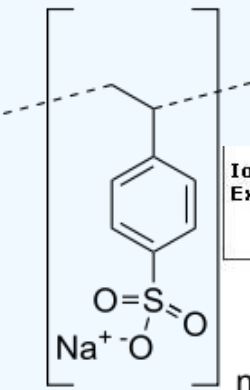


Spent Ion Exchange Resins: Challenges and Management - presentation of international trends and future expectations concerning management of spent resins

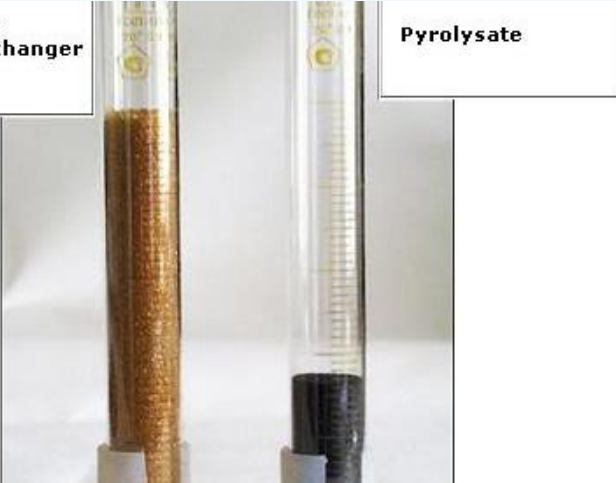
NUKEM's capabilities and experience concerning treatment of spent resins, spent solvent, alpha waste, bituminized waste

**Dr. Georg Braehler, CTO NUKEM Technologies**





$$\left[ \text{C}_6\text{H}_4(\text{CH}_3)(\text{SO}_3\text{Na}) \right]_n$$

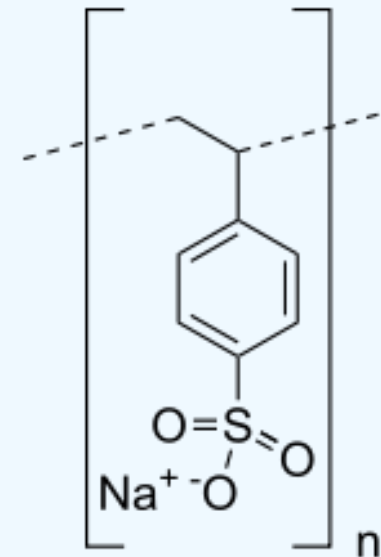
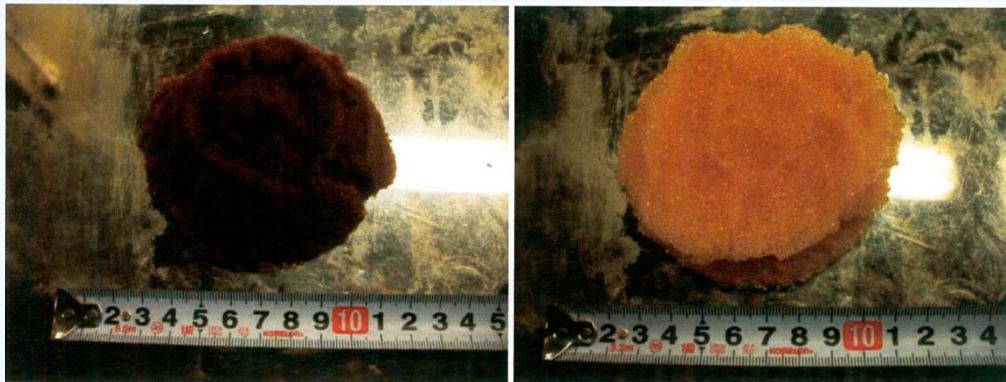


[http://www.extrapackaging.com/radioactive/images/radioactivewaste\\_polybag.jpg](http://www.extrapackaging.com/radioactive/images/radioactivewaste_polybag.jpg)

# IEX

## The Disposal Challenge

- IEX resins are used to remove radionuclides from the primary coolant
- Cation and anion exchangers
- Depending on the water regime 3 to 10 m<sup>3</sup>/year spent ion exchange can be produced in a 1300 MW class unit
- Radioactivity is predominantly from Cs-134/137, Co-60, Sr-90
- Specific activity levels can vary (E5 to E7 Bq/g )



