Workshop C

R A D W A S T E T R E A T M E N T

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MOBILE LLW AND ILW SOLIDIFICATION UNIT

AND

TREATMENT OF TRU-BEARING, COMBUSTIBLE WASTE

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1. MOBILE LLW AND ILW SOLIDIFICATION UNIT

1.1 Introduction

To meet final waste disposal specifications in the FRG, homogeneous fixation into a leach-resistent matrix like concrete is mandatory.

Many of the power station originated wastes are liquids or semiliquids as evaporator bottoms, precipitates, sludged filter aids, decontamination effluents or spent resins. These have to be either solidified in station-own equipment or transported to solidification units elsewhere, e. g. at nuclear research centers.

As an alternative, NUKEM and it's subsidiary TRANSNUKLEAR developed a mobile solidification unit licienced and commissioned at the end of 1977, which since has been operated in three power stations. The solidified wastes were shipped to the Asse salt mine for ultimate disposal.

Because waste solidification units in power stations usually are operated only a few weeks per year, it is attractive to station operators to run in external service companies specialized in this field. A service, performed on the basis of mobile processing units is especially attractive because the station operator

- saves space and own equipment
- saves own, trained crew
- can transfer risk to the service company

A mobile service could be offered successfully, because the design verified the following principles:

- compact construction
- negligable set-up time
- high performance
- high throughput
- closed, HEPA filtrated system without contamination risk
- easily adaptable to all kinds of approved drums
- homogenous product
- no secondary waste generation

1.2 General unit design

As shown on the isometrical cross-section Fig. 1 the unit consists of a strong cubicle frame, supported on four turnable, telescopical stems. Inside the frame there is a tightened SS-cell, outside iron shielded. Inside the cell are placed mainly

- double-helicoil stirrer with vertical drive and adjustable 340° angle planetary gear
- liquid or semiliquid metering pot connected to the 2" waste-circulating loop, which ends outside in two 2" double-ballvalve couplings, and auxiliary
- ultrasonic level sensing device
- circular dedusting pipe connected to the dustfilter
- another 2" liquid concrete supply pipe
- shielding windows, flexible cleaning spray nozzles, connected inside and glove openings.

At both front elevations are positioned folding or dismountable, bottom shielded operating platforms. The right platform supports the control panel.

The unit is supported upon a support-frame at the floor. Inside the frame there is the roller conveyor and the hydraulical driven cask lifting device.

Maximum cask dimensions are 1.10 m diameter and 1.50 m in height. Due to the stirrers orbit adjustability and dependent on transportation shielding requirements resulting from waste activity the following casks are used

- 200 l drums either with or without outer concrete shielding

- 400 l drums either with or without internal concrete shielding

All safety aspects have been analysed and approved by the TÜV-Baden technical inspection authority. The mobile solidification unit is licensed for processing wastes up to an activity inventory of 6 Ci/ m^3 at 1.25 MeV dose rate. If higher levels are required, the design permits additional shielding up to 20000 kg.

1.3 Set up and supply requirements

Fig. 2 shows the transportation arrangement on truck with total load of about 34000 kg. All dimensions are kept below international road transportation allowances.

For setting up 6 m by 3.3 m floor space with a loading capacity of 9000 kg/ m^2 and total height of 4.53 m or 5.40 m are required. The unit can be operated with own HEPA-filter or connected to on-site HEPA-plenum.

Set up time is 1-1.5 days influenced by particular site structural conditions.

Connecting values are

- 380/220 V, 63 Amps. electrical power
- 3/4" demineralized water supply
- 3/4", 6 bar, dustfree, dry, compressed air
- both 2" "Argus" type ballvalve-couplings to waste circulation loop inlet and outlet. Other types on request.
- 2" concrete suspension supply.

On request the unit may be equipped with power generating station and air compressor.

