

TECHNICAL REPORTS SERIES NO. 427

Predisposal Management of Organic Radioactive Waste



IAEA

International Atomic Energy Agency

PREDISPOSAL MANAGEMENT
OF ORGANIC
RADIOACTIVE WASTE

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FOREWORD

The processing of organic waste is a rapidly developing field. Various treatment and conditioning options are being investigated, developed and widely applied in several IAEA Member States. The organic nature of waste, or the presence of organic components in waste, should be taken into account during all steps of radioactive waste processing, particularly during final disposal. Modern acceptance criteria for radioactive waste disposal include requirements for a minimum organic content in final waste packages. The management of organic radioactive waste was specifically addressed in IAEA Technical Reports Series No. 294, *Options for the Treatment and Solidification of Organic Radioactive Wastes*, published in 1989. Since that time new developments have been reported for the processing and immobilization of organic radioactive waste and other radioactive waste which contains substantial amounts of organic components. Therefore it was decided to revise and update that report to reflect new developments and experience on the subject of processing of organic radioactive waste.

The initial draft of this report was prepared in July 2001 by consultants from the Netherlands and the United Kingdom. In May 2002 the draft was revised and further developed by experts from nine countries, and then further modified in March 2003 by consultants from Canada, the Netherlands and the United Kingdom. The IAEA would like to express its thanks to all those who took part in the preparation and revision of the report. The IAEA officer responsible for this publication was V.M. Efremkov of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

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1. INTRODUCTION

Since the discovery of the phenomenon of radioactivity at the end of the nineteenth century there has been a continuous increase in the use of radiation and radioactive material in conventional industry, research, medicine, and for power generation. At the same time, the potential hazards of radiation and radioactive material were recognized at an early stage, and international standards for radiation protection are concerned with the uses of radiation and radioactive material. One of the areas of concern is the proper management of radioactive waste generated during different applications of radioactive material and in the nuclear power industry.

There is a broad international consensus on the principles of the management of radioactive waste [1, 2]. Many reports have been published by the IAEA on various technical aspects of radioactive waste management [3–8]. The current report focuses on the management of organic radioactive waste. This differs from the management options applied for purely inorganic radioactive waste in that organic compounds may have specific properties which need to be dealt with during the treatment and conditioning processes. Typical features of organic waste are volatility, combustibility, thermal, chemical and radiolytic instability or biotoxicity. These do not normally apply to inorganic radioactive waste. The chemical toxicity of organic components was addressed in Ref. [9] and is therefore not explicitly addressed in this report.

Management of organic radioactive waste should take full account of both its radioactive and organic nature. These issues were addressed in Ref. [10]. This report is an update and revision of that publication.

1.1. OBJECTIVES

The primary objective of this report is to provide an overview of the technical options and approaches available for the treatment and conditioning of organic radioactive waste, as part of an integrated waste management system. The information is aimed at persons and organizations looking for practical solutions for disposal of a limited amount of organic radioactive waste in the light of possible severe economic constraints.

In order to select an appropriate waste management strategy it is important to establish the nature of the waste, which will largely be determined by the origin, use and characteristics of the radioactive material. Therefore this report will review the origins of organic radioactive waste, covering both

nuclear fuel cycle facilities and various other applications of radioactive material, including those in research establishments and medical centres.

1.2. SCOPE

Radioactive waste generally consists of a mixture of discarded materials or components arising from the production or use of radioactive material. Some of these wastes may be wholly or largely organic, whereas others will only contain a small fraction of organic material. Normally, the specific activity of a waste material or its point of origin determines whether it is considered to be radioactive under national regulations, but it is not easy to similarly define it as 'organic'. This is a more qualitative judgement. The mere presence of organic materials does not make the waste organic. This report provides information that can be used to develop appropriate strategies both for the management of wholly organic waste and that containing only a fraction of organic material which is, however, significant with respect to the behaviour of the overall waste stream. It addresses all types and origins of organic material that appears in radioactive waste.

1.3. STRUCTURE

Section 2 of the report describes the origin and characteristics of organic radioactive waste, along with some general precautions that should be taken when dealing with it. Section 3 addresses the selection of a waste management strategy and outlines various strategy options. Typically, one of the following options could be applied:

- (a) Storage and containment without special treatment (e.g. for decay);
- (b) Destructive or non-destructive treatment with or without subsequent conditioning (solidification, packaging) of treated and secondary waste;
- (c) Direct solidification;
- (d) In some special cases, decontamination.

Selection of a strategy will depend on criteria such as the quantity of the waste and its radiological characteristics, the available treatment systems, the national disposal policy, costs, and environmental factors. Section 4 provides information on the storage of untreated material and the transport of organic radioactive waste. The hazards arising from the organic nature of the waste are specifically addressed. Section 5 describes the various treatment techniques

that are in use, with examples of existing installations. This section also briefly addresses techniques that are under development and some techniques that were studied but failed to become operational. Several of the techniques produce secondary waste that also needs to be treated. These are also addressed in Section 5. The properties and performance of the conditioned radioactive waste forms are described in Section 6. A summary of the necessary quality assurance and quality control measures is given in Section 7, and the conclusions of the report are set out in Section 8.

2. ORIGIN AND CHARACTERISTICS OF ORGANIC WASTE

Organic radioactive waste can occur in solid, liquid or, infrequently, gaseous form. Examples of each of these are discussed in this section, but it should be noted at the outset that it becomes increasingly difficult to isolate and control the waste when it is in the liquid or gaseous form. In general, organic components of radioactive waste can change form more easily than most inorganic components, for example due to their low melting point, their response to radiolysis or their volatility. This property can significantly affect the strategy adopted for their management. Organic waste is often very heterogeneous in nature, with several types of waste being present in one container.

The radionuclide content of organic waste can generally be traced to contamination or mixing with other radioactive streams. Organic materials are widely used in nuclear power plants and research facilities where they can become contaminated with fission and activation products or, rarely, even with fuel particles. Due to their low melting point and vulnerability to radiolysis, they are not used in high temperature and radiation environments such as reactor cores, so direct neutron activation can usually be precluded. However, the use of organic materials as lubricants in reactor cooling pumps or for neutron shielding can lead to the production of small amounts of activation products (e.g. ^{14}C). Organic materials are also used in the construction of targets for accelerators, so small volumes of activated organic material may arise. The production of labelled organic compounds for use in medical diagnosis and research is a special case, in which the radioactive content is distributed throughout the material and is not confined to surface contamination.

Apart from their physical nature, radioactive wastes can also be classified according to their radioactive content. Classification is primarily based on the concentration of radioactivity in the waste, causing it to be put into the high, intermediate or low level waste category. Wastes can also commonly be classified as alpha or beta/gamma waste, short or long lived waste, plutonium contaminated material (PCM) or transuranic waste. Further details on classification systems are given in Ref. [11].

2.1. SOLID ORGANIC RADIOACTIVE WASTE

The solid organic materials most widely used in the nuclear industry are plastics, rubber and cellulose (covering paper, wood and natural fibres such as cotton). Less common solid organic materials include ion exchange resins. Materials that consist of elemental carbon, such as graphite, are explicitly excluded from consideration in this report. Solid organic waste originates from processes throughout the nuclear industry – at nuclear power reactors, fuel fabrication facilities, reprocessing plants, research establishments and medical facilities.

The largest volumes of solid organic waste tend to arise from operations at power plants and research centres, where ‘general trash’ is produced containing high proportions of plastic, rubber and cellulose. Solid organic radioactive waste from power reactors is often heterogeneous and ill defined, but characterization of this class of waste from pressurized heavy water reactors showed that paper and plastic typically average about 70% of the total waste volume and were roughly equal in quantity. The remainder of the waste consisted of materials such as natural and synthetic rubber, cotton and fibreglass [12]. Other types of reactor produce similar mixtures of organic material accounting for up to 50% of the waste volume. Reprocessing operations and research activities can produce significant quantities of PCM, which includes a large proportion of organic material [13].

2.1.1. Origins of solid organic radioactive waste

2.1.1.1. *Plastic and rubber*

The use of plastic is widespread in the form of protective sheets, gloves and clothing, as well as for electrical insulation or as manufactured items, for example containers, bottles, syringes and laboratory equipment. These items can become contaminated and, due to their low cost, are commonly discarded

after a single use. The use of polyethylene in neutron shielding can lead to low levels of activation products.

Natural and artificial rubber, including latex, is also commonly used in protective gloves, glovebox gauntlets, gaskets and sealing rings for drums. They can become contaminated with radioactivity from external sources. These materials are generally more expensive than plastics and are designed for longer service lives. However, once they fail they are discarded as waste.

2.1.1.2. Cellulose

Cellulosic waste arises from a variety of uses, including paper or cloth wipes, filters, wooden frameworks and clothing. These can also become contaminated with radioactivity from external sources. Clothing is often washed to allow reuse. Filters using organic filtration material are changed on a regular basis and together with wipes are generally discarded after a single use.

2.1.1.3. Ion exchange resins

Organic ion exchange resins are used in specialized applications to remove contaminants from water (for example in water reactor circuits and prior to discharge of effluents into the environment). Therefore they accumulate a radionuclide burden. They are expensive materials that are used with care and regenerated if possible. They are discarded as waste only when this is necessary or economically justified.

2.1.2. Key characteristics of solid organic radioactive waste

The radionuclide content of solid organic waste is generally caused by contamination, so effective containment measures must be applied. However, with the exception of loaded ion exchange resins, such waste will tend to present a low radiation hazard and can generally be handled and stored without significant shielding. Some solid waste (e.g. ion exchange resins) tends to be stored underwater.

In dry conditions most solid organic waste is relatively stable. However, in the presence of water or aggressive chemicals, or when exposed to radiation, this waste may be subject to chemical and radiolytic degradation, yielding a variety of products including non-aqueous phase liquids and gases (e.g. hydrogen). The mechanisms of such degradation are complex and the products may be poorly characterized. The products of such degradation may complicate further handling, storage and processing of this waste (see Section 4).

Therefore care should be taken to properly segregate and store this waste prior to appropriate treatment and conditioning (see Section 3).

2.1.3. Potential hazards posed by solid organic radioactive waste

Solid organic waste is generally combustible or can support combustion of other waste, but is not inherently hazardous or toxic. The presence of PVC in older stored waste can affect the integrity of storage containers due to corrosion. It is now accepted good practice to avoid the use of PVC since this material forms corrosive chloride ions or radicals when irradiated. Certain types of organic ion exchange resin (quaternary amines) are known to become unstable if they dry out, and there have been cases of explosive detonations when this type of material has not been appropriately managed. Ion exchange material may concentrate fissile material during storage or following disposal, which may increase the criticality hazard.

2.2. LIQUID ORGANIC RADIOACTIVE WASTE

A wide variety of organic liquids are used in the nuclear industry. These can be broadly categorized as lubricants, solvents, process fluids and diluents, and decontaminants. Typically, liquid organic wastes comprise a low proportion of the total organic waste generated. It is generally agreed that aqueous waste with a significant organic content, including soluble organic decontamination agents, should be considered to be liquid organic waste. This class of waste could be characterized as wastewater with a high chemical or biological oxygen demand (COD/BOD).

2.2.1. Origins of liquid organic radioactive waste

2.2.1.1. Lubricants

Lubricants include both oils and greases. They are present in the gas and water circulators used in power reactors, and in smaller applications such as vacuum pumps and experimental facilities.

Radioactive oil waste produced in nuclear power plants consists of lubricating oils from primary heat transport pumps, hydraulic fluids from fuelling machines, and turbine oils. These are normally low level wastes containing only relatively small quantities of beta/gamma emitting radionuclides. They can become contaminated with volatile radionuclides or by contact with radioactive materials, but low levels of activation products may

develop in power plant lubricants due to exposure to neutrons. These liquids become waste as a result of regular servicing of equipment, or when an item of equipment is discarded.

The removal of tritium from heavy water in the heat transport system of pressurized heavy water reactors can produce intermediate level tritiated oil waste through contamination of vacuum pump oil by gaseous tritium, which then becomes organically bound through isotopic exchange. This waste oil may contain up to 1.8 TBq of tritium per litre and the estimated annual arisings are about 75 L [14].

2.2.1.2. Organic solvents

A large variety of organic solvents are used in research and medical establishments, for many purposes. Ultimately they can become waste.

The solvent extraction systems employed in reprocessing generate organic radioactive liquid wastes. Solvents include ethers and tributyl phosphate (TBP) and its diluant (usually a light saturated hydrocarbon such as dodecane or a mixture of paraffins). Both TBP and its diluant are subject to degradation by hydrolysis and radiolysis. Eventually the degradation significantly reduces the solvent's performance so as to prevent recycling and thus the fluids are diverted for storage as waste. As the solvents are in direct contact with dissolved nuclear fuel solutions, they can be among the most highly contaminated organic waste, containing uranium, plutonium and fission products.

A range of solvents are used for cleaning and degreasing. Chlorinated or fluorinated hydrocarbons have been used for this purpose, although this is no longer considered good practice. After use such solvents also become liquid organic radioactive waste. Perchloroethylene and similar solvents are used for dry-cleaning of contaminated garments, with the resulting sludge being treated as an organic waste.

2.2.1.3. Scintillation liquids

Scintillation liquids are generated from routine radiochemical analyses of radionuclides with low energy emissions. The scintillant 'cocktails' typically consist of mixtures of toluene and xylene although proprietary mixtures, including water soluble species, are also common. Large volumes of scintillation liquids are generated each year. New techniques are being developed which might reduce the use of such liquids in future.

2.2.1.4. *Decontamination liquids*

A wide variety of organic decontamination agents are used in nuclear facilities to remove radionuclides and reduce doses to operators. After use, these can be regarded as liquid organic waste. Some of these agents are organic phase liquids, whereas others are dissolved in water (e.g. citric acid, ethylene diamine tetra acetate (EDTA)). All become contaminated as part of their service life, which can be only a single use. As noted above, organic liquids such as chlorinated hydrocarbons are no longer used for this purpose due to international restrictions on the use of ozone depleting substances.

2.2.2. Key characteristics of liquid organic radioactive waste

The most important feature of liquid organic wastes is their mobility. They will drain under gravity and contribute to the spread of contamination, so they need to be effectively contained. Many are volatile and combustible, or will support combustion of other wastes. They can also provide a source of nutrients for microbial activity.

Many organic fluids are immiscible with water and can be classed as non-aqueous phase liquids which require special care due to their potential to migrate rapidly in the environment (the lighter fraction can float on water whereas the dense fraction cannot). This distinction may be of significance for waste collection, storage and processing (see Sections 3, 4). Some of the decontaminants (chelating agents) can form water soluble complexes with radionuclides (especially the actinides).

2.2.3. Potential hazards posed by liquid organic radioactive waste

Many liquid organic materials are flammable, some with low flash points. Degradation during storage, for example by radiolysis, can produce gases and lead to lighter fractions with lower flash points, and hydrogen. This requires careful management to prevent fires (e.g. by ventilation or blanketing with inert gas). Some organic materials are also toxic, and exposure to fumes should be avoided.

2.3. GASEOUS ORGANIC RADIOACTIVE WASTE

Gaseous organic effluents are normally not accumulated for storage and treatment. Process design is usually optimized to ensure that organic material in gaseous form is minimized, although it is recognized that some processes that

use volatile organic substances may discharge organic species to the environment in gaseous or vapour form. These substances have a negative impact on the environment since they contribute to the greenhouse effect and can attack the protective ozone layer in the stratosphere. They may also be chemically hazardous and present a toxicity concern for the workforce.

Where gaseous or vapour phase materials are present in relatively high concentrations, the possibility of a flammability hazard should be recognized. The vapour phase is unlikely to contain high levels of radioactivity unless the species incorporates ^{14}C and ^3H , which may be the case for radioactively labelled compounds. Other radioactive gases, such as Kr, Xe and Rn, do not normally form organic compounds.

2.4. MIXED PHASE ORGANIC RADIOACTIVE WASTE

Many forms of mixed phase waste can be identified. In this context, mixed means the presence of more than one physical state, with at least one being predominantly organic. These wastes can include sludges, colloidal suspensions and emulsions. They can range from almost solid (i.e. paste-like) materials, through mixtures of inorganic or organic liquids, to liquids with a high content of dispersed solids. Used ion exchangers and precipitates from liquid treatment can also be present as sludges.

A number of special cases can be considered mixed phase organic waste, including absorbents containing liquids, animal carcasses, some waste from the medical sector, and contaminated soil. Absorbed liquids are usually not irreversibly bound to a matrix, so their original characteristics are maintained although some of the hazardous properties such as mobility and flammability are mitigated. Animal carcasses and vegetable material mainly result from research into biological processes and can be subject to rapid degradation by microbial processes. Contaminated soil is produced in relatively small quantities from research activities, but may also be present in huge quantities as the result of accidents and incidents. Contaminated soil in the Chernobyl area and the large quantities of contaminated soil resulting from the radiological incident in Goiânia (Brazil) are both relevant examples of this [15, 16].

3. SELECTION OF A WASTE MANAGEMENT STRATEGY

As described in Section 2, organic radioactive waste has diverse characteristics that require careful consideration when selecting management options. In order to deal effectively with the potential hazards associated with organic radioactive waste an overall strategy should be developed with the objective of stabilizing the organic waste and eliminating or mitigating the potential hazards. This will often include pretreatment processes, which may change the form and properties of the original waste.

