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Radioactive Sodium Waste Treatment and Conditioning

Review of Main Aspects

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FOREWORD

Sodium and sodium–potassium eutectic (NaK) have been used as coolants in several research reactors as well as in a small group of prototype and commercial nuclear reactors with fast neutrons. Some of the reactors are still in operation; however, most of them have been already shut down either for their age or for economic reasons. Sophisticated sodium cooled reactors with fast neutrons are considered as a prime candidate for the next generation of future reactors with advanced fuel cycles maximizing resource utilization and minimizing waste production.

Radioactive sodium waste management is not covered in the IAEA publications. Only general and limited information is available in publications dealing with decommissioning of nuclear reactors. Recognizing this fact and the requirements of the Member States, the Agency prepared this publication to address specific issues of radioactive sodium waste handling, processing and disposal in the global context of management of radioactive waste from operation through decommissioning of nuclear facilities.

The first draft report was prepared at the meeting 18–22 June 2001 by four consultants: M. Berte (France), N. McLean (United Kingdom), B. Michelbacher (United States of America) and Yu. Shtynda (Russian Federation). The status report on the subject was prepared by M. Berte. The technical meeting (TM) was held in April 2002 in Lyon, organized by IAEA in cooperation with Framatome ANP. Ten participants from nine countries discussed various aspects of radioactive sodium waste management and contributed to substantial improvement of the draft publication. At the meeting 5–9 May 2003, N. McLean (United Kingdom), B. Michelbacher (United States of America) and S. Nakai (Japan) consolidated all comments and prepared a final draft publication. A subsequent consultant's review was performed by J.J. Kelly (United States of America) 3–6 March 2006 for editorial purposes, structural revisions, and verification the contents remain reliable and relevant.

The IAEA wishes to express its appreciation to all those individuals who took part in the preparation and publication of this report. Particular acknowledgement is due to M. Berte (France), who chaired the TM and put great effort into the completion and technical polishing of this publication.

The officer at the IAEA responsible for initiating this report was R. Burcl from the Division of Nuclear Fuel Cycle and Waste Technology. J.L. González Gómez and J.J. Kelly of the same Division finalized the report for publication.

EDITORIAL NOTE

CONTENTS

SUMMARY

Within the nuclear industry, the use of sodium and sodium-potassium alloys (NaK) is closely associated with Liquid Metal Fast Reactors (LMFR). Both of these alkali metals are used in liquid form as a neutron moderator and a coolant for thermal energy transfer from the reactor core. Relatively few power and research reactors with sodium and NaK have been constructed an operated worldwide, and these are either shut down, being decommissioned, or near the end of their design life.

During normal plant operation, sodium waste does not represent a significant waste stream. However, radioactive sodium waste arising during decommissioning reactors and sodium waste generated during operation and refurbishment of operable reactors requires complex planning and implementation of several unique operations related to the extremely high chemical reactivity of sodium. Special procedures must be implemented from the first steps of dismantling sodium or sodium residue-containing facilities and equipment, through processing of bulk sodium waste and sodium contaminated surfaces, to final conversion of the resulting alkali to environmentally friendly compounds.

Radioactive sodium waste management is not addressed in the IAEA publications. With the majority of sodium-cooled reactors in permanent shut down or decommissioning, an extensive examination of sodium applications, hazards and waste management practices within the nuclear industry is needed.

This publication provides a comprehensive review of worldwide management practices for sodium, NaK, mixtures of the two, and the arising radioactive wastes from nuclear facilities. This review includes:

- Sodium and NaK applications;
- Hazards and hazard mitigation;
- Radioactive sodium waste generation, handling, processing and dispositioning; and
- Conclusions and recommendations for radioactive sodium waste management.

This publication provides a comprehensive review of the hazards associated with sodium waste management. Given the large quantities of sodium waste arising during decommissioning or reactor refurbishment, as well as the challenges and varied techniques associated with removal of 100% of all sodium and NaK bulk quantities and residues during decommissioning, a hazards review and analysis is a critical component in planning the dismantling and waste management activities.