1.4 Operating methods and performance

Due to waste conditions, operating methods after prescription is established are:

- drums with weighed in cement powder are supplied and, after connection to the cell liquid or semiliquid waste is added portionwise through the metering pot and stirred in

- drums are supplied with portioned in powder or granulated waste, connected to the cell, and mixed in.
  Concrete or its suspension, in this case, is supplied from outside through a 2" auxiliary line.
- decommissioned parts are supplied in drums, connected to the cell and poured with concrete suspension.

Casks are delivered up to the roller conveyor and hauled off by a forklift truck.

The performance reached over all is dependent on specific activity of the waste and resulting shielding requirements at one hand, and the dry substance contents at the other.

- 1.8 - 2.2 m^3/d are solidified into outside shielded 200 l drums or inside shielded 400 l drums
- 3.6 - 4.6 m^3/d are processed if 400 l drums are used.

Some statistical data are given in Table I.

The reliability reached not regarding failures caused by on site is 95%.

While processing slurries with an activity of about 4 Ci/m^3, containing of 15% Cs-134, 44% Cs-137, 36% Co-60, and 5% Mn-54. The detected dose rates were 3 mrem/h at the cell surface and 0,35 mrem/h at the operators place.

The applied personnel dose rate still remained below 10 mrem/d and man.

Because of rising interest in mobile waste solidification service, an improved unit equipped with hydraulical driven stirrer is under development.

Table I

Statistical data of mobile waste solidification

Stations: 1 BWR Gundremmingen 2 PWR Neckarwestheim 3 PWR Biblis

Period	Station	type of waste	cask	no. of	pers. expos. mrem/ man /d
Nov. Jan.	1	filter aid	200 l drum lost shielding	679	10
March April	1	decont. effl.	200 l drum	134	6
May June	2	boric acid	200 l drum lost shielding	193	5
Sept.	1	decont. effl.	400 l drum	42	10
Sept.	3	boric acid	400 l drum	65	8
Oct.	1	filter aid	200 l drum lost shielding	84	10
Nov.	2	boric acid	400 l drum	63	5
Nov.	2	boric acid	400 l drum	113	12
Nov.	2	spec. effl.	400 l drum	10	8
Nov. Dec.	3	boric acid	200 l drums lost shielding	282	20

