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Management of low and intermediate level radioactive wastes with regard to their chemical toxicity

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FOREWORD

Low and intermediate level radioactive waste (LILW) contains radioactive and non-radioactive components that may adversely affect humans and the environment. Therefore the management of such wastes should take into account both radioactive and non-radioactive components and their associated hazards. This report provides a preliminary overview of management options for LILW with regard to its chemical toxicity. In particular, it identifies and describes the following issues associated with the management and safe disposal of chemically toxic materials in LILW:

- the origin and characteristics;
- the regulatory approaches;
- the pre-disposal management;
- the disposal;
- the safety assessment.

The information provided in this publication is intended to contribute to a timely and rational development of processes and procedures for Member States' LILW management programmes as they develop and mature.

The report was prepared by a series of consultants meetings and an Advisory Group meeting held in November 1999 in co-operation with the Waste Safety Section, Department of Nuclear Safety. A list of contributors to drafting and review of the material collected is provided at the end of this report. The IAEA is grateful to those who participated in preparing the report, in particular R. Little of the United Kingdom, who was involved in the revision and preparation of the final version of the report. The IAEA officer responsible for the report was V. Efremenkov of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

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1. INTRODUCTION

1.1. BACKGROUND

To protect human health and the environment from hazards caused by radioactive waste and to avoid any undue burden to future generations, the treatment and disposal of low and intermediate level radioactive waste (LILW) is carried out subject to assessment of the potential impacts [1, 2]. This assessment generally focuses on the hazards to human health and the environment from the radioactivity in the waste. In addition to the radioactive components, LILW may contain non-radioactive components (such as, heavy metals and organics) that can result in harmful effects on human health and the environment. In some cases, radionuclides can exhibit chemical toxicity as well. The disposal of LILW containing such hazardous materials must comply with appropriate regulations and their properties need to be taken into account in the safety assessment of disposal options.

A number of Member States are now initiating management activities for LILW that consider all their associated hazards (both radioactive and non-radioactive) and associated implications for historic, current, and future disposals. Some Member States already have experience in addressing the potential non-radiological hazards of LILW, in particular, the associated chemical toxicity effects. They have addressed the chemical toxicity effects in the safety assessments of waste disposal. This requires an analysis of the impact of the chemical toxicity on the disposal system performance, and the identification of pre-disposal management technologies that support protection of human health and the environment.

1.2. OBJECTIVE

In light of the above, this report is intended to identity and describe the issues associated with the management and safe disposal of chemically toxic materials in LILW. By highlighting these issues, the publication is designed to contribute to improved efforts of Member States in their development, regulation and operation of LILW management and disposal facilities. This report does not prescribe how the chemical toxicity problems associated with LILW are to be solved, although analysis of these problems and summaries of the existing experience may suggest solutions in some cases.

1.3. SCOPE

This report focuses on the management of LILW with regard to their chemical toxicity. Key aspects are discussed in accordance with the regulatory, technological, and safety assessment approaches for dealing with toxic chemical components contained in LILW during pre-disposal and disposal phases. The publication focuses on LILW from:

- nuclear fuel fabrication,
- operation of nuclear power plants (NPPs),
- spent fuel reprocessing,
- decontamination and decommissioning of nuclear facilities, and
- other institutional and industrial facilities, including research laboratories.

High level waste (HLW) and wastes from mining and milling of uranium ores are not specifically considered in this publication. Industrial waste contaminated by naturally occurring radioactive materials (NORM) also are not discussed, even though these wastes are considered as LILW in some countries. It is pointed out, however, that similar management approaches for the wastes considered in this report could also be applied to these other wastes. Waste from biomedical applications of radionuclides/radioisotopes is also not considered in this report since this subject has been recently covered in another IAEA publication [3].

While some countries have specific legal definitions of so-called “mixed waste” (waste which is both radioactive and chemically toxic), this term is not used in the report since a common definition has not been agreed in all countries.

It is recognised that LILW can contain materials that pose a variety of hazards, for example, radiological, chemical, and biological. The focus of this report is the hazard posed by the chemical toxicity of non-radioactive materials in LILW rather than other hazards, such as flammability, corrosiveness and reactivity. Nonetheless, much of the discussion is still relevant to those other hazards.

1.4. STRUCTURE

After this introductory section, Section 2 identifies the nature and sources of chemically toxic materials contained in waste from the five sources of LILW listed in Section 1.3. Section 3 discusses regulatory approaches and practices dealing with the chemical toxicity in radioactive waste with regard to disposal and provides some examples of Member States application of these approaches. The section is supplemented by Appendix A, which provides a summary of the regulatory framework in the USA with regard to chemically toxic LILW. Section 4 then presents factors to be considered for pre-disposal management of toxic components in LILW and technology options available for compliance with the established requirements. Appendix B describes the options in more detail, whilst Appendix C describes some selected technologies applied for treatment of specific waste types. Section 5 discusses disposal approaches, and Section 6 discusses safety assessment aspects related to chemically toxic contents of LILW. Examples of safety assessments dealing with the chemical toxicity in Member States are given in Appendix D. Lastly, Section 7 provides the summary and conclusions derived from the specific subjects discussed in this publication.

2. ORIGIN AND CHARACTERISTICS OF CHEMICALLY TOXIC LILW

Operations in the nuclear power industry, academic and industrial research, and biomedical research and treatment facilities produce a wide variety of radioactive wastes. Wastes are generated in all sectors that handle radioactive materials, and include almost any process material or equipment used in that sector. These wastes may include small amounts of process chemicals, spent chemical analysis solutions, spent ion exchange resins, scintillation cocktails, and discarded laboratory and process equipment. In addition, very large quantities of waste are generated from the dismantling of nuclear power reactors and nuclear industry facilities.

Plant operations in the nuclear sector some times require hazardous materials whether acids, bases, or some of the various organic solvents considered hazardous. Research sectors may require use of very toxic materials such as pesticides or inorganic chemicals such as cyanide or arsenic. Any of these widely varied materials may be present in wastes streams. The concentration or fraction of the chemical hazardous material may range from trace levels up to comprising a major fraction of the waste.

Radioactive wastes can be described at a number of levels: the individual package, the consignment (a package or group of packages transported together), or the waste stream (a series of wastes resulting from a particular source and with consistent character). To keep the discussion manageable, wastes described below are described on the basis of their source.

To discuss the waste and their associated hazardous and toxic components in enough detail to understand the potential compliance with disposal requirements, both the contaminant characterisation and the bulk waste stream physical and chemical characteristics (the matrix) need to be understood. Therefore, the following discussion is provided to describe the waste from various sources by the matrix description (ion exchange resins, evaporator bottoms, etc.), as well as the chemical and radioactive contaminants. However, the particular operations that generate these wastes are not discussed.

2.1. WASTE FROM NUCLEAR FUEL FABRICATION

LILW from fuel fabrication include filter media from wash water cleanup, waste oils, spent acids and bases, spent analytical solutions, decontamination and cleaning solutions and discarded scrap metals and equipment. Any of these wastes may be contaminated with hazardous chemicals and uranium. Plutonium contamination is present from facilities manufacturing mixed oxide fuel.

Table I lists typical waste arisings at a fuel fabrication facility per 1000 tonnes of uranium throughput [4]. Many of the arisings listed in Table I can be minimized by source reduction, recycling or reuse of valuable materials and components from potential waste streams after appropriate cleaning and control.

TABLE I. Typical waste arisings from the fuel fabrication facility for 1000 tonnes uranium throughput [4]

Arisings	**Quantity**	**Classification**	**Process/origin**
Ammonium fluoride solution	4000 m^3	By-product	AUC
Ammonium nitrate solution	5000 m^3	By-product	AUC + ADU
Extraction residues	10 m^3	Material for treatment	AUC + ADU
Sludges	1 m^3	Material for treatment	AUC + ADU
Hydrogen fluoride	1000 t	By-product	IDR
Magnesium fluoride	450 t	By-product	Magnox
Graphite	300 t	Material for treatment	Magnox
Zircaloy	1 t	Material for treatment	Water reactor fuel
Stainless steel	1 t	Material for treatment	Gas cooled reactor
Miscellaneous metal Scrap	40 t	Material for treatment	All
Ventilation filters	100-200 m^3	Material for treatment	All
Mixed combustible material	300 m^3	Material for treatment	All
AUC = Ammonium uranyl carbonate process, ADU = Ammonium diuranate process, IDR = Integrated dry route process.			

2.2. WASTE FROM OPERATION OF NUCLEAR POWER PLANTS

Many toxic, non-radioactive contaminants may be found in LILW from NPP operation, such as chromium and nickel contaminated activated metals, spent ion exchange resins and contaminated oil, etc. Operational wastes from NPPs may also contain mercury, cadmium, and beryllium, as well as a number of chemically toxic organic compounds. For example, beryllium is used in neutron sources (e.g., Be/Am and Be/Pu sources) and as a reflector material in research reactors [5].

The main process waste streams derived from NPP operation are:

- sludges and fine particulates from aqueous precipitation and filtration of liquid radioactive waste,
- spent ion exchange resins used for purification of process water,
- the evaporator concentrates, and
- miscellaneous solid, dry active waste,

The sludges are generally comprised of hydroxides of iron, magnesium, calcium and aluminum (along with mineral based materials) and are generally of low toxicity. However, some sludges, may contain toxic residual components (e.g. Cr, Cu, Ni). The ion exchange resins are likely to include toxic and non-toxic metals (e.g. Fe, Cu, Zn, Mn, Ni, B). The most common toxic material in evaporator concentrates is boric acid [6]. In addition to boric acid, evaporation concentrates generally contain a mixture of fission and activation products.

NPP maintenance and repair operations produce discarded equipment, organic solvents (used for degreasing and cleaning), and organic complexing agents from decontamination activities. In addition to these organic compounds, these wastes may contain metals such as lead, mercury, and barium.

The power plant cooling water generally contains chromium or other chemical anti-fouling materials. Therefore, cooling water blowdown, or associated filtrate sludge will contain these chemicals. Any radionuclides in the plant coolant may appear in the cooling tower water.

Most of the materials making up dry active waste (i.e., miscellaneous trash, organic and inorganic rubble) are comprised of cellulosic materials (paper, rags, clothing and wood), rubber gloves and boots, plastics, steel and building debris, and would not usually be regarded as hazardous waste. However, these wastes may contain trace amounts of toxic elements. Dry active waste generally contains only small amounts of the soluble forms of toxic elements. For miscellaneous trash and refuse, it is often the case that there is little information concerning the low levels of chemically toxic substances present in these wastes. The toxic metal content can sometimes be inferred from the analysis of incinerator ash after treatment of dry active waste. The polymers that comprise plastic waste packaging are expected to be non-toxic, but a variety of hazardous materials may be present as surface contamination because plastic sheeting is frequently used for isolating areas during decontamination, and as packaging materials. More detailed data on toxic constitients in LILW from NPPs operation can be found in [7].

Lead is widely used in NPP operations for shielding as lead blankets and bricks, and it is sometimes used as a liner material in radioactive waste containers. Waste containers lined with lead have been emplaced in repositories in several countries. Lead blankets and bricks may become contaminated with radionuclides and hazardous chemicals. However, the lead can be separated for treatment, recycling or disposal as appropriate.

Tables II and III provide further example information on inorganic and organic compounds in NPP wastes.

TABLE II. Non-radioactive, chemotoxic substances in example NPP wastes streams [7]

Waste	**Waste Volume (m^3)**	**Toxic Substance**	**Concentration ($kg.m^{-3}$)**	**Mass of Substance (kg)**
Operational LLW	200,000	Cd	-	4000
		Hg	-	4000
		Be	-	20 000
		Se	-	8000
Evaporator Concentrates	3300	B	45	150 000
Ion Exchange Resins	1000	Cr	0.5	500
		Ni	0.7	800

TABLE III. Non-radioactive organic contaminants in example operational NPP low level waste [7]

Waste Volume (m^3)	Solvent	Concentration ($kg.m^{-3}$)
2E+5	Acetone	2E-1
	Dichlorobenzene	4E-1
	Ethanol	2E-1
	Isopropyl alcohol	7E-2
	Methylethyketone	2E-1
	Toluene	8E-2
	Trichloroethane	8E-2

As Table III shows organic solvent concentrations are not high, ranging from about 50 to 500 ppm, in this case. Other solvents and organic contaminants may be present in measurable quantities in waste arisings from non-routine NPP operations.

Abnormal events at NPPs can also give rise to appreciable volumes of radioactive wastes containing chemically hazardous constituents [8]. Abnormal events could include events such as unplanned major modifications, process upsets and accidents of various kinds. The waste arisings from abnormal events may include large quantities of miscellaneous refuse contaminated with decontamination chemicals, process chemicals and cleaning solvents and adsorbents for organic liquids contaminated with pump oils and hydraulic fluids.

2.3. WASTE FROM SPENT FUEL REPROCESSING

In countries that reprocess spent fuel, there is a backlog of stored radioactive waste, both intermediate and high level, with very complex and sometimes not clearly defined composition. The disposal strategy for many of these wastes is still under development in many countries.

LILW wastes containing hazardous or toxic contaminants from reprocessing of spent NPP fuel range from activated or fission product contaminated metals to water treatment filters. The separated fission product waste streams are normally acidic and may contain erosion or corrosion products from plant process equipment. Equipment cleaning for maintenance includes degreasing agents, which may include halogenated solvents, and decontamination and metal cleaning agents which often contain strong acids, oxidizing agents, and complexing agents. Any of these waste streams may become contaminated with fission products, uranium, and plutonium.

In some countries the first stage separation of uranium and plutonium in fuel reprocessing is considered as HLW. All other processing liquid waste streams, all fuel cladding (the cladding remains undissolved in the fuel dissolution step), all maintenance wastes and discarded equipment, support laboratory and analytical equipment and solutions are considered to be LILW.

Activated and highly contaminated metals derived from cladding of spent nuclear fuel generally have low or moderate toxicity since the metallic materials are either of low toxicity, such as magnesium and iron, or low solubility such as zirconium and stainless steels.

Nitrate is a significant component of a number of reprocessing waste streams because nitric acid is used for spent fuel dissolution. Spent solvents can arise from the solvent extraction processes used for chemical separations. The most commonly used extraction solvent is tributylphosphate (TBP). The TBP is diluted for the extraction process, usually with a light saturated hydrocarbon, such as dodecane or a mixture of paraffin hydrocarbons. Chemicals that can arise in waste from spent fuel reprocessing in LILW [9, 10] are:

- TBP (tributylphosphate) and other organic extractants
- Nitric acid and alkali metal nitrates
- Organic solvents
- Complexing agents
- Metals as Zr, Cr, Ni, Fe, Al and their nitrates
- Alkali metal fluorides/chlorides
- Mercury-contaminated scrap metals (processing equipment)
- Uranium-contaminated metals
- Full cladding mills.

Table IV provides further information on inorganic compounds present in reprocessing wastes.

TABLE IV. Examples of waste arisings from reprocessing facilities [7]

Waste stream	**Volume (m^3)**	**Substance**	**Concentration ($kg \cdot m^{-3}$)**	**Total mass (kg)**
Ministry of Defense Pu Finishing LLW	5500	Be	3.3	18 000
Sellafield operational	86 000	Ni	1.3	110 000
Sellafield Vitrification plant LLW	26 000	Zn	1.6	41 000
Sellafield soil and rubble	69 000	Asbestos	26	1 800 000

2.4. WASTE FROM DECONTAMINATION AND DECOMMISSIONING OF NUCLEAR FACILITIES

Decontamination and decommissioning activities generate a significant volume of waste, including radioactive scrap metal, contaminated concrete debris, spent decontamination solutions and sludges, contaminated isolation and shielding materials, asbestos containing piping insulation and thermal shielding, etc. For example, the US DOE is decommissioning hundreds of surplus buildings associated with former reprocessing activity, and this decommissioning generates chemically and radioactive toxic wastes [11]. Decommissioning waste consists of all facility construction materials including metallic materials from plant dismantling, and concrete rubble from demolition. The plant metallic equipment can be expected to be contaminated with many types of chemicals and radionuclides that were used in the processes. Recycling of metals from decommissioning of large facilities has been successfully carried out in several countries to reduce the volume of wastes [12, 13].

Representative volumes of radioactive decommissioning wastes from dismantling of nuclear facilities can be found in [13, 14].

A wide variety of chemicals are used for decontamination of the various materials/surfaces found in nuclear facilities. Decontamination chemical agents range from nitric and hydrofluoric acids to a variety of organic complexing agents such as citric acid, EDTA etc. [13]. The decontamination solutions often contain toxic metals. Table V shows the toxic metal and radionuclide composition of a spent acid solution obtained by decontamination of scrap metal and metallic components [15].

TABLE V. Metal and radionuclide content in spent acidic decontamination solutions [15]

Contaminant	Cr	Ni	Fe	Cu	^{60}Co	$^{134/137}$Cs	^{241}Am ^{54}Mn	Anions (NO_3, Cl^-, F^-)
Concentration	1.6 kg•m^{-3}	2.0 kg•m^{-3}	12.5 kg•m^{-3}	74 mBq•m^{-3}	3000 MBq•m^{-3}	111 MBq•m^{-3}	37 MBq•m^{-3}	>10%

The majority of building and facilities that will undergo decommissioning in the near future were constructed 40–50 years ago. At that time asbestos was a common material used for thermal isolation formulated together with magnesium citrate, diatomaceous earth, and silica. Decommissioning of these facilities will require special considerations for protection of workers both from asbestos inhalation, as well as conditioning and disposal of this material. Decommissioning of auxiliary systems with electrical equipment could contain PCB (Poly Chlorinated Biphenyls) and some chemotoxic fluids from decontamination that need special consideration for human protection and safe handling.

2.5. WASTE FROM INSTITUTIONAL AND INDUSTRIAL FACILITIES

Institutional and industrial LILW is widely variable in composition [17]. Many of the wastes are generated in small quantities from experiments or operations, which change over time. They therefore can have unique characteristics, and so, with the exception of scintillation cocktails[1], it is difficult to define waste streams for these processes. This waste category may require characterisation of individual waste source or waste containers. However, for these wastes, it is possible, by examining the physical matrix and contaminants, to gather wastes into similar groups to allow for practical management.

Sources of institutional and industrial LILW include:
- research activities,
- research reactor operation,
- industrial application, and
- biomedical applications (considered in [3]).

Waste from research activities can contain a very large spectrum of inorganic and organic chemical toxic compounds. Typical inorganic hazardous material may be toxic heavy

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[1] Liquid scintillation cocktails are a waste stream common to many radioactive material handling industries, and these contain organic solvents. Scintillation cocktails are used in measurement of low levels of alpha and beta emitting radioisotopes. These scintillation fluids historically contained benzene, toluene and/or xylene, but modern less toxic solvents have come into use in recent years [16].

Waste from research activities can contain a very large spectrum of inorganic and organic chemical toxic compounds. Typical inorganic hazardous material may be toxic heavy metals, reactive metal salts, anions like nitrates, sulphates, chlorides, chlorates, strong oxidisers, solutions of corrosive acids and bases.

