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MARTIN MARIETTA

WASTE MANAGEMENT PROGRAM

Waste Treatment at the La Hague and Marcoule Sites

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
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Energy Systems Waste Management Organization

Waste Treatment at the La Hague and Marcoule Sites

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1. INTRODUCTION

This report responds to the requirements of Phase 2, Task 2, "Waste Treatment," of the contract for Low-Level Radioactive Waste Technology Information awarded to Numatec, Inc., by Martin Marietta Energy Systems, Inc.

In this report, an overview of waste treatment and solidification facilities located at the La Hague and Marcoule sites, which are owned and/or operated by Cogema, will be provided. The La Hague facilities to be described in this report include the following:

- the STE3 liquid effluent treatment facility, which is in operation;
- the AD2 solid waste processing facility, also in operation; and
- the UCD alpha waste treatment facility, which is currently under construction.

The Marcoule facilities described in this report, both of which are in operation, include the following:

- the STEL-EVA liquid effluent treatment facilities for the entire site; and
- the alpha waste incinerator of the UP1 plant.

This report is organized into four sections: this introduction, low-level waste treatment at La Hague, low-level waste treatment at Marcoule, and new process development, including the solvent pyrolysis process currently in the development stage for Cogema's plants.

1.1 EXECUTIVE SUMMARY FOR TASK 2.2

In Task 2.2, Numatec provides information on the design, operation and performance of low-level waste treatment systems in at the La Hague and Marcoule sites in France. Specific areas of interest include incineration, chemical treatment, stabilization, and physical volume reduction. This report will be an overview rather than an exhaustive treatise of the subject and will serve as the basis for identifying more detailed information requests.

This report describes the systems that are in use for the treatment and conditioning of solid and liquid low-level waste and alpha wastes produced in the COGEMA reprocessing plants at La Hague and Marcoule, including:

- the definition of the different types of waste and their main characteristics;
- the processes and technologies used for each categories of waste;
- a description of the performance parameters for each process, such as throughput, decontamination performance, volume reduction, etc.; and
- the main operation conditions.

New processes under development by the CEA will also be described briefly, including cold crucible techniques and the solvent mineralization process.

2. TREATMENT AND SOLIDIFICATION OF LOW-LEVEL WASTE AT LA HAGUE

2.1 OVERVIEW OF THE LA HAGUE REPROCESSING PLANTS

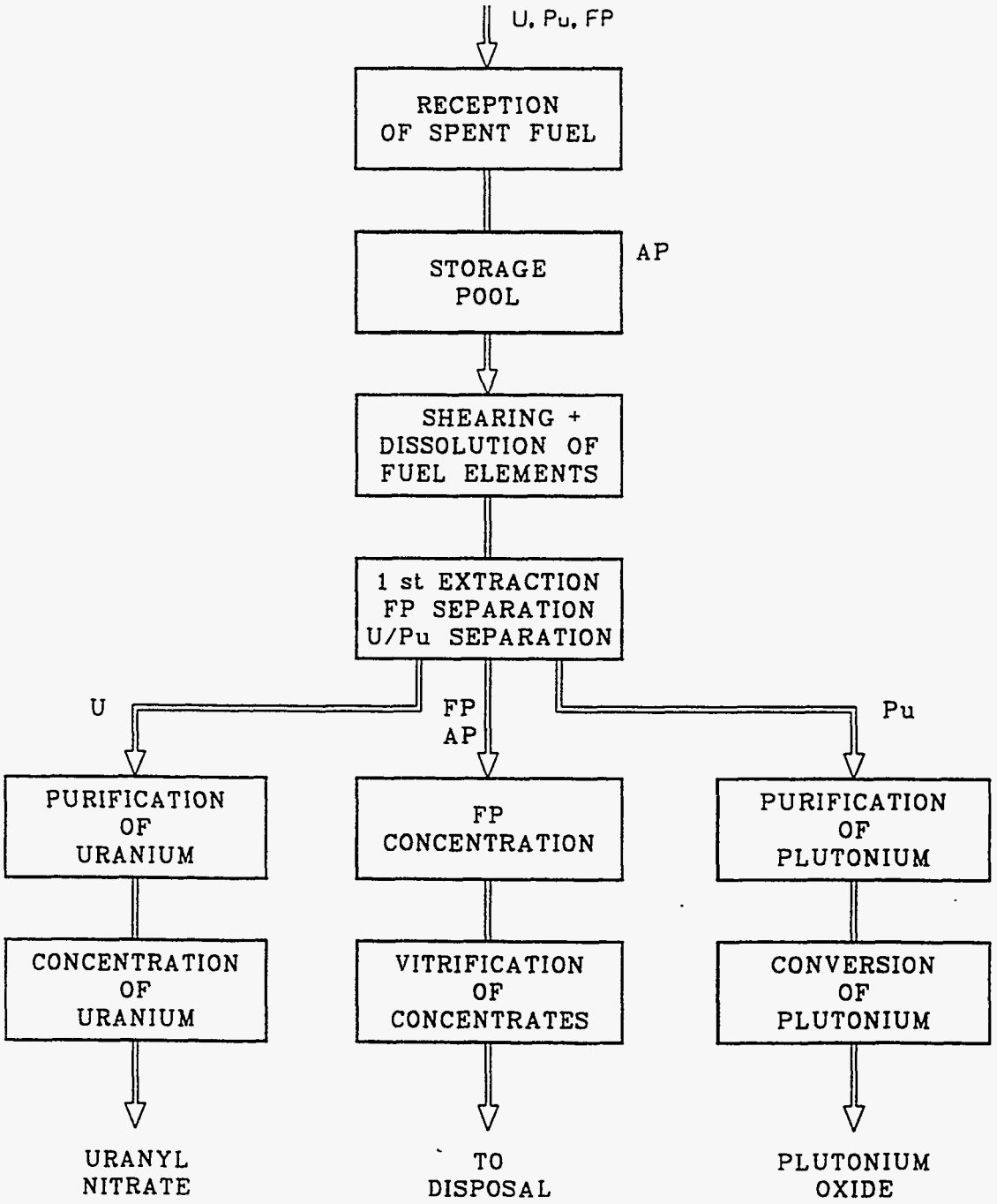
La Hague is a commercial reprocessing complex for spent fuel from nuclear power reactors. The first reprocessing plant at La Hague was the UP2-400 plant, which could reprocess up to 400 metric tons of uranium (MTU) per year of both gas-cooled reactor (GCR) and uranium oxide fuel from light water reactors (LWR). The total reprocessing capacity at the La Hague site has been increased over the past ten years by the construction of the UP3 plant, which has a nominal capacity of 800 MTU per year. The UP2-400 plant itself will be upgraded to the same capacity through the UP2-800 project, which is currently under construction and scheduled to enter service by the end of 1993.

The La Hague expansion project involved major process modifications to accommodate advanced technologies, new trends in reactor fuel design such as higher burnups and the use of mixed oxides, and increasingly stringent nuclear safety regulations, site release limits, and environmental monitoring requirements. The new plants are still based on the Purex process, in which uranium, plutonium and fission or activation products are separated chemically with a series of liquid extraction operations.

As shown on the conceptual flow diagram of a Purex plant in Figure 1, the incoming streams are separated into their various components, resulting in very different ranges of radioactivity from one part of the plant to another. The activity distribution corresponding to activity of the incoming fuel may be found only at the head-end of the reprocessing plant. Other streams with well-characterized activity distributions are:

- the spent fuel storage pools, which contain primarily activation products (AP);
- the fission product stream (FP), which is highly radioactive and contains most of the fission and activation products and a minute amount of fissile material;
- the uranium stream (U), containing the majority of the uranium, trace amounts of fission products and a very small amount of plutonium; and

Figure 1. Conceptual flow diagram of a Purex plant



- the plutonium stream (Pu), containing the majority of the plutonium and minute amounts of uranium and fission products.

The behavior of the radioelements contained in these streams has been well-characterized. Since all uranium and plutonium isotopes exhibit homogeneous chemical behavior, their isotopic composition may be considered to be constant as the uranium or plutonium process stream moves through the plant; variations in composition over time may be attributed to differences in the composition of the various spent fuels fed to the plant.

All other elements, generally beta/gamma ($\beta\gamma$) emitters, including fission and activation products, are contaminants; these are routed from the reprocessing plant to the vitrification facility. These elements exhibit a wide variety of chemical behaviors, and their distribution between the different plant facilities varies significantly. Nonetheless, the $\beta\gamma$ composition of these elements may be considered to be constant for a given feed within a given plant facility insofar as operating parameters are consistently the same.

The processes of decay occurring in the plant may modify the isotopic compositions of the various streams. The most noticeable illustration of this phenomenon is the build-up of americium-241 at various locations in the plant because of plutonium aging.

In addition, to optimize site operations, most plant support systems are shared by several facilities in a given plant, such as radioactive laboratories, or by the entire site, such as the liquid effluent treatment facility. Consequently, the distribution of activity in these units may be quite different from that of the principal process units.

Despite this wide range of activity distributions, experience has shown that the overall activity distribution for each facility does not vary significantly when averaged over periods of several months. This is due to several factors: the composition of the incoming fuel does not vary significantly over long periods of time, the process flowrates are highly stable, and the process itself remains constant.

It may also be assumed that the activity distribution of so-called technological waste, that is, dry solid waste, generated in the same zones of various plant units will be the same.

2.2 LA HAGUE WASTE CHARACTERISTICS

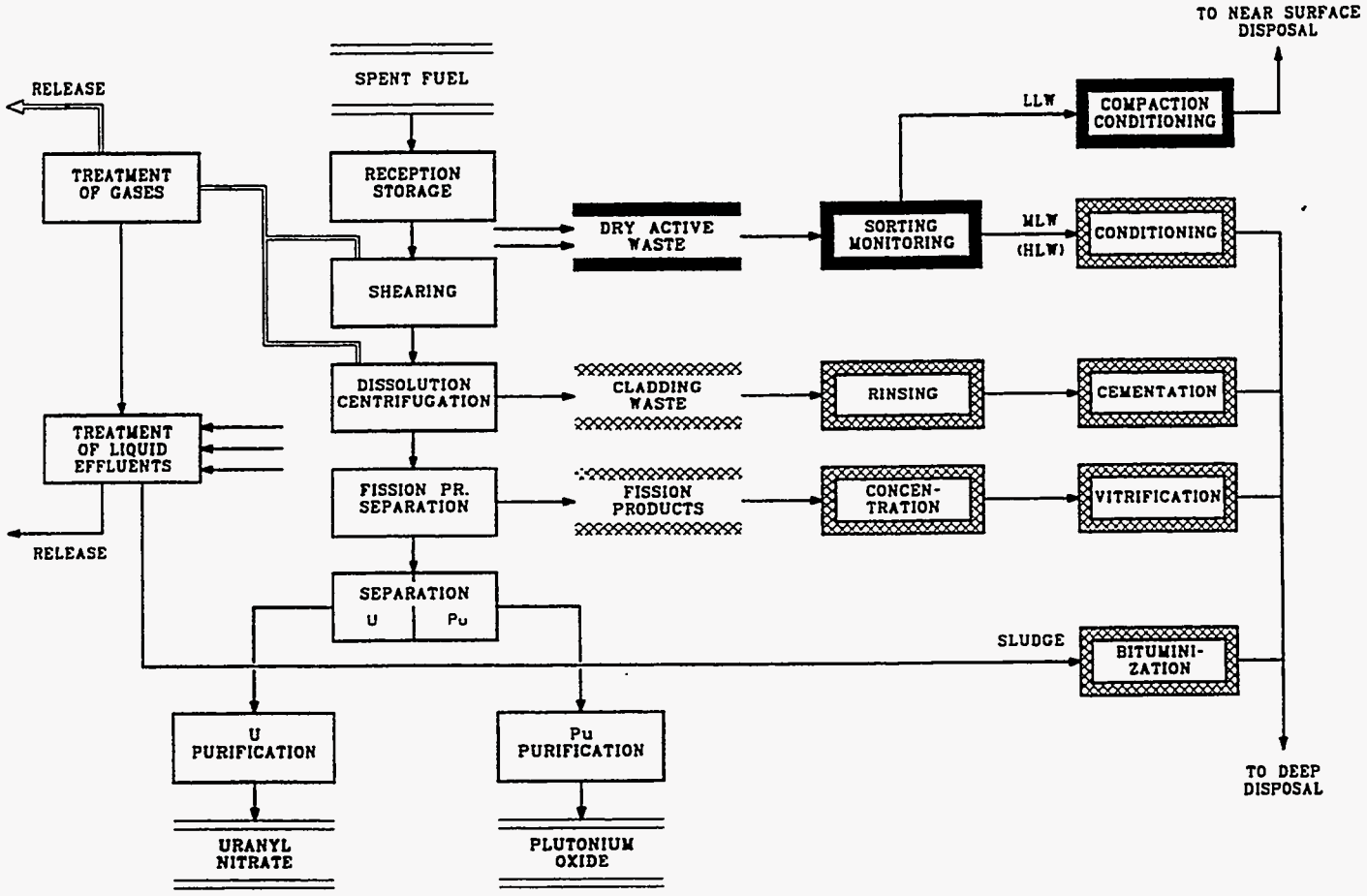
The waste management practices of the La Hague site are illustrated in the conceptual waste management flow diagram provided as Figure 2.

Waste generated by reprocessing operations is classified into two major categories: *process waste*, or waste generated by the process itself, and *plant waste* (called technological waste in French) resulting from repair and maintenance operations.

Because process waste is concentrated at La Hague, thereby increasing radioactivity concentrations, all process waste will be disposed of in a geologic repository. Plant waste is routed to the AD2 solid waste processing facility at La Hague and subsequently to a near-surface disposal facility. Plant waste is generated during repair and maintenance operations and consists of contaminated waste such as used or failed equipment and components from restricted-access areas and consumable items such as gloves, cotton swabs, and vinyl shielding from work areas. Higher activity plant waste from hot cells is removed from the cell in specially-designed transfer casks and routed to a separate processing line in the AD2 facility, where it is sorted and packaged for deep geologic disposal.

Plant waste from work areas and spent ventilation filters are routed to another processing line in the AD2 facility, where they are compacted and packaged for final disposal. The resulting packages are routed to an intermediate storage building before shipment to the near-surface disposal facility.