Note:"boric acid " stands for evaporator bottoms containing boric acid

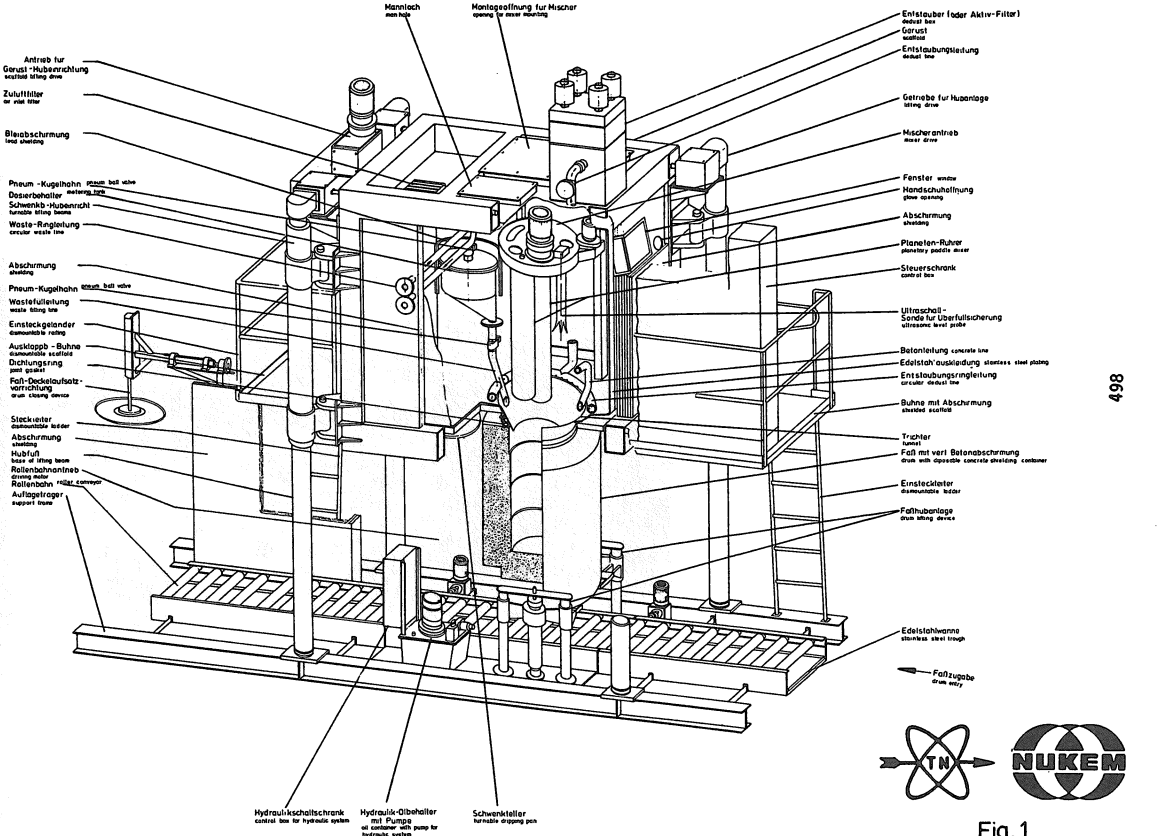

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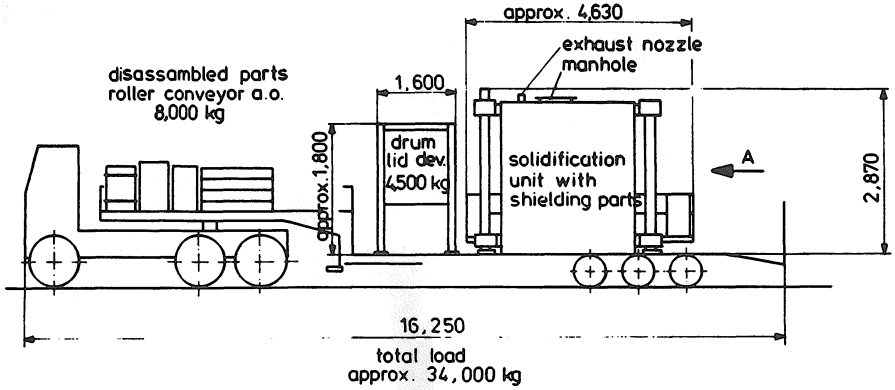
Fig. 1

Dm - Darstellung
Mobile Waste - Anlage


approx. 4,630
exhaust nozzle
manhole
disassambled parts
roller conveyor a.o.
8,000 kg
1,600
drum
lid dev.
4,500 kg
approx.1,800
solidification
unit with
shielding parts
A
2,870
16,250
total load
approx. 34,000 kg

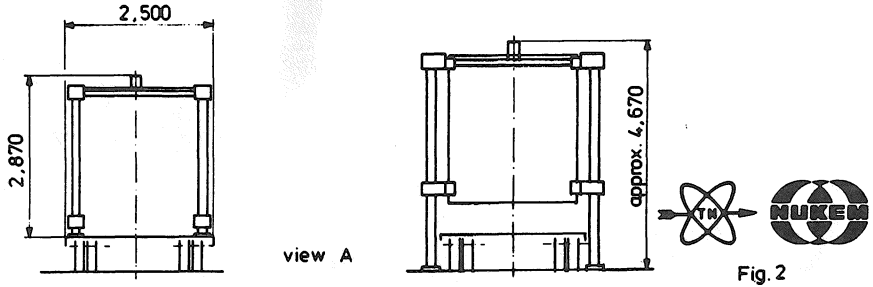

2,500
2,870
during transportation
view A
approx. 4,670
before settling on truck

Fig. 2

2. PYROHYDROLYSIS

2.1 Introduction

Final disposal of combustible waste from Pu-fuel element fabrication containing up to 120 g Pu/m³ may not cause only technical problems because of H_2 or He generation but due to long half life, time, and ecological aspects are of public interest.