3.1. SELECTION CRITERIA

A wide range of technical and non-technical criteria must be considered in the development of an appropriate waste management strategy. Distinctions and interrelationships between different components of a strategy should be considered and evaluated. The main criteria to be considered when selecting an appropriate strategy for organic radioactive waste management are briefly summarized below, including the main issues that should be addressed. Depending on the nature of the waste and conditions in a country, there may be other relevant criteria that are not listed here. If so, these can be added as required.

3.1.1. Technical criteria

Many technical factors and criteria influence and determine the selection of a waste management strategy. In most cases, organic radioactive waste forms only part of a total waste inventory. Therefore the strategy selected for organic waste should be part of a more general waste management strategy. In the case of an individual strategy for a particular organic waste stream, this strategy may be more specific. General technical criteria for selection of a waste management strategy include, but are not limited to, the following factors:

- (a) Waste characteristics, which include the physical form, chemical, radiological, toxic, biological and other properties important for selection of a waste treatment and conditioning technology;
- (b) Total waste quantities and generation rates, which define the scale of technology application;
- (c) Availability of technology and its compatibility with particular waste types;

- (d) Maturity and robustness of the technology;
- (e) Complexity and maintainability of the technology;
- (f) Secondary waste generation and the complexity of further treatment/conditioning;
- (g) Quality of the final waste product.

Table 1 provides examples of other technical criteria to be considered when selecting treatment options and a management strategy for radioactive organic waste.

3.1.2. Non-technical criteria

In recent years the costs of disposal and the uncertain availability of a disposal route have been the driving forces of efforts to reduce the volume of final waste product. Minimization of waste volume should be a criterion to be examined from an economic perspective, as well as from the environmental and sustainability points of view. The economic criteria, together with other non-technical criteria important for selection of a waste management strategy, are summarized in Table 2.

Highly sophisticated and complex techniques are not always a feasible choice for a small volume of waste. The overall economic situation in a country will also be an important factor and will possibly have an impact on competitiveness. Small volumes of waste can sometimes be treated by very simple and cheap techniques. An example of such an elegant solution is the cleaning of slightly contaminated oils with demineralized water (see Section 5.1.4).

Various users can share technical solutions. Mobile equipment exists. In the Czech Republic, for example, a mobile super compactor is contracted every ten years to treat the solid waste from the nuclear power plants. This is standard practice in some other countries as well, and is not determined by the organic nature of the waste. Mobile equipment is also industrially available for the conditioning of liquids, sludges and ion exchange resins [17]. Sharing of installations will have an economic benefit, as well as allowing improvements in the treatment process as well as in the final product. Sharing of installations will mean that more skilled, specialized and experienced operators will be involved.

In the United States of America it is common practice to use commercial industrial companies for waste treatment. Therefore untreated waste may be transported over relatively long distances and will certainly cross state boundaries. It is noted, however, that crossing the boundaries of independent States to optimize the utilization of low level waste treatment installations is more rare, but there are examples of commercial operators doing this [18].

TABLE 1. TECHNICAL CRITERIA FOR SELECTING TREATMENT OPTIONS AND A MANAGEMENT STRATEGY FOR RADIOACTIVE ORGANIC WASTE

| Criterion | Comments |
|--|--|
| Potential radiological and non-radiological hazards | Are the current hazards significant and can they be eliminated or mitigated by the proposed strategy? |
| Current storage arrangements | Do the current storage arrangements meet the required standard/are wastes deteriorating? |
| Storage improvement requirements | Can storage arrangements be improved by new construction or refurbishment? |
| Complexity of the treatment and conditioning process | Is the proposed process simple and reliable and are the maintenance requirements acceptable? |
| Availability of the treatment and conditioning process | Can the proposed process be implemented now or is further development required? |
| Safety of the process | Does the proposed process provide optimal safety? |
| Volume changes | Does the proposed process result in an increase or decrease in waste volume? |
| Environmental factors | Does the proposed process have an acceptable environmental impact? |
| Disposability of the waste form | Does the envisaged process lead to a waste form which is directly disposable or does it at least not jeopardize its later conversion into a disposable form? |

From Canada some organic liquid radioactive waste is sent to facilities in the USA for treatment. From the economic as well as from the quality point of view more regional co-operation would be beneficial, but the attitudes of the regional, transboundary populations are a key factor influencing such co-operation.

3.2. WASTE MANAGEMENT OPTIONS

A number of strategies which are widely applied to the management of radioactive waste in general are also applicable to organic radioactive waste. The approaches described in the following should not be considered to be complete strategies, but rather components of an overall strategy for the

TABLE 2. NON-TECHNICAL CRITERIA IMPORTANT FOR SELECTION OF A WASTE MANAGEMENT STRATEGY

| Criterion | Comments |
|---------------------|--|
| Financial viability | Can the process be financed and what would be the source of finance? |
| Investment benefit | Are the waste management costs reasonable considering the nature of the waste, arisings and investment potential? |
| Use of synergies | Have all features which might decrease costs been considered (e.g. equipment/personnel sharing such as in the case of mobile treatment facilities, or provision of treatment in a central facility)? |
| Waste policy | Is the process consistent with national waste management policy? |
| Regulatory approval | Has the process been approved by a regulatory body or does the process require additional regulatory approval prior to operation? |
| Stakeholder views | Is the process likely to result in an adverse response from the public or non-governmental organizations/pressure groups? |

management of this waste. The overall strategy is likely to evolve with time, for example as new technology is developed, new waste treatment facilities become available and disposal concepts progress.

3.2.1. Waste minimization and segregation

The principle of minimization of waste arisings is widely recognized. This element of a strategy should be consistently applied to organic material which might end as radioactive waste, but should be used only where the practice can be justified. A straightforward example of waste minimization is switching from single use protective clothing to reusable, washable clothing. Although the intrinsic value of most organic materials is relatively low, their treatment to allow recovery, recycle or reuse may also represent an appropriate strategy. This would prevent unnecessary accumulation of waste and conserve resources. The filtration of contaminated oils to remove accumulated sludges or the ‘washing’ of contaminated items to remove surface contamination are examples of treatment processes that would allow recovery and reuse of organic materials. Such processes may also allow waste to be put into a

different category, possibly allowing cheaper disposal in a surface facility, or even dispatch to a non-nuclear facility for incineration.

The segregation of waste is also seen as an important principle because of the difficulties experienced with the characterization and treatment of stored historic heterogeneous waste. Thus it is recommended that organic radioactive wastes be segregated at source wherever possible. Such segregation allows consideration of a wider range of treatment processes. This strategy should be applied to future waste arisings although, where sorting of existing wastes can be shown to be consistent with the ALARP (as low as reasonably practicable) principle, they can be also be segregated. It is recognized that wastes are often segregated on the basis of their radionuclide content to facilitate subsequent waste management. Organic wastes should also be segregated by activity content.

3.2.2. Continued storage as raw waste

The strategy of extended storage of the waste as generated should represent a positive decision to maintain the status quo rather than 'do nothing'. Evaluation of the hazards associated with the waste, the expected lifetime of the storage arrangements or the half-life of the associated radionuclides may lead to the conclusion that continued storage is appropriate. For example, if sufficient decay occurs during storage, the waste may eventually be treated as non-radioactive. However, improvements may be required in the way the waste is stored, possibly including the development of new facilities. Consideration should also be given to centralizing the storage of the waste, possibly requiring its movement within or between sites. The technical issues associated with the storage and transport of raw waste are addressed in more detail in Section 4.

3.2.3. Conversion to a less hazardous form

As noted previously, some organic wastes pose significant hazards due to their volatility and flammability, their toxicity, or their chemical instability. It may be possible to convert organic material to a less hazardous form, thus allowing its continued storage without production of a final waste form for disposal. This may be particularly attractive in cases where a disposal facility is not yet available or where relevant waste acceptance criteria (WAC) have not been determined. The conversion may yield a less hazardous organic species or result in an inorganic form.

Some organic radioactive waste is generated and stored in liquid form. An obvious choice of disposal method would be incineration of the liquid.

Where such a process is available and the resulting secondary waste is acceptable, this route can be taken. However, high temperature processes are not simple techniques, especially when alpha containment is required.

Another option for liquid waste might be solidification. This is a specific class of conversion process. It has significant advantages for liquid waste, in particular for ongoing storage, as well as for transport, as the mobility of the waste is controlled and is not dependent on active containment. Also, the flashpoint of the resulting solid product will be much higher, reducing the risk of fire. Solidification may be achieved in various ways. The most common will be absorption into a porous solid material or mixing with a material that subsequently sets to form a solid mass. The conversion of a liquid to solid form may be temporary or permanent.

Absorption can often be reversed, although not with total efficiency, and thus can be considered to be a temporary solidification strategy. It would facilitate the stabilization of the waste for a period of time, but would not preclude the development of a final waste form for disposal using an alternative approach (although in this case the absorbent will probably form a secondary waste also requiring disposal).

In contrast, the solidification of a liquid waste using a setting agent, such as cement or polymers, cannot easily be reversed and should be considered to be permanent. If this option is to be pursued, the disposability of the solidified waste must first be considered in detail.

In the absence of a disposal facility and associated WAC it may be appropriate to consider the production of solidified waste in relatively small unit volumes so that in the future they can be overpacked in standard containers, with additional matrix material if required to meet future WAC.

In many countries it is common practice to immobilize dispersible radioactive waste by mixing it with or adding agents which ultimately yield a solid, low dispersible waste form. This strategy aims to decrease possible activity release under normal or accident conditions during (long term) storage and transport, but may also be necessary to comply with the acceptance criteria for a disposal facility. It is noteworthy that organic material such as bitumen has been used as an embedding agent for the conditioning of special waste, resulting in organic waste forms [19–21]. The overall benefits and disadvantages of such applications have to be assessed carefully before startup of a process and re-analysed from time to time to take ongoing developments and boundary conditions into account.

3.3. DECISION MAKING

The waste management strategy to be adopted should result from a decision making process which is based on a set of previously identified case specific management options. As part of this process, a number of criteria such as those addressed in Section 3.1 are analysed. These criteria should be linked to casespecific weighting factors in order to arrive at an overall, optimized final decision.

The framework and application of such analyses are covered in more detail in other IAEA publications [3, 22]. Typically, these analyses will include technical, regulatory and economic factors. They may also include societal factors such as the acceptability of various technologies.

4. INTERIM STORAGE AND TRANSPORT OF UNTREATED ORGANIC WASTE

4.1. STORAGE

Interim or temporary storage of untreated waste is a standard part of most waste management systems. Following generation, all wastes will be kept in storage for some time before they are treated to obtain a product that is suitable for long term storage, disposal or recycling. Generally, the quantities stored in raw, untreated form should be as small as possible and the storage time as short as possible because in untreated form the waste will possess a higher hazard potential. It may be more mobile, unstable, flammable and/or biologically active. During storage, all of these aspects, as well as the radiological aspects, must be carefully considered.

Storage facilities for untreated waste are usually associated with either the generator of the waste or with a treatment facility. Depending on national laws and policies, it may be more cost effective to operate a small number of centralized storage facilities (e.g. connected to a centralized processing facility) rather than a large number of smaller storage facilities, especially where waste volumes are small or special storage conditions are required.

Specific considerations for storage of treated or conditioned waste are discussed in Section 6.2. While it is recognized that, ideally, different types of waste should be segregated during storage (keeping liquids separate from solids, untreated waste separate from treated waste, etc.), practical limitations,

such as efficient utilization of resources, often result in the sharing of waste storage facilities among several waste forms or types. However, even in these cases, physical or administrative controls can be applied to meet the objectives outlined below.

4.1.1. Solid waste

By nature, most organic waste is flammable. As a fundamental safety consideration, the fire hazard posed by the stored material should be controlled. In most cases, the following practices can be easily implemented to reduce the fire hazard:

- (a) Storing waste in relatively small quantities in rugged, non-flammable containers such as closed metal drums or containers.
- (b) Avoiding the mixing of different types of waste or wastes from different sources in the same storage container if the chemical compatibility of the waste materials is not certain.
- (c) Equipping the storage area with smoke detectors, heat detectors and/or flammable gas detectors.
- (d) Equipping the storage area with the capability for isolation by closure of the ventilation openings.
- (e) Providing fire extinguishers near the storage area to fight a fire as soon as it starts. The use of dry or gas type extinguishers will prevent the radioactivity from spreading to the surrounding area, as might happen when water is used. Manual operation of the system may be required for reasons of personnel safety; e.g. automatic operation of a CO₂ fire extinguishing system should be avoided since this may cause injury or death if triggered while people are working in the area.

A controllable drainage system, possibly with alarms, might be installed when it cannot be guaranteed that no liquids are present in the unconditioned waste. Microbiological activity within organic materials can produce large amounts of heat, which may eventually lead to combustion. This possibility increases with increasing ambient temperature. Therefore it is good practice to keep the waste stored in a shaded, cool area. It is also important to prevent access to the waste by animals, as they will tend to spread the activity.

4.1.2. Liquid waste

Generally the same fire safety requirements as for the storage of solid waste should be applied for liquid waste. In many cases, the fire safety

requirements will be more rigorous than for solid waste due to the increased mobility and volatility of liquids. In particular, water should not be used for fighting liquid fires.

Liquid waste is more dispersible than solid waste and therefore requires tighter packaging. Depending on its nature and quantity, the waste will be stored in tanks, carboys, bottles, drums or other containers suitable for liquids [6]. The chemical nature and other properties of the waste will determine whether metal, plastic, glass fibre or a combination of these is used for the storage container. It should be noted that aggressive reactions towards both metals and plastics do occur.

Mixing of poorly defined liquids in the same container should be avoided. In addition, plastic containers should be avoided where the risk of fire is high since the plastic could melt and release the liquid, possibly spreading the fire. Glass storage bottles are not ideal for storage due to their fragility. If their use is unavoidable, they need to be protected from accidental breakage (e.g. from mechanical damage or from freezing of the contents if water is present).

Attention should be given to the possible formation of explosive vapours. This will determine whether or not special regulations apply for the electrical installations and the use of electrical and other equipment. Special requirements may be necessary to keep the liquid cooled (to minimize its volatility) and to avoid static electricity which may provide an ignition source (spark).

A good drainage system and/or the availability of leakage collection will be required to counter the possibility of leakage from tanks, drums or containers. If the possible hazard requires it, double containment with leakage tracing may be used.

4.1.3. Liquid–solid waste mixtures

If the waste mixture is formed by a combination of solid and liquid material, the requirements set forth in Sections 4.1.1 and 4.1.2 should be considered. Additional requirements for some common wastes in this category are given below.

For sludges, it should be noted that the solids may settle in the tanks or containers. This can not only result in a very uneven dose distribution but also cause problems in retrieving the sludge from the container for future processing. The longer the sludge is stored, the greater the risk of phase separation.

For animal carcasses and equivalent material, the only widely accepted temporary storage method is in a deep frozen form. Freezing systems should be equipped with a reliable temperature control system and an alarm device

[8, 23]. When a freezing container is available it might also be a suitable place for the temporary storage of other mixed wastes. Animal carcasses should be packaged in smaller containers that can be incinerated directly. Sealing of the containers may be required in order to contain any odours from putrefaction. Any direct handling of carcasses should be avoided because of the potential biohazard. This risk can increase when needles or other pieces of equipment are still present which could easily lead to physical injuries to the personnel handling the waste.

Small carcasses can also be vacuum sealed in heavy plastic bags (such as those commonly used in the food industry to protect meats and other perishable products), especially when long term freezing is undesirable due to unreliability of the local electric power supply or where there may be delays between generation of the waste and its transport to a centralized storage facility.

Freeze drying of biological material prior to interim storage has also been practised in some countries. This can be considered a pretreatment process.

4.2. TRANSPORT

The transport of radioactive material is controlled by internationally accepted rules and regulations, as defined in Ref. [24], which are implemented as international and national rules and laws. For chemicals posing a fire or explosion hazard, toxicity or biohazard, other national and international rules also apply. It is clear that in the case of transporting radioactive organic materials all the requirements must be met.

For on-site transfers it is not always necessary to apply the same rules as for off-site transport, unless this is required by national or local regulations. However, whenever possible it is prudent to adhere as closely as possible to the established rules for off-site transport.

5. TREATMENT AND CONDITIONING TECHNIQUES

The aim of applying treatment and conditioning techniques is to obtain a waste product that can be stored or disposed of more safely. A general processing scheme is given in Fig. 1, showing treatment in the context of the entire life cycle of the organic waste.

This section describes techniques for the treatment and conditioning of organic waste. Some of the processes chemically alter or destructively modify the organic nature of the waste. Thus, the techniques are grouped as follows:

- (a) Non-destructive techniques, which primarily involve a physical change in the properties of the material to enhance additional treatment, storage or disposal but do not destroy the organic components (e.g. absorption, compaction, immobilization);
- (b) Destructive techniques, which primarily involve a chemical change in the waste product (e.g. incineration, pyrolysis).

The following two sections briefly describe a variety of techniques used in the management of organic radioactive waste. These techniques are summarized in Table 3. The first column of this table gives an overview of all the non-destructive and destructive techniques that are addressed. For each technique, a general description is given setting out the principles behind the process. Examples of use of the technique are given for reference purposes where possible. The focus has been to consider the operational status of known facilities to highlight the changes from the last IAEA review that was undertaken in 1989 [10]. Lastly, the advantages and disadvantages of the process are discussed.