Figure 2. Conceptual waste management flow diagram for the La Hague Site



2.3 STE3 LIQUID EFFLUENT TREATMENT FACILITY

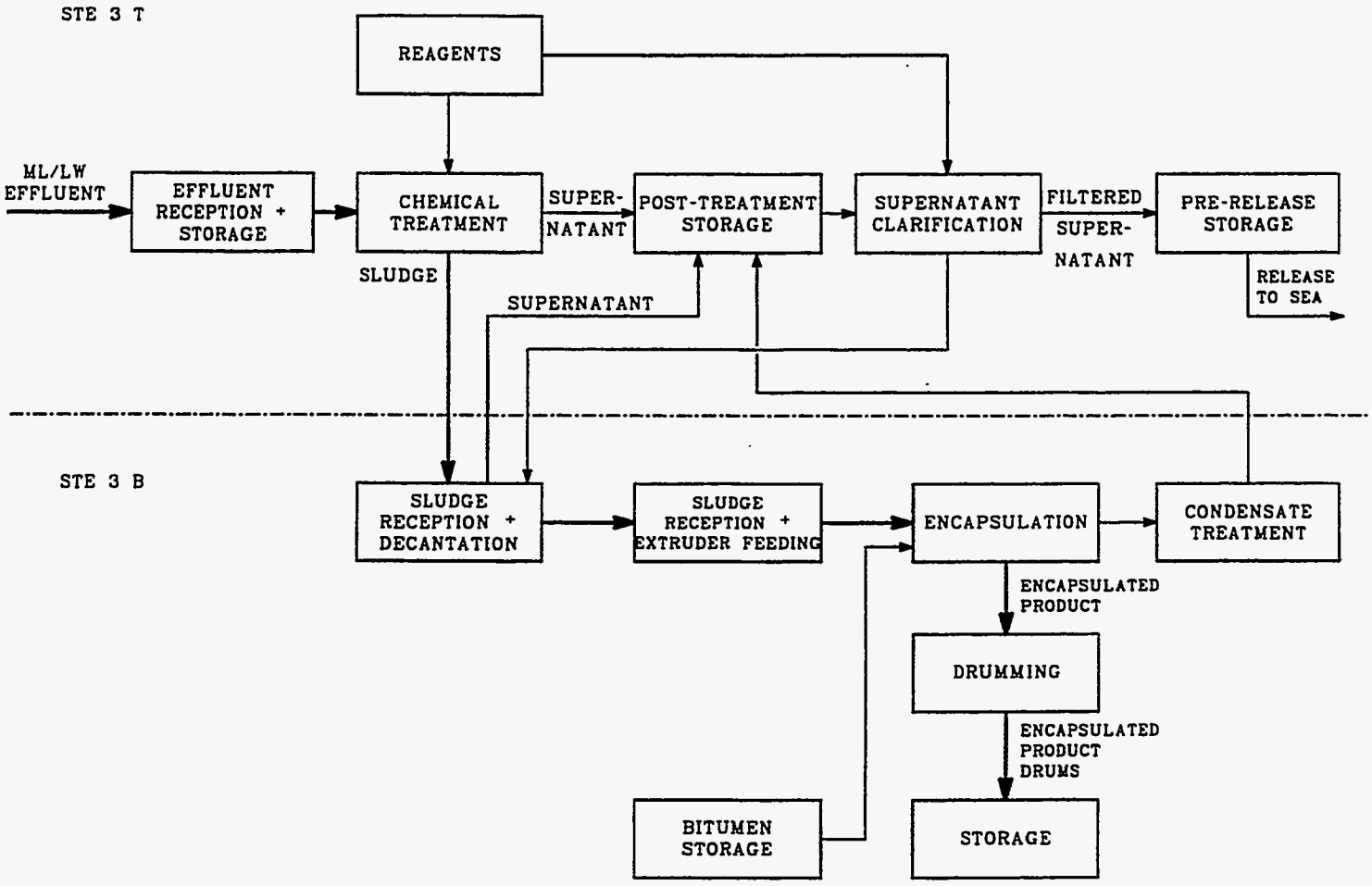
The STE3 liquid effluent treatment facility (see Figure 3) began operating in 1988. It is the third liquid treatment facility in France for reprocessing, and services both the UP2 and UP3 reprocessing plants at La Hague. The facility decontaminates low- and medium-level liquid effluent generated by site operations before release to the sea; solidification of waste generated by effluent treatment operations is integrated into the process. The facility, designed to treat 100,000 m^3 (or 3.5 million ft^3) of effluent per year, is divided into two principal sections:

- a treatment section for effluent decontamination by chemical coprecipitation; and
- a solidification section where radioactive sludge from the chemical coprecipitation treatment section is solidified in bitumen.

2.3.1 Effluent Characteristics

The STE3 facility receives process effluent and effluent generated by maintenance operations from the UP2 and UP3 reprocessing plants. The range of activity in effluent from a given plant facility is a function of the chemical operations used in the process. The activity distribution for the La Hague effluent corresponds to the following range of activity for beta/gamma emitters:

Figure 3. STE3 diagram



Co^{60}	0.01 - 2%
Sr^{90}	1 - 12.5%
Y^{90}	1 - 12.5%
Ru^{106}	12.5 - 48%
Rh^{106}	12.5 - 48%
Sb^{125}	0.5 - 4%
Cs^{134}	0.5 - 4.5%
Cs^{137}	1 - 13%
$Ba^{137}m$	1 - 12%
Ce^{144}	0.2 - 20%
Pr^{144}	0.2 - 20%
Pm^{147}	0.3 - 1.3%
Eu^{154}	0.3 - 1.5%
Eu^{155}	0.1 - 0.8%
Other	0.1 - 0.3%
including	$H^3 \leq 0.1\%$
	$I^{129} \leq 0.001\%$
	$Tc^{99} \leq 0.01\%$

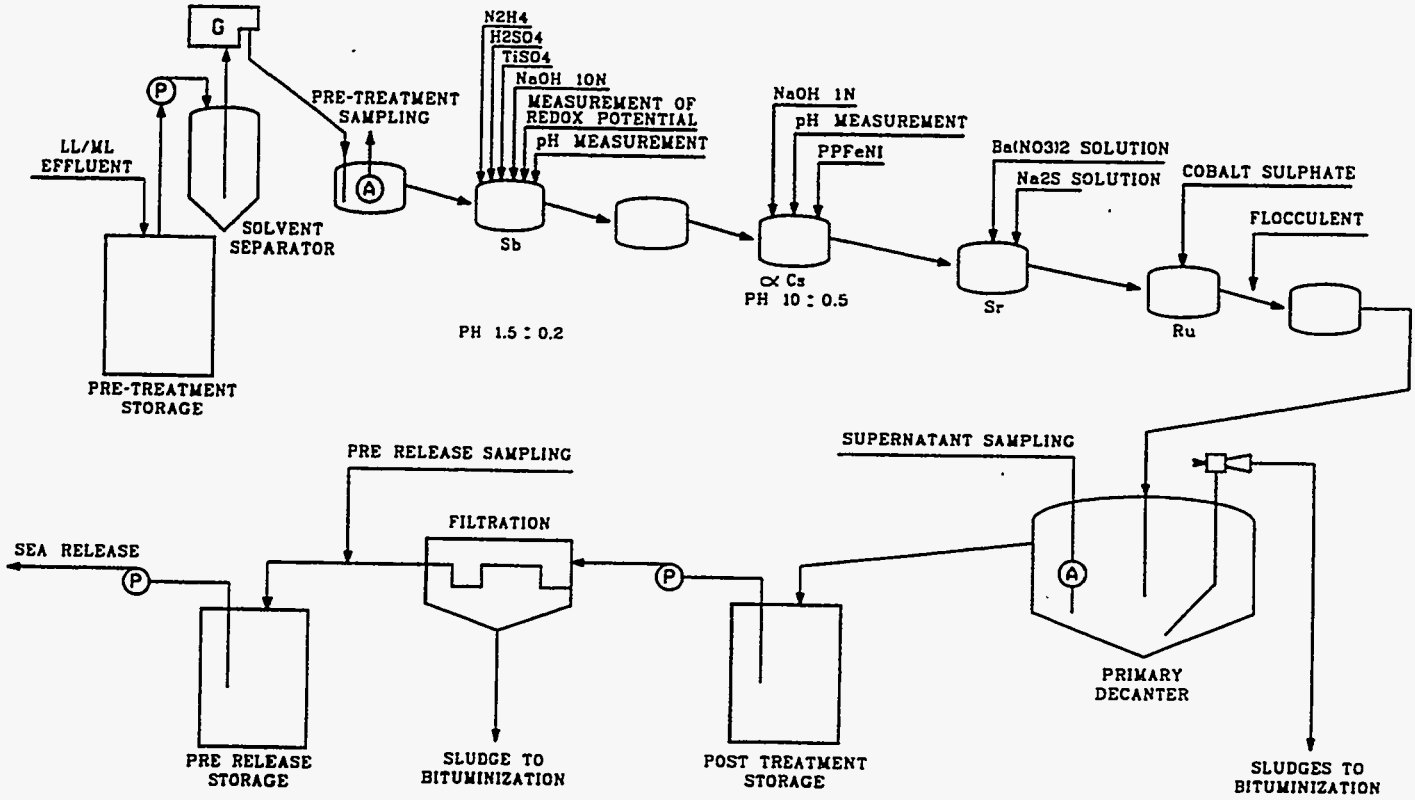
The average activity of the effluent treated in the STE3 facility varies from 1 to 4 Ci/m^3 (or from 1 to 4.2 GBq/ft^3) for beta/gamma emitters and 4×10^{-2} to 7×10^{-2} Ci/m^3 (or 42 MBq/ft^3 to 73 MBq/ft^3) for alpha emitters. Most of the effluent are acidic, with their acidity primarily nitric varying from 0.3 to 0.5 N.

2.3.2 Treatment Operations

The functions of the treatment section of the STE3 facility are shown in Figure 4 and described below:

- effluent receiving and storage before treatment;
- chemical treatment of effluent by coprecipitation; and
- post-treatment separation of:
  - decontaminated effluent (supernatant) before release to the sea; and of
  - sludge containing most of the radioactivity separated during chemical treatment operations, which is transferred to the bitumenization section of the facility for solidification.

Figure 4. STE3 - chemical treatment



- Effluent receiving and storage

Effluent are received and stored in five 600-m^3- (or 160,000-gal-) tanks and two 60-m^3- (or 16,000-gal-) tanks at La Hague. Both types of tanks are mechanically stirred. The tanks provide approximately one week of buffer storage capacity in the event that the chemical processing line is unavailable. The maximum receiving capacity at STE3 is 50 m^3/hr (or 13,000 gal/hr), which is the maximum capacity of the rotary distributors.

- Chemical treatment

Chemical reagents are added to form insoluble precipitates containing the radioelements in order to separate radioelements selectively. The precipitated product is referred to as the chemical coprecipitation sludge, while the decontaminated effluent is called the supernatant.

The following precipitates are formed in the treatment section of STE3:

- pre-formed precipitate of nickel and potassium ferrocyanide (PPFNi) to insolubilize cesium;
- barium sulfate to insolubilize strontium;
- cobalt sulfide to remove ruthenium from the effluent to be treated; and
- titanium sulfate to remove antimony from the effluent and to enhance the removal of alpha emitters, which are also separated in hydroxide form in an alkaline medium.

The following reagents are added to the effluent at STE3 to form these precipitates:

- PPFNi is added in liquid form;
- cobalt sulfide is formed by the addition of cobalt sulfate and sodium sulfide;
- barium sulfate is formed by the addition of sulfuric acid and barium nitrate; and
- titanium sulfate is added in liquid form.

Certain ions can reduce the effectiveness of chemical treatment because of their complexing capabilities or to their behavior in relation to a specific treatment. Before any chemical process is implemented on an industrial scale, its performance is verified on a large-volume sample in a shielded cell.

The chemical processing line is continuously fed with a 17 m^3/hr- (or 4,500 gal/hr-) GEDEON, or immersed aperture flow generator, after any traces of solvent present in the effluent aaare skimmed off with a solvent separator.

GEDEON routes the feed to the chemical treatment reactors, which are arranged in a cascade formation, allowing them to be fed by gravity overflow. Reagents are added to the reactors either by gravity or at low pressure, depending on reagent type.

Certain parameters must be regulated to ensure efficient treatment:

- the oxidation-reduction potential must be regulated at the head-end of the chemical treatment line; and
- the PH must be adjusted at the end of the treatment line for optimum decontamination factors.

At the end of the treatment line, a continuous separator separates the supernatant from the coprecipitation sludge by decanting.

Whenever the contents of a 600-m^3- (or 160,000-gal-) tank are treated, samples taken of the effluent feed at the head-end and of the supernatant at the back-end are analyzed and compared to determine the effectiveness of each treatment campaign.

- Post-treatment storage and release

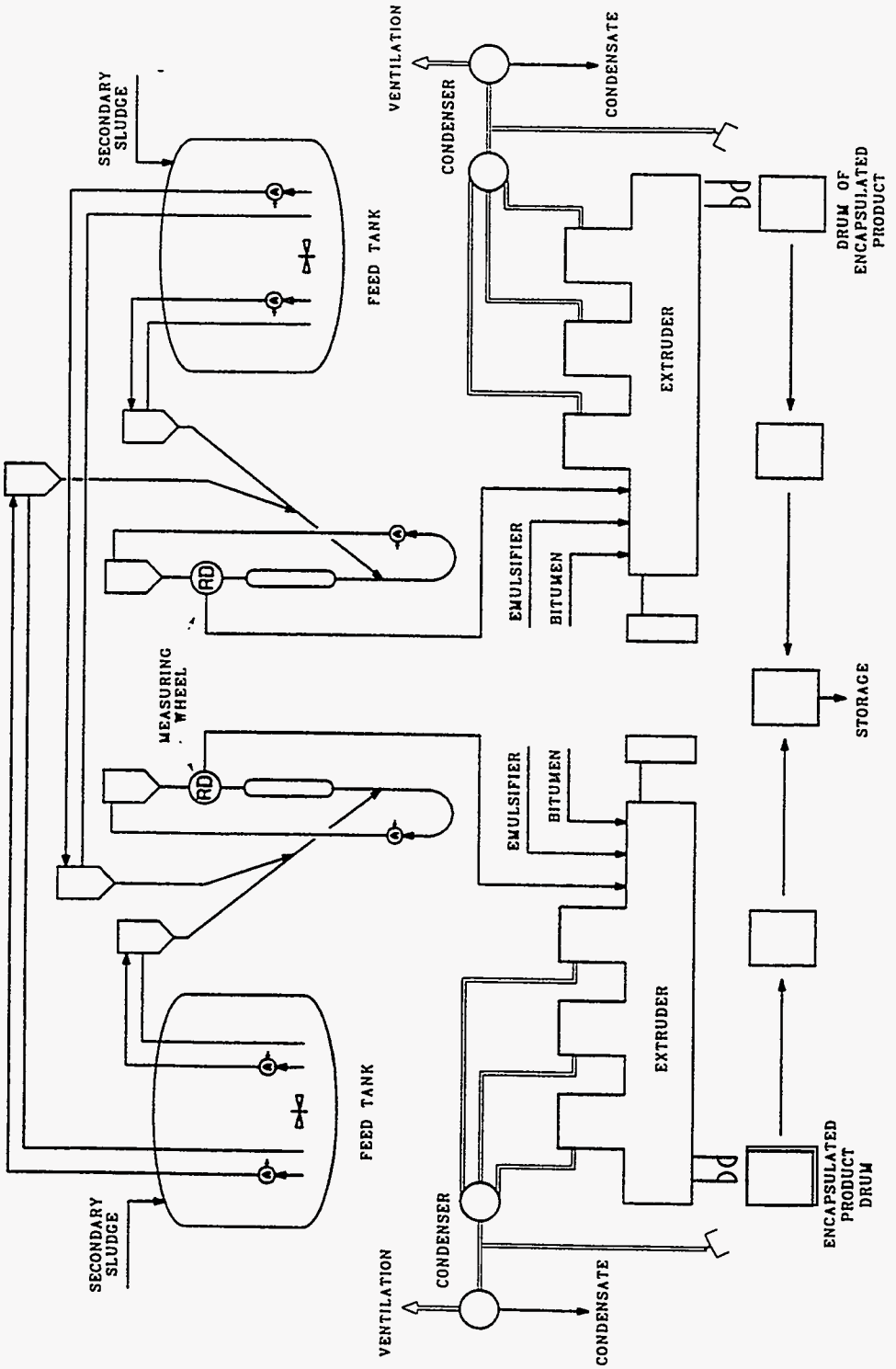
The supernatant produced by chemical coprecipitation passes through a diatomaceous filter and is routed to a storage unit, where it is sampled and analyzed before release to the sea. This filtration method produces supernatant containing suspended solids with particle sizes of less than 25μ, in compliance with the criteria of the Decree published in the *Journal officiel* of 1 November 1 1980.