Roughly half of this publication focuses on sodium waste generating, handling and treatment processes. This includes draining sodium and NaK from plant systems; in situ treatment of residual sodium; cutting techniques for pumps, valves, piping and other components; cleaning of components; potential reuse of sodium; and removal of selected radionuclides from sodium waste with the objective of reducing the waste classification or converting it to exempt waste. The focus is on proven techniques and technologies, and each discussed method includes a review of the associated principle or theory, practical

applications, advantages and disadvantages, limitations, industry experience, and final waste products.

A review is provided of final management practices for treated sodium and NaK wastes, including conditioning of radioactive sodium waste and subsequent storage/disposal considerations. The review of conditioning practices includes those designed for the nuclear industry, as well as industrial conditioning technologies which are directly applicable or readily adaptable to nuclear applications. This review includes both successes, failures, and failure analysis.

Throughout this publication, emphasis is placed on industry experience and application of sodium and NaK and industry experience with the techniques and technologies used to manage sodium waste. Reactor-specific examples are abundant and include both successes and failures.

Throughout the publication, the emphasis is on proven methodologies, including their advantages, disadvantages, limitations and hazards. In fact, sodium-related hazards and associated safety considerations are extensively annotated throughout.

This publication can be used most effectively during the planning stages for sodium and NaK removal and treatment activities, including in situ treatment for the purpose of conversion to non-reactive species (e.g. salts, acids). Once radioactive sodium waste or sodium-contaminated components are removed for disposition, this publication is best used as a review of conditioning and dispositioning options, as well as for developing the associated waste management plan. With regard to planning in general, this publication is especially useful in identifying the potential hazards and hazard mitigation considerations at each stage of the removal, treatment, handling and conditioning activities.

1. INTRODUCTION

1.1. BACKGROUND

Sodium waste in the nuclear industry is closely associated with the development of Liquid Metal Fast Reactors (LMFR). Sodium or sodium-potassium alloys (NaK) are used in liquid form as a low moderating effect coolant fluid to extract and transfer thermal energy from the core.

Only a few power and research reactors with sodium coolant have been constructed and operated worldwide. They are close to the end of their design lifetime and, in some cases, the decommissioning is in progress. Sodium radioactive waste does not constitute one of the main waste streams; nevertheless, it represents a significant technical and safety problem during operation and decommissioning of liquid metal cooled nuclear reactors. In addition to the challenges arising from radioactive contamination of sodium waste, the extremely high chemical reactivity of sodium and sodium eutectics must be taken into account.

Each work activity with sodium should be properly planned and managed to avoid potential chemical reactions or explosions with a high risk of consequent environmental contamination. Special procedures should be implemented for removing and processing bulk quantities of sodium, sodium residuals in internal spaces and on internal surfaces of equipment.

Given that the safe and sound management of sodium radioactive waste is a necessary step for successful decommissioning, several Research and Development (R&D) programmes have been initiated. Conducted by countries that have operational experience with LMFR, these R&D programmes are intended to provide a solid basis for design and operation of sodium waste processing facilities as well as for decommissioning planning. Knowledge and experience acquired at this stage of work will be useful in the future development of liquid metal cooled reactors (as a part of advanced fuel cycles) as well as other applications, e.g. in connection with transmutation of heavy radionuclides.

There are a limited number of comprehensive publications dedicated to radioactive sodium waste management, and the available literature on this topic is oriented largely toward chemical behavior of sodium and sodium eutectics.

1.2. OBJECTIVE

The objective of the report is to provide information on present technologies for radioactive sodium and NaK eutectic waste management, mainly in the context of liquid metal coolant processing during decommissioning of fast breeder reactors. Special emphasis is given to radioactive sodium waste treatment and conditioning technologies for final disposal.

The purpose is to provide operators, decision makers, and other involved bodies (e.g. regulatory bodies) with technologically oriented information on the present status and recent achievements on the subject and to facilitate planning and preparatory work for decommissioning LMFRs. Another purpose is to provide designers with technical information necessary for design and construction of technological facilities for radioactive sodium waste processing.

1.3. SCOPE

This publication covers the most important topics related to radioactive sodium waste management, mainly in connection with decommissioning of sodium or sodium potassium (NaK) eutectics in nuclear reactors. Available technical information and good operational practice are discussed and evaluated. Radioactive sodium waste sources, generated volume, typical properties, treatment and conditioning procedures and final transformation to disposable waste form are discussed.