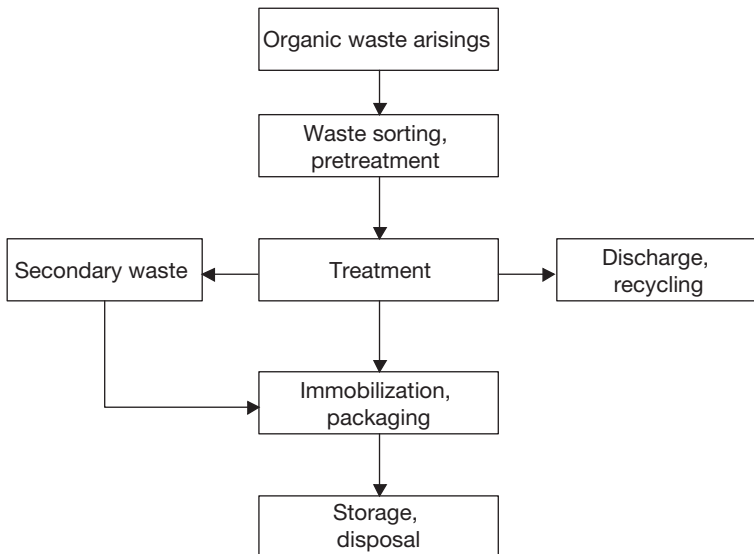


FIG. 1. Generalized diagram of the life cycle of organic waste.

Section 2 gave a general description of the characteristics of organic waste. Depending on the characteristics, the choice of a treatment technique can be narrowed down because not all techniques are generally applicable or suitable. The matrix in Table 3 can help to select a suitable technique for a specific waste stream.

5.1. NON-DESTRUCTIVE TECHNIQUES

The non-destructive techniques for the processing of organic radioactive waste, as listed in Table 3, are described below.

5.1.1. Drying and evaporation

Technique

Drying and evaporation is generally used as a technique to remove (free) water. It may be used for solid waste that contains a significant amount of water (drying) or for aqueous waste streams, resulting in a solid or sludge-like evaporate concentrate that contains the major part of radioactivity (evaporation). In the case of evaporation, the waste material is heated. Heat may be applied in the drying process also. To advance the process, moist air can be removed by ventilation. Drying and evaporation can be carried out using readily available equipment scaled to the needs of the particular waste generation/treatment facility.

Examples

For some organic radioactive waste, drying and evaporation may be quite suitable prior to subsequent treatment or immobilization. For example, ion exchange resins may be dried prior to immobilization in a monolithic solid matrix.

For disposal purposes, the waste acceptance criterion of no (or negligible) free liquid being present is commonly applied. Materials with free liquids must, therefore, be dried before disposal.

Evaporation is widely employed in the chemical processing industry. The technique is useful to drastically reduce the volume of aqueous waste streams that also contain organic materials. However, the large scale use of evaporation needs to be evaluated from the point of view of economics and its impact on radiological safety. The use of thermal evaporators may result in secondary waste (e.g. air filters) which also requires treatment and disposal.

TABLE 3. POSSIBLE APPLICABILITY OF TECHNIQUES

| Technique | Waste type | | | | | | | |
|---|--------------------|-----------|---------------------------|------------------------|--------------|------------|---------------------|---------------|
| | Rubber/ plastic | Cellulose | Ion exchange resins | Biological material | Mixed solids | Lubricants | Organic solvents | Other liquids |
| Non-destructive techniques | | | | | | | | |
| Drying and evaporation | N | Y | Y | Y | Y | | Y | Y |
| Distillation | N | N | N | N | N | | Y | |
| Physical conditioning | | | N | N | Y | N | N | N |
| Decontamination | Y | Y | N | N | Y | Y | Y | |
| Absorption | N | N | N | N | N | Y | Y | Y |
| Compaction | Y | Y | Y | | Y | N | N | N |
| Direct immobilization | Y | Y | Y | | Y | N | N | N |
| Destructive techniques | | | | | | | | |
| Incineration | Y | Y | Y | Y | Y | Y | Y | Y |
| Pyrolysis/steam reforming | Y | Y | Y | Y | Y | Y | Y | Y |
| Alkaline hydrolysis (TBP/ odourless kerosene (OK)) | N | N | N | N | N | | Y | |
| Vitrification | Y | Y | Y | Y | Y | | | |
| Plasma treatment | Y | Y | Y | Y | Y | Y | Y | Y |
| Molten salt oxidation | Y | Y | Y | N | Y | | Y | |

TABLE 3. POSSIBLE APPLICABILITY OF TECHNIQUES (cont.)

| Technique | Waste type | | | | | | | |
|----------------------------------|--------------------|-----------|---------------------------|------------------------|--------------|------------|---------------------|---------------|
| | Rubber/ plastic | Cellulose | Ion exchange resins | Biological material | Mixed solids | Lubricants | Organic solvents | Other liquids |
| Electrochemical treatment | N | N | N | N | N | | Y | Y |
| Direct chemical oxidation | | | | | | | Y | |
| Acid digestion | Y | Y | | Y | Y | | Y | |
| Wet oxidation | | | Y | | | Y | Y | Y |
| Advanced oxidation | N | N | N | N | N | | | Y |
| Supercritical water oxidation | Y | Y | Y | | Y | | Y | |
| Biological treatment | | Y | Y | Y | | | | |
| Thermochemical treatment | | | Y | Y | | N | N | N |
| Microwave treatment | | | Y | Y | | | | Y |

Note: Y: Known or likely to be appropriate; N: Not an appropriate technique; Blank: Unknown or possible.

Advantages/disadvantages

Drying techniques are generally quite simple to use and result in negligible or only small quantities of secondary waste. Evaporation is more complex and results in discharges to the environment as well as the production of some secondary waste.

5.1.2. Distillation

Technique

The distillation technique has two steps, evaporation and condensation. By application of a heat source, one component is made volatile, and when it is cooled down this component is recovered as a clean liquid.

Examples

Distillation has been investigated as a method of decontaminating spent reprocessing solvents such as TBP for possible reuse. A detailed description of this is given in Ref. [10]. The method is still in use at reprocessing facilities in France and the United Kingdom.

Advantages/disadvantages

Advanced equipment is needed for the large scale distillation of organic liquids. The technique is very useful if the distillate can be used again, so it is mainly used for specific liquids such as TPB. It is also useful when it makes the liquid suitable for free release or treatment in commercial facilities. A disadvantage is that volatile radionuclides such as tritium are not removed from the distillate.

5.1.3. Physical conditioning/separation

Technique

Physical conditioning/separation means that waste is separated into two or more components. For solid waste this can be done with mechanical techniques such as shredding and sorting, or by phase separation for liquids.

Examples

For liquids, phase separation has been used in the past to treat reprocessing liquids. Reference [10] gives descriptions of this process. However, none of the reported installations are operating at present.

For solid waste, shredding is sometimes used prior to immobilization or incineration. In the case of immobilization this is done to obtain a better inclusion of the waste in the matrix. A more homogeneous mixture is obtained when each fragment is encapsulated by the immobilizing medium. The advantage of shredding prior to incineration is that a more homogeneous feed can be processed and smaller pieces will prevent clogging of the feed system.

Shredders are also used for scintillation vials. Here the aim is to separate the glass and plastic of the vials from the liquid that was present in them. Because the scintillation liquids generally have low flashpoints, care must be taken to prevent fires and explosions [25].

Advantages/disadvantages

Phase separation of liquids does not seem to be a technique that has wide applicability. Solid waste shredding can create considerable amounts of dust and movement of particles. Therefore radioactive waste shredders have to be adequately enclosed to prevent the spread of contamination, and this level of confinement will increase the cost of dedicated equipment significantly.

5.1.4. Decontamination of organic radioactive solids and liquids

Technique

Decontamination of organic radioactive solids and liquids is a technique whereby the radioactive contaminants are removed from the solid or from the liquid. This is usually a mechanical process, but chemical decontamination is also practised.

Examples

A number of decontamination techniques have been used successfully to separate/concentrate the radioactive components in both solid and liquid radioactive waste. These include solvent cleaning, washing of surfaces and surface cleaning using CO₂ in the supercritical state (temperature and pressure greater than 32°C and 300 bar, respectively).

Solid organic radioactive waste may be decontaminated by solvent cleaning and washing of surfaces. This includes the laundering/dry cleaning of clothing and rags and the scrubbing and washing of surfaces to remove loosely held contamination. In general, secondary waste will arise from these treatments, requiring additional treatment.

Solid surfaces can also be cleaned using supercritical carbon dioxide (CO₂). An example of application of this technique (for the separation of oil from metallic chips or sludges) has been reported in Germany. This method was mainly used for the supercritical extraction of oil from chips and sludges that resulted from the cutting of metal and glass objects using CO₂. In the supercritical state, CO₂ has unique solvent properties. At a pressure of 400 bar, 1 kg of supercritical CO₂ was able to dissolve 100 g of oil [26].

Contaminated oils have been decontaminated by liquid–liquid extraction. A set-up used at a Czech nuclear power plant is shown in Fig. 2 [27]. A mixture of oil and water is pumped into a closed tank with a capacity of 1 m³. The mixture consists of 500 L of oil and 100–200 L of demineralized water. Circulation can take 1–3 hours, and when the phase equilibrium has been established water is discharged from the lower part of the tank. The water will contain the radioactive contaminants and is treated in a water purification system. The cleaned oil can be disposed of as inactive waste. During oil collection it is necessary to segregate non-chlorinated oils from chlorinated substances as the latter are either unacceptable for incineration or their incineration would be very expensive (see Section 5.2.1).

Advantages/disadvantages

Decontamination is a widely used technique, laundering perhaps being the most common method. Secondary waste will be produced with every decontamination method and before applying a method the consequences of treating the resulting product must be evaluated. The reuse of material or the possibility of disposal in the non-radioactive area is a general advantage of decontamination.

5.1.5. Absorption

Technique

Liquid organic waste can be absorbed into various materials. The liquid is simply brought into contact with the absorbent, resulting in a solid product.

Examples

A number of absorbents are available, from clays to special polymers, with the resultant material varying from dry particles to jelly-like solids, or to hard and dry solid mass. Before an absorbent is employed the following factors should be taken into consideration:

- (a) Whether the organic material is fully integrated into the matrix so that it cannot be released.
- (b) Whether the material is likely to comply with long term storage acceptance criteria. This may be important in selecting an organic based absorbent, because it may require that the absorbed material be immobilized in cement.
- (c) Long term stability and resistance to degradation of the absorbent material.

Absorption should therefore be considered as part of an overall integrated waste management strategy, possibly for improving storage conditions of existing liquid waste. It may also be used prior to other treatments such as immobilization or incineration. In the latter case liquids on absorbents can be fed into incinerator systems that are not supplied with special liquid feeding systems.

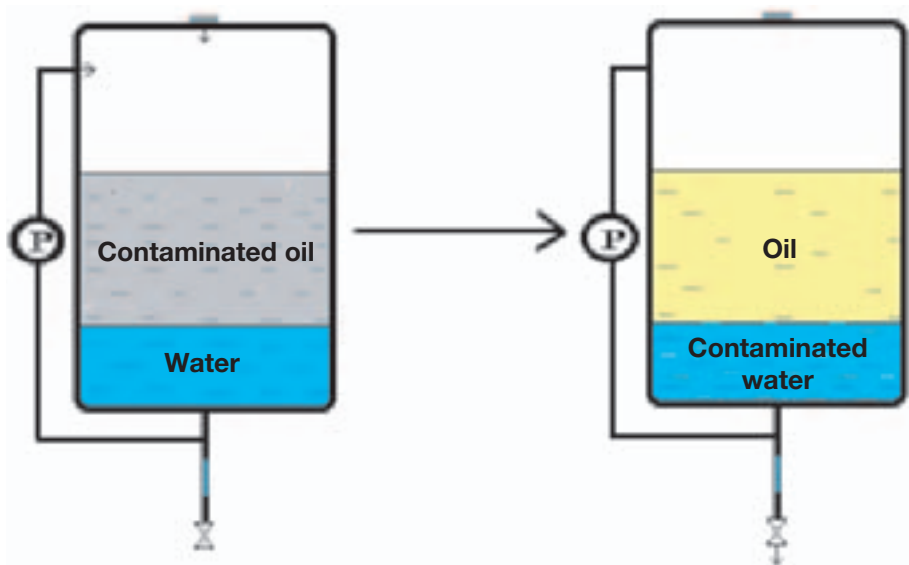


FIG. 2. A simple set-up used in the Czech Republic to clean contaminated oils (P: pump).

Development work in the 1980s reported the use of special cements for the solidification of many types of organic liquid waste such as lubricating oils and scintillation fluids [28]. More recently, other absorbent polymers have been used to solidify tritiated oil. Polymers have been demonstrated in the USA for treatment of tritiated oils. These oils also contained other chemicals, such as cyclohexane, which were added to inhibit coagulation. This specific polymer has been developed based on experience gained from major oil spill operations. The method of deployment is simple. Waste oil is mixed with the absorbent by pumping the oil into a drum containing the polymer and the oil is absorbed without mechanical mixing. This facilitates the reduction of personnel dose and the possibility of remote handling to minimize potential exposure to tritium. The polymer composition is tuned to the individual components of the waste oil to be treated. Assumptions made to account for these individual properties include, for example, the possibility that the water content in the oil might be 5% or greater due to condensation after decades of operation. Both inactive and active laboratory trials were conducted [29].

Advantages/disadvantages

Absorption is a simple and cheap technique that can be applied to a wide range of liquids. However, the liquids may not be permanently absorbed in all cases and therefore it may not be compatible with disposal requirements.

5.1.6. Compaction

Technique

Compaction is an old technique that is widely used. The principal aim of compaction is to reduce volume. It is normally done with raw waste in sacrificial thin walled steel drums which form ‘pucks’ after compaction. The volume reduction achieved is strongly dependent on the nature of the waste to be compacted and on the compaction force used. Originally, only modest compaction forces of less than 1 MN were used. Developments in the 1980s made supercompactors available with forces in the 10–15 MN region, which in the 1990s increased to 20 and even 50 MN. Apart from volume reduction, voids are eliminated and a waste form with cohesive properties is produced. In most cases further processing is required, for example immobilization of the pucks by grouting into a larger container.

The composition of the waste must be compatible with the compaction process. Compressed gases and explosive materials must be excluded prior to compaction. Large quantities of powders or bulky items are unlikely to form a

cohesive monolith on compaction, and the latter may even damage the compactor. Administrative controls should be adopted to segregate bulky (metallic) waste at source. Each waste management organization should develop and monitor appropriate WAC for the use of waste compaction equipment, depending on national circumstances.

Examples

Some operational supercompactors and their present operational status are shown in Table 4. This table, which is not intended to be an exhaustive list, points out their widespread application. Figure 3 shows the supercompactor at the COVRA facility in the Netherlands. Supercompaction followed by encapsulation is used in many countries. In the Netherlands, 100 L drums of waste are supercompacted and the reduced packages are placed in galvanized 200 L drums and further encapsulated in cement. In France, the waste is supercompacted in 200 L drums that are then placed in an 870 L container and the whole is encapsulated within a bituminous/cement matrix. In the UK also, 200 L drums containing waste are compacted and the resulting pucks are grouted into 500 L stainless steel drums. In the UK, low level waste is also compacted prior to disposal at the Drigg site, whereas supercompaction is applied to some solid intermediate level waste at Sellafield. In the latter case PCM is subjected to 2000 tonnes of pressure in 200 L drums, with the resulting pucks being grouted into 500 L stainless steel drums. The collection and treatment of liquid effluents is an important part of the process here. Compaction of intermediate level waste from spent fuel reprocessing is also practised in France. Mobile supercompactors have been developed and used in Germany, Italy, the UK, the USA and elsewhere.

Advantages/disadvantages

A wide range of solid organic waste can be compacted. This reduces the volume, free liquid is pressed out and voids are eliminated. If desired, mobile equipment is available. Ordinary compaction into drums or other containers, without further treatment, is a simple process requiring relatively inexpensive equipment. High pressure supercompaction equipment has a high capital cost and, if combined with remote computer controlled handling and encapsulation, becomes a sophisticated operation needing skilled personnel. The technique is effective for most solid organic waste. Secondary waste, both liquid and airborne, must be adequately treated.

5.1.7. Direct immobilization

Technique

With the direct immobilization technique, raw waste is directly mixed with a binding material. The original product does not change, but is wholly embedded and thus isolated from the environment.

Direct immobilization of organic waste allows the production of a waste form that is suitable for disposal in a single step. It is widely applicable to solid and liquid waste, and the immobilization material may be selected from a range of possible types, including cement, bitumen and polymer matrices. The waste is usually physically mixed with the encapsulant. Direct immobilization can be done near the source of waste generation.

Examples

There is a wide range of examples of the use of direct immobilization for organic waste. Organic ion exchange resins are directly encapsulated in epoxy



FIG. 3. The supercompactor at COVRA in the Netherlands.