The amount of hazardous constituents also varies widely in waste from research reactor operation and depends mostly on the irradiation programme of the particular research reactor (activation analysis, irradiation of biomedical materials, etc). Because of the wide range of research activities, many different hazardous materials can appear in these wastes. Associated organic liquids include oils, metal cleaning solvents with halogenated organics, flammable organic solvents, alcohols, aldehydes, and possibly toxic materials such as organic phosphorus compounds. The various types of small volume organic liquid waste arisings have been described in more detail in other IAEA publications [17]. Metal wastes will include lead shielding, discarded equipment, gloveboxes, and laboratory analysis apparatus.

Waste from research and industrial applications include spent sealed sources, ignitable organic liquids, organic solvents including halogenated solvents, waste solutions from laboratory analysis, bulk corrosive solutions, metal fines, mercury waste, and toxic metal wastes. The wastes include radioisotopes produced by activation analysis, nuclides used in tracer experiments. Secondary waste, such as incineration ashes, evaporator concentrates, sludges from chemical treatment, etc. may contain much higher concentration of hazardous components than initial waste streams.

Liquid radioactive wastes are generated during research reactor operations, isotope production and operations involving the application of radioisotopes (e.g. medicine, research, education, etc.). The type of waste produced depends upon the particular operation being conducted and can vary extensively in both chemical and radionuclide content. Most operations, particularly the larger ones, will also produce a variety of radioactive liquid wastes from activities such as showers, laundries, analytical laboratories, and decontamination services [17].

3. REGULATORY APPROACHES FOR WASTE MANAGEMENT

3.1. THE HIERARCHY AND SCOPE OF REGULATIONS

In considering the regulations for waste management among the various Member States, it is clear that there is a hierarchy of regulations ranging from broad principles to objectives and enforceable standards. These principles, objectives and standards should all be self-consistent.

At the "top" of the hierarchy are the waste management "principles" that embody policy at the highest level. Principles include, for example, the broad goals of minimising the production of waste and the impacts of waste disposal on humans and their environment. Such principles are couched in general terms in legislation and often place the onus on the waste-producing industry to show compliance with the spirit of the principle.

The "objectives" reflect the principles. One example is the requirement to limit waste disposal by the application of optimisation procedures to control the release of pollutants from either a single source to a specific medium, or, more generally, from a number of sources to and across various media. Other examples include the prevention or limitation of deleterious health effects that would arise from a disposal practice, and the need to preserve natural resources (such as groundwater) for future use.

"Standards" occupy the "bottom" tier of the hierarchy. These are quantitative measures that can be applied either to the nature and magnitude of the waste stream and the performance of its disposal method, and/or to concentrations of various pollutants in environmental media.

The regulations can cover a broad range of issues relevant to the management of waste, in particular:

- define the wastes of concern;
- identify procedures for collection, treatment, and disposal of the waste;
- regulate waste disposal facility site selection and characterisation;
- contain definitions and prescriptions, at differing levels of detail, concerning, for example:
    - the overall performance criteria,
    - particular performance requirements,
    - how the performance is to be demonstrated (demonstration of compliance with the regulation);
- define/establish the responsible authorities;
- define the responsibility of the different parties (e.g. implementor and regulatory authorities).

Such regulations may be formulated as criteria that must be met or as guidelines that should be followed.

3.2. RADIOACTIVE AND NON-RADIOACTIVE WASTE REGULATIONS

Most countries have developed or are developing regulations that separately cover the management of radioactive and non-radioactive waste. The basic principle behind the regulations for radioactive and non-radioactive wastes is essentially the same, i.e. to protect humans and the environment against potential harm. However, the actual standards used to achieve these principles differ among countries and between radioactive and non-radioactive waste types. Indeed, in some countries, the standards for the management of radioactive and non-radioactive waste can be inconsistent, and so, it can be difficult to fulfill the regulatory standards if a waste contains both radioactive and chemically toxic materials. Such differences can be compounded in certain countries by radioactive and non-radioactive waste being regulated by different bodies. In the United States of America (USA), the generation, storage, and disposal of chemically toxic low level radioactive waste (called mixed waste in the USA) is subject to dual regulation. The US Nuclear Regulatory Commission (NRC) regulates the radioactive contamination under the Atomic Energy Act and the US Environmental Protection Agency (EPA) regulates the chemically hazardous nature of the waste under the Resource, Conservation and Recovery Act. Appendix A provides some more details on regulatory framework for chemically toxic LILW in the USA to illustrate the dual regulation of this waste.

Key differences between radioactive and non-radioactive waste regulations are itemised below.

- Regulations concerning the management of chemically toxic waste, in general, define waste and system requirements, often in much detail and in a prescriptive manner (for example waste leaching rates, barrier properties, and monitoring requirements). They deal with protection of the public and the environment during operation and during a limited period after closure, typically a few tens of years. Long term safety assessments are, generally, not required and hence the long term evolution of the disposal system and its associated barriers is not usually considered. However, some quantitative consideration of the potential impact of the waste on groundwater quality, but not human health, may be required.

- Regulations concerning the management of radioactive waste, define, in general, the requirements on the overall performance of the disposal system and require a safety assessment to be carried out of both operational and post-closure impacts. Post-closure impacts may be assessed over certain period of time (hundreds or thousands of years) depending upon the half-life of the radionuclides and the regulatory requirements. They have the aim of demonstrating that the disposal of the waste is safe and is not placing any undue burdens on future generations consistent with the principles given in the IAEA Safety Fundamentals “The Principles of Radioactive Waste Management” [18]. Safety is here measured as radiation dose or risk to humans, although some times detailed requirements on the performance of the individual barriers are also defined (for example the Waste Isolation Pilot Plant in the USA and the associated 40 CFR Part 191 regulation). Protection of the environment is often addressed by assuming that protection of humans ensures adequate protection of non-human biota, although some countries are starting to consider the impact on non-human biota explicitly. Within the post-closure assessment, there is explicit recognition that there will be eventual loss of active and passive institutional control over the disposal facility, often over the timescale of several hundred years.

Although there are separate regulations governing radioactive and non-radioactive waste, in the past there have been relatively few regulations that explicitly consider the issue of chemically toxic materials in radioactive waste. However, there is now a growing recognition of the need to consider explicitly not only the radiological but also the non-radiological impacts of LILW management. For example, in recent guidance from the IAEA, explicit reference is made to the need to take due account of non-radiological hazards and impacts when considering waste management options [2, 19]. Furthermore, there is now a European Commission directive [20] that requires an Environmental Impact Statement (EIS) to be undertaken prior to the development and construction of facilities such as radioactive waste disposal facilities. It requires consideration to be given to the different types of hazards associated with the facility, including the effects of the chemical toxicity of the waste.

3.3. APPLICATION OF THE REGULATIONS

Comparison of the actual waste properties with the definitions in the regulations concerning radioactive and non-radioactive wastes should show whether the wastes are, in principle, to be considered chemically toxic waste, radioactive waste or both. The relevant properties to be compared might not only be the concentration or amount of chemically toxic and radioactive substances but also their chemical nature (e.g. oxidation state) or physical form (e.g. as solute, as respirable dust or in an immobilized form).

If the waste is, in principle, to be considered both as being radioactive and chemically toxic, several possibilities exist.

- The regulatory system determines that both the regulations relating to radioactive waste and chemically toxic waste have to be followed in their respective fields. However, as noted in Section 3.2, the regulations concerning radioactive waste and chemically toxic waste may be inconsistent.
- The regulatory system determines that only the regulations relating to radioactive waste have to be followed. These regulations on radioactive waste may include how to deal with chemical toxicity (for example in the Czech Republic Atomic Law No. 184/97 par. 24, and Czech public notice of the State Office for Nuclear Safety No. 18/97).
- The regulations on radioactive waste may not contain statements about chemical toxicity (implicitly or explicitly assuming that the requirements for chemical toxicity would be fulfilled), for example in Switzerland (Swiss Technical Ordinance on Wastes TVA, SR 814.600 of 10.12.1999, and Swiss Ordinance on Protection against Accidents, StFV, SR 814.012 of 27.02.1991).
- The regulations on chemically toxic waste may not contain any statement about radioactivity.

A comparison of Russian Federation maximum permissible concentrations (MPCs) for non-radioactive metals and permissible specific activities (PSAs) for radionuclides in water is given in Figure 1. Comparing these regulatory requirements it can be seen that the MPCs of non-radioactive metals in water are generally three to seven orders of magnitude greater than MPCs for radionuclides.

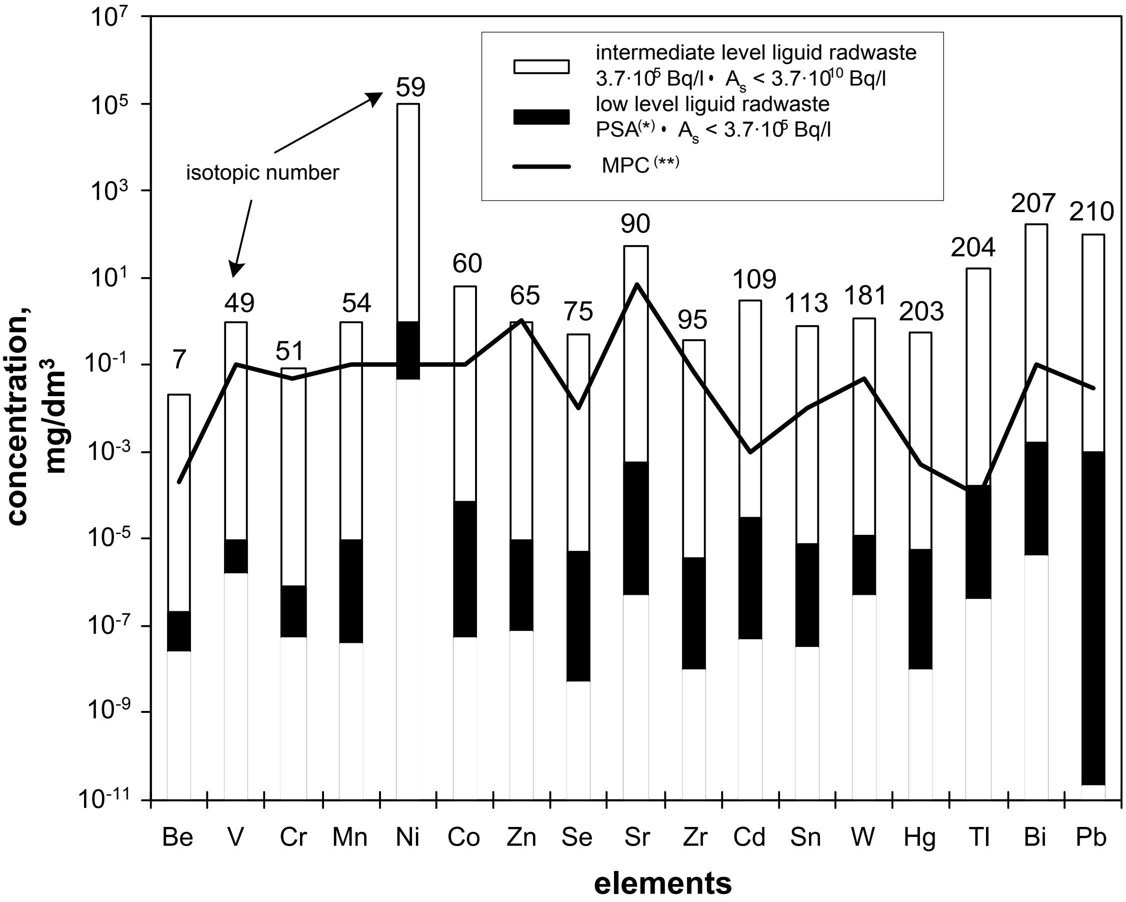

Fig. 1. Comparison of Russian Federation Maximum Permissible Concentration (MCAs) of non-radioactive metals in water (RF Sanitary Hygienic Standard) and Permissible Specific Activities (PSAs) of radionuclides in water (RF Standard on Radiation Safety).

In the absence of clear regulatory guidance on the chemically toxic components of LILW, an assumption has sometimes been made that the "stringent" disposal regulations, which apply to the radioactive components of the waste, will automatically ensure that the wastes are managed in a safe manner. Many countries have recognised that this assumption is not necessarily valid and so, in order to help ensure the safe management of the waste, they have introduced the concept of waste acceptance criteria (WAC) for waste packages during handling, transport, interim storage, and final disposal (for example Spain, Switzerland, UK, and USA that can relate to the non-radioactive as well as radioactive component of LILW. Such WAC can provide limits for the concentration of chemically toxic contaminants, as well as specifying the nature of pre-disposal treatment and providing a list of materials to be excluded from the disposal facility. In addition, disposal facility operators have been pragmatic in their approach and have undertaken assessments with the objective of addressing both regulations for radioactive and non-radioactive waste to demonstrate that the principle of protection of humans and the environment against harm is met (see Section 6).

4. PRE-DISPOSAL MANAGEMENT OF LILW CONTAINING CHEMICALLY TOXIC COMPONENTS

Pre-disposal activities are those that occur after generation of the waste and prior to disposal. Many pre-disposal activities are already practiced in radioactive waste management, while others are commonly used in the management of non-radioactive wastes.

Chemically hazardous components of wastes are, in certain cases, more amenable to treatment and stabilisation than radionuclides. Treatment methods are basically subdivided into those that deal with inorganic compounds, and those that deal with organic compounds. For example, incineration or vitrification can destroy the hazardous organic components of a waste stream, yet leave the inorganic components unaltered. Chemical precipitation can stabilise dissolved inorganic ions by creating insoluble solids that are leach resistant. One of the main goals of treatment is to stabilise, destroy and neutralise wastes that pose an immediate hazard (e.g., explosive hazard, strong oxidizing agents, corrosive gases).

During pre-disposal management of waste with respect to their chemically toxic components the following issues are considered.

- Waste minimization or waste avoidance (Section 4.1). This has been very successfully employed by many Member States thereby reducing the problem of waste and its chemically toxic components.
- Waste characterization (Section 4.2). It is essential to ensure that hazardous constituents are identified, and that the waste is entered into the appropriate regulatory framework. Characterization is necessary in order to define the waste management system and to support its successful operation through, for example, the collection of data to allow demonstration of compliance with the treatment/disposal system acceptance criteria.
- Waste processing (Section 4.3). The objective of waste processing (sorting treatment and conditioning) is to reduce the volume, destroy or neutralise toxic components and to stabilise waste into stable form suitable for storage, transport and disposal.

4.1. WASTE MINIMISATION

The generation of LILW with hazardous contaminants is undesirable, but it is not always avoidable. An important waste management consideration is the minimisation of the volume of LILW with toxic non-radioactive components. Some examples of the application of this concept are given below:

- Training of operational personnel on the requirements, procedures and effects of the generation of radioactive waste with toxic contaminants may lead to improvement of the operational culture and the reduction of waste with chemically toxic constituents.
- The evaluation and selection of alternative materials, such as substituting solvents for scintillation fluids, can eliminate hazardous components in some waste streams.
- Careful sorting and segregation of wastes at their points of generation can minimise spreading of contamination and facilitate subsequent treatment requirements. This also

can lead to the reduction and avoidance LILW arisings containing chemically toxic constituents.

- Careful selection of treatment processes and introduction of associated chemicals may help to avoid production of radioactive waste with chemically toxic constituents. For instance, the replacement of chromates for biological control in cooling tower waters can eliminate production of waste contaminated with heavy metal constituents.
- Planning and organizing of maintenance operations in a manner that minimises the generation of chemically toxic LILW.
- Selection of decontamination processes serve to minimise secondary wastes generation. For example the replacement of chemical decontamination by dry ice blasting and use of ultrasonic techniques.
- The recovery of chemically toxic materials for recycling and reuse, such as nitric acid and ammonia.

Careful consideration of the above and other waste minimisation options may help substantially reduce waste generation and facilitate subsequent treatment, conditioning and disposal of waste.

4.2. WASTE CHARACTERISATION

Careful waste characterisation is a necessary tool to ensure the selection and application of appropriate treatment and conditioning options to satisfy requirements for waste storage and final disposal to protect human health and the environment [21]. In defining the required treatment for stabilisation of each waste stream, it is necessary to identify the radioactive and non-radioactive hazardous constituents. For both the radionuclides and the chemically toxic contaminants, it is important to know their chemical forms and the original concentrations. It is also important to have an understanding of their expected behaviour in candidate treatment processes, their toxicity, and the potential release rates of the components from the final waste form. Besides characterising the physical matrix of waste, the following characterisations are important.

- Inventory of radioactive elements, their concentrations (specific activities), their half-lives, their chemical forms that may influence their release rate, and their specific radio-toxicity.
- Identification of chemically toxic inorganic substances (toxic stable elements and inorganic compounds). These stable components may undergo the same release phenomena as the radioactive components, and these constituents may be leached from the waste and released to the environment long after the radioactivity has decayed away. For each component, the original concentration, toxicity, release rate, and potential for adsorption along the release path should be determined.
- Identification of chemically toxic organic components (solvents, complex organic compounds, complexing agents, certain monomers or polymers, etc.). This class of contaminants is also subject to chemical reaction and release to the environment through common mechanisms. The original concentration, toxicity, release rate, and potential for adsorption or destruction along the release path should be determined.

Determination of waste volumes is critical to the design of a treatment process. Low volume waste streams may be treated batch-wise without concern for process efficiency. Alternatively, high volume waste streams can justify the use of dedicated processing systems.

Waste characterisation includes but is not limited to the following main components, which are briefly discussed below. More detailed information is provided in [22].

- Process knowledge,
- Radio-assay results,
- Intrusive sampling and analysis, and
- Radiographic examination.

4.2.1. Process knowledge

Process knowledge of how the LILW was produced is a cost effective and reliable method of providing insight on the probable constituents of a waste stream. It also may provide a basis for precluding consideration of a wide range of contaminants. For instance, if the waste stream itself does not include, nor has ever been exposed to toxic organic solvents or compounds, then it is not necessary to remove or destroy such constituents. Process knowledge is especially important for defining the presence of hazardous components in the initial waste streams, for selecting the appropriate waste management option(s) and for controlling their content through the whole waste management process.

4.2.2. Radio-assay results

Radio-analyses provides information used for safe handling of a waste stream as well as defining the waste category for treatment, conditioning and disposal. The radiological properties of the waste stream or package determine whether manual (contact) or remote handling is necessary. In addition, the activity levels of long lived radioisotopes must be ascertained to help define the disposal option and, ultimately, disposal site selection. Typically, the determinations include:

- Beta/gamma survey (determines the waste handling category),
- Gamma spectroscopy (to identify particular radionuclides), and
- Passive or active neutron interrogation (to determine transuranic element content).

4.2.3. Intrusive sampling and analysis

If there is possibility that chemically toxic substances may exist in a waste stream, an analyses can be undertaken to confirm the range of their concentrations. The information is important in helping to select the treatment option. Sampling for common waste streams which are homogeneous is generally straightforward. However, obtaining a representative sample of a heterogeneous mixture may be very difficult. For some applications, a simple sorting of the waste into the specific components and weighing the various fractions may provide adequate information if the composition of the sorted waste is known. In practice intrusive sampling requirements are statistically based to minimise analytical costs, and to minimise the hazard to the sampling personnel.