The report is oriented toward managing of radioactive sodium and NaK waste generated in the context of LMFR development, operation and decommissioning. If not otherwise specified, the words “sodium waste” and “liquid metal waste” always mean both sodium and NaK waste.

Non-radioactive sodium waste is not considered in this report. However, the approach, procedures, and recommendations that apply to safe management of radioactive sodium waste are largely applicable to non-radioactive sodium.

1.4. STRUCTURE

The publication consists of six sections. Following this Introduction, the general context of sodium waste generation is discussed in Section 2. In Section 3, main characteristics relevant to sodium waste management, predominantly in the context of nuclear facilities decommissioning, are presented and discussed. Sections 4 and 5 are dedicated to approaches and procedures for processing radioactive sodium waste to final form for disposal. Conclusions and recommendations are summarized in Section 6.

It should be noted that inputs from France, Japan, Russian Federation, the United Kingdom, and the United States of America are predominantly referred to in this publication, given that these countries have accumulated the most extensive knowledge and experience on the subject.

2. GENERAL CONTEXT OF SODIUM WASTE GENERATION

2.1. STATUS OF LIQUID METAL COOLED REACTORS

There are a number of Liquid Metal Fast Reactors (LMFR) and other nuclear facilities using liquid metal in operation or being decommissioned throughout the world. The status and the main characteristics of these plants and facilities are summarized in Table I. Most of them are cooled by sodium (Na) or sodium potassium (NaK) eutectic.

TABLE I. MAIN LMFR AND LIQUID METAL TEST FACILITIES WORLDWIDE
(Operation period from the 1st criticality)

Name	Purpose	Country	Coolant circuit principle	Power (MWth/e)	Coolant Prim. circ./total (metric tons)	Operation period	Status December 2005 **
RAPSODIE	R&D	France	Loop	40	Na 37/57	1967 - 83	SE
KNK II	R&D	Germany	Loop	58/21	Na 36/88	1972 - 91	DIP
DFR	R&D	UK	Loop	60/14	NaK 57/167	1959 - 77	DIP
EBR I	R&D	USA	Loop	1.4/0.2	NaK 15/18.5	1951 - 63	D
SEFOR	R&D	USA	Loop	20	Na	1969 - 72	SE
EBR II	R&D	USA	Pool	62/20	Na 286/327	1961 - 94	SE
FERMI 1	R&D	USA	Loop	300/61	Na 290/421	1963 - 72	DIP
FFTF	R&D	USA	Loop	400	Na 500/900	1980 - 92	SD
JOYO	R&D	Japan	Loop	140	Na 126/199	1977 -02	SD
BR-5/10*	R&D	Russian F.	Loop	10	Na 2/14	1959-02	SD
SRE	R&D	USA	Loop	20	Na 27	1957 - 64	D
HALLAM	R&D	USA	Loop	254	Na 260/370	1963 - 64	D
BOR-60	R&D	Russian F.	Loop	60/10	Na 22/42	1968-	OP
FBTR	R&D	India	Loop	40/13	Na 27/150	1985-	OP
PHENIX	Prototype	France	Pool	563/250	Na 800/1281	1973-	OP
PFR	Prototype	UK	Pool	670/250	Na 915/1450	1974 - 94	DIP
BN-350	Prototype	Kazakhstan	Loop	1000/350	NaK 550/1040	1972 - 99	DIP
MONJU	Prototype	Japan	Loop	714/280	Na 912/1675	1995-	OP
SUPER PHENIX	Commerc.	France	Pool	3000/1250	Na 3300/5520	1985-98	DIP
BN-600	Commerc.	Russian F.	Pool	1470/600	Na 770/1600	1980-	OP

* The BR-5 was upgraded in 1964; thereafter it was referred to as the BR-10.

** OP – in operation; SD – shut down; SE- safe enclosure; DIP – decommissioning in progress; D-decommissioned

LMFR technology and its “breeding” capability to convert plentiful uranium 238 into fissionable fuel — plutonium 239 — was seen until the late 1980s as the way to overcome the predicted shortfall of uranium 235 due to its extensive use in nuclear energy generation in many countries. However, the uranium market did not develop as expected. In a number of countries, liquid metal cooled reactors and the test facilities supporting their development became obsolete. Today, sodium waste management challenges are linked more with decommissioning activities than with operation.

