cerium, being more reactive than magnesium, reacts easily and the focus on the first set of trials was to ensure a safe process and not risking an escalating oxidation process. As a result of the trials and parameter optimisation a mixture of Ce and oil can be treated in three steps. These three steps are described and explained in the example given below, including Figures 2-5.

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Two crucibles were placed in the pyrolysis vessel. One crucible contained two Ce-ingots and oil and the other only two Ce-ingots. The first step is when the oil can be gasified without oxidising any Ce. In Figure 2 it is seen that the temperature in the ABC is increased under a period of time because of oxidation of gases from gasification of oil in the pyrolysis vessel.
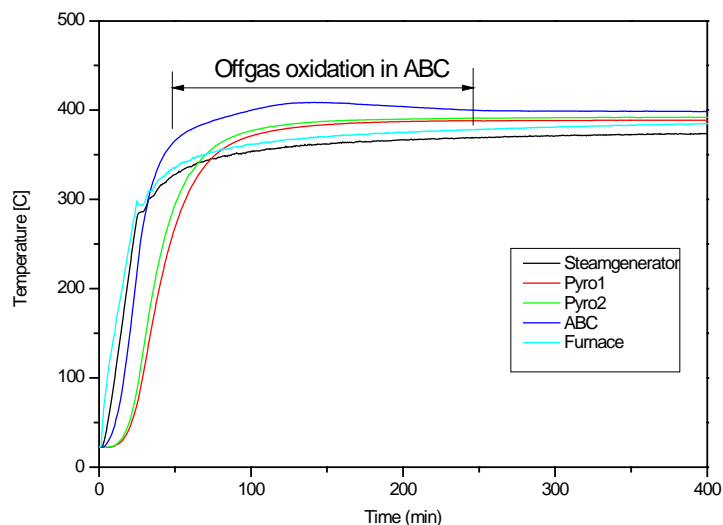
Fig. 2. Gasification of oil in Ce-oil mixture

In the second step the cerium is partially oxidised and then quenched. This is obtained by adding steam and when increased temperature in the pyrolysis vessel is observed the addition of steam is terminated. As a last step, step three, the remaining Ce can be oxidised by adding oxygen and/or steam, see Figure 3 and Figure 4. When no further increase in temperature can be observed despite addition of oxygen and steam the oxidation process is considered as finalised.

After gasification of oil approximately 2.2 % of the Ce has been oxidised. After the last step when oxygen and steam has been added more than 99.75 % of the Ce is oxidised.
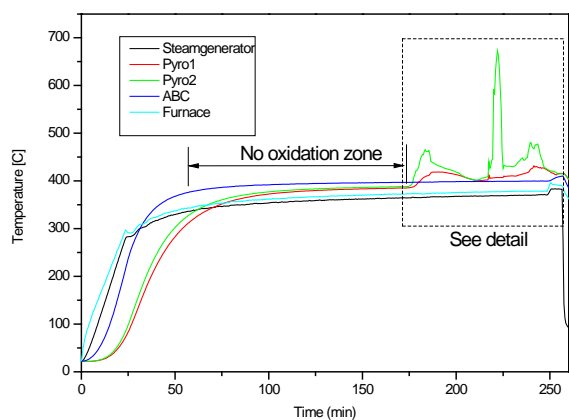
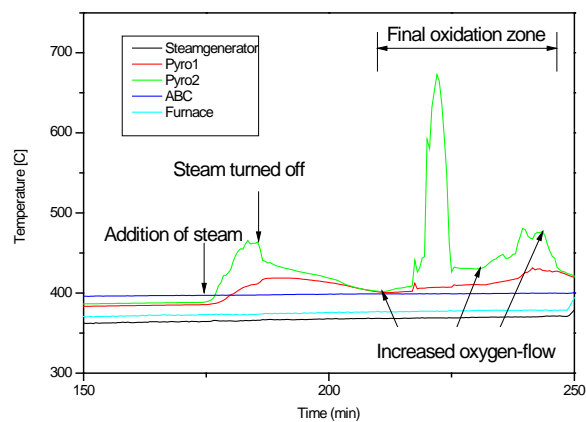Fig. 3. Quenching of process and oxidation for Ce

Fig. 4. Quenching of process and oxidation of Ce, detail.