The information required from intrusive sampling is entirely dependent on the waste types and the expected treatment process. Common determinations for hazardous constituents may include:

- Standard tests for flammability or ignitability,
- pH control (for corrosivity),
- Standard tests for reactive chemicals,
- Standard tests to identify and quantify solvents and organic compounds, and
- Standard test to identify and quantify toxic metals and complexes.

4.2.4. Radiographic examination

Radiography has been used to image waste packages as a means of confirming inventory information of waste packages and facilitating safe handling. Identification of unacceptable items in waste packages, such as aerosol cans and free liquids, is important for safe handling and for compliance with disposal acceptance requirements.

4.3. WASTE PROCESSING

Once the presence of hazardous constituents and the probable range of concentrations is defined, then consideration is given to selection of potential technologies to separate, stabilise or destroy the hazardous constituents. Currently employed management practices for LILW emphasises volume reduction and stabilisation of waste to reduce leachability, and to optimise disposal site capacity and performance. For example, organic constituents are destroyed by high temperature treatment used for volume reduction and stabilisation of radioactive materials. Similarly, a disposal system based upon retention of long lived radioisotopes may simultaneously retain heavy metals, such as lead or cadmium. Alternatively, numerous technologies have been developed specifically for the processing of hazardous non-radioactive wastes, which may be used for the processing of chemically toxic components of LILW.

The selection of the specific waste processing options for dealing with the chemical toxicants depends on both the waste contaminant and the general characteristics of the waste stream. The physical characteristics of the waste and the fraction of organic and inorganic chemical constituents are important for choosing the management approach and especially the selection of treatment and conditioning processes.

There are various technical options for the processing of LILW which may be applied to waste containing chemically toxic components. These include:

- sorting;
- size reduction;
- separation;
- incineration and thermal treatment;
- vitrification;
- biological treatment; and
- solidification and immobilisation.

Table VI provides a summary of the advantages and limitations of these options. Details of these options are given in Appendix B, whilst Appendix C describes some selected example technologies, applied for processing of chemically toxic components in LILW.

In some cases these techniques may be applied directly to these wastes, in other cases they may be applied after appropriate pre-treatment to separate, neutralise, or to destroy chemically toxic hazardous components in waste. Where practical the pre-treatment of these wastes may include segregation of organic and inorganic ingredients which require different treatment and conditioning options. However, often it will not be practical to separate hazardous inorganic material from organic matrices. It is then more convenient to destroy the organic material and then deal with the residue. Similarly, hazardous organics adsorbed onto inorganic matrices may be best dealt with directly by thermal destruction. After treatment, basically the same immobilisation techniques may be used, which are applied for conditioning of conventional LILW (cementation, bituminization, incorporation into polymers, glass matrixes, ceramics, etc.). The application of the procesing options to various waste types containing chemically toxic components is briefly discussed below and sumarised in Table VII.

4.3.1. Aqueous liquid wastes inorganic and organic toxic contaminants

Treatment options for these wastes are based on conventional wastewater treatment processes.

The primary treatment provides removal of suspended solids and neutralisation, if required, before further processing. Suspended solids may be separated and treated with inorganic sludges (see Section 4.3.3), if they are expected to contain regulated contaminants. Acidic or basic wastes are treated by simple neutralisation.

Evaporation may be used to concentrate the dissolved inorganic compounds before the residue is sent to the immobilisation process. High salt content wastes may be not amenable to stabilisation in many common immobilisation agents, such as Portland cement. These salt streams may be concentrated or dried and then stabilised with polymers or other salt tolerant media, such as glass or ceramic matrix. The immobilisation process usually retains both the radionuclides and inorganic toxic materials.

Reactive chemicals in wastes, such as strong acids, bases, oxidisers, cyanides, etc. may be deactivated, which must be defined for each type of chemical compound. A number of special chemical processes may be required, which normally are within the capabilities of a typical chemical or chemical engineering research laboratory.

4.3.2. Organic liquid wastes

Some hazardous organic materials may be separated from liquid waste streams, purified, and recycled. Assuming that the recycling of such materials has been maximised, the remaining organic hazardous materials are best treated by a destruction technology, commonly by a thermal treatment (Appendix B). It is important to demonstrate that the thermal treatment process is capable of destroying the hazardous organic material which may be present.

TABLE VI. Advantages and limitations of treatment and conditioning options for LILW containing chemically toxic components

Treatment/Conditioning Technology	**Advantages**	**Limitations**
Sorting	• Simplifies treatment and disposal of wastes by segregating them into appropriate categories. • Minimises the volume of LILW with chemically toxic components.	• Manual sorting can expose operators to hazardous materials. • Additional space and containers are required. • Staff training required.
Size reduction	• Can reduce volume and voidage for transport, storage and disposal. • Well developed, commercial technology.	• Potential for dust (and hence secondary waste) generation. • Increase hazards to workers due to use of cutting tools.
Separation	• Potentially allows waste to be re-classified. • Well developed, commercial technologies available.	• Chemical separations not 100% efficient. • Re-classification of waste might not be straightforward or easily acceptable.
Incineration and thermal treatment	• Organics are nearly all completely destroyed. • Residual ask amenable to immobilisation, stabilisation in agents. • High volume reduction for combustible waste. • Well developed, commercial technology.	• Need to limit off-gases (generates secondary waste). • Poor public acceptance.
Vitrification	• Low volume, low leaching final waste form. • High volume reduction for combustible waste. • Organics are nearly all completely destroyed.	• Need to limit off-gases (generates secondary waste). • Need to control variations in waste feed.
Non-thermal destruction	• Reduced volume of off-gases such as dioxins, furans and mercury. • High volume reduction for combustible waste.	• Low production rates for oxidation relative to thermal technologies. • Sorting of waste required to preclude unacceptable items. • Large volumes of corrosive chemicals required. • Expensive corrosive resistant construction required for major process vessels.
Biological treatment	• Unlikely to generate dioxins or furans. • Low cost. • Public acceptance.	• Compound specific. • Slow production rates. • Sorting of waste required to preclude unacceptable items.
Solidification and immobilisation	• Well developed, commercial technologies. • Low temperate technologies preclude volatile metal emissions.	• Need to ensure compatibility with organic materials and high-salt content. • Increased volume for disposal.

TABLE VII. Applicability of treatment and conditioning options for various types of LILW containing chemically toxic components

	Sorting	**Size reduction**	**Separation**	**Incineration and thermal treatment**	**Vitrification**	**Non-thermal Destruction**	**Biological Treatment**	**Solidification and Immobilisation**
Aqueous liquid wastes	--	--	X	--	--	--	X	X
Organic liquid wastes	--	--	X	X	--	X	X	X
Inorganic sludges	--	--	X	--	X	X	X	X
Organic sludges	--	--	X	X	X	X	X	X
Organic rubble	X	X	X	X	X	X	X	X
Inorganic rubble	X	X	X	--	X	--	--	X
Inherently hazardous, miscellaneous, and special wastes	X	--	X(a)	X(a)	X(a)	X(a)	X(a)	X(a)

(a) Selection of treatment and conditioning option would depend on particular waste characteristics.

4.3.3. Inorganic and organic sludges

These waste categories could also be called homogeneous or wet solids. Industrial operations involving radioactive materials produce a variety of relatively homogeneous sludges or similar wastes. These can be both the organic or inorganic. Sludges may contain a very high percentage of water, however, their high content of dissolved solids makes them non fluid, they are generally not pumpable, and do not flow on their own, or else flow extremely slowly.

A commonly occurring inorganic sludge is water treatment filter cake; commonly produced from water treatment processes. These sludges may contain silica filter aides, iron oxide used as a scavenger in the precipitation processes, and various salts precipitated out from the process solution. Inorganic sludges are generally amenable to immobilisation in common agents, such as Portland cement.

Organic sludges are heavy, highly viscous oil or grease, or may be organic liquids adsorbed onto inorganic materials such as vermiculite, clay or onto organic adsorbent materials. Some inorganic stabilising agents will solidify oil with as little as approximately 25 wt % added inorganic. Processing of organic sludge is more difficult than the treatment of liquid wastes discussed in Section 4.3.1. The objective is to remove or destroy organic material so that the remaining inorganics many be stabilised for disposal. A description of some separation and destruction techniques is provided in Appendix B.

4.3.4. Rubble

The term rubble is used to cover a broad category of discarded materials. In some regulations, these materials are defined as debris. These materials may have been in contact with the hazardous and radioactive materials used in the facility, and therefore become contaminated. Rubble also includes the steel and concrete from demolition of nuclear facilities.

Pre-treatment options for rubble include sorting of the waste to segregate the organic contaminants and size reduction. Treatment options include organic material destruction, separation of contaminants by thermal desorption, and finally, stabilisation of treated residuals. Organics should be removed from rubble to such a level that they will not interfere with the stabilising materials used to produce the final waste form, nor create an environmental hazard after disposal.

4.3.5. Inherently hazardous, miscellaneous, and special wastes

Inherently hazardous wastes include materials like cadmium, mercury, beryllium, and lead that cannot be deactivated or neutralised by treatment but remain hazardous after treatment. This special waste category may require special handling capabilities not readily available in a facility designed for processing the more general plant waste streams.

Treatment processes for these materials require specific approaches and may include recycling, reuse, or stabilisation and disposal. Mercury often can be cleaned or distilled producing a clean material for recycling together with a distillation waste, which can be stabilised and packaged for disposal. Lead also may be cleaned for storage or reuse. Substantial amounts of lead that is no longer required have been removed during decommissioning of power and research reactors. In general, about 60% of this lead is not contaminated and therefore it could be recycled/reused, or sold for scrap value. Oxide and scale removed from the lead is sent to grout stabilisation.

5. WASTE DISPOSAL

5.1. DESIGN OBJECTIVES

The disposal can be seen as the final stage in waste management operation. The implementation of a disposal solution should be consistent with the internationally accepted principles and requirements for the management of radioactive waste [18]. The overall objective of the design of a disposal facility is to provide design features that ensure the facility can be built and waste received, handled and disposed of without undue risk to human health and the environment, both during facility operation and after facility closure [2]. In order to achieve this primary objective, the following secondary objectives ought to be satisfied.

I. ***Isolation of waste/control of releases*** - The design of a facility should provide adequate isolation of the disposed waste for an appropriate period of time, taking account of the waste and site characteristics and the appropriate safety requirements [2]. It is recognized that, especially in the long term, there might be certain processes and events that might result in the release of contaminants from the disposal facility. However, the design, as well as other aspects of the disposal system (e.g. the geosphere characteristics), should strive to ensure that such releases do not have an unacceptable impact on humans and the environment during either the operational or post-closure phases.

II. ***Minimisation of impacts*** - The design of the disposal facility should minimize the exposure of workers to hazards during the operational phase and the public and the environment during the post-closure phase period.

5.2. DESIGN FEATURES

To achieve the required waste isolation and impact minimisation a series of diverse, independent, and robust barriers are installed. The required characteristics of the disposal system can be defined as:

- *diverse* - the performance of the different barriers is governed by various physical, mechanical, and chemical processes, so that a high level of complementarity can be guaranteed;
- *independent* - the performance of one barrier may not heavily depend on the correct functioning of the other barriers; in case of an ineffective performance of one barrier, the performance of the other barriers should not be negatively influenced; and
- *robust* - the estimated or designed performance of the barriers is highly independent of remaining uncertainties.

For disposal of radioactive waste, the multi-barrier system is commonly applied [2]. A similar approach is used for non-radioactive waste. Consideration of disposal facilities for non-radioactive waste is beyond the scope of this report, however, review and comparison of disposal options used in both cases can be found in [23].

5.3. SAFETY FUNCTIONS

When chemically toxic components in LILW are considered, their presence should be accounted in the safety assessment of the disposal system. Consistent with the design objectives and features, the following four safety functions of a disposal system ought to be considered in the safety assessments of the radioactive and chemically toxic contaminants in the waste:

- physical confinement;
- retarded release;
- dilution and dispersion; and
- limited accessibility.

Each of these safety functions is considered in turn below.

5.3.1. Physical confinement

This safety function refers to the initial isolation of the waste. As long as this safety function is effective, no release of the contaminants in the waste may occur. This function is performed by the conditioned waste package and the engineered barriers. Indefinite isolation of waste cannot be guaranteed since the various barriers will physically degrade over time, even if natural materials are used, and their performance as chemical barriers will also diminish, although at a potentially slower rate. As a consequence their ability to isolate the waste from processes such as the infiltration will decrease as a function of time.

The confinement of the waste allows benefit to be taken from the decay of the radionuclides and resulting decrease in activity levels. Although a similar benefit can be gained from the confinement and resulting degradation of chemically toxic organic contaminants in LILW, such a benefit is not gained from the confinement of many chemically toxic inorganic contaminants due to their stable nature.

5.3.2. Retarded release

As the role of the first safety function diminishes, the role of second safety function becomes increasingly important, particularly for the contaminants released in liquid form. Due to the degraded state of the barriers, water may reach the waste and start leaching the contaminants. The radionuclides and chemically toxic components of the LILW will not be released immediately from the disposal facility, because physico-chemical processes (e.g. sorption, diffusion, precipitation and co-precipitation) occur in the disposal facility and the geosphere and retard the release to the biosphere. Retarded release allows benefit to be taken from the decay of radionuclides and degradation of organic contaminants.

5.3.3. Dilution and dispersion

Once the contaminants start to be released and migrate from the disposal facility, they are discharged into the surrounding geosphere and may then reach the biosphere. As a result of dilution and dispersion processes taking place in the geosphere and biosphere, the contaminant concentrations that may became accessible to humans are further reduced.

5.3.4. Limited accessibility

The waste should be disposed of in such a way that the probability and consequences as of involuntary access by humans are sufficiently low once the access to the site is no longer controlled. In a deep disposal system, it is mainly the geosphere that performs this function. For a near surface disposal facility, it is the institutional control period, and to a lesser extent, the engineered barriers, even if they are partially degraded.

5.4. DISPOSAL FACILITIES

Various engineered disposal facilities have been developed for LILW, each with their own specific engineering features depending upon factors such as site and waste characteristics, national radioactive waste management strategies and regulatory approaches, and social and economic factors [24]. Disposal of LILW is currently considered in above or below grade near surface disposal facilities, or in deep geologic formations (in excess of 100 m depth). Most LILW disposal facilities have been built on the surface or within about 10 m of the surface.

Despite the differences in design, it is possible to identify the following common engineered barriers that are used to meet the design objectives:

– *the waste package*, comprising the waste matrix (cement, bitumen, polymers, glass and ceramics) and overpackage (carbon steel, concrete or stainless steel containers);
– *the disposal unit*, comprising the engineered structures/isolation layers (concrete, porous medium for drainage, bitumen, polymers, clay), and lining and backfilling materials (concrete, fly ash, clay mixtures); and
– *the man-made cover* (not required for cavern disposal facilities) comprising a series of alternative low and high permeability layers.

When considering the appropriateness of different disposal options, consideration should be given to the chemically toxic components in LILW and their characteristics. For example, it may be possible that a facility concept suitable for disposal of short lived radionuclides is unsuitable for certain chemically toxic constituents present in the LILW due to their persistent nature [25]. There is also a need to ensure that the hazardous substances in the waste do not compromise the performance of the engineered and natural barriers.

As noted in Section 3, many countries have developed waste acceptance criteria (WAC) to help ensure the safe disposal of LILW. They can relate to the non-radioactive as well as radioactive component of waste. Such WAC can provide limits for the concentration of radioactive and chemically toxic contaminants, as well as specifying the nature of pre-disposal treatment and providing a list of materials to be excluded from the disposal facility. They may also specify the physical, chemical and biological properties of the waste (e.g. only solid/solidified wastes not containing flammable, pyrophoric, organic and liquid sludge wastes); and procedures for the configuration and identification of waste packages.

Unlike very prescriptive requirements for chemically toxic waste disposal facilities, radioactive waste management approach is performance-based, which allows the disposal site owner to design and operate the facility as appropriate to achieve the performance standards.

5.4.1. Geological disposal

In the field of radioactive waste disposal, deep geologic formations are mainly envisaged for wastes containing significant quantities and concentrations of long lived radionuclides. However, deep geologic formations are also considered for disposal of LILW, including those containing chemically toxic components.

The disposal facility might be purpose built tunnels and/or silos, or be in an existing mine. The walls of tunnels/silos/mine can be lined by a low permeability barrier (for example bentonite) to control the ingress and egress of water. The exact nature of waste conditioning and packaging varies depending on factors such as waste and site characteristics. Conditioning can consist of waste immobilisation in a media such as concrete, bitumen or polymer. Steel drums and/or cubic/cylindrical boxes (steel or concrete) can be used as packaging containers. Such conditioning and packaging can provide both a physical and chemical barrier to the migration of radionuclides and other contaminants, especially in the short term. Any backfill material used can be high permeability or low permeability material depending upon particular design requirements.

An example of geological disposal in operation is the Waste Isolation Pilot Plant (WIPP) site in New Mexico, USA. WIPP has been excavated in salt deposits at about 650 m deep. Specific restrictions relate to water and humidity, explosive or pyrophoric materials, and volatile organic carbons. The safety model of WIPP is essentially based on the stability and impermeability of the salt formation. Since no material is supposed to move out of the repository formation and human intrusion is considered highly improbable no further restrictions are proposed for disposal. However, the final licensing may possibly consider other restrictions.

Several geological repositories are in the licensing procedure (e.g. the Konrad mine in Germany), whilst others are still in the R&D and feasibility phase (e.g. the proposed Wellenberg repository in Switzerland). See Section 6 and Appendix D for more detail.

5.4.2. Near surface disposal

Near surface disposal is currently practised or envisaged for LILW, essentially short lived (half life not in excess of 30 years) with long lived radioisotopes being limited to very low concentrations. Two broad categories of disposal facilities can be identified:

- above grade disposal facilities or those built within about 10 m of the surface; and
- deeper cavern facilities built at depths of up to 100 m.

For above grade disposal facilities or those built within 10 m of the surface, the disposal units or vaults are typically concrete lined and can be sub-divided into cells by internal concrete partitions to ensure that the operational area used for disposal at any given time is not too large. Each cell is filled in turn. There is usually some form of drainage system to channel any infiltrating water away from the waste. Depending on the position of the disposal unit with respect to the groundwater table, additional barriers might be constructed around the disposal unit in an attempt to control the movement of water into and out of the disposal unit.

As with deep geological disposal, the exact nature of the conditioning, packaging and backfilling varies depending on factors such as waste and site characteristics, and design requirements. Following filling of all disposal units, a graded final cap can be placed over the entire facility with the purpose of limiting the infiltration of precipitation into the disposal facility, reducing the probability of inadvertent intrusion by humans and/or other biota, and delaying or even preventing the erosive processes. Typically the final cap consists of a series of alternating high and low permeability layers. The low permeability layers limit infiltration, whilst the high permeability layers allow infiltrating water to be channelled along the layers and way from the disposal facility by a drainage system. In addition, a layer of rubble or concrete blocks can be introduced to dissuade inadvertent intrusion.