2.2. HAZARDS ASSOCIATED WITH ALKALI METALS

In addition to the risks associated with the manipulation of radioactive products, sodium waste creates a specific hazard due to chemical properties of the alkali metals. Sodium and sodium potassium (NaK) are highly reactive with numerous materials. Reactions with water, air and oxygen are generally violent and produce hazardous by-products, such as hydrogen or caustic substances. It is therefore recommended that all sodium waste be transferred, handled and stored under an inert atmosphere and that transfer and manipulations in open air be avoided.

2.2.1. Reaction with water

Sodium and potassium react strongly with water, even at ambient temperatures, especially when water is in excess. The basic chemical reactions are:

$$Na + H_2O \rightarrow NaOH + 1/2\ H_2\ (\Delta H = -139.6\ KJ/mol)$$

$$K + H_2O \rightarrow KOH + 1/2\ H_2\ (\Delta H = -140.5\ KJ/mol)$$

Reactions are fast, largely exothermic, and produce hydrogen, which is flammable (explosive) in air with oxygen at concentrations above 4%. Sodium and potassium hydroxides, which are harmful due to their caustic properties, are also generated.

2.2.2. Reaction with air and oxygen

Alkali metals react with moisture in the air. Sodium can burn in air at temperatures above 115–130°C. It may also burn in air at lower temperatures, depending on the size and physical condition of the exposed surface and other factors such as humidity. When finely divided into particles such as aerosol deposits or sodium hydrides, sodium can burn in humid air at room temperature.

Sodium burning produces large amounts of high-density, opaque, white fumes composed of sodium oxides that react with the humidity in ambient air to produce caustic sodium hydroxide.

Several accidental sodium fires have occurred at various plants throughout the world. They were generally started by sodium leaking from circuits or vessels. One of the most significant accidents was the sodium fire that completely destroyed the Almeria solar plant in Spain in 1986, wherein heat was transported by a sodium circuit.

2.2.3. Specific hazards associated with NaK

Even in sodium-cooled reactors, NaK is sometimes utilized for its physical, thermodynamic (liquid at ambient temperature and high heat transfer capacity), or chemical properties (strong reducer). For example, the oxygen and humidity content in fresh argon cover gas at the inlet of the Phenix and SuperPhenix reactors are controlled by gas bubblers filled with NaK. After a period of operation, these devices are filled with a mixture of metallic and oxidized NaK. Oxidized products are in solid form and impede draining of the component.

Potassium reacts with air at room temperature to form peroxides, which may react explosively. Among all oxides, potassium superoxide (KO_2) is very reactive (explosive reactions have been reported under specific conditions) with sodium and potassium metal. In the presence of hydrated peroxides or hydrated hydroxides, a reaction is possible between hydrated compounds and NaK, producing heat and hydrogen. The heat can promote KO_2 decomposition with oxygen release; at that point, all conditions exist for a hydrogen explosion.

Such conditions can also occur when abnormal operating situations lead to contact between NaK and oxygen or ambient air. This was the case at SuperPhenix, when air was accidentally admitted into the reactor cover gas circuit and circulated through a NaK-filled safety valve. This rather large component (height 3.5 m; diameter 1.5 m) was filled with approximately 60 kg of products from NaK oxidation.

Serious accidents with NaK have been reported from NaK-cooled LMFR operations in the United Kingdom and the USA. In a 1999 example, an accident occurred at Oak Ridge National Laboratory, USA, due to a NaK spillage during the replacement of a NaK-cooled furnace crucible. Eleven workers were injured [1].

Therefore, NaK waste should be given special attention due to the high chemical reactivity of NaK, especially when the presence of oxidized products is expected. Violent reactions are possible during the treatment of such waste, and specific solutions must be applied on a case-by-case basis.

When NaK systems are drained, the empty system must maintain a positive seal to prevent ingress of air until careful cleaning of the entire system from NaK residuals is assured. For example, at EBR-II, the residual NaK quantities in the drained NaK systems (associated with the purification system and the shutdown coolers) were reacted using water vapour nitrogen mixtures, subsequently flushed with water, and finally dried to assure potassium superoxide compounds are not formed.

2.3. SODIUM WASTE GENERATION DURING REACTOR PRE-COMMISSIONING

The quality (purity) of the liquid metal coolant prior to reactor operation has an impact on the downstream decommissioning activities due to the potential activation of impurities in the sodium. The process of purification generates inactive alkali metal waste.