## IEX Treatment Processes

- Drying
  - no reduction in volume referring to dry matter
- Cementation
  - increase the volume
  - no destruction of organic matter
  - poor resistance to fire
- Embedding  
(bitumen, resin)
  - increase of the volume and organic matter
  - problems of combustibility and radiolysis
- Combustion
  - technically complex because of the poor combustibility
  - difficult maintenance at higher radioactivity levels  
(contamination of the brick lining)
  - Cs nuclides in flue gas
- Hot Compaction
  - Good volume reduction
  - synergy with existing equipment (supercompactor, grouting)
  - no destruction of organics

**NUKEM has experience with all of them, can supply respective facilities**

## IEX Future Perspectives

- Application of IEX
  - In future reactors liquid effluents minimized
  - AP 1000 UK: no Boron recycling, no evaporator
  - Just IEX, with increasing specific activity (E7 Bq/g)
  - All liquids released free of radioactivity
- Disposal of spent IEX
  - Clear tendency in worldwide final disposal projects: no organics
  - Radiolysis, chemical reactions, fire resistance, ...
  - Without organics safety case much simpler
- Requirement: To find a process which:
  - reduces the volume
  - yields an inert/mineralized product
  - works at temperatures of not more than approx. 650°C
  - can be run in a simple facility

## Basics Pyrohydrolysis (aka Hydrolysis)



- Since 1850 town gas (CO+H<sub>2</sub> from coal + H<sub>2</sub>O)
- Applied in energy and chemical industry (steam reforming)



## Pyrohydrolysis Characteristics

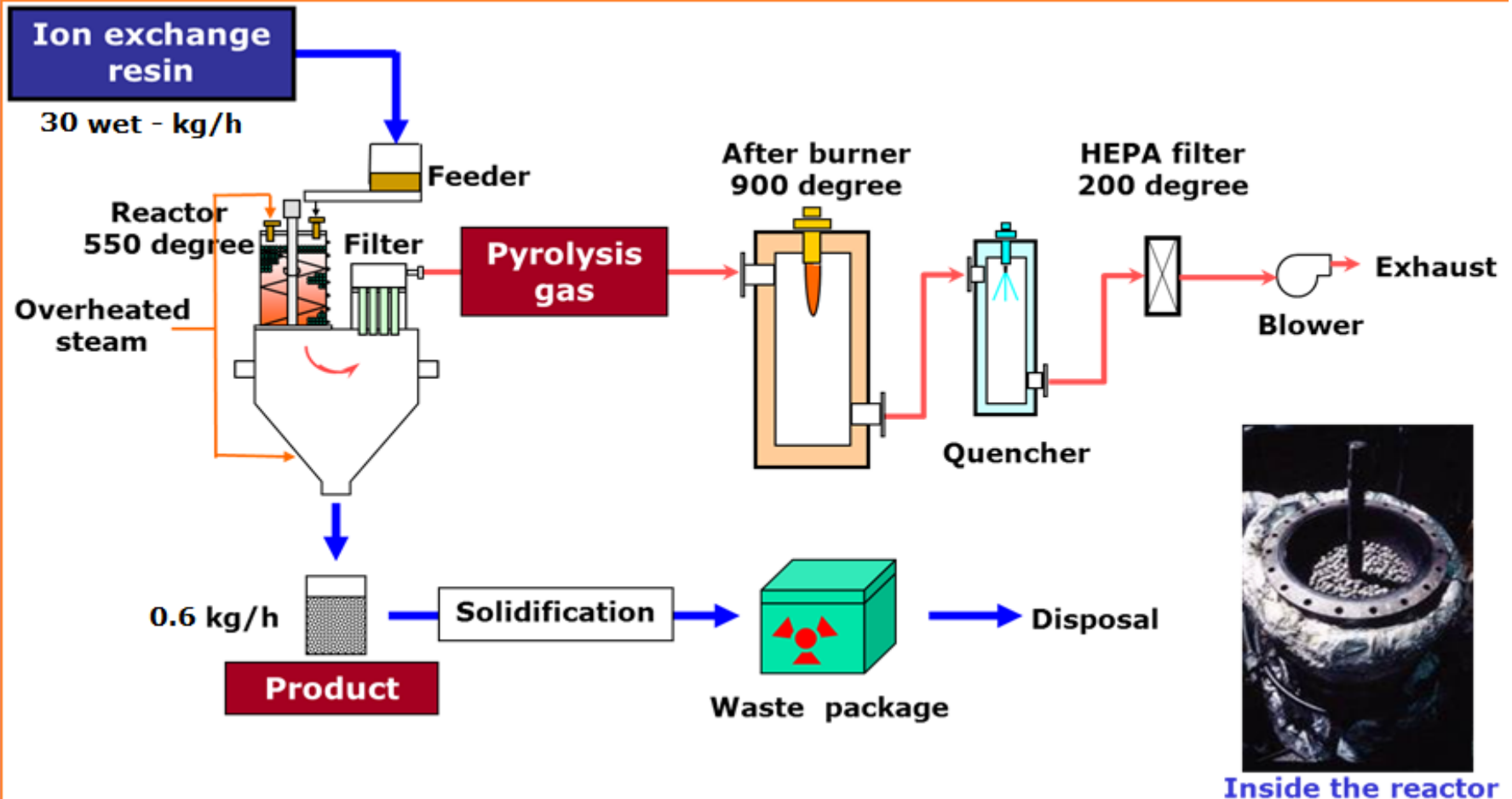
- Reaction temperature 400 – 900°C
- No residue from carbon and hydrogen content
- Constituents like Nitrogen (Amino, Nitro, ..), Oxygen (keto, carboxyl,..), sulfur (sulfonyl, ..), halogens (F, Cl) in unlimited concentrations gasified
- Ingredients which cannot be gasified ( eg fillers in polymers, like silica, titania, gypsum) etc. remain in ash
- Small (sub-stoichiometric) amounts of Oxygen accelerate reaction
- Pyrohydrolysis optimum tool for destruction of organic radwaste
  - High volume reduction (depending on inorganic content in feed: up to 100)
  - Excellent safety features (stops immediately after shut down of power and steam supply)
  - Low temperature (no Cs volatilization, metallic construction material)