Operating examples of near surface disposal facilities or those built within about 10 m of the surface include Centre de l'Aube (France), Rokkasho (Japan), El Cabril (Spain), and Drigg (UK) [24].

Cavern disposal facilities have similar characteristics to the deep geological facilities descried in Section 5.4.1. An example is the SFR disposal facility in Forsmark, Sweden, which is located under the seabed and has been receiving LILW for disposal since 1988 [24].

All these near surface disposal facilities have WAC that place limitations upon the disposal of certain non-radioactive hazardous materials. For example, in France, the WAC prohibit the disposal of organic liquids, free liquids, metallic sodium or sodium alloys, alloys likely to give rise to violent chemical reactions and biological toxicants. The reason for their prohibition is that they can increase the mobility of the radionuclides contained in the waste either through complexation or because they can cause degradation of the confining materials. In addition, a safety assessment of certain chemically toxic components in the waste is required to allow appropriate disposal limits to be established. The disposal agency in France (ANDRA) has developed guidance for waste producers to allow them to declare the quantity and nature of the chemically toxic components of the waste. It requires information to be collated concerning a variety of chemically toxic contaminants including: As, Cd, Cr, Hg, Ni, Pb, Sb, Se, B, Be, U and asbestos.

6. SAFETY ASSESSMENT

The waste management includes many stages during which safety must be ensured. During treatment, packaging, transport, handling, storage and operational disposal, the safety is ensured through the enforcement of regulations, the implementation of essentially active protection systems (for example ventilation) and the implementation of corrective measures in the case of occurrence of any abnormal situation. Such an approach cannot be applied to safety during the disposal post-closure because, consistent with the IAEA principles on radioactive waste management [18], the safety should not be built on active measures to be taken by future generations.

The overall objective to protect human health and the environment from any deleterious effects of the waste must be applied to disposal over the short term (operational phase of the disposal facility) as well as over the long term (post-closure phase). For the demonstration of the safety of radioactive waste disposal, procedures including site-specific radionuclide transport and fate models have commonly been developed and applied to assess the radiological impact [1]. Performing such an assessment involves:

- the definition of the source term;
- the definition of the possible transfer pathways and the evaluation of the resulting end-points; and
- the analyses of the overall acceptability and safety.

The use of safety assessments with detailed site-specific contaminant transport and fate calculations to estimate health effects is not common for non-radioactive waste in general (because there is often no regulatory requirement) and chemically toxic components in LILW in particular (some exceptions are given in the case studies in Appendix D). However, such calculations can provide a unique insight into: the relative hazards of radiological and chemically toxic components; the usefulness of radioactive waste safety assessment methodologies for the assessment of chemically toxic components; and the long term safety of disposal practices for a LILW containing radioactive and chemically toxic components.

6.1. SAFETY ASSESSMENT APPROACH APPLIED TO CHEMICALLY TOXIC SUBSTANCES

6.1.1. Source term definition

The source term definition consists of the determination of the waste content and the subsequent selection of the toxic substances with the highest potential hazard according to a first screening.

(a) Waste contents

The knowledge of the waste content (nature, quantities, chemical form(s)) is of primary importance in developing a strategy for managing LILW with regard to its chemical toxicity. Records should be kept of all waste constituents with special attention for radioactive and potentially chemically toxic constituents. Such information is essential for the evaluation and understanding of the long term evolution of the source terms. Furthermore, experience indicates that possible later remediation is much more problematic if the source term is not characterised or is insufficiently characterised.

- ***Chemically toxic components.*** This step consists of identifying all the substances considered as chemically toxic and to be dealt with in the safety assessment. Potentially chemically toxic by-products resulting from the decomposition and transformation of the constituent chemicals in the waste should be considered, as well as chemically toxic substances included in the waste matrix or added to the package (for example metallic lead used for shielding).

- ***Non-toxic components.*** It is important to identify and account for possible consequences of the non-toxic components of the waste (e.g. organics such as cellulose containing materials, low molecular weight organics, and high molecular weight organics) since, during decomposition, they may give rise to complexing substances which may enhance mobility of radioisotopes or other chemically toxic components. The potential production of gas may also be accounted for.

(b) Selection of the chemically toxic substances with the highest potential hazard

The objective of this step is to determine among all the chemically toxic substances identified in the source term, those for which a stringent safety assessment should be undertaken because of their expected harmful consequences on human health and/or the environment. A screening methodology can be applied to eliminate those substances that definitely do not lead to hazards under the conditions considered and to select the critical substances for which most effort in terms of assessment resources and parameter identification should be undertaken.

6.1.2. Definition of the possible transfer pathways and evaluation of the resulting end-points

The transfer pathway definition consists of the inventory of the potential transfer pathways by which humans may be exposed (scenarios) during the operational period and the post-closure period. The evaluation consists of the quantification of the calculated end-points through mathematical models.

(a) Scenarios

The investigation of the transfer pathways aims at identifying the initial routes by which any component of the waste is likely to come into contact with humans and the environment. Generally, such an investigation has already been undertaken within the framework of the radiological safety assessment. These pathways may be the same for the chemically toxic substances. The knowledge of the transfer pathways allows scenarios to be developed within the context of the assessment. Since the transfer pathway are generally the same, the scenarios identified within the framework of the radiological safety assessment can be applied to the chemically toxic substances.

Three kinds of scenarios are commonly distinguished:

- Air-vector scenarios (release of gas from the waste through the air vector);
- Water-vector scenarios (release of hazardous substances resulting from the leaching of the waste); and
- Intrusion scenarios (resulting from human and/or natural intervention).

(b) Evaluation of the resulting end-points

This part of the assessment is aimed at calculating the quantities of chemically toxic contaminants that may be transferred out of disposal facility and their subsequent impact on human health and the environment. The resulting end-points can be:

- release rates from the waste and/or the disposal facility;
- environmental concentrations (groundwater/river, soil, air, flora…);
- intake rates (ingested and inhaled quantities); and
- health effect risk.

The end-points quantification can be undertaken by using calculational codes. The calculations need many data related to the behavior of the substances within the disposal system (conditioned waste, engineered barriers, geosphere, biosphere, etc.). Efficiency of retention or containment applies to radioactive as well as to chemically toxic materials, organic as well as inorganic materials. Understanding and quantification of these phenomena currently receives much more attention for the radionuclides and has become the basis for widely used and accepted safety assessment methodologies (see for example [26]).

Many physicochemical data (corrosion, sorption/retention) currently exist or can be derived for many inorganic and organic chemically toxic contaminants. New assessment scenarios and new data may be required but they could fit into the assessment models currently used for radionuclides. Nevertheless, it is important to note that, contrary to most radionuclides, the chemically toxic contaminants can be in significant quantities in the waste, and hence the phenomena governing the transfers may differ. In particular, precipitation and dissolution might have to be considered, as well as the presence of complexing agents, colloids, etc. Note that the influence of such phenomena also may be accounted for within the framework of certain radiological safety assessments.

6.1.3. Analyses of the overall acceptability and safety

In the case of radiological impact assessment, the common safety indicator used to evaluate health effects` is the dose or risk consistent with the regulator requirements. It takes account for the contribution of all radionuclides and all exposure routes (inhalation, ingestion, external exposure).

To assess the impact of chemically toxic contaminants, it is necessary to compare the calculated environmental concentrations and/or exposure levels with impact levels considered as acceptable. These values should be consistent with :

- the nature and the chemical form of the toxic;
- the exposure time (chronic/acute); and
- the exposure route.

Several indicators may be used. Some are related to environmental concentrations (indirectly related to health effects), whilst others are related directly to the resulting health effects. A summary of potentially relevant indicators is given in [7, 25].

(a) Environmental concentrations

Indicators related to environmental concentrations include:

- drinking water standards,
- air quality guidelines (public, workers),
- soil quality guidelines, and
- natural background levels in the environment (water, air, soil…).

(b) Health effects

The health effects may be `threshold` and `no threshold` related. The former refers to cases where adverse effects occur only at exposures above a given level and it is proportional to the exposure, whereas the latter assumes that the probability for example of developing cancer or mutations is proportional to exposure levels (stochastic effects like most cancers). Different guidelines exist that reflect the differences in exposure pathway, chemical form of the substance, exposure time, etc.

- Stochastic effects (non threshold effects): risk unit for ingestion and inhalation
- Systemic effects (threshold effects): reference dose (RfD) for ingestion, reference concentration (RfC) for inhalation, others.

Values for risk, RfD and RfC can be found in databases such as the US Environmental Protection Agency's Health Effect Summary Tables.

The acceptability of the impact depends on the position of the calculated end-points relative to the acceptable level for the indicators. For the environmental concentrations, and systemic health effects, the associated end-points should be below the acceptable level. This points out the importance of the choice of the indicator value and hence the chemical form of the toxic substances considered. In the case of risk end-points with regard to stochastic effects, the calculated value should be below the risk level considered as acceptable. This level can be set up by the Members States regulations or derived from other risk levels.

It should be noted that the combined effects between several chemically toxic substances and/or between chemically toxic substances have radionuclides are generally not been taken into consideration currently because of the lack of data available. However, the acceptability of the impact may be subject to discussion according to the probability of occurrence of the considered scenario and the conservativeness of the calculation (model, data…). Thus, a significant impact associated with a scenario with a very low probability of occurrence might under certain circumstances be considered as acceptable.

6.2. EXAMPLES OF SAFETY ASSESSMENT

Several studies have been published that address the safety assessment of the chemical components present in LILW. The studies may differ in several respects, for instance in the type of chemical components considered (organic or inorganic, or both), the methodology applied, the repository concept (deep versus near-surface), etc. The case studies given in Appendix D illustrate some of these differences, and include both examples for deep geological disposal (Germany), above grade near surface (Belgium and France) and below grade (cavern) near-surface disposal (Sweden). Other examples of equally well documented case studies have been reported in the UK [27], and Switzerland [28]. Note that intrusion scenarios have generally not been considered in the assessment studies mentioned here, with the exception of generic studies reported in [7] and [25].

Existing safety assessment studies for geological disposal of LILW containing organic and inorganic components have shown that no hazards for humans and environment are associated with this waste type. For near surface disposal facilities, similar conclusions have been drawn although for particular elements concentrations in groundwater exceeded the existing guidelines (assuming very conservative assumptions in the calculations).

7. CONCLUDING REMARKS

The management of chemical toxicity in LILW has not been widely addressed in a direct manner previously. It is considered more complex due to the inhomogeneous nature of LILW compared with HLW. This report provides a background understanding of the issues associated with chemically toxic materials in LILW and the role that waste treatment and conditioning alternatives can play in supporting their safe disposal.

Radionuclide concentrations in LILW are generally more extensively assessed than chemical constituents, and process knowledge is often the only source of information for identifying non-radiological contaminants of concern. Various compositions of chemically toxic materials constitute LILW from different nuclear energy sectors, and they can be categorised into five waste types, namely: aqueous liquid wastes with organic and inorganic toxic contaminants, organic liquid wastes, inorganic and organic sludges, rubble, and inherently hazardous, miscellaneous and special wastes.

Most countries have developed or are developing regulations that separately cover the management of radioactive and non-radioactive waste. The basic principle behind the regulations for both types of waste is essentially the same, i.e. to protect humans and the environment against potential harm. However, the actual standards used to achieve the principle differ between the countries and between the two waste types. In the absence of clear regulatory guidance on the chemically toxic components of LILW, many countries have introduced waste acceptance criteria that relate to the non-radioactive as well as radioactive component of LILW. In addition, disposal operators have undertaken assessments with the aim of addressing both sets of regulations. There is now a growing recognition of the need to consider explicitly not only the radiological but also the non-radiological impacts of LILW management.

Traditional (dual purpose) technologies for radioactive waste treatment combined with special methods and processes for destruction/stabilisation of chemically toxic materials demonstrate solid technical basis for the processing of toxic constituents in LILW. Few individual technologies can provide a combination of organic destruction, radionuclide immobilisation, other toxic materials immobilisation after transferring them into less toxic form. Therefore, a waste treatment system (a train of technologies) is required to address the full range of toxic constituents in LILW.

Disposal of LILW is currently considered in near surface repositories and in geological repositories. When considering the appropriateness of different disposal options for LILW, consideration must be given to the chemically toxic components in the LILW. There is also a need to ensure that the substances in the wastes do not compromise the performance of the engineered and natural barriers. To help ensure the safe disposal of LILW, many countries have developed waste acceptance criteria that relate to the non-radioactive as well as radioactive component of the waste.

Safety assessment can be carried out in the same or comparable manner for both the radionuclide and the chemically toxic substances in the radioactive waste. In the context of chemical impact assessment, many end-points may be considered. The choice of the value of the associated impact indicator is of most importance because it can widely influence the conclusion about the acceptability of the impact. However, the question of the long term fate of the chemically toxic substances is just starting to be addressed for radioactive as well as the chemical waste disposal. A consistent approach to the assessment of both radioactive and chemically toxic substances would better ensure their safe disposal.

Existing safety assessment studies for geological disposal of LILW containing organic and inorganic components have shown that no hazards for humans and the environment are associated with this waste type. For near surface disposal facilities, similar conclusions have been drawn, although for particular elements concentrations in groundwater exceeded the existing guidelines (assuming very conservative assumptions in the calculations). This points out that the assessments need to be considered case by case with regard to the chemically toxic substances and the scenarios of concern.

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Appendix A

REGULATORY FRAMEWORK FOR CHEMICALLY TOXIC LOW LEVEL WASTE IN THE UNITED STATES OF AMERICA

In the United States of America chemically toxic radioactive waste is called mixed waste. Mixed waste management is subject to dual regulation, i.e. the US Nuclear Regulatory Commission (NRC) regulates the radioactive contamination and the US Environmental Protection Agency (EPA) regulates the chemically hazardous nature of the waste. The following description of the mixed waste regulatory requirements was compiled from several documents on the EPA's mixed waste web site; http://www.epa.gov/radiation/mixed-waste. The reader is directed to that web site for specific regulatory citations and additional detail on the regulation of mixed waste in the USA.

It is also noted that a new rule was signed into law on October 29, 1999 which may substantially alleviate the burden of dual regulatory authorities, if the conditions apply. This new rule is described in Section A.7.

A.1. AN OVERVIEW OF MIXED WASTE

Mixed waste contains radioactive and hazardous waste. A dual regulatory framework exists for mixed waste, with the EPA or authorized states regulating the hazardous waste and the NRC, NRC agreement states, or the US Department of Energy (DOE) regulating the radioactive waste (radioactive constituents). The NRC (or agreement states, where applicable) generally regulates commercial and non-DOE federal facilities. DOE is currently self-regulating and its orders (regulations) apply to DOE sites and contractors.

Using the Atomic Energy Act (AEA) authority, the NRC and DOE regulate mixed waste with regard to radiation safety. Using the Resource, Conservation, and Recovery Act (RCRA) authority, the EPA regulates mixed waste with regard to hazardous waste safety. The NRC is authorized by the AEA to issue licenses to commercial users of radioactive materials. RCRA gives the EPA the authority to control hazardous waste from "cradle-to-grave". Once a waste is determined to be a mixed waste, the waste handlers must comply with both AEA (NRC) and RCRA statutes and regulations.

Commercially generated Mixed LLW is produced in all 50 states at industrial, hospital, and nuclear power plant facilities. Radioactive and hazardous materials are used in a number of processes such as medical diagnostic testing and research, pharmaceutical and biotechnology development, pesticide research, as well as nuclear power plant operations. Based on the results of a survey conducted by the NRC and EPA (NUREG/CR-5938), approximately 4,000 m^3 of Mixed LLW were generated in the USA in 1990. Of this amount, approximately 2840 m^3 (or 71%) was liquid scintillation cocktail (LSC). Organic solvents such as chlorofluorocarbons (CFC's), corrosive organics, and waste oil made up 18%, toxic metals made up 3%, and "Other" waste made up the remaining 8%.

Under the 1984 Amendments to RCRA, Land Disposal Restriction (LDR) regulations prohibit disposal of most mixed waste, including Mixed LLW, until it meets specific treatment standards. While most of the commercial mixed waste that is generated and stored can be treated to meet the LDR's by commercially available treatment technology, there still exists a small percentage of commercial mixed waste for which no treatment or disposal capacity is available. Commercial mixed waste volumes are very small (approximately 2%) compared to the total volume of mixed waste being generated or stored by the DOE.

A.2. THE LAND DISPOSAL RESTRICTION (LDR) LEGISLATIVE FRAMEWORK

The 1984 Hazardous and Solid Waste Amendments (HSWA) to RCRA restrict the land disposal of hazardous wastes, including mixed waste. Waste treated in accordance with treatment standards set by RCRA are not subject to the prohibitions and may be land disposed. The statute requires EPA to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short term and long term threats to human health and the environment are minimized".

A.3. MIXED WASTES SUBJECT TO THE LAND DISPOSAL RESTRICTIONS

The LDR regulations currently apply to all hazardous waste, including mixed waste, listed or identified as of November 8, 1984. They also apply to several hazardous wastes newly listed after November 8, 1984 for which treatment standards have been developed. The methodology for establishing whether a low level waste is mixed waste is as follows:

A.3.1. Step 1: Identify LLW

Step 1 in the methodology requires that the generator to determine whether the waste is LLW as defined in the Atomic Energy Act. LLW is a radioactive material that (a) is not high-level radioactive waste, spent nuclear fuel, or by-product material as defined in the AEA (i.e., uranium or thorium mill tailings) and (b) the NRC classifies as LLW consistent with existing law and in accordance with (a). If the generator determines that the waste is LLW, the generator should proceed to Step 2. If the determination is negative, then the waste cannot be Mixed LLW because it is not LLW. However, the waste may be another radioactive or hazardous waste regulated under AEA, RCRA, or both statutes.

A.3.2. Step 2: Identify listed hazardous waste

In Step 2, the generator determines whether the LLW contains any hazardous wastes listed in Subpart D of 40 CFR Part 261. LLW is Mixed LLW if it contains any hazardous wastes specifically listed in Subpart D of 40 CFR Part 261. Listed hazardous wastes include hazardous waste streams from specific and non-specific sources listed in 40 CFR Parts 261.31 and 261.32 and discarded commercial chemical products listed in 40 CFR Part 261.33. The generator is responsible for determining whether LLW contains listed hazardous wastes. The determination should be based on knowledge of the process that generates the waste. For example, if a process produces LLW that contains spent solvents that are specifically listed in the tables of Subpart D of Part 261, the generator should suspect that the waste is Mixed LLW.