TABLE 4. STATUS OF SUPERCOMPACTION FACILITIES IN SOME MEMBER STATES

| Country | Facility/site | Start of operations | Pressure (MN) | Comments |
|-------------------|----------------------------------|---------------------|---------------|--|
| Austria | Seibersdorf | 1995 | 20 | Old unit Fakir 1 — resold |
| Belgium | Mol-CILVA | 1993 | 20 | |
| China | China Institute of Atomic Energy | 2000 | 20 | |
| France | La Hague/Cogéma | 1986 | 15 | |
| | Soulaines | 1991 | 15 | |
| | La Hague/Cogéma | 1997 | 25 | Intermediate level waste |
| | La Hague/Cogéma | 1997 | 25 | Intermediate level waste |
| | EdF Bugey | 1990 | 20 | Mobile/also used in other locations |
| | Framatome | 1999 | 15 | |
| Germany | Brunsbüttel | 1983 | 20 | |
| | Forschungszentrum Karlsruhe | 1984 | 15 | Scrapped in 2001 |
| | Forschungszentrum Karlsruhe | 2001 | 15 | Commissioned in 2001 |
| | Forschungszentrum Karlsruhe | 1997 | 20 | |
| | Amersham Buchler | | 20 | Operated by AEA Technology |
| | Philippsburg | 1994 | 20 | Not willing to disclose data |
| | Jülich | 1996 | 15 | Fakir 6/GNS property/ service contract |
| | Würgassen | 1997 | 20 | |
| | GNS-Dortmund facility | | 20 | Own usage |
| | Energie Nord/Lubmin | | 20 | Fakir 7 |
| Gundremmingen/KRB | | 20 | Fakir 4 | |
| | KWU-Karlstein | 1988 | 16 | |

TABLE 4. STATUS OF SUPERCOMPACTION FACILITIES IN SOME MEMBER STATES (cont.)

| Country | Facility/site | Start of operations | Pressure (MN) | Comments |
|--------------------|--------------------------|---------------------|---------------|---|
| Italy | ENEA Casaccia | 1988 | 20 | Mobile system |
| Japan | Tokyo Electric Power | | 20 | |
| Netherlands | COVRA-Vlissingen | 1993 | 15 | |
| Republic of Korea | Kepeco | 1992 | 20 | Mobile system |
| Russian Federation | Balakova NPP | 2001 | 20 | |
| | RADON Moscow | 1980/1997 | 15 | Old unit from Petten, Netherlands |
| Slovakia | Bohunice | 1998 | 20 | |
| Spain | El Cabril | 1992 | 20 | Fakir 3 |
| UK | UKAEA Dounreay | 1990 | 20 | Mobile system |
| | BNFL Sellafield-SDP | 2000 | 20 | Two units installed, operation planned for 2005 |
| | WTC | 1996 | 20 | Used for PCM |
| | UKAEA | 1986 | 20 | |
| USA | BWX Technologies (B & W) | 1986 | 15 | Operational at naval fuel plant |
| | INEEL | 2001 | 20 | |
| | GTS Duratek | 1990 | 50 | |
| | GTS Duratek | 1987 | 15 | |
| | DOE Savannah River site | 1986 | 10 | Former West Valley |
| | ATG Hanford | 1992 | 15 | |
| | Hanford WRAP | 1996 | 20 | Supplied by INET |
| | Race Co. | | 20 | Rented from INET |
| | DOE Rocky Flats | 1989 | 20 | Never operational |

TABLE 4. STATUS OF SUPERCOMPACTION FACILITIES IN SOME MEMBER STATES (cont.)

| Country | Facility/site | Start of operations | Pressure (MN) | Comments |
|---------------|----------------------------|---------------------|---------------|---|
| | Chem Nuclear Chicago | | 12 | Fakir 2; formerly at Chicago/buried at Barnwell |
| | Northern States Power | 1985 | 20 | Mobile, never moved |
| Taiwan, China | Taipower at Kuosheng plant | 1990 | 20 | |
| Ukraine | Chmelnitzki NPP | 2001 | 20 | |
| | South Ukraine NPP | 2001 | 20 | |

resin by British Nuclear Fuels Ltd (BNFL) at the Trawsfynydd power plant [28]. The technique of immobilization of spent resin in polymer is used commercially in France and India [30, 31]. In the process of immobilization, the spent resins are incorporated into a polyester styrene monolithic block. The matrix has been tested for chemical and biological durability and for thermal and radiological stability. Operation is fully remote, in a hot cell. Plutonium contaminated materials have been shredded for direct grouting in cement at a number of nuclear facilities. In Germany, the Netherlands, Sweden, the USA and various other countries, ion exchangers and sludges are directly immobilized in cement. Mobile equipment is available for this operation [17].

Bituminization is used for dry ion exchange resins in Belgium, France and Sweden. A bituminization plant has been set up in Slovakia and has been in operation since 1995. A bituminization plant for ion exchange resins has also been in operation at the Cernavoda NPP in Romania since 1997 [32].

Advantages/disadvantages

The advantage of direct immobilization is that a disposable product is obtained at the production site in a single step. Sometimes pretreatment of the waste is needed and complex mechanical equipment may be required for waste products with high activity contents, such as ion exchange resins.

5.2. DESTRUCTIVE TECHNIQUES

This section describes those techniques summarized in Table 3 that result in the destruction of the organic material, generally by vigorous oxidation. Many of these technologies can normally be applied to both solid and liquid waste.

It should be noted that destructive techniques will often result in concentration of the radionuclides in the treated waste product. This may lead to operational concerns such as increased dose rates, as well as criticality issues when fissile nuclides are involved.

5.2.1. Conventional incineration

Technique

Incineration is an exothermic reaction process which uses heat and oxygen to destroy organic material through combustion. In many cases, the combustion of waste itself provides sufficient heat to maintain the reaction. In other cases a supplemental fuel source such as natural gas or oil is used. Incineration is a well developed technology that has been extensively employed as a part of the treatment of organic waste. It is currently in use in a number of countries such as Austria, Belgium, Canada, France, the Netherlands, the Russian Federation, Slovakia, the UK and the USA.

The combustibility nature of organic material makes incineration an ideal technology for the complete destruction of organics. The process also significantly reduces the volume and mass of waste. The products from complete incineration are carbon dioxide and water, and the oxides of other constituent components, e.g. phosphorus, sulphur and metals. Incineration is an appropriate technique for both liquid and solid organic waste forms. Sufficient air is provided to burn all the waste and is favoured for high volumes of low level waste. A related process, pyrolysis (or air starved incineration), can be used to prevent vigorous burning conditions and mobilization of the ashes leading to deposition within the incinerator. Incineration is also used for putrescent waste, e.g. medical waste and animal carcasses [8, 23], as well as for alpha bearing waste [33].

A number of different incineration technologies are available:

- (a) Excess air incineration is characterized as a one step process. The excess air added is significant (50–75%), resulting in considerable entrainment of particulate matter in off-gas. If a vertical shaft incinerator is used, off-gas quality is relatively low.

- (b) Controlled air incinerators achieve complete combustion of the waste by using multiple combustion chambers in sequence. The waste initially burns at 600–800°C in the primary chamber at near stoichiometric air ratios; the gases are then burnt at 1000–1200°C in the secondary chamber with excess air. In this case off-gas quality is good.
- (c) Starved air (pyrolyzing) incinerators make use of two combustion chambers. The first thermally decomposes material in an oxygen deficient atmosphere. The gases are then mixed with excess air and burnt in the second chamber. This process produces good quality off-gas.
- (d) Fluidized bed incinerators generally operate as single chamber, excess air systems with beds of granular material to heat the waste, where waste is injected directly onto the bed. They can process liquids, slurries or solids. Air is heated by exhaust gases and goes through waste, causing agitation or fluidization.
- (e) Slagging incinerators operate as a multi-chamber process, similar to controlled air incinerators. A mixture of combustible and non-combustible waste is transported through the first chamber under stoichiometric air conditions. The waste then goes into a high temperature chamber where non-combustible residues are melted. The melt is gravity fed into another chamber where it is quenched and converted into a highly insoluble basaltic slag.
- (f) Slagging kiln incinerators operate with a primary chamber at temperatures high enough to melt all waste materials into a slag. A secondary combustion chamber is needed to aid complete destruction of hazardous constituents.
- (g) Rotary kiln incinerators are based on a large, horizontal (slightly inclined) tubular hearth which rotates at a low speed, providing agitation of the waste and efficient mixing with air. They can accept a large range of waste liquids and solids. As the wastes come into contact with the air, they oxidize and gravity moves the remaining waste to the lower end of the kiln. The exhaust gas enters a secondary combustion chamber to provide for complete oxidation of residual organics.
- (h) Agitated hearth incinerators are used mainly for homogeneous waste streams that are difficult to oxidize and/or have a high water content, such as ion exchange resin and filters.
- (i) Multiple hearth incinerators can be used for calcining, roasting and activated carbon regeneration. A series of circular hearths are arranged in a vertical configuration; air cooled rabble arms pile and move the waste to the various hearths. As the waste gets lower it is heated, dried and combusted, then cooled. This is particularly well suited to treatment of sludges, tars and solids which generate low heat.

- (j) Cyclone incinerators can be used for sludges and liquids. They consist of a vertical cylindrical vessel with a single hearth. High shear cyclonic flow provides intense mixing and complete combustion.

While complete destruction of an organic material can be easily achieved by combustion/incineration techniques, concerns remain about the formation of environmentally regulated materials such as dioxins or furans, and radioactive emissions which may require complex off-gas equipment for their containment. The amount of chlorinated plastics (e.g. PVC) processed through an incinerator should be restricted so as to minimize corrosion by chloride. Phosphorus feeds are usually also restricted due to a potential for buildup of P_2O_5 , although this can be mitigated by adding sodium carbonate to the off-gas cleaning system. Sulphur containing feeds (such as ion exchange resins and rubbers) should be limited to minimize H_2SO_4 formation and corrosion.

The application of incineration for organic waste treatment cannot be considered in isolation but should include an overall consideration of final waste disposal. A typical concept for incineration is shown in Fig. 4, which identifies both final products and secondary waste. Such a scheme would be applicable for both solid and liquid waste. For solids, the pretreatment step may involve shredding, whereas for liquids this may be a mixing/homogenizing step to aid delivery to the incinerator. Incineration of PCMs is normally preceded by shredding of the waste to provide a consistent form and improve the efficiency of combustion.

Examples

A number of operational facilities are described in Ref. [10]. Since that publication, the use of incinerators has declined somewhat as changes in airborne discharge regulations and public perceptions have led to the selection of other processes. However, new incineration facilities have been constructed in several countries for various types of radioactive waste.

Figure 5 is a simplified schematic diagram of the Ontario Power Generation (OPG) radioactive waste incinerator at OPG's Western Waste Management Facility in Canada. The incinerator, which was commissioned in 2003, replaced an older batch loaded, starved air design that operated from 1976 to 2001. The new incinerator is licensed for 2 tons per day of low level radioactive solid and 45 litres per hour of liquid radioactive waste based on continuous feed. It operates with a starved air primary chamber and an excess air afterburner. The off-gas treatment includes lime injection to neutralize acid gases. The new system was retrofitted into the same building as the old system.

An existing industrial facility for incineration of both burnable solid and liquid radioactive waste is situated at Belgoprocess in Belgium [34]. This incinerator started nuclear operation in 1995 as a part of the centralized facility for processing low level radioactive waste (CILCA plant). The radioactivity limit of the waste to be incinerated is 40 gBq/m³ for beta–gamma emitters and 40 MBq/m³ for alpha emitters, with a maximum dose rate at the surface of each package of 2 mSv/h. A general flow diagram of the incinerator system is given in Fig. 6. The radioactive waste undergoes a combined process of combustion and pyrolysis. The primary combustion chamber operates at a temperature range of 900–950°C. The unburned gases and soot particles entering the second combustion chamber are mixed with access air to complete oxidation. The access air supply is controlled by an oxygen analyser–controller at the outlet of the secondary combustion chamber. The size of this chamber is meant to

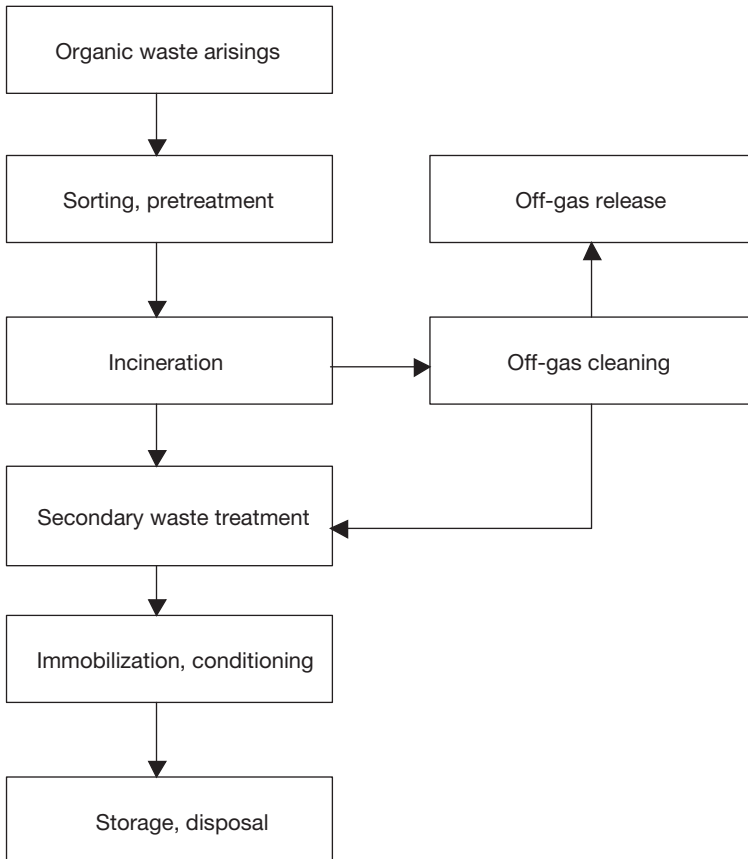


FIG. 4. Conceptual diagram of an incineration process.

provide a minimum of two seconds residence time at the designed waste feed rate and at a temperature of 1050°C.

In the Netherlands, COVRA has installed two incinerator systems for the treatment of organic liquid waste and solid biological matter (e.g. animal carcasses) at Vlissingen-Oost. For the incineration of liquid organic waste, the liquids can be pretreated to remove the inorganic components and then combusted at 1200°C. This liquid waste incinerator has been operating since 1994 [35]. Operational difficulties encountered at this facility were separation of the inorganic components, as the feed was often more complicated than anticipated, gels blocking the feed supply and corrosive species affecting both the incinerator and the off-gas equipment. It was also observed that the increased operating temperatures required to prevent dioxin formation led to the generation of more NO_x, the removal of which was not economic. In comparison, the incinerator for animal carcasses has operated effectively by pyrolysis at 650°C and combustion at 850°C, followed by afterburning at 1000°C.

An oil burner has been operational at Sellafield, UK, since January 1998. The aerial effluent is discharged through a chimney, with small amounts of solid waste accumulating in the combustion chamber in the form of slag. This is periodically removed and disposed of at the low level waste disposal facility at Drigg. An incinerator previously operated at Dounreay, UK, for processing solvent has also experienced difficulties with buildup of corrosive phosphorus oxide products. It was shut down in the 1990s.

It should be noted that public opinion in many countries is adverse to new incinerators and considerable consultation would be required before the construction of such proposed installations. In many cases the proposed construction of large scale incinerators for waste treatment is opposed by local

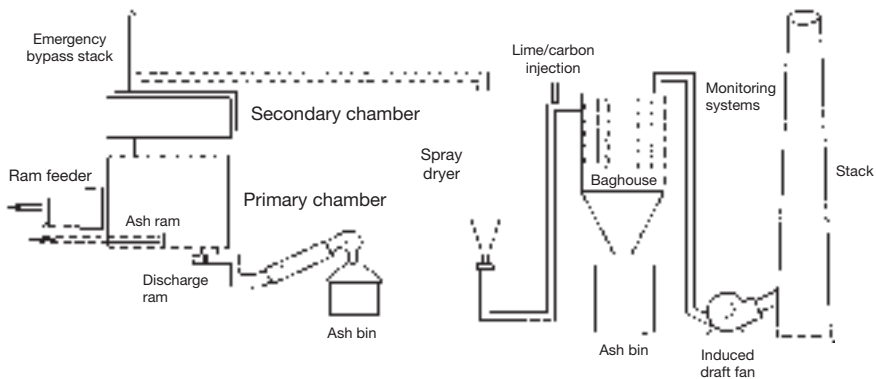


FIG. 5. Schematic diagram of the OPG incinerator, Canada.