2.3.3 Bitumenization Operations

The functions of the bitumenization section of the STE3 facility are shown in Figure 5 and described below:

- receiving and storage of chemical coprecipitation sludge;
- additional sludge decanting to increase the facility's overall concentration factor;
- solidification of the resulting sludge in a bitumen media; and
- storage of resulting waste drums in specially designed storage modules.

Figure 5. STE3 - bitumenization unit



- Sludge receiving and decanting

The sludge routed to the bitumenization section of the STE3 facility has already undergone an initial decanting step in the chemical treatment section of the facility; it will undergo a second decanting operation in the bitumenization section. This additional decanting enhances the facility's overall concentration factor by a factor of about two.

The supernatant produced during the second decanting operation is rerouted to STE3's treatment section, while the remaining sludge is transferred to the extruder feed unit.

- Extruder feed

The extruder feed unit has two ordinary feed tanks which feed chemical coprecipitation sludge to both bitumenization process lines. The bitumen used for solidification is made by direct distillation. The sludge is transferred to the extruder feed regulator from the tanks by a dual air lift.

- Solidification

The chemical coprecipitation sludge is solidified in a bitumen media in two bitumenization lines, each with its own extruder. The extruder comprises a series of seven modules:

- a bitumen feed module, which receives bitumen and an emulsifier at a regulated flowrate in two separate streams;
- an active effluent feed module;
- a sealed module;
- three off-gas modules, which release off-gas to the condenser through a large opening at the top; and
- an extruded product module, with solidified material exiting at the bottom.

Four V-shaped screw shafts arranged in pairs inside the modules extrude the final product, which is a bitumen-coated dry extract.

- Drum storage

The STE3 facility has four drum storage modules, each capable of storing 5,000 drums. The storage modules are currently being upgraded to include drum load-out facilities.

- Condensate treatment

Condensates produced during bitumenization operations are routed to the condensate treatment line at STE3. The condensates contain tar and light oils produced by the lighter compounds of bitumen, which are separated by a decanting operation. The purified aqueous phase is rerouted to the chemical process in the facility's treatment section, just as the supernatant from secondary decanting operations was.

2.3.4 Solidified Waste Characteristics

The bitumen-solidified sludge produced at STE3 has the following average characteristics:

- cold fill rate: 70 to 80%
- maximum weight of solidified waste: 250 kg (or 550 lb)
- solidified product composition:

. dry extract	39%
. bitumen	58%
. surfactant	1%
. water	2%

The maximum activity of each drum is calculated with the following equation:

$$A_1 + 80A_2 \leq 140 \text{ Ci}$$

where: A_1 = beta/gamma activity other than Pu^{241}, and

A_2 = alpha activity.

The approximate dose rate for the 100 Ci ßγ/0.5 Ci α- (or 3.7 E^{12} Bq βγ/18.5 GBq-) pair (excluding Pu^{241}) with an average activity spectrum is the following:

- direct contact: 75 rad/hr
- at 1 m: 5 rad/hr

A total of three 200-l drums of bitumenized sludge is produced at the STE3 facility per MTU processed at the La Hague reprocessing plant.

2.3.5 STE3 Operating Results

- Decontamination factor

The decontamination factors recorded at the STE3 facility are highly dependent on the activity of the effluent prior to treatment. However, the average activity of the supernatant is invariable, with the following decontamination factors (DF) achieved:

- 5×10^{-3} Ci/m^3 (or 5.24 MBq/ft^3) for ruthenium-106 (DF of 200 for activity of 1 Ci/m^3, or 1 GBq/ft^3, before treatment);
- 1.2×10^{-2} Ci/m^3 (or 12.6 MBq/ft^3) for strontium-90 (DF of 20 for activity of 0.25 Ci/m^3 (or 262 MBq/ft^3) before treatment);
- 4×10^{-3} Ci/m^3 (or 4.2 MBq/ft^3) for cesium-137 (DF of 250 for activity of 1 Ci/m^3, or 1 GBq/ft^3, before treatment);
- 10^{-4} Ci/m^3 (or 0.1 MBq/ft^3) for alpha emitters (DF of 1000 for activity of 0.1 Ci/m^3, or 0.1 GBq/ft^3, before treatment).

- Concentration factor

The concentration factor of the STE3 facility, which is the volume of effluent generated over the volume of drums produced, is approximately 75.

2.3.6 Process Enhancements

It is noteworthy that the volume and activity of low- and medium-level effluent generated by operations of the UP3 plant at La Hague are substantially lower than estimated during the design stage. The principal reason for this is the very high efficiency of the extraction cycles, which results in lower than expected activity levels for some effluent. In addition, excess evaporative capacity resulting from the gradual ramp-up of plant operations was applied to the concentration of some of these effluents, with the concentrate being routed to the vitrification facility. These two factors contribute to a current production of bitumenized sludges which, if extrapolated to an 800-MTU per yr reprocessing plant, would amount to about 70% of the design value. Nonetheless, the total volume of bitumenized waste is still four times greater than that of vitrified high-level waste, yet it accounts for less than 1% of all waste activity. This fact,

together with the excellent operating performance of the UP3 plant, indicated that there was room for improvement in the management of low- and medium-level effluent generated at La Hague.

Measures already being taken to reduce effluent volumes and activity at La Hague will continue in the form of process modifications designed to achieve effluent segregation based on chemical content and activity level and to increase plant evaporative capacities.

Enhanced effluent segregation will make it possible to discharge very low-level streams to the sea after filtration and monitoring, without a corresponding increase in total released activity. This is already the practice for aqueous effluent from the solvent distillation unit of the UP3 plant.

The remaining effluents are routed to the STE3 facility from the analytical laboratory. These effluents usually consist of a mixture of excess process samples and chemical reagents which are not used in the main process, and they contain varying levels of alpha and beta/gamma activity. In their case, enhanced effluent management relies primarily on appropriate segregation in the analytical laboratory. Segregated analytical laboratory effluent will be returned to the plutonium purification cycles, in the case of alpha-bearing effluent, or will be routed to the vitrification facility whenever possible, which would be the case for beta/gamma effluent. Effluent containing undesirable chemicals will be transferred to a special coprecipitation unit to separate the alpha activity. Furthermore, the amount of unwanted ions, such as phosphates, sulfates, and chlorides, is being substantially reduced through the use of alternative analytical methods.

When the new units come on line, virtually all of the activity, in the form of concentrates, will be routed to the existing vitrification facilities. This will have the direct benefit of eliminating the need for effluent coprecipitation and sludge bitumenization, under normal operating conditions, for all low- and medium-level effluent generated by the UP3 and UP2-800 plants by 1995. The incremental increase in activity in the vitrified product will not significantly increase the volume of glass produced.

2.4 AD2 SOLID WASTE PROCESSING FACILITY

The UP2 and UP3 reprocessing plants generate various types of waste, including:

- process equipment and components, such as pumps, valves, ejectors, etc.;
- laboratory materials, such as glass, beakers, etc.; and
- various types of waste from plant operations, including cotton swabs, vinyl, cardboard, and the like.

This type of waste is collected in metal drums, cans, or shielded transfer casks and is transferred to the AD2 facility, where it is processed without breaching containment before shipment to the disposal facility. The facility features two dedicated processing lines, one for solid process waste and one for plant waste, both of which are described below.

2.4.1 Solid Process Waste Processing

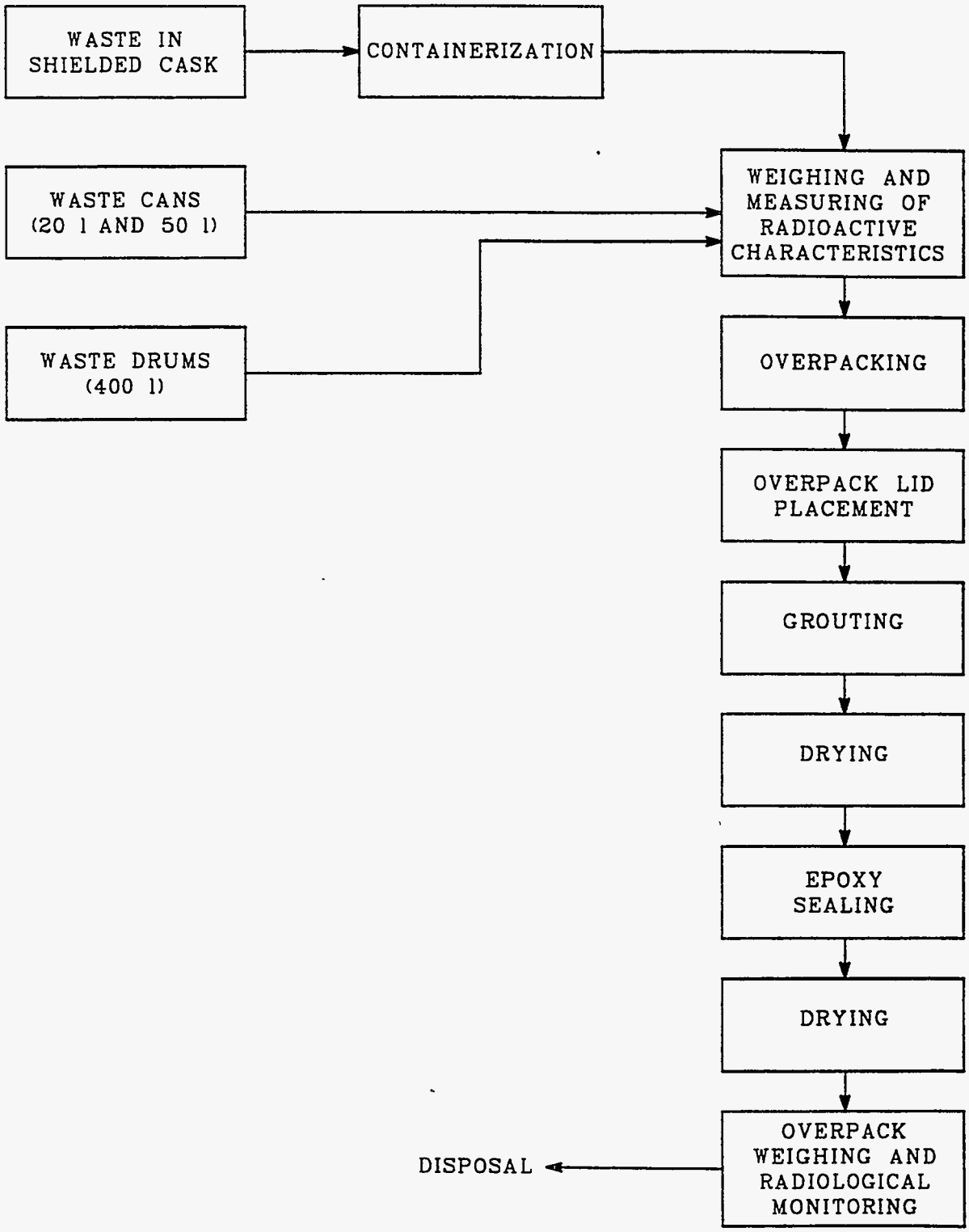
- Process principle

The process principle for solidification of solid process waste is illustrated in Figure 6. Individual solid process waste components from the UP2 and UP3 plants are transferred to the AD2 facility in a shielded cask, in 20- or 50-l cans wrapped in vinyl, or in 400-l drums.

Upon arrival in the AD2 facility, the waste is processed as follows:

- Waste transferred to the facility in shielded transfer casks is unloaded into a canister under containment.
- The waste is weighed and assayed to determine the radioactive characteristics of waste in cans, canisters, or drums. The $\beta\gamma$ and α activity of the waste is determined with a dose rate measurement method and correlation to a standard activity spectrum for that waste type. This is supplemented by passive neutron counting for waste from areas where large amounts of alpha emitters are present (see paragraph 2.4.3 below).
- The waste is placed in an asbestos-cement overpack called a CAC in French.
- A lid is placed on the CAC and locked onto the body of the overpack.

Figure 6. Solidification of process waste



- The annulus between the CAC and the container of waste is completely filled with grout by injection through a nozzle in the center of the CAC lid.
- The CAC is stored to allow the grout to solidify.
- An epoxy resin sealant is injected through the nozzle of the CAC lid until the lid is completely covered.
- The CAC is stored to allow the sealant to solidify.
- The CAC is weighed, and its radiological characteristics are determined by measuring the gamma dose rate and checking for the absence of loose alpha contamination and surface beta/gamma contamination.

