

IAEA-TECDOC-1527

*Application of  
Thermal Technologies for  
Processing of Radioactive Waste*



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International Atomic Energy Agency

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## FOREWORD

Large quantities of radioactive waste, with varying characteristics, are generated from the operation and maintenance of nuclear power plants, the nuclear fuel cycle facilities, research laboratories and medical facilities. These wastes should be treated and conditioned into a form acceptable for safe storage and disposal.

There are increasing demands for further improvements in efficiency and safety of waste treatment, conditioning and disposal methods. This has stimulated efforts to develop new processes or utilize existing but improved conventional waste processing technologies. Thermal technologies have attracted significant attention and development as they provide advantages regarding stabilization of the waste form and high volume reduction.

This publication can be used most effectively as an initial cutting tool to identify whether any given technology will best serve the local waste management strategy in terms of the waste generated, the technical complexity, the available economic resources, the environmental impact considerations, and the end product (output) of the technology. If multiple thermal technologies are being actively considered, this publication should be instrumental in comparing the technologies and assisting the user to reach an informed decision based on local needs, economics and priorities.

Many IAEA publications discuss various waste treatment and conditioning methods with varying levels of detail on specific thermal technologies. However, there is no IAEA publication focusing specifically on thermal technologies as a group. This publication goes beyond previous work by addressing the applicability of each technology to nuclear programs of specific relative size, and by addressing thermal technologies for processing solid, liquid, organic and inorganic radioactive waste streams.

The IAEA wishes to express its appreciation to all those individuals that took part in the preparation and publication of this report. Particular acknowledgement is due to J. Deckers and L. Morton who participated in the entire report development process, including the Consultants Meeting and the Technical Meeting. The officers at IAEA responsible for initiating and finalizing the report were V. Efremenkov and J.J. Kelly from the Division of Nuclear Fuel Cycle and Waste Technology.

### *EDITORIAL NOTE*

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## SUMMARY

### 1. BRIEF STATEMENT OF NEED FOR PUBLICATION

It is important for Member States to adopt a mix of radioactive waste processing technologies which is optimally suited to the country-specific types and quantities of wastes generated. Increasing demands for enhanced efficiency and safety of waste processing technologies has focused attention on thermal technologies, as they provide advantages regarding stabilization of the output waste form and high volume reduction efficiencies.

However, there are other key factors which influence the selection of processing technologies, such as economics, disposal site availability, regulatory and social considerations, and environmental impact. Any single or combination of these non-technical factors may strongly promote, inhibit, or rule out the selection of one or more thermal technologies. This publication examines each thermal processing technology by offering a broad perspective of the technical and non-technical selection influencing factors.

### 2. APPROACH

This publication discusses the primary technical and non-technical factors which influence technology selection. It also suggests technical and operational criteria which should be included in the selection process. Each thermal processing technology is then examined in terms of its advantages, limitations and operational experience, as well as the potential impact of the non-technical selection factors. This approach recognizes that thermal technology selection is highly dependent on the overall size (waste generating capacity) of the national program and the intended application of the technology, as well as the non-technical influencing factors.

### 3. PRIMARY NON-TECHNICAL FACTORS INFLUENCING TECHNOLOGY SELECTION

**Economic considerations** – Most thermal technologies are very expensive to procure, install and operate. For countries with very small nuclear programs and small waste generating capacities, most thermal processes are not economically feasible.

**Availability of disposal site** – An available repository with a large capacity and low disposal fees is a disincentive to investment in most thermal technologies. In contrast, where disposal capacity is limited or not available, or where disposal fees are high, the enhanced efficiency of thermal processing technologies makes them a more attractive option.

**Regulatory and social considerations** – Regulatory and national policy issues, as well as public perception, may either preclude or mandate the use of specific processing methods.

**Environmental considerations** – Many thermal processes require gaseous effluent treatment systems for environmental protection. The complexity and cost of such systems can strongly influence the selection of thermal technologies.

### 4. INCLUDED THERMAL TECHNOLOGIES

The experts who participated in the development of this publication reviewed all of the thermal pre-treatment, treatment and conditioning technologies known to be deployed at nuclear power plants, nuclear fuel cycle facilities, and centralized radioactive waste

processing facilities around the world. In so doing, the authors were not constrained by differentiating between operational and decommissioning activities, although some technologies clearly are more relevant to one particular phase of the nuclear life cycle. The listing was then narrowed to focus on those thermal technologies which have been demonstrated to be proven, routinely used technologies, with only brief mention given to promising but infrequently used technologies. The net result is a comprehensive review and comparison of those thermal technologies which are most likely to be evaluated and adopted as mainstream technologies within a national waste processing strategy.

Brief descriptions of thermal technologies are provided to differentiate among the technical aspects. Also included are discussions of the advantages, limitations, operational experience, and other significant technology selection considerations, such as non-technical selection factors. The included technologies are:

- |                                 |                            |
|---------------------------------|----------------------------|
| — Calcination                   | — Thermochemical treatment |
| — Wet combustion                | — Metal melting            |
| — High temperature incineration | — Plasma                   |
| — Incineration                  | — Synroc                   |
| — Molten salt oxidation         | — Vitrification            |
| — Pyrolysis                     |                            |

## 5. GENERAL CONCLUSION

This publication is a review of the most commonly used thermal processing technologies, and it examines the key factors influencing the selection of thermal technologies as part of a national waste management strategy. Accordingly, the structure and content of this publication is intended to assist decision-makers, regulators, and those charged with developing such strategies to identify and compare thermal technologies for possible inclusion in the mix of available, country-specific waste management processes.

This publication can be used most effectively as an initial cutting tool to identify whether any given technology will best serve the local waste management strategy in terms of the waste generated, technical complexity, available economic resources, environmental impact considerations, and end product (output) of the technology. If multiple thermal technologies are being actively considered, this publication should be instrumental in comparing the technologies and assisting the user to reach an informed decision based on local needs, economics and priorities. A detailed set of conclusions is provided in Section 7.

# 1. INTRODUCTION

## 1.1. BACKGROUND

Large quantities of radioactive waste, with varying characteristics, are generated from the operation and maintenance of nuclear power plants, nuclear fuel cycle facilities, research laboratories, and medical facilities. These wastes should be treated and conditioned into a form acceptable for safe storage and disposal.

There are increasing demands for further improvements in efficiency and safety of waste processing. This has stimulated efforts to develop new processes or utilize existing but improved conventional waste processing technologies.

There are many reports previously published by the IAEA which discuss radioactive waste management and processing technologies, such as references [1-5]. A more recent report focuses exclusively on the management and processing of organic radioactive waste [6]. This TECDOC expands on those publications by focusing on thermal technologies for processing solid, liquid, organic and inorganic radioactive waste streams. This publication also goes beyond previous work on thermal processes by addressing the applicability of each technology to national or regional nuclear programs of specific relative size (major advanced programs, small-to-medium programs, and emerging programs with other nuclear applications). The advantages, limitations and operational experience of various thermal technologies are also explained.

## 1.2. OBJECTIVES

The primary objective of this publication is to provide an overview of the various thermal technologies and their applicability to various solid and liquid, organic and inorganic radioactive waste streams.

The target audience for this publication is those individuals employed by regulatory or governmental agencies who may be involved in permitting, licensing or policy for the recommended thermal technologies. The target audience also includes persons — typically middle managers, such as technical managers — who are seeking information about thermal technologies to make informed decisions about — and possibly recommend to higher level management — thermal technologies as a solution to various radioactive waste management challenges. Proper selection and evaluation of various thermal processes for application in a Member State are important components of an overall waste management strategy.

## 1.3. SCOPE

Thermal technologies covered by this publication are those processes which:

- by the assistance of heat, break down organic components of the wastes, producing end products which are inorganic, non-flammable, chemically inert, and much more homogeneous than the initial waste;
- destroy organic components of the waste while melting its inorganic components by reaching and exceeding their melting temperatures; or
- Involve the assistance or application of heat at temperatures in excess of 600° C.

Other technologies exist for treatment of radioactive wastes but failed to meet the above criteria for inclusion in this report, such as wet oxidation and melt densification. Those technologies are described in References [6, 7].

Finally, the publication focuses on those thermal technologies which are in use in one or more Member States and have been demonstrated to be proven, routinely used technologies. Where a technology is emerging and appears promising (e.g. Synroc), it may have been included but only briefly. Those technologies which are strictly research-based and have not demonstrated commercial viability are not included.

#### 1.4. STRUCTURE OF THE PUBLICATION

The technical content of this publication is presented in Sections 3 to 6. Section 2 provides a brief summary of the key considerations and conclusions.

Section 3 describes the considerations for choosing any given thermal technology over a non-thermal option. It further includes considerations for choosing a specific thermal technology among the many available.

Sections 4 through 6 provide detailed descriptions of specific technologies, their advantages, limitations and relevant operational experience. For the purposes of this report, the thermal technologies were categorized as follows (see Reference [8] for formal definitions on treatment and conditioning):

- *Pre-treatment processes*: processes whose end product typically requires further treatment; included in this category are: pyrolysis, steam reforming, calcinations, sintering, thermochemical treatment, and molten salt oxidation. Those technologies are described in Section 3.
- *Treatment processes*: processes which change the characteristics of the waste and may result in an end product which is, in itself, an appropriate waste form for disposition, such as incineration. Those technologies are described in Section 4.
- *Conditioning processes*: processes which result in an end product which is in itself a waste package suitable for handling, transport, storage and/or disposal. Vitrification, melting and plasma arc technologies are included in this category. Those technologies are described in Section 5.

The conclusions of the report are set out in Section 6. A brief Appendix captures some important lessons learned related to thermal technologies and technology selection.

#### 1.5. KEY DEFINITIONS

Reference [8] should be referred to for most terms used in this publication. The following terms are also used within the context of this publication but are not defined in reference [8]:

*Combustion* – A sequence of chemical reactions between a fuel and an oxidizing element accompanied by the production of heat and/or light. In the context of this publication, a combustion process is one which involves an open flame.

*Technology cost ranges* – A general scale which indicates the order-of-magnitude cost for typical procurement, installation, operation, maintenance and decommissioning of a given technology over its anticipated life cycle. The intent is to assist Member States to recognize

the entire life cycle cost for any given technology, which typically goes far beyond the basic purchasing cost. The general scale is low, medium and high cost, which are further defined below.

*Low cost technology* – A technology for which the entire life cycle costs (design, operating, maintenance and decommissioning) are less than \$ 1 M US dollars (USD).

*Medium cost* – A technology for which the entire life cycle costs (design, operating, maintenance and decommissioning) are between \$ 1 M USD and \$ 10 M USD.

*High cost* – A technology for which the entire life cycle costs (design, operating, maintenance and decommissioning) are above \$ 10 M USD.

## 2. CONSIDERATIONS FOR SELECTION OF THERMAL TECHNOLOGY

Many IAEA publications discuss the criteria to be considered when selecting a waste management strategy, e.g. [1, 6]. These same criteria apply when considering whether to use thermal technologies for a given waste stream and when considering which particular thermal technology to pursue.

There are many issues affecting whether the use of specific thermal technologies might be applicable. Some of these issues are purely technical in nature, and some are economic or political. The decision to pursue any specific option will normally be based on balancing these potentially conflicting issues. The key considerations are discussed in this section:

### 2.1. GENERAL ADVANTAGES AND DISADVANTAGES

Thermal technologies may provide the best potential for effective volume reduction of generated wastes. A further advantage of employing thermal processes is an improvement of homogeneity and quality of the waste form obtained after treatment and conditioning. Considering the high overall costs of waste disposal and the growing requirements for improved quality of the final waste form, the benefits offered by thermal processing become very significant.

Thermal methods also have disadvantages which may restrict their applications in radioactive waste processing strategies. The primary consideration is meeting the environmental safety requirements, such as gaseous effluent restrictions, which may lead to higher complexities and costs of these technologies. Higher implementation costs may make a specific technology cost prohibitive for some Member States or applications.

### 2.2. ECONOMIC CONSIDERATIONS

Technologies that are already available will be more attractive. A large investment is often required to provide a new processing technology, and this would have to be justified. The application of advanced thermal technologies may not be economically justified in some waste management schemes because of insufficient waste volumes to be processed. When the volume of waste to be treated is large, consideration can be given to investing in establishing a thermal treatment facility. When the volume is low, this investment may not be justified and other approaches need to be considered, such as mobile treatment equipment (including skid-mounted), transporting waste to a central waste processing facility (national or regional), or use of an alternative treatment method.

The size of the waste management program has a significant impact on which technologies can be pursued and how they might be pursued. Some thermal technologies can be very expensive to procure, operate and maintain. For Member States with advanced programs, many nuclear reactors and fuel cycle facilities, large waste volumes, and corresponding large budgets, many options are available. For Member States with small-to-medium programs and smaller waste volumes, the options will be more limited, with development of some major technologies not being economically feasible in that country. For Member States with emerging nuclear programs with only a limited number of nuclear applications, such as medical or academic uses, and which have very small waste volumes, few thermal technologies will be economically viable.

Consider the following simple example and the summary in Table I.

*Assumptions for a combustible waste technology economic analysis:*

- 20-year life cycle cost of a specific large incinerator = \$40M USD = \$2M/a average
- Annual volume of waste generated:
  - Member State with advanced, major nuclear program ..... 50,000 m<sup>3</sup>/a  
 Amortized (average annual) cost ..... \$40/ m<sup>3</sup>
  - Member State with small-to-medium nuclear program ..... 500 m<sup>3</sup>/a  
 Amortized (average annual) cost ..... \$4,000/ m<sup>3</sup>
  - Member State with other nuclear applications..... 5 m<sup>3</sup>/a  
 Amortized (average annual) cost ..... \$400,000/ m<sup>3</sup>

TABLE I. SUMMARY FOR EXAMPLE TECHNOLOGY ECONOMIC ANALYSIS

<b>Program size</b>	<b>Annual combustible waste generation</b>	<b>Amortized cost</b>	<b>Economic feasibility</b>
Advanced, major nuclear program	50,000 m <sup>3</sup> /a	\$40/ m <sup>3</sup>	Very economical
Small-to-medium nuclear program	500 m <sup>3</sup> /a	\$4000/ m <sup>3</sup>	Marginal; competes with direct disposal
Other nuclear applications	5 m <sup>3</sup> /a	\$400,000/ m <sup>3</sup>	Not economically feasible

The above example clearly illustrates the relationship between the annual waste generation volume and the average cost/ m<sup>3</sup> for the processing technology. Regardless of the volume reduction efficiency of the example technology, it would be very difficult for a country with a small nuclear program to cost-justify such a financial commitment. For the Member States that cannot justify the cost of local, site-specific implementation of these technologies, there may be options to use national waste processing facilities which support multiple nuclear facilities, use mobile technologies, or negotiate with neighboring countries to combine resources and share facilities (i.e. establish a regional central processing facility).

### 2.3. AVAILABILITY OF DISPOSAL SITES

The availability and cost of disposal and/or storage capacity can have a significant impact. Where capacity is limited and disposal costs are high compared to the cost of a given thermal technology, there is incentive to pursue a high volume reduction. In contrast, where capacity is large and disposal costs are much lower than the cost of a given thermal technology, there is less incentive to reduce volume aggressively. In this second case, less expensive treatment methods with reduced volume reduction potential may be more appropriate.

## 2.4. REGULATORY AND SOCIAL CONSIDERATIONS

There may be regulatory or national policy issues that preclude or mandate the use of some specific waste processing methods. Public opinion can also have an impact. As an example, combustion methods that involve the use of a flame are unpopular in some Member States due to a presumption of high radioactive effluent rates. In addition, there may be disposal waste form criteria that place constraints on the types of processing methods that may be used.

## 2.5. ENVIRONMENTAL CONSIDERATIONS

Most of the thermal processes described herein will require some type of gaseous treatment system due to the requirement, in all jurisdictions, to meet regulatory limits for both radiological and chemical emissions. There are many designs of off-gas systems and individual components may vary greatly. Therefore the complexity of the overall system may increase even if the thermal processing system itself is relatively simple. A previous publication by the IAEA provides further information on off-gas systems [9, 10] although it should be noted that the referenced publication is dated relative to current technologies and standards.

In addition to an off-gas treatment system, most thermal technologies will also require off-gas monitoring systems for both radiological emissions and chemical emissions. Generally, the permits or licenses from regulatory agencies will stipulate numerical emission limits or reference known standards to be met. They will often be very prescriptive in the requirements for data collection, analysis and reporting. Radioactive monitoring of such parameters as particulate, radioiodine, tritium and carbon-14 may be required. Typical chemical parameters requiring on-line monitoring may include oxygen (O<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), nitrous oxides (NO<sub>x</sub>), and opacity. Therefore, depending on the rigor of the regulatory requirements, the off-gas monitoring system can become a complex, costly component of implementing the overall thermal technology which must be factored into the life cycle economic analysis.

## 2.6. CRITERIA FOR CONSIDERATION WHEN SELECTING A THERMAL TECHNOLOGY

### 2.6.1. Chemical composition of the waste

The waste composition will have a great effect on the choice of thermal technologies, as well as the nominal capacity of the machine, the construction material, and the design of the off-gas cleaning system. Consider the impact of the following waste types on the selection of a thermal technology:

#### *Solid radioactive organic waste*

This low level solid waste stream is quite often heterogeneous (highly variable or mixed composition) in nature. Depending on the sorting and segregation facilities available either at the generation point or at the waste management facility, eliminating or controlling this heterogeneity may not be practical. As such, the heterogeneous nature of the waste stream usually translates to a high variability of heat content (from as low as 2000 kCal/kg for wood to 11,000 kCal/kg for some plastics). This can make the control of some thermal processes difficult, thereby limiting the applicability of any given thermal technology.

### *Solid radioactive inorganic waste*

The higher melting points of this waste stream must be considered. Some thermal technologies cannot generate the minimum heat required to achieve complete melting of the waste.

### *Liquid radioactive organic waste and aqueous wastes*

When selecting a thermal technology for processing liquid wastes (organic liquids, oil, borated aqueous waste, etc.), it should be considered that these liquids could contain solid particles and corrosion products. Some technologies will permit organic liquids — such as oils, solvents, and scintillation liquids — to be treated together with the solid waste stream (i.e. the processing system simultaneously accepts both liquid and solids within reasonable limitations). Other technologies may require solid and liquid waste streams to be separated.

Table II summarizes the applicability of thermal technologies described in this publication for the treatment of each type of waste.

## **2.6.2. Specific activity of incoming waste and radiological releases**

Each waste to be treated has a certain specific activity for beta, alpha and gamma emitters. For some wastes, the specific activity of the as-generated waste may prohibit one or more thermal technologies. A maximum contact dose rate of 2 mSv/h, which can be correlated to a certain permissible radioactivity level in the waste, is often applied as an acceptance criteria for thermal treatment of low level waste for the following reasons:

- (a) It must be recognized that a thermal technology concentrates the radioactivity of the incoming waste stream, consideration must be given to special requirements for handling and disposing of the end product. It is possible to have an unexpected impact from the specific activity of the untreated waste. If the specific activity of the as-generated waste is close to the threshold for a higher waste disposal classification, then volume reduction could result in a waste form that must meet the more restrictive disposal acceptance criteria associated with that higher waste classification. In this case, high efficiency volume reduction may not be desirable. Therefore, consideration should be given to setting limits on the activity concentration for wastes destined for a given processing method to avoid generation of waste forms of a higher disposal classification.
- (b) If the incoming waste stream has a high specific activity, the levels of contamination of the internal parts of the thermal processing system increase along with the dose rates, thus increasing the personnel protection requirements for maintenance activities.
- (c) Some thermal technologies will have little effect on reducing the resulting environmental release of radionuclides. However, other thermal technologies will be very effective at capturing the radionuclides and may result in negligible releases. Once again, this will have an effect on the permissible activity levels of the incoming waste. For licensing purposes, the specific activity of the incoming waste will be required for modeling and calculating the maximum radiological release and the potential radiological impact on critical population groups and the environment.

TABLE II. APPLICABILITY OF THERMAL TECHNOLOGIES TO COMMON WASTE TYPES

Technology	Section	Waste type						
		Organic liquids	Inorganic liquids	Organic solids	Inorganic solids	Mixed organic-inorganic solids	Mixed organic-inorganic liquids	Spent resins
Calcination	3.1	NA	A	NA	NA	NA	NA	NA
High temperature incineration	4.1	A	A	A	NA *	A *	A	A
Incineration	4.2	A	A	A	NA *	A *	A	A
Melting	5.1	NA	NA	NA	A	NA	NA	NA
Molten salt oxidation	4.3	A	NA	A	LA	LA	LA	A
Plasma	5.2	A	A	A	A	A	A	A
Pyrolysis	4.4	A	NA	A **	A **	A **	A	A
Synroc	5.3	NA	NA	A	A	A	NA	NA
Thermo-chemical treatment	4.5	NA	NA	A	A	A	NA	A
Vitrification	5.4	NA	A	A **	A **	A **	NA	A
Wet combustion	3.2	A	NA	A	NA	NA	NA	A ***

**Legend:**

A Technology is applicable to this waste type.