## NUKEM Pyro(hydro)lysis Spent Ion Exchange Resins IEX

- Ion exchange resin is organic matter, pyrolysis and pyro-hydrolysis (= pyrolysis with water steam added) processes to decompose.
- Advantage, compared to incineration
  - low process temperature, keeps volatile nuclides like Cesium in the solid
  - endothermic character, overheating and thermal runaway impossible
- Pyro(hydro)lysis/ process in stirred pebble bed reactor.
  - Wet resins fed together with steam into the reactor at 500-550°C
  - decomposed while passing the moving pebble bed,
  - resulting residue (the pyro-ash) separated from the pyro-gas by hot gas filtration
  - pyro-gas sent to incineration and flue gas treatment
- Many tests with resins done
- Close cooperation with Japanese company NGK



# System Flowsheet





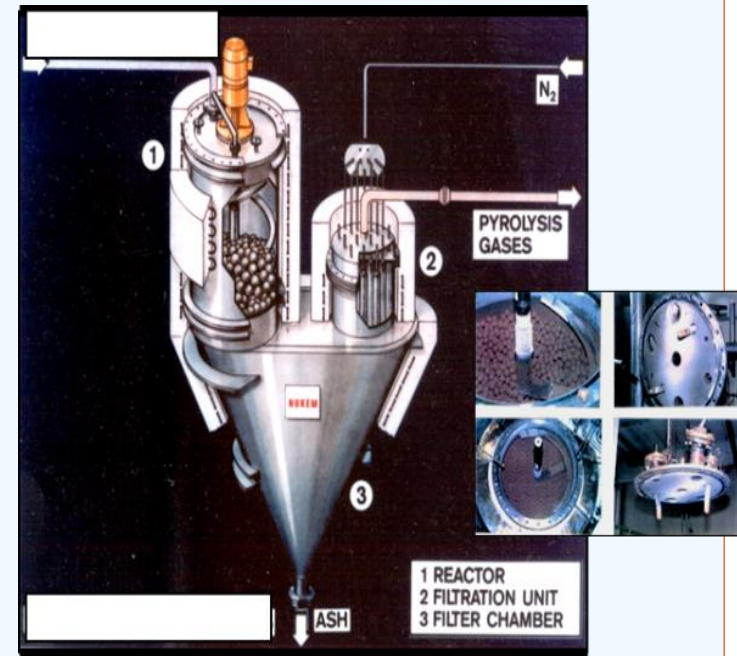
## Pyro(hydro)lysis of Spent IEX Summary