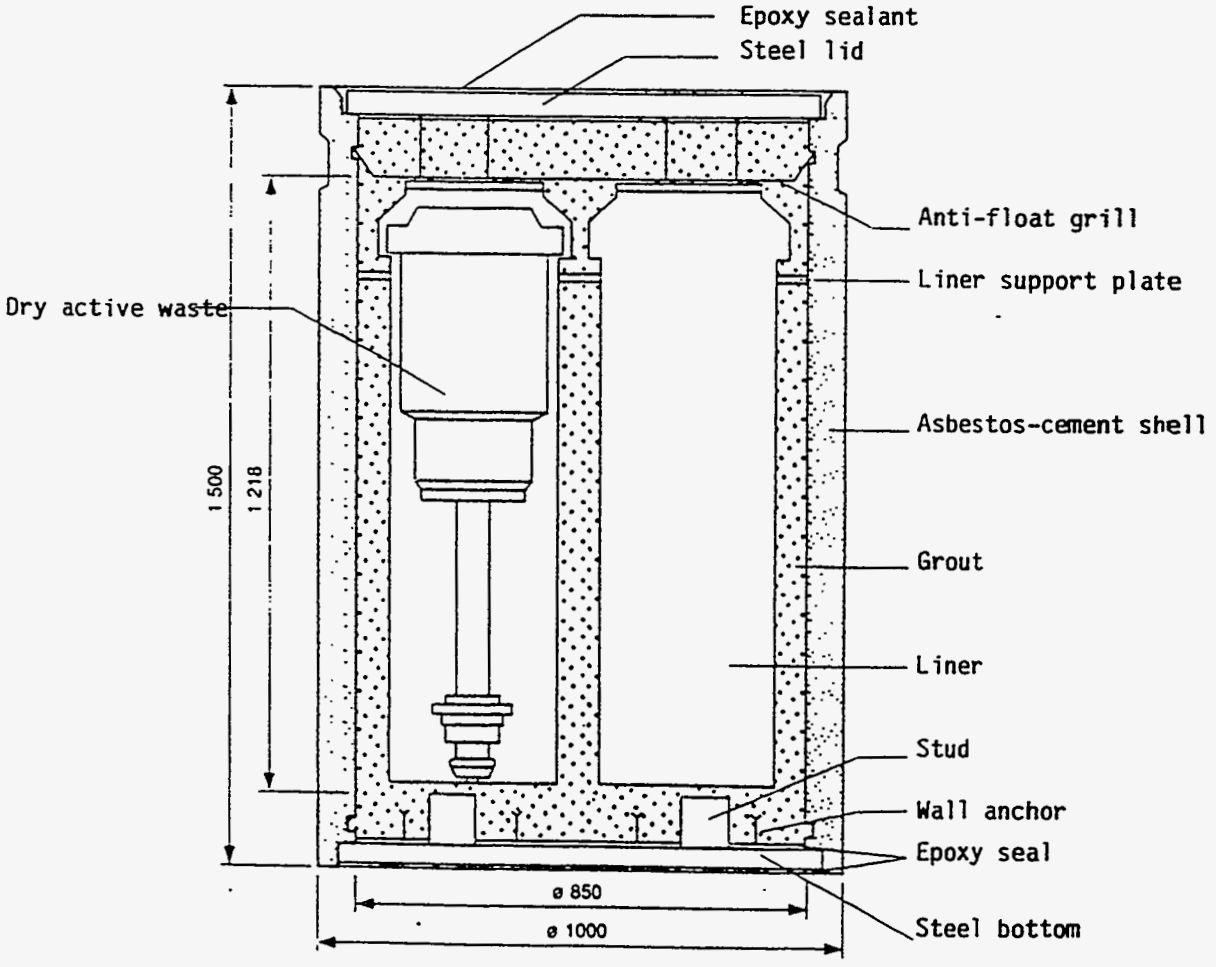
• Grouted process waste characteristics

Asbestos-cement overpack (CAC)

The asbestos-cement overpack (CAC) is illustrated in Figure 7. The CAC consists of:

- a cylindrical body made of asbestos-cement with 75-mm- (or 3-in-) thick walls;
- an inside bottom plate glued to the overpack made of 920-mm- (or 3-ft-) diam, 30-mm- (or 1 3/16-) thick steel with wall anchors and carbon steel studs to support the waste container;
- a lid made of a 902-mm- (or 2 ft-, 11-in-) diam, 30-mm- (or 1 3/16-in-) thick carbon steel plate with two openings:
  . a 120-mm- (or 4 ¾-in-) diam center nozzle for the injection of grout or sealant;
  . a 170-mm- (or 6 11/16-in-) diam side opening which serves as a vent and to monitor the grout level; and
- a carbon steel anti-float grill which acts as an anchor for the waste container, preventing it from rising when the grout is injected.

Figure 7. Asbestos-cement overpack



Individual process waste containers

The process waste from the various facilities of the UP2 and UP3 plants consists primarily of equipment installed in mechanical cells, chemical process cells, analytical laboratories, and shielded enclosures; this equipment was designed for rapid remote replacement. The principal characteristics of the containers for this type of waste are described below.

Canisters: Irradiated materials from hot cells are placed in carbon steel canisters, which come in five diameters and various lengths to accommodate waste of different sizes, all of which can be processed in the AD2 facility.

Type of Canister	Overall Diameter	Overall Height
Diameter 135	220 mm	ranging from 475 to 1,203 mm inclusive
Diameter 300	380 mm	
Diameter 400	480 mm	
Diameter 580	660 mm	
Diameter 650	760 mm	

Cans: Analytical laboratory waste and waste from temporary shielded enclosures is placed in polyethylene cans.

Can Size	Overall Diameter	Overall Height	Useful Volume
20-l	320 mm	440 mm	approximately 20 l
50-l	320 mm	740 mm	approximately 40 l

400-l drums: Mechanical equipment that has low activity levels and does not fit into canisters or cans is placed in carbon steel drums.

Drum Size	Overall Diameter	Overall Height	Useful Volume
400-l	800 mm	1,200 mm	450 l

Grout

A grout of CLC 45 cement with minimum exudation and appropriate viscosity is used to completely surround the container of waste inside the overpack.

Sealant

Epoxy resin is used as a sealant.

Final grouted waste form

The principal characteristics of the finished grouted overpack are as follows:

- Average weight: 2,200 kg (or 4,850 lb)
- Average activity upon production of the final waste package:

  . beta/gamma 20 Ci (or 740 GBq)

  . alpha 2 Ci (or 74 GBq)

- Average gamma dose rate upon production of the final waste package:

  . direct contact 730 mRad/hr

  . at 1 m 130 mRad/hr

- Number of CAC overpacks per MTU of reprocessed uranium: approximately 1.4.

2.4.2 Solid Plant Waste Processing

- Process principle

Bagged waste placed in 100-l and 200-l metal drums of plant waste is transferred from the various facilities of the UP2 and UP3 plants to the AD2 solid waste processing facility (see Figure 8). Bagged ventilation filters are packed in cardboard boxes. Upon arrival at the AD2 facility, plant waste is processed as follows:

- Containers are weighed and assayed to determine the radioactive characteristics of the waste contents. A dose rate measurement is taken of the container and is correlated with the typical activity spectra for its waste contents to determine the $\beta\gamma$ and α activity of the waste. This method is supplemented by passive neutron counting for waste from areas with high alpha radiation (see section 2.4.3 below).
- Cardboard packages undergo preliminary compaction, are placed in 100-l drums, and are fed to the high-pressure compaction system.
- The 100-l drums are compacted and placed in 200-l drums. A 200-l drum can accommodate five to six compacted 100-l drums. Compacted drums are transferred to one of eight positions on a sorting table and are selected so as to maximize the fill ratio of the 200-l drums (see Figure 9).
- The 200-l drum is placed inside a fiber-reinforced concrete overpack.
- An anti-float plate made of fiber-reinforced concrete is inserted inside the overpack.
- Filler material made of the same fiber-reinforced concrete as the overpack is injected into the annulus between the overpack and the 200-l drum until the mixture is flush with the top of the overpack.
- The overpack is stored to allow the filler concrete to set.
- The overpack is weighed and radiologically monitored using a gamma dose rate measurement for surface alpha and beta/gamma contamination.

Figure 8. Solidification of dry active waste

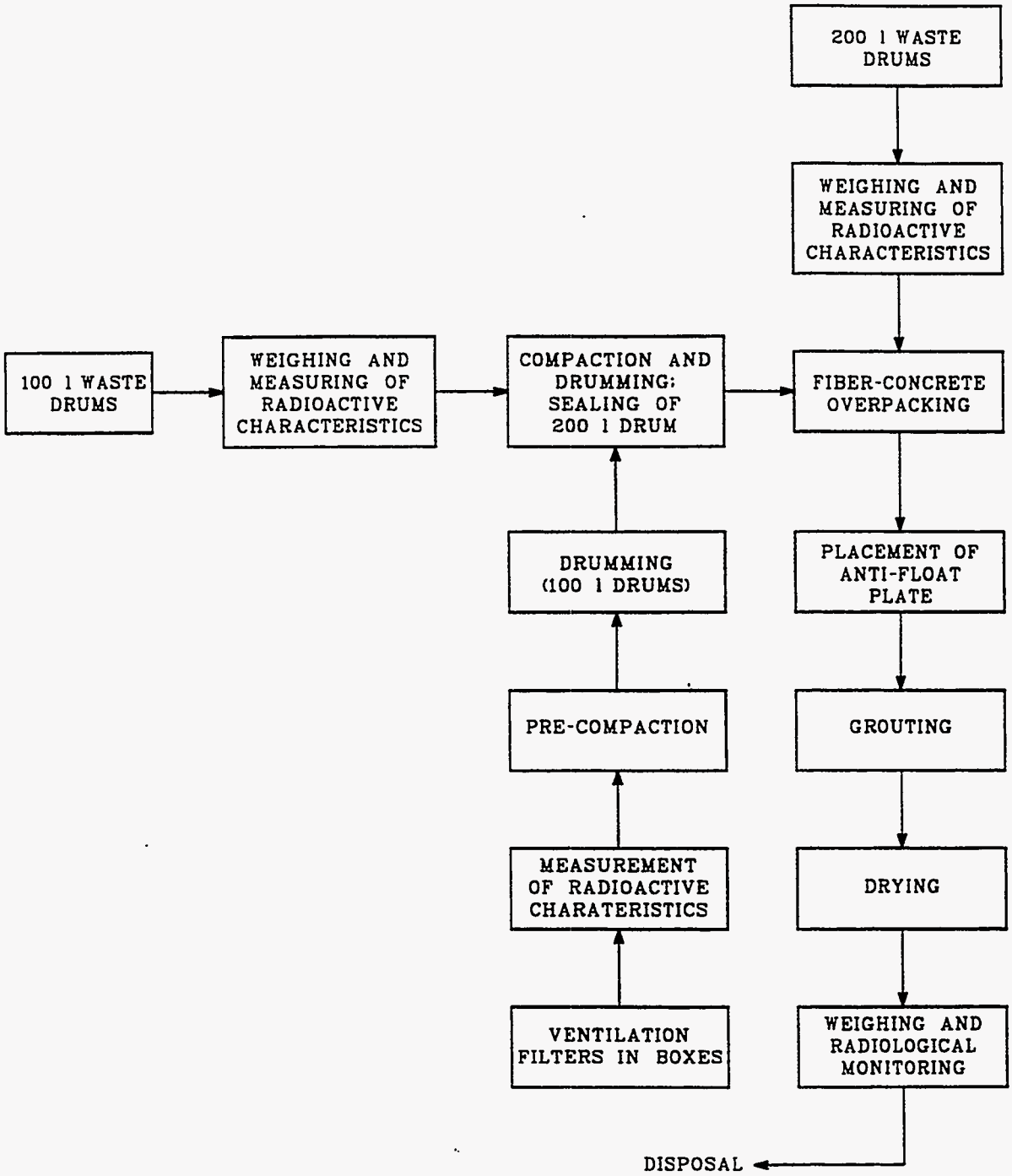
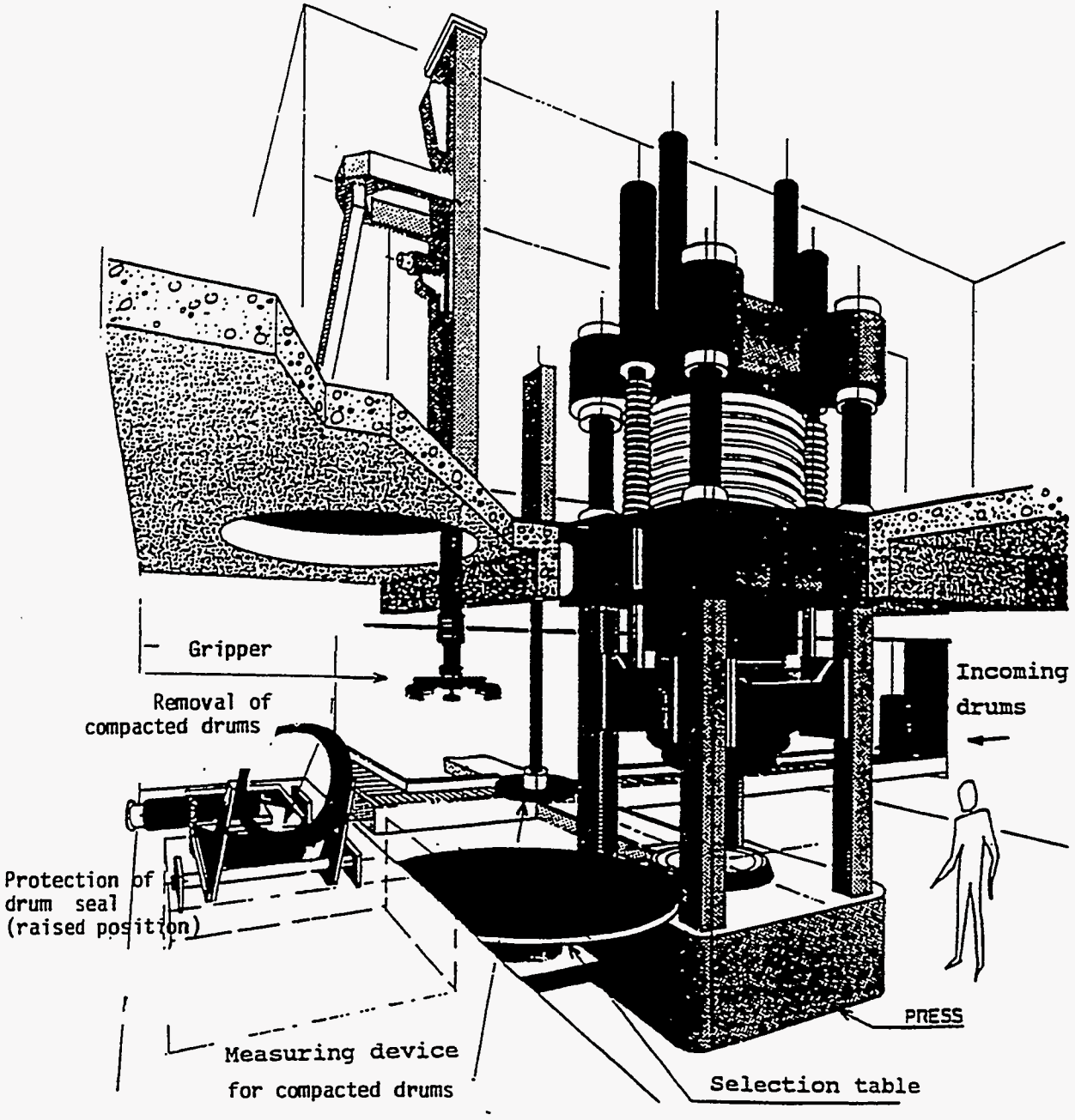


Figure 9. Conceptual design for a 100-l drum compaction unit



- Grouted plant waste characteristics

Fiber-reinforced concrete overpack

The fiber-reinforced concrete overpack, shown in Figure 10, is a poured concrete product made of CLC 45 cement and cast iron fibers. The overpack includes an anti-float plate made of a single poured section of the same fiber-reinforced concrete used to fabricate the overpack; the plate has an opening in the center to allow filler material to be injected into the overpack and a side opening that acts as a vent.