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In Figure 5 pictures are shown prior to and after the oxidation step. Picture A shows virgin material where the left crucible contains two Ce-ingots and approximately 40 cm3 of hydraulic oil and the right crucible contains two Ce-ingots and no oil. Picture B shows same crucibles after first, oil gasification, step. In this step only nitrogen is used as a carrier gas to transport gasified oil to the ABC. Picture C shows the oxidised cerium after thermal treatment and picture D is a close-up.
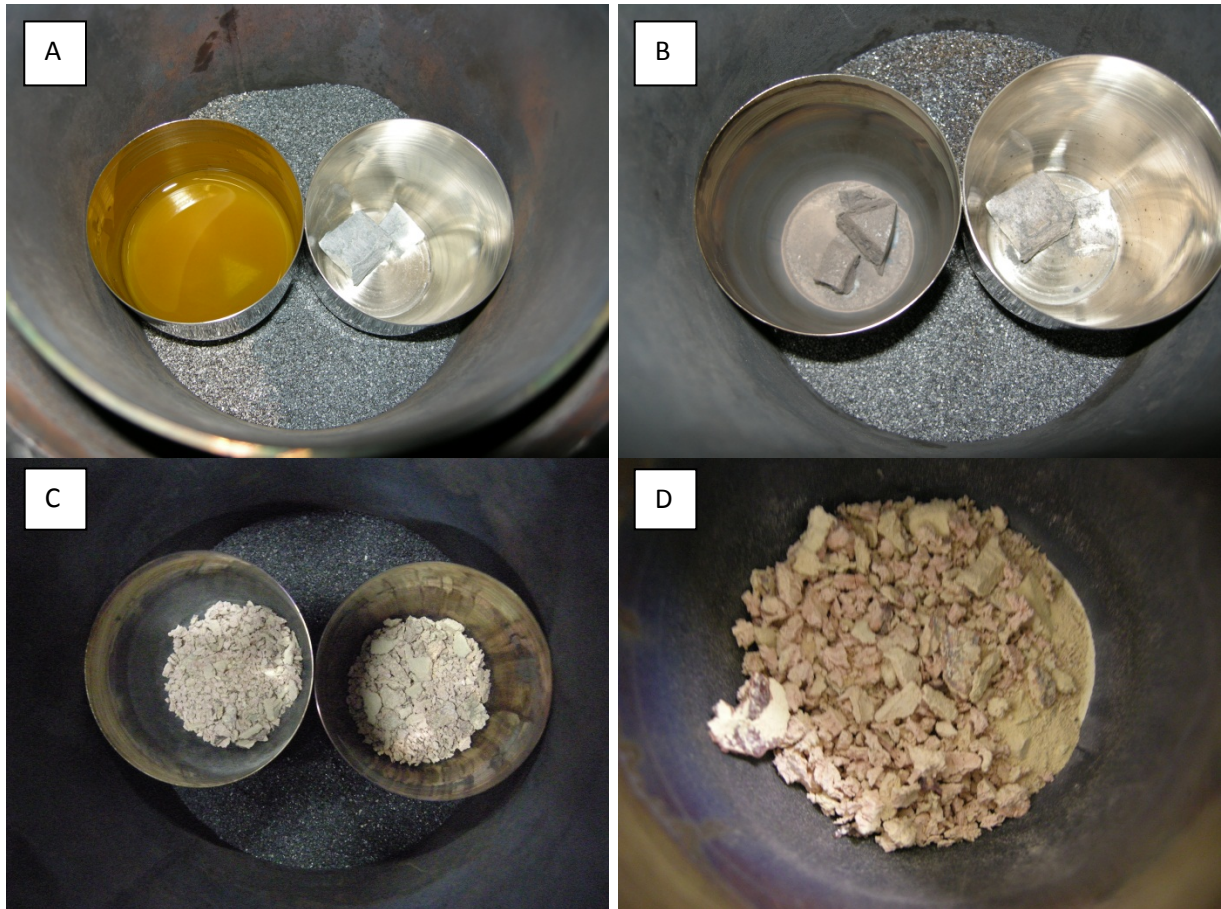

Fig. 5. Cerium blocks prior and after oxidation steps.