Processes, allowing the recovery of Pu-values from this waste therefore are of particular interest.

In the past, pyrohydrolysis was used at NUKEM in order to recover high enriched uranium from combustible process waste like cellulosic and cotten wipes. The waste has been loaded in shuttles, pushed through a sintering tunnel furnace, and contacted with counter flowing, superheated steam. After a reaction time of 3 hours at temperatures of 800 - 1.000° C complete decomposition into gases and nearly carbonfree ashes were observed.

Further preliminary tests carried out by the NUKEM research division in an simplified arrangement demonstrated the applicability to the decomposition of other materials contained in combustible TRU-waste.

2.2 The process chemistry

Organic materials treated with steam at temperatures of 800 - 1.000°C are reacting as follows:

paper / cotton : $1/n\ (C_6H_{10}O_5)_n + H_2O \rightarrow 6\ CO + 6\ H_2$

PVC : $1/n\ (CH_2 - CHCl)_n + 2\ H_2O \rightarrow 2\ CO + 3\ H_2 + HCl$

rubber : $1/n\ (C_5H_8)_n + 5\ H_2O \rightarrow 5\ CO + 9\ H_2$

neoprene : $1/n\ (C_4H_5Cl)_n + 4\ H_2O \rightarrow 4\ CO + 6\ H_2 + HCl$

polyethylene : $1/n\ (CH_2 - CH_2)_n + 2\ H_2O \rightarrow 2\ CO + 4\ H_2$

A nearly quantitive decomposition is obtainable if sufficient reaction time is given.

2.3 Laboratory and bench scale results

To verify the preliminary results mentioned above, tests are being performed in first; laboratory mostly glass made micro-line and second; in a bench scale reactor, constructed of stainless steel,with uncontaminated materials.

In the laboratory equipment, batches of the particular materials have been treated in 0.5 to 1 g batches at 800°C and 1000°Cand the offgas has been analysed.

Table I Offgas Composition

material	reaction Temp °C	percent by volume CO_2	CO	H_2	Alkane
Paper	800	17	31	44	7
	1000	15	34	45	6
PE	800	2	4	28	50
	1000	7	26	59	4
Rubber	800	4	6	32	39
	1000	8	18	64	6
PVC	800	9	22	56	9
	1000	11	26	60	3
Neoprene	800	4	26	56	8
	1000	9	27	60	2

When treating PVC and rubber, HCl, respectivly H_2S have been observed in addition to the off gas constituents, mentioned in Table I.

A bench scale unit was set up, consisting of steam superheater, electrically heated reactor and steam condensing line.
In this unit, particular materials as well as simulated waste, composed of such materials are being processed, first in 0.7 kg batches and offer same improvements semi-continously up to 1.5 kg/ h.
Reference waste compositions varied as shown in Table II.

Table II Variations of waste composition

	weight %
PVC	50-70
Rubbers (Latex + Neoprene)	15-20
Cellulose and cotton	10-15
Other plastics (Polyethylene, PS, PTFE)	5-15

To determine decontamination efficiency some batches have been spiked with enriched Uranium. Some results after 3 hours reaction time at a temperature of 800°C are shown in Table III.

Table III Weight reduction and C-content

	weight reduction %	C-content % of the ashes
PVC	90	14
Polyethylene	100	---
Paper	99	2
Rubber	87	---
Neoprene	80	27

Further results and observations are:

- at reaction temperatures of 1000° C the condensate contains less organic destillates than at 800°C.
- If no HCl is entrained, offgas feedback into the reaction chamber results in complete decomposition.
- The decontamination factors, measured by U_{235}-tracing are: 2×10^3 - 2×10^5 between condensate and feed
  10^6 between offgas and feed
  without filtering the offgas.
- Samples of pyrohydrolysed ashes have been mixed with PuO_2, and treated another 3 hrs at 850°.
  Subsequent dissolution of these ashes in 10 M nitric acid for 5 hours yielded in 90 % Pu dissolved.