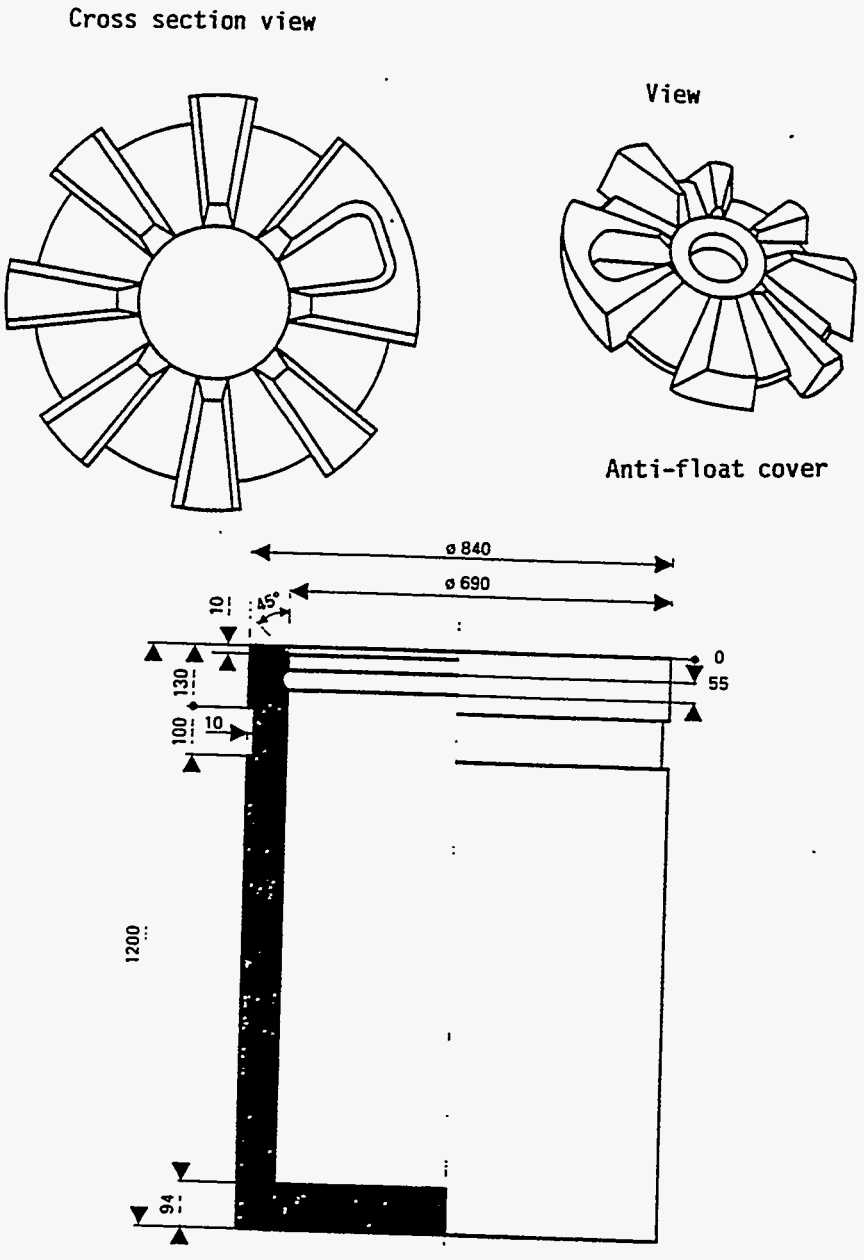
Plant waste

Plant waste generated by the UP2 and UP3 plants consists primarily of solid materials used for cleaning, for decontamination, and for maintenance operations; consumable packaging and shielding materials; and debris from cutting and dismantling operations.

The tables below summarize the principal characteristics of the containers used for plant waste before processing in the AD2 facility.

Drums: Carbon steel drums are used to contain solid waste such as paper, cardboard boxes, vinyl, gloves and shoe covers; scraps from cutting and dismantling operations, including debris, cuttings, and filings; discarded analytical equipment from ventilated laboratory benches and enclosures, such as glass and scientific instrumentation; and miscellaneous discarded mechanical equipment, including valves and pumps.

Figure 10. CBFC1 fiber-reinforced concrete overpack



Drum Size	Overall Dimensions	Useful Volume
100-l	ϕ 495 mm - H 765 mm	120 l
200-l	ϕ 600 mm - H 915 mm	225 l

Cardboard boxes: Ventilation filters with low contamination are packaged in cardboard boxes for transfer to the AD2 facility. The filters are bagged before packaging.

Type of Package	Overall Dimensions	Useful Volume
Cardboard Package	L 690 mm W 320 mm H 630 mm	130 l

Filler material

The annulus between the overpack walls and the waste container is filled with concrete the composition of which is identical to the fiber-reinforced concrete used to fabricate the overpack and the anti-float plate. The filler concrete is poured into the overpack by gravity; the overpack is vibrated during filling to ensure void-free filling.

Final grouted waste form

The principal characteristics of the final grouted plant waste are as follows:

- Average weight: 1,200 kg (or 2,650 lb)
- Average beta/gamma activity upon production of the final waste package: 0.1 Ci (or 3.7 GBq)
- Average gamma dose rate upon production of the final package:

. direct contact: 10 mRad/hr

. at 1 m: 1 mRad/hr

- Number of fiber-reinforced overpacks per MTU of reprocessed uranium: about 5.4.

2.4.3 Radioactivity Measurements Based on Standard Spectra

Individual containers of waste and groups of waste containers are labeled at the generating facility of the La Hague plants and are documented on a waste production sheet. The main information on the production sheet is as follows:

- type of waste;
- area of the facility where the waste originated;
- individual identification codes for each container of waste; and
- dose rate and unfixed surface contamination of each container of waste (information required for shipping).

A bar code label and the corresponding identification number are printed on each container of waste. Data from the waste production sheet are entered into the AD2 operating control system; when the bar code label of a given waste container is scanned into the system, it automatically generates a waste manifest that is used to track the waste during processing operations.

The waste tracking system also calculates the specific activity of the waste containers, using the following information:

- results of gamma and/or neutron radiation measurements and of weighing;
- information on each container transmitted to the AD2 facility by the waste generator, including:
  - container identification code;
  - the zone of origin of the waste, which establishes the following:
    . the distribution of beta-emitting radioelements;
    . the distribution of alpha-emitting radioelements;
    . the ratio of α activity/ß activity; and

. the chemical form of any plutonium contained in the waste;
- the geometric characteristics of the waste;
- information on the chemical form of the waste; and
- the presence of any shielding.

Computer algorithms are used to correlate the above information with either neutron or gamma dose rate measurements to determine the α and $\beta\gamma$ activity.

The standard spectra method used at La Hague to determine radioactivity concentrations was developed as part of a lengthy characterization and testing program undertaken in France. The program, which has been approved by ANDRA, the French waste management agency, identifies radioactivity spectra for standard waste types and establishes transfer functions between the dose rate of a given container of waste and its activity concentrations.

2.4.4 Planned Process Enhancements

Enhancements to the AD2 solid waste processing facility are currently under review, prompted by several years of operating experience and by recent changes in European regulations. The changes for each processing line of the facility are described below.

- Solid process waste processing

Solid process waste is packaged in the CAC asbestos-cement overpack. However, European regulations now prohibit the fabrication of materials containing asbestos. Fabrication of the CACs will therefore be stopped in the near future and a substitute will be needed. One concern in identifying a substitute for the CAC overpack was of course to minimize the impact of this change on the structure of the AD2 facility and on the facility's handling equipment. The new CBF-C2 fiber-reinforced concrete overpack was selected to replace the CAC overpack because it matches the external mechanical interfaces of the AD2 facility. The selection of the new overpack was also motivated by the objective of increasing waste management flexibility, since the new overpack has been licensed for near-surface disposal, although this will depend on the type and activity of the waste contents of the overpack. The latter option implies that waste

packaged in CBF-C2 overpacks must be sorted by activity in order to benefit from the cost savings associated with substantially reducing the volume of waste requiring deep geologic disposal.

- Solid plant waste processing

Operating experience from the solid plant waste processing line of the AD2 facility has also given rise to a review of potential process enhancements. In particular, experience has shown that the activity of plant waste is much lower than projected during the process design phase. Much of this waste could be processed by placing compacted drums in a 200-l drum and simply stabilizing them with grout rather than with fiber-reinforced CLC concrete. This modification alone will significantly reduce the volume of grouted plant waste, and it is simpler and more amenable to a wide range of grout formulations.

Plant waste with higher activity concentrations will continue to be immobilized in a fiber-reinforced concrete slurry because of the latter's radioactive containment properties.

2.5 CENTRALIZED ALPHA WASTE TREATMENT UNIT

2.5.1 Introduction

Alpha waste management is integral to Cogema's overall waste management program, which is based on volume reduction and on the reduction of transuranics contained in high-level waste. The implementation of this program created a new requirement at La Hague: removal of plutonium from metallic and plastic alpha waste to make it acceptable for near-surface disposal, as opposed to deep geologic disposal.

The process selected to decontaminate metal and plastic alpha waste also proved to be suitable for the treatment of ash from the incineration of alpha waste, performed at Marcoule, and a separate processing line was therefore included in the design to accommodate the incinerator ash. Both process lines are under construction in the R2 facility of the UP2-800 plant at La Hague, where the plutonium will be recovered and reprocessed.

2.5.2 Waste Type

Alpha waste from both Marcoule and La Hague will be processed at the La Hague treatment unit and will include the following types of waste:

- plutonium-rich metal waste consisting of:
  - empty PuO_2 containers,
  - incinerator ash bins,
  - depleted uranium slugs from the shredders used in the MOX fuel fabrication process,
  - molybdenum baskets from pellet sintering furnaces; and
  - miscellaneous stainless steel equipment;
- ash from the incineration of contaminated organic materials used in glove box shielding, such as latex gloves, neoprene, polyurethane sheeting, cotton swabs, cellulose, and packaging and sleeving made of PVC, polyethylene or polyurethane; and
- unincinerated plastic waste.

2.5.3 Process Principle

The solid alpha waste treatment process involves the removal of alpha-emitting contaminants, primarily plutonium, which adhere to the surface of the waste matrix in varying degrees, and to solubilize these elements.

Fixed plutonium in the waste and plutonium in incinerator ash is in the form of quadrivalent PuO_2 oxide, which is particularly resistant to dissolution by conventional processes. Dissolving the plutonium in a nitric solution alone is very weak thermodynamically, but can be achieved by using nitro-hydrochloric acid at boiling temperature, although this causes substantial corrosion to process equipment made of materials such as stainless steel, chromium, zirconium, and uranus 65, and it generates corrosive ions which are difficult to control. The preferred method is to bring the plutonium to the +V oxidation degree (PuO_2^+), then +VI (PuO_2^{2+}), which can be solubilized in a nitric solution with an electrochemical mediator. Series II silver was chosen to accomplish this. The AgII/Ag system is most effective as an electron carrier because of its high apparent normal potential and because of the more rapid electron exchange between the pair than for other systems, such as CeIV/CeIII.

The AgII oxidant is continuously regenerated on a platinum electrode by the passage of forced anodic current, which minimizes the amount of series I silver used.

In parallel with the plutonium solubilization reactions, the surface of the waste is leached by Ag II, causing radionuclides that have migrated internally to emerge and dissolve.

Silver is added to the solution in the form of silver nitrate. The reaction between the PuO_2 and AgII occurs very rapidly, with the rate of AgII generation governing the rate of PuO_2 dissolution.

2.5.4 Processing Operations

Because of the different pretreatments involved, the waste is treated in three separate lines at the centralized alpha waste treatment unit, each of which is adapted to a particular waste type. However, the process is identical in terms of operations. The three lines are:

- line A for incinerator ash,
- lines B and C for metallic and plastic waste.

The existing CEA prototypes were extrapolated to the maximum reasonable level for the design of the La Hague process lines, giving the following capacities:

- line A: 2 t/yr of incinerator ash with an average of 10 kg Pu/t (or 22 lb);
- lines B and C: the equivalent of 400 100-l drums per year per line.

Waste undergoes pretreatment operations prior to leaching in the centralized facility, as described in the following paragraphs.

2.5.5 Treatment of Incinerator Ash

Incinerator ash bins from Marcoule arrive at La Hague in casks. The ash is crushed before treatment to increase the leaching surface, thereby increasing the dissolution rate.

The ash is then treated to remove chlorine ions, which can be precipitated with the Ag ions added in the next stage of the process.

After these operations, the ash is oxidized. The waste produced by this treatment must be separated from the leaching solution, the latter being transferred to a plutonium extraction cycle by TBP in the R2 chemical separations facility by TBP.

2.5.6 Treatment of Metals and Plastic

The oxidation treatment for metals and plastic must be adapted to the chemical composition of the waste. Molybdenum, uranium, and stainless steel wastes all behave differently when exposed to AgII++. This type of waste is first sorted, then treated in separate batches.

In addition, it is sometimes necessary to add a preliminary mechanical treatment step to the process to increase the waste's leaching surface, thereby increasing the dissolution rate. Empty PuO_2 containers and incinerator ash bins are segmented before treatment, while plastic waste is shredded.