As much as 99.76 % of the metallic Ce was oxidised when weights before and after oxidation are compared. The theoretical amount of oxidised metal, called *F* and expressed as a percentage of theoretical amount of CeO_2, is calculated as:

$$F = \frac{(\text{Weight after oxidation} - \text{Initial weight of metallic sample})}{(\text{Theoretical weight as } CeO_2 - \text{Initial weigth of metallic sample})} \quad \text{(Eq.1)}$$

Trials with cerium powder show the same behavior as with blocks/ingots.

EXPERIMENTAL – ACTIVE MATERIAL

As for trials on active material several different mixtures have been used. The active material has been both metallic uranium in the shape of shavings (grams/shaving) mixed with organic material (oil and sawdust) as well as solid blocks (>700 grams). Also solid blocks (approximately 100

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grams each) of Mg-Th alloy have been thermally treated.

Metallic uranium as shavings from fuel manufacturer

Several trials have been performed with metallic uranium (slightly enriched) from a fuel manufacturer where one waste stream from the manufacturing process was metal shavings of uranium and the cutting oil. As uranium metal shavings are pyroforic these shavings and oil were stored in drums, and wood chips or sawdust was added to bind any free oil.

The uranium residue in its original form is not suitable for direct disposal but it can be thermally treated to remove organics and oxidise any residual metallic uranium to create a residue that may be capable of further processing to a form suitable for acceptance at a disposal facility. The residues will also be subject of leachability tests before disposal is possible, this was not part of the treatment test. Three different waste forms were examined. The uranium content varied between 5-75%.

Before any heating of the samples were done N_2 was added to remove all oxygen from the vessel and to help transport of pyrolysis-gas to the after-burner. Nitrogen was added until the oxidation step was started, at about 380 °C then a very small amount of steam was added. If a reaction could be observed no more steam is added. If no reaction was observed the amount of steam was increased. Finally oxygen was added to help oxidise any remaining uranium. The final temperature during these trials was 600°C.

When no further increase in temperature caused by addition of oxygen (by adding steam and/or oxygen gas) could be observed, the experiment was ended and the furnace was set to cool-down. N_2 was added through the cool-down process.

Figure 6 show the time-temperature curve for one of the trials and it was soon concluded that the necessary oxidation occurred at the lower temperature, 400 C.
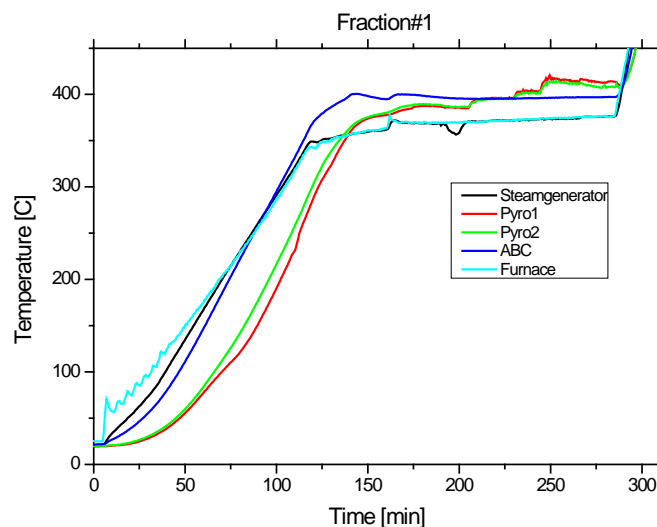