NA Technology is *not* applicable to this waste type.

LA Technology has limited applicability to this waste type.

\* Small pieces of inorganic are acceptable without causing damage or plugging of the system.

\*\* Applicable only for the granular or powder form of this waste type.

\*\*\* Applicable only to organic spent resins.

### 2.6.3. Permitting and licensing requirements

Any thermal treatment system will require licensing or permitting from a regulatory authority. However, when considering which thermal technology to pursue, one would have to get a clear understanding of the regulatory environment. For example, some regulators may be wary of incineration as a process and, as such, the regulatory process may be difficult and lengthy. However, other regulators may be wary of lesser known technologies (such as vitrification or plasma) and, as a result, may require much more up-front information in order to approve a license.

### 2.6.4. Existing operational industry experience

When selecting a thermal technology, one should first invest an appropriate amount of time investigating the existing operational experience within the nuclear industry and other industries. A thorough investigation of this operating experience would provide a balanced view of the advantages and limitations of certain operating systems. The following should be considered:

- Is the technology in common commercialized industrial use?
- Has the technology been demonstrated only at the research stage?
- Are there other users of the technology world-wide who can be consulted for further operational experience?
- What are the capital costs compared to other technologies?
- What are the operating costs and labour demand compared to other technologies?
- What are the licensing requirements and hurdles to be overcome compared to other technologies?
- What is the availability of central or regional thermal treatment facilities?
- What are the input requirements for economical operation as compared to the expected waste generation rates?

### 3. PRE-TREATMENT METHODS

The order of technologies in the remainder of this publication is not intended to suggest that any particular technology is better than any other technology. For this reason, the technologies are presented in alphabetical order within each section.

For consistency and easy user interface, the information on every technology is presented using the same generic structure:

- (1) Basic description
- (2) Advantages
- (3) Limitations
- (4) Operational experience
- (5) Other considerations

#### 3.1. CALCINATION

##### 3.1.1. Basic description

###### *3.1.1.1. Process description*

Two-stage vitrification processes utilize preliminary calcination of the waste. The oldest calcination technique is “pot calcination,” in which the entire procedure takes place in a “pot.” The liquid waste is added batch-wise to the container, which is enclosed in a zoned furnace. As the water boils, calcination of waste salts takes place, and a crust of calcine forms on the sides and bottom. The process is continued until the container is about 90% filled with solid material. The batch nature of this process limits its use for any large-scale application, and quality control is more difficult than in most other methods.

In spray calcination (Figure 1a) the waste is introduced into the top of an externally-heated reaction chamber through a spray orifice along with a jet of atomizing air. Water is driven off of the falling droplets, and the waste is largely converted to oxides and is collected in the form of a fine spheroidal powder ( $\leq 1\text{mm}$ ). The reaction furnace is operated to produce a  $100^\circ\text{C}$  wall temperature, although the calcine temperature itself is typically in the  $350\text{--}550^\circ\text{C}$  range. The technique is able to handle waste of almost any concentration.

Fluidized bed calcination (Figure 1b), much like spray calcinations, can accept wastes at almost all concentrations. In this process the wastes are kept in suspension by air jets from below and heated internally to  $500\text{--}600^\circ\text{C}$ . Evaporation occurs from the surfaces of the original bed particles and results in a product consisting of granular bed material and powdered calcine, both of which are continuously removed from the reactor. Heating of the bed was originally done by means of an exterior furnace, but this resulted in high losses of Ru and Cs. Heating accomplished by kerosene combustion in the bed resolves this problem. Figure 1c shows a variation of a fluidized bed system.

The rotary kiln calciner (Figure 1(d)) has been largely developed by the French. The equipment consists of an externally-heated ( $500\text{--}600^\circ\text{C}$ ) rotating cylinder tilted at a slight angle from the horizontal so that the waste introduced at the upper end is dried and almost completely denitrated before it exits at the lower end. A loose bar in the barrel keeps the calcine free-flowing and prevents build-up of wall deposits. The rotary kiln calciner is mostly

used for two-stage vitrification processes. Powdered silica is added to the feed stream to enrich calcines in silicates, which are more readily knocked loose by vibrating hammers acting on the outside of the walls.

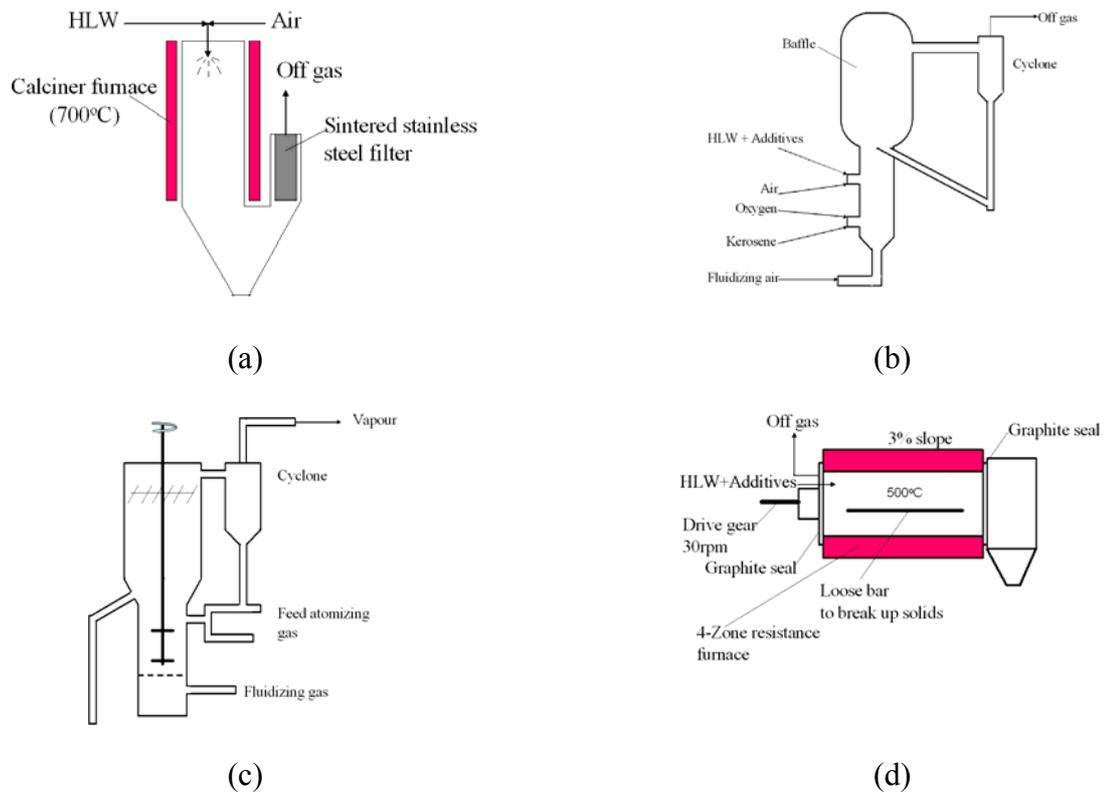


FIG. 1. Schematic of four main types of calcination processes. (a) – spray; (b) – fluidized bed; (c) – stirred bed; and (d) – rotary kiln.

### 3.1.1.2. Applicable waste types

Almost all concentrates of inorganic liquid wastes can be handled with a calciner. However, high sodium nitrate content, typical of many wastes, creates problems in all of the calcination processes. This salt has a melting temperature of 307°C and, upon melting, forms a viscous, sticky mass that resists further decomposition. The addition of finely divided metallic iron to the wastes helps with this problem. Processes have also been developed where much of the nitrate in the wastes is destroyed by pretreatment with formaldehyde or formic acid.

### 3.1.1.3. Expected end product

Most calcines as originally produced will still contain traces of substantial quantities of un-decomposed nitrate salts, as well as small quantities of residual water. Calcines produced by the fluidized bed process typically have high levels of either aluminum or zirconium. Table III presents some data on calcination products [11]. These properties are obviously highly dependent on the compositions of the original wastes, which can vary considerably.

TABLE III. PROPERTIES OF CALCINES

Property	----- Calcine type -----			
	Pot	Fluidized bed	Spray	Rotary kiln
Bulk density, g/cm <sup>3</sup>	1.1-1.4	2.0-2.4	1.0-2.4	1.0-1.3
Highest operating temperature, °C	420	600	700	600
Thermal conductivity, W/m K	0.35-1.0	0.2-0.3	0.2	0.2
Specific area, m <sup>2</sup> /g	0.1-5.0	0.1-5.0	10-20	0.1-5.0
Porosity, %	40-85	45-80	30-75	70-80

### 3.1.2. Advantages

The general advantages of the calcination technologies are high efficiency waste volume reduction, elimination of water, decomposition of soluble salts, and almost complete transformation of the as-generated waste product into an oxide form, which has a much lower water solubility than the as-generated waste.

### 3.1.3. Limitations

The process results in a powder waste form, which in many cases is not acceptable for disposal without additional conditioning/packaging into different containers, such as High Integrity Containers (HIC).

### 3.1.4. Operational experience

Calcination is industrially used as a preliminary stage in the two-stage vitrification processes in France and UK [11, 12]. Calcination is also used in the USA [13] where it has been proposed as a final waste form (e.g. supercalcine [11] or fluidised bed steam reforming product [14]).

### 3.1.5. Other considerations

Calcination is only a pretreatment method leaving the end product, which is typically fine powder. Thus, they are relatively dispersible, which is a serious consideration in the event of a transportation accident. The untreated calcine materials are also easily leachable/soluble in water. These two characteristics have largely eliminated calcines from consideration as a final disposal form. Calcinated wastes also require further processing, such as vitrification.

The technology costs for calcination methods are generally low to medium.

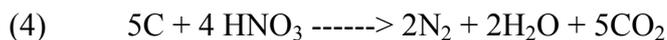
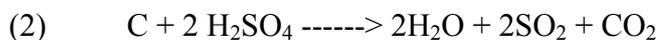
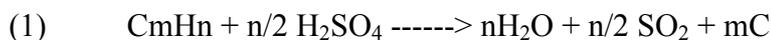
## 3.2. WET COMBUSTION (HOT ACID DIGESTION)

### 3.2.1. Basic description

#### 3.2.1.1. Process description

Wet combustion/hot acid digestion is a thermal desorption process involving carbonization of organic wastes in hot commercial sulphuric acid and oxidation of the resultant carbon by commercial nitric acid. It has been used most commonly for the recovery of Pu from organic solid wastes and is also used for treating alpha-bearing solid wastes.

In the wet combustion process, the bulk of the waste is converted to carbon-dioxide and is released with the off-gas stream. The radioactive contaminants in the waste will be retained in the digester residue as insoluble sulphates. The primary chemical reactions involved in the acid digestion process can be represented by the following four reactions:



The sulfuric acid serves both to carbonize the waste material and to oxidize it to CO<sub>2</sub> as shown in reactions (1) and (2) above. Sulphuric acid also serves as the high temperature medium, as its boiling point is above 300°C. This is particularly necessary for digestion of aged plastic materials, such as PVC, neoprene and polyethylene, where an acid temperature near 250°C is necessary to obtain complete oxidation of the waste at a reasonable rate. Reaction (2) is slower than reactions (3) and (4). Nitric acid serves as a better oxidant due to faster kinetics and according to reactions (3) and (4).

The solid combustible wastes typically must be sorted and shredded in advance of digestion. This is required to increase the surface area per unit mass of waste, thereby improving the rate of digestion. The shredded wastes will be carbonized in hot commercial H<sub>2</sub>SO<sub>4</sub> and oxidized by commercial HNO<sub>3</sub> in a digester vessel. Experience in India has demonstrated that a decontamination factor for alpha-bearing wastes of around 105 can be achieved at the digester vessel [15, 16]. The volume reduction efficiency is also high at roughly 99:1.

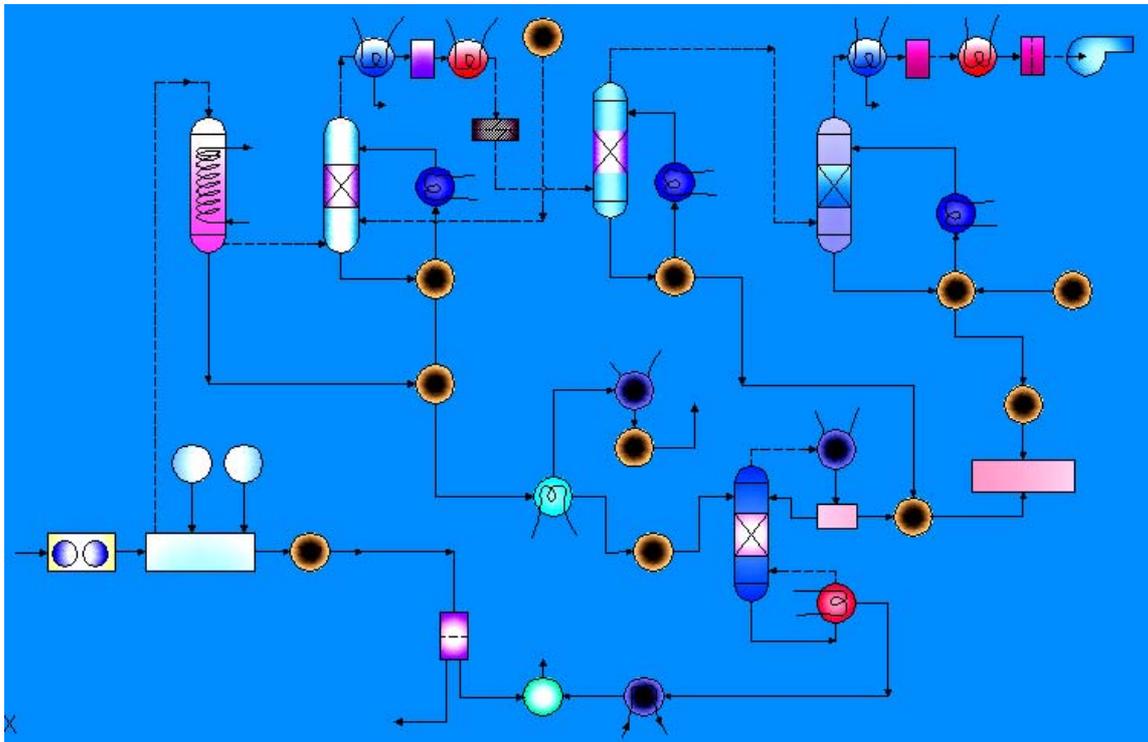
After cooling the digester contents, the solid residue is separated by batch type pressure filtration, and the filtrate is recycled to a digester. The residue, which contains TRUs and other activities can either be treated for recovery of Pu or can be fixed in suitable matrix.

After passing through a cooler/condenser, the off-gas is contacted with a counter current water/acid scrub solution in the presence of air/oxygen. This is accomplished in two separately packed columns in series for oxidizing the gaseous effluents to the acid anhydrides and being absorbed as H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl. The off-gas finally will pass through another scrubber where alkali/hydrogen peroxide is used to scrub the solution for removal of traces of NO<sub>x</sub>. After removal of pollutants from the off-gas stream, it is passed through a chiller, heater and a set of absolute filters before being released into the area ventilation system. As a result

of the low off-gas emissions, the complexity of the off-gas system is relatively low, reducing the overall cost of the system.

The  $H_2SO_4$  and  $HNO_3$  will be recovered from the scrub solutions by pre-distillation for removal of  $HCl$  and subsequent rectification/counter-current distillation for recovery of  $H_2SO_4$  and  $HNO_3$ . Around 90% to 95% of  $H_2SO_4$  and around 50% of  $HNO_3$  consumed at the digester can be recovered by proper design of the scrubbing system. Small amounts of secondary low level liquid wastes will be produced as a top product/condensate from the scrubbing solution recovery unit.

The acid digestion process is a semi-batch process. A typical process flow sheet of the Wet Combustion process under development in India is enclosed in Figure 2.



*FIG. 2. Typical process flow sheet of wet combustion system under development at Kalpakkam, India.*

Considering the inhalation and ingestion hazard potential of transuranic (TRU) contaminated solid wastes, the supporting waste management facility should be designed for handling these wastes inside a suitably ventilated containment. Containment is required up to the first stage absorption column of the process and for the filtration unit and any subsequent residue handling units of the process. However, the use of HEPA filters in key positions in the off-gas system, together with the inherent decontamination factor (DF) for radioisotopes between the digester and the off-gas system, normally produces a gaseous effluent stream which is expected to be non radioactive.

The corrosive nature of the acids and wastes to be handled must also be taken into consideration. For example, the candidate materials of construction of a digester vessel are glass, tantalum or glass-lined steel. As the vapour phase temperature in the Dilute Acid Scrubber and Alkali Scrubber will be well below 100°C, FRP/PVC columns can be used the construction material for subsequent scrubbers.

#### *3.2.1.2. Applicable waste types*

All organic solid wastes, including spent resins and organic liquids can be treated by this process. Based on the extent of the contamination, shielding may be required.

#### *3.2.1.3. Preparation*

The solid, combustible waste inputs normally require pre-sorting and shredding. The cost of a shredder represents an additional expense.

#### *3.2.1.4. Expected end product*

The end product is an easily leachable inorganic sulphate residue. It requires a subsequent treatment/conditioning process prior to recovery of Pu or disposal. The residue can be dissolved in HNO<sub>3</sub> and can be sent to a reprocessing plant for recovery of Pu.

The residue can be encapsulated in a cement matrix based on levels of TRU content and disposed in an appropriate repository. If TRU contamination is high, it may require a post-treatment calcination step and subsequent fixation in a glass or Synroc matrix prior to disposal.

### **3.2.2. Advantages**

The process is a reasonably low temperature wet process providing low turbulence at the digester. Hence, radioactivity carryover to the off-gas stream is minimal. This provides an advantage of containment integrity and potential for a conventional contact manageable off-gas treatment system. Due to the relatively low temperature as compared to other thermal technologies, wet combustion provides a very high recovery of Pu from wastes and into an easily dissolvable residue. The reported percent recovery of Pu from wastes is above 90%. The process provides a high volume reduction factor comparable to that of air incineration (i.e. around 99:1). The process can treat a wide variety of wastes, including almost all organic wastes.

### **3.2.3. Limitations**

The major limitation is that the process is a low throughput process. Due to the high oxidizing environment, the material of construction for the digester is very limited — glass, glass-lined steel, or tantalum. Due to the aqueous medium which serves as a neutron moderator at the digester, safety aspects have to be considered in terms of the potential for criticality if planned for treatment of fissile contaminated wastes.

### **3.2.4. Operational experience**

The process was originally developed at Hanford Engineering Development Laboratory, United States of America, and was subsequently demonstrated in a Radioactive Test Unit for Defense Wastes (organic solid wastes). The process was first deployed commercially at

Karlsruhe, Germany, and at Eurochemic, Belgium, for volume reduction and recovery of Pu from organic solid wastes. The process was also developed and used in Japan. In India, a laboratory feasibility study has been completed, and a radioactive demonstration facility for treating alpha bearing solid waste by wet combustion at a throughput of 5 Kg/hr is being designed and constructed at Kalpakkam. Figure 2 illustrates the process flow for the Kalpakkam wet combustion system.

### 3.2.5. Other considerations

- The process is a low throughput process; a throughput of up to 5 kg/hr has been demonstrated.
- The comparable technology cost of the process is low, and the cost and complexity of the off-gas system is low. However, a shredder is normally used to prepare the input waste stream, which represents an added cost. The system is an immobile/fixed unit.
- Since the process achieves a volume reduction factor of 99:1, there is a potential for the higher specific activity of the output residue from the digester to increase in waste classification depending upon the activity levels of input waste stream.
- The radiation shielding requirement and remote handling requirements for the process must also be considered at the design stage consistent with the intended waste to be processed.

#### 3.2.5.1. Process safety

Four general considerations must be carefully evaluated to ensure the overall chemical safety aspects of a wet combustion system for engineering design and operation:

- (1) Combustibility and/or explosiveness of the digester gases;
- (2) Nitration reactions in the digester;
- (3) Nitration reactions in the recycle acid; and
- (4) Volatilization of organics.

## 4. TREATMENT METHODS

### 4.1. HIGH TEMPERATURE INCINERATION

#### 4.1.1. Basic description

A conventional incinerator is a self-sustaining process, because only combustible wastes are treated and at temperatures of around 1000°C. With high temperature incineration (HTI), a powerful burner is installed which employs fuel and mostly pure oxygen as a combustion gas. Operating temperatures can exceed 1500°C; therefore, a small percentage of metal, air filters, and insulation material can be incinerated together with organic wastes. The waste is melted in a rotating furnace and then discharged at a controlled rate and with water cooling to produce a granular product. The organic material is decomposed and vaporized, and the gasses are sent to a secondary combustion chamber to obtain complete combustion of the primary oxidation products.

The end product is a glass-like granulate.