- Weight reduction ratio is approx. 97-98 %
- Doping material Zn, Cs, Li remain in product
- No Cs (source of radioactivity, volatile) is found in scrubber solution.
- No organic content remains in product
- Sulfur and Li remain in product as  $\text{Li}_2\text{SO}_4$



## Spent Solvent TBP Stirred Pebble Bed

- TBP from UNF reprocessing
- Thermochemical decomposition,  $\text{Ca}(\text{OH})_2$  added
- Fed onto stirred pebbles in heated ( $550^\circ\text{C}$ ) reactor
- Ca-phosphate product leaving, pyrogas filtered, incinerated
- Typical capacity 20 kg/h
- Most of world's spent TBP processed
  - AREVA La Hague
  - JNFL Rokkashomura
  - BELGOPROCESS Dessel
  - CNNC site 821

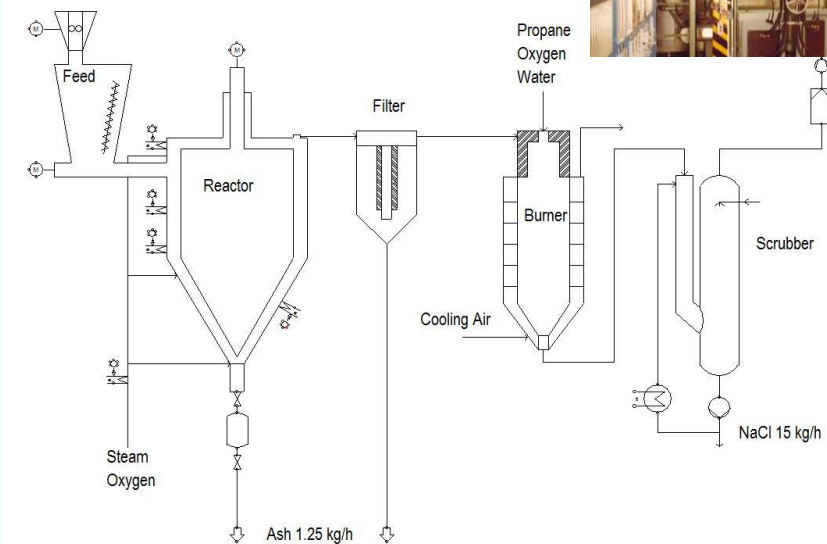


## ALPHA Waste

- Pu processing (reprocessing, MOX fab) generates Vinyl (PVC) waste
- Pyrohydrolysis demonstration facility built
  - 25 kg/h
  - 40 – 120 g Pu/m<sup>3</sup> waste
  - Max. T 850°C (soluble PuO<sub>2</sub>)
  - Safe geometry
  - Metallic construction
- Successful operation 2 000h with Uranium
- With Gorleben exit abandoned