A.3.3. Step 3: Identify hazardous characteristics

If the LLW does not contain a listed hazardous waste, Step 3 of the methodology requires the generator to determine whether the LLW contains hazardous wastes that cause the LLW to exhibit any of the hazardous waste characteristics identified in Subpart C of 40 CFR Part 261. This determination can be based on either (1) an assessment of whether the LLW exhibits one or more of the hazardous waste characteristics because it contains non-AEA materials (i.e., materials other than source, special nuclear, and by-product materials) based on the generator's knowledge of the materials or processes used in generating the LLW, or (2) testing of the LLW in accordance with the methods identified in Subpart C of Part 261. Except for certain ores containing source material, which are defined as source material in 10 CFR 40.4(h), and uranium and thorium mill tailings or wastes, NRC and EPA interpret the definitions of source, special nuclear, and by-product materials to include only the radioactive elements themselves. Generators should identify non-AEA materials contained in the LLW by examining the process that generates the waste. For example, if the process mixes by-product material (an AEA material) with a volatile organic solvent (a non-AEA material), the generator would determine either through their knowledge or testing of representative samples of the LLW that contain the solvent waste whether the waste exhibits any of the hazardous waste characteristics because it contains the solvent.

If the wastes are tested, the generator should collect and test representative samples of the LLW to determine if the waste exhibits any of the characteristics identified in Subpart C because it contains the non-AEA materials. These characteristics include ignitability (Section 261.21), corrosivity (Section 261.22), reactivity (Section 261.23), and Extraction Procedure (EP) toxicity (Section 261.24). The purpose of the characteristics tests is to identify hazardous wastes that are not specifically listed in Subpart D of 40 CFR Part 261. Test methods to collect representative samples of wastes are described in Appendix I of 40 CFR Part 261. The samples should then be tested using the referenced testing protocols.

If LLW contains a listed hazardous waste or non-AEA materials that cause the LLW to exhibit any of the hazardous waste characteristics, the waste is Mixed LLW and must, therefore, be managed and disposed of in compliance with EPA's Subtitle C hazardous waste regulations in 40 CFR Parts 124, and 260 through 270, and NRC's regulations in 10 CFR Parts 20, 30, 40, 61, and 70.

Management and disposal of Mixed LLW must be conducted in compliance with state requirements in states with EPA-authorised regulatory programmes for the hazardous components of such waste and NRC agreement state radiation control programs for LLW.

A.4. BEST DEMONSTRATED AVAILABLE TECHNOLOGIES TO TREAT WASTE TO LDR STANDARDS

RCRA Section 3004(m) requires EPA to "promulgate regulations specifying those levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste”. To meet this requirement, EPA chose to promulgate only the technology-based level or Best Demonstrated Available Technologies (BDAT) approach.

To date, EPA has set special treatment standards for four categories of mixed waste. They include:

1. radioactive lead solids with a BDAT treatment standard of macrocapsulation;
2. radioactive elemental mercury with a BDAT treatment standard of amalgamation;
3. radioactive hydraulic oil contaminated with mercury and a BDAT standard incineration; and
4. radioactive high level wastes generated during the reprocessing of fuel rods with a BDAT standard of vitrification.

The remaining mixed wastes are subject to those promulgated treatment standards that apply to the hazardous portion of the waste unless EPA publishes specific standards for mixed waste treatability groups in the future.

A.5. THE LDR STORAGE PROHIBITION

In addition to prohibiting the land disposal of hazardous wastes, RCRA also prohibited the storage of any waste which is prohibited from land disposal unless "such storage is solely for the purpose of the accumulation of such quantities of hazardous waste as are necessary to facilitate proper recovery, treatment, or disposal".

A.6. DISPOSAL REQUIREMENTS

RCRA regulations identify the design and operating requirements for owners and operators that dispose of hazardous waste in landfills. These regulations involve requirements for the installation of two or more liners and a leachate collection and removal system above and between the liners to protect human health and the environment. Exceptions to the double liner and leachate collection system requirements are allowed if alternative design and operating practices, together with location characteristics, are demonstrated to EPA's Regional Administrator to be equally effective in preventing the migration of hazardous constituent into the ground water or surface water.

NRC regulations in 10 CFR Part 61 Licensing Requirements for Land Disposal of Radioactive Waste, indicate that long term stability of the waste and the disposal site require minimisation of access of water to the waste [61.7(b)(2)] and that the disposal site must be designed to minimise to the extent practicable the contact of water with waste during storage, the contact of standing water with waste during disposal and the contact of percolating or standing water with wastes after disposal [61.51(a)(6)]. The primary objective of the above NRC regulations is to preclude the possibility of the development of a "bath-tub" effect in which the waste could become immersed in liquid (e.g. from infiltration of surface water runoff) within a disposal unit below grade with a low-permeability bottom surface

A.7. ENVIRONMENTAL PROTECTION AGENCY PROPOSED RULE FOR STORAGE, TREATMENT, TRANSPORTATION, AND DISPOSAL OF MIXED WASTE

On October 29, 1999 the EPA signed a proposed rule for storage, treatment, transportation and disposal of commercial mixed waste. In general, this rule exempts commercially generated mixed waste from the dual regulatory requirements if:

- The waste is in tanks or containers,
- The waste is generated at a NRC licensed site,
- The waste meets the requirements of the EPA's Land Disposal Restrictions, and
- The waste meets the waste acceptance criteria of a licensed disposal site.

The new rule is intended to alleviate the dual regulatory issues created under RCRA.

Appendix B

PRE-DISPOSAL PROCESSING OPTIONS FOR LILW CONTAINING CHEMICALLY TOXIC COMPONENTS

Selection and application of appropriate pre-disposal techniques for processing of radioactive waste containing chemically toxic constituencies is especially important for optimisation of the whole waste management scheme in terms of cost, efficiency and safety. This Appendix details some important steps and components of waste processing options mentioned in the main text and specifically applied for this type of waste.

B.1. SORTING

It is always best to avoid co-mingling of the wastes that require different treatment processing prior to disposal. So the sorting and segregation of both solid and liquid waste with different characteristics is widely practiced by generators. It provides a number of advantages:

- Simplifies documentation requirements for shipment and handling by minimising the volume of LILW with toxic constituents,
- Simplifies treatment by limiting the input to any process to those items it is specifically designed to treat; and
- Simplifies disposal of the wastes by segregating them according to disposal waste categories and disposal acceptance criteria.

The sorting of relatively low active waste (contact handled) may be done safely by the generator. Wastes that were generated and simply stored without regard for their treatment requirements may require re-sorting into categories that are compatible with new treatment technologies or with disposal site acceptance criteria. However, the sorting of stored wastes may be disadvantageous as it exposes staff to radioactive and physical hazards during the sorting process.

Common solid waste sorting categories include the following:
- combustible waste,
- rubble (e.g. non-combustibles including concrete from building dismantlement),
- non-toxic metals (e.g. equipment and structure),
- toxic metals (e.g. lead, etc.), and
- solids (those contaminated with toxic organic and inorganic constituents).

Proper sorting requires staff training for segregation at the various points including generation and treatment. Additional space and containers in the waste collection and storage areas are required.

B.2. SIZE REDUCTION

Some wastes may require reduction in size or shape changes to be acceptable for feeding to process equipment. A number of techniques can be used.

Shredding, chopping, shearing, grinding, or torch cutting can be used for reducing waste volumes for disposal and also for sizing of wastes for feeding to treatment processes. Larger pieces of rubble type waste, such as spent process equipment, may be cut with remote saws or other techniques. As many nuclear facilities enter the decontamination and decommissioning phase of their lives, the size reduction of large metal objects is becoming an industrial challenge. Options include gas torches, plasma torched, grinders, saws, shears etc. In some cases such size reduction techniques may enhance the process effectiveness by providing increased surface areas for reaction. Furthermore, size reduction can reduce waste handling, storage, and shipment costs. However, grinding dust and saw chips may be hazardous and may require the introduction of secondary waste control. There also may be increased hazards to worker due to use of the cutting tools and the physical hazards of handling the sharp and heavy materials.

B.3. SEPARATION

The separation of the toxic or radioactive constituent from the waste stream is an effective means of reclassifying the waste and simplifying management into either the toxic or radioactive regulatory classification.

For volatile or semi-volatile organic materials, these separations can be accomplished using common industrial technologies. Heating will readily volatilize simple organic compounds in particular from solids or sludges. Several processes have been commercialised for the thermal desorption of organic contaminants from soils and sludges. [B-1] described the supercritical carbon dioxide extraction (SCDE) technology that has been used successfully for the removal of hazardous organic compounds from LILW.

For inorganic materials may be removed by extraction with suitable solvents. Extraction technology is a widely used industrial processes and has been successfully demonstrated for radioactive wastes (see for example [B-1]). To be most effective, extraction requires that an appropriate solvent is carefully matched to the separation which is desired and that the characteristics of the feed material are consistent.

Chemical separations are generally not 100% efficient and some contaminant often remains in the original waste stream. Separation technologies may substantially simplify regulatory process for decontaminated waste, however, the change of regulatory status may not be straightforward or easily acceptable (i.e., the materials continue to be regulated as toxic/radioactive). At the same time the separated or concentrated contaminants may present an additional regulatory challenge.

B.4. INCINERATION AND THERMAL TREATMENT

Incineration, which is used for volume reduction of lightly contaminated and sometimes highly contaminated combustible waste, also provides almost complete destruction of hazardous organic compounds and flammable solvents. For example, destruction of greater than 99.99% is required by the US Resource Conservation and Recovery Act (Title 40 Chapter 264.340 of the US Code of Federal Regulations) and many systems document capabilities exceeding 99.9999%. Simple batch operated incinerators were used for lightly contaminated radioactive waste in the late 1950s [B-2]. In the 1970s several commercial radioactive waste incinerator designs were marketed utilizing fixed hearth, fluidised bed and pyrolysis designs.

Incineration technology is now well developed and systems are commercially available (see Table B-I). For example, for the last 20 years, radioactive waste has been incinerated at the Austrian Research Center at Seibersdorf [B-3]. The US Department of Energy operates three incinerators with the appropriate licenses and permits to treat organically contaminated LILW.

LILW incineration system should include the following components:

- Waste receipt and storage area, with capabilities to sort and blend materials;
- Primary combustion system with a design specifically selected to address the waste form, waste stream quantity and contaminants of concern;
- Secondary combustion chamber to complete destruction of the organic compounds in the off-gases from the primary chamber;
- Ash removal system to safely cool and remove non-combustible material from the combustion chamber;
- System for immobilization of the ash;
- Air pollution control system to remove particulate matter and other pollutants of concern from the combustion gases.

Volatile metals, such as mercury, ought be addressed in the design to avoid unacceptable emissions. Dioxin/Furan emissions should be limited by the appropriate designs. The air pollution control system generates a secondary waste that may represent an additional regulatory concern. A further disadvantage with incineration is that it is poorly accepted by the public in some countries.

B.5. VITRIFICATION

Vitrification was developed for radioactive high level waste applications, but has been suggested as a technology for LILW solid and liquid wastes. Vitrification uses joule heating of glass matrices to melt inorganics such as ash and other inorganic materials. The product is a high density glass-like final waste form. Application of vitrification to these solid wastes generally requires all the subsystems of an incineration system.

The advantages of vitrification include:

- a leach resistant, low volume final waste form;
- a high volume reduction for combustible waste;
- organic and nitrate destruction efficiency equivalent to incineration;
- for waste streams treatable by direct vitrification, overall waste processing is simplified compared to a separate organic destruction process followed by blending and solidification.

However, there are certain limitations associated with vitrification. Care must be taken to avoid unacceptable emissions of volatile metals, such as mercury, and dioxins and furans. The associated gas cleaning system generates a secondary waste which may present additional regulatory problems. Furthermore, if there are variations in the waste feed, it is necessary to control the melt composition and therefore assure the melted waste form properties are satisfactory.

TABLE B-I. Some characteristics of selected thermal treatment technologies applicable to LILW

Technology	Waste Streams Treated	Temperature/ Pressure	Destruction and Removal Efficiency	Emission	Secondary Wastes Generated
Steam reforming	Organic liquids, solids, sludges	850 to >1100°C/ ambient	>99,99%	HCl, CO_2, H_2O	Ash, scrubber solutions
Supercritical water oxidation or hydrothermal oxidation	Aqueous w/dissolved or suspended organics	400 to 650°C/ >250 atm	>99,99%	CO_2, H_2O, N_2, N_2O	Salts, acids, oxides
Packed bed reactor	Vapor phase organics	870 to 1000°C/ambient	>99,99%	CO_2, H_2O, acid gases	Scrubber solutions/ filters
Thermal reduction	Chlorinated hydrocarbon vapor	>850°C/ambient	>99,99%	H_2, CH_4, CO, H_2O	Scrubber sludge
Photo reduction	Gas phase halogenated hydrocarbons	<500°C/ambient	N/A	HCl	Hydrocarbons
Plasma pyrolysis	Organic liquids	5000 to 15000°C	>99,99%	CO_2, H_2O, CO, NO_x, particulates	Powdered carbon
Fixed Hearth Incinerator	Organic solids	>850°C/ambient	>99,99%	CO_2, H_2O, acid gases	Scrubber solutions/ filters
Fluidized Bed Incinerator	Organic solids	>850°C/ambient	>99,99%	CO_2, H_2O, acid gases	Scrubber solutions/ filters
Rotary kiln incinerator	Organic solids	>850°C/ambient	>99,99%	CO_2, H_2O, acid gases	Scrubber solutions/ filters
Molten salt oxidation	Organic solids	>850°C/ambient	>99,99%	CO_2, H_2O, acid gases	Spent salt, scrubber solutions/ filters

B.6. NON-THERMAL DESTRUCTION TECHNOLOGIES

The limitations associated with thermal treatment technologies (in particular the generation of off-gases) has led to a new category of waste destruction technologies generally know as non-thermal destruction technologies or alternative oxidation technologies. These technologies generally provide destruction of organic constituents, matrix or contaminants, leaving the residual non-oxidisable materials in a sludge form. They have the advantage of reducing off-gas emissions and if used for waste with high content of organics, the volume reduction will be high. Table B-II summarizes some common non-thermal destruction technologies under development.

Most low temperature oxidation processes used in waste treatment systems involve the production of free radicals in sufficient quantity to oxidise and destroy organics. However these processes vary in the methods used to generate the radicals and often use a combination of strong oxidants (e.g. O_3 and H_2O_2), catalysts (e.g. transition metal ions or photocatalysts) and irradiation (e.g. ultraviolet, ultrasound, or electron beam). Direct chemical oxidation of organic compounds is also achieved by exposing the target compounds to strong oxidising agents, such as oxygen or air, ozone, hydrogen peroxide, nitric acid, catalysed hydrogen peroxide, or certain ions in an oxidised state (as in electrochemical oxidation processes).

Low temperature oxidation is most commonly used to destroy dilute organic contaminants in aqueous waste. However, oxidation processes such as mediated electrochemical oxidation, wet air oxidation, catalytic chemical oxidation and acid digestion are being developed for treatment of waste sludges, organic liquids, and solids. The processes may also be used to solubilise toxic metals and radionuclides to decontaminate debris.

Issues to be aware of when considering non-thermal destruction technologies include:

- generally low production rates for oxidation relative to thermal technologies;
- extensive sorting of the waste to preclude unacceptable items is required;
- large volumes of highly corrosive chemicals are required;
- most technologies require expensive acid resistant alloy construction for major process vessels.

B.7. BIOLOGICAL TREATMENT

Biological treatment refers to the degradation and detoxification of waste using micro-organisms such as bacteria and fungi. The process residues generated are generally biomass in the form of sludge, water and carbon dioxide, and organic by-products in the case of incomplete mineralisation. Aqueous or organic liquid waste streams are most suitable for being treated using biological treatment technologies. For example, biosorption of metals can result in the removal of metals from aqueous solutions. In addition, biological treatment (oxidation or reduction) can alter important properties such as a metal’s solubility in water and mobility. When implemented successfully, biological treatment systems are simpler, less expensive and less disruptive compared to conventional physical/chemical treatment methods. In addition, they are often more acceptable to the public than alternative physical/chemical treatment methods. Potential areas of biological treatment application are listed in Table B-III.

TABLE B-II. Characteristics of selected non-thermal destruction technologies applicable to LILW

Technology	**Waste Streams Treated**	**Temperature/ Pressure**	**Destruction and Removal Efficiency**	**Emission**	**Secondary Wastes Generated**
Electrochemical oxidation	Organic liquids, cellulosics, some plastics	Ambient/ambient	90 to >99%	CO_2, CO, No_x, HNO_2	Depleted acid, inorganic sludge
Photo oxidation	Dilute aqueous, no solids	Ambient/ambient	>99,9%	CO_2	Organic by-products
Ultrasonic oxidation	Dilute aqueous, <10% solids	Ambient/ambient	>99,9%	CO_2	Organic by-products
Electron Beam oxidation	Dilute aqueous, <5% solids	Ambient/ambient	>99.9%	CO_2	Organic by-products
Gamma Ray oxidation	Dilute aqueous, contained sludges	Ambient/ambient	>99,9%	CO_2	Organic by-products
Acid Digestion	Organic liquids, cellulosics	200°C/Low Pressure		CO_2	Gaseous NOX, sludge
Direct Chemical Oxidation	Organic Liquids, Cellulosics	200°C/Low Pressure	99.9%	CO_2	
Catalytic Chemical Oxidatin	Organic Liquids and sludges	200°C /100 psi.		CO_2	

TABLE B-III. Potential candidates for biological treatment technologies

Chemical class	Status of biological treatment technologies	Evidence of future success
Hydrocarbons and Derivatives		
Gasoline, fuel oil	Established	
Polycyclic aromatic hydrocarbons	Emerging	Aerobically biodegradable under a narrow range of conditions
Alcohols, ketones	Established	
Ethers	Emerging	Biodergradable under a narrow range of conditions using aerobic or nitrate-reducing microbes
Halogenated Aliphatics		
Highly chlorinated	Emerging	Cometabolized by anaerobic microbes; cometabolized by aerobes in special cases
Less chlorinated	Emerging	Aerobically biodegradable under a narrow range of conditions; cometabolized by anaerobic microbes
Halogenated Aromatics		
High chlorinated	Emerging	Aerobically biodegradably under a narrow range of conditions; cometabolized by anaerobic microbes
Less chlorinated	Emerging	Readily biodegradable under aerobic conditions
Polychlorinated Biphenyls		
Highly chlorinated	Emerging	Dehalogenated by anaerobic microbes by cometabolization
Less chlorinated	Emerging	Aerobically biodegradable under a narrow range of conditions
Nitroaromatics		
Nitroaromatics	Emerging	Aerobically biodegradable; converted to innocuous volatile organic acids under anaerobic conditions
Metals		
Cr, Cu, Ni, Pb, Mg, Cd, Zn, U, etc.	Possible	Solubility and reactivity can be changed by a variety of microbal process

Potential limitations associated with biological treatment technology include:

- the technologies are compound specific and so are not “robust” as incineration;
- the production rates relative to competitive technologies are slow;
- sorting of the waste is required to preclude unacceptable items.

B.8. SOLIDIFICATION AND IMMOBILISATION

Wastes may be stabilised either by blending with a solidification/immobilisation agent and casting the mixture in a container (microencapsulation), or, for large objects such as discarded equipment, by placing the items into a container and pouring in a stabilising material (macroencapsulation). Both techniques result in an increase in the volume to be disposed. However, this is off-set by the reduction in void space and improved leaching characteristics. Solidification and immobilisation has been widely used for both liquid and solid wastes for a number of years using a range of commercially available simple technologies that generally operate at low temperatures (see Table B-IV). In some processes, the agent merely immobilises or encapsulates the hazardous waste. In other cases, however, liquid or sludge wastes may become an integrated part of the physical or chemical structure of the stabilising solid. Three types of stabilisation agent can be used.