#### 4.1.2. Advantages

The principal advantages of HTI are:

- The final end product is stable.
- The volume reduction factor (VRF) for light metals, air filters, and insulation is typically in the range of 3:1 to 5:1, while for other combustibles the VRF can rise as high as 99:1.
- The waste feed can contain some proportion of non-combustible material.

#### 4.1.3. Limitations

Limitations of the HTI are:

- Very sensitive to waste composition; deviations may shut down the system.
- Some knowledge of the waste composition is necessary; otherwise pre-sorting is required.

#### 4.1.4. Operational experience

An HTI test facility was set up in Belgium, started nuclear operation in 1978, and treated beta and alpha containing wastes with a capacity of about 50kg/h. In 1988, the plant was shut down due to a strategic decision by the Belgium Research Centre (SCK) to pursue further development.

Different HTI systems are in still in operation in Japan for treating low level waste.

#### 4.1.5. Other considerations

The installation costs for an HTI system are relatively high. In fact HTI can be seen as a precursor for plasma technology systems (see section plasma). HTI has waste feed limitations (i.e. some wastes will still not be combusted at 1500°C), the higher temperature plume of a plasma torch (5000°C or more) eliminates these limitations.

## 4.2. INCINERATION

### 4.2.1. Basic description

#### 4.2.1.1. Process description

A generic “incineration system” consists in its entirety of the “incinerator” itself (a combustion system comprising of one or more combustion chambers completed with auxiliary equipment, instrumentation and process controls), the waste feed preparation and loading (metering) system, the ash removal system, and the off-gas treatment system. These are depicted in a block diagram in Figure 3. For the purposes of this report, the term “incinerator” is used to refer to the combustion system only, while the term “incineration system” is used when referring to the total system.

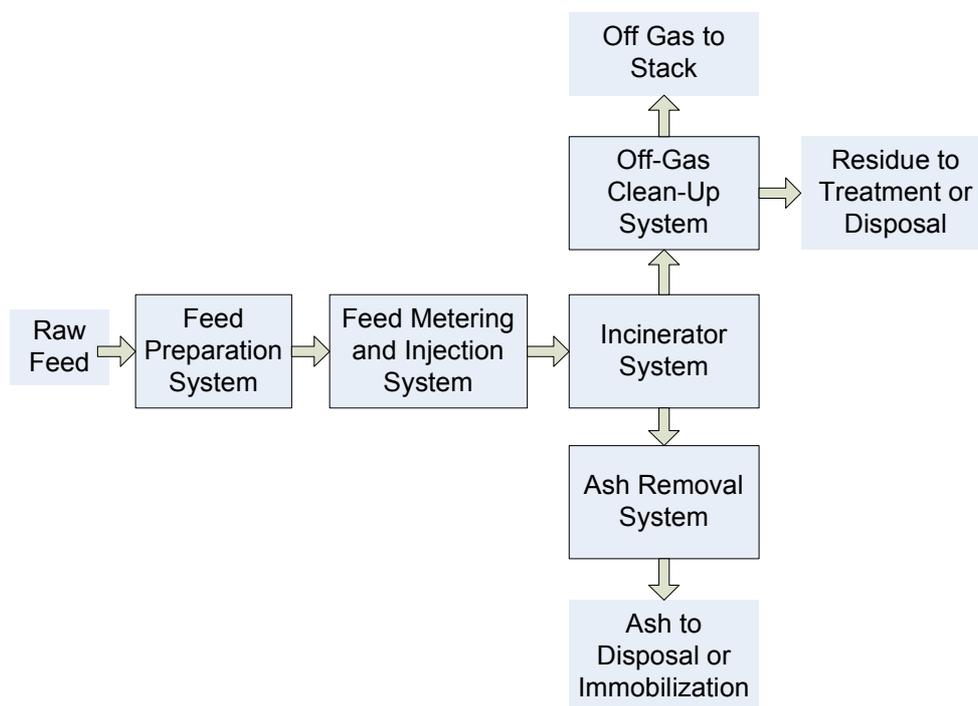


FIG. 3. Incineration system block diagram.

Once the waste feed is in the incinerator (combustion chamber), waste can be transported by gravity, by mechanical means, or by media flow (infrequent) to the ash removal system.

Incineration of radioactive wastes can be accomplished in a single stage or a multiple stage operation. In a single stage (single chamber) incinerator, the waste is burned under excess oxygen conditions in one combustion chamber, producing a solid waste residue (ash) and a stream of off-gas which do not contain organic materials. In a multiple-stage system, the waste is first gasified in a primary combustion chamber under controlled (oxygen-deficient) air conditions. This produces a mixture of combustible gases which are subsequently burned in an oxygen rich environment in a secondary combustion chamber(s); the solid residue (ash) remains at the bottom of the pyrolysing chamber to undergo a carbon burn-out.

Radioactive waste incinerators can be designed using horizontal combustion chamber(s), vertical (shaft) chamber(s), or a combination of the above. The combustion chambers may be refractory lined cylindrical steel vessels (or true pressure vessels), or they may be constructed of bricks and structural steel in a cubical geometry with appropriate refractory linings. Refractory damage can occur in an incinerator but can be mostly avoided with proper operation, including minimizing thermal shock resulting from rapid heat up and cool down.

The configuration of the primary chamber dictates the design of the waste feed system, the transport of the waste/ash through the primary chamber, and finally the ash removal system. Primary chambers can be designed so that the solid waste feed is:

- placed on a stationary grate or a furnace bottom;
- moved by gravity from the top of a vertical shaft downwards;
- a combination of these two;
- introduced into a fluidized bed of granules;
- agitated by tumbling (in rotary kilns).

The combustion chamber burners may be operated with propane, natural gas, fuel oil, waste oil, etc.

The complete oxidation of all combustibles in the waste material is the primary objective for the incinerator design and operation. To achieve complete combustion of the organic portion of the processed waste, the basic requirements are adequate reaction temperatures, sufficient excess air supply, ample mixing of air and gas/vapors, and an adequate reaction time. Incomplete combustion will lead to miscellaneous operating problems, including formation of deposits on the system components (e.g. heat exchanger tubes, combustion air tubes), premature clogging of the off-gas filters. This will typically increase maintenance requirements and operating costs, create fire hazards, and reduce system availability. Furthermore, incomplete combustion may affect the ash removal process and result in a lower ash quality, produce a need for manual intervention inside the radioactive zone, and cause a lower overall system volume reduction.

There have been many designs of incinerators over the last several decades. A good description of various types of incinerators can be found in Reference [6]. In a successful incinerator design, careful consideration is given to the provision of adequate access and to the appropriate location of air supplies. In addition, the combustion temperature is carefully controlled; the off-gas velocities are adequately low; and the gas residence times are comparatively long.

The end product of incineration of radioactive materials is ash, the composition and characteristics of which vary with the combustion process used, as well as with the composition of the initial waste feed. In essence, the end products of incineration are the elemental oxides of the initial substance composition. Ash is a heterogeneous substance that, in practical terms, also contains all of the non-combustibles that were originally present in the waste feed. Ideally, ash should contain no fixed carbon, which is achievable as long as the carbon burn-out can take place in an oxygen-rich atmosphere and for a sufficiently long residence time.

Ash can be discharged from the primary chamber by gravity, removed by mechanical or hydraulic means, or melted and granulated by high temperatures. Regardless of the system used for ash transport and removal, considerations need to be taken for control of radiological contamination and for radiation exposure to personnel.

Incinerators also produce fly ash, which is an easily dispersible material collected from the incineration off-gas system. The fly ash can be collected into a separate drum or together with the incinerator ash.

As is the case for all high temperature processes, the off-gas from incinerators has to be cooled to temperatures that are compatible with the components of the off-gas treatment system which deal with chemical pollutants as well as remaining nuclides. The need for an off-gas treatment system is described in Section 2. When designing an incinerator system, the design of the off-gas treatment system must be carefully considered, as they are tightly linked.

#### *4.2.1.2. Waste feed characteristics*

One of the advantages of incineration is its versatility in terms of the waste feed characteristics. Dry solid organic wastes from nuclear power plants remain the principal feed for radioactive waste incinerators. Note that the rated throughput of an incinerator is normally based on this typical waste feed. However, organic liquids can also be processed. These are usually co-processed with the solid waste, but incinerators also can be designed to process organic liquid waste exclusively. Aqueous wastes can be treated by incineration, but incineration technology would not necessarily be the primary choice if aqueous waste was the only waste stream required to be treated. In summary, the following waste streams can be generically treated by incineration, depending on the incinerator concept employed:

- (a) Dry solid wastes
- (b) Ion exchange resins\*
- (c) Organic liquids\*
- (d) Aqueous liquids\*

\* with operating limitations

Incineration of low activity spent ion exchange resins has been successfully accomplished; resins are now routinely processed by modern incinerators, and considerable operational experience has been collected [15]. However, processing of resins needs to be acknowledged in the incineration system design phase, and design provisions may need to be incorporated. Design challenges include considerations for heat quenching (temperature reductions) due to the entrained water of hydration inherent in spent resin. Other important challenges are the significant potential release of tritium through the gaseous effluent stream from incineration of primary resin (a design specification and operational issue), as well as the exceptionally high potential dose rates of some spent resin (i.e. a shielding design and operational issue). Usually, the resins would be co-processed together with dry solid wastes, and there would be a set limit for the resin types, mass, and radioactivity. If incineration of resins has not been considered in the incinerator design phase, their processing may affect performance and the rated throughput of the incinerator.

Organic liquid waste can be fed into the combustion or post-combustion chamber, as most incinerators are furnished with nozzles or burners for incineration of these liquids. Due to the high heating value of the oils, the design throughput of the system as calculated for the

solid waste (i.e. in kg/hr) is then reduced to only a fraction of its nominal throughput if introduced in combustion chamber. However, if acknowledged in the design phase, there would be a throughput rating determined for the nominal (solid) waste and the co-processed organic liquid. Organic liquids, when generated in nuclear power plants, may be a mixture of oils, lubricants, solvents, etc. and may contain a certain fraction of water. When incinerating these liquids, the burner has to be set up to handle a sudden “slug” of low heat content water/liquid (much the same as when incinerating spent resin). This may extinguish the burner; therefore precautions must be exercised to ensure that a large quantity of low-btu content liquid is not injected into the chamber prior to igniting the burner, and that the combustion chamber temperature is monitored to maintain satisfactory burn temperatures.

Aqueous liquids may also be co-processed in an incinerator when their volume is relatively low and the system operator has a need to dispose of these liquids. (Note that in some cases, aqueous liquids originate during the operation of the incineration system.) In summary, it must be recognized in the system design and operation that aqueous liquids have effectively a negative heating value, and their feed into the incinerator must be strictly controlled .

#### 4.2.1.3. Preparation

Each incinerator concept has unique requirements for the solid waste feed form. Solid waste materials can be fed into the combustion chamber simply by gravity (vertically), by mechanical devices (horizontally), introduced in a shredded form or as a fluidized bed, etc. While some systems require careful sorting of the waste feed, other systems may accept the waste feed form as-generated. Some systems require that waste be shredded; other systems require pre-packaging the waste feed in bags, cardboard boxes, or incinerable (cardboard, fiberboard, plastic) drums since the heating value of the combustible materials in the heterogeneous waste feed varies widely between 4 600 and 42 000 kJ/kg, it is typically necessary to ensure during sorting of the waste feed that the total heating value of the waste package is consistent within certain limits.

Pre-sorting in order to eliminate materials that would not be compatible with either the combustion system design or the off-gas treatment capabilities may be required.

As an example, the following waste items or materials may need to be controlled (either eliminated, minimized, or limited), depending on the incinerator type and the ash removal system limitations:

- Non-combustibles
- Metal objects
- Plastics (halogenated or not)
- Materials with excessive heating value
- Excessive radioactivity\*
- Explosion hazard

*\* The radioactivity of combustible dry solid LLW, which is the primary feed to most incinerators, as well as that of contaminated liquids are usually very low and enable contact collection and handling. Since incineration increases the specific activity of the ash residue, upper activity limits may have to be set for the waste feed in order to keep the activity of the ash within limits for further handling, storage, and disposal and without increasing the waste classification.*

A final inspection of waste prior to incineration is usually completed to ensure that the waste does not include undesirable items. Activity detectors, metal detectors, and X ray systems are routinely utilized to detect undesirable items.

#### *4.2.1.4. Expected final product*

Incineration destroys organic material, transforms it into a stable product free from liquids, and complies without doubt with the acceptance criteria for long-term storage or final disposal. Indeed the ash and fly ash collected (e.g. in 200 l drums) can be supercompacted and loaded in overpacks. Subsequently the overpacks can be embedded with grout (if stabilization is required) in preparation for storage or disposal. The ash can also be encapsulated, which means immobilization of dispersed solids (ash) by suspending within a cement or other matrix acceptable for disposal.

Bear in mind that volatile isotopes, such as H-3, C-14 and I-129 are transferred to the off-gas. They are partly absorbed into the scrubber water — if a scrubber is installed — and partly emitted into the atmosphere by way of the stack.

#### **4.2.2. Advantages**

Incineration is the most commonly used thermal process for treatment of solid LLW and certain ILW in the nuclear industry. The principal advantages of incineration are:

- Well-proven technology.
- Very high volume reduction of processed waste, especially when processing power plant dry solid LLW.
- High versatility, in that it can process a broad spectrum of dry solid wastes, organic liquid wastes, and to some extent also aqueous liquid wastes.
- End product of incineration is a stable and chemically inert residue that is free of organic materials and can be conditioned by various commonly used methods into a waste form that meets radioactive waste disposal criteria.
- High throughput process (i.e. a large incinerator can treat 10 t or more per day of solid waste).
- Process continuity (i.e. process can operate on a continual basis 24 hours/day).

#### **4.2.3. Limitations**

- Due to heterogeneity of waste stream sorting, segregation and, for some systems, shredding is required. Metal objects in waste feed, if not removed, may create mechanical operational problems.
- Relatively high capital cost for investment, so it is not generally economical unless there is a sufficient minimum annual waste input volume that needs to be continuously processed during the lifetime of the incineration system. (It is not unusual for some incinerators to be operated on a part time basis, but this is not the optimum situation, and the heat-up time has a significant impact on throughput.)
- Public acceptability of incineration may be difficult in certain jurisdictions.
- Combustion process controls need to be carefully designed to compensate for the process variables (i.e. waste characteristics and heating value of a batch feed, ingress of air, etc.) to ensure safety of the combustion process.

- Well proven combustion and de-ashing systems need to be utilized to eliminate the need for manual interventions that are associated with exposure to radioactivity.
- Certain systems may generate increased volumes of secondary waste (i.e. systems incorporating hot gas ceramic filters).

#### 4.2.4. Operational experience

Incineration is a mature and proven technology and has demonstrated successful operation and accumulated credible operating experience. Most incinerators are controlled air, multi-stage incinerators and are operating on a commercial and industrial scale (i.e. large input and continuous operation). Table IV gives an overview of different incinerator plants currently in operation in some Member States.

TABLE IV. INCINERATOR FACILITIES IN OPERATION IN SOME MEMBER STATES

Country	Facility/ Site	In-service date	Capacity	Notes
Austria	Seibersdorf Research Center	1983	40 kg/h solid	
Belgium	CILVA, Belgoprocess	1995	80 kg/h solid 50 kg/h liquid	Solids, liquids and ion exchange resins
Canada	Ontario Power Generation, Western Waste Management Facility	2002	2 t/d solid 45 l/h liquid (license limit)	Continuous feed, starved air system.
India	BARC Kalpakkam	1990's	50 kg/h solid	Organic solids without Cl and S
France	Socodei Centraco	1999	2000 t/yr solid 1100 t/yr liquid	Commercial LLW treatment facility
Germany	Karlsruhe	Since 1980's	40 kg/h liquids 50 kg/h solids	Solids and liquids
Japan	PNC, Tokai-Mura	1991	50 kg/h solid	
Netherlands	COVRA, Vlissingen-Oost	1994	60 kg/h solid 40 l/h liquid	Two incinerators, one for liquids, one for animal carcasses and other solids
Russian Federation	RADON	1982	100 kg/h solid 20 l/h liquid	
Slovakia	Jaslovske Bohunice BSC	2001	50 kg/h solid 10 kg/h liquid	Used in campaigns for LLW
Spain	ENRESA El Cabril	1992	50 kg/h total solid and liquid	Located at LLW disposal facility
Sweden	Studsvijk	1977	150 kg/h total solid	

Country	Facility/ Site	In-service date	Capacity	Notes
UK	Hinkley Point B	Since 1970's		Located at a nuclear power plant
Ukraine	Zaporizhzhе NPP	1993	40 kg/h solid 20 kg/h liquid	
USA	Consolidated Incineration Facility, Savannah River	1997	400 kg/h solids 450 kg/h liquids	Designed for PUREX reprocessing solvents, LLW and mixed waste.
USA	Duratek, Oak Ridge	1989	2 incinerators, approx 400 kg/h each	Commercial LLW treatment facility

A first example of a controlled air multi-stage incinerator is the CILVA incinerator at Belgoprocess in Belgium which started nuclear operation in 1995 [18]. Figure 4 shows the layout of the incineration system which treats the following types of radioactive waste:

- Un-compacted and compacted solid waste such as clothing, gloves, rags, cotton, rubber and plastics (PVC quantity 3 % average, caloric value of about 25 MJ/kg)
- frozen animal carcasses
- spent ion exchange resins in wet or dry condition
- organic liquid waste such as scintillation liquids and organic solvents (caloric value of about 35 MJ/kg)
- aqueous liquid waste whether or not containing organic components and solid particles
- spent oil (caloric value of about 40 MJ/kg)

Based on a weekly operating time of 100 h the capacity is about 8 tons/week of solid waste, besides 1 to 5 ton of liquid wastes. The radioactivity limit of the waste is 40 GBq/m<sup>3</sup> for beta-gamma emitters and 40 MBq/m<sup>3</sup> for alpha emitters, with a maximum dose rate at the surface of each package of 2 mSv/h. The collected ashes and fly ashes, which contain the concentrated radioactivity, are super-compacted and embedded with grout.

The incineration system consists of the following main components:

- A primary combustion chamber in which the radioactive waste undergoes a combined process of combustion and pyrolysis at a temperature range of 900°C to 950°C;
- A secondary combustion chamber in which the unburned gases and soot particles are mixed with excess air to complete oxidation to primary combustion components;
- A boiler to cool the off-gases;
- Off-gas filtration and radiological purification, consisting of a bag-houses with bag filters and high efficiency particulate air (HEPA) filters;
- A wet off-gas scrubbing system, consisting of a quench tower and a counter current scrubbing tower to remove HCl and SO<sub>2</sub>.

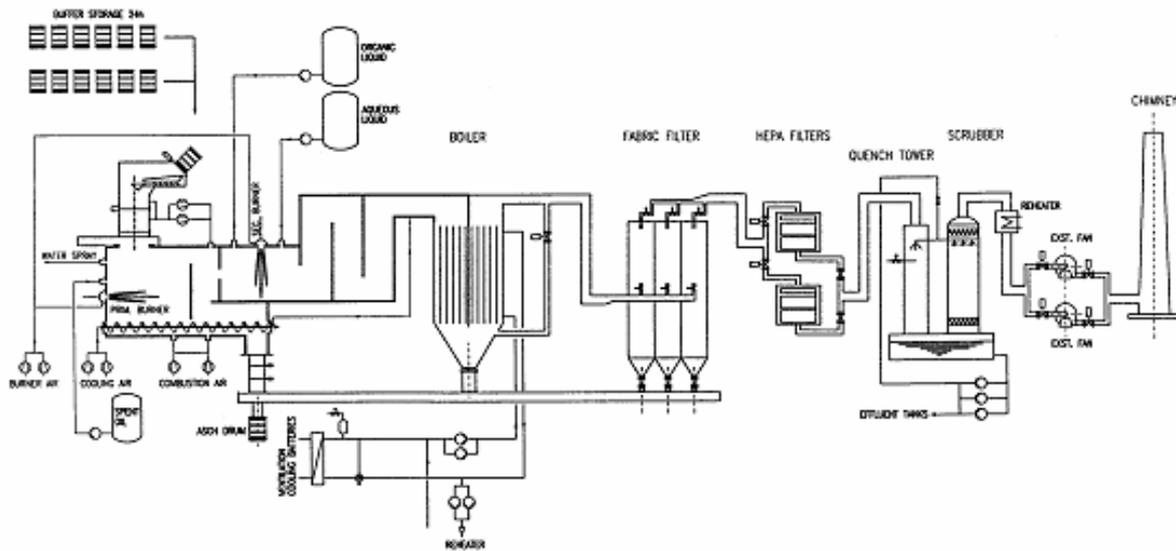


FIG. 4. CILVA low level waste incinerator facility, Belgium.