Fig. 6 Typical time-temperature curve from uranium shavings oxidation

Figure 7 show pictures of one of the fractions prior to and after treatment. By comparing weights, Table 1, before and after thermal treatment it is seen that the residue fulfil the set expectation regarding weight. 1-2% of the residual weight is considered to be residual carbon originating from the organic material.
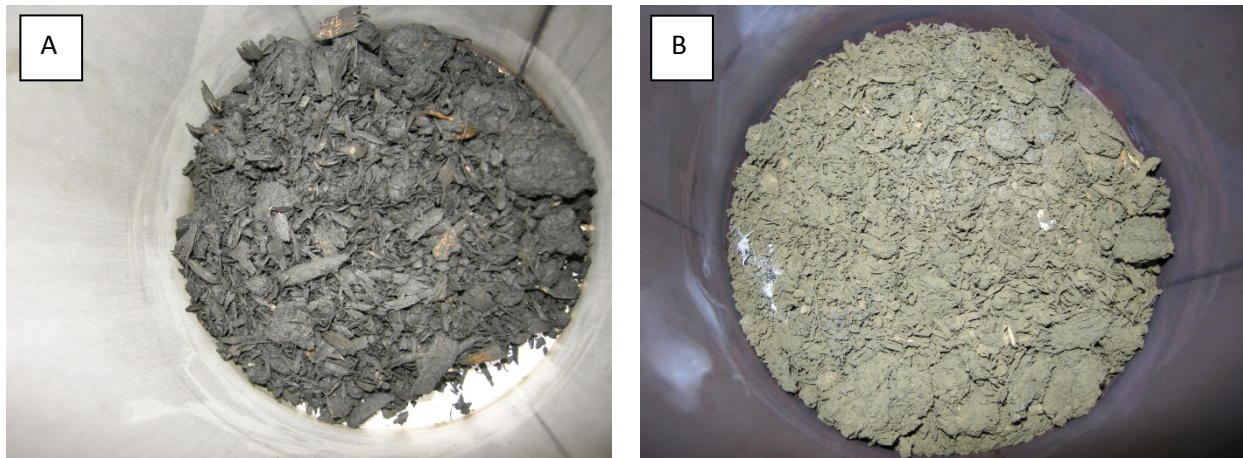

Fig. 7 Uranium, saw dust and oil mixture prior to (A) and after treatment (B)

TABLE 1. Examples of weights prior to, and after treatment of uranium/metal/oil mixture

	Fraction#1	Fraction#2
Weight, material [g]	143.55	166.09
Uranium content, [%]	38.45	66.32
Theoretical amount of UO_2, [g]	62.62	124.96
Weight, residue, [g]	64.00	127.98