For example, prior to commissioning of a Fast Breeder Test Reactor (FBTR) in India, the non-availability of reactor grade sodium led to the construction of a sodium purification facility. This was a dedicated facility to convert commercial grade sodium with impurities of about 1 mass per cent to reactor grade sodium. A total of 152 tonnes of sodium were processed and 1.5 tonnes of waste were generated.

2.4. SODIUM WASTE GENERATION DURING REACTOR OPERATION

There are several sources of sodium waste during operations. One of the most important is residual sodium on and within components removed from sodium circuits. Residual sodium may consist of a thin layer wetting the surfaces or may be larger quantities retained in pockets that cannot be drained during component removal. There are several reasons for performing a careful cleaning of such components:

- It is generally preferable and easier to work in an ambient air atmosphere. Therefore, cleaning sodium from components is normally a safe prerequisite to other work activities. Reaction of any residual sodium with air may result in a fire generating caustic aerosols.
- Reaction with humidity in ambient air forms sodium hydroxide, which may lead to caustic corrosion problems on components intended for reuse.
- It is sometimes necessary to decontaminate the components to reduce radiation levels.
- It is sometimes necessary to remove sodium from the components in order to continue operation, e.g. fuel handling machines.

Fuel assemblies unloaded from the reactor must also be cleaned of residual sodium before storage in air or water and before reprocessing.

In normal operation of sodium circuits, there is a need to control the sodium purity regarding dissolved oxygen and hydrogen by using cold trap systems. It is also necessary that radioactive elements remain at reasonable levels with regard to radiation shielding aspects during maintenance using specific traps, e.g. caesium traps. The oxygen and humidity content of reactor cover gas is sometimes controlled by gas bubblers filled with NaK. After an extended period of operation, these devices must be replaced. Any used sodium or NaK containing impurities must be processed as waste.

Any maintenance, repair or modification carried out on a circuit or a component wetted with sodium metal generates sodium-contaminated gloves, tissues, tools, metallic parts, etc. During these activities, it may be necessary to remove quantities of residual sodium, which must be processed as waste. During storage of such residual sodium and sodium-contaminated items, it is important to avoid contact with air, because sodium residues are subject to reaction with oxygen and moisture in air and represent a significant fire hazard.

2.5. SODIUM WASTE GENERATION DURING REACTOR DECOMMISSIONING

Waste management challenges during decommissioning and dismantling of LMFR sodium circuits are more or less the same as during operation and include the following:

- Eliminating residual sodium from dismantled components and structures;
- Managing various sodium-contaminated items (gloves, tools, etc.) used during dismantling operations; and
- Treating specific devices such as cold traps or NaK bubblers.

Chemical reactivity and associated hazards are strong incentives for neutralizing the sodium metal on components, structures and various items that must be treated as waste at an early stage of decommissioning operations. The main reason for sodium metal processing (neutralization) is that sodium in metallic form is not generally accepted by the organizations responsible for radioactive waste management, storage and disposal.

When treating sodium waste, there are a few significant differences between the operational and decommissioning phases. The following issues arise during decommissioning:

- Waste quantities are considerably larger because all sodium circuits finally become waste;
- Bulk sodium drained from the main circuits impedes any reuse in classical industry and generally becomes waste; the lack of new LMFR projects leaves few opportunities for reuse in the nuclear field;
- The large size of primary vessels and piping in commercial power plants or other large nuclear facilities may have high radiation levels that require in situ treatment of residual sodium after draining; and
- There is little likelihood of reusing cleaned components; therefore, there is no concern with regard to caustic corrosion, stress corrosion cracking, or other component defects.

2.6. SPECIFIC ASPECTS OF SODIUM COOLED REACTOR DECOMMISSIONING STRATEGY

Most LMFRs were not designed with decommissioning in mind. For this reason, draining the primary and secondary circuit vessels often requires developmental activities. Many sodium circuits rely on primary pumps and/or immersion heaters or external heat sources, such as heated nitrogen and external electrical heaters, to keep the primary sodium molten. As draining commences, the primary coolant pumps can no longer function, and the immersion heaters become uncovered, making them less effective in transferring heat to the sodium. In the case of SuperPhenix, electrical contact heaters were applied to the base of the primary tank to keep the sodium molten. For EBR-II, heated air was circulated through the annular space between the guard vessel and primary tank to keep the sodium molten during draining operations. At BN-350, a similar heated air system was used to keep sodium molten. At JOYO, a heated nitrogen system has been used during reactor vessel sodium filling and primary cooling system draining to maintain molten conditions.