A second example of a controlled air multi-stage incinerator is the CENTRACO incinerator plant from SOCODEI in France, which started nuclear operation in 1999. Figure 5 shows the layout of the incinerator which treats the following types of radioactive waste:

- Un-compacted and compacted solid waste such as clothing, gloves, rags, cotton, rubber and plastics (PVC quantity 5 to 12 %, average caloric value of about 25 MJ/kg)
- frozen animal carcasses (several tons per year);
- spent ion exchange resins in wet or dry condition (up to 10 % of solid waste);
- organic liquid waste such as scintillation liquids and organic solvents (caloric value up to 45 MJ/kg);
- aqueous liquid waste whether or not containing organic components and solid particles (boron concentrates, etc.);
- spent oil (caloric value of about 40 MJ/kg).

Based on a continuous operation time the capacity is about 60 tons/week of solid waste, besides 40 to 80 tons/week of liquid wastes. The radioactivity limit of the waste is 20 GBq/t for beta-gamma emitters and 37 MBq/t for alpha emitters, with a maximum dose rate at the surface of each package of 2 mSv/h. The collected ashes and fly ashes, which contain the concentrated radioactivity, are embedded with grout I metallic casks of 400 l. The incineration system consists of the following main components:

- A primary combustion chamber in which the radioactive waste undergoes a combined process of combustion and pyrolysis at a temperature range of 850°C to 1050°C;
- A secondary combustion chamber operating at 1100°C in which the unburned gases and soot particles are mixed with excess air to complete oxidation to primary combustion components;
- A partial quench tower to cool the off-gases;
- Off-gas filtration and radiological purification, consisting of a bag-house with bag filters and high efficiency particulate air (HEPA) filters;

- A wet off-gas scrubbing system, consisting of a quench tower and a counter current scrubbing tower to remove HCl and SO<sub>2</sub>.
- A catalytic reactor to remove all nitrogen oxides and dioxins and furans.

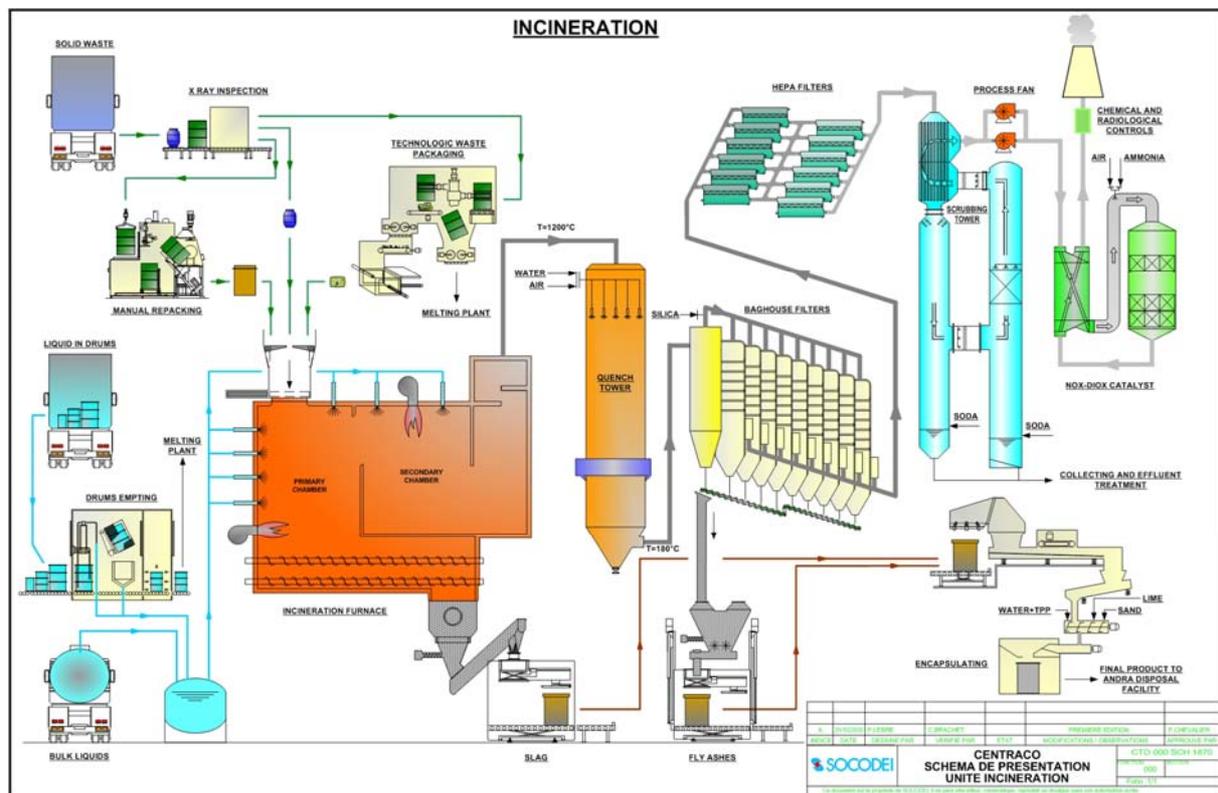


FIG. 5. CENTRACO incineration plant.

## 4.2.5. Other considerations

### 4.2.5.1. Scale/throughput

There are various sizes and throughput capacities available for radioactive waste incinerators. Incinerators can range in solid waste feed capacity from approximately 40 kg/hr to as much as 500 kg/hr. In addition, liquid waste feed capacity can range from 10 kg/hr to as high as 500 kg/hr.

### 4.2.5.2. Costs

Incineration is typically a very costly technology relative to some smaller scale technologies. It may not be economically justifiable for small waste volumes. However, for large waste volumes and many waste types, incineration will be cost beneficial. If the incinerator is processing only solid waste streams, then the cost benefits may not be realized. The biggest economic gains can be achieved when processing liquid wastes due to the difficulty of treating them in conventional water treatment plants and the expense of treating exotic liquids.

equivalent capital costs. However, incinerators with capacities above 150 kg/hr up to approximately 500 kg/hr will have much higher costs.

It should not be assumed that smaller capacity incinerators lead to a smaller off-gas treatment system. This is due to the fact that the high instantaneous heat release of the waste and the resulting off-gas production will still dictate the size and design of the off-gas system. It should be noted that even for small scale incinerators, the overall operation and maintenance costs will not be proportionally reduced – again due to the requirements for an off-gas treatment system.

#### *4.2.5.3. Mobile or fixed*

Most incinerators are mounted as fixed units in centralized facilities. It is possible to construct a mobile incineration system for small capacities. The entire system would have to be skid-mounted and able to be transported in multiple 40-foot ISO containers. Then it would have to be assembled at the site in a controlled area.

#### *4.2.5.4. Environmental/regulatory issues*

Incineration is not always favorable with regulators. The regulatory environment in the Member State would have to be considered. Depending on where it is installed, air quality permits may be needed for either a fixed or a mobile system, and obtaining such permits may be a determining factor for feasibility. Once contaminated, transport regulations would have to be considered.

Of course, the local regulations may also have an effect on the design of the entire incineration system, particularly the off-gas system, and therefore will affect costs.

#### *4.2.5.5. Lessons learned*

The main lesson learned is that only proven incineration systems that have demonstrated successful operation and accumulated credible operating experience that is applicable and of value to a new proposed installation should be considered for new acquisitions.

## 4.3. MOLTEN SALT OXIDATION

### 4.3.1. Basic description

Molten salt oxidation is a flameless thermal desorption process. The waste is introduced into a bath of molten salts, typically at temperatures between 500-950°C. This has the effect of oxidizing the organic constituents of the waste. Carbon dioxide, nitrogen and water are produced. The end product is an organic-free salt residue which captures radionuclides, metals and other inorganics. The production of acid gas emissions is inhibited by the formation of the stable salts.

### 4.3.2. Advantages

Molten salt oxidation results in the complete destruction of organic material and efficiently captures ash and radioactive particles within the salt bath. The lower operating temperature, relative to other thermal technologies, may result in reduced fuel costs. Low levels of gaseous emissions are produced.

### 4.3.3. Limitations

The process is still in the developmental and assessment phase with limited experience (described below). It has a high capital cost, and requires specialized techniques for adequate conditioning of the salt product.

### 4.3.4. Operational experience

The operational experience to date has been fairly limited. In the United States, molten salt extraction was used at the Rocky Flats facility to remove americium from plutonium metal by oxidizing and extracting the americium ion into the molten salt matrix [19]. A bench scale facility was also developed and demonstrated on thirty types of waste streams at Lawrence Livermore Laboratories in USA in 1997 [20]. A third facility was constructed in South Korea in 2001; further information on the operational experience of that facility was not available at the time of publication of this report.

### 4.3.5. Other considerations

- limited commercial experience
- applicable to small and medium waste programs
- could be further developed as a mobile technology
- technology costs are relatively low

## 4.4. PYROLYSIS

By definition pyrolysis is a flameless, dry distillation process where organic matter is externally heated in the absence of air or oxygen to temperatures where the organics are fractured into several volatile components with high caloric values. The main output products are generally methane, ethane, benzene, toluene, tars and char. In general organics are thermally unstable and process temperatures of 500–600°C will fracture most organics. When organics are fractured, excess carbon is left as a carbon-rich char.

Pyrolysis might be performed in different types of reactors utilizing downdraft, updraft, bubbling fluidized bed, or entrained flow. Most common are bubbling fluidized beds as they offer good gas-solids contact and mixing, high thermal efficiency, and good temperature control. They also can handle significant variations in fuel quality, have good thermal control, and are easy to start up and shut down

#### 4.4.1. Basic description

##### 4.4.1.1. Process description

Processing radioactive organic waste by pyrolysis has been utilized in several bench scale, pilot plant scale, and industrial plant applications. Pyrolysis is generally applied with steam reforming or incineration as a second stage process to remove the carbon content in order to produce higher volume reductions and improve the final waste form.

In radioactive organic waste, the organics are contaminated by inorganic radionuclides. The organics are mostly non radioactive; it is the inorganic constituents which introduce most of the radioactivity. The pyrolysis process separates the organic fraction of the waste from the radionuclides by gasification of the volatile organic species. The radioactivity remains in the solid residue generally in the form of reduced metal oxides. Relatively low temperatures are effective in achieving successful pyrolysis; control of the temperature band becomes critical as a means of retaining volatile nuclides in the final resulting waste form. The temperature should be kept as low as possible to retain the radionuclides in the solid pyrolysis residue. At temperatures of up to 750°C, Cs and Ru, the most volatile radionuclides, are still retained almost completely in the solid residue.

Pyrolysis thus achieves a substantial volume reduction by removing the original organic fraction and evaporating the aqueous portion of the waste. However the final product contains a significant amount of carbon in the form of char. Subsequent removal of the char will result in higher volume reduction ratios.

A process favoured to remove the carbon fraction is steam reforming. Steam reacts with carbon according to the following formula:



The endothermic character of the above reaction and the moderate reaction rate at the temperature of interest favour good temperature control and, in practice, is performed using the same steam which is used to fluidize the fluid bed reactor. Alternative measures for char removal could include incineration, which oxidizes the carbon directly with atmospheric oxygen.

A typical pyrolysis/steam reforming plant is the Studsvik Processing Facility in Erwin, TN, USA [21]. The Studsvik Processing Facility employs the THERMAL ORGANIC REDUCTION (THOR<sup>sm</sup>) process, developed and patented by Studsvik. The THOR<sup>sm</sup> process utilizes two fluid bed contactors to process a wide variety of solid and liquid wastes. Figure 6 provides an overview flow diagram of the THOR<sup>sm</sup> process.

Radioactive waste feeds are received from waste generators and stored in hold up tanks. Solid, dry, granular wastes, such as charcoal, graphite, soil, etc., are metered into the pyrolyzer by the solids feeder. Liquids and slurry wastes, such as ion exchange resins, sludges, oils, antifreeze, solvents, cleaning and decontamination solutions, are metered into

the pyrolyzer by a pump. In the pyrolyzer, the input feed is distributed by a fluid gas (which is superheated to near operating temperature) and mixed with the fluidizing media. The fluid gas includes steam, which is important to the steam reformation stage of the process. The fluidizing media enhances heat transfer. The fluidizing media is retained in the pyrolyzer by gravity, while the pyrolysis residue follows the pyrolysis gases and fluid gas into the filter house. Ceramic filters separate the solids from the gas. The solids are transferred to a steam reformer where steam is introduced. Carbon fines left over in the solid residue is completely gasified, and the radioactive solid retained in the bottom of the steam reformer is drained into high integrity containers for final disposal.

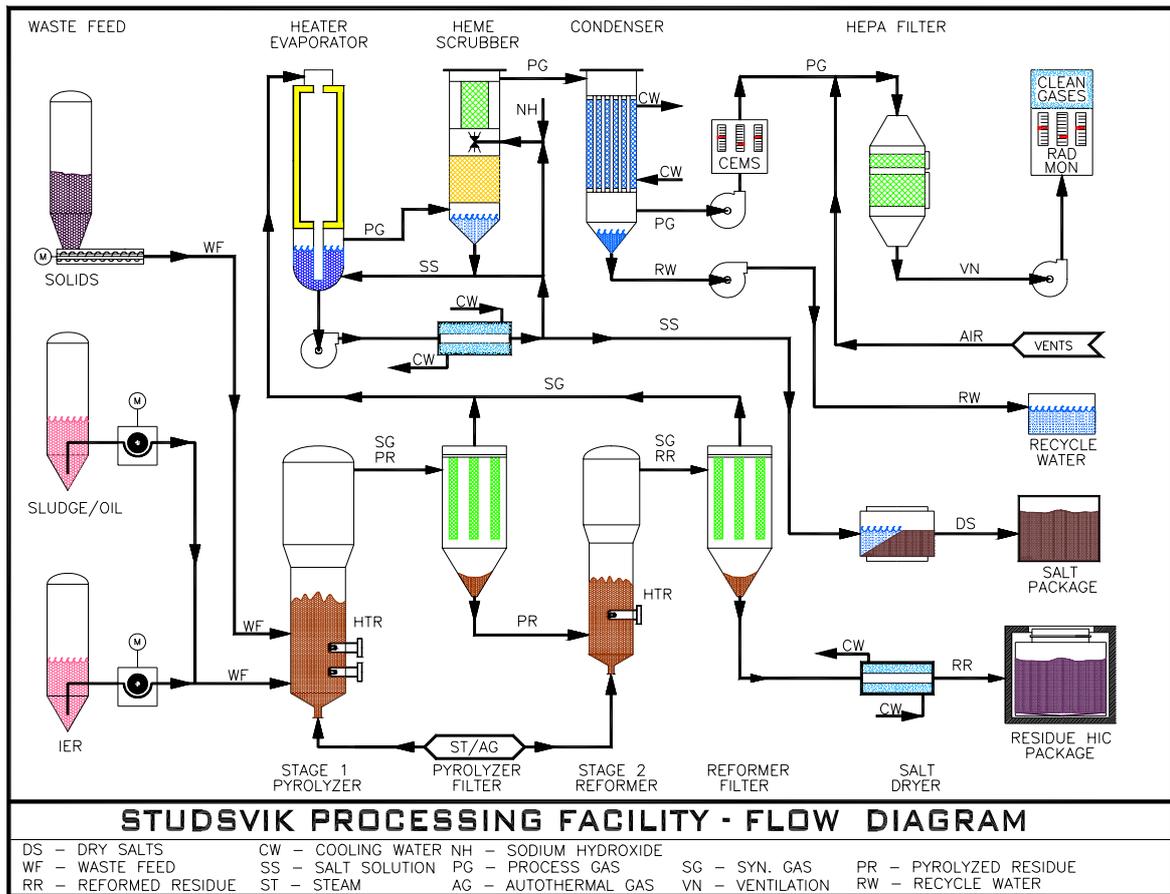


FIG. 6. Flow diagram for pyrolysis processing facility.

The gas leaving the filter has a high caloric value, and constituents like sulfur will be present in normally a oxidized state as sulphur dioxide. There are several options for gas treatment. The option chosen by SPF is oxidation by pure oxygen in a thermal oxidizer, followed by quenching in a quencher/scrubber containing a sodium hydroxide water solution. Sulfur is efficiently trapped in the scrubber. The off-gas system is a classical design. One unique feature of the THOR<sup>sm</sup> process is that mineralizing additives can be injected into the pyrolyzer to convert halogen and sulphur salts and alkali metals directly into water insoluble aluminosilicate minerals that can provide very efficient removal of acid gases even without the use of a downstream scrubber.

#### 4.4.1.2. *Applicable waste types*

General types of waste suitable for pyrolysis are ion exchange resins, oils, organic solvents, sludges, plastics, filters, rubbers, cellulosic materials and soils. Of particular value, fixed pyrolysis plants are capable of processing highly radioactive wastes (e.g. 1 Sv/hr).

Specific examples of wastes suitable to pyrolysis are salt cakes and supernatant solutions that contain high concentrations of sodium, aluminum, nitrates, nitrites, nitric acid, hydroxides, and sulfates contaminated with substantial amounts of radionuclides, chlorides, fluorides, phosphates, heavy metals, and many other inorganic elements as well, organic solvents, spent activated carbon, sludges, off-gas scrubber recycle streams, decontaminating solutions, oils, ion exchange media and resins, plastics, sodium hydroxide solutions, and wastes with high concentrations of Cl, F, S, P, and heavy metals.

Wastes with high activities and dose rates are suitable to pyrolytic processes. For example:

- Alpha activities to 4.8E+07 Bq/l
- Beta activities to 8.6E+06 Bq/l
- Total activities to 5.22E+12 Bq/m<sup>3</sup>
- Exposure rates on the order of 4 Sv/hr

Wastes from plutonium production glove boxes, plutonium extraction solvent facilities, NPP production facilities, and various other types of facilities have been successfully processed through pyrolytic systems.

#### 4.4.1.3. *Expected end product*

The primary end product of pyrolysis/steam reforming is a granular flowable material of a highly inorganic nature, where the inorganic materials are mostly metal oxides and salts. The activity concentrations are higher than the input waste, as is to be expected, and consideration should be made as to waste classification and disposal criteria for the resultant waste stream prior to processing. Blending of various activity wastes is often required to achieve the desired waste classification in the end product. If a monolithic form is required, post treatments, such as those below, can be employed:

- solidified monolith using polymer sulphur cement, portland cement, thermoplastics or polymers;
- vitrified monolith using borosilicate or phosphate glass; or
- melted metal monolith
- compacted, cold-sintered, high density, metal oxide monolith;

Secondary wastes are also produced as part of the routine operation of the pyrolysis plant, with the most significant quantities being protective clothing worn by workers within the plant. Scrubber salts are also generated by the off-gas scrubbers.

#### 4.4.2. **Advantages**

The following advantages apply to pyrolysis:

- Low process temperatures. Volatile species of concern such as ruthenium and cesium are retained within the pyrolyzer residues.
- Low gas flows limit the entrainment of radionuclides by flowing gas.
- Ability to process waste with high water and organic content.
- Can be used for high dose rate wastes.
- Can handle a wide variety of mixed wastes, including wastes with high alkali metal, heavy metal and acid gas content.
- Retention of radioactivity in the pyrolyzer residue is > 99.99%. Tritium, carbon-14 and volatile iodine is not retained (are released to the off-gas system).
- Can be shut down quickly in case of unexpected incidents.
- Pyrolysis has thus far been accepted by the public in currently installed locations.
- Low gas flow rates (compared to incineration); hence smaller and more compact off-gas handling equipment is required.
- Insignificant NO<sub>x</sub> production, as the process is reducing and, by definition, does not use free oxygen.
- End product is easily managed (although highly concentrated) and can either be directly disposed [22], vitrified, or solidified with cement, plastic polymers, wax, etc.
- End product can be suited to elemental separation for recycling (especially of fissile isotopes).
- Higher activities and high alpha emitter concentrations are possible, because the lower gas flow rates do not present significant carryover issues.
- The processes can be heated externally, thus minimizing gas flows which would otherwise require radiological control.

#### **4.4.3. Limitations**

The following limitations apply to pyrolysis:

- A specific pyrolyzer rarely is able to handle all types of waste and extensive waste pre-treatment can be required, which increases overall costs. In practice, the choice of pyrolyzer is related to specific applications. There are several engineering options as to pyrolyzer design. Pyrolyzers could utilize fluidized bed, flash pyrolysis, entrained flow, fixed bed, horizontal moving bed and rotary kiln to mention some.
- In general the pyrolysis residue (end product) is granular whereas the user of the system may require a monolithic form. If the monolithic form is required, a secondary conditioning process is required, which again would increase overall costs.
- Feed form is preferably as gas, liquid, slurry or solids. The particle size must generally be below 5 cm to enhance heat transfer; however, larger size objects have been successfully processed.
- Sodium/potassium bearing waste might cause operational problems for fluidized bed pyrolyzers. Alkali metals have the capability to form low melting eutectic salts which make the solid fluidizing media ineffective because the eutectic are condensed on the media. The THOR<sup>sm</sup> process has solved the problem by introducing additives to the

feed which complex the salts to form higher melting point species which will not melt at the lower operating temperatures.

- If halogenated plastics are processed, off-gas treatment may have to address dioxin and dibenzofuran constituents.
- Pyrolysis has extensive commercial experience in the processing of high organic content waste, but it has limited experience in processing of inorganic waste with a stabilized (monolithic) end product.