Solid blocks of metallic uranium

In Figure 8 the time-temperature curves for the oxidation of a solid block of uranium are shown. In zone 1 and 2 both steam and oxygen is added without giving rise to any increase in temperature. When oxygen concentration exceeds a certain level the temperature increases rapidly. The temperature is controlled by quenching oxygen and steam addition. Solid metallic uranium blocks between approximately 350 and 750 grams have been oxidised in a series of trials. Example of a block of metallic uranium prior to and after thermal treatment is shown in figure 9.
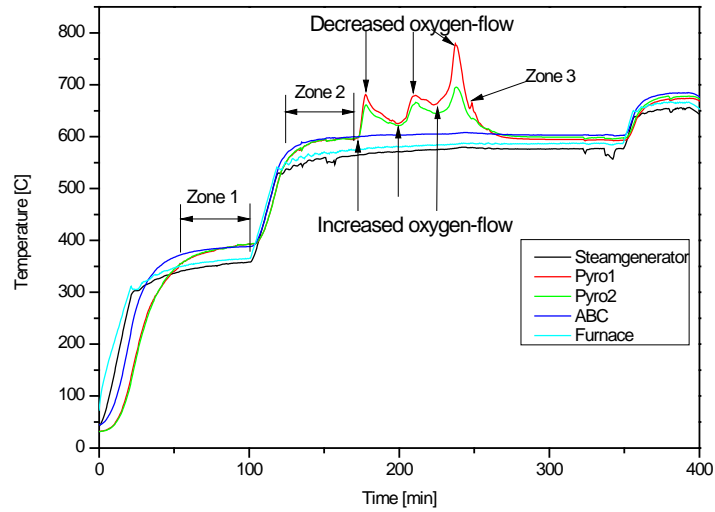
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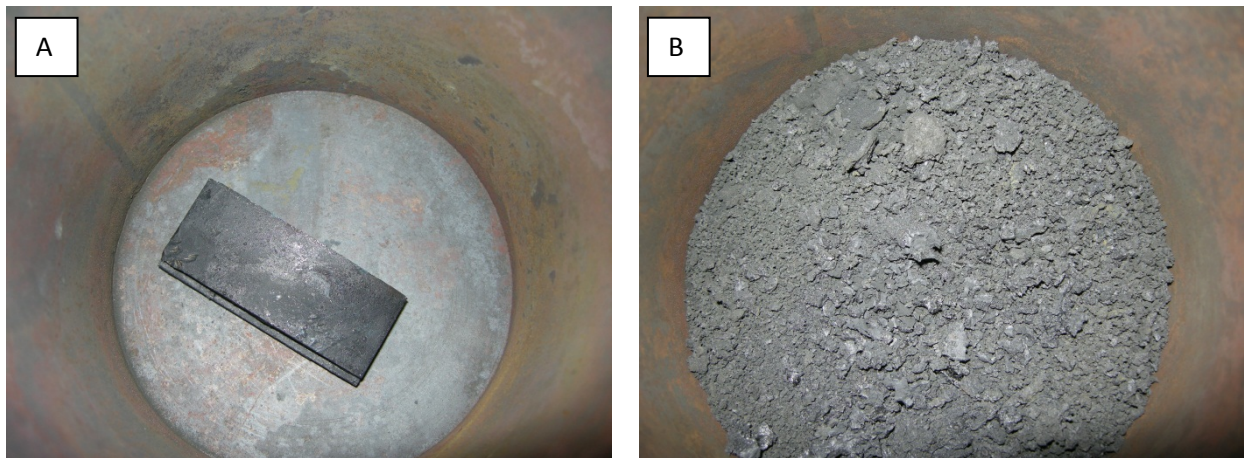Fig. 8. Time-temperature curves for oxidation of metallic uranium block

Fig. 9 Solid block of uranium (A) prior to and uranium oxide (B) after thermal treatment

Magnesium-Thorium alloy

Trials on material consisting of a Mg-Th alloy were conducted to assess the suitability for thermal treatment. The time-temperature curves for oxidation of a solid block of Mg-Th alloy are shown in Figure 10.
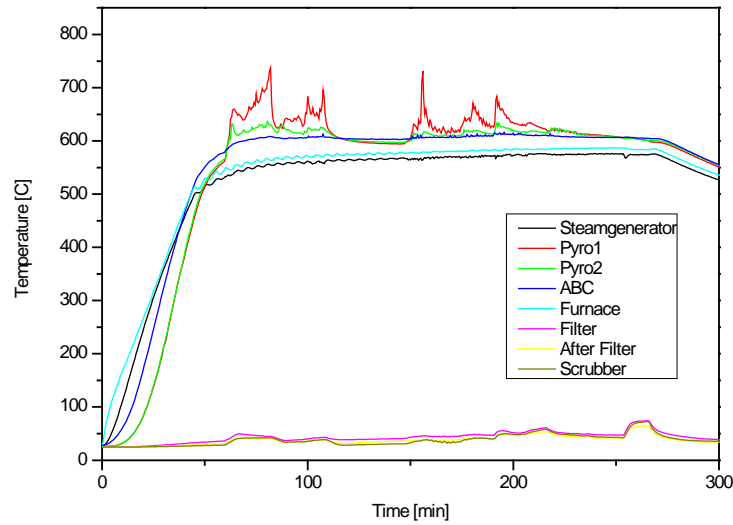
Fig. 10 Time-temperature diagram for oxidation of Mg-Th