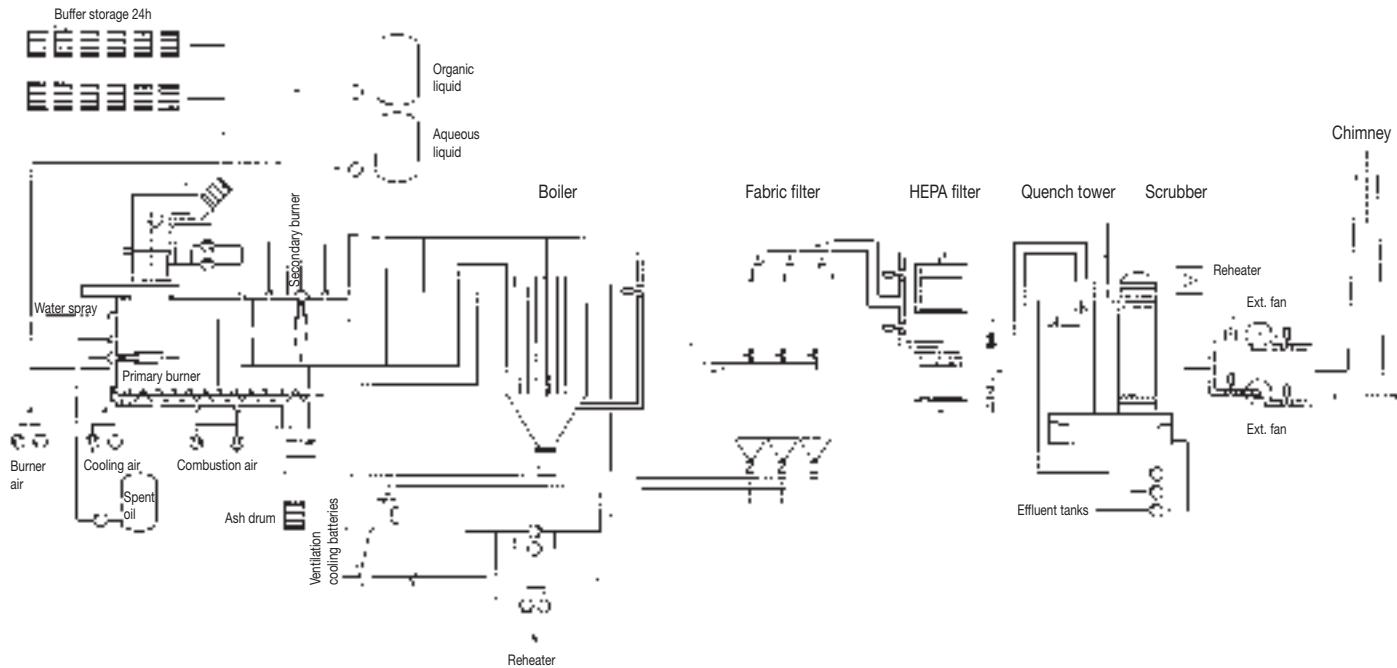


FIG. 6. Schematic diagram of the CILVA incineration facility, Belgoprocess, Belgium.

communities. Table 5 shows some operational incinerators and their present status.

Where operational incineration facilities remain, consideration should be given to pretreating other organic feeds to ensure optimization of the incinerator while remaining within the facility's acceptance criteria. Reference [36] defines the principal requirements for design and operation of incineration facilities for radioactive waste.

Special purpose incineration systems are also being developed. For example, a 15 kg/h system for PVC and rubber is under development in Japan. The system uses a water cooled primary chamber constructed of corrosion resistant alloy [37].

Although TBP/OK could be destroyed in a dedicated incinerator, none is yet operational, principally owing to the difficulties associated with component corrosion. In conditions of sub-stoichiometric oxygen, TBP and OK will pyrolyse on heating. TBP decomposes to form phosphoric acid and a number of organic compounds, such as butanol and butene. In excess air incineration the phosphate is converted to phosphorus pentoxide. The OK and the butyl groups from the TBP are oxidized to carbon dioxide and water vapour. The phosphorus pentoxide combines readily with moisture in cooler parts of the incinerator off-gas plant to form phosphoric acid. Thus, either mode of incineration leads to the formation of phosphoric acid. At high temperature, this acid is very corrosive and leads to a problem in selecting an appropriate corrosion resistant material. Alternatively, means can be provided to convert the phosphorus into an inert phosphate. This can be done in several ways, and incinerators developed for burning solid waste have been tested for burning TBP/OK. These facilities include:

- (1) The fluidized bed incinerator at Rocky Flats, USA, where the sodium carbonate granules in the fluidized bed were used to fix the phosphorus from the TBP;
- (2) The fluidized bed calciner at Idaho National Environmental Engineering Laboratory (INEEL), USA, where less than 86% of the phosphorus was fixed on the alumina/zirconia granules in the bed [38];
- (c) The controlled air incinerator at Savannah River, USA, where only about 42% of the phosphorus was immobilized after slurring of the TBP with calcium hydroxide and feeding it either into cartons or as a spray.

Tributyl phosphate/OK has also been burned experimentally in the cyclone incinerator at Mound Laboratory, USA, and, in small quantities, in liquid waste incinerators at Cadarache, France, and Karlsruhe, Germany [39].

TABLE 5. STATUS OF INCINERATION FACILITIES IN SOME IAEA MEMBER STATES

| Country | Facility/site | Start of operations | Capacity | Comments |
|---------|--|---------------------|---|--|
| Austria | Seibersdorf Research Center | 1983 | 40 kg/h solid | |
| Belgium | CILVA, Belgoprocess | 1995 | 61 kg/h liquid, 79 kg/h solid | Solids, liquids and ion exchange resins |
| Canada | Ontario Power Generation, Western Waste Management Facility | 1976–2001 | 17 m ³ /day solid, 9 L/h liquid | Batch loaded system; shut down in 2001 for replacement |
| | Ontario Power Generation, Western Waste Management Facility | 2002 | 2 t/d solid, 45 L/h liquid (licence limit) | Continuous feed, starved air system |
| France | Cadarache | 1988 | 20 kg/h | |
| | Socodei Centrac | 1998 | 3500 t/a solid 1500 t/a liquid | Commercial low level waste treatment facility |
| | Melox | 1994 | 20 kg/h | Designed for solid alpha contaminated waste |
| | IRIS, Valduc | 1996 | 7 kg/h | Solid alpha contaminated waste |
| Germany | Grenoble | | 20 kg/h | |
| | Karlsruhe | Since 1980s | 50 kg/h solids, 40 kg/h liquids | Solids, including fabric, plastics, rubber; liquids, including oils, solvents, emulsions |
| India | Narora NPP | 1990s | KG/h solid | Used in short campaigns of a few days every few months for solid low level waste |

TABLE 5. STATUS OF INCINERATION FACILITIES IN SOME IAEA MEMBER STATES (cont.)

| Country | Facility/site | Start of operations | Capacity | Comments |
|--------------------|--|---------------------|-------------------------------------|--|
| Japan | PNC, Tokai-Mura | 1991 | 50 kg/h solid | |
| Netherlands | COVRA, Vlissingen-Oost | 1994 | 40 L/h liquid, 60 kg/h solid | Two incinerators, one for liquids, one for animal carcasses and other solids |
| Russian Federation | RADON | 1991–2001 | 20 L/h liquid, 100 kg/h solid | |
| Slovakia | RADON | 2002 | 250 kg/h solid | Uses plasma torch |
| | Jaslovske Bohunice Nuclear Power Plant Research Institute (VUJE) | 1982 | 30–60 kg/h | Used in campaigns for low level waste |
| Slovakia | Jaslovske Bohunice waste processing facility (BSC) | 2001 | 10 kg/h liquid, 50 kg/h solid | Used in campaigns for low level waste |
| | ENRESA-El Cabril | 1992 | 50 kg/h total solid and liquid | Located at low level waste disposal facility |
| Spain | ENRESA-El Cabril | 1992 | 50 kg/h total solid and liquid | Located at low level waste disposal facility |
| Switzerland | PSI Würenlingen | 1974 | 25 kg/h | Shut down in 2003, to be replaced by Swiss Central Storage Facility (ZWILAG) plasma arc system |
| UK | Hinkley Point B | Since 1970s | | Located at a nuclear power plant |
| USA | TOSCA Incinerator, Oak Ridge | 1991 | 700 kg/h solids and organic liquids | Designed for mixed chemical/ radioactive waste |
| | Los Alamos | Shut down in 2000 | | |

TABLE 5. STATUS OF INCINERATION FACILITIES IN SOME IAEA MEMBER STATES (cont.)

| Country | Facility/site | Start of operations | Capacity | Notes |
|-------------|--|---------------------|---|---|
| USA (cont.) | Consolidated Incineration Facility, Savannah River | 1997 | 400 kg/h solids, 450 kg/h liquids | Designed for PUREX reprocessing solvents, low level and mixed waste |
| | Duratek, Oak Ridge | 1989 | Two incinerators, approximately 200 kg/h each | Commercial low level waste treatment facility |

The primary product of the incineration process is ash, which is usually immobilized (e.g. in cement) prior to storage or disposal. Incinerator operation is generally accompanied by secondary waste arisings, typically:

- Solid and liquid effluents from a pretreatment step,
- Scrubber liquors and/or salts from the off-gas equipment,
- Filter media from the off-gas equipment (possibly including organic matter if paper filters are used).

Advantages/disadvantages

The general advantages of incineration are that it leads to complete destruction of the organic material to an inorganic residue, with very high volume and mass reduction factors. It can be applied to a wide range of solid and liquid materials and mixtures of materials. The ash product is readily incorporated into standard immobilization matrices such as cement to produce a fully conditioned waste form ready for long term storage or disposal. However, incineration has a relatively high capital and maintenance cost and can lead to the production of environmentally regulated by-products in the off-gas (e.g. furans and dioxins). Although technology exists to prevent the release of by-products, this increases the cost of the facility. Generally, public perception of incineration as a waste treatment technology is negative.

5.2.2. Pyrolysis

Technique

Pyrolysis is related to incineration, but is based on thermal decomposition of organic materials under an inert or oxygen deficient atmosphere to destroy the waste and convert it into an inorganic residue. Whereas incineration is utilized for low level waste, pyrolysis is more often applied to intermediate level waste. The pyrolysis gas generated is burned in a simple combustion chamber and then treated in a flue gas cleaning section. At 500–550°C the operating temperature for pyrolysis is significantly lower than for conventional incineration. At these temperatures the problem of corrosive species such as phosphoric oxides is removed as the oxides readily form stable inorganic phosphates. Also, at the lower temperatures and reduced oxygen levels, volatile species of concern, such as ruthenium and caesium, are largely retained within the pyrolysis reactor.

Examples

A pebble pyrolysis reactor using calcium hydroxide was developed in Germany for treatment of intermediate level waste, radioactive resins and spent reprocessing solvent (TBP) in kerosene and has been in use since 1989 [40, 41]. The feed system differs for treatment of solid or liquid waste. The moving balls improve heat transfer and can also crush the solids produced by the pyrolysis. The resultant dry product (calcium phosphate from TBP treatment) can be either directly stored in an appropriate container or immobilized immediately for long term storage or final disposal. There have been difficulties in obtaining a consistent calcium phosphate based final product from TBP treatment. This has implications on the product envelope specifications for a final cemented waste form.

Volume reduction can be achieved for the treatment of ion exchange resins where the pyrolysed resin can be incorporated into a conditioning matrix at a higher loading factor than the non-pyrolysed resin. Several facilities which can do this have been constructed in countries such as Belgium, France and Japan [42].

The pyrolysis process can be initiated in a fluid bed system such as that at Rocky Flats in the USA, which uses a two stage system. The first stage includes incineration in a regulated atmosphere (nitrogen + air) using Na_2CO_3 and a catalyst at temperatures of less than 600°C. Afterburning of the off-gases takes place in a second chamber using a bed of pseudo-fluidized Al_2O_3 and a catalyst (Cr_2O_3) at a temperature of 550–600°C. Lower temperatures allow a decrease

in the use of thermal insulation, minimizing the total amount of secondary waste. Aggressive off-gases are neutralized by Na_2CO_3 , which decreases corrosion of the processing equipment. The capacity of the plant is approximately 80 kg/h, but it is not operational at present.

Processing facilities which use pyrolysis in combination with steam reforming technology for volume and weight reduction and stabilization of organic waste, such as the THOR processing facility in Erwin, Tennessee, USA [43, 45], have been constructed. This facility has the capability of processing ion exchange resins, charcoal, graphite, sludge, oils, solvents and cleaning solutions with contact radiation levels of up to 1 Sv/h. The process utilizes two fluid bed contactors to process a wide variety of solid and liquid low level waste. The low level waste is injected into the electrically heated, fluidized pyrolyser where water is rapidly vaporized and superheated and the organic compounds are converted into syngas. The syngas is subsequently oxidized to carbon dioxide and water in a secondary heater/energy recovery system. The off-gas passes through a system of high temperature filters, scrubbers and a final HEPA filter before discharge to the environment.

Residual solids from the pyrolysis of low level waste (including fixed carbon, over 99% of the incoming radionuclides, metal oxides and other inorganics in the waste feed) are removed from the pyrolyser and collected in the first stage ceramic filter vessel. The pyrolyser is fluidized with superheated steam and added gas. The second stage reforming contactor is designed to operate at up to 800°C. Pyrolysed solid residues from the first stage filters are transferred to the reformer, which is an electrically heated fluidized bed where the fixed carbon is converted to dioxide by contact with the superheated fluidizing gases (superheated steam and additive gases). Pyrolysis has also been investigated for various wastes in Sweden [46] and Japan [47].

Advantages/disadvantages

The general advantages of pyrolysis are that it operates at lower temperatures than conventional incineration, thus reducing the problems associated with material corrosion, and corrosive POx is transformed into relatively inert inorganic phosphates rather than phosphoric acid. Similarly to conventional incineration, pyrolysis can be applied to a wide range of solids and liquids and results in a great reduction in volume and mass. The capital and operating costs for the equipment are similar to those for a conventional incinerator. However, the specialized pretreatment equipment required for some waste types (such as PCM or higher dose rate ion exchange resins) can increase these costs significantly. In addition, the final waste product is often not as homogeneous as that of a conventional incinerator.

5.2.3. Alkaline hydrolysis

Technique

Alkaline hydrolysis is a wet, chemical extraction process in which a liquid organic waste is put into contact with an aqueous alkaline solution. Hydrolysis reactions alter the nature of the organic species and result in transfer of the radioactivity to the aqueous phase. Subsequent separation of the phases results in a clean organic liquid. This technique has been employed primarily for the treatment of waste solvents from spent fuel reprocessing, e.g. TBP/OK, allowing the diluant to be recycled. It is described in detail in various references, e.g. Refs [9, 10].

Examples

Alkaline hydrolysis is the main chemical treatment method employed at the solvent treatment plant (STP) at Sellafield, UK. This plant has been designed to treat 750 m³ of TBP/OK from both the THORP and Magnox reprocessing operations. It was commissioned in 2001 to treat historic waste (stored since 1983) and future arisings, and has a prospective lifetime of 30 years.

In the STP, solvent washing is employed if the uranium content of the solvent is high to prevent precipitation of uranium complexes at a later stage. This is then followed by alkaline hydrolysis using 7.4 M sodium hydroxide. The process results in three phases:

- (1) Odourless kerosene: This has little associated activity and is separated for treatment in a vortex combustor.
- (2) Sodium dibutylphosphate: This is the major product of the process and is permitted for sea disposal on account of its solubility and low ecotoxicity.
- (c) Sodium hydroxide: The majority of the initial activity is contained within this phase and is routed for treatment at existing effluent treatment plants using flocculation and cementation processes.

The treatment of the sodium hydroxide phase shows that, for this process to be used on a large scale, considerable thought needs to be given to treatment of the final waste. In the UK, the enhanced actinide removal plant at Sellafield is used to separate the radioactivity from the aqueous phase by iron hydroxide flocculation (chemical treatment), with the resultant floc waste being encapsulated in cement. This particular application of alkaline hydrolysis has been designed to be free of solids. Treatment of waste containing considerable

amounts of solids may require some pretreatment, for example by filtration. Alkaline hydrolysis has also been used at the former WAK facility in Germany [10] and has been studied in India for recycling of TBP [48].

Advantages/disadvantages

Alkaline hydrolysis is a well established chemical process for the treatment of spent fuel reprocessing solvents. Its main advantages are the low operating temperature and its size flexibility for operation, from benchtop to full sized industrial plant. However, it has very limited application for radioactive organic waste and often produces complex waste products that require further treatment before they are suitable for storage or disposal.

5.2.4. Vitrification

Technique

Vitrification involves combining feedstock materials with glass forming compounds at high temperature, usually to produce a solution of radionuclides in a glass matrix which is poured into a container and allowed to cool to form a monolithic block. The high temperature destroys any organic species in the waste which would otherwise result in the discharge of volatile and gaseous species and require scrubbing in an off-gas system prior to discharge.

A closely related technique is molten glass incineration, by which solid low level waste (usually shredded) is fed directly into a bed of molten glass. The organic material combusts in the pool of glass, leaving a residue encapsulated in the glass matrix. The waste product resulting from molten glass incineration is generally not as homogeneous as that from true vitrification.

Examples

Vitrification has been researched extensively and applied to the solidification of high level waste in France, the Russian Federation, the UK and the USA. In these applications it is important that the feedstock be fully calcined and the radionuclides dissolved in the glass. There has been considerable interest, particularly in France, in the application of vitrification technology to waste other than high level radioactive waste, for example sludge waste containing organic species that might act as radionuclide complexants. Several approaches are possible, including the direct feed of organic aqueous waste into the glass crucible without separate calcination of the feedstock, such

as the Russian Joule melting process [49]. A 500 L/h plant has been constructed in the Russian Federation.

Pilot plants for vitrification of low level waste have been built in the Republic of Korea [50] and in France [51]. Vitrification of low level waste has also been studied at the Pacific Northwest National Laboratory in the USA. Some commercial waste processing facilities in the USA also employ low level waste vitrification systems [52]. A volume reduction factor of up to 200:1 and a mass reduction factor of 10:1 with a processing rate of about 70 kg/h are claimed for these commercial systems.

Advantages/disadvantages

The general advantages of vitrification are that it yields a robust waste form suitable for long term storage or disposal, results in total destruction of the organic material and can be applied to a wide range of liquid and solid waste. However, it is a complex and expensive technology that is generally only applied to high level waste and specialized waste that is difficult to treat with other technologies. The high operating temperatures often dictate the use of exotic construction materials.