#### 4.4.4. Operational experience

Operational experience is provided for three different operating pyrolyzers designed for specific applications and which provide a representative perspective of overall experience and the diversity of pyrolysis systems.



*FIG. 7. Pyrolysis plant at Belgoprocess, Belgium.*

A pebble pyrolysis reactor using calcium hydroxide was developed in Germany for treatment of ILW radioactive resins and spent reprocessing solvent in kerosene [23]. One such system was started in 1999 at Belgoprocess in Belgium for treatment of TBP (tributylphosphate), kerosene and hydraulic oil containing significant amounts of  $\alpha$ -emitters (magnitude of 1 GBq/m<sup>3</sup>) [24]. This type of thermal process was selected because it can cope with  $\alpha$ -emitters and the resulting, aggressive phosphoric acid by-product.

Compared to other pyrolysis units, the difference in process for treatment of the liquid waste is the feed system. The moving balls improve heat transfer and can also crush the solids produced by the pyrolysis. At a temperature of about 600°C and under an inert atmosphere of nitrogen, the TBP, kerosene and oil is broken down into phosphoric acid and hydrocarbons.

The phosphoric acid reacts with the calcium hydroxide and is converted to calcium phosphate. This end product is collected in drums along with the ashes at the bottom of the pyrolyzer, and they are subsequently solidified in a 400 l drum with cement. The evaporated hydrocarbons are transferred to the afterburner where they are converted to CO<sub>2</sub> and water at a temperature of about 1000°C. As in all waste processing facilities the off-gases are scrubbed and filtered before being released to the atmosphere.

Another example of a pyrolysis process is the IRIS plant at Valdouc in France which treats  $\alpha$ -bearing solid waste (Figure 8). The plant started up in 1996 and has a capacity of 7kg/h. A typical waste composition includes 55% plastics (polyvinylchloride/PVC and polyethylene/PE), 35% latex and neoprene rubber, and 10% cellulose. A waste pre-treatment (sorting and segregation) is necessary in order to remove metal constituents. The waste is then pyrolyzed at 550°C in an electrically heated, rotating cylindrical kiln under inert gas. The resulting solid residue is then calcined at about 900°C in an electrically heated rotating kiln in oxygen enriched air. The pyrolysis and calciner off-gasses are ducted to an afterburner furnace for complete combustion of all flammable gases. The obtained ash is experiences a nearly complete burnout (carbon content lower than 1%), and it is possible to extract the plutonium out of the ashes [25] Table V provides the results of the first two test campaigns at the IRIS Facility.

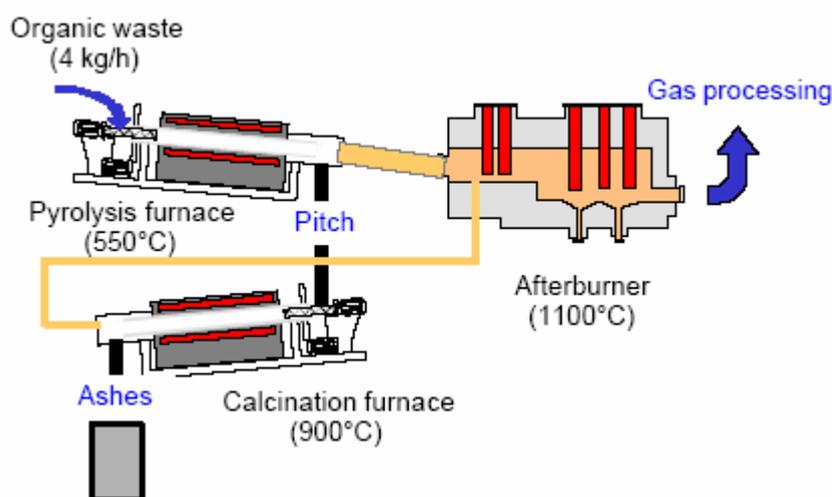


FIG. 8. IRIS Plant in Valdouc, France.

TABLE V. TEST CAMPAIGNS DATA FOR IRIS FACILITY, FRANCE

Parameter		1 <sup>st</sup> Campaign	2 <sup>nd</sup> Campaign
Incinerated waste weight	(kg)	395.0	360.0
Waste activity	(GBq·kg <sup>-1</sup> )	0.2	1.1
Ash weight	(kg)	16.0	20.3
Waste/ash weight ratio		24.7	17.7
Pu in waste stream *		33.8	179.0
Pu in ash **		29.3	162.0

\* Measurement uncertainty:  $\pm 20\%$

\*\* Measurement uncertainty:  $\pm 12\%$

A commercial pyrolysis processing facility has operated in Erwin, Tennessee (USA) since 1999. The Studsvik Processing Facility (SPF) is heavily shielded, can handle highly radioactive wastes (e.g. 1 Sv/hr), and has the capability to process a wide variety of radioactive streams, including ion exchange resins, charcoal, graphite, sludge, oils, solvents, cleaning solutions, and solids such as filters, plastic, wood, rubber, etc. Volume reductions of up to 70:1 and weight reductions of up to 30:1 have been achieved.

The design throughput is 0.25 kg/h. As of May 2006, the total volume and weight of resins processed since start up amounts to 191,967 ft<sup>3</sup> (5 430 m<sup>3</sup>) and 9,750,538 lbs (4,432 metric tonnes), respectively [25]. The total activity processed over the same period was 67,537 Curies (2.5E+03 TBq). During 2004 and 2005 the average contact dose rates for spent ion exchange resin were 0.16 Sv/h. However, wastes with contact doses as high as 400 R/h (4.0 Sv/hr) have been processed.

#### 4.4.5. Other considerations

Depending on the design, a pyrolytic system is generally a high technology cost and can be applied to small to large volume waste streams. Cost is driven by the complexity and the degree of regulation (e.g. fissile, mixed) of the waste to be treated. Refer to Table VI for a brief assessment of the implementation considerations for pyrolysis.

TABLE VI. IMPLEMENTATION CONSIDERATIONS FOR PYROLYSIS

Consideration	Range
System procurement Cost	Medium to High
Life Cycle Cost	High
Waste Volume	60 m <sup>3</sup> to 1200 m <sup>3</sup> (current systems)
Environmental Implications of System	Low environmental impact High degree of regulation
Regulatory Requirements for System	High degree of Regulatory work in construction and operation
Throughput	<1 Kg/h to 12 Kg/h current systems Can be extended to beyond 500 Kg/h

## 4.5. THERMOCHEMICAL TREATMENT

### 4.5.1. Brief description

Thermochemical treatment is a thermal desorption process using powdered metallic “fuel,” such as aluminum or magnesium, which interacts with the waste both chemically and physically through reaction with the water present in the waste. This results in the formation of hydrogen gas and heat; the subsequent combustion is used to destroy the organic material, resulting in solid slag or ash. The hydrogen gas burns because of the presence of enough oxygen, and in co-reaction the waste is combusted and brought into a slag-like form. The presence of excess metal powder suppresses the production of corrosive gases.

### 4.5.2. Process description

Thermochemical processing technologies are used for treating and conditioning problematic radioactive wastes. The thermochemical processing uses powdered metal fuels (PMF) that are specifically formulated for the waste composition and react chemically with the waste components. The composition of the PMF is designed in such a way as to minimize the release of hazardous components and radionuclides in the off-gas and to confine the contaminants in the ash residue. The thermochemical procedures allow decomposition of organic matter and capturing hazardous radionuclides and chemical species simultaneously.

A significant advantage of thermochemical processing is its autonomy. Thermochemical treatment technologies use the energy of exothermic reactions resulting from combining radioactive or hazardous waste with PMF. By using the energy of exothermic reactions as the heat source, the problems concerned with heating method choice, appropriate heating equipment operation, and maintenance of equipment reliability are excluded. Generally, the PMF consists of combustible powder metal, an oxygen containing component, and some additives (pre-forming materials, stabilizers, surface-active substances, and others), with a predominance of metal powder. As would be expected, a thermodynamic simulation is applied widely during the design stage of the PMF.

#### 4.5.2.1. Waste types applicable

The thermochemical treatment technologies were developed and demonstrated to be feasible as follows:

- (1) Thermochemical decontamination of metals, asphalt, and concrete.
- (2) Processing of spent ion exchange resins, plastics, polymers, medical waste, biological objects.
- (3) Autonomous vitrification of ash residues, calcinates, spent inorganic sorbents, contaminated soils, and the like.
- (4) Processing of carbon with  $^{14}\text{C}$  retention (reactor graphite, lubricants, moulds, etc.).
- (5) Processing of fuel rod zirconium by chemical including into mineral-like materials.

#### 4.5.2.2. Expected end product

Due to heating, the radionuclides are mostly volatilized and subsequently trapped in the slag layer, which is produced as a result of PMF combustion. Thermochemical interaction with the slag layer can also result in removal of a near surface layer along with contaminating radionuclides.

### 4.5.3. Advantages

The following advantages apply to thermochemical treatment:

- Complete destruction of organic molecules.
- Avoidance of emissions of radionuclides, heavy metals, and chemically hazardous species.

- The heat source for a thermochemical treatment technology is the energy of exothermic reactions from mixing radioactive or hazardous waste with PMF.
- This eliminates many of the challenges inherent in most other thermal technologies, such as heating method choice, appropriate heating equipment operation, and maintenance of equipment reliability.
- The environmental impact is expected to be relatively low.

#### 4.5.4. Limitations

The following limitations apply to thermochemical treatment:

- The production of hydrogen gases requires great care.
- A thermodynamic simulation must be applied widely at the design stage for the PMF. This requires significant technical skill and appropriate software, which adds to the expense and lead time for implementation.

#### 4.5.5. Operational experience

This process has not fully matured through broad implementation. However, it has been used in batch processes in the Czech Republic to decontaminate surfaces, process ion exchange resin, incinerate animal cadavers, vitrify contaminated clays, stabilize reactor graphite (and retain the predominate quantities of C-14), and stabilize irradiated Zr. A photograph of a mobile facility is provided in Figure 9. Some results from preliminary uses are included in Tables VII and VIII. Additional information can be found in reference [26].



*FIG. 9. Mobile test facility for thermochemical treatment of ion exchange resins.*

TABLE VII. THE CHARACTERISTICS OF THERMO-CHEMICAL DECONTAMINATION PROCESS.

Radioactive waste content (wt. %)		Maximum process temperature (°C)	Carry over of aerosols (wt. %)	Carry over of <sup>137</sup> Cs (%)	Leach rate (g/(cm <sup>2</sup> ))	
Ash residue	Soil				<sup>137</sup> Cs	<sup>239</sup> Pu
50	-	1530	1.9	0.9	9.0 10 <sup>-6</sup>	5.4 10 <sup>-6</sup>
60	-	1200	1.0	0.3	7.9 10 <sup>-5</sup>	7.0 10 <sup>-5</sup>
-	45	1900	2.2	3.1	1.0 10 <sup>-5</sup>	-
-	56	1520	1.0	1.3	2.1 10 <sup>-6</sup>	-

TABLE VIII. PARAMETERS OF RADIOACTIVE WASTE THERMOCHEMICAL TREATMENT PROCESS AND END PRODUCT

Radioactive waste content (wt. %)		Maximum process temperature (°C)	Carry over of aerosols (wt. %)	Carry over of <sup>137</sup> Cs (%)	Leach rate (g/(cm <sup>2</sup> ))	
Ash residue	Soil				<sup>137</sup> Cs	<sup>239</sup> Pu
50	-	1530	1.9	0.9	9.0 10 <sup>-6</sup>	5.4 10 <sup>-6</sup>
60	-	1200	1.0	0.3	7.9 10 <sup>-5</sup>	7.0 10 <sup>-5</sup>
-	45	1900	2.2	3.1	1.0 10 <sup>-5</sup>	-
-	56	1520	1.0	1.3	2.1 10 <sup>-6</sup>	-

#### 4.5.6. Other considerations

##### 4.5.6.1. Design scale

The thermochemical treatment process can be designed for small to large applications.

##### 4.5.6.2. Cost

The technology cost for a thermochemical treatment base process is expected to be low. However, the safety aspects related to the generation of hydrogen will most likely significantly increase the costs.

##### 4.5.6.3. Mobile or fixed

Mobile units may be applicable if the safety aspects can be handled. Certainly decontamination of building surfaces is inherently a mobile process.

##### 4.5.6.4. Environment/regulatory issues.

Because the process is not restricted to a fixed facility, each application of the process may require licensing. For example, the hazard analyses associated with fire and deflagration

(intense heat), as well as the containment and monitoring of off-gas emissions, will require permitting or licensing for each application.

The process includes a somewhat open flame, which presents certain fire control requirements and which will also require permitting or licensing for each application.

## 5. CONDITIONING METHODS

### 5.1. METAL MELTING

#### 5.1.1. Brief description

Metal melting is a thermal desorption process. Melting of metals can have several purposes, including:

- minimizing the disposal volume of metals;
- homogenization of the material for disposal;
- binding the activity to the metal;
- simplifying and obtaining more precise measurements of activity in the material; and if possible
- allowing the resultant metal monolith to be cleared for unconditional release or conditional reuse.

Melting is a simple process from a technical perspective. It involves applying enough energy to a component to raise its temperature above the melting point and hence melt the original component into liquid material. The liquefied material can be poured into moulds and allowed to cool into a solid mass with a reduced disposal volume. The overall volume reduction is attributable to the elimination of void spaces and the resultant increase in density.

In metal melting, the waste feed material, usually scrap metal, is fed into a furnace. Additives (such as fluxing agents) may be used to improve slag separation and trapping of certain radionuclides. After melting, the slag is removed, samples for determination of the remaining content of radioactivity are taken, and the molten metal is poured out into a solid form.

The most commonly used furnace type for melting metals from the nuclear sector is the induction furnace, which is illustrated in Figure 10. It is an alternating current (AC) electric furnace in which the primary conductor generates, by electromagnetic induction, a secondary current that develops heat within the metal charge. The induction furnace has the added advantage over other furnace types that induction ensures the material in the furnace is fully homogenous.

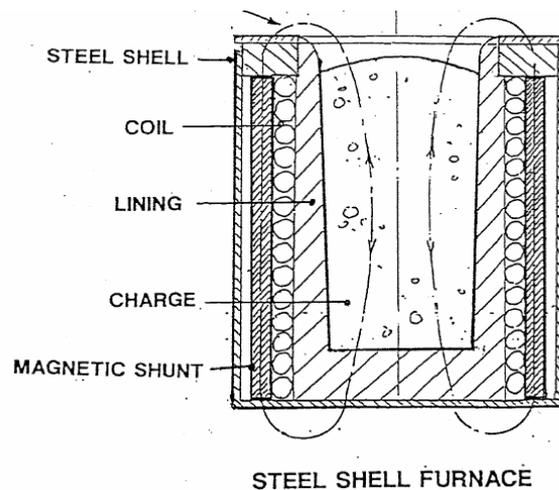


FIG. 10. Principal structure of a steel shell induction furnace.

The homogeneous melted metal can be formed into different final forms depending on requirements. It can be poured into molds and cooled to make ingots; centrifuged to make waste container cylinders; or poured into waste containers which are then directly suitable for disposal or storage. If the residual radioactivity level of the final product is acceptable, it may be cleared and recycled to the conventional metal industry [27] or reused within the nuclear industry (as shielding blocks for example).

During the melting process different elements and their radioactive isotopes are redistributed between the slag, the metal, and the off-gases depending on elemental properties. The more volatile elements (including their radioactive isotopes) – such as cesium, iodine or hydrogen (tritium) – leave the melt and are essentially transferred to the off-gases or, in some cases, to the slag. Some metallic elements (including radioactive isotopes) – such as cobalt, nickel, chromium, iron, zinc and manganese – mainly remain within the melt. Transuranic elements can be readily oxidized and will transfer to the slag [28].

#### 5.1.1.1. Process description

The melting process consists of:

- Preparation (e.g. segmentation, sorting, decontamination (if required))
- Melting
- Sampling and analysis
- Conditioning of secondary waste
- Recycling, decaying or final storage of metal product

#### 5.1.1.2. Waste types applicable

Most metal components can be subjected to melting. The required preparation and radiation protection arrangements will depend on the size, activity content, material, etc. The following materials are routinely processed in nuclear metal melting facilities;

- Ferrous metals (carbon steel and stainless steel)
- Aluminum
- Lead
- Copper and brass

The radioactivity of a metallic component can either be in the form of surface contamination or as activation of the metallic component, both of which can be melted. A combination of surface contamination and activation is also possible.

#### *5.1.1.3. Preparation*

Pre-sorting of the waste is required, as the melter will be dedicated to a specific purpose. For example, a metal melter will be limited to metals (ferrous metals, aluminum, lead, etc.) due to different melting points, furnace lining requirements, and contamination profile. In addition, metals must also be segregated as they have different properties and downstream applications (e.g. steel melts at a higher temperature than aluminum and, as an end product, makes a better radiation shield).

It is very important to verify that the metal does not include closed compartments. A closed compartment, especially if it contains a liquid, will cause a very dangerous situation when heated within the furnace as a result of the increase in volume of trapped liquids/gases (e.g. a steam explosion). This may cause severe damage to operators and facility. Therefore, careful inspection of the metals to be melted is required prior to melting.

Also prior to melting, most materials need to be segmented. The required size reduction is depending on the size of the furnace and access port to be used.

To reduce the activity content in the end product, different decontamination methods can be used either prior to melting or as part of the melting process. For example, decontamination could be necessary in order to minimize the radiation exposure to the personnel during the pre-treatment and melting process. Decontamination prior to melting is beyond the scope of this report. Decontamination of metals by melting comprises additives, and special procedures are applied during the melting step in order to redistribute the radioactive elements.

#### *5.1.1.4. Expected end product*

The final product (ingot, shielding block, centrifugated steel cylinder, etc.) is homogeneous, stable, and has the remaining activity content bound in the metal. Melting can produce a conditioned waste form suitable for direct disposal.

The melting process, including the preparation processes, produces the following waste types:

- Pre-sorted material not suitable for melting which must be managed separately.
- Cutting residues from segmentation.
- Decontamination residues (wet or dry waste from chemical decontamination, blasting residues from mechanical decontamination and various residues/activity carriers from thermal decontamination methods).

- Slag from melting.
- Dust from melted filters.
- Operational waste, such as the lining from the furnaces.
- Homogenised end product (mixed metals) that is not suitable for recycling.
- Heterogeneous end product (e.g. steel shield block) suitable for recycling.

Normally, the amount of secondary waste is in the range of 2% to 5% (by weight), excluding any final product and operational waste (e.g. used lining, replaced filters etc.).

### **5.1.2. Advantages**

Metal melting provides the following advantages:

- Extensively proven technology.
- High volume reduction, typically 5:1 to 20:1 [27]. If recycling is possible, volume reduction factors (from a disposal perspective) of up to 100:1 are possible.
- The end product can be well categorized with regard to activity content and from a metallurgical stand point.
- The end product is typically homogeneous and stable with the remaining activity content bound in the metal.
- A heterogeneous end product has the potential to be re-used or recycled within the nuclear industry or after clearance within the conventional metal industry.

### **5.1.3. Limitations**

Metal melting has the following limitations:

- For the purposes described in nuclear waste management applications, melting is limited to metals.
- Pre-sorting is usually required due to dedicated melt furnaces and differences in melt temperatures of the different metals.
- Treatment by melting of mixed metal components (such as small electric motors) is normally not economical.

### **5.1.4. Operational experience**

An alphabetical summary of the operational experience from melting of scrap metal from the nuclear industry at major nuclear melting facilities is provided in Table IX.

TABLE IX. SUMMARY OF OPERATING EXPERIENCE FOR METAL MELTERS

Facility, start of operation	Furnace type	Types of metal treated	Charge size (ton)	Products	Radiological limitations	Quantity of scrap melted	Recycled/ released
CAPENHURST UK, 1994	Induction	Aluminum, brass, copper	4	Ingots		7,000 t	Recycling
CARLA, Siempelkamp Germany, 1989	Induction	Carbon steel, stainless steel, aluminum, copper and lead	3.2	Ingots, shield blocks, waste containers	Max 200 Bq/g (beta/gamma), Max 100 Bq/g (alpha), separate for uranium	15,000 t (1989-2005)	Most metal recycled in nuclear industry. A minor amount have been recycled for free release .
CENTRACO, France 1999	Induction	Carbon steel, stainless steel and to less extent non ferrous metals	4	Ingots and tubes	Max 20 000 Bq/g (beta/gamma), Max 370 Bq/g (alpha)	12,000 t (1999-2005)	Recycling in nuclear industry
DURATEK Plant, Oak Ridge, United States of America, 1992	Induction	Carbon steel, stainless steel, aluminum (planning to melt copper and titanium)	20	Ingots, shield blocks, waste containers and reinforcing steel	Normally <2 mSv/hr	2,000 t	Recycling in nuclear industry
ECOMET-S, Russian Federation	Induction	Carbon steel	2.5	Ingots	Max 100 Bq/g	8,000 t	Recycling
INFANTE, Marcoule France, 1992	Electric Arc	Carbon steel, stainless steel	12	Ingots, shield blocks, waste containers	Max 250 Bq/g for Co-60, other limitations for other nuclides	5,000 t	Stored, recycling in nuclear industry
STUDSVIK, Sweden, 1987	Induction	Carbon steel, stainless steel, aluminum, brass, copper and lead	3.5	Ingots, shield blocks on request	Varies with type of material and preparation to be done	12,000 t (1987-2005)	95% recycled directly or after free release

### 5.1.5. Other considerations

#### 5.1.5.1. Scale/throughput

A melting facility for radioactive scrap metal is normally to the scale of a small foundry. It is important to optimize the size of the furnaces. A small furnace requires more preparation

work (segmentation). A larger furnace requires a higher investment and larger melt batches. Based upon the experience from the operators of metal melters within the nuclear industry, the furnace should have a typical capacity of at least 3 tonnes of steel. A 3-tonne furnace allows melting of about 6-10 tonnes per eight hour shift.