After this preliminary treatment stage, the waste is introduced into batches for leaching. The leachate is recycled to the plutonium extraction cycle in the R2 facility via an extraction cycle with TBP, while the waste is assayed for plutonium before transfer to the AD2 solid waste processing facility described in section 2.4 above.

2.5.7 Auxiliary Systems

Two auxiliary systems are installed. Solutions rich in plutonium, uranium, and other α emitters are transferred to the main extraction cycle of the UP2-800 plant at La Hague. These solutions sometime contain species that interfere with the main partitioning cycle, especially those produced by the treatment of incinerator ash containing dissolved silica. Before the solutions are transferred to the R2 extraction cycle, they undergo preliminary extraction in the centralized alpha waste treatment unit, which involves extraction, rinsing, re-extraction and simplified solvent treatment.

The substantial amount of silver nitrate required for treatment operations in the alpha waste treatment unit motivated the installation of a silver extraction unit for the raffinate from the extraction cycle.

2.5.8 Pre-operational Testing

The process to decontaminate solid alpha waste by leaching with electrically-generated Ag II was developed by the French Atomic Energy Commission (CEA). The process was applied to the treatment of alpha-contaminated solid waste generated at the CEA's Fontenay aux Roses site and to the recovery of plutonium from incinerator ash in the Prolixe and Elise facilities.

- Metal waste

Over 300 kg of metal waste heavily contaminated with α, ß, and γ emitters was decontaminated in the Prolixe facility and met ANDRA's acceptance criteria for near-surface disposal (α activity < 0.1 Ci/t after 300 years).

- Plastic waste

Experimental testing on wet oxidation of plastic waste is currently in progress. Tests have already shown that compounds which oxidize readily, such as cellulose, cannot be treated in this manner. These materials completely dissolve in solution, and the kinetics of oxidation are controlled by the very slow dissolution of the cellulose. However, decontamination of organic

waste other than cellulose is feasible, subject to the use of a high-efficiency electrolyzer and repetition of the wet oxidation operations.

- Incinerator ash

Tests performed on several kilograms of PuO_2-rich incinerator ash served to establish the process design bases and to define general operating procedures for a total plutonium recovery yield of 98% or more.

3. TREATMENT AND SOLIDIFICATION OF LOW-LEVEL WASTE AT MARCOULE

3.1 SOLID WASTE TREATMENT

Since plant operations began at the Marcoule site in the 1950s, waste has been collected in a wide variety of containers:

- 100-l to 5,000-l drums,
- cylindrical or parallelepipedic concrete overpacks,
- 5 m^3 boxes, and
- 7 to 20 m^3 capacity metal cans and receptacles for loose or drummed waste.

To make waste collection practices more consistent, Cogema launched a study the objective of which was to collect all waste generated at the Marcoule site in containers identical to those used at the La Hague site.

3.1.1 Waste Types

As a result of this study, the following waste containers were chosen for use at Marcoule:

- the CO drum for waste requiring stabilization;
- the CBFK overpack for waste to be shipped to a surface disposal facility;
- the CBFC2 overpack for waste which may potentially be shipped to a surface disposal facility; and
- the CV canister, identical to high-level vitrified waste canisters, for waste which may potentially be shipped to a surface disposal facility (1 CBFK can accommodate 9 CVs).

The waste will be sorted by activity ($\alpha\beta\gamma$) and by type to simplify processing and ensure compatibility with these containers. With respect to waste activity, three categories were established:

- waste to be stabilized,
- waste to be immobilized, and
- waste not acceptable for surface disposal.

With respect to waste type, waste will be sorted into low-level/medium-level and high-level as follows:

LLW/MLW: . compactible and combustible waste in 120-l drums,
. uncompactible waste in 213-l drums, and
. oversized waste in boxes;

HLW: . waste in La Calhène cans or other containers.

3.1.2 Processing Operations

The principal objective of solid waste processing is to reduce waste volumes for disposal and to dispose as much of it as possible in near-surface facilities.

- Low- and medium-level waste

Very low-level and medium-level waste will be routed to the TFA facility at Marcoule, where the following preliminary functions will be performed:

- radiation monitoring, spectrometry, and weighing;
- alpha assaying by active neutron counting;
- low-level 6γ measurements for containers the activity of which is close to the immobilization threshold and which must therefore be measured as accurately as possible.

Waste will then be processed by type and activity level as follows:

- 120-l drums of combustible waste will be processed in the TFA incinerator, producing a vitrifiable ash;
- compactible 6γ waste requiring stabilization will be compacted in a 3-dimensional press, which has three 100 T cylinders and an oversized compaction chamber, and placed in CBFKs for grouting (up to 100 compacted drums per CBFK);

- compactible α and $\beta\gamma$ waste requiring immobilization will be shipped to the AD2 facility at La Hague for compaction, since the TFA press is restricted to very low-level $\beta\gamma$ waste;
- uncompactible waste requiring stabilization will be grouted in the 213-l CO-type containers;
- 213-l drums of uncompactible waste requiring immobilization will be concreted in CBFK containers, which can hold up to 5 drums each; and
- oversized waste in boxes will be size-reduced in a cutting cell and compacted in the TFA press, if feasible, and placed in CBFK containers.

- High-level waste

High-level solid α waste will be routed to the TDA facility, while high-level solid $\alpha\beta\gamma$ waste will be routed to the HA facility.

TDA Facility: Solid α waste will be processed in this facility in one of two ways:

- waste which can be decontaminated will be segregated and decontaminated with Series II electrogenerated silver so that it can be processed as low-level alpha waste (see above);
- waste which cannot be decontaminated will be placed in 400-l drums and routed to the HA facility (see below) for immobilization in CBFC2 containers.

HA Facility: Solid $\beta\gamma$ and $\alpha\beta\gamma$ waste will be monitored for $\beta\gamma$ activity and assayed with a passive neutron counting method before processing in one of two ways:

- compactible waste will be compacted one-dimensionally in an 800-kg (or 1,764-lb) press and the compacted drums will be placed in CV containers;
- uncompactible waste will be placed in CBFC2 containers for surface or other disposal.

3.2 STEL-EVA LIQUID EFFLUENT TREATMENT FACILITY

3.2.1 Facility Description

Radioactive liquid effluent produced throughout the Marcoule site are collected in an underground network of radioactive drains which converge at the STEL liquid effluent treatment facility, where the following functions are performed:

- effluent receiving, sorting and storage;
- effluent decontamination and release; and
- solidification of by-product sludge in a bitumen media.

The STEL was constructed in 1958 and upgraded in 1990 with the start-up of the EVA evaporator.

3.2.2 Effluent Characteristics

- Activity

Effluents are sorted into three categories, based on their activity: low-level (LL), medium-level (ML) and high-level (HL), as shown in the table below.

Category	Beta/Gamma Activity	Alpha Activity
LL	$\beta\gamma$ $< 10^{-2}$ Ci/m^3 Cs^{137} $< 10^{-3}$ Ci/m^3 Sr^{90} $< 10^{-3}$ Ci/m^3	$\alpha < 10^{-5}$ Ci/m^3
ML	$10^{-2} < \beta\gamma < 1$ Ci/m^3	$10^{-5} < \alpha < 3 \times 10^{-2}$ Ci/m^3
HL	$1 < \beta\gamma < 50$ Ci/m^3	$10^{-5} < \alpha < 3 \times 10^{-2}$ Ci/m^3

In addition, there is a fourth category of effluents, special medium- and high-level effluent (SML, SHL), which cannot be processed in the EVA evaporator, either because they are already concentrated or because they contain undesirable elements. SML/SHL effluents are segregated and processed separately from the others.

- Chemical composition

The acidity of low-level and medium-level effluent ranges from 0.2 to 0.4 N, while the acidity of high-level effluent is around 1 N. The salt content of the effluent ranges from 5 to 25 g/l, with an average $NaNO_3$ content of 85%.

- Throughput

The STEL facility receives 80,000 m^3 (or 2.8 million ft^3) of effluent per year on average containing 200,000 Ci of $\beta\gamma$ and 900 Ci of α activity. Approximately 55,000 m^3 (or 1.9 million ft^3) of the effluent is low-level, 22,000 m^3 (or 780,000 ft^3) is medium- and high-level, and 3,000 m^3 (or 120,000 ft^3) is special medium- and high-level.

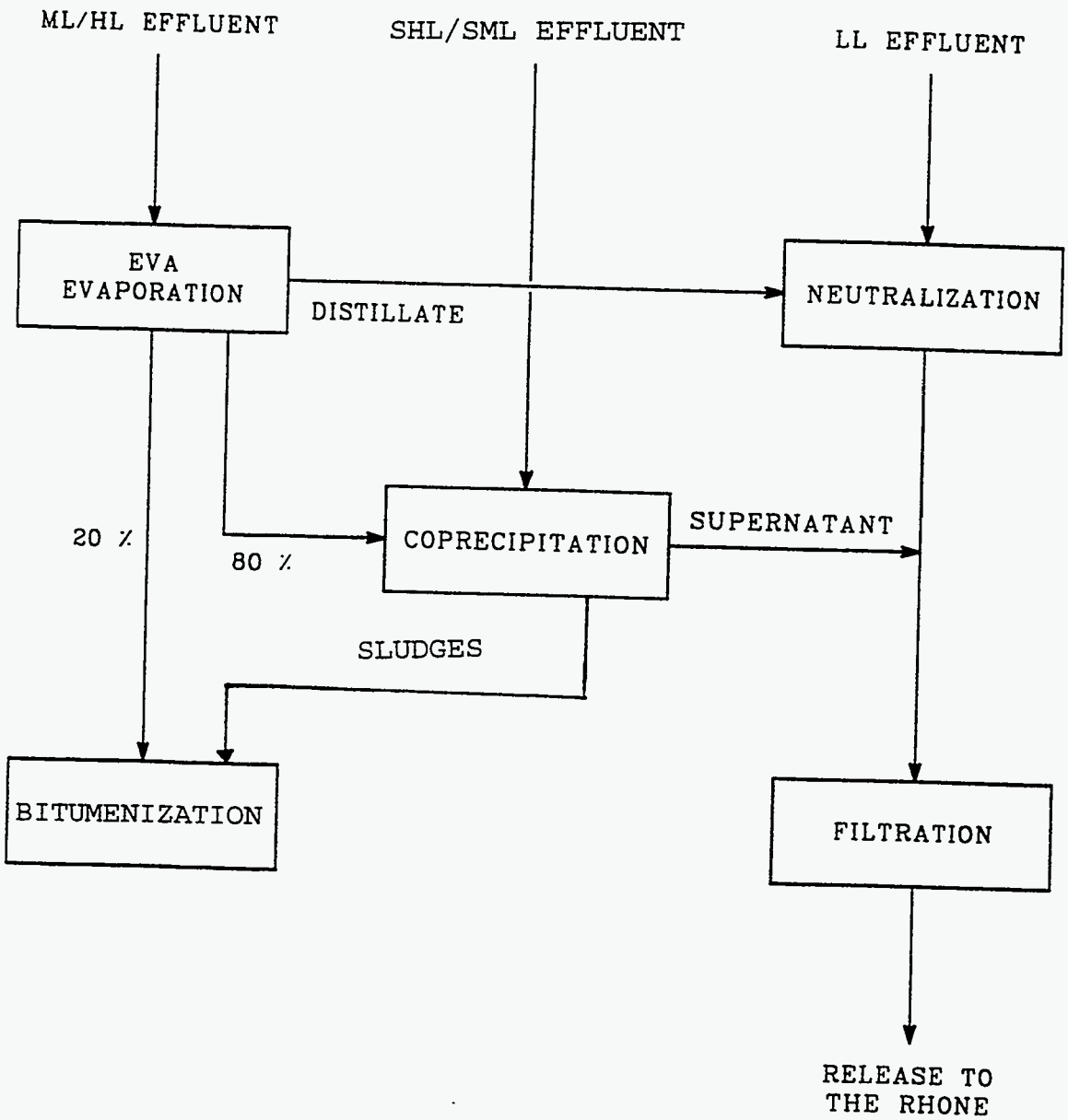
3.2.3 Process Principle

The principal process used in the STEL facility, as illustrated in Figure 11, is based on evaporation in an acid medium. About 90% of the medium- and high-level effluent is treated in this manner, while the special medium- and high-level (SML/SHL) effluent is treated directly by chemical coprecipitation.

Approximately 80% of the evaporator concentrates is neutralized and chemically treated. The remaining 20% of the concentrates, the activity of which exceeds 108 Ci/m^3 (or 113 GBq/ft^3), making it too active to be treated by coprecipitation, is routed directly to the bitumenization processing line with the sludge from chemical coprecipitation treatment.

Evaporator distillate and low-level effluent are neutralized as part of the overall process and are transferred with the supernatant exiting the coprecipitation treatment line to holding basins, where they are filtered to 25 μm and released to the Rhône River.

Figure 11. STEL-EVA effluent treatment concept



3.2.4 EVA Evaporation Process

- Process principle

The EVA evaporation unit, shown in Figure 12, consists of two identical, independent evaporation lines, which can operate concurrently or back each other up in an emergency. Each evaporation line comprises:

- a mechanically stirred 300 m^3- (or 10,600 ft^3-) effluent feed tank;
- an 8 m^3/hr- (or 3,520 gal/mn-) thermosiphon evaporator which operates by natural circulation at atmospheric pressure and includes a 3-m- (or 9-ft-, 10-in-) diam, 10-m- (or 32-ft, 10-in-) high column and a 1.5-m- (or 4-ft, 11-in-) diam, 5-m- (or 16-ft, 5-in-) high boiler;
- a condenser, which gravity-feeds a distillate neutralization tank;
- a evaporator concentrate receiving tank at the end of the evaporation cycle;
- a system to produce superheated water (4 bars at 136°C, or 58 PSI at 277°F) and a water cooler; and
- a 250 m^3- (or 66,000-gal-) tank which feeds evaporator concentrates to the bitumenization line.

- Processing operations

The evaporation cycle varies in direct relation to the salt concentrations in the effluent to be treated, with the objective of reaching a final salt concentration of 400 g/l and an activity lower than 450 Ci/m^3.