Organic matrix materials: Examples of low temperature stabilization processes or materials of interest includes organic matrix materials such as bitumen and polymers. Bitumen, being as an organic material, has an advantage in its potential for retention of mobile organic compounds on in the waste; the material has been applied for stabilization of both organic and inorganic wastes. It is especially resistant to potential leaching (e.g., by groundwater). Polymer stabilization has been demonstrated for the solidification of salts. Polymers are used for blending with chopped or shredded wastes and casting into containers for disposal. Polymers also may be used for macro encapsulation of solids such as lead bricks or whole entire pieces of equipment.

Inorganic matrix materials: Inorganic matrix stabilisation materials include cements and grouts. The cements and grouts category also covers a very wide range of material formulations and approaches to waste stabilisation. Ordinary Portland cement is used in waste stabilisation by the blending and casting of small items and shredded (or chopped) solid wastes into drums or boxes producing a packaged monolithic form for disposal. Finely divided wastes, such as rubble, contaminated soil, ion exchange resin, etc., are mixed with Portland cement much as the sand and gravel used normally in making concrete. Special grout formulations have been developed to incorporate high salt content wastes that could not be retained with Portland cement alone. These formulations use other grout type materials including foundry slags and coal fired power plant fly ash.

Particulate materials: Liquid solutions may also be stabilised by sorption onto particulate materials and through reactive formation of stable insoluble chemical compounds. There are many variations of physical sorption used to produce stable, disposable waste forms. Acidic or basic solutions may react and affect effect the cement grouts adversely when combined directly with Portland cement. Alternatively, acids, bases, or aqueous/organic solutions may be adsorbed onto vermiculite or similar solids. These particulate type materials with the sorbed solution may be satisfactory for disposal or may be further stabilised by incorporation into grout or cement formulations. The sorption of the liquids onto the inert particulate materials may reduce the potential for the liquid to interfere with the solidification reactions of the grouts or cement. Specially modified clays can be added to organic liquids and sludge to form a solid waste. These final form solids are reported to have desirable physical properties and good leach resistant characteristics. Similar materials from the same manufacturers are used to stabilise aqueous solutions containing toxic metals and radionuclides. Many metals form very insoluble sulphuric compounds. Solutions and sludges that contain toxic metals e.g. lead, silver, cadmium, or and mercury can be treated with sulphide solutions to produce the corresponding metal sulphides.

TABLE B-IV. Some characteristics of selected solidification and immobilisation, technologies applicable to treatment of LILW

Treatment Technology	**Waste Streams**	**Temperature/ Pressure**
cement stabilisation	aqueous waste, sludges, solids	ambient/ambient
bitumen	aqueous waste, sludges	elevated/ambient
sulphur polymer cement	aqueous waste	ambient/ambient
chemically bonded phosphates	aqueous waste, sludges	ambient/ambient
polymer microencapsulation	aqueous waste/ sludges/partiuclates	variable/ambient
polymer macroencapsulation	dry active waste	variable/ambient

REFERENCES TO APPENDIX B

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[B-2] PERKINS, B. L., Incineration Facilities for Treatment of Radioactive Wastes: A Review, Los Alamos National Laboratory, USA, Report LA6252, February (1976).

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Appendix C

EXAMPLE TREATMENT TECHNOLOGIES FOR LILW CONTAINING CHEMICALLY TOXIC COMPONENTS

C.1. SEPARATION TECHNOLOGIES

C.1.2. Supercritical carbon dioxide extraction

Supercritical carbon dioxide extraction (SCDE) has been used successfully for the removal of hazardous organic compounds from low-level mixed waste streams [C-1].

For supercritical fluids in general, the relative high material densities yield high capacity for solutes, while supercritical fluids exhibit significantly larger molecular diffusivities than normal fluids, and the viscosities are nearly as low as those of gases. These characteristics allow supercritical fluids to permeate a matrix quickly and facilitate transfer out of a matrix. Since the compressibility of carbon dioxide allows broad changes in properties with relatively small operational changes, solvent recovery is accomplished with relatively small temperature and pressure reductions. In addition, experimental results indicate that the flow of carbon dioxide plays more of a role in the extraction of solvents than does pressure and temperature.

Bench-scale testing has demonstrated that SCDE is a viable technology and can extract volatile as well as semi-volative organic compounds, with varying polarities, from several types of solid materials (Table C-1). Motor oils and machine coolants that contain paraffin and long chain polymers tended to be more difficult to extract in SCDE than other organic compound; however, these oils were extracted with longer extraction times.

TABLE C-1. Typical results for volatile/semivolatile extractions with SCDE

	Sample Age	**Solvent Loading**	**Solvent Removed**
Carbon tetrachloride, Trichloroethane, Acetone Mixed Matrix	170 hours	Various	99,96%
Di/trichlorobenzene, Cotton/Paper	260 hours	270%	99,95%
Di/trichlorobenzene, Polyethylene	110 hours	380%	99,94%
Di/trichlorobenzene, Neoprene	310 hours	160%	99,81%
Water, Cotton/Paper	0 hours	390%	63%

The pilot-scale extraction system configuration is shown in Figure C-1. The system is designed to separate volatile and semivolatile organic compound leaving the extraction vessel, thereby allowing the carbon dioxide to be recycled. It is capable of extracting hazardous contaminants from 60 liters of waste within approximately 20 minutes.

The system is designed so that a second extraction vessel can be added, making the system a semi-continuous process. With two extraction vessels this system is capable of treating one cubic meter of waste per shift.

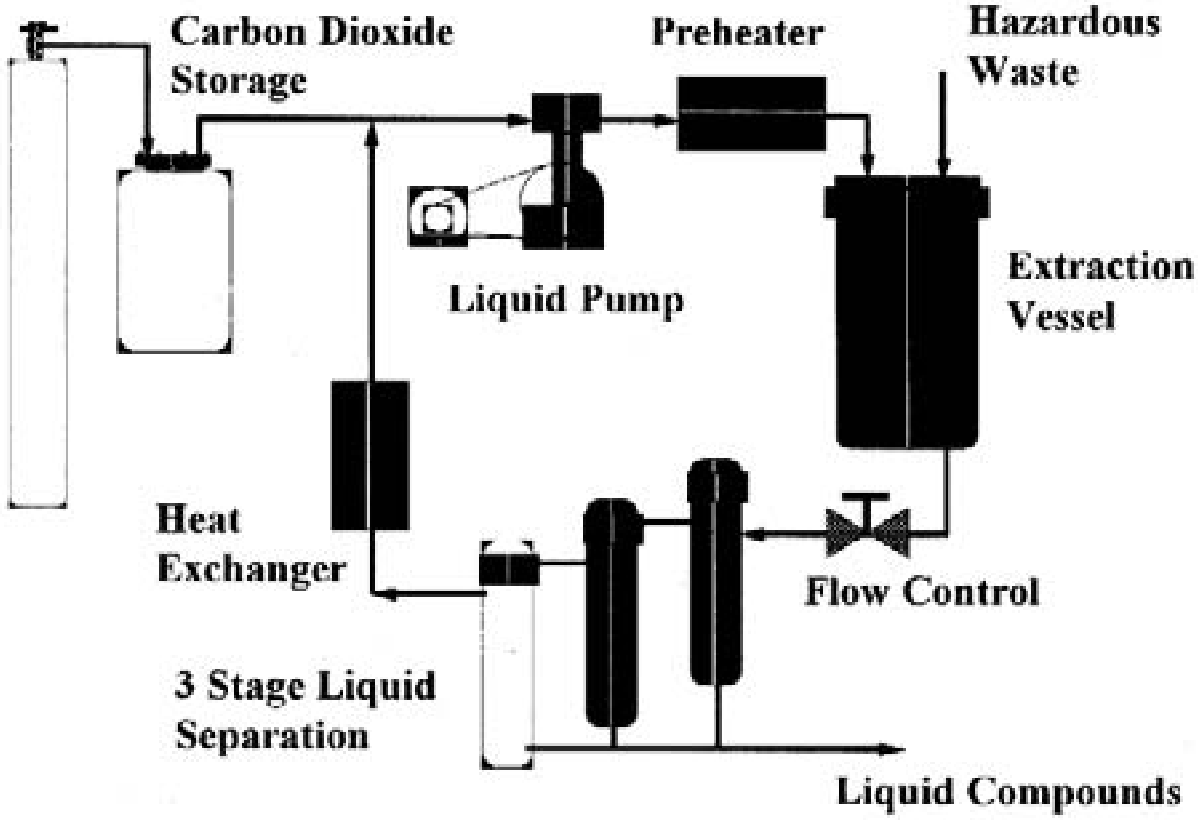

Fig. C-1. Pilot-scale supercritical carbon dioxide system configuration.

C.2. INCINERATION AND THERMAL TREATMENT TECHNOLOGIES

C.2.1. Fixed Hearth Incineration

One of the earliest incinerator designs was the simple fixed hearth, sometimes called the “controlled air incinerator. In its earliest configuration, the fixed hearth was a rectangular, refractory lined chamber combustion chamber with a refractory lined door, which is opened for manual waste charging. The door was closed and a burner was turned on to heat up the chamber to combustion temperatures. Commonly, the amount of air injected into the primary combustion chamber was less than that required for complete combustion; therefore the name controlled air incinerator. This controlled airflow provides the operator with control over the oxidation temperature and oxidation rate in the primary combustion chamber. The incompletely oxidised gases from the primary combustion chamber pass through a secondary chamber where excess air is added, the gas temperatures are raised, and combustion is completed. Figure C-2 shows a simple representation of such a system.

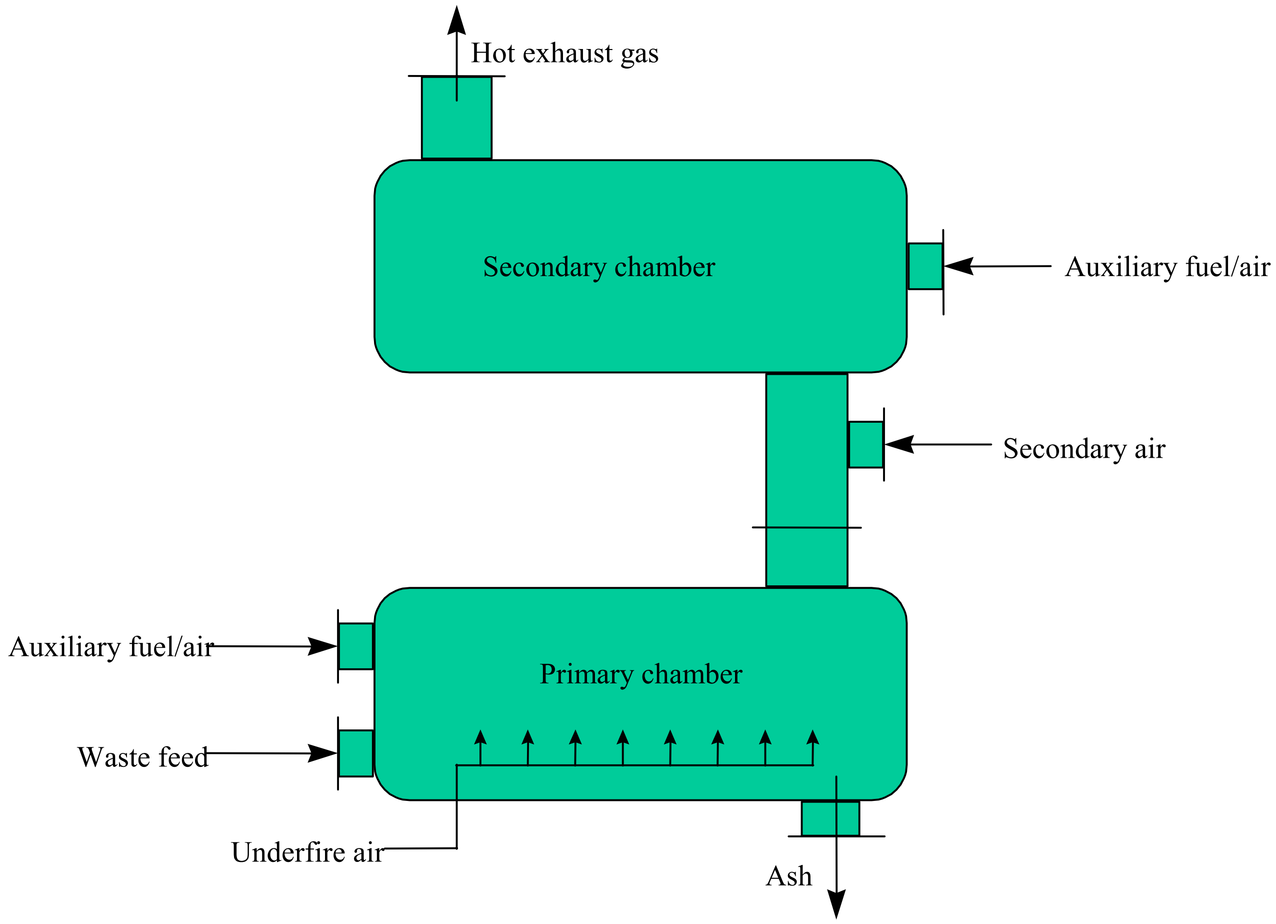

Fig. C-2. Fixed hearth incinerator.

As the wastes continue to burn in the primary chamber, there is a time when the volatile gas emissions require less oxygen than the air provides, and the chamber temperature reduces. In the simple batch processes the primary combustion chamber burner would be started to maintain the system temperature. Thereby, the gaseous "volatiles" and most of the fixed carbon in the waste were oxidized leaving only ash in the primary chamber floor, or hearth. In most systems, the incinerator was allowed to cool and the ash manually removed.

Configurations of the fixed hearth for radioactive waste facilitate continuous operation wherein packaged waste is fed to the primary combustion chamber in a "semi-batch" basis. In this operation, the primary chamber is maintained at a relatively low combustion temperature (500–700°C) throughout the feeding operation by injecting more waste when the chamber temperature gets too high. Because of these substoichiometric conditions, adding more waste cools the chamber and reduces the temperature. A supplemental fuel burner controls the secondary chamber temperature. Typically, the secondary combustion chamber temperatures (1000–1200°C) are controlled to give nearly complete destruction of organics. Note that the minimum airflow use in the radioactive application minimises turbulence in the primary chamber and thereby minimises radioactive particulate entrainment. This simplifies the design of the subsequent secondary combustion chamber and off-gas cleanup systems. In this continuous operation, the fixed carbon material remaining in the primary chamber must be periodically burnt off by ceasing feed and allowing the chamber to slowly advance from oxygen deficient to oxygen rich. In this fashion the fixed carbon content of the ash is reduced, although not to the same level that is commonly achieved by systems with agitation and mixing of the solids in the primary chamber.

In one fixed hearth application processing “mixed” waste, the waste is packaged and fed to the primary combustion chamber through using a ram feeder. The solids residence time in the incinerator is approximately 16 hours allowing for complete oxidation of all organics and fixed carbon in the waste.

Fixed hearth incinerator advantages include:
- Accepts packaged waste and provides well oxidised off-gases;
- Inexpensive simple design commonly shop fabricated; and
- Low particulate emissions.

Fixed hearth incinerator limitations include:
- Batch operation requires periodic cooling for manual ash removal;
- Low throughput leads to high unit treatment cost, and
- Ash quality typically not as good as other incineration technologies.

C.2.2. Rotary kiln incinerators

Rotary kilns have been used in the processing industries for gas/solid contacting since the early 1900s. Currently, they are used extensively in the manufacture of cement, a basic industry in both developed and undeveloped countries. The knowledge base for the design and operation of rotary kilns for incineration was developed in the late 1950’s. Since that first rotary kiln incinerator, the rotary kiln has become the workhorse of the hazardous waste and contaminated soil treatment markets. For example, in the thermal remediation of soils, the rotary kiln design has processed more wastes than all other technologies combined.

As in the case of fixed hearth systems, the rotary kiln incineration system is commonly a two-stage operation, the first stage being the rotating kiln barrel, and a secondary combustion chamber for completion of the oxidation. Figure C-3 provides a schematic of a system. The rotating kiln barrel is a refractory-lined cylinder installed at a slight slope to cause the solid material to tumble over itself and travel down the length of the barrel. Rotary kilns can be configured to accept liquid, solid, and sludge wastes. This feature is one of the reasons that rotary kilns have found such wide application in the commercial incineration field.

As in the fixed hearth system, combustion gases and volatilised organics from the kiln are then treated in a downstream secondary combustion chamber for complete oxidation. The kiln is typically operated at relatively high temperatures, 700 to 1300°C. Tumbling action in the kiln continually exposes fresh waste surface to the high temperature radiant heat from the burner and refractory walls and to the oxygen in the combustion air. Ash and non-combustibles are continuously discharged into an ash handling system. Seals are provided at both ends of the rotating kiln shell to minimise air inleakage. In radioactive waste applications particular attention must be given to design and maintenance of these seals to minimise the potential for fugitive emissions or radioactive particle release.

There are several types and configurations of rotary kiln incinerators, each providing specific operating advantages and disadvantages. In radioactive waste applications, the waste and air typically travel through the kiln in the same direction. However, other applications utilise counter-current flow. Radioactive waste applications operate at temperatures below the melting point of the ash, but other applications use a “slagging mode”.

Rotary kiln incinerators can be designed to operate either in a controlled air or excess air mode. The advantages and applications of these modes of operation were previously discussed for the fixed hearth incinerator and apply equally to rotary kilns.

In some large commercial incineration systems, 200 liter drums filled with waste can be fed into the rotary kiln. Design for injection of whole drums rotary kiln is a challenge mechanically and operationally. The operational challenge is maintaining good destruction conditions with the instantaneous input of energy from the volatilisation and subsequent combustion of the wastes. Additionally, the drums could damage the refractory as they fall into the kiln. The US Department of Energy operates rotary kiln “mixed” waste incinerators at the Oak Ridge and Savannah River sites.