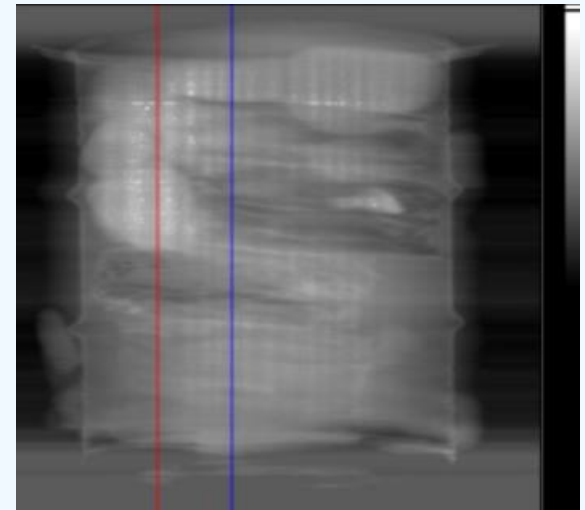


Alpha Waste 25 kg/h



## Bitumen Matrix Material

- Widely applied as matrix for conditioning of many kinds of low and intermediate level radioactive waste
  - Homogeneous conditioning of evaporator concentrates and sludge
  - Homogenous embedding of spent ion exchange resins
  - Heterogeneous embedding of technological waste (metal)
  - Heterogeneous embedding of mixed waste (compacted drums, clothing, rubber, plastics)
- Challenges raised
  - Certain degree of degradation
  - Radiolysis gases
  - Acceptance in underground repositories: flammability, lack of long time stability
- Rework needed



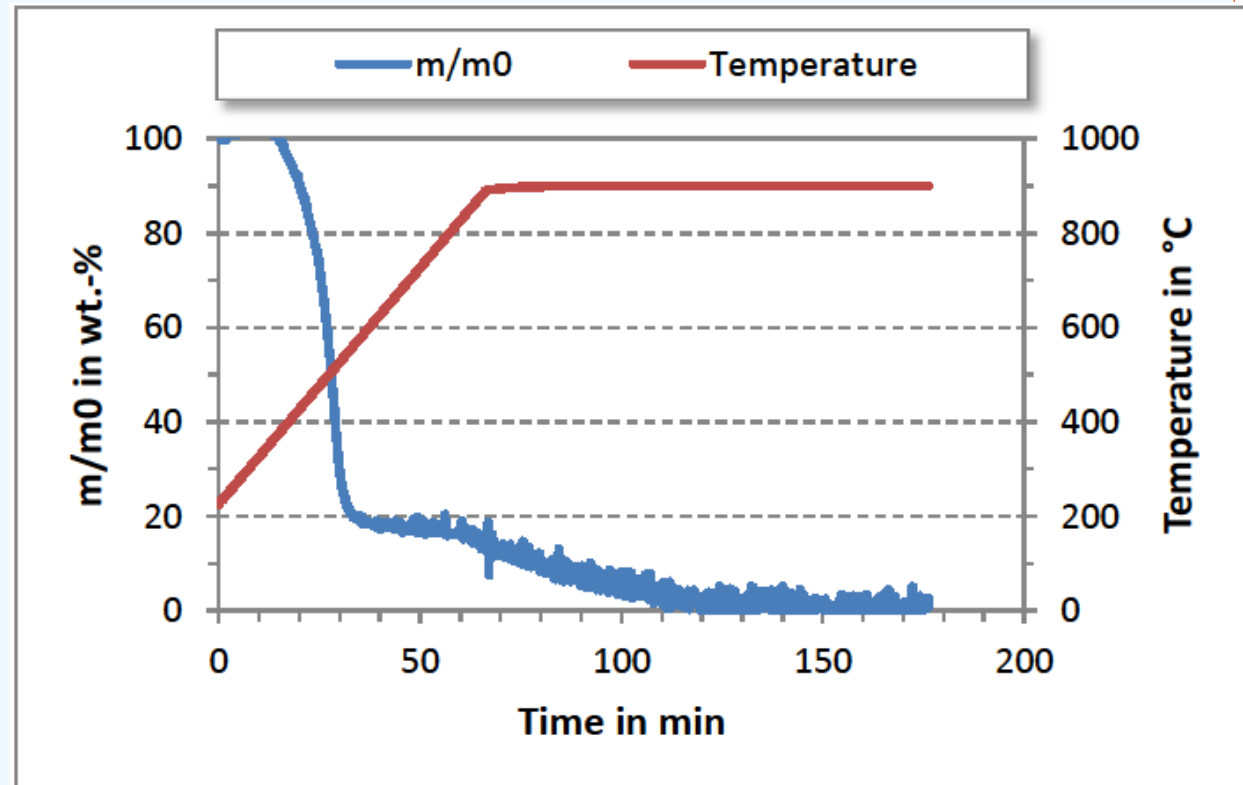
## Bitumen Rework

- Overpack
  - Increase of volume
  - Basic challenges remain
- Melting, removal of bitumen, incineration
  - Handling of sticky materials
  - Safety questions
- Dissolving in organic liquid, separation, incineration
  - Flammability
  - Complex facility