2.4 Discussion

The pyrohydrolysis process incorporates four concepts, which sets it apart from conventional incineration:

- endothermic process resulting in uniform temperature without any local peaks and smooth reaction avoiding generation of refactory Pu
- it can be accomplished in critical safe geometry.
- minimum offgas release
- metallic construction equipment easy to decontaminate or decommission

An engineering design covering the further demands is completed

- throughput 25-50 kg waste/ h in compositions as shown in table II
- Pu-content 60-120 gr/m³ of waste
- critical safe reactor design
- no safety risk in case of energy supply failure

2.5 Production size unit, brief description and improvements

(Simplified flowsheet is given in Figs 1-3)

The unit consists of:

- Feed preparation with shredder, hopper and feeder.
- Pyrohydrolysis reactor, consisting of outside electrical heated vertical kiln with internal slow rotating displacer. Understoichiometric oxygen may be added to steam, in order to lower C-content in the ashes. Gas velocity controlled between 0.05-0,2 m/s prevents particulate entrainment.
- Afterburner with outside air cooling. Burnout of all organic compounds with oxygen keeps the offgas quantity low and prevents explosion hazard.
- First scrubber is operated at 93°C removing HCl as NaCl-solution. This secondary waste is ready to be solidified. The quantity depends on PVC-content in the waste feed.
- Second scrubber operates at 50°C condensing most of the steam and releases CO_2 with excess O_2, saturated with water. This offgas is heated to 90°C prior to HEPA filtration.
- The following, proved decontamination factors are expected:

reactor	10^3 (in tests reached 10^3-10^5)
afterburner	1
first scrubber	10^2
second scrubber	10
HEPA filter	10^2 (proved values are 10^3)
over all	greater than 10^8.

2.6 The development program

The goals are:

- Detail engineering and equipment manufacturing up to the and of 1979

- Optimize the on stream parameters at reaction temperatures 750-850°C with throughput 25-50 kg/h up to April 1980 testing:
  - construction material behavior
  - reliability of components
  - Pu solubility of ashes
  - activity distribution
  - nuclear safety
  - energy supply and other failures by simulation

In parallel, bench scale tests will be continued.

After the test program the major components will be dismounted, transferred to the Karlsruhe Research Center and there adjusted to alpha techniques for hot operation.

If second start up will be successful, first contaminated waste and later on original production waste from Pu fuel element production shall be processed.