#### *5.1.5.2. Cost*

Metal melting a high cost technology from life cycle perspective. The cost to construct a melting facility with a 3-tonne furnace is in the range of \$5 to \$10 million USD if the facility is built on a nuclear site with the required infrastructure pre-existing. If constructed and licensed as a new separate or commercial enterprise, the capital costs are considerably higher. The overall investment is much larger considering operating costs and decommissioning.

#### *5.1.5.3. Mobile or fixed*

A mobile melting facility is typically not economical. However, the pre-treatment steps (segmentation and decontamination) can be mobile. Large commercial melting facilities are available internationally and transport of metal to these facilities for processing is an option.

#### *5.1.5.4. Environmental/regulation issues*

Licensing should not be a major issue, since all major risks for a properly designed facility are the same as for conventional foundries (i.e. they are well-known and mitigated through extensive experience). However, the possibilities for licensing of a nuclear melting facility may vary between different Member States.

The environmental impact from a melting facility with a state of the art off-gas filtration system is very limited. The positive environmental impact is that metals can be recycled. For example, compared to the energy cost of producing virgin aluminum from raw materials, it requires just 5% of the energy to recycle aluminum.

## 5.2. PLASMA

### **5.2.1. Basic description**

Plasma sources of heating (plasma torches) are devices alternative to liquid-fuel nozzles or gas burners. In contrast to the latter, plasma sources provide deep thermal conversion of organic materials and produce an end product in the melted state. Plasma torches use the energy of an electric discharge (electric arc) for heating working gases transmitted through it. Both chemically inert gases (nitrogen, argon, helium) and chemically responsive gases (oxidizers = oxygen, air; reducers = hydrogen) can be used as the working media. The temperature of the gas stream at the output of the plasma torch can achieve several thousand degrees centigrade.

In contrast to radioactive waste incineration and other technologies which rely on the combustion of an organic (hydrocarbon) fuel, plasma torches enable thermal conversion to occur in a relatively small volume with high efficiency. This is due to the fact that plasma torches provide a high degree of concentration of the thermal energy in the plasma jet.

Plasma technology has been used extensively and for many years outside of the nuclear industry for the production of high purity metal alloys and for the plasma synthesis of acetylene. Plasma treatment introduces the required energy directly into the waste material.

As a result, the relatively higher flame temperature of the plasma burner ensures continuous melting and decomposition of the waste material.

The treatment of solid radioactive waste using plasma heating sources occurs in primary reaction chambers. Subsequent stages include those of thermal conversion of waste materials with formation of inorganic slag, gasification of organic components, homogenization, melting slag residue, and pouring of the melt into receiving containers. The process may be carried out either in periodic (batch loading) or continuous mode.

Liquid radioactive waste may also be treated by injection into the stream of plasma gas or simultaneously with solid waste in the primary reaction chamber.

Due to the higher temperature range of the plasma treatment process compared to conventional methods of radioactive waste incineration, the range of applicable waste types is much greater. The waste feed can include not only solid organic waste, such as paper, wood, plastics and rubber, but also inorganic and mixed materials (debris, soil, scrap metal, thermal insulating materials, glass,). The percentage of inorganic materials in the total waste volume can be as high as one hundred percent depending on the waste origin and composition.

#### *5.2.1.1. Plasma torches*

The plasma torch is a design comprised of several concentrically-arranged tubes that are water cooled. The outermost tube is also clad with refractory material to enable the burner to withstand the high temperatures within the processing chamber.

Plasma torches contain the following main components:

- Torch with electrodes
- Power supply unit
- Control and instrumentation system
- Cooling water circuits
- Process gas supply (e.g. N<sub>2</sub>, air or O<sub>2</sub>)

There are two main torch types :

- Transferred torches
- Non-transferred torches

In transferred torches , the plasma torch transfers electrical energy from the anode to the molten slag which serves as the cathode. By this principle the energy is transferred directly and more efficiently into the waste material to be heated. An example of a transferred torch is presented in Figure 11 [29].



*FIG. 11. Example of a transferred torch.*

A non-transferred torch contains two metallic tubular electrodes (upstream and downstream of the plasma flow direction) separated by a gas injection chamber. An electrical arc flows between the negative and positive electrodes; therefore, the gas flow injected into the chamber is ionized. The result is a high temperature gas flow coming from the downstream electrode in a plasma jet.

Transferred torches normally induce higher temperatures to the waste material. Power ratings typically range from 100 kW to several MW. Process conditions can be varied from inert (e.g. Ar or N<sub>2</sub>) to oxidizing (e.g. air or pure O<sub>2</sub>) through the selection of the plasma gas.

The most sensitive components on plasma torches are the copper electrodes. The first electrodes had service lives of only several hours, which has been improved considerably (up to 500 hrs).

The typical temperature of the plasma “flame” from a non-transferred torch is about 5,000°C, which is lower than that of transferred torches but still high enough to treat a variety of heterogeneous wastes with different melting points.

#### *5.2.1.2. Feeding systems*

The choice of feeding systems has a direct effect on processing parameters. Two possible feeding systems are:

- Batch feeding system
- Continuous feeding system

In a batch feeding system, the entire package or container filled with radioactive waste - such as metals, concrete debris and organic material -- is transferred via a feeding system into the primary chamber. In a continuous feeding system, the pace of loading of packed or shredded radioactive waste into the primary chamber is dependent upon the technology of treatment. With either approach, the feeding system should be hermetic (completely sealed) and prevent mechanical destruction of the inner surfaces of the high temperature zone inside the reaction chamber.

#### 5.2.1.3. End product

The end product of the plasma treatment system is a solid, glass-like material packed in metal or ceramic containers and suitable for direct disposal without any further treatment. The radioactive materials are immobilized. This end product has very high mechanical and chemical durability exceeding the equivalent properties of the glass matrices.

The homogeneous form of the slag consists mainly of amorphous material with a 10% to 20% crystalline phase. Treatment of radioactive waste of mixed types containing both organic and inorganic materials may result in obtaining a heterogeneous slag where the different residues of molten debris, metal, etc. form different inclusions or layers within the waste block. This technically has no direct impact on the acceptability of the final waste form for disposal.

The final product of plasma treatment may have a specific activity several times higher than the as-generated waste depending on the waste composition and volume reduction factor. This may impact the waste classification and acceptance criteria for the disposed package.

#### 5.2.2. Advantages

The following advantages apply to plasma technology:

- One single process can treat the waste as-generated (i.e. no prior treatment is necessary). This reduces the infrastructure costs and reduces the radiation exposure to personnel from duplicative handling of the waste.
- The final waste form is robust, free of organic material, and suitable for long term storage and disposal.
- Volume reduction factors can range from 6:1 (typical ZWILAG results) for waste containing mostly metals and debris (including the waste containers) to 10:1 for treatment of mixed waste (typical RADON results) and to more than 100:1 for primarily organic waste.
- Since the heat source is a plasma instead of fossil fuels, there is less production of certain flue gases and the greenhouse gas CO<sub>2</sub>. This may lead to better public acceptance. (However, this is not to suggest that off-gases are eliminated, as is discussed in the limitations.)

#### 5.2.3. Limitations

The limitations of the plasma system are:

- If a homogeneous slag end product, similar to that of vitrification, is desired, then the process is expensive to construct and operate.

- There is limited full-scale plant experience. A first plasma unit for LLW came into commercial operation in 2004. However, several facilities are in advanced stages of start-up.
- To ensure efficiency of the unit, a waste acceptance criteria is required which covers the maximum allowable content of each waste type in the raw waste package.
- Compared to radioactive waste incineration, off-gases of some plasma processes may contain tens of grams of combustible components per kilogram of off-gases, along with increased concentrations of radioactive particles and nitrogen oxides. Therefore, the demands on an off-gas treatment system may be more considerable.

#### **5.2.4. Operational experience**

##### *5.2.4.1. ZWILAG plant*

The first full-scale plasma system, the ZWILAG facility in Switzerland, began operation with radioactive waste in 2004. The ZWILAG plant, serves to process combustible solid and liquid wastes, as well as metals and mineral substances (concrete, gravel, etc.). The maximum capacity of the facility is 200 kg/h of combustible waste and 300 kg/h of fusible waste [30]. At the ZWILAG site, the delivered, untreated wastes destined for processing are stored temporarily in buffer stores designed specifically for this purpose, and where they are assembled into actual processing cycles of approximately 300 drums per cycle. The plant is currently operated twice a year, each time for about six weeks. (This is due to the limited waste generation volume and is not a technology restriction.)

The process principles for the ZWILAG plasma system are shown in Figure 12 [31]. The processing of waste takes place by charging the plasma furnace with 200-litre drums of untreated waste, which are then introduced to the plasma stream and processed in batches. This means that only the contents of a single drum undergo processing at any given time. The entire process is largely automated and controlled remotely. This results in reduced radiation exposure for the operating personnel.

From the horizontal drum feeder, the waste falls onto the molten slag. Inorganic material is melted and becomes slag. Organic material is vaporized, and the remaining volatile gases are fed to the afterburner chamber. A rotating crucible (centrifuge) in the primary processing chamber moves the molten slag. Centrifugal forces keep the slag from the pour hole during processing. Pouring is achieved by opening the outlet of the throat and slowing down the centrifuge. The slag moves towards the centre and pours through the throat into a mold located directly below the throat in the slag collection chamber.

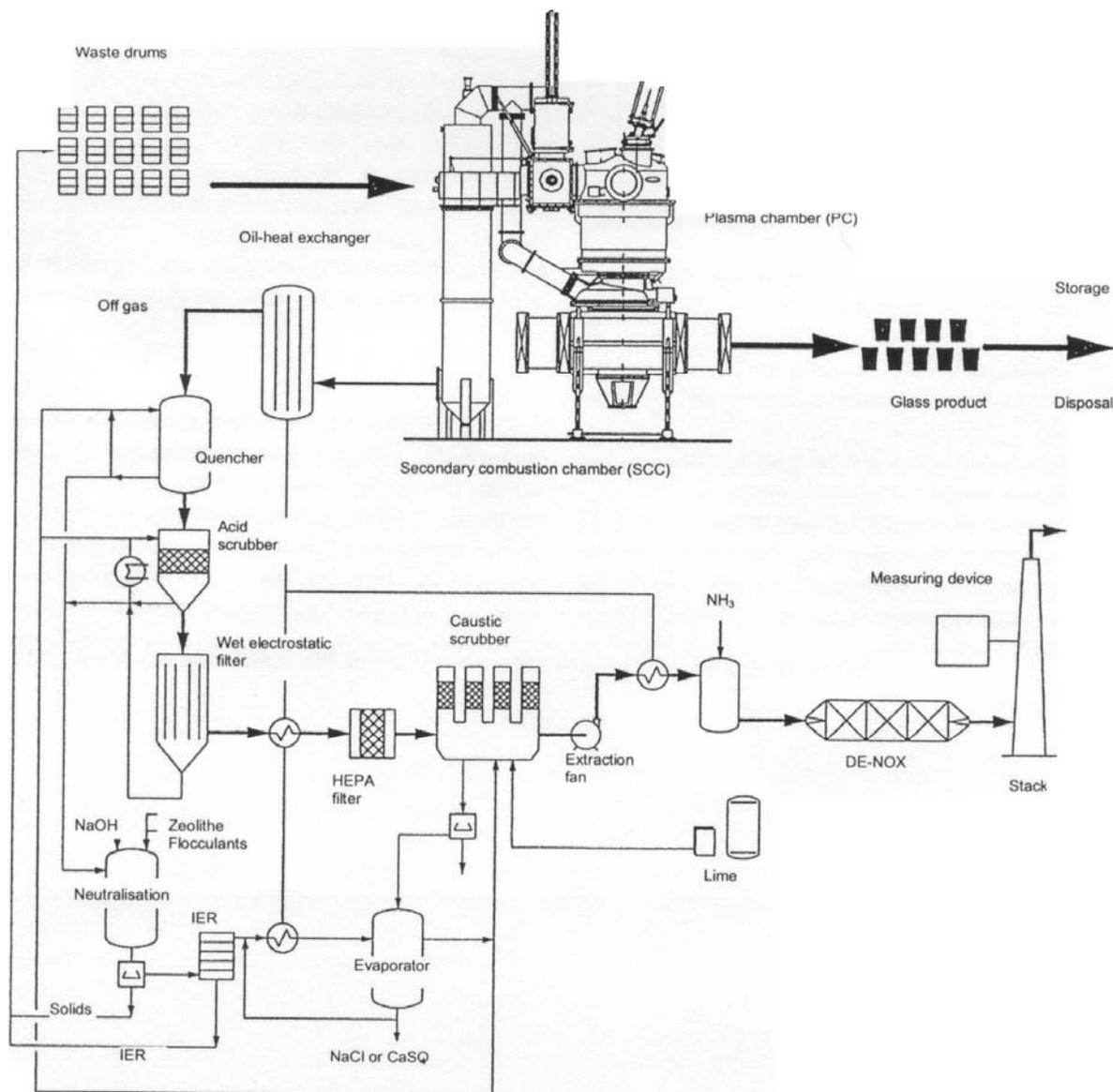


FIG. 12. Process diagram of ZWILAG plasma process, Switzerland.

After complete oxidation in a secondary combustion chamber, the flue gases emitted from the centrifuge chamber are routed to an off-gas treatment system, which can be divided into a wet physical and a wet chemical process. The wet physical process comprises a quencher, acid scrubber, and wet electrostatic filter, enabling a large portion of the gaseous and particulate materials to be separated. After passing through the HEPA filters, the caustic scrubber absorbs the remaining portions of acids, gaseous contaminants, and sulphur dioxide.

Redundant flue gas exhaust fans propel the flue gas stream through the off-gas treatment system and also maintain the required continuous negative pressure inside the entire system. Any nitric oxides still remaining in the flue gas are removed in the DENOX (de-nitrogen oxide, or nitrogen oxide removal) system through selective catalytic reduction. The clean gas attained by this purification method is permanently subjected to conventional emissions monitoring prior to being released into the environment from the building's integral

flue stack. Figure 12 includes a process diagram for the off-gas treatment system in the ZWILAG plasma melting plant.

The volume of waste processed to date is approximately 150 000 kg (80 000 kg active waste, 70,000 kg inactive waste). The current mean throughput is approximately 50 000 to 60 000 kg/yr. A target throughput of 80 000 kg/yr is being pursued.

#### *5.2.4.2. The industrial-scale plant “Pluton”*

SIA RADON, in Moscow, Russian Federation, operated an experimental plant named “Pluton” for plasma treatment of mixed solid radioactive waste. It operated with a throughput of about 40 kg/hr from 1998 to 2001 (see Figure 13 and Table X). SIA RADON then built an industrial-scale plant for treatment of mixed radioactive waste in a plasma shaft furnace with melted slag pour, which has a capacity up to 200 to 250 kg/h.

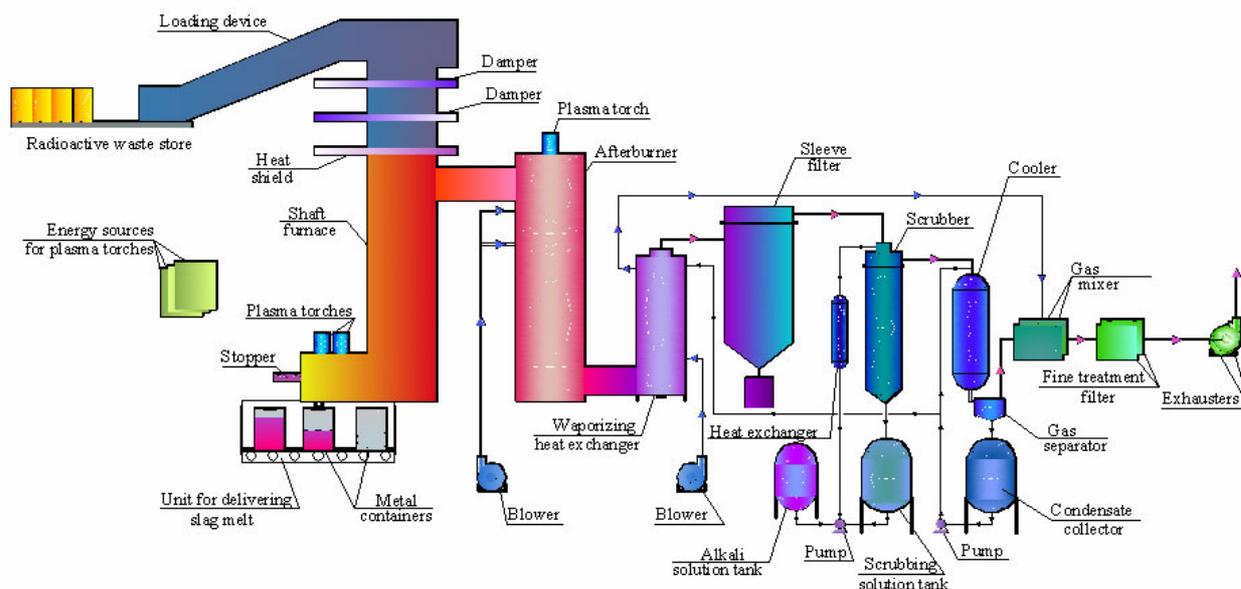


FIG. 13. The technological flow sheet of the plant PLUTON, SIA RADON.

TABLE X. THE COMPARATIVE CHARACTERISTICS OF THE SIA RADON PLASMA PLANTS FOR TREATMENT OF THE RADIOACTIVE WASTE,

Parameter name	"Pyrolysis"	"Pluton"
Capacity of solid radioactive waste, kg/h	40–50	200–250
Dimensions of the plant, m	8x8x10	12x18x12
Number of Plasma torches	1	2
Electrical capacity of the plasma torch, kW	70–120	100–150
Start up time (till beginning of loading), hours	3–4	6–10
Electric energy usage of plasma torches, kWh/kg waste	1–2	0.5–1.5
Degree of radionuclides escape from the furnace ( $^{137}\text{Cs}$ ), %	5–12	7–10

The shaft furnace is a refractory-lined steel hull. The height of the shaft from the hearth is 6.4 m with an internal cross section 0.8m x 0.8 m. The volume of the shaft filled with waste is 3.5 m<sup>3</sup>. The melting chamber is adjoined at the bottom of the shaft. Two plasma torches, rated 100 - 150 kW and providing a melt temperature of 1,500 to 1800° C, are placed in an oval vault. At the bottom of the hearth is a horizontal pouring channel and a stopper device for regulating the melted end product pouring into the containers through the vertical discharging branch pipe.

Waste packages are gravity -fed into the shaft and are subjected to heating, drying and pyrolysis in an oxygen-deficient atmosphere. The coke residue is gasified at the bottom part of the shaft.

Slag melt is collected in a melting bath, homogenized and then poured through the discharge unit into metal containers installed in a collecting box. The off-gas temperature at the output of the shaft furnace does not exceed 250 to 300°C. The cooled and solidified slag is sent to a long term radioactive waste storage site pending future availability of a repository.

Pyrolysis gases from the shaft furnace are directed into an afterburner (see Figure 14), where the combustible gaseous and solid aerosol components are burned at a temperature range of 1,200 to 1,300°C. Further off-gases are cooled to 300°C in a contact heat exchanger, and aerosol particles are trapped in a sleeve filter. The gaseous components (HCl, NO<sub>x</sub>, SO<sub>2</sub> etc.) are neutralized in the absorber and washed with an alkaline solution. The off-gases are then cooled, filtered and released into the atmosphere.