Pumping systems used to drain the sodium from the primary circuit are also used for removing sodium. A specially designed annular linear induction pump was used for primary sodium removal from EBR-II. At PFR, a pneumatic (nitrogen driven) diaphragm pump was used. Drilling operations are also common to gain access to the lower-most regions of the primary circuit vessels to drain sodium.

For many LMFRs, the decision has been made to place the reactor and its systems in a safe enclosure and postpone core and containment dismantlement for several decades. To ensure that the information pertaining to the status of the systems is maintained, it is important to provide a concise, well-documented status report for each system.

For EBR-II and proposed for BN-350, the ’lay-up plan method’ was adopted. Using this method, a lay-up plan is generated for each reactor and non-reactor system identifying the hazards associated with the system. The plan also defines the desired safe enclosure conditions for each system and the actions necessary to achieve this state. The lay-up plan should document the conditions of the system including quantities and locations of any unreacted sodium and any other hazards that exist within the systems. The lay-up plan also defines the necessary surveillance and maintenance required to assure the system remains in a safe, stable condition for the duration of the safe enclosure period.

3. SODIUM AND SODIUM-POTASSIUM WASTE IN THE CONTEXT OF LMFR DECOMMISSIONING AND DISMANTLING

3.1. BULK SODIUM FROM MAIN CIRCUITS

3.1.1. Quantities

After draining the main circuits of a reactor to be decommissioned, bulk sodium or NaK is waste. The amounts of waste alkali metal are generally large (several tonnes) and constitute a significant hazard, especially in the course of decommissioning/dismantling activities.

In the case of reactors, the quantity of alkali metal depends on the size and purpose of the reactor (see Table I). They are approximately as follows:

- 20 to 900 metric tonnes of sodium for research reactors, e.g. 900 metric tonnes for FFTF, which is the biggest reactor used for testing purposes;
- 900 to 1700 tonnes for prototype power plants with LMFR;
- 1600 to 5500 tonnes for commercial-sized power plants with LMFR.

The biggest NaK-cooled reactor is DFR at Dounreay in the UK with a total inventory of 167 tonnes, most of which had already been processed by the end of 2005.

Several sodium-cooled reactors also have a relatively small inventory of NaK used in auxiliary circuits, e.g. about 13 tonnes for the PFR prototype power plant in the UK and 7 tonnes for the commercial power plant SuperPhenix in France. In both reactors, Na in primary circuits is the main coolant.

Bulk sodium from critical or non-critical R&D facilities other than reactors is present in smaller amounts ranging from a few kilograms to a few tonnes (e.g. 5 metric tonnes for CEA's Cabri/Sura facility in France).

Test facilities, such as sodium loops, containing up to several hundreds tonnes of sodium, have been built to develop and test full-scale mock-ups of actual components for reactors; however, they are generally operated with non-radioactive sodium.

3.1.2. Radiological inventory

3.1.2.1. Primary circuits

There are several sources of radioactivity in bulk Na or NaK from primary circuits:

- Activation of sodium and potassium by neutrons in the reactor core; ^{22}Na and ^{40}K are the main generated radionuclides;
- Contamination by actinides and fission products due to initial surface contamination of fresh fuel by fissionable material, fuel cladding failures during operation, or use of leaking fuel pins. Typical actinide contaminants are Pu, Am, Cm and U isotopes; the most common fission products are isotopes of caesium. Tritium is also present;
- Contamination by activated corrosion products from fuel cladding and primary circuit structures, such as ^{54}Mn and ^{60}Co.

The concentration of radioactive products in primary sodium is highly dependent on the operational history of the reactor. Major contributors to the radiological inventory are generally ^{137}Cs, ^{22}Na (and ^{40}K in NaK) and ^{3}H.

Due to its short half-life of 2.2y, ^{22}Na concentration depends on the irradiation time and the decay period after reactor shutdown and is typically on the order of 2 to 12 kBq/g of sodium at two to five years after reactor shutdown.