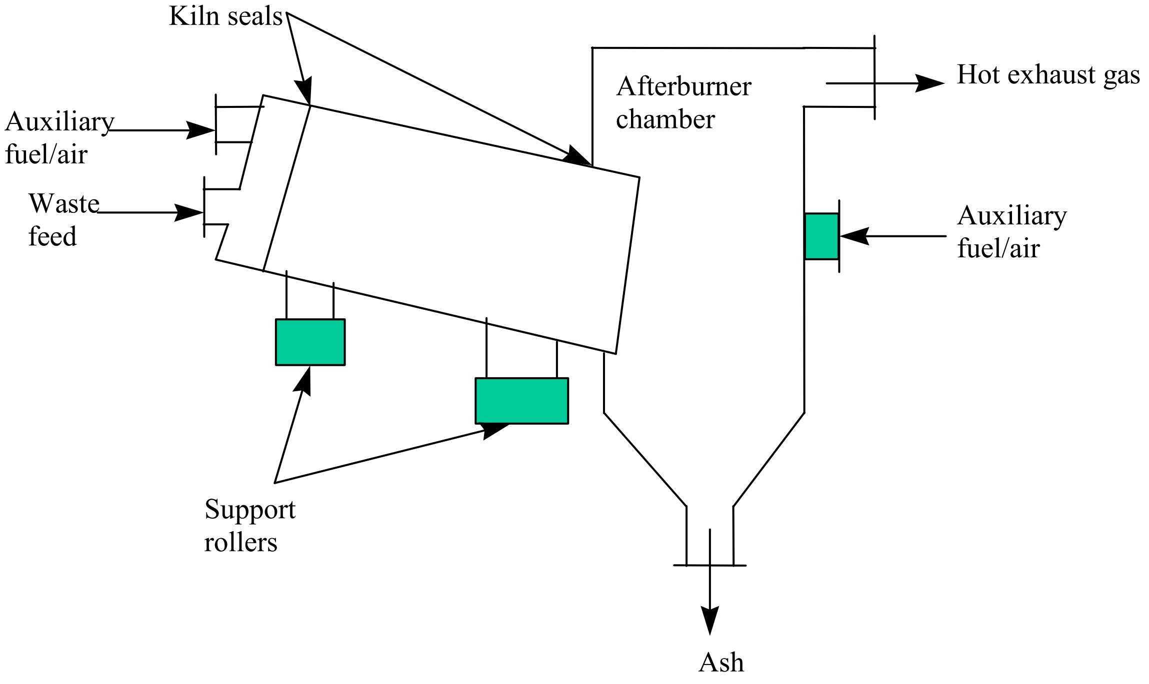

Fig. C-3. Rotary kiln incinerator.

Rotary kiln incinerator advantages include:

- Accepts all waste forms (solid, liquids, sludges);
- Large continuous systems are economical, and
- Well developed technology with established designs.

Rotary kiln incinerator limitations include:

- Radioactive waste applications require special designs for the kiln seals;
- Kilns are typically large volume systems, atypical for radioactive waste applications; and
- Not amenable to routine cycling.

C.2.3. Catalytic combustion

Catalytic combustion is a technology option that is being developed to address some waste destruction issues. In catalytic combustion of waste the fuel is totally oxidized on the surface of solid catalysts at low temperature without flame [C-2, C-3]. A facility (Figure C-4) was designed to treat liquid organic waste from nuclear materials processing plants in the Siberian Region of Russia.

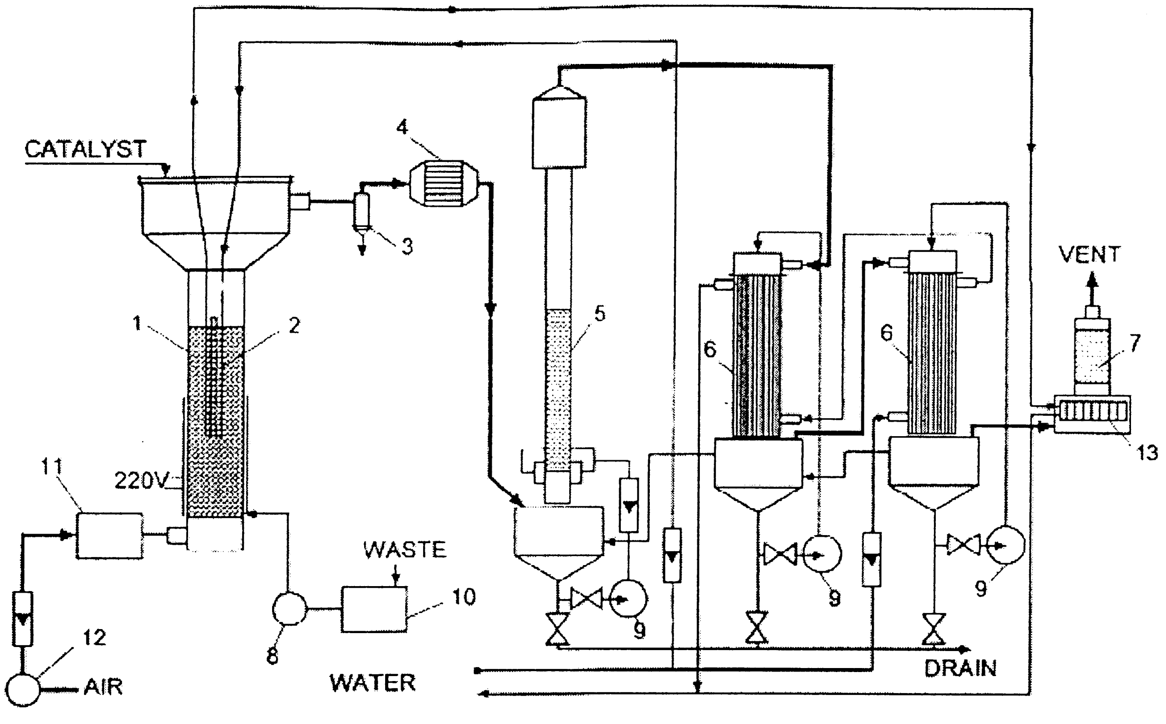

Fig. C-4. Schematic diagram of organic waste catalytic combustion and off-gas treatment: 1-fluidized bed reactor, 2-heat exchanger, 3-cyclone, 4-CO catalytic converter, 5-jet scrubber, 6-absorber-condensers, 7-aerosol filter, 8-waste pump, 9-water pumps, 10-tank with wastes, 11-electric reactor, 12-compressor, 13-heat exchanger.

The fluidized bed of catalyst material is preheated to 500–600°C with a combination of electrically preheated air and in-bed combustion of kerosene. After the bed temperature reaches 500–600°C, waste feed is initiated. A waste is fed from the tank to the reactor with a fluidized catalyst bed. The compressed air is supplied to the reactor by compressor at a flow rate which is sufficient to provide catalyst fluidisation and total waste combustion at the temperatures in the range of 700–780°C.

The flue gas from the catalytic reactor contains combustion products CO_2, H_2O, small quantities of CO (40–300 ppm), NO_x (5–20 ppm), SO_2 (0–25 ppm), P_2O_5, HCl (when phosphorous and chlorine containing compounds are burned), and particulates. From the reactor, the gas enters the cyclone where large particles (>30 µ) are separated and the temperature is further decreased to 200–300°C.

For the removal of CO admixture from flue gas, a catalytic converter for CO oxidation to CO_2 is installed after the cyclone. The converter contains platinum catalyst on monolithic honeycomb aluminosilica support. At the next stage, the gas passes through a foam jet scrubber, which acts both as a gas and dust trap and as a regenerative heat exchanger. In this apparatus, the strong jets form highly turbulent foam layers with a constantly refreshed surface, providing quantitative separation of medium-sized particles (>3 μ) from the gas stream, the capture of acid gases (SO_2, HCl, P_2O_5) and the gas cooling to 70–90°C.

The same category of technologies for treatment of toxic and hazardous waste includes specific methods/processes allowing the treatment of radioactive and hazardous wastes that exhibit the reactive characteristics (lithium hydride, sodium and potassium metal), and chemical plating wastes containing cyanides, ammonia, Cr(VI) and heavy metals, as well as the grout technology for reliable encapsulation of mixed waste.

C.2.4. Supercritical water oxidation (SCWO)

Another thermal treatment alternative that is in development relies on waste oxidation using supercritical water oxidation (also known as hydrothermal oxidation). The rationale behind using supercritical water ($P = 22.1$ MPa, $T = 374^{o}C$) as a reaction medium for the destruction of organic compounds is based on the very specific properties of supercritical water, with very significant effects on the relative contributions of various intermolecular reactions. The reduced contribution of the hydrogen bond, in particular, results in miscibility at any proportion with organic compounds and oxygen. The advantages of continuous SCWO processes include:

- very short reaction times (less than a minute);
- complete reactions, ensuring that the process waste streams contain no intermediate organic compounds;
- reaction containment, allowing control of process waste, and notably a cold gas stream directly compatible with the environment.

Limitations of the process are:

- it is limited to liquids and sludges that can be pumped to high pressures;
- the low solubility of inorganic elements and salts requires careful design to avoid system plugging.

Organic solutions contaminated by radionuclides are particularly well suited to this technology. Specifically, supercritical water at $500^{o}C$ and 30 MPa provides an excellent reaction medium allowing complete oxidation of dodecane and TBP. Under optimum conditions, destruction of the organic mixtures was better than 99.98 % with a residence time of less than 30 seconds [C-4]. The off-gas contained only N_2, O_2, and CO_2, while the liquid waste stream was pure water (with orthophosphoric acid when TBP was oxidised).

C.2.5. Steam Reforming

[C-1] notes that for several decades, steam-reforming technology has been applied commercially and world wide for the production of synthesis gas from coal. More recently the technology has been modified for application to waste management. Steam reforming is the reaction of steam with organic materials at elevated temperature (300°C to 1200°C) to yield synthesis gas comprised of CO, CO_2, H_2, H_2O, CH_4, and other light organic gases.

Steam reforming is usually accomplished in multiple stages. In the first stage waste is destroyed pyrolyticaly and/or has volatile constituents removed. Exposure to steam or a mixture of steam and recycled synthesis gas at temperatures between about 300°C and 800°C produces synthesis gas from any organic material present. Volatile organic species generated in the first stage are further reacted in the second stage with steam at temperatures up to 1200°C to produce additional synthesis gas. The final residues from pyrolysis of organic material include coke or char together with non-volatile inorganic ash materials. A drum reaction chamber is used for packaged or contained wastes. A full of drum of waste may be introduced into the processor with the drum serving as the reaction vessel. Aqueous and organic liquids and slurries are processed in fluidized beds or moving beds (re-circulated inorganic or inert spheres). Shredded debris or rubble waste and contaminated soils are treated in shredders and/or screw conveyors.

For waste treatment application, acid gasses (mainly HCl) are scrubbed or adsorbed from the synthesis gas; the cleaned gas is then burned to produce CO_2 and H_2O for release to the environment.

The process is energy intensive. Most wastes do not contain sufficient organic material to provide the heat required to sustain the process.

Steam reforming advantages include:

- complete destruction of fragments or products of incomplete combustion/pyrolysis and removal of chlorine prior to release of the treated gas;
- a relatively omnivorous process, although each waste stream may require a unique primary evaporation system;
- minimisation of dioxin and furan formation.

Steam reforming limitations include:

- the process requires handling large volumes of hydrogen and other fuel gasses (internal re-circulating) at high temperature;
- the second/third stage unit used for the thermal destruction of volatile organic and products of incomplete combustion/pyrolysis makes this treatment the essentially equivalent to two-stage incineration;
- the process generally requires a different reactor for each waste matrix to be treated.
- high-temperature electrically heated reforming reactors have exhibited severe corrosion during processing of halogenated hydrocarbons.

C.3. NON-THERMAL DESTRUCTION TECHNOLOGIES

C.3.1. Wet air oxidation

Wet air oxidation (WAO) is a commercially available process that has potential for treating organic contaminated aqueous wastes which are too dilute to incinerate and too toxic to biologically treat [C-5]. Commercial system designs are based on extensive bench- and pilot-scale experiments; these however usually are directed to a specific waste or relatively narrow range of waste types. WAO's usual role has been as a pre-treatment process to reduce waste strength and toxicity and render it suitable for final treatment and disposal by other means.

Waste materials in dilute aqueous solution or suspension are contacted with dissolved oxygen at elevated temperatures (150°C to 325°C) and pressures (2000 kPa to 21000 kPa) but below the critical point of water. Organic materials are partially carbonised. Dissolved oxygen reacts catalytically at the carbon sites to produce hydrogen peroxide that then decomposes to generate highly reactive oxygen and hydroxyl free radicals. These hydroxyl radicals react with the carbon to form carbon dioxide.

Most organic compounds are completely oxidised, the carbon going to carbon dioxide, the hydrogen to water, any halogens to halides, sulphur to sulphate, phosphorous to phosphate, and organic nitrogen to ammonia or nitrogen gas. Single-pass conversion of waste compounds is often limited by the solubility of oxygen in water at these high temperature process conditions. Incomplete or partial oxidation may result in production of low-molecular weight compounds such as acetaldehyde, acetone, acetic acid, methanol, etc. These compounds are sufficiently volatile that they will distribute into the off-gas. The liquid effluent also will contain only partially oxidised compounds such as carboxylic acids, carbonyl compounds, suspended solids.

Soluble metal salts and acids also will remain with the liquid effluent. Acids formed by the oxidation of halogen, sulphur, and phosphorous containing compounds are very aggressive at the required process conditions. Commercial WAO units for hazardous waste treatment are necessarily constructed with titanium clad or other alloy steel.

Most organic compounds are destroyed with a destruction efficiency greater than 99% in 15 to 60 minutes at temperatures in the range from 200°C to 280°C. Some compounds, which are difficult to carbonise, such as acetic acid, may require longer residence times and higher temperatures to be substantially degraded. Halogenated aromatic compounds (PCBs, chlorobenzenes, etc.) are very refractory and degrade slowly (70% destruction in 60 minutes) unless at least one electron-donating functional group (hydroxyl, amino, methyl, etc.) is present on the ring.

Use of WAO technology for other than pre-treatment purposes implies extensive effluent storage, analysis, and recycle.

WAO advantages include:

- Organic waste compounds are oxidised and mineralised without formation of NO_X, SO_X, products of incomplete combustion, or particulate in the off-gas;
- Recombination products, such as dioxins or furans are generally avoided.

Issues associated with WAO include:

- WAO cannot predictably and reliably destroy a wide range of contaminants. Destruction efficiencies for most waste constituents are below 99.9% and are very dependent on waste composition (physical and chemical) and waste strength.
- WAO processing requires substantial sampling, analyses, and characterisation of both feed and product materials to assure satisfactory destruction of waste materials.

- Without substantial pre- and post-treatment, WAO is limited to processing a relatively narrow range of wastes, and designs are based on extensive laboratory and pilot plant tests.
- WAO requires processing in relatively large, high-alloy, pressure vessels to achieve even modest throughput.

C.3.2. Electrochemical oxidation, cerium mediated electrochemical oxidation (MEO)

In the MEO process an electrochemical cell is used to generate an oxidant species in acidic solution at the anode [C-1]. Balancing electrochemical reactions at the cathode must either decompose water or another species in solution. MEO is typically operated in nitric acid solution; in that case, the species decomposed at the cathode is nitric acid. Process economics usually require that the decomposed nitric acid be recovered and reused.

The oxidant solution is pumped from the electrochemical cell into the primary reactor. After reaction, electrolyte is recycled from the reactors back to the electrochemical cell for regeneration of the oxidant. The waste feed rate is based on the destruction time required for the organic in the feed stream.

MEO has been tested with a number of different electrochemical oxidants including Ag(II), Co(III), Ce(IV), and Fe(III). Aqueous media tested included nitric and sulfuric acids.

The MEO system operates at 50°C to 60°C and atmospheric pressure. The electrolytic cell consists of a parallel set of chambers with Nafion membranes between the anode and the cathode chambers. Each cell contains approximately 60 pairs of electrodes. An electrolyte solution of nitric acid and ceric nitrate is circulated through a set of cells in the MEO unit. The ceric ion in solution is oxidised from the +III to +IV oxidation state. This oxidised metal ion acts as the primary active oxidiser in solution. The metal ion reacts either directly with the organic species, or with water to produce a reactive intermediate such as the hydroxyl radical (OH·) that then reacts with the organic material. Eventually the organics are broken down into carbon dioxide and water. Reaction may occur any place in the circulating loop from the electrolytic cell to the primary reactor.

The extent of reaction depends on the time allowed for reaction with the active agents. The process is expected to achieve destruction up to 99.99% of most organic compounds.

Some of the water formed by oxidation of the organic compounds migrates through the membrane to the cathode side eventually reducing the nitric acid concentration below 6 molar (M). Water must be removed continually from the catholyte to maintain the nitric acid concentration at 6M to avoid formation of hydrogen. Ce(III) and Ce(IV) ions do not migrate through the membrane. A slip stream of the catholyte is removed and processed for acid recycling. A much smaller slip stream from the anolyte is combined with the catholyte stream for the removal of salts to prevent build up of in the anolyte. The combined electrolyte "blowdown" stream consists of water, nitric acid, ceric nitrate, metals ions, unreacted organic waste materials, and miscellaneous inorganic ions, such as sulphate, chloride, and phosphate, which result from oxidation of the waste material.

MEO advantages include:

- Cerium based MEO has been shown to destroy a wide array of chemical compounds and some solid materials that suspended in aqueous streams;

- Cerium is not a hazardous metal;
- There should be no electrolytic production of hydrogen (a process hazard) from the cathode if nitric acid concentration maintained above 6M;
- Chloride from destruction of chlorocarbon compounds does not precipitate cerium. (Chloride ion will precipitate silver from solution).

Issues associated with MEO include:

- The process is practical only for liquid, finely divided, or emulsifiable organic materials. The oxidant is short lived and cannot be stored.
- It is necessary to recovery and recycle cerium metal for economic and waste minimisation reasons.
- Re-oxidation of oxides of nitrogen in the off-gas is required for pollution control and for economics of the process.
- The system is somewhat complex because of the requirement for acid recovery and cerium metal recycle.
- The process does not dissolve hard plastics, as shown for poly vinyl chloride (PVC).
- Successful operation depends on the integrity of the membrane. Acid appears to move through the membrane which may be degraded by corrosion and radiation effects.
- The process needs to be carefully controlled. Excess waste feed (concentration too high for set conditions of feed to bleed) will lead to too high organic concentration in the bleed stream for treatment and discard.
- Depleted acid <2M will lead to destruction of water to release H_2 along with NOx in the cathode off-gas creating a potentially explosive mixture.

C.3.4. Aqueous phase ultraviolet photolysis and photo-oxidation

Photolysis and photo-oxidation are related processes that use light to cause the destruction of hazardous organic materials [C-5]. In photolysis light energy is adsorbed directly by the organic molecules leading to energising the molecule causing breakage of bonds and thereby destruction of the material. In general, the breaking of a hazardous organic compound in to fragments will lead to simpler and less hazardous reaction by-products. For destruction to occur, a light source must emit at a wavelength in the UV region that can be absorbed by the contaminant such that the molecular bonds are broken. In the direct photolysis process, organic by-products may not absorb UV light and continue the decomposition process into non-hazardous molecules. Because of the difficulty in matching the wavelength of the light source with the absorption band of all the contaminants, the organic compounds are typically destroyed through an indirect photochemical process.

Photo-oxidation defines a set of indirect photochemical processes that use light to generate strong oxidising agents in solution. Typically the UV energy is used to photolyze either hydrogen peroxide or ozone to generate hydroxyl radicals ($OH\cdot$). These strong oxidants react with the organic materials in a series of steps leading eventually to destruction of the hazardous materials to produce carbon dioxide, water, and some reaction by-products.

Application of these two technologies is generally limited to aqueous solutions that contain only small amounts of organic contaminants. The primary application is to reduce or eliminate organic contaminants so that the water can be discharged or recycled. Destroying the organic directly in the aqueous solution rather than separating it out avoids the effort of separating and then destruction of the organic in an additional process. After the organic contaminant is destroyed, precipitation and filtration, or ion exchange may remove any inorganic or radioactive contaminants present.