5.2.5. Plasma treatment

Technique

Plasma treatment uses an electric arc to generate a temperature in excess of 20 000°C. This temperature causes the molecular structure of materials to be broken into their constituent atoms. The electric arc can be generated by a conventional plasma torch (used in many industrial processes) or by one or more graphite electrodes. Power ratings typically range from several hundred kilowatts to several megawatts. The process can be applied to vaporize organic materials (and other volatiles) and to melt metallic or inorganic constituents in radioactive waste. The vaporization conditions can be changed by changing from a reducing plasma gas (e.g. Ar or N₂) to an oxidizing one (e.g. air, O₂).

The resulting vapour phase is passed through an afterburner or catalytic converter for complete oxidation, followed by appropriate treatment of the off-gas. This is a multi-step procedure aiming to eliminate chemical compounds and radioactivity in the released off-gas to levels which safely comply with conventional and radiological regulations. The molten residues (metal and/or slag) which contain most of the radioactivity are transferred into an external vessel and cooled. In general, they form solid phases which are deemed to be directly suitable for storage and disposal. Direct vitrification of the slag by the

addition of glass frit into the crucible during the treatment may yield a waste form with enhanced properties [53].

Depending on the nature of the off-gas treatment system, the process will lead to the production of some secondary waste (e.g. HEPA filters, sludges, aqueous solutions) which, depending on the nature of waste and on the treatment strategy, might be radioactive and require subsequent treatment, one option for this being incinerator feed.

Examples

This technique has been applied in various forms for the destruction of problematic chemical waste, later on extended to incineration/melting of low level waste [54, 55]. A first full scale plant for processing low level waste, the plasma arc centrifugal treatment plant (PACT) at the ZWILAG facility in Switzerland, shown in Figs 7, 8, is in the clearance process for active operation [56].

The system is supplied with a drum feed (drum sliced to reduce its size before entering the crucible), and the final waste form is a vitrified slag. A similar system is currently being installed in Japan [57]. A graphite electrode plasma system has been installed at the KAERI waste treatment centre in the Republic of Korea (Fig. 9) [58].

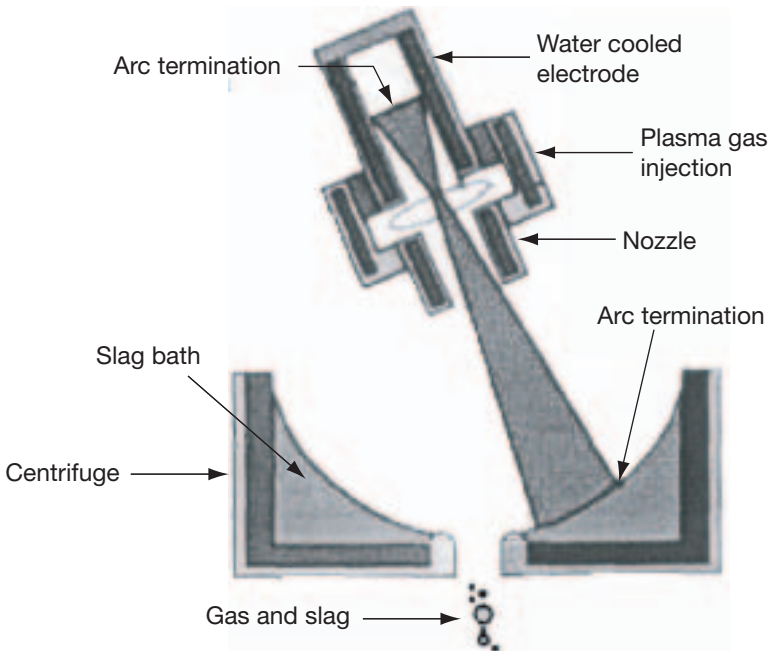


FIG. 7. The PACT concept.

Advantages/disadvantages

The general advantages of the plasma treatment process are similar to those of vitrification. It yields a robust waste form suitable for long term storage or disposal, results in total destruction of the organic material and can be applied to a wide range of liquid and solid waste. Unlike other forms of thermal processing, plasma treatment does not require any pre-separation of different waste materials. Entire drums of waste can be fed into the system (drum included) with no prior sorting of the contents. Similar to vitrification, the process is expensive to construct and operate. In addition, there is as yet no full scale plant experience with low level waste. However, several such facilities are in the advanced stages of startup.

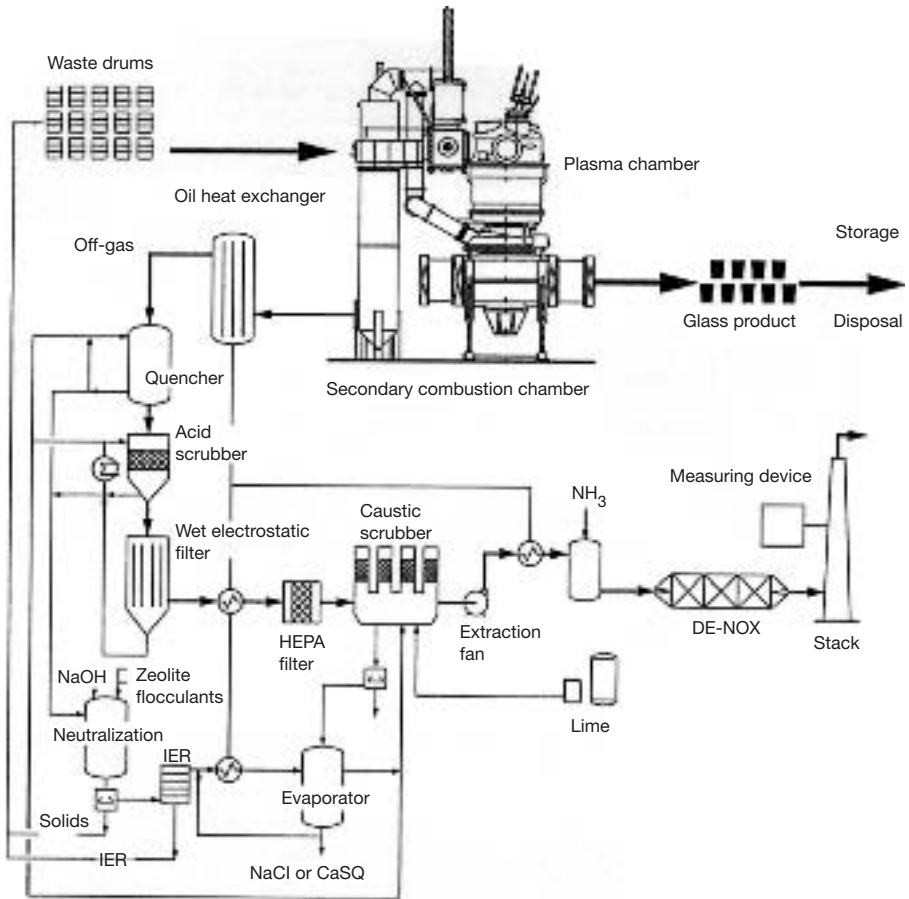
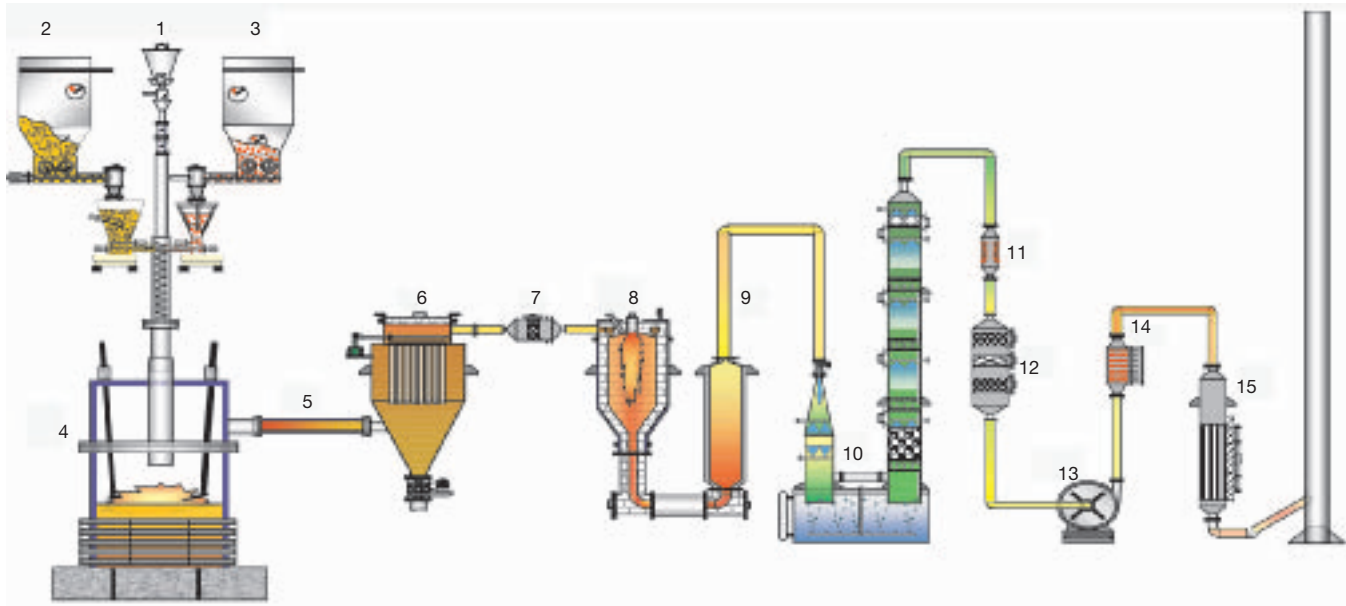


FIG. 8. Flow sheet of the ZWILAG plasma system process.



- | | | |
|------------------------|---------------------------|---------------------------------|
| 1 Glass frit feeder | 6 High temperature filter | 11 Reheater 'A' |
| 2 DAW feeder | 7 HEPA filter | 12 Activated carbon/HEPA filter |
| 3 Resin feeder | 8 Post-combustion chamber | 13 Extraction fan |
| 4 Cold crucible melter | 9 Off-gas cooler | 14 Reheater 'B' |
| 5 Pipe cooler | 10 Scrubber | 15 DeNOx system |

FIG. 9. Schematic diagram of the KAERI waste treatment facility in Daejeon, Republic of Korea.

5.2.6. Molten salt oxidation

Technique

Molten salt oxidation has been developed as an alternative to traditional incineration of organic waste. The combustible organic species are oxidized in a bath of alkaline molten salts at temperatures between 500 and 950°C (Fig. 10). The organic components react with oxygen to produce carbon dioxide and water, and the inorganic component residues formed (including actinide species) are contained within the molten salt. Any acid gases produced in the oxidation, such as hydrochloric acid, are scrubbed by the alkaline salt. Recycling of the salt removes the residues from the bath for immobilization.

Examples

There are a number of examples of molten salt use for nuclear waste. A bench scale facility has been developed at Lawrence Livermore Laboratories in the USA [59]. The process is generally used for mixed waste. Other facilities have been constructed in the Republic of Korea and in the USA for military waste [60].

The spent salt produced in the process can be converted to a ceramic as part of the process. Extensive off-gas equipment is generally employed, producing additional quantities of scrubber liquors and/or salts.

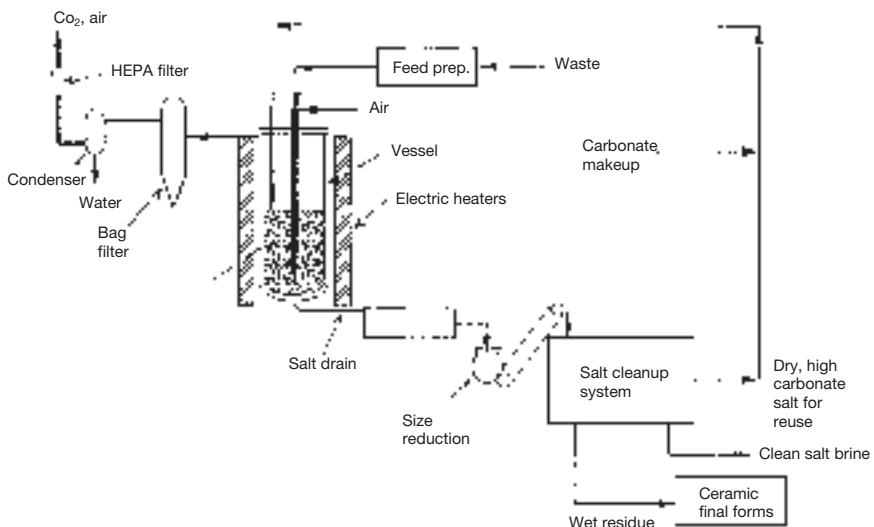


FIG. 10. Integrated molten salt oxidation system.

Advantages/disadvantages

The general advantages of the molten salt oxidation process are that it results in the complete destruction of organic material (even complex poly-aromatic compounds that are difficult to destroy with other methods); it operates at a lower temperature than vitrification, plasma or conventional incineration systems; it results in negligible dioxin and furan production; and the radioactive species are captured in the salt bath, which also scrubs acid gases from the off-gas system. The process is still in the development phase, has a high capital cost and requires specialized techniques for adequate conditioning of the salt product.

5.2.7. Electrochemical methods

Technique

Electrochemical methods are based on the creation of highly reactive ions and their subsequent use to break organic bonds and destroy the organic material. The most commonly described method utilizes a highly reactive form of silver, Ag^{++} ions in a standard electrochemical cell, and is informally known as the silver II process. The feedstock is fed to the reaction vessel containing a nitric acid and silver nitrate solution in an anolyte circuit. The anolyte solution is circulated through the electrochemical cell where the natural Ag^+ ions are transformed into highly reactive Ag^{++} ions which attack the organic feed. The organic matter is broken down into carbon dioxide, insoluble inorganic salts and water, which migrates across a membrane, preventing bulk mixing of the anolyte and catholyte.

The reaction turns the Ag^{++} ions back into Ag^+ ions which are recycled to continuously generate the active Ag^{++} species. The insoluble inorganic precipitates are extracted from the anolyte circuit using a hydrocyclone. The cathodic reaction involves reduction of nitric acid and protons to nitrous acid, NO_x and water. The nitrous acid and NO_x are oxidized to nitric acid through reaction with oxygen and water. There is no volatilization of low molecular weight species which are formed as intermediates during the destruction process, and the process can be readily started and stopped by switching the current on or off.

Examples

This patented technology has been developed to 4 kW pilot plant scale and operated on a semi-continuous basis at Dounreay in the UK [61]. The Silver II technology has also been investigated in Belgium [42].

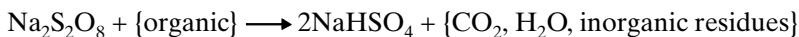
Advantages/disadvantages

The general advantages of electrochemical oxidation processing is that it is capable of treating a range of liquid organic wastes, even with an organic content of as much as 100% and with low temperature and pressure. However, it is a complex technology with a relatively high capital and operating cost. It is not suited for solid waste unless this can be finely dispersed in a liquid suspension.

5.2.8. Direct chemical oxidation

Technique

This method has been used specifically to describe a process developed at Lawrence Livermore National Laboratories [62]. It was designed to retain the benefits of an aqueous system (capturing dust while products remain within a liquid medium) but increase the efficiency of oxidation in an aqueous process by specifically utilizing sodium or ammonium peroxydisulphate. The peroxydisulphate ion is a strong oxidant and the oxidation reactions require no catalysis.



The operating temperature is normally 80–95°C and the final bisulphate ion is recycled to produce new oxidant by conventional electrolysis. The organic material is converted to carbon dioxide and the inorganic residue products can be collected for immobilization in cement.

Examples

This technique is still at the development stage, although it has been tested on organic materials including TBP and other solvents. Direct use of other oxidizing chemicals has not been reported in this context. However, acid digestion, described in the next section, is the most closely related technique.

Advantages/disadvantages

The general advantages of the direct chemical oxidation technique are its use of low temperature and pressure aqueous reaction media combined with improved oxidation efficiency. It is only suitable for liquid organic waste.

5.2.9. Acid digestion

Technique

The acid digestion technique uses hot, strong mineral acids (nitric and sulphuric acids at about 250°C) to oxidize the organic components of the waste, producing a range of gases and an aqueous sludge consisting of inorganic oxides.

Examples

This technique was pioneered in Belgium in the 1970s and was studied in a number of countries during the 1980s, but only in Germany and the USA was experience obtained with a large scale plant [63]. The process was proven successful for TBP, but organic liquids like trichloroethane and also toluene are not easily digested. The process is not currently used on an industrial scale but is being re-examined for the processing of mixed (chemically hazardous and radioactive) waste in the USA [64].

5.2.9.1. Advantages/disadvantages

The acid digestion technique is capable of treating a range of organic wastes and operates at low pressure. Because of the extremely corrosive nature of the acid mixture, the process needs to be performed in equipment made of expensive, highly corrosion resistant materials. The oxidative reaction results in the formation of sulphur and nitrogen oxide. As these gases cannot be discharged to the environment, extensive off-gas treatment is necessary. The residual waste also requires neutralization before immobilization in cement.

5.2.10. Wet oxidation

Technique

The wet oxidation technique uses soluble salts of redox sensitive elements with hydrogen peroxide or air/oxygen to effect the chain reaction oxidation of

organic materials, producing carbon dioxide, water and inorganic salts. In 1994, Fenton investigated the use of soluble iron salts with hydrogen peroxide for the oxidation of organic material by the formation of the highly oxidizing hydroxyl radical [65]. On contact with organic molecules this radical abstracts hydrogen atoms or adds across unsaturated bonds to form organic radicals. Reduction or oxidation by the transition metal ion, which is now present in both its principal oxidation states, can stabilize the organic radical, allowing further attack by hydroxyl radicals. Eventually the original organic carbon structure will be completely converted in a reaction analogous to incineration. This basic chemical reaction has been much developed since and finds application today in the treatment of radioactive organic material.