^{137}Cs concentration is low in reactors with short operating times and no fuel element failures (such as SuperPhenix), or those equipped with caesium traps (such as FFTF). It is quite high for R&D reactors used for fuel testing, such as Rapsodie or DFR (see Table II).

TABLE II. ^{137}CS CONCENTRATION IN PRIMARY SODIUM OF VARIOUS LMFR REACTORS

Reactor	Caesium traps Yes/No	Cladding failures Yes/No	Cs^{137} concentration (Bq/g)	Date measured	Reference
FFTF	Y	Y	3.5	1996	[2]
EBR II	Y	Y	370	1994	[3]
SuperPhenix	N	N	7	2000	[4]
Rapsodie	N*)	Y	5800	1985	[4]
BN-350	N**)	Y	$9\ 10^{5}$	2001	[5]
PFR	N	Y	$3.3\ 10^{3}$	1998	[6]
DFR	N	Y	$8.2\ 10^{6}$	1999	[7]
BR-5/10	N*)	Y	10^{5}	1998	[8]
KNK II	Y	Y	$6.4\ 10^{3}$	1996	[9]

*) Caesium purification during or prior to sodium processing
**) Caesium concentration reduced to 370 Bq/g after purification operations in 2003

^{3}H concentration is of the order of 3 to 15 kBq/g three to five years after shutdown. At BR-5/10 during operation, the ^{3}H in primary sodium was 3.6 to 13 kBq/g [10]. At BOR-60, which is still in operation, the ^{3}H concentration in primary sodium is 80 to 100 kBq/g. At Monju, the ^{3}H concentration was about 1 to 3 kBq/g a half year after start of operation.

3.1.2.2. Secondary circuits of reactors

During normal operation, the sodium of secondary circuits is physically separated from the primary sodium by intermediate heat exchangers. However, some of the tritium generated in the primary circuit diffuses through the walls of heat exchanger tubes and contaminates the secondary sodium. In the secondary circuit, tritium may diffuse through walls of the steam generators or be collected in cold traps.

If an intermediate heat exchanger should fail, the secondary sodium may be slightly contaminated by the primary sodium, although secondary circuits are designed generally to maintain a small overpressure margin relative to the primary circuit.

In pool type reactors, secondary sodium could be activated by neutron flux from the core. However, the main activation product, ^{24}Na, poses little radiological hazard due to its very short half-life (15 hours).

In pool type reactors, activated corrosion products on the secondary side of heat exchanger walls may be swept along by secondary sodium. However, given the operating temperatures of secondary circuits, corrosion is negligible, and the resulting radioactivity in sodium is typically below detection limits.

Finally, the main radioactive contaminant of secondary sodium is tritium. One to two years after shutdown, the order of magnitude of the activity ranges from hundreds to thousands of Bq/g. For example, at EBR II tritium activity in the secondary circuit has been found at the 0.75 kBq/g level; at BOR 60 it is at the 2–4 kBq/g level.

3.1.2.3. Other bulk sodium

In addition to sodium that comes from reactor main circuits, sodium exists in the fuel storage facility of the SuperPhenix reactor. This sodium was contaminated by primary (radioactively contaminated) sodium from the main vessel during fuel assembly transfer. The radioactivity level is very low because the facility had not been operated for a long time.

Facilities used for fuel development, fuel post irradiation examination, or core safety research may contain significantly higher radioactive sodium. In some cases, actinides and other alpha emitters may be present.

3.1.3. Chemical purity

3.1.3.1. Sodium from reactor main circuits

The sodium loaded in the reactor circuits prior to start up and for commissioning is likely to be of nuclear quality, which means that chemical impurities are on the order of a few ppm.

Although reactor circuits are under inert gas atmosphere, small oxygen and hydrogen ingress is inevitable during operation and maintenance. Due to its chemical properties, sodium tends to react with oxygen and hydrogen, resulting in the formation of sodium oxides and hydride. The concentration of sodium oxides and sodium hydride in sodium coolants should be maintained below saturation limits to prevent any precipitation of solid particles that may impede coolant flow through the core. Sodium cooled reactors are equipped with purification systems based on cold traps for maintaining oxygen and hydrogen concentrations at an acceptable level.