Several processes that use direct UV radiation have been developed; the differences are wavelength of light sources, different oxidants, and methods to enhance the production of hydroxyl radicals. Light sources that have been studied include medium and low-pressure mercury lamps, xenon lamps, and lasers with wave lengths that match the chemical bonds targeted in the hazardous organic compound. Due to the high cost of laser systems and xenon lamps and the difficulty in matching the required wave lengths for primary and secondary compounds in the destruction paths, investigators of direct photo chemical technologies have usually reverted back to indirect photo-oxidation processes. Oxidants used include; peroxide, ozone, and Fenton's reagent (oxidation by iron +3 which after reduction to +2 is continually re-oxidized to +3 for additional reactions). In addition, catalysts and additional energy sources, such as hydrodynamic cavitation, are used to enhance the production of $OH\cdot$ and the destruction of organic bonds.

UV photolysis advantages include:

- These systems work in aqueous solution at ambient conditions and mild solutions. The process conditions are moderate and not especially corrosive.
- Processes are easily controlled.
- For the targeted wastewater streams (containing a few percent organic), technology should easily satisfy most regulatory requirements.
- Systems are modest sized, usually skid-mounted and portable, permitting on-site treatment.
- Only innocuous chemicals are added, none of which is solid-waste forming and no secondary waste is generated.
- They are "clean" technologies with minimum air emissions. However, an off-gas system will be required to ensure volatile organic materials are not released with the CO_2.
- The H_2O_2/UV process can be modified by the addition of chemical agents that enhance the decomposition of the more refractory organics.
- For streams with limited number of organic contaminants there is always the potential to use UV lamps that emit in the short UV and produce direct photolytic destruction of the contaminants.

UV photolysis limitations include:

- These oxidation technologies cannot be used as generic destruction techniques. The process is only applicable to relatively dilute solutions of organic materials in water. The resulting solution needs to be nearly transparent to permit the activating light to penetrate the system.
- Insoluble organics and suspended solids must be removed for efficient operation.
- Slightly soluble or highly volatile organic materials may be swept out of the solution rather than destroyed. While this leaves the solution cleaned of the organic the volatilization transfers the organic destruction problem to the gas stream.
- The choice of a particular system, and the optimum oxidant concentration, flow rate, and wavelength, will depend on the specific contaminant, or range of contaminants, and the characteristics of the water to be treated. Therefore, the design and operation of any system is waste composition specific.

- When the processes involve ozone, solubility of gaseous ozone in the aqueous phase becomes the limiting factor. Although H_2O_2 can eliminate this mass transfer problem, the decomposition of H_2O_2 by UV light generated by inexpensive mercury lamps is relatively inefficient.
- Hydroxyl scavengers, such as carbonates and bicarbonates, must be removed from the waste stream for efficient application of this technology. Contaminants that oxidise in the UV process and form insoluble species that may deposit on the lamp window may also require detection and removal from the waste stream.
- The peroxide/ozone process is of limited utility for oxidation of organohalides that have relatively low rate constants with OH· such as chloroalkanes.
- The optimum proportion of oxidants for maximum destruction or removal efficiency cannot be predetermined, but must be determined by tests on a case-by-case basis. Hydrogen peroxide, used as the source of the hydroxyl radicals, also is a free radical scavenger, and may compete with the organic contaminants for the hydroxyl radicals. Ozone can react directly with hydroxyl radicals consuming both ozone and radicals.

C.4. WATER REACTIVE WASTE TREATMENT SYSTEM

Some LILW may react readily and violently with water, and because of that they must be treated to remove such hazardous components as lithium hydride, sodium metal and potassium metal before they are disposed.

The treatment process involves directly immersing the water-reactive waste in a volume of water. Reaction rate is controlled by the rate of addition of the waste to the reactor. In this system, a nominal amount of nitrogen is introduced as purge gas, but there is no attempt to maintain the hydrogen content below 4%. The possibility of explosion is avoided by excluding oxygen. All off-gas is scrubbed, filtered, and discharged. During processing, the liquid volume charged gradually accumulates alkaline hydroxide strength. After pH adjustment, the waste water is sent to a wastewater processing plant.

The advantages of this approach are the following:

- Either powdered or large solid pieces of water-reactive waste can be fed, with acceptable reaction rates. Simple solids introduction methods can be used.

- Extraneous materials can be processed with the water-reactive waste. For instance, if lithium hydride is bonded to another non-water-reactive substance, the whole mass can be introduced to the reaction system to reliably remove the water-reactive waste from the non-reactive substrate.

- The volume of water in the reaction system provides an effective heat sink for the exothermic reaction. The reaction system is sized to limit the temperature rise to 20 ^{o}C if the cooling system fails.

- Accumulations of solid alkaline hydroxide layers that could stop the reaction are minimised because the excess water dissolves the accumulations. This factor also eliminates the need for separate dissolution and rinse procedures.

- The amount of water-reactive waste treated per run is limited only by the liquid volume in the reaction system and the solubility of the alkaline hydroxide or neutralized hydroxide, and not by the volume of the reactor itself.

Figure C-5 shows a simplified flow diagram of the process. The treatment skid consists of individual modules. Each module weighs a maximum of 2 tons and has maximum dimensions of 1.5 m wide × 3.0 m long × 3.5 m high. The structural system is designed so that it can be easily cleaned for removal to storage. This requirement necessitates welded stainless steel construction that greatly minimises cracks, crevices, and corrosion products such as rust. All reasonable effort has been given to meeting this goal with standard industrial equipment. When stainless construction is not possible, epoxy painting for nonstainless metal parts is specified.

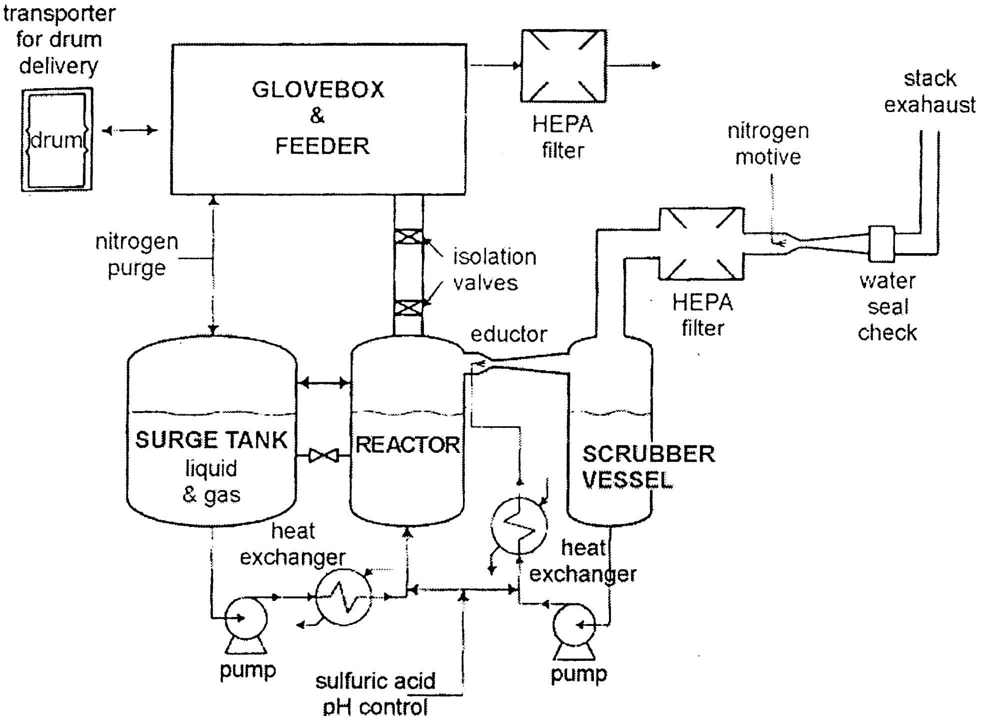

Fig. C-5. Simplified process flow diagram for the water reactive waste treatment system.

Explosion-proof design uses a combination of explosion-proof enclosures, purging, and intrinsic safety barriers. The instrument and control portion of the skid design allows local and remote control of all critical portions of the process.

The reaction produces hydrogen gas and an alkaline metal hydroxide solution that is continuously neutralised with sulphuric acid. Reactor vent off-gases are scrubbed with water in a venturi-eductor scrubber before passing through a HEPA filter to the stack. Cooling water is applied to the reactor and scrubber cooling exchangers using an intermediate heat-transfer loop. An intermediate cooling loop prevents environmental contamination by ensuring that the main cooling system is isolated. The nitrogen-hydrogen mixture is monitored for tritium and volatile radionuclides and vented to atmosphere. All waste water is collected and processed.

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Appendix D

SAFETY ASSESSMENT CASE STUDIES FOR GERMANY, BELGIUM, FRANCE AND SWEDEN

This appendix provides a summary of some example safety assessments that have been undertaken to assess the impact of the disposal of the chemically toxic component of LILW in a number of different disposal systems. Assessments are presented for a deep geological disposal facility in Germany (Section D.1), an above grade facility in Belgium (Section D.2), an above grade facility in France (Section D.3), and below grade, cavern in Sweden (Section D.4). More detailed descriptions of these assessments are provided in references [D-1 to D-5]. Examples of other country specific assessments that have assessed the chemically toxic component of LILW are given in references [D-6, D-7], whilst references [D-8, D-9] present generic assessments.

D.1. DEEP GEOLOGICAL FACILITY: CASE STUDY FOR GERMANY

The chemical toxicity of radioactive waste with negligible heat generation has been evaluated for the Konrad repository as a part of the overall long term safety assessment [D-1, D-2]. This waste contains mainly non-radioactive materials (99.98–99.99 % on a weight basis). About 98% of the waste on a weight basis is inorganic and about 2 % is organic material.

Konrad is a planned geological disposal facility (up to 1300 m deep) located in Salzgitter, Germany. The long term safety assessment was based on the scenario that radioactive waste and its chemotoxic inventory are assumed to come into contact with water originating from the surrounding rock ('formation water') in the post-operational phase and that toxic constituents could be transported by groundwater into the biosphere. The safety assessment was carried out for organic and inorganic components.

The results of calculation showed that for the Konrad repository a water transfer time from the repository to the biosphere would be about 300 000 years. It was therefore estimated that the chemotoxic organic compounds in the Konrad repository be hydrolysed before they could reach the biosphere. This applies even to the environmentally 'persistent' chlorinated organic compounds such as 2,3,7,8-TCDD.

Under the site-specific conditions of the Konrad repository (60^{o} C, pH ~ 7 assumed), it was estimated that most of the chemotoxic substances would be decomposed before the period of 10 000 years, so that for the majority of the compounds it was estimated that no restrictions in waste acceptance requirements would be needed. Within a time span of 20 000 years, essentially all organic toxic substances would be decomposed perhaps with the exception of a few substances such as 2,3,7,8-TCDD which might need to be restricted in their amounts.

With respect to the inorganic components, it was shown that the chemotoxicity of the radioactive waste stayed below the radiotoxicity up to a time span of approximately 100 000 years. Furthermore, the concentration of the chemotoxic elements in the 'diluted repository water', should it reach the biosphere, approached the concentration limits specified in the drinking water standards only in the case of a few elements.

The overall conclusion was that, in case of this repository, the chemotoxicity of the radioactive waste posed an acceptable risk to the public and that no new unknown hazard potential would arise from the chemotoxic substances being present in the LILW.

D.2. SURFACE REPOSITORY: CASE STUDY FOR BELGIUM

In Belgium two options for disposal of low-level radioactive waste disposal are studied, i.e. a surface repository and an underground repository. The ongoing safety assessment studies for both disposal options are dealing with several aspects such as effects of gas generation on repository safety and consequence analysis for radiological and non-radiological substances present in the waste. The safety analysis for inorganic non-radiological substances in case of surface disposal is briefly discussed below.

The safety analysis for inorganic non-radiological elements considered a state of the art surface disposal facility in combination with a generic setting [D-3]. The surface disposal refers to engineered concrete structures at ground level covered by a multi-layer barrier system [D-4]. In the study, the only exposure pathway considered was by pollution of groundwater owing to leaching of contaminants from the surface disposal. The analysis of the groundwater pathway was considered generic because average, literature-based properties were used to describe sorption onto sediment particles, together with flow parameters that were representative for hydrogeological conditions in Northern Belgium.

The degree of pollution of the groundwater by leaching of contaminants from the surface disposal was assessed in a two-step approach. First, a conservative screening calculation was performed to assess the 41 inorganic non-radiological elements present in the waste. Elements were screened on the basis of five criteria to decide whether they further required detailed assessment. The first three criteria were quantitative whereas the final two were qualitative: (i) comparison between estimated concentrations in groundwater and current groundwater standards, (ii) comparison between chemical and radiological toxicity, (iii) comparison between elemental solubility and current groundwater standards, (iv) abundance in the geosphere, and (v) miscellaneous criteria. In a more detailed analysis, the groundwater concentrations of the remaining elements were calculated by applying a numerical flow and transport model to the disposal facility and the underlying aquifer.

On the basis of the five independent screening criteria considered, 30 elements were removed from the list of potentially toxic elements. The final list of elements to be considered in the detailed calculation was as follows: B, Be, Cr, Cd, Cl, Hg, I, Nb, Pb, and Sb, and Zn. For each of these elements maximum groundwater concentrations were numerically calculated and compared with the standards and background concentrations. The effects of organic degradation products present in the waste (in particular high molecular weight organics originating from organic polymers such as polyethylene, polyurethane, etc.) on the chemical mobility was also accounted for, notably by considering an experimentally determined sorption reduction factor in a sensitivity analysis.

The results showed that the numerically calculated maximum groundwater concentrations at distances ranging from 100 to 1000 m downstream of the repository were below the current drinking water standards for the majority of the eleven elements. Only for B, Cd, Sb, and Zn did the maximum concentration slightly exceed the standard, considering several conservative assumptions. It is noted that maximum background concentrations obtained from a literature survey for these four elements were often higher than the standards. For instance, background concentrations for Zn measured in seventeen wells throughout Northern Belgium were nearly as high or even higher than the standard.

D.3. SURFACE REPOSITORY: CASE STUDY FOR FRANCE

The first surface disposal facility for LILW in France is the Centre de la Manche whose operation was terminated in late June 1994 with about 500 000 m^3 packages disposed. Operating feedback from the Centre de la Manche was used to design the second French disposal facility, located in the Aube, which has been receiving LILW since 1992.

A chemical impact assessment was performed within the framework of the definitive safety report of the Centre de l'Aube, in 1996. This was the first time such an assessment had been performed for a nuclear disposal facility in France. The assessment considered essentially the long term impact, occurring after the closure of the disposal. The methodology applied was similar to the methodology used for radioactive impact assessment. It consisted of the determination of the transfers of the elements from the waste package to the environment and the human exposure levels and associated risks under various scenarios. The objective was to use indicators of unit risk and minimum risk levels, according to the administrative route and the nature of the effect (stochastic and/or threshold effects). The level of these indicators were the values defined in international databases such as ATSDR, US-EPA, and WHO.

The estimated inventory was established on an *a posteriori* research basis. The choice of the chemically toxic elements to be assessed was made by considering the intrinsic toxicity and the estimated quantities at the closure of the disposal.

The safety scenarios used to define the context of the safety assessment with regard to the chemically toxic substances were the same scenarios used to assess the radiological impact. An air transfer scenario, as well as a water transfer scenario were been investigated. Only water transfer scenario related conclusions are reported below.

The classification of the toxic elements from a first screening based on the quantity and the ingestion toxicity was: Pb > Cr(VI)> B > Cd > Sb > Ni > Be. Most of the lead present in the waste comes from screens used for worker shielding. It is in metallic form.

In light of the transfer data available, detailed calculations of the concentrations of elements within the downstream river and the different compartments of the biosphere have been undertaken for lead and nickel. The result are expressed in terms of concentration within the water and soils and in terms of quantities ingested and/or inhaled by humans. Studies are on-going to obtain the data for the calculation of the transfers from the repository to the biosphere of the other elements.

Results for lead for the water- transfer scenario.

The maximum average calculated concentration of lead within the river water was shown to be significantly below the 10 mg m^{-3} drinking water standard. The concentration of lead in the cultivated soil did not exceed the guideline value applied in Holland (85 mg•kg^{-1}), which is the value adopted because no criterion existed in France at the time of the assessment. The daily intake following the chronic exposure was estimated to be much lower than the Provisional Tolerable Weekly Intake (PTWI) (25 µg/kg of body weight/week according to the 1993 World Health Organization standard, or about 90 $mg \cdot y^{-1}$ for a 70 kg human).

Results for nickel for the water transfer scenario

The maximum average calculated concentration of nickel within the river water was estimated to be about 0.01 $mg \cdot m^{-3}$, significantly, below the 20 $mg \cdot m^{-3}$ drinking water standard. The average concentration of nickel in the cultivated soil (0.4 $mg \cdot kg^{-1}$) does not exceed the guideline value applied in Holland (35 $mg \cdot kg^{-1}$). The average intake following the chronic exposure to nickel was estimated to be about 4 $mg \cdot y^{-1}$ through ingestion. The value of the ingestion route indicator is the oral reference dose (RfD) for soluble Ni salts from the US EPA database (IRIS), which is 0.02 mg/kg of body weight/day or about 510 $mg \cdot y^{-1}$ for a 70 kg human.

D.4. NEAR-SURFACE REPOSITORY: CASE STUDY FOR SWEDEN

Disposal of LILW in Sweden takes place in Forsmark. The near-surface repository is located approximately 50 m below the bottom of the sea. The wastes that are currently being stored originate from nuclear power reactors (mainly ion exchange resin filters from the water cleanup system, but also trash and scrap), from research, and from medical and industrial applications of radioactive sources.

The long term safety assessment of the repository with respect to the potentially chemotoxic components in the LILW focused on the behaviour of metals and solvents [D-5]. Metal ions were mainly present in ion exchange resins (typically Zn, Cr, Ni, and Co) and sludge residues. Another source of metals considered was scrap (80% Fe, 10% Ni, and 10 % Cr).

The safety assessment study considered all relevant physical (diffusive transport through concrete and bentonite barriers, groundwater flow in the host rock and caverns, advective transport in caverns) and chemical (sorption of metals on solid surfaces of engineered barriers) processes that would occur in the conditioned waste, the engineered barriers, and the host rock.

The safety calculations showed that the increase in metal concentrations in the seawater will be negligibly small. For example, considering the most conservative calculations, the increase in Cr, Ni, and Zn would be about 1 mg m^{-3}. This is due to the contribution of the different barriers to the overall safety of the repository. First of all, a major contribution to the safety is from the conditioned waste, i.e. the concrete or steel containers with operational waste in a concrete matrix. A second contribution is from the engineered barriers that are responsible for retardation and thus result in a dilution in time. The host rock also contributes to this retardation due to the low groundwater velocities. Finally, at the time the chemical components reach the sea above the repository, they are considerably diluted [D-5].

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