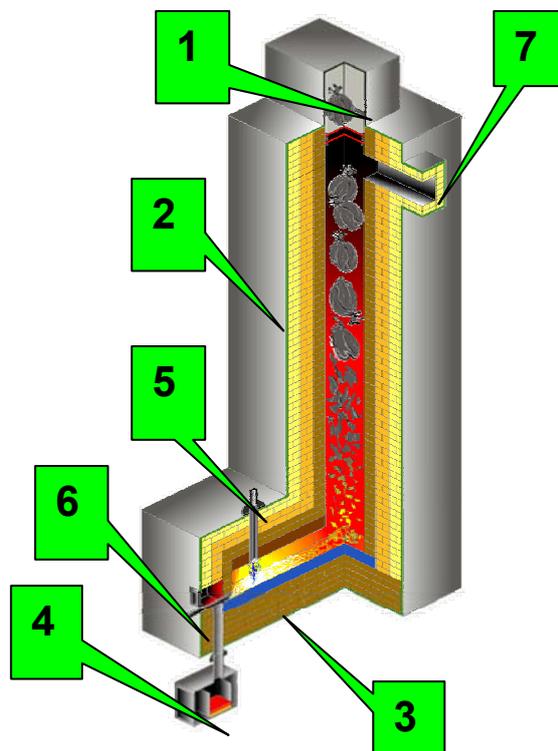


FIG. 14. Shaft furnace:

1 – loading unit, 2 – shaft, 3 – hearth, 4 – slag receiving box, 5 – plasma torch, 6 – stopper, 7 – pyrogas outlet.

## **5.2.5. Other considerations**

### *5.2.5.1. Scale and throughput*

A plasma treatment facility is normally tailored to the desired scale and throughput (expected annual as-generated volume) of the waste streams to be processed. There is no such facility to be obtained “off the shelf.”

### *5.2.5.2. Costs*

Life cycle costs are high for plasma technology. Therefore, it is crucial to operate with a sufficient input waste stream to justify the investments.

### *5.2.5.3. Mobile or fixed*

Being a rather sophisticated technology, the choice would be to have a fixed installation, either at existing nuclear facilities where the amount of waste production is sufficient or at a central or regional processing facility. Commercial mobile applications are not currently considered feasible for this technology. However, for specialty work, such as military site remediation or working on smaller test/research quantities, a mobile installation could be possible, but has not yet been realized.

### *5.2.5.4. Environmental/regulatory issues*

The installations existing to date meet the highest environmental and regulatory standards of the day. An effective off-gas treatment system is a must to achieve the regulatory standards for both nuclear and conventional emissions. These aspects are a vital part of the investment costs.

### *5.2.5.5. Technical issues*

On the one hand, specific energy consumptions of plasma treatment processes are comparable to the same characteristics of vitrification processes and much higher than the same indices for incineration technologies. On the other hand, it is possible to obtain with a single processing stage the conditioned product suitable for disposal and whose properties are competitive with vitrification.

Plasma technologies require special refractory lining materials which are durable to the extremely high temperatures and aggressive influence of the melting process and the melted residue. Using fluxes decreases the melting temperature of slag residue and makes pouring the melt easier; it also increases the potential for corrosion of the inner refractory lining. Similarly, to prevent untimely destruction of the facility equipment, the user of the plasma technology should restrict the content of chlorine and sulfur in the waste to be treated (e.g. PVC, rubber, ion-exchange resins, etc.).

Construction of a high-temperature reactor (melter) should contain a minimal quantity of water-cooled units to provide most the most effective heating slag and to prevent superfluous heat losses.

### 5.3. SYNROC

#### 5.3.1. Basic description

Synroc is a particular kind of “synthetic rock” which was invented in 1978 by the Australian National University. Synroc is a titanite ceramic-based matrix similar to naturally occurring minerals which incorporate actinides in nature.

##### 5.3.1.1. Process description

In this process, a “Precursor” is prepared (e.g. a tailored mixture of titanium oxide, zirconium oxide, calcium oxide, etc. which are the basic constituents of hollandite, perovskite, zirconolite and rutile). The Precursor is mixed with waste to form a slurry feed. The mixture is fed to a calciner where they are dried and calcined in a reducing atmosphere. The calcined product is then normally mixed with Titanium metal powder (around 2%) to act as an oxygen getter and first cold pressed. The cold pressed mixture is loaded in to a hot isostatic press, where it is pressed at 14–21 MPa at temperatures of around 1150<sup>0</sup>C. Increased waste loading has a desirable effect on SYNROCK processing, as it leads to a reduction in temperature required for compaction during the hot pressing phase.

One form of Synroc is called Synroc-C. The main minerals in Synroc-C are hollandite (BaAl<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>), zirconolite (CaZrTi<sub>2</sub>O<sub>7</sub>) and perovskite (CaTiO<sub>3</sub>). Table XI identifies the phase constituents of Synroc-C containing 20 wt% high level waste (HLW) [32]. The table demonstrates which radionuclides are incorporated into the various mineral phases.

TABLE XI. COMPOSITION AND MINERALOGY OF SYNROC-C

Phase	Wt.%	Radionuclides in lattice
Hollandite Ba(Al,Ti) <sub>2</sub> Ti <sub>6</sub> O <sub>16</sub>	30	Cs, Rb
Zirconolite CaZrTi <sub>2</sub> O <sub>7</sub>	30	RE, An *
Perovskite CaTiO <sub>3</sub>	20	Sr, RE, An
Ti oxides	10	
Alloy phases	5	Tc, Pd, Rh, Ru, etc

\*RE, An = rare earths and actinides respectively

Other alternatives to Synroc-C have been developed. The most favorable for the immobilization of plutonium has been pyrochlore-rich ceramics. Pyrochlore is similar to zirconolite and can be incorporated up to 50% by mass of PuO<sub>2</sub> and/or UO<sub>2</sub> [33].

##### 5.3.1.2. Expected final products

The end product is a solid monolith of Synroc, which has a high mechanical strength (> 200 MPa) and high density (4 to 4.35 g/cubic centimeter). It is impermeable to liquids and

gases, as its porosity and hydraulic conductivity are not measurable. It is highly resistant to oxidants and other corrosive environments. From a radiological perspective, it is highly compatible with wastes, has a high radiation resistance; and alpha decay damage is confined almost exclusively to pervoskite and Zirconolite phases. Thermal conductivity is low ( $< 2.0 \text{ W/m K}$ ), and it has a high thermal expansivity ( $> 5 \times 10^{-6} / ^\circ\text{C}$ ).

### **5.3.2. Advantages**

- Very effective means of immobilising high level radioactive wastes for disposal.
- Can be used to immobilise those wastes which can not be incorporated into a glass vitrification matrix.
- Chemically insoluble, high durability, low leaching characteristics.
- Suitable matrix for TRU.
- A wide range of radionuclides can be incorporated in to the crystalline lattices of the form.
- Crystalline phases are more stable and hence are more durable than amorphous solids such as glass.
- Possible to incorporate higher levels of actinides than borosilicate glass.
- Expected to be suitable for isolation for millions of years since it simulates natural rocks.

### **5.3.3. Limitations**

- There is limited commercial operational experience.
- Most efforts have been research-based.
- Generally not economical for low and intermediate level wastes.
- The Synroc waste form must be tailored to suit the particular characteristics of the nuclear waste to be immobilised.

### **5.3.4. Operational experience**

- Synroc was first developed in 1978 and R&D efforts have been conducted at the Australia Nuclear Science and Technology Organization (ANSTO) Research Facility.
- A pilot plant to manufacture Synroc using only radioactive material was constructed at Lucas Heights, Australia. The ANSTO demonstration plant can produce 50 kg monoliths with a throughput of 10 kg/hr.
- ANSTO and Argonne National Laboratory in the United States of America participated in a joint project in 1997 to demonstrate the technology on a commercial scale. Current status is unknown.
- ANSTO collaborated with Minatom in the Russian Federation for a pilot plant. Current status is unknown.
- ANSTO entered into an agreement with Nexia Solutions in the United Kingdom to treat five tonnes of plutonium waste at Sellafield in 2005. Current status is unknown.
- China has completed research into the chemical durability and performance assessment of Synroc [34].

### **5.3.5. Other considerations**

#### *5.3.5.1. Scale/throughput*

The Synroc technology is currently designed as small scale operations and with a relatively low throughput. There are no known commercial installations in operation.

#### *5.3.5.2. Costs*

Long term operating costs are unknown. Capital investment costs are likely low. However, research costs to develop a commercial installation are likely to be high.

#### *5.3.5.3. Mobile or fixed*

Likely the technology could be made mobile. Current facilities are local to existing nuclear facilities, although a central processing facility is a reasonable potential.

#### *5.3.5.4. Environment/regulatory issues*

As this is an emerging technology, regulatory issues will need to be explored further for each new installation. As the form simulates natural rock and is suitable for isolation of radionuclides, it is expected to be an acceptable waste form for achieving regulatory requirements.

## **5.4. VITRIFICATION**

### **5.4.1. Basic description**

#### *5.4.1.1. Process description*

Vitrification is defined as the process of incorporating materials into a glass matrix or glass-like form [8]. Vitrification involves melting of waste materials with glass-forming additives so that the final vitreous product incorporates the waste contaminants in its macro- and micro-structure. Hazardous waste constituents are immobilized either by direct incorporation into the glass structure or by encapsulation. In the first case, waste constituents such as Si, B, P are dissolved in the glass melt, thereby being included as part of the glass network upon cooling. In the encapsulation process, waste constituents such as Cs, K, Na, Li, Ca, Pb, Mg are confined within glass melt as modifiers (discrete components within the glass).

Encapsulation is applied to elements and compounds with a reduced solubility in the glass melt and which do not fit into the glass microstructure; they are neither network formers nor modifiers. Immiscible constituents which do not mix easily into the molten glass are typically sulfates, chlorides, molybdates, noble metals such as Rh and Pd and refractory oxides with high boiling point such as  $\text{PuO}_2$ , noble metal oxides and spinels. (Spinels are any of a group of minerals that are oxides of magnesium, iron, zinc, manganese, or aluminum.)

Encapsulation is carried out either by deliberate dispersion of the insoluble compounds into the glass melt, during the immiscible component phase separation at cooling (i.e. separation of materials which will not mix nor blend with the glass), or by sintering of glass and waste powders so that the waste form produced is a glass composite material. However, this requires a more complex melter facilitated with a stirrer.

The vitrification technology comprises several stages, starting with evaporation of excess water from liquid radioactive waste. This is followed by batch preparation, calcinations, glass melting, and cooling. The final waste form consists of vitrified waste blocks and potentially small quantities of secondary waste (Figure 15).

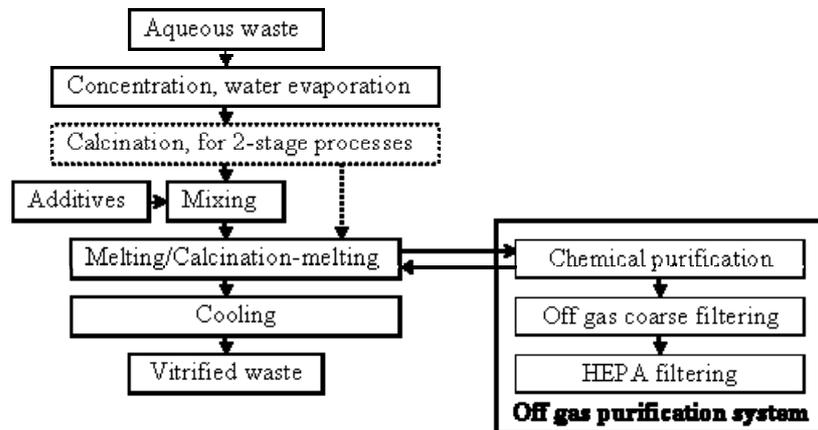


FIG. 15. Schematic of a vitrification process.

In a one-stage process, both waste calcination and melting occur in the same apparatus (the melter). In a two-stage process, waste calcination is carried out in a separate apparatus (the calciner) prior to melting in melter.

In the one-stage vitrification process, glass forming additives are mixed with concentrated liquid wastes, which is the glass-forming batch (often in the form of a paste). This batch is then fed into the melter, where further water evaporation occurs, followed by calcination and glass melting (Figure 16).

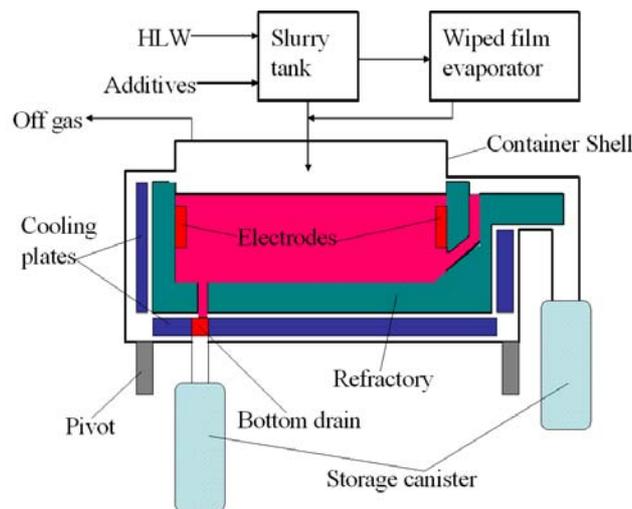


FIG. 16. Schematic of one-stage vitrification processes in a JHCM used in United States of America, Russian Federation, Germany-Belgium and Japan.

In the two-stage vitrification process with separate calcination, the waste concentrate is fed into the calciner (Figure 17).

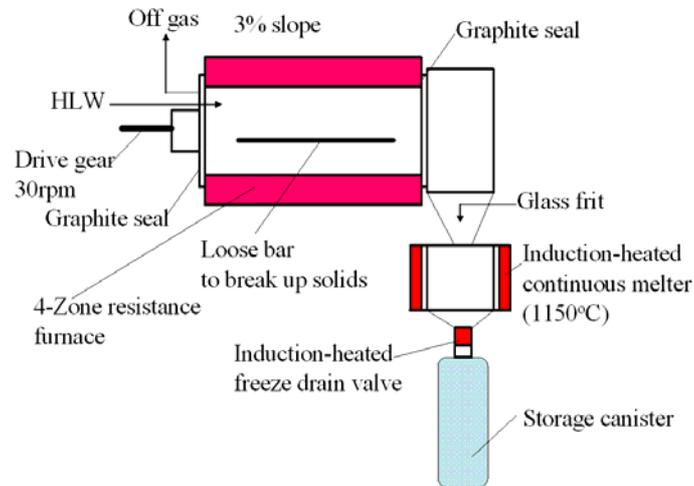


FIG. 17. Two stage vitrification process AVM used in France and United Kingdom.

After calcination, the required glass-forming additives (usually as a glass frit) are fed into the melter along with the calcine. The melted waste glass from the melter is poured into canisters. The canisters may then be slowly cooled (annealed) to reduce cracking of glass matrix.

The off-gas stream from the melter goes to the gas purification system. This is usually a complex system that removes from the off-gas not only radionuclides but also chemical contaminants [10, 35]. Operation of this purification system leads to generation of secondary waste.

As an alternative to an induction heated batch melter, a continuous process of melting the glass referred to as a Joule-Heated Ceramic Melter (JHCM) can be used. It consists of a tank constructed from refractory ceramic blocks and uses submerged electrodes in the melter. An electric current is passed through the molten glass to achieve the continuous melting and increase throughput. Typically, calcined HLW is mixed with glass frit or glass forming additives and fed into the JHCM. Cold material covering the surface of the molten glass (referred to as a cold cap) reduces evaporation losses.

Recent developments include the application of cold crucible induction heated melters (CCM) [7, 35] and thermochemical self-sustaining processes [36]. These technological advances immobilize the wastes which are difficult to melt. They are also used to produce glass composite materials for immobilization of wastes.

In a CCM, the glass melt is heated by induction currents. The melt is preserved inside a cooled volume of glass-batch material referred to as the skull. The skull isolates the high temperature melt from the water-cooled stainless steel or copper tubes, which make up the cold crucible walls (Figure 18). CCM are used either to melt waste with glass frit or melt calcined waste with glass frit. A colder surface layer or cold cap of dried batch is formed in both CCM and in JHCM, reducing the losses of aerosols and volatilized radionuclides from

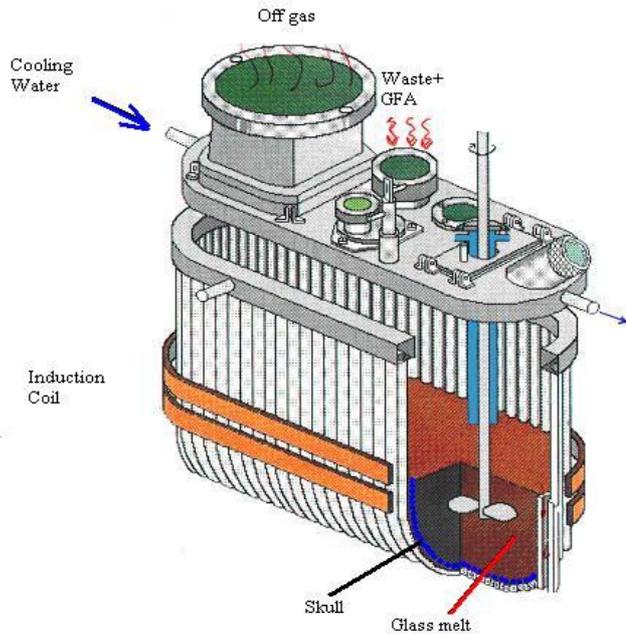
the glass melt. Table XII illustrates the main process parameters of a CCM compared to a JHCM

TABLE XII. PROCESS PARAMETERS OF JHCM AND CCM.

Parameter	Melter type	
	Joule heated (JHCM)	Cold crucible induction (CCM)
Melt capacity, kg/h	25	25
Specific melt capacity, kg/m <sup>2</sup> h	40-120	170
Melting ratio, (kW h)/kg	2.5-3.2	4.4-6.4
Operating temperature, °C	<1300	≥3000
Corroding in melt	Refractory and electrodes	No
Gross weight of loaded melter, kg	>1000	<200
Operating mode	Continuous	Continuous or Batch

The construction elements of a CCM are transparent to the electromagnetic field produced by the induction coils, thereby allowing induction currents to be generated inside the waste contained in the crucible. The cooling water in the tubes is at a temperature less than 100°C so that molten glass in contact with them can be kept at ~200°C. Even during melting, the tubes remain cold, and a protective layer (a cold cap) made of glass batch material forms between the melt glass and the tubes, thereby insulating them from the melt. This protective skull means that the refractory liners required in other melters are not needed. Since active refractory materials are difficult to immobilize, they cannot be melted easily. This is a distinct advantage of this technology.

Waste vitrification using CCM may be either one or two stage (i.e. with preliminary calcination or with calcination occurring in the melter). CCM are well suited for obtaining high throughput in a small waste package. CCM's supplied with stirrers have enhanced throughputs as well as enabling production of glass composite materials to immobilize wastes which are difficult to melt. Since the weight of the crucible is relatively lower, it facilitates easy dismantling and produces smaller quantities of secondary waste compared to conventional melters. Neither glass nor metal adheres to the cooled wall, and hence the crucible is relatively less contaminated.



Note: GFA = glass forming additives

FIG. 18. Schematic of an induction-heated cold crucible melter (CCM).

In situ vitrification (ISV) uses an electric current to melt soil or other waste-earthen mixtures [37-40]. The ISV is carried out via JHCM by passing electric current through electrodes installed into the contaminated materials (Figure 19). Typically it is applied on bulk soils or other contaminated wastes with the objective of leaving them in place as a stabilized disposition method.

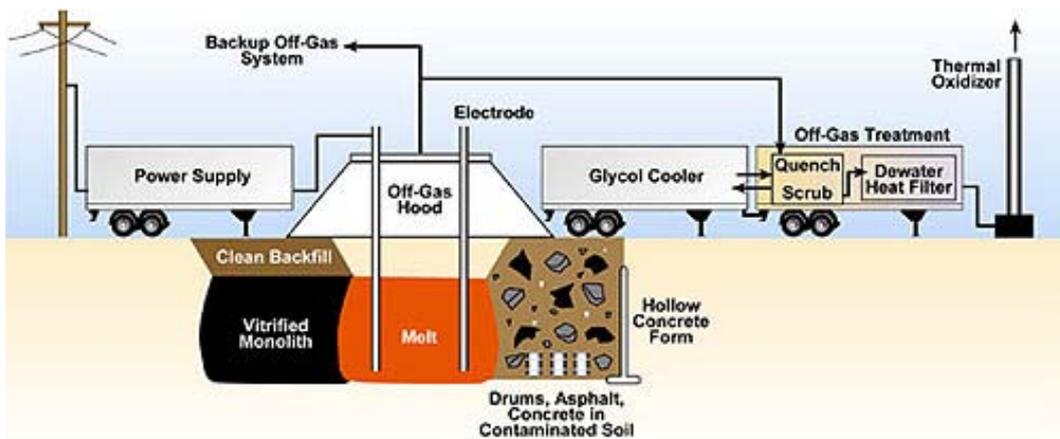


FIG. 19. Schematic of in situ vitrification system.

Once melting starts, most soils are conductive enough to sustain electrical currents sufficient to continue the vitrification process. If the molten soils are not sufficiently conductive, the soil is preconditioned by the addition of components that will impart the required conductivity on melting. The process typically operates in the temperature range

between 1600 – 1900°C and uses standard off-gas cleaning systems to contain and treat emissions.