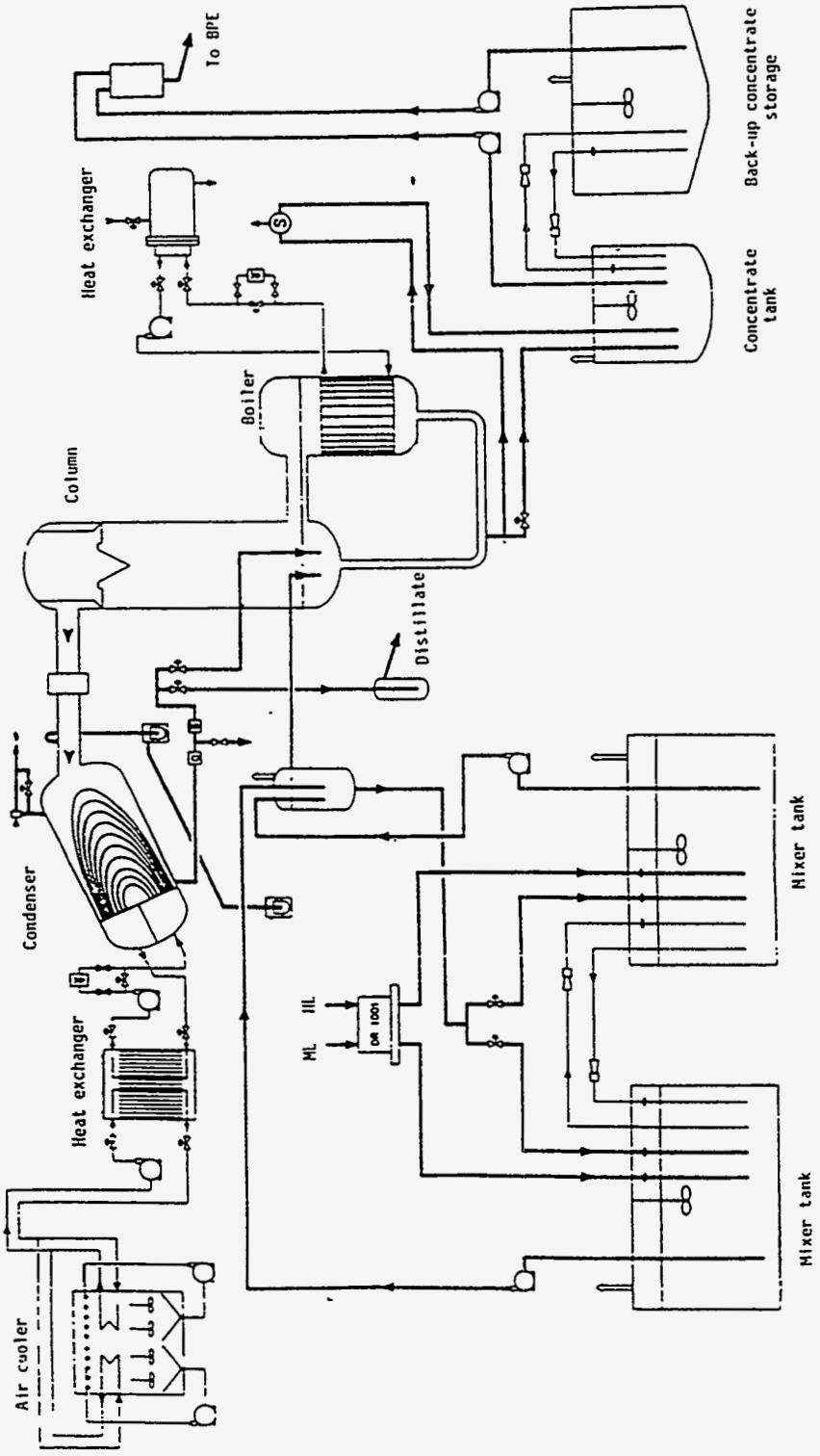
At the same time, the evaporation cycle is extended if the acidity of the concentrate exceeds 1 N. The addition of water to the evaporator directs the acid to the distillate by a salt effect.

- Process efficiency

Decontamination factor: DF $\simeq 10^4$

Concentration factor: The salt content of the effluent before treatment is about 5 to 25 g/l at 85% $NaNO_3$, while the salt content in the evaporator concentrates is 400 g/l, giving a CF of $\simeq$ 30 to 35.

Figure 12. EVA



3.2.5 Coprecipitation Treatment

- Process principle

Evaporator concentrates and special medium- and high-level effluents are decontaminated using a chemical process in which most of the radioelements they contain attach to a precipitate which separates them from the concentrates and effluent. The batch coprecipitation treatment is performed in mechanically stirred tanks.

Reagents to be added to the process are determined based on automated gamma spectrometry analysis of concentrate and effluent samples. The automated system is also used to gauge the efficiency of the process by monitoring the decontaminated supernatant produced by this chemical treatment. In particular, three different reagents are added in succession in an alkaline medium for the special treatment requirements of the following radioelements:

- ruthenium, the most difficult radioelement to decontaminate because of its complex anionic, cationic, or non-ionic forms, is coprecipitated by a mixture of iron and copper hydroxides;
- strontium is separated by a barium sulfate precipitate; and
- cesium is decontaminated with a colloidal solution of a preformed precipitate of nickel ferrocyanide.

These special reagents are also effective for the separation of zirconium, niobium, cobalt and alpha emitters. The precipitate from the insolubilization process are flocculated and decanted following chemical treatment. The supernatant is monitored to verify the effectiveness of the treatment and is routed to holding basins before release, while the concentrated precipitate is routed to the bitumenization process.

- Process efficiency

DF ß $\simeq$ 20

DF $\alpha \simeq$ 400

3.2.6 Bitumenization

The chemical compounds and radioelements contained in the effluent treatment sludge are solidified in a bitumen media to form a solid waste package providing safe and lasting containment for transportation, storage and disposal.

- Process principle

The chemical treatment sludge and the evaporator concentrates are stored in two mechanically stirred feed tanks, where they are monitored before being fed alternately to separate bitumenization lines in the STEL facility. The sludge is concentrated on a diatomaceous-coated filter operating under a vacuum.

The concentrates are bitumenized with a four-screw extruder. Water is continuously evaporated from the concentrates by the heat from the extruder, while the screws produce a homogeneous mixture of bitumen and dry extract. Depending on the activity level, the re-condensed water is routed either to the chemical coprecipitation process or, if it is very low-level, to the effluent monitoring and neutralization unit. The hot bitumen mixture is poured into 217-l carbon steel, chrome-lined drums. The drums are placed on two turntables and filled through a Y-shaped pour spout with two valves to ensure an uninterrupted drum fill. The drums are filled to 90% capacity in three stages, and are allowed to cool naturally between each stage. The 160°C (or 320°F) pour temperature of the bitumen mixture is monitored continuously with an infrared camera.

The drums of solidified waste are handled by a semi-automated traveling crane and transferred to a cool-down area in the drum filling unit, where they are cooled to a core temperature which is below the softening point of the solidified waste. The drums are then transferred to storage vaults, where they are weighed to record density and verify in/out production figures and where a crimped lid is placed on them, their gamma dose rate is measured, and they are labelled.

The storage vaults have a capacity of 3,000 to 7,000 drums. The drums are stacked four deep in the vaults using a self-propelled shielded transporter controlled from the cab by an operator.

- Process efficiency

The solidified waste package produced at the STEL facility is homogeneous and contains about 60% bitumen and 40% dry extract with less than 5% water, which complies with guidelines and ensures long-term integrity.

The solidification capacity of the facility for evaporator concentrates is on the order of 700 m^3 (or 24,700 ft^3) of concentrates per year. The overall decontamination factors for the chemical coprecipitation process and the evaporator concentrate bitumenization process are:

DF ß = 300

DF α = 2,000

3.3 ALPHA WASTE INCINERATION AT MARCOULE

3.3.1 Incinerator Description

In 1972, after two years of inactive testing, a 1 kg/hr- (or 2.2 lb/hr-) incinerator began processing waste containing fissile materials at Marcoule (see Figure 13). The average composition of the waste to be incinerated is as follows:

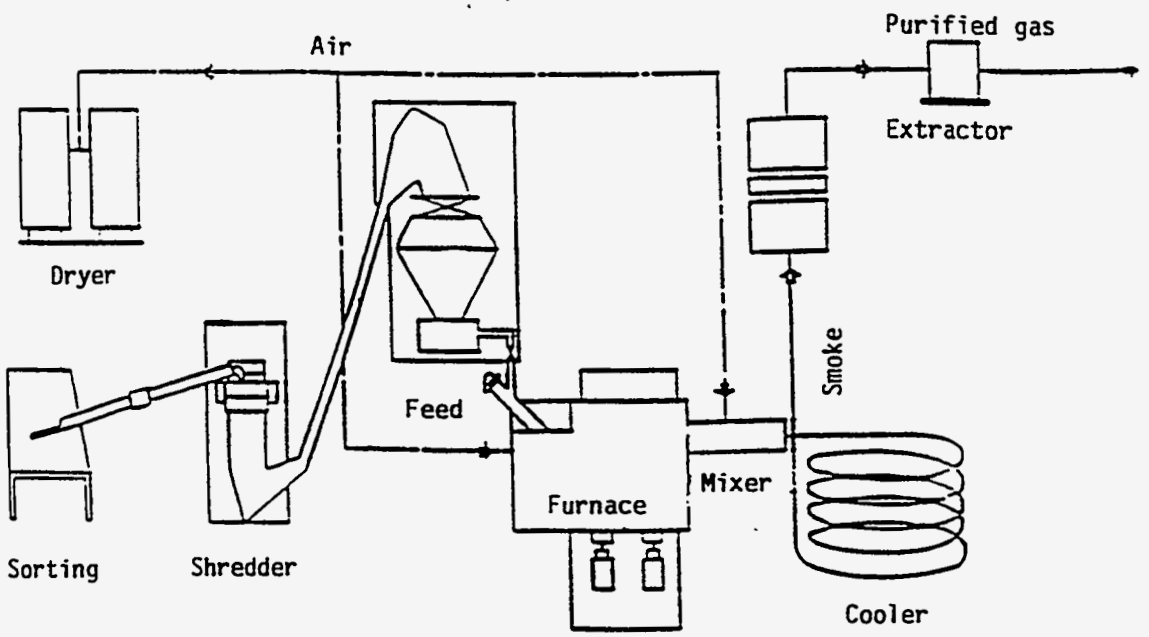
- rubber 40%
- PVC 40%
- cellulose 10%

After careful sorting by the waste generator, combustible waste, consisting primarily of welded glove box sleeves, PVC and cellulose, is placed in drums and transferred to the incinerator unit. Waste is emptied from the drums in a glove box and is passed in front of a metal detector that operates by electrical field deformation. The operator manually segregates metal components and oversized objects, such as sheets of polyethylene, which might impede waste shredder operations.

The rotary shredder has four-bladed cutters. Shredding operations are conducted in a nitrogen atmosphere. Pieces larger than 5 mm are collected on a screen underneath the cutters and recycled to the shredder. The cutter blades are changed an average of once a year.

The shredded waste falls into a bin which is transferred to the incinerator feed hopper in an adjacent glove box. The waste is continuously fed to the incinerator through a chute at the bottom of the hopper, assisted by a worm screw that pushes the waste into the incinerator feed tube. A continuous mixing system was installed in the hopper to prevent the formation of a vault in the waste feed. In the event of fire in the hopper, a fire detection system stops the feeding process, closes the valve to the incinerator and extinguishes the fire.

Figure 13. Marcoule alpha waste incinerator



The incinerator itself performs two essential functions: combustion of waste and combustion of incinerator off-gas. The incinerator is made of refractory brick which acts both as a heat shield and as biological shielding, and is housed in a seal-welded steel enclosure. Heat is supplied by ten electrical resistance-heated elements made of Super-Kanthal which are contained in vertical sleeves. The ends of the heating elements and their electrical connections are located in sealed glove boxes with nuclear ventilation which are attached to the incinerator glove box and which can be easily removed.

Waste is fed by gravity through the incinerator feed tube at the top of the incinerator inlet and 300°C (or 572°F) combustion air is injected through a horizontal flue.

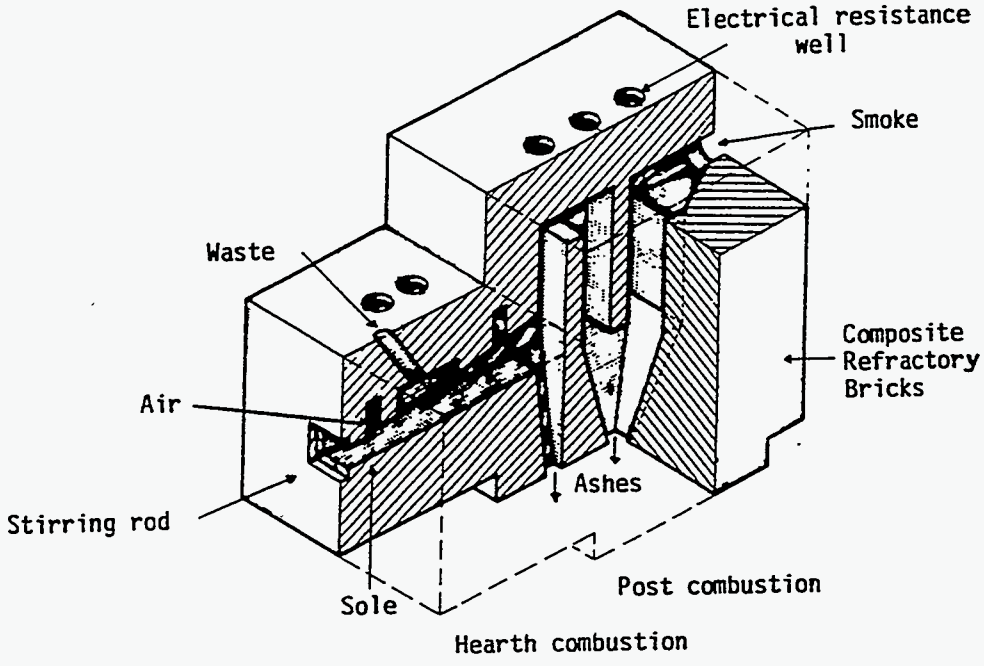
As illustrated in Figure 14, the incinerator has two sections. Waste is incinerated at 700°C (or 1292°F) in the first section, which consists of a arched chamber penetrated by four refractory steel sleeves housing the electrical heating elements. The vertical incinerator feed tube, which is inside a water sleeve, empties into this chamber, as does the horizontal flue for the combustion air. A trap door at the inlet to the first section of the incinerator provides access to a refractory steel poker used to push the ash to the bottom of the hearth, where it falls into a refractory bin.

Combustion off-gas is burned in the second section of the incinerator at a temperature of 1,100°C (or 2012°F). This section consists of three vertical flues, each containing electrical heating elements, arranged in a baffle formation. One ash bin is at the bottom of the first flue, and the two other flues share a second ash bin.