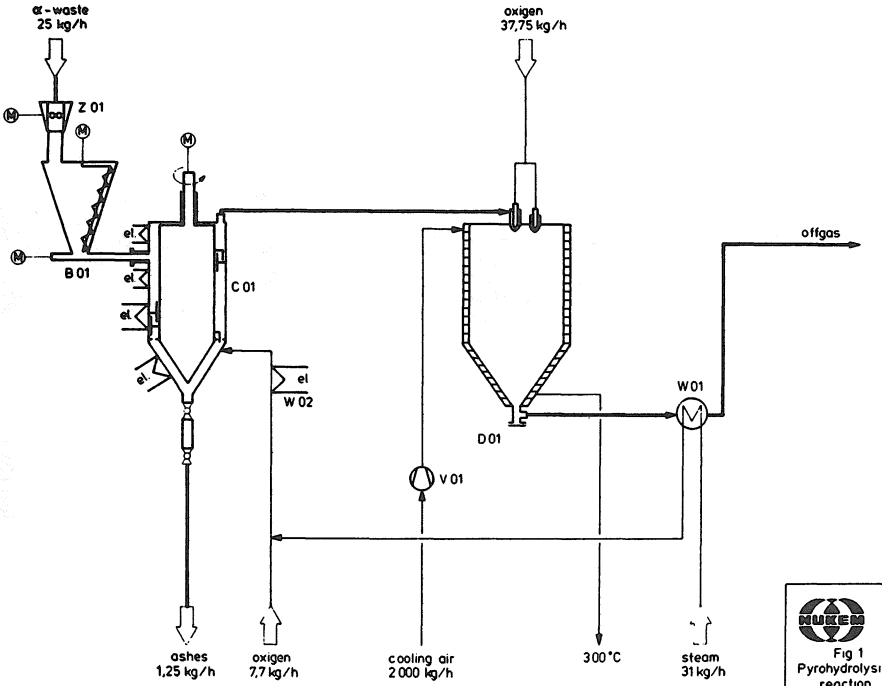


Fig 1
Pyrohydrolysis
reaction

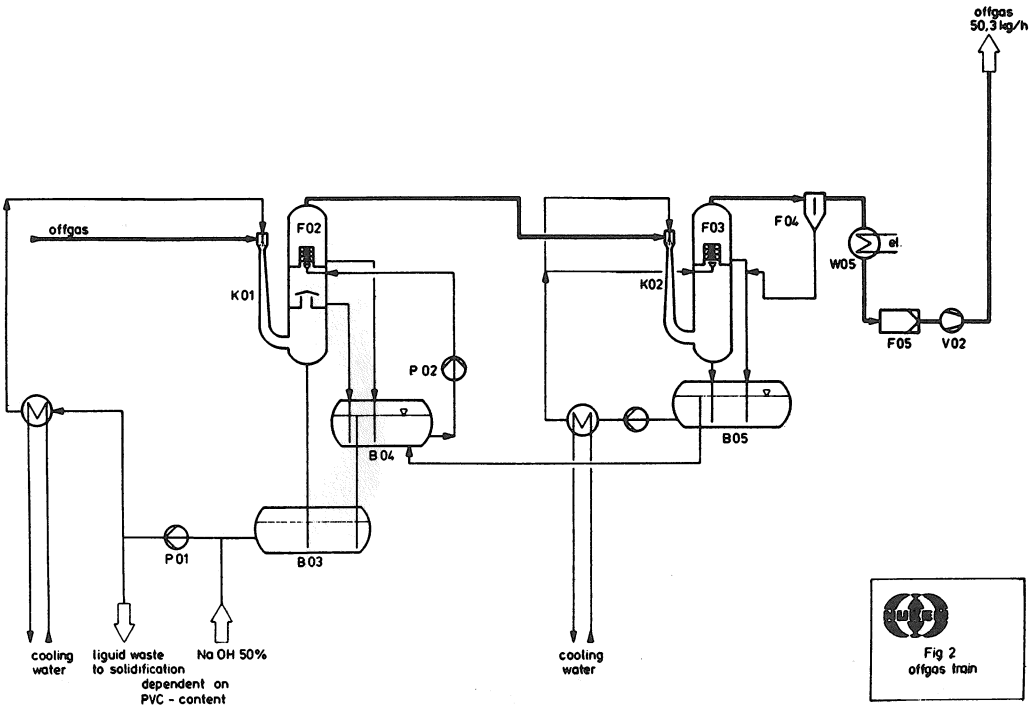


Fig 2
offgas train

Legend

Z	01	shredder
B	01	hopper
C	01	reactor
D	01	afterburner
V	01	air blower
W	02	superheater
W	01	heat exchanger
K	01	venturi
F	02	demister
K	02	venturi
F	03	demister
F	04	aerosol removal
W	03	heat exchanger
W	04	heat exchanger
W	05	preheater
F	05	HEPA - filter
P	01	pump
P	02	pump
P	03	pump
B	03	vessel
B	04	vessel
B	05	vessel
V	02	exhaust blower

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Fig. 3