Wet oxidation can be applied at low temperatures and pressures, generally using hydrogen peroxide (H_2O_2), sometimes with a catalyst, or at high temperatures and pressures using oxygen or compressed air as the oxidant. The method is applied to liquid waste or small particulate waste (e.g. ion exchange resins or sludges). Once initiated, the oxidation reaction is generally exothermic.

Examples

Application of this chemical method has been proven for treatment of ion exchange resins with either an iron or copper catalyst. For example, a 99% organic carbon reduction and 78% volume reduction for the treatment of cation resin were achieved [66]. These promising results led to the development of a mobile treatment plant in the UK. It was designed to treat up to 100 L of organic ion exchange resin per day and was contained within a single ISO transport container. The resultant slurry residues are encapsulated in cement. This provides a volume reduction factor comparable to direct encapsulation of the original organic waste. The mobile demonstration plant was built and licensed in accordance with UK regulations and demonstrated the treatment of 360 L of ion exchange resins containing over 100 MBq of activity contaminated with EDTA and citrate.

Other related systems include a chromium catalysed destruction process, patented by BNFL [67]. However, the implications of the production of large volumes of aqueous waste containing chromium requiring treatment, for example by immobilization, would appear to outweigh the advantages. This system is most applicable to water miscible organic components (e.g. glycols).

A full scale wet oxidation system using air was operated by Ontario Hydro in the mid-1990s to process EDTA based boiler chemical cleaning solutions from nuclear power plants [68]. Although the solutions contained detectable amounts of radioactivity (mostly ^{60}Co and tritium), these were

below regulatory limits and it was therefore classified as a non-radioactive system. The two stage system operated at approximately 5 MPa and 250°C, using compressed air as the oxidant and steam for the initial heating. Once started, the process was exothermic and required no additional heat. Sludge was removed in a filter press. The oxidized effluent was polished using an ultrafiltration and reverse osmosis system and discharged to a sewage treatment plant. The system processed more than 5 000 000 L of solvent before it was shut down. Operational experience with the system suggested that it required high maintenance due to the buildup of iron hydroxide sludge in the reactor vessels and piping. Wet air oxidation using H₂O₂ at atmospheric pressure and less than 100°C has also been investigated in Egypt on a bench scale for cellulose, IX resins and liquid scintillants [69].

Advantages/disadvantages

The technique uses degradable oxidizing agents (e.g. H₂O₂), and is suitable for low concentration water miscible organic feeds. It can be operated as a mobile treatment plant, and can be implemented with simple equipment at low temperature and pressure. However, it frequently relies on soluble heavy metal catalysts and can result in incomplete oxidation, leaving alcohols. For safety reasons, the H₂O₂ content should not exceed about 6%. Where a high temperature is required, the systems require special alloys to sustain high pressure and resist corrosive attack. There is evidence of high levels of maintenance.

5.2.11. Advanced oxidation processes

Technique

Advanced oxidation processes are a class of waste treatment methods that include the use of ultraviolet light and oxidants (hydrogen peroxide or ozone), sometimes combined with catalysts, to destroy organic materials, producing carbon dioxide and water (with inorganic salts if catalysts are present). These techniques are similar to wet oxidation and are applied industrially to wastewaters containing small amounts of organic species. The waste stream must be of low turbidity to enable penetration by UV light. A possible application for nuclear waste streams may be removal of the organic component of an aqueous radioactive waste so that the aqueous stream can then be treated by a conventional method such as biological treatment or flocculation. It is unlikely that there would be any benefit in dilution of a

concentrated organic to the extent that this technique could be applied, as the increase in volume would be significant.

Although organic species could be directly oxidized by UV light, this would require tuning of the wavelength to the absorption band of the contaminant. Photochemical decomposition of hydrogen peroxide under UV light produces strong oxidants capable of oxidizing organic material to carbon dioxide and water. It has also been used on the effluent from wet oxidation systems containing Fenton's reagent (as described in Section 5.2.10) to ensure complete oxidation of the original organic material.

Another advanced oxidation process is catalytic chemical oxidation using platinum coated alumina as a catalyst to promote decomposition of organic materials in a non-flame process at high temperature (450–750°C). Complex dedicated equipment is required, including that for emission reduction of off-gases.

Examples

Advanced oxidation has been applied to industrial and 'Superfund' sites in the USA to destroy halogenated solvents [70]. It has been demonstrated in a laboratory environment on oxidation of oxalic acid and TBP in nitric acid. A pilot scale system for the treatment of radioactive laundry waste has been constructed in the Republic of Korea [71] and an evaluation trial for organically contaminated radioactive wastewater has been reported from Japan [72]. Catalytic chemical oxidation remains under development and has not been demonstrated on a large scale.

Advantages/disadvantages

Advanced oxidation uses degradable oxidizing agents (e.g. H_2O_2), and is suitable for low concentration water miscible organic feeds. It can be used in a mobile treatment plant, with simple equipment at low temperature and pressure. However, successful application requires dilute aqueous systems, and experience of its application to radioactive waste is very limited. For safety reasons, the H_2O_2 content should not exceed about 6%. Catalytic chemical oxidation is a non-flame process in which the catalysts can be recycled frequently, but it is not ready for commercial exploitation.

5.2.12. Supercritical water oxidation

Technique

The supercritical water oxidation technique uses the properties of water at above its critical temperature and pressure, combined with air, to oxidize organic material, producing carbon dioxide and water with inorganic components, resulting in insoluble precipitates. The supercritical conditions require a substantial plant operating at high temperatures and pressures.

Supercritical water oxidation can be considered to be an advanced form of wet oxidation. Water oxidation of organic material is possible at temperatures and pressures exceeding the critical point of water (374°C and 22 MPa). In these conditions, water acts like a non-polar fluid and all organic material becomes soluble. This supercritical water can be mixed with oxygen in any proportion, and by increasing the temperature and pressure to 400°C and 25 MPa all organic matter becomes unstable. In general, metals are converted to their oxides and are precipitated from the supercritical fluid.

Examples

Supercritical water oxidation has been applied to industrial waste with some success [73]. Modular transportable units have also been developed for small volumes of waste. The technique has been investigated in Japan for low level and mixed waste [74]. A system for alpha contaminated waste including solvents, rags, filters and IX resins is operated at Los Alamos National Laboratory in the USA. Supercritical water oxidation is also widely used for the destruction of chemical waste, military toxic waste and explosives in the USA, as well as in France, Germany, Spain, Sweden and Switzerland, and has been applied to municipal sewage in several countries.

Advantages/disadvantages

This technique can provide rapid and efficient oxidation of organic materials in aqueous media without generation of NO_x or SO_x . It is an efficient means of separating dissolved heavy metals and fission products from dilute aqueous solutions and can be applied in a mobile treatment plant. However, the high pressure and temperature requirements may limit maximum equipment size, and systems are generally limited to processing solutions and slurries containing 2–25% organics with particulate not exceeding 100 μm in diameter. The chemical environment in the reaction chamber is very challenging, as mineral acids are formed (e.g. from Cl, F). Strong alkalis may

need to be added to the feed material to control corrosion. The oxidation is exothermic and the process must be controlled to ensure that excessive temperature rises do not occur. The inorganic product forms a concentrated sludge which will need to be effectively immobilized.

5.2.13. Solvate electron oxidation

An innovative decontamination technique is the solvated electron technique, which can be used for reducing the toxicity of organic species such as PCBs and pesticides. The technique uses the powerful reducing properties of free electrons to destroy the aggressive or toxic functional groups of organic compounds, producing non-aromatic hydrocarbons. The solvated electrons are formed by dissolving sodium metal in liquid ammonia. The process is patented in the USA and has seen commercial application at Superfund sites.

5.2.14. Biological treatment

Technique

The biological treatment technique uses the ability of bacteria to metabolize and digest the organic components of waste. Under aerobic conditions, the gaseous product is carbon dioxide, but anaerobic conditions will produce a 50:50 mixture of carbon dioxide and methane. Inorganic material will remain associated with the biomass. Industrial experience of using bacteria for the biological treatment of waste shows that the biological agents are often most effective when used for a specific substrate and low concentration organic containing aqueous streams.

Examples

A proprietary method for the treatment of organic waste has been patented in the USA [75]. It utilizes preselected bacteria at 35°C to hydrolyse low activity organic solvents and absorb any remaining products other than carbon dioxide and water onto a silica substrate which can then be disposed of in a low level waste disposal facility. It is also believed that the biomass is absorbed onto this substrate, which is discharged periodically for immobilization in cement. Generally the bacteria need to be selected for the substrata, so the biological agents need to be changed if a wide variety of wastes are to be treated. The technology is not utilized at present, although a pilot facility has been constructed for Electricité de France.

A pilot plant for biological treatment of ion exchange resins has been constructed at Loviisa in Finland [76–77]. Fermentation of cellulose waste using fungi and yeast has also been studied on a bench scale in the Russian Federation [78]. However, with the exception of conventional sewage treatment plants, which in some cases may accept low level liquid effluents from research or medical facilities, biological processes are not currently employed on an industrial scale for the treatment of radioactive waste.

Advantages/disadvantages

Biological methods are the subject of much industrial and academic research. Prior to embarking on such a route for the treatment of organic waste it should be noted that it is only suitable for low volume, low concentration streams. Because biological matter is usually substrate specific, biological treatment is not very suitable for mixed waste, and there is a need for subsequent treatment and disposal of biomass and of a large volume liquid stream. If the waste contains ^{14}C or tritium the gaseous products will be active, and will require additional management. The technique is not recommended for destruction of solid organic waste.

5.2.15. Advanced thermochemical treatment process

Technique

This process uses a powdered metallic ‘fuel’ such as aluminium 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, and combustion to destroy the organic material, resulting in solid slag or ash. The hydrogen gas burns because of the presence of enough oxygen, and in a 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.

Examples

This process was developed in the Russian Federation for a variety of organic and biological wastes [79]. It has been used for incineration of spent ion exchange resins, plastics, biological and medical waste. It can be used for in situ destruction of animal carcasses as demonstrated in an experiment in the Czech Republic [80]. The process has also been used for decontamination of organic surfaces such as asphalt.

Advantages/disadvantages

The technique is a relatively simple process that can be applied to mixed solid waste. However, the waste product may present challenges for conditioning to a disposable form. For safety reasons, the production and burning of hydrogen gas requires great care.

5.2.16. Microwave treatment

Technique

Microwave treatment of organic waste uses microwave energy to heat the waste and destroy organic components. The microwave energy is applied to the waste, which can be either in batch form (in a container) or on a continuous transport system (e.g. a conveyor belt). The energy causes molecular vibration in dipolar molecules, which in turn heats the waste as well as breaking down organic chemical bonds. Steam or other moisture can be added to dry waste to increase the efficiency of the microwave heating. Large waste may be shredded first, in order to provide more even energy distribution. Very high temperatures can be achieved, and the process produces an inorganic fused solid mass.

Examples

Microwave energy has been used to dry wet waste (such as IX resins and sludges), to melt waste (such as plastics), to induce chemical reactions to destroy organic components of waste [81, 82], or to sterilize radioactive medical waste [8]. Systems can be constructed to handle a few kilograms to many hundreds of kilograms per hour. High power microwave systems can also be used to melt inorganic residues such as salts in scrubber concentrates or sludges, or as a source of heat for vitrification systems.

Advantages/disadvantages

This is a relatively simple technique, which may be applied using mobile equipment, and has the potential for high throughput. However, the fused solid product may present a challenge to subsequent conditioning for disposal, and the off-gas produced during the processing of this waste may require further treatment prior to discharge.

5.3. CONDITIONING OF TREATED AND SECONDARY WASTE

Many of the treatment technologies described in this section produce intermediary waste products and secondary waste. These are generally inorganic and may include ashes, salt residues, liquids, sludges and compacted pucks. Technological and maintenance waste will also be produced by most of the processes. Conditioning technologies for these materials generally follow conventional technologies for direct immobilization, as described in Section 5.1.7. However, some special considerations may be necessary, as described below.

5.3.1. Solid waste and residues

Some of the treatment options for organic radioactive waste discussed elsewhere in this section result in direct, effective immobilization of waste in a disposable form. These processes include direct cementation, plasma arc treatment and vitrification, the products of which require no further conditioning. Some of the other treatment methods result in effective immobilization but do not result in a product ready for disposal. In these cases the conditioning process can take account of the properties of the treated waste in producing a fully immobilized waste form. An example would be high force compaction of PCM to produce stable pucks that can then be grouted into a container using cement.

Some treatment processes produce a dry salt or ash, either as a conversion product of the original waste or as a secondary waste, such as from an off-gas scrubber system. Although these are generally inorganic high salt concentrations or finely divided metallic residues (from mixed organic/inorganic waste), they may require special formulations of solidification matrices to ensure that a waste form is suitable for storage or disposal. Technological waste (e.g. mechanical components replaced during maintenance) is also often conditioned by encapsulation in a matrix (usually cement grout) in a container.

5.3.2. Liquid secondary waste

Treatment processes which utilize wet chemistry (e.g. acid digestion) produce a liquid secondary waste which must be further conditioned prior to disposal. The absorption of liquids on porous materials may provide a suitably treated waste although the potential for subsequent release of the liquid burden, for example during transportation or following geological disposal,

should be evaluated. If the retention of absorbed liquids is compromised, further conditioning or packaging of the waste will be necessary.

Wet chemical processes may also produce liquids with extreme pH values (i.e. highly acidic or highly alkaline). These liquids may require neutralization prior to conditioning, depending on the conditioning process employed. The effects of the neutralization step must be considered in the overall process. For example, sudden major changes in pH may cause dissolved chemical species to change form or to precipitate, and may produce significant heat.

5.3.3. Sludges

Many of the remaining treatment processes result in wet particulate or sludge residues which require further conditioning to produce a disposable product. The most common method for processing these is to mix them with a material that subsequently sets to form a solid mass. It is worth noting that the integrated, commercial application of some of these waste treatment processes results in the direct production of conditioned waste forms.

Use of hydraulic cements to immobilize particulates or sludges is widespread, but the development of a suitable formulation can be difficult. The chemical and physical nature of the residue is crucial to the success of this approach. Potentially difficult residues would include metastable intermediates with a high demand for water, hydrophobic material that is difficult to mix in aqueous systems, or extremes in pH (either acidic or alkaline, as these may interfere with the immobilization process). The development of an appropriate formulation is therefore crucial.

5.3.4. Off-gases

Many waste treatment processes, especially ones utilizing or generating heat, produce an off-gas stream. Depending on the nature of the waste being treated, the off-gas stream may require further treatment prior to discharge. This treatment may include scrubbing to remove acid gases or other noxious substances, filtration to remove particulate, absorption (e.g. charcoal bed) to remove volatiles, or further heating to destroy toxic or hazardous substances (e.g. dioxins, furans). Each of these steps may result in the production of secondary solid or liquid waste that must then be managed as described above. The presence of radioactive gases such as tritium and ^{14}C in the off-gas stream needs to be considered.

For comparison, the principal features of the various disposal techniques described in this section are summarized in Table 6.