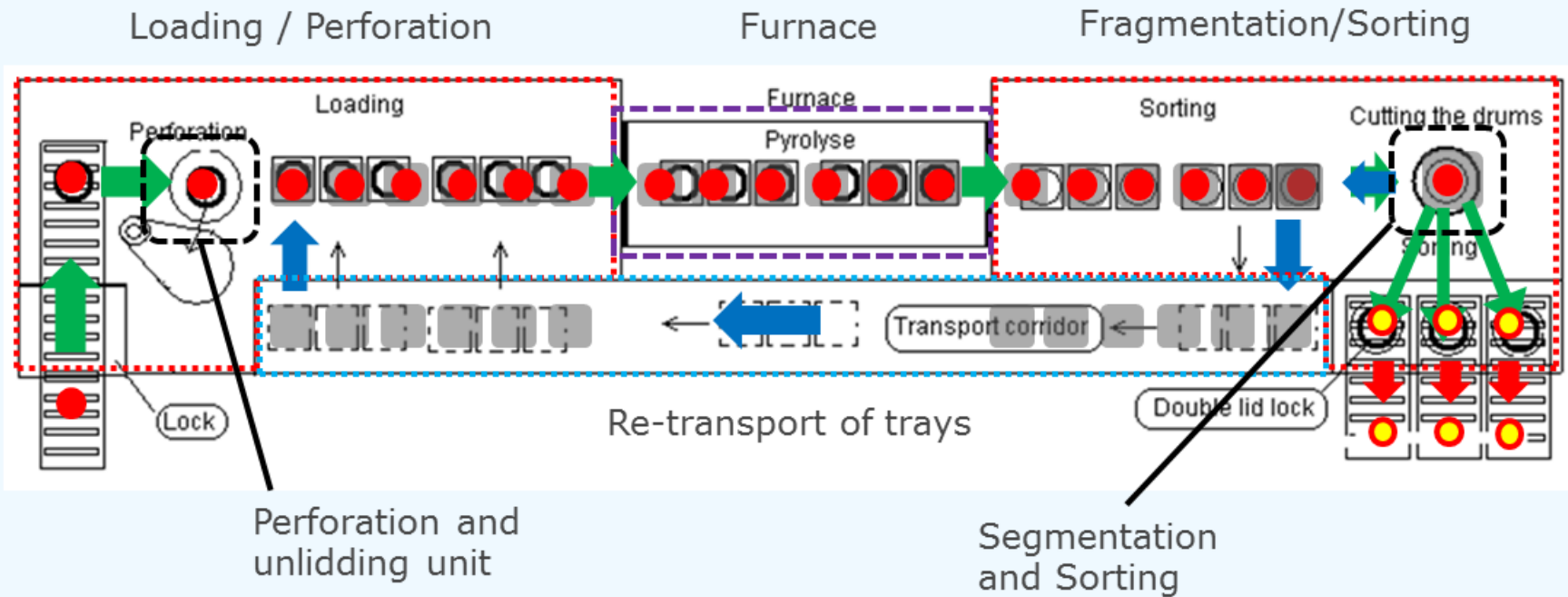


## Bitumen Basic Investigations

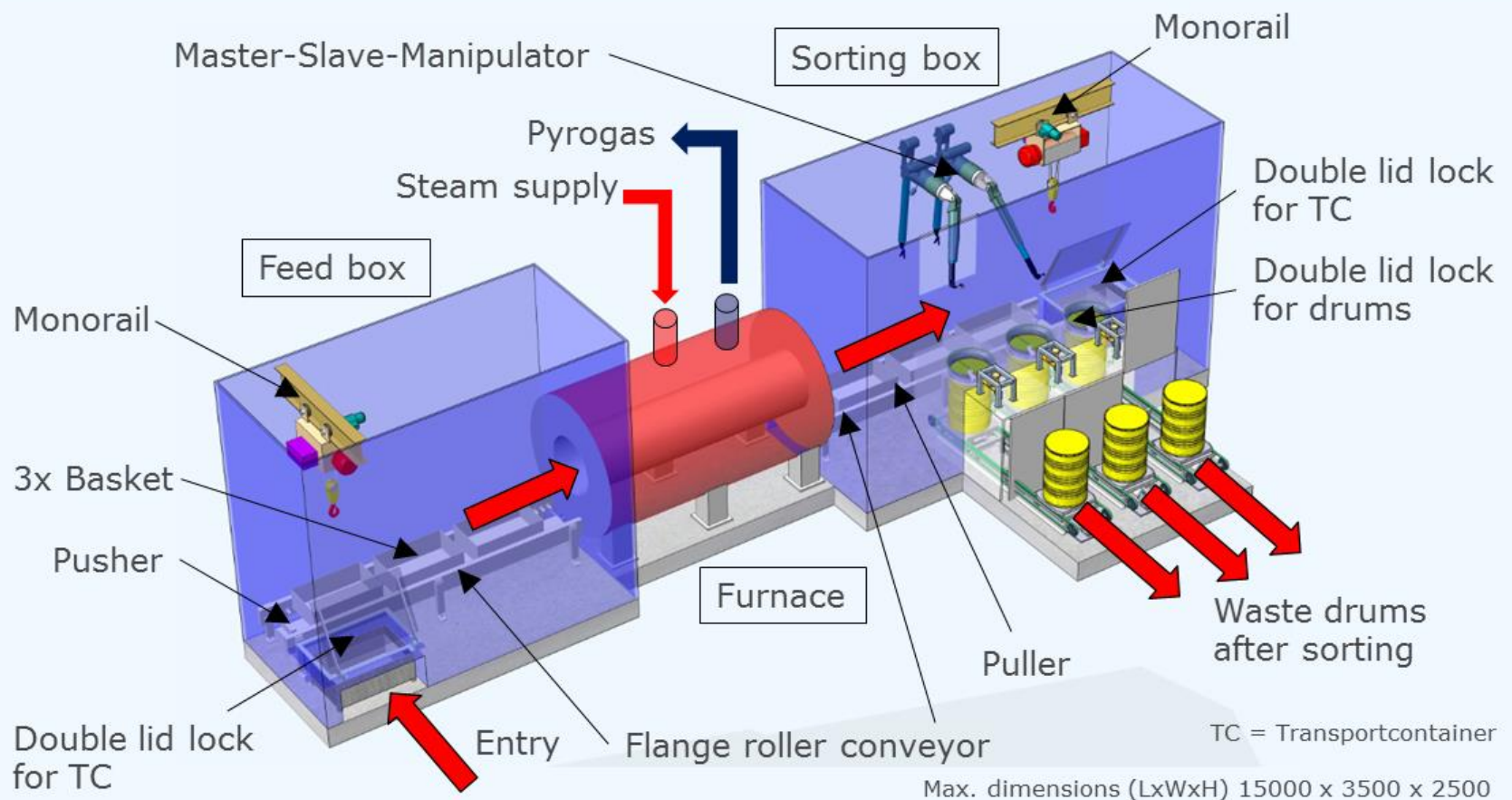
- At low T pyrolysis
- Above 750°C further mass loss
- At 800 – 900°C total gasification achieved



# Bitumen Facility Design Whole Drums



# Bitumen Facility Design Partly Emptied Drums





## Conclusion

- Thermal processes allow for complete destruction of organic matter in radioactive waste
- Compared to the high temperature processes like incineration and plasma decomposition, pyrohydrolysis offers significant advantages:
- **The low process temperature prohibits the transfer of volatile radionuclides like Cs-134/7 into the flue gas**
- **Metallic construction materials avoid the accumulation of radioactivity in bricks and linings**
- **The endothermic process offers unique safety features**
- **The variety of applicable reactors (muffle, shaft, fluidized bed, stirred pebbles, rotary kiln, ..) allows the choice of the optimum facility of all kinds of waste**
- **The pyrolysis product (ash) is virtually free of organics, suitable for intermediate storage and final disposal, or, since not sintered and not molten, fit for further treatment, e g the leaching of valuable materials**

## Contact

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