There are two methods of organizing ISV: conventional top-down and planar directions. The conventional top-down melting produces melts typically wider than the depth process. The planar melting produces tall and thin planar melts. These are important capabilities to an in situ process, as the waste configuration defines the optimum directional approach.

Another viable alternative is the application of a self sustaining vitrification process [41] for inorganic solids, which utilizes the energy released during exothermic chemical reactions in a mixture of radioactive waste with specially designed powder metal fuels (PMF). This technology emerges from a self-propagating high temperature synthesis method. Self sustaining vitrification utilizes PMF to melt the waste and form a glass-like material without requiring an external power supply. This process is controlled by the composition of the initial mixture of waste and PMF [42].

The composition of the PMF is designed to release sufficient heat to sustain waste melting and to produce a mineral or glass-like end product. Suitable PMF compositions and PMF/waste ratios are determined through computer simulation minimizing carryover of hazardous components and ensuring retention of contaminants in the final waste form.

Additives are selected for their affinity to waste radionuclides (e.g. natural zircon can be used to immobilize uranium and plutonium). PMF provide sufficiently high temperatures to facilitate the chemical reactions that bind radionuclides in the final product, which can be a mineral-like material or a glass composite material. Moreover, the self-sustaining vitrification occurs through formation of melts and produces monolithic waste forms. Self-sustaining vitrification chemical reactions can be described by:



As with any process involving the use of PMF, chemical reactions in self-sustaining vitrification are carried out within carefully selected, stable and controlled regimes. Self-sustaining vitrification compositions ensure efficient immobilization of hazardous components into the final waste form. In addition, during the self-sustaining vitrification, the release of contaminants due to volatilization or through emission of contaminated aerosols is minimized. Self-sustaining vitrification is carried out without melting devices and utilizing simplified off-gas purification systems.

Two main glass types have been accepted for nuclear waste immobilization: borosilicates and phosphates. The exact compositions of nuclear waste glasses are tailored for easy preparation and melting, avoidance of phase separation, uncontrolled crystallization, and acceptable chemical durability (e.g. leaching resistance). Vitrification can be performed efficiently at temperatures below 1200°C, which is necessary because of the volatility of vitrified fission products, most notably Cs and Ru. This avoids excess radionuclide volatilization and maintains viscosities below 10 Pa to ensure high throughput and controlled pouring into canisters. A low viscosity glass melt is preferred to minimize blending problems.

Phase separation while melting is most important for waste streams containing constituents immiscible in a glass matrix. However, these can be immobilized in a dispersed phase (separate phase). The leaching resistance of nuclear waste glass matrices is a paramount criterion, as it ensures low release rates for radionuclides in potential contact with water.

Table XIII gives the compositions of several glass frits for nuclear waste glass matrices used for ILW or LLW. Molten phosphate glasses are highly corrosive to refractory linings. This behavior has limited their application.

TABLE XIII. COMPOSITIONS OF SOME GLASS FRITS FOR NUCLEAR WASTE GLASS MATRIX (IN WEIGHT %).

Glass/Country	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	Others
K-26 Commercial LILW, Russian Federation	48.2	-	7.5	2.5	15.5	-	16.1	10.2
AG8W1, Republic of Korea LILW	43.1	0.4	10.0	12.3	4.8	2.1	17.6	9.7

Containers of vitrified waste are the final product containing almost all of the waste contaminants. Volume reduction factor (*VRF*) is crucially dependent on the waste composition. For a typical vitrification process, *VRF* is on the order of 5:1 for solids and, although variable for liquids, is significantly higher.

#### 5.4.1.2. Applicable waste types

Vitrification is a mature technology and has been used for high level nuclear waste (HLW) immobilization for more than 40 years in France, Germany, Belgium, Russian Federation, United Kingdom, Japan and the United States of America. The total production of all vitrification plants by the end of 2000 was ~10 000 t of radioactive glass in ~20 000 canisters [41, 43–45].

Although developed initially for HLW, vitrification is being currently used for immobilization of intermediate and low level radioactive wastes (LILW) generated from operation and decommissioning of nuclear power plants [35]. Vitrification is one of several technologies chosen to solidify 18 000 tons of geologic mill tailings at Fernald, Ohio, USA [46]. Plans are in place to vitrify vast volumes of waste; for example the vitrification of the low level radioactive waste at Hanford, USA, is expected to produce over 160 000 m<sup>3</sup> of glass [47].

Self-sustaining vitrification is suitable particularly for small volume hazardous wastes. The possibility of such processes has been demonstrated for a number of waste streams, including calcined radioactive waste, contaminated clay soils, ash, and spent inorganic ion exchange materials, such as clinoptilolite.

Refer to Table 14 for generic waste types applicable to vitrification. Table XIV also shows the characteristics of waste forms obtained in self-sustaining vitrification.

#### 5.4.1.3. Expected end product

Vitrified waste is generally poured/ cast into canisters resulting in a unit geometrically conducive to handling/storage. The canisters will require a cooling period of 20 to 30 years (dependant on fuel burnout, loading, fuel cool down time prior to processing) prior to final placement in a disposal cell.

The final vitrified radioactive waste form is a chemically durable material which reliably retains active species. Normalized leaching rates (*NR*) of vitrified waste forms are typically below  $10^{-6}$  g/cm<sup>2</sup> day (Table XV). As glasses and glass composite materials are highly corrosion resistant, their high nuclide retention is expected to last for thousands of years.

TABLE XIV. CHARACTERISTICS OF SELF-SUSTAINING VITRIFICATION AND WASTE FORMS OBTAINED

Waste type and waste loading, wt. %	Process temperature, °C	Density, g/cm <sup>3</sup>	Compressive strength, MPa	Leach rate, g/cm <sup>2</sup> ·day		
				<sup>137</sup> Cs	<sup>239</sup> Pu	
Ash	50	1530	2.8	20	9.0·10 <sup>-6</sup>	5.4·10 <sup>-6</sup>
	56	1356	2.8	17	4.9·10 <sup>-6</sup>	2.8·10 <sup>-6</sup>
	60	1245	3.0	16	7.9·10 <sup>-5</sup>	7.0·10 <sup>-5</sup>
Soil	45	1905	2.4	10	1.0·10 <sup>-5</sup>	-
	50	1627	2.0	10	8.1·10 <sup>-6</sup>	-
	56	1530	1.5	8	2.1·10 <sup>-6</sup>	-
Klinoptilolite	55	1476	1.74	9	4.0·10 <sup>-5</sup>	-

TABLE XV. PROPERTIES OF BOROSILICATE GLASSES AND GLASS COMPOSITE MATERIALS

Properties		Borosilicate glasses	Glass composite materials
Waste oxide content, wt. %		30-35	30-35 + up to 15vol.% of yellow phase
Viscosity, Pa-s, at 1200 °C		3.5-5.0	3.0-6.0
Resistivity, Ω m, at 1200 °C		0.03-0.05	0.03-0.05
Density, g/cm <sup>3</sup>		2.5-2.7	2.4-2.7
Compressive strength, MPa (annealed)		80-100	50-80
<i>NR</i> , g/(cm <sup>2</sup> day), (28-day IAEA test)	<sup>137</sup> Cs	10 <sup>-5</sup> -10 <sup>-6</sup>	~10 <sup>-5</sup>
	<sup>90</sup> Sr	10 <sup>-6</sup> -10 <sup>-7</sup>	10 <sup>-6</sup> -10 <sup>-7</sup>
	Cr, Mn, Fe, Co, Ni	~10 <sup>-7</sup> -10 <sup>-8</sup>	10 <sup>-7</sup> -10 <sup>-8</sup>
	Rare Earth Elements, Actinides	~10 <sup>-8</sup>	~10 <sup>-8</sup>
	Na	10 <sup>-5</sup> -10 <sup>-6</sup>	10 <sup>-4</sup> -10 <sup>-5</sup>
	B	<10 <sup>-8</sup>	≤10 <sup>-8</sup>
	SO <sub>4</sub> <sup>2-</sup>	~10 <sup>-5</sup> -10 <sup>-6</sup>	~10 <sup>-4</sup> -10 <sup>-5</sup> at content up to 15vol.% of yellow phase

### 5.4.2. Advantages

The most significant advantage of vitrification is the long, stable life of the end product. New glass forms continue to be developed, including Synroc, which is a stable, long-lived glass formulation discussed earlier in this publication. Several titanium based glasses are found in nature, such as obsidians (volcanic glasses), fulgarites (formed by lightning strikes), tektites found on land in Australia and associated microtektites from the bottom of the Indian Ocean, moldavites from central Europe, and Libyan Desert glass from western Egypt. Some of these glasses have been in the natural environment for about 300 million years with low alteration rates: only tenths of a millimeter per million years.

The excellent durability of vitrified radioactive waste ensures a high degree of environmental protection. In addition to good volume reduction factors, waste vitrification enables the utilization of simpler disposal facilities for LLW and ILW (i.e. for wastes not containing long-lived isotopes like TRUs) [48]. Vitrification for LILW is more for the purpose of meeting waste acceptance criteria and less for economic reasons.

CCM have the following advantages:

- Larger operating temperature range. Since the CCM are protected from the glass melt by a cold glass batch layer, glass can be produced at higher temperatures, which increases flexibility in terms of the glass formulation range.
- Because the melt comes in contact only with solid material of the same composition as the glass frit, the end product has a high degree of quality in terms of meeting end product criteria.
- High reliability of immobilization and durability of the final waste form.
- High chemical resistance of glass allows it to remain stable in corrosive environments, as are found in nature, for thousands of years.
- High glass throughput into significantly smaller size packages.
- Extended operational lifetime of vitrification facility.
- Small volume of the resulting waste form.
- Large number of elements can be incorporated in the glass.
- Refractory liner not required.

Self-sustaining vitrification has the following additional advantages:

- does not require high temperature equipment, as simplified off-gas purification systems can be used either remotely or at point of generation
- Well suited to small volume inorganic waste streams.
- During self-sustaining vitrification the release of contaminants due to volatilization or through emission of contaminated aerosols is minimized.
- Carried out without melting devices.
- Utilizes simplified off-gas purification systems.

In-situ (bulk) vitrification (ISV) allows for the final waste form to remain in place: waste retrieval, transport, and disposal of the vitrified product are avoided.

### 5.4.3. Limitations

Vitrification is most suitable for liquid radioactive waste. The drawbacks of vitrification are:

- High initial investment cost.
- High operational cost.
- Complex technology requiring high qualified personnel.
- High specific energy consumption.

In-situ (bulk) vitrification (ISV) is not suitable for liquid wastes but instead is most effective with diverse, bulk solid wastes. A considerable limitation in ISV is the need for pretreatment of waste to be vitrified. This is especially applicable where a potential exists for the presence of undesirable materials, such as explosives, large quantities of organic contaminants, sealed drums of flammable and explosive materials, and large quantities of water. Pretreatment of the subject waste area may be required to achieve the safe and efficient operation of ISV. Final waste characteristics cannot be pre-evaluated.

Self-sustaining vitrification has limited use and experience — it has only been used for calcined or ash-like material. Final waste characteristics cannot be pre-evaluated.

### 5.4.4. Operational experience

Immobilization of HLW by vitrification has been studied extensively over the last 40 years in Denmark, Canada, China, Germany, Belgium, Italy, India, Japan, Republic of Korea, Russian Federation (former USSR), the United Kingdom and the United States of America. The first LILW vitrification plant based on CCM was put into operation in 1999 in the Russian Federation [35]. This plant has a melt capacity of 75 kg/h and is currently operated as a prototype plant for the vitrification of operational radioactive waste from nuclear power plants (NPP).

France is intensively developing CCM for both HLW and LILW. Several CCM test platforms have been built at the Marcoule pilot facilities. These programs were initially focused on the treatment of HLW solutions from light water reactor fuel, producing simulated R7/T7 glass. The feed systems allow simultaneous controlled input of solids (frit, powders) and liquids (surrogate solutions, sludge).

Italy is introducing French CCM technology to vitrify most of the active waste at the Eurex reprocessing plant [49]. CCM melting was also intensively studied for Hanford site wastes in the United States of America [50].

South Korea plans to operate a waste vitrification plant based on CCM to vitrify LILW from its NPP. Pilot plant tests have been successfully completed for various waste types [51]. A demonstration vitrification plant is operational at Daejeon. The facility uses CCM vitrification process for shredded combustible solid waste, spent ion exchange resins, and concentrated borated liquid waste, either directly or in granular/pellet form. Volume reduction factors of 99:1, 35:1 and 8:1 were obtained for organic solid waste, spent ion exchange resins, and concentrated borated liquid waste, respectively. Table XVI gives data on radioactive waste vitrification facilities.

TABLE XVI. DATA ON LILW RADIOACTIVE WASTE VITRIFICATION FACILITIES

Facility	Waste type	Melting process	Operational period	Performance	Reference
Radon, Russian Federation	LILW	CCM	Since 1999	75 kg/h, continuous	[35]
Torch, Russian Federation	LILW, ash	PMF	Since 2001	10 kg/h, batch process	[42]
WTP, Hanford, United States of America	LLW	JHCM	Since 2005	No data available	[43, 50]
Ulchin Npp, Republic of Korea	LILW	CCM	Under construction expected 2007	No data available	[51]
Saluggia, Italy	LILW	CCM	Under development	No data available	[49]
Slovakia	LILW	JHCM	Since 1996	No data available	[52]

**Acronyms used in Table XVI:** LILW – low and intermediate level waste, LAW – low activity waste, JHCM – Joule heated ceramic melter, CCM – cold crucible induction melter, PMF – powder metal fuelled thermo-chemical process.

Over 80 demonstration ISV-projects were carried out by Geomelt (Geosafe) Corp in the USA at scales from 0.1 to 1200 tons of vitrified product. Moreover, ISV is being used for the treatment of Pu-contaminated soil at Maralinga test site in Australia [37, 38]. ISV is also under consideration for low level waste vitrification at Hanford, USA [39, 40].

Moscow SIA “Radon,” Russian Federation uses self-sustaining vitrification to immobilize ashes from the radioactive waste incinerator [42].

#### 5.4.5. Other considerations

##### 5.4.5.1. Scale and throughput

Due to the relative complexity of vitrification and the high initial cost of equipment, this technology is well suited to large volume waste streams, such as toxic waste, commercial HLW from decommissioning activities, and LILW. However, many large waste generators would be needed to bring down the unit cost significantly. In addition, a range of accumulated wastes of different composition and properties from bulk waste streams have been generated during various activities of both industrial facilities and research institutions, although usually in relatively small quantities. Examples include spent ion exchange resins, wastes from research centers, contaminated soils and incinerator ash. Due to the relatively small volumes of such wastes the use of conventional vitrification technologies is difficult to justify.

Glass formulation for LILW vitrification is somewhat difficult due to the heterogeneous content of LILW. This includes both the solid components and broad range of minerals such as Si, Ca, Ti, Li, B, Na, etc. Also, quality control of LILW vitrified forms seems to be a significant challenge, because of inconsistencies in LILW waste streams.

#### *5.4.5.2. Costs*

Life cycle costs are high for vitrification technologies. Thus it is difficult to justify in the absence of a large volume of waste or in the absence of a specialty application as the most feasible technology.

#### *5.4.5.3. Mobile or fixed*

There are no mobile vitrification systems, except for in-situ vitrification.

#### *5.4.5.4. Environmental/regulatory issues*

For vitrification, the same environmental/regulatory issues are valid as for incineration. However, the volume of off-gas is smaller than that of incineration.

#### *5.4.5.5. Technical issues*

A LILW vitrification melter generates fly ash and other low volatiles, like Ru and Cs. These should be recycled to the melter in order to keep the properties of glass melt constant and to reduce carryover of radioactivity.

## 6. CONCLUSIONS

This publication will serve as an abbreviated technical reference on thermal technologies for Member States and organizations seeking to develop a waste processing strategy or facility involving one or more such technologies. Of particular benefit are the included discussions which suggest the economic impacts and the waste throughput requirements which are essential for including the various technologies as viable local options. The following additional conclusions apply:

- (1) It should be emphasized that the volumes of LLW that require treatment in Member States expands proportional to the number of nuclear applications, new power plants, new decommissioning projects, etc. Accordingly, high efficiency volume reduction processes provide an important contribution to the mix of available technologies. Thermal treatment processes are, in general, among the most efficient volume reduction (VR) technologies.
- (2) This publication provides a review of the available thermal technologies, with the extent of the included information being consistent with the complexity and the range of technical variations applicable to each technology.
- (3) This publication can be used most effectively as an initial cutting tool to identify whether any given technology will best serve the local waste management strategy in terms of the waste generated, the technical complexity, the available economic resources, the environmental impact considerations, and the end product (output) of the technology. If multiple thermal technologies are being actively considered, this publication should be instrumental in comparing the technologies and assisting the user to reach an informed decision based on local needs, economics and priorities.
- (4) High VR processes are not always the most economical. If the volume of waste is low, the investment may not be justifiable on a cost basis. In such situations, it may be better to use a less efficient but more cost effective approach. From a life cycle perspective (including procurement, installation, operation, maintenance, decommissioning), thermal technologies are usually among the most expensive of the available waste processing technologies.
- (5) Before embarking on the use of a thermal process, it is essential to research the process thoroughly and understand the characteristics of the wastes to be processed, volumes of wastes to be processed, regulatory strategy and regime, disposal options available, etc. This is essential to developing and comparing options objectively.
- (6) A full economic assessment is crucial to choosing among options. Obtaining accurate data can sometimes be difficult, especially when assessing long range factors such as operating costs, maintenance costs, and decommissioning costs. Many economic analyses have focused only on initial procurement, failing even to take into consideration the high costs of installation.
- (7) The need for and cost of ancillary facilities or service requirements must be taken into considered in the overall processing needs assessment and in the economic assessment. For example, if the objective is to obtain a final conditioned waste package suitable for disposal, and if the selected thermal technology is designed only for pre-treatment or treatment, then the selection and cost of the subsequent conditioning technology must

be included in the overall evaluation. The overall structure and the included discussions in the publication will assist the user in making such determinations.

- (8) It is often more economical to make use of centralized or regional waste treatment facilities, especially for very expensive processes. This is especially true for technologies with a high cost and high waste throughput demand, whereby the processing of waste from many waste generators will make the overall technology cost more economical.
- (9) It may be possible to improve the return on investment if multiple waste types can be treated by the process. When an expensive thermal technology is designed for a single waste type or a narrow range of small volume waste streams, then the cost per unit of waste processed can be far more difficult to cost justify. The discussions in this publication assist the user to identify the various waste streams which can be processed with each technology.
- (10) Off-gas systems are needed for most thermal technologies. These can be very complex and expensive for some processes (e.g. up to 60% of the initial capital investment). Design of the off-gas system must be closely linked to the chosen processing technologies and expected waste properties.

## 7. LESSONS LEARNED

The contributors to this report identified many lessons learned from experience with various thermal technologies. The following are the most important of those lessons:

- (1) It is best to stick with well-developed and proven technologies. It is important to be aware of the risks involved with the evolutionary development of technologies. The involved investments are large, and gambles on design improvements often are not successful.
- (2) Focus on standard components where possible. Again, new designs and design improvements which are unproven often adversely impact the overall budget and effectiveness of implementing the technology.
- (3) If planning to make a large investment in a thermal technology, small investments to visit a similar facility (preferably of similar size and complexity) and to set up small scale trial processes can be extremely worthwhile.
- (4) When planning to invest in a given technology it is important to consult experienced operators of this process to truly understand operating experience, limitations, past problems, etc.
- (5) Obtain an thorough understanding of the types and quantities of waste to be treated before proceeding. Large technology investments have been made in the past based primarily on stored waste volumes (as opposed to current generation); it was later discovered that the continuing input volumes to be processed were too small to justify the investment.
- (6) Be aware of being “blinded” by a large investment. Once a very large investment has been made, there is sometimes a tendency to feed waste types to the process even if it is not the best process for those wastes. For example, if a large VR process has been procured, there may be the tendency to ignore waste minimization at the source in order to keep the processing technology fully implemented.
- (7) Be aware of the impact of large VR processes on the subsequent disposal classification. If the incoming waste has a high specific activity, a highly efficient VR process will further concentrate the activity with two possible negative outcomes: a requirement for remote handling of the end product, or the resultant waste form has a higher disposal classification (which translates to more restrictive waste acceptance criteria and increased disposal costs).
- (8) Due to the potential expense and complexity of the off-gas system requirements, it is important to fully understand the anticipated off-gas characteristics before contracting to procure the system. Off-gas (and subsequent gaseous effluents) are an important area of attention for regulators, typically requiring air quality permits, special licenses, operating restrictions, reporting requirements, etc. In many cases, the thermal technology will not be approved by the regulatory authority at all or will need to meet economically prohibitive emission restrictions. Off-gas requirements and systems should be recognized as a potential show-stopper to the implementation of any given technology in any given location. For this reason, it should be given a high and early assessment priority.



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