TABLE 6. SUMMARY OF ORGANIC WASTE PROCESSING TECHNIQUES

| Technique | Feed | Nature of the waste after treatment | Suggested conditioning | Features of the technique | Current status | Secondary waste issues |
|-----------------------------------|------|--------------------------------------|-----------------------------|--|---|--|
| <i>Non-destructive techniques</i> | | | | | | |
| Drying and evaporation | S, L | Dried solids or concentrated sludges | Incineration or cementation | Necessary step for some waste types | Widely used | Off-gas system needed if active discharge possible |
| Distillation | L | Concentrated residues | Incineration or cementation | Allows possible reuse of the organic materials | Widely used to separate wastes and reduce volume | Off-gas system needed if active discharge possible |
| Physical conditioning | S, L | Separated wastes | Incineration or cementation | Necessary step for some waste types — allows access to a wider range of techniques | Waste should be segregated at source — applies mostly to historic waste | |
| Decontamination | S, L | Cleaner waste | Incineration or cementation | Allows possible reuse of the organic materials | Widely used (laundry, etc.) | Off-gas system needed if active discharge possible |
| Absorption | L | Solid with absorbed liquid | Cementation | Waste remains liquid and may drain in future | Widely used in research laboratories | |

TABLE 6. SUMMARY OF ORGANIC WASTE PROCESSING TECHNIQUES (cont.)

| Technique | Feed | Nature of the waste after treatment | Suggested conditioning | Features of the technique | Current status | Secondary waste issues |
|-------------------------------|------|-------------------------------------|---|--|--|--|
| Compaction | S | Compacted waste pucks | Cementation | Volume reduction of waste, supercompactors available | Widely used | Expressed liquids (squeezeate) |
| Direct immobilization | S, L | Complete waste packages | Not applicable | Broad acceptability, mature technology | Applied widely to ion exchange materials and sludges | |
| <i>Destructive techniques</i> | | | | | | |
| Incineration | S, L | Ash | Cementation | Complex technology, high capital and operating costs | Some older facilities operational at power plants, new licensing difficult | Off-gas equipment required due to volatile species |
| Pyrolysis/steam reforming | S, L | Powder | Cementation | Complete oxidation of organic material; more applicable to PCM waste | Licensed for treatment of TBP waste solvent — Facility in the USA since 1999 | Off-gas equipment required due to volatile species |
| Alkaline hydrolysis (TBP/OK) | L | NaDBP, OK and caustic waste | Sea disposal, vortex combustor and flocculation and cementation | More developed for spent reprocessing solvent treatment | Basis of STP at Sellafield, UK | |

TABLE 6. SUMMARY OF ORGANIC WASTE PROCESSING TECHNIQUES (cont.)

| Technique | Feed | Nature of the waste after treatment | Suggested conditioning | Features of the technique | Current status | Secondary waste issues |
|---------------------------|------|-------------------------------------|-------------------------------|---|--|--|
| Vitrification | S, L | Glass blocks | Not applicable | Waste loading limited by solubility in glass, but can operate as encapsulation system | Operational facilities in France, Russian Federation, UK, USA | Off-gas equipment required due to volatile species |
| Plasma treatment | S, L | Final waste product | In-furnace slag vitrification | Combined incineration/melting, one step process for generation of disposable waste forms; complex technology, high capital and operating cost | Full scale low level waste plant in Switzerland started active test operation in 2003; related system being installed in Japan and the Republic of Korea | Off-gas equipment required due to volatile species |
| Molten salt oxidation | S, L | Spent salt | Ceramification | Applicable to mixed waste of high organic concentration, retains activity in salt | Pilot plant developed at Lawrence Livermore National Laboratories | Off-gas equipment required due to volatile species |
| Electrochemical treatment | L | Electrolyte | Cementation | Applicable to mixed waste of high organic concentration | Pilot plant operational at Dounreay, UK, technology to be deployed in the USA for treatment of military waste | Off-gas equipment required due to volatile species |

TABLE 6. SUMMARY OF ORGANIC WASTE PROCESSING TECHNIQUES (cont.)

| Technique | Feed | Nature of the waste after treatment | Suggested conditioning | Features of the technique | Current status | Secondary waste issues |
|-------------------------------|------|-------------------------------------|------------------------|---|--|--|
| Direct chemical oxidation | L | Inorganic salts | Cementation | Low temperature incineration | Still in the development stage at Lawrence Livermore National Laboratories, USA | Off-gas equipment required due to volatile species |
| Acid digestion | S | Acidic sludge | Cementation | Highly corrosive system | Used previously in Eurowatt process in Germany — now being decommissioned | Off-gas equipment required due to volatile species |
| Wet oxidation | L | Inorganic sludge | Cementation | Low capital cost | Pilot plant developed in UK, ion exchange resin treated as part of EU funded programme | Off-gas equipment required due to volatile species |
| Advanced oxidation | L | Inorganic sludge | Cementation | Several variants — UV/H ₂ O ₂ uses 400 nanometre UV light | Best suited to industrial wastewater treatment | |
| Supercritical water oxidation | L | Inorganic sludge | Cementation | High temperatures and pressures required | Pilot plant in use | |

TABLE 6. SUMMARY OF ORGANIC WASTE PROCESSING TECHNIQUES (cont.)

| Technique | Feed | Nature of the waste after treatment | Suggested conditioning | Features of the technique | Current status | Secondary waste issues |
|---------------------------|------|-------------------------------------|----------------------------|--|---|--|
| Biological treatment | L | Inorganic waste (and biomass) | Cementation (incineration) | Applicable to specific substrate in low concentration organic aqueous stream | Used in wastewater treatment to lower COD/BOD. Pilot scale test in Finland for IX resins. | Spent biomass and large volume of water for disposal |
| Thermo-chemical treatment | S | Ash and fused solids | Cementation | Residues from powdered metal fuel present a challenge | Demonstrated on a range of waste types | |
| Microwave treatment | S | Fused solids | Cementation | Wide applicability, high throughputs possible | Demonstrated on a range of wastes | |

Note: S: solid; L: liquid.

6. PROPERTIES AND PERFORMANCE OF CONDITIONED WASTE FORMS

Waste conditioning has to meet three main objectives. The resulting waste packages must:

- (1) Be acceptable for storage,
- (2) Enable their safe transport,
- (3) Comply with disposal requirements.

These objectives may be achieved by a process or processes yielding a convenient solid waste form which is permanently encapsulated in packaging suitable for all subsequent waste management steps. Temporary or permanent overpacking would be a possible and acceptable option to enhance safety at a later point in time, if required. The waste form should, under storage and disposal conditions and over the timescales envisaged, efficiently immobilize the incorporated radionuclides, have and keep adequate physical properties and not be significantly deteriorated by chemical and radiolytic degradation processes.

6.1. REQUIRED PROPERTIES

The conditioned waste form should have adequate physical and mechanical properties such as strength, permeability and diffusivity, thermal stability and thermal conductivity. It may also be necessary to control the retained voidage and heterogeneity of the waste form. National programmes may set quantitative requirements for these parameters, but in many cases the use of well developed encapsulating materials, such as hydraulic cements, will ensure that the necessary properties are achieved. As noted in Sections 5.1.7 and 5.3, special formulations may be required when dealing with organic waste forms or the products resulting from the destruction of organic waste forms.

Depending on national regulations, repository acceptance criteria and modelling approaches, it may be necessary to meet a quantitative requirement for leach resistance of the conditioned waste form. In other cases, testing of the leaching behaviour can give useful insight into the effectiveness of the conditioned waste form. Standard leach tests have been defined, many of which can readily be applied to small scale samples. Testing of full scale samples is more difficult, although simple immersion tests have been used to test for

certain types of waste. Typical properties and limits of waste forms are described in other IAEA publications, e.g. Refs [18, 20, 83–86].

6.2. PERFORMANCE IN STORAGE

Conditioning of waste may take place many years before disposal, in which case there will be a need to store the packages until a disposal facility is available. In the case of waste containing only short lived radionuclides (such as those with half-lives of less than a few years), it may be advantageous to intentionally store the conditioned waste until the radionuclides have decayed to background levels, then dispose of the waste as non-radioactive material. In either case, it is necessary to consider the possible degradation of the waste during this period of time, which may extend to many decades.

Degradation mechanisms include corrosion of the container, physical breakdown of the waste form, general loss of waste package integrity, etc. and may affect the physical or chemical properties of the waste form. These mechanisms are principally influenced by the chemical characteristics of the waste form and the environmental conditions of the storage facility. Degradation may occur from outside or inside of the package, but controlling the environmental storage conditions will play a significant role in ensuring that the conditioned waste package will be suitable for disposal when it is retrieved. The key threats are considered to be temperature (maximum, minimum and degree of severe fluctuations), water availability (flooding and atmospheric humidity), and the presence of aggressive ions (e.g. chloride). Further guidance on these issues is provided in Ref. [86]. Long term decomposition of organic materials is generally not considered to be an issue for most properly conditioned organic waste. An important exception to this is the acidic micro-environment that can be produced in compacted waste by the decomposition products from some chlorinated plastics such as PVC and sulphonated ion exchange resins.

A stable waste form is particularly important where long term storage is required (e.g. where disposal will not be available in the foreseeable future). In this case, slow degradation over extended periods of time may result in a waste form that no longer meets disposal WAC. In this case, or if disposal WAC are not known at the time of conditioning, future reconditioning may be required to ensure that the waste form meets the acceptance criteria at the time of disposal. In any event, the package or waste form must be in a suitable state for safe retrieval at the end of the storage period (e.g. physically intact and safe to handle) and it must meet the requirements for transport as well as for subsequent phases of waste management.

6.3. PERFORMANCE AT DISPOSAL

The conditioned waste form plays an important role in the safety case for most radioactive waste repositories. In addition to providing physical strength and stability to prevent subsidence of repository cover systems, the waste form is also required to contain or minimize the release of radioactivity into the environment for hundreds of years or longer.

The conditioned waste form should display adequate chemical, mechanical, thermal and radiolytic stability. These properties should be evaluated as part of the development programme for the conditioning process. The conversion of organic waste to inorganic residues is likely to result in adequate stability under most conditions, but the retention of the organic nature of the waste in some treatment processes, notably compaction, means that these waste forms are more vulnerable to degradation.

The key degradation products include gases and liquids. Gases can be generated from corrosion, microbial degradation and radiolysis, whereas liquids can be released from absorbents or by the microbial degradation of biological solids such as animal carcasses. In both cases, the degradation will result in increased voidage, and the generation of gases may lead to cracking if they cannot be dispersed efficiently. These degradation processes can, therefore, result in a conditioned waste with inferior physical and mechanical properties that becomes increasingly deficient over time. The decomposition products themselves may also have the undesirable effect of carrying radionuclides directly to the environment (e.g. as dissolved species or as radioactive gases/vapours), or of increasing the mobility of radionuclides in the environment (e.g. acidic decomposition products may adversely alter partitioning and transport parameters in the near field environment) and non-aqueous phase liquids may provide an additional radionuclide transport pathway.

7. QUALITY ASSURANCE AND CONTROL

An essential element of an efficient waste management system is the establishment and maintenance of a workable system of quality assurance and control. Various national and international standards such as ISO, DIN, BS and NNI exist on this subject, and special guidance documents are available from the IAEA on quality assurance and control [87–91]. Generally, the requirement to implement and maintain an appropriate quality assurance

system will be part of the licensing agreement between the regulatory authority and the waste manager.

However, the existence of a quality system, a quality manager or even a complete quality management department does not automatically mean that a good quality product is delivered. Good quality of a product, and also the good quality of a waste management system, is only obtained if the workforce has integrated the quality system into their behaviour. A quality assurance programme is just a tool, and this tool should be properly handled. Correct handling of the tool should be part of the quality control system.

7.1. QUALITY ASSURANCE PROGRAMME

A quality assurance programme should describe, in a concise and systematic manner, the organization, responsibilities, requirements and specifications to be met, and all of the steps in the process that must be controlled in order to ensure the final quality of the product. It is important to set up a system that is optimal for the specific situation. The key elements that influence the quality of the final product should be well defined. Care must be taken not to describe and control every detail of the process because then the system can develop into a paper system that does not reflect reality. Management's attitude towards the quality assurance programme is more important than their written statements. Equally important, however, is direct input from the workforce. A widely supported bottom up approach is likely to be more effective than a rigorous top down approach. For organic radioactive waste, separate quality assurance programmes may be set up for:

- The management (administrative) system,
- The temporary storage system,
- The transport system,
- The treatment and conditioning system,
- The final disposal or discharge system.

If, as is often the case, only one organization is in charge of all of these segments, all programmes will be integrated into a single one. When various organizations are involved, adequate co-ordination is vitally important.

The quality assurance programme should focus on the design, procurement, construction, commissioning and operation of both facilities and equipment. Waste packages should be seen in this context as being essential for the safe management of organic radioactive waste. The conditioning and packaging operations must be harmonized with the expectations of the waste

recipient at the disposal facility and be in accordance with established acceptance criteria. Waste acceptance criteria should be clearly described, as well as regulations and licensing conditions that have to be fulfilled.

7.2. WASTE ACCEPTANCE CRITERIA

Acceptance criteria are normally in written form for standardized processes. They are intended to harmonize waste treatment with the safety needs of the disposal site. When these acceptance criteria are met, and this has been verified by means of a validation exercise, the standard processes can be carried out. This should not necessarily cause a blockage when compliance cannot be verified. Waste, by its nature, is a diverse 'product' and not everything can be foreseen or predicted. The quality assurance programme should clearly describe what route to follow to solve a problem with non-standard waste and how the final waste product should be received. Acceptance criteria may be established to cover the following:

- Radionuclide inventories (i.e. for the unit waste package, for the facility),
- The surface dose rate of a package,
- The level of radioactive contamination of a package,
- The chemical nature of the waste,
- The physical state, dimensions and weight of a package,
- Toxicity of the waste,
- Biohazard posed by the waste,
- Flammability of the waste,
- Explosion hazards,
- Nuclear criticality of the waste,
- Physical and chemical stability of the waste,
- Integrity of the package,
- Identification/markings,
- Resistance to crushing from external impacts.

Characterization of the waste and/or performance qualification testing of the final product normally demonstrate conformance with WAC. The required tests and analysis protocols, which may range from simple documentation of the characteristics, through knowledge of the process originally generating the waste, to complex chemical and radiochemical analyses, are often established by national regulations or by standards organizations. Additional information on characterization can be found, e.g. in Ref. [91].

7.3. RECORD KEEPING

The quality assurance programme will determine which parameters have to be measured and how the results of these measurements are to be recorded. The records may have to be kept for a very long time (years or decades). They should be kept in multiple locations and formats which are not dependent upon specific technologies which may evolve or even become obsolete. Records may also need to be provided to all the organizations involved. Straightforward and absolutely clear instructions must be available for the record keeping process, with care taken to define the necessary units of measurement, etc. For example, older records do not always explicitly state the units of measurement (i.e. whether information on the radioactive content of packages is given in bequerels, megabequerels or millicuries) [87]. In addition, older records were not always created and maintained according to a documented quality assurance programme. Therefore, these records should be carefully evaluated before being relied on in critical applications.

7.4. QUALITY CONTROL

The essential steps in the processes defined in the quality assurance programme will require specific controls. These controls can focus on compliance with WAC or with specific conditions for a treatment process. Compliance with the administrative process should also be controlled. Internal and external audits must be performed on a regular basis in order to ensure that implementation has occurred and that the operational effectiveness of the quality assurance programme is maintained.

8. CONCLUSIONS

Organic waste forms a significant part of the radioactive waste produced at many nuclear facilities, including power reactors, nuclear fuel cycle facilities, research centres and medical facilities. The organic waste may be in solid, liquid or, less commonly, gaseous form.

The organic nature of the waste often introduces additional hazards not encountered with inorganic waste, such as susceptibility to radiolysis and biodegradation, flammability, volatility, chemical toxicity and inherent biological hazards. This results in special requirements and considerations for

storage, treatment, conditioning, packaging and disposal of this waste. These requirements and considerations vary depending on the waste and the selected treatment/conditioning process, and are generally recorded in WAC for the treatment, storage and disposal facilities. Depending on the overall waste management strategy and how it is implemented, there may be different WAC as the waste moves through the different phases of waste management and the nature of the waste form evolves from raw waste to treated and conditioned form.

Characterization and documentation of organic waste is important for many treatment/conditioning processes. Depending on the treatment/conditioning process, various physical, chemical, radiological, and biological properties are of interest. These properties can be elaborated by direct measurement, knowledge of the process, and/or inference from other properties, as appropriate for the waste type. Chemical interactions (sometimes with violent results) between various types of waste, especially liquids, can occur. Therefore, until waste is properly characterized it should be kept segregated and not mixed in the same storage container.

The primary goal of any treatment or conditioning is to produce a waste form that is physically and chemically stable, with limited mobility of the radionuclides and is suitable for all subsequent phases of waste management including interim storage, transport to a repository and, ultimately, disposal. This can be achieved by destroying the organic structure of the waste, for example by incineration or other oxidation processes to produce an inorganic residue, and/or by encapsulation in a suitable matrix and container.

For very small quantities of waste which are infrequently generated, simple benchtop processes may be appropriate. For medium quantities of waste, or where similar wastes are generated at multiple facilities, a versatile, centralized treatment/conditioning plant can be considered. For large quantities of a given waste type, a dedicated treatment/conditioning plant may be appropriate. Once such a plant exists, the prospect of using the plant to treat other waste streams is often considered. Other options, such as use of mobile treatment/conditioning facilities, shared among a number of waste producers or provided by an independent contractor, and use of existing facilities in other regions or countries, have also been employed and should be encouraged.

When storage of the untreated waste is included as part of a waste management strategy, the effects of biodegradation need particular attention, especially for medical or research waste such as animal carcasses and other biological material where putrefaction may occur. The effects of slow degradation of some treated and conditioned organic waste over the long term also need to be considered if interim storage prior to disposal is included as part of the waste management strategy. Certain decomposition products, such

as HCl from the decomposition of chlorinated plastics, may locally alter the near field chemistry in a repository, leading to undesirable effects such as the enhanced mobility of some radionuclides.

A wide variety of treatment and conditioning techniques are available for organic waste (see Section 5). Selection of the most appropriate management strategy and treatment/conditioning technique for a given waste is often a complex process. Factors such as economics, local regulations and perceptions, versatility of the process to treat a range of wastes, quantity of waste generated, as well as technical performance of the process, all need to be considered.

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CONTRIBUTORS TO DRAFTING AND REVIEW

| | |
|---------------------|---|
| Chopra, S.K. | Nuclear Power Corporation of India Ltd, India |
| Clark, D. | DEC Enterprises, United States of America |
| Codée, H. | COVRA, Netherlands |
| Efremenkov, V. | International Atomic Energy Agency |
| Garamszeghy, M. | Ontario Power Generation Inc., Canada |
| Gresley, M. | British Nuclear Fuels Ltd, United Kingdom |
| Kulovaný, J. | Dukovany NPP, Czech Republic |
| Masanov, O.L. | A.A. Bochvar All-Russian Scientific Research Institute of Inorganic Materials, Russian Federation |
| Schweingruber, M.R. | NAGRA, Switzerland |
| Steyer, S. | Bundesamt für Strahlenschutz, Germany |
| Wisbey, S. | UK Nirex Ltd, United Kingdom |

Consultants Meetings

Vienna, Austria: 2–6 July 2001, 10–14 March 2003

Technical Committee Meeting

Vienna, Austria: 13–17 May 2002