Figure 11 show pictures of a solid Mg-Th block prior to (A) and after thermal treatment (B). Even if the virgin material is a metal block, the result of the MgO-ThO$_2$ mixture is more like a powder.
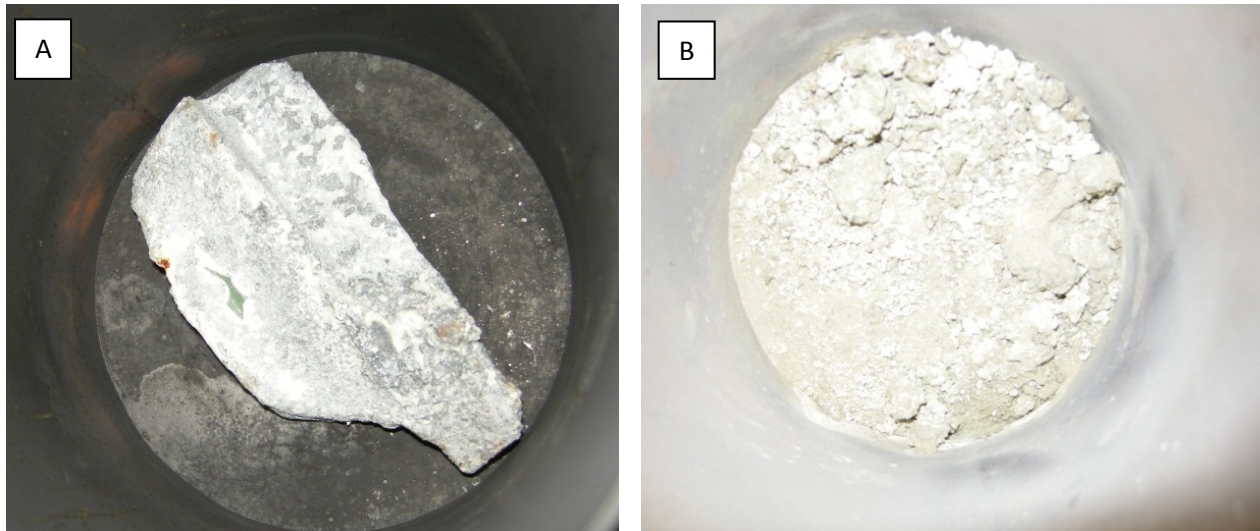

Fig. 11 Mg-Th alloy prior to and MgO/ThO$_2$ after thermal treatment

FUTURE

Scale-up from lab-scale to production scale can be done in two ways, pilot scale trial in a pilot sized plant or full scale testing where small amounts of material is treated in a full-sized plant.

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.

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. Figure 12 shows the modus operandi from lab to full scale.
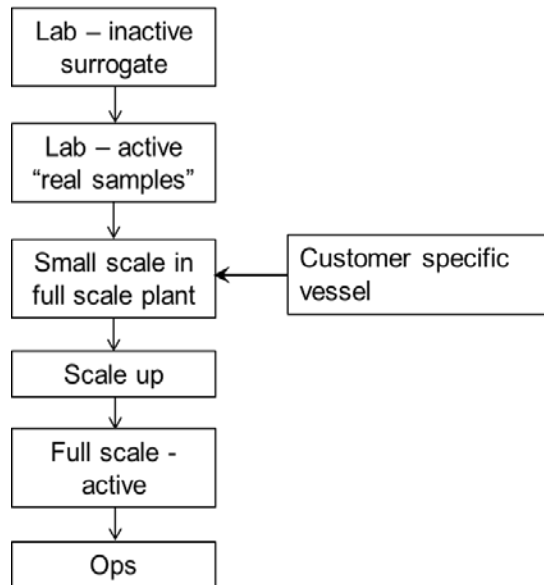
Fig.12 Modus operandi – from lab to full scale

CONCLUSIONS

The oxidation of all examined metals and metal-alloys could be performed in a safe and controlled manner. All reactions were possible to quench by lowering or totally shutting off the supply of oxygen either in the form of pure oxygen or as free oxygen in steam.

It is possible to achieve a complete oxidation of metal even if the metal is shaped as big blocks (in the magnitude of several hundreds of grams) as in the case with the uranium and Mg-Th metal. For the uranium case one solid block of metal weighing approximately 750 grams was totally oxidised in a 2 litre crucible in a controlled process. Metal powder or shavings are processed in the same manner and the process is as controllable as for solid metal blocks.

ACKNOWLEDGEMENTS