The ash is collected from the bins and placed in 3-l metal boxes for storage prior to chemical treatment. The ash is removed from the bin through a sealed glove box connected to the incinerator unit.

Gases produced in the post-combustion chamber are first cooled to 300°C (or 572°F) by mixing them with fresh, dry air, and are then cooled to 60°C (or 15.6°F) by passing them through a serpentine heat exchanger whose mangle is fed with borated water.

Figure 14. Incinerator concept



The cooled gases are then filtered twice, first through a primary filter made of fireproof paper to capture dust and soot, then through a flash wall to a high-efficiency fiberglass filter. The gases are exhausted from the facility by a roots fan, which is also used to maintain low pressure in the incinerator.

3.3.2 Results of Operations

The Marcoule alpha waste incinerator achieves volume reduction factors in the range of 20 to 40, depending on the type of waste.

If the waste is properly sorted manually, the waste shredder and incinerator feed system are relatively trouble-free under normal operating conditions, which is also the case for the incinerator itself.

Table 1 provides the distribution of incinerator ash throughout the system, while Table 2 provides the plutonium balance for the unit. The difference in in/out balances are due to the inaccuracy of certain measurements used to determine plutonium activity.

Table 1. Distribution of ash in weight %

Primary Combustion Ash Bin	92.5
Secondary Combustion Ash Bin	2.1
Cooling Diffuser	0.5
Serpentine Heat Exchanger	0.4
Filters	1.5
Miscellaneous deposits	2.0

Table 2. Plutonium balance in weight %

Incoming -	Plutonium in Waste	100
Outgoing -	Plutonium in Ash	81.5
	Plutonium on Filters	1.5
	Plutonium in Liquid Waste	1.7
	Total Outgoing Plutonium	84.7
Difference		15.3

Ash analysis:

- Lost in combustion (1,100°C) 12%
- Plutonium 3%
- SiO_2 + CaO 45%
- Miscellaneous metals (oxides) 22%
- Cl^- ion 12%

Some problems were experienced with waste with a high content of rubber, which produced carbon and tar during combustion that clogged the filters.

The most significant difficulties occurred in the gas cooling system and were due to the presence of chlorides. The waste contains metals such as Zn, Mo, Fe, Cu, lead and the like, which release gaseous chlorides during combustion when attacked by HCl. These compounds can form deposits at the tail end of the process in the gas cooling system. Compounds containing Fe and Zn are the most prevalent. Operating experience has shown that the amount of fouling by deposits of such compounds was proportional to the heat of the combustion area. It is therefore recommended that the furnace be kept at a temperature ranging from 650°C (or 1202°F) to 700°C (or 1292°F).

4. NEW PROCESS DEVELOPMENT

In this section, the solvent mineralization process under development for commercial use by Cogema at its La Hague plants will be described.

4.1 SOLVENT MINERALIZATION PROCESS

4.1.1 Effluent to be Mineralized

- Origin

The solvents used in the extraction cycles of the UP2-800 and UP3 plants at La Hague are regenerated in the organic effluent treatment unit, or TEO, installed in the R2 facility of the UP2-800 plant and in the T3 facility of the UP3 plant. The solvent is regenerated by separating it into three principal phases:

- TPH diluent, which is recycled to the process;
- 80% TBP for the solvent adjustments in the process; and
- a small volume of organic effluent containing most of the alpha, beta, and gamma emitters and the solvent decay products.

The organic effluent is currently transferred to a storage tank in the STE3 facility, where it will remain until the storage facilities for MDSA solvent mineralization facility are operational.

- Production

The TEO of the UP3 plant is in operation and generates approximately 12 m^3 (or 424 ft^3) of organic effluent per year. Some 70 m^3 (or 2,472 ft^3) of effluent has been produced to date. The total volume of effluent generated in the TEO units of both the UP2-800 and the UP3 plants will reach approximately will 250 m^3 (or 8,800 ft^3) by the year 2000.

- Characteristics

  The organic effluent has the following average concentrations by volume:

- TBP ≃ 90% (including ~ 0.5% of TBP decay products)
- TPH ≃ 10%

  Other solvents which may also be mineralized include:

- recycled TPH diluent;
- oils from the UP3, UP2-800 and UP2-400 plants; and
- organic phases from the chemical coprecipitation and bitumenization sections of the STE3 effluent treatment facility.

- Effluent activity

  The ßγ and α activity of the organic effluent are as follows:

- average ßγ activity of UP3 effluent ≃ 5 x 10^{-2}Ci/m^3 (or 52 MBq/ft^3); and
- average total α activity of UP3 effluent ≃ 2 x 10^{-4}Ci/m^3 (or 0.21 MBq/ft^3).

The ßγ and α activity of the recycled TPH diluent, oils, and organic phases are very low, and less than the activity of the organic effluent.

4.1.2 Pyrolab Pilot Pyrolysis Unit

Cogema acquired a license from NUKEM for a pyrolysis process and contracted with SGN to construct a pilot pyrolysis unit to perfect the process for commercial use at the La Hague plant (see Figure 15).

The 3 kg/hr TBP pyrolysis pilot unit, located in the Beaumont Research Center near La Hague, entered service in October 1991, and development testing was conducted from that time through the end of December 1992.

- Process principle

TBP in organic effluent from the TEOs at La Hague is thermochemically decomposed with a neutralizing agent (lime or magnesia) in the pyrolysis process, producing a mineral product which can be solidified in cement.

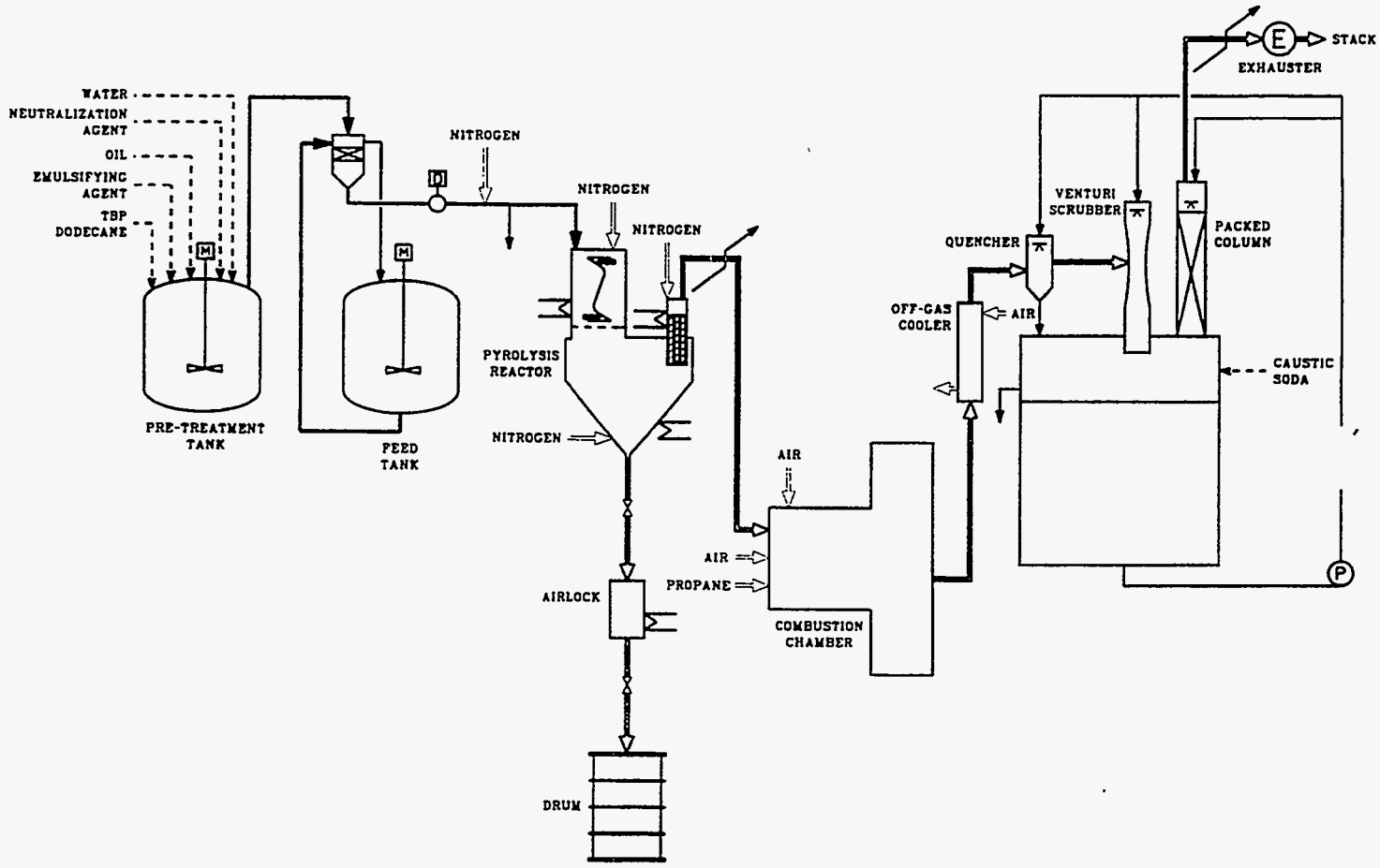
The slurry of organic products and milk of lime (or magnesia) is fed to the pyrolysis machine from the feed tank at a controlled rate. The slurry thermochemically decomposes in the pyrolysis reactor, which is stirred and filled with a layer of marbles. The TBP decomposes in butene, butanol, and phosphoric acid at temperatures greater than 350°C (or 660°F). The phosphoric acid reacts with the neutralizing agent which coats the surface of the marbles, producing calcium or magnesium phosphate ash. The TPH diluent, oil, and water in the feed evaporate.

The ash produced by pyrolysis reactor settles at the bottom of the pyrolysis vessel, where it is removed through a trap door beneath the vessel.

Off-gas from pyrolysis is filtered through vents at the top of the pyrolysis vessel and is propelled into a combustion chamber, where it is burned at around 900°C (or 1650°F), releasing only carbon dioxide, nitrogen, oxygen, and steam to the environment. Before release, the trapped combustion gases are cooled, rinsed, and filtered with the following equipment:

- a quencher to cool the gas,
- a venturi scrubber, and
- a packed filtration column.

Figure 15. Process flow diagram of the Pyrolab Pilot



- Pilot unit description

The pyrolysis pilot unit performs the following functions:

- slurry preparation and feeding;
- pyrolysis of slurry;
- separation of ash and gases and collection of ash;
- combustion of off-gas from pyrolysis; and
- combustion off-gas cooling, rinsing, and filtration before release to the environment.

Slurry preparation andf feeding

The reactor is fed continuously from two feed tanks:

- a mechanically stirred slurry preparation tank; and
- a mechanically stirred feed tank.

The slurry is prepared in batches sufficient for 48 hours of operation.

Pyrolysis of slurry and ash/gas separation

The pyrolysis vessel is the principal component of the solvent mineralization pilot unit. It comprises:

- a high-temperature, mechanically stirred cylindrical reactor heated with coils and filled with marbles in which the thermochemical reaction occurs;
- a funnel-shaped tank which separates the ash from pyrolytic off-gas;
- a filtration chamber formed by a series of back-flushable candle filters; and
- a trap door at the funnel outlet to transfer ash into a drum periodically without interfering with the pyrolysis operation.

Combustion of pyrolytic gases

The pyrolytic off-gas is around 400°C to 500°C (or 750°F to 930°F) when it enters the propane-fired burner, where it is heated to the ignition point. Additional gas combustion occurs in the combustion chamber, which has three main sections:

- a cylindrical chamber including both the burner and the combustion chamber;
- a vertical post-combustion chamber in the form of a parallelepiped; and
- a bundle of gas/air cooling coils.

- Test program

Purpose of tests

The principal objectives of the test program for the Pyrolab pilot pyrolysis unit were the following:

- to establish operating parameters for safe and continuous operation of the pyrolysis process;
- to validate operating conditions and operating interfaces through long-term testing; and
- to qualify and optimize the technological aspects of the process.

Principal test parameters

The principal parameters tested were the following:

- the wall temperature of the pyrolysis reactor;
- the type of neutralizing agent to be used;
- the specific composition of the TBP/TPH/oil organic phase;
- the type of marbles to be used; and
- the slurry injection method.

Principal operating parameters tested

The principal operating conditions and operating ranges validated on the pilot were as follows:

Reactor wall temperature: An increase in the reactor wall temperature improves the kinetics of pyrolysis and the quality of the ash. A reactor wall temperature of $\geq$ 550°C (or $\geq$ 1022°F) was selected for the pyrolysis process.

Neutralizer: Long-term tests conducted with both lime and magnesia under identical operating conditions yielded favorable results:

- homogeneous, fluid slurry;
- proper operation of pyrolysis machine; and
- cement-solidifiable ash.

Organic phase composition: The pyrolysis machine operated satisfactorily for solvents with a TBP concentration in the range of 70% to 100% by volume. Solvent containing up to 10% oil by volume can be pyrolyzed.

Reactor technology: Long-term testing was performed to validate the selection of the marbles and the method of injecting the slurry into the reactor.

4.1.3 MDSB Solvent Mineralization Facility

The MDSB solvent mineralization facility currently in the design phase will process organic waste generated primarily by the UP3 and UP2-800 plants and solidify residual organic effluent as part of the overall process. The facility will used the pyrolysis process for effluent mineralization to produce ash which can be incorporated into a cement medium.

- Treatment capacity

The facility will feature of 3 kg/hr- (or 6.6 lb/hr-) TBP pyrolysis line, which is equivalent to the capacity of the Pyrolab pilot pyrolysis unit.

- Processing operations

The principal process functions to be performed in the MDSB facility are as follows:

- effluent removal from storage tanks;
- slurry preparation and feeding;
- slurry pyrolysis;
- incineration of pyrolysis off-gas;
- cooling, rinsing and filtration of combustion gases; and
- cement-solidification of ash.

The first and last of the above functions are described in the following paragraphs; the other functions have already been described in the section on the Pyrolab pilot pyrolysis unit (section 4.1.2).

Effluent removal from storage tanks

The effluent to be processed is transferred to the feed make-up tank of the MDSB facility in large enough batches to produce two drums of waste. The tank is stirred and then sampled to determine the chemical and radiological composition of the effluent to be treated and of the final waste package.

Cement solidification of ash

The ash is collected and cooled in a vibrating hopper in an amount sufficient to make two 223-l drums. The ash is mixed with water, cement and a fluidizer in a high-efficiency mixer operating in batch mode to produce a homogenous cement-solidified waste form. The cemented ash is poured into a standard 223-l drum licensed for disposal in a near-surface facility.