For example, in the French Fast Reactors, oxygen and hydrogen concentrations during operation are about 5 ppm O_2 and 0.5 ppm H_2.

Other sources of chemical impurities in primary circuits are corrosion/erosion of primary components and materials and ingress of seal alloy materials and lubricants from primary pumps.

After final shutdown of the reactor, the content of chemical impurities in sodium may increase, especially concentrations of oxides and hydride, depending on shutdown and safe storage conditions, time since shutdown, operation of purification systems, etc.

3.1.3.2. Other sodium

The radionuclide inventory and chemical purity of bulk sodium used at other than LMFRs depends on the purpose and operational history of the particular facility. This is the case of PFR fuel post irradiation examination cells (fuel caves). While the fuel was stored, various operations performed in these cells degraded the chemical quality of the sodium. Fuel debris may also be present.

3.1.4. Main waste management problems

Two principal issues can be identified for bulk radioactive alkali metal waste processing:

- For alkali metal from reactor main circuits, the difficulties encountered and potential hazards are generally associated with the large quantities involved. As there is little possibility of recycling, alkali metal must be processed. The main question is how to handle the large quantities of secondary waste: Should it be released to the environment according to existing authorizations, or should it be conditioned for final storage/disposal?
- Alkali metal from R&D and test facilities and auxiliary (in reactor) fuel storage is generally in smaller quantities compared with reactor circuits, but it may be more radioactive and chemically contaminated. The difficulties of processing such metals are closely linked to the choice of a safe and reliable processing technology.

It may be beneficial to reduce the radioactivity level of the sodium before its processing in order to facilitate subsequent treatment and conditioning and to simplify the required processing efforts. This could also have an impact on the final product of processing. Caesium radionuclides and tritium are the main contaminants generally considered in sodium decontamination processes. Caesium is the main gamma contaminant in the liquid phase, and tritium is the main contaminant of gaseous effluents generated during sodium neutralization.

3.2. RESIDUAL SODIUM FROM REACTOR MAIN CIRCUITS AFTER DRAINING

3.2.1. Draining of reactor circuits

Draining of reactor circuits during the course of decommissioning operations may result in sodium being trapped inside. The capability of the reactor circuits to be completely drained depends on the general concept (loop or pool type) and also on the particular design features of each reactor.

3.2.1.1. Primary circuits

Loop type reactors

The draining aspects of the primary piping and components of loop type reactors are globally similar to that of secondary circuits, with limited quantities of retained sodium (see below).

The reactor vessel is a specific case. The complex geometry of its internal structures, organized to form a cold and a hot plenum, could lead to non-self-draining zones. In some cases the reactor vessel constitutes the lowest point of the circuit. For safety reasons, design provisions are taken that prevent the primary vessel from being drained by gravity with normal means. Consequently, a bottom puddle is often left in the reactor circuit at the end of the final draining during decommissioning.

Pool type reactors

The primary vessel of pool type reactors is not, in general, fully self-draining for the same reasons that loop type reactors are not. This concept leads to a bigger vessel, and the quantities of residual sodium can be quite significant.

3.2.1.2. Secondary circuits

Secondary circuits are generally designed with the capability of being drained during normal operation of the reactor. The quantity of sodium left inside the loops is minimal. Apart from the thin film of residual sodium wetting the surfaces, secondary pumps and steam generators are the main areas that retain sodium. Limited quantities of sodium may remain in components, such as auxiliary pumps, valves or specific devices (temperature measurement, hydrogen detection, etc.) due to their geometry.

Residual sodium may remain inside the circuits when bulk sodium is drained through small holes or narrow annular spaces, which may plug when draining conditions are not favourable (high impurity level, presence of debris, low temperature, etc.). In addition, small diameter pipes may not completely drain.

3.2.1.3. Main storage tanks

Bulk sodium from reactor main circuits is drained and collected in dump tanks that are part of the primary or secondary systems or in specially built storage tanks. These tanks are then considered waste and may contain a pool of residual sodium at the bottom that cannot be pumped out.

Some fast reactors have sodium-filled spent fuel storage vessels, generally of a large capacity. This was the case for SuperPhenix reactor. Due to the failure of this vessel, it was dismantled after draining and in situ treatment of the residual sodium.

3.2.2. Quantities

3.2.2.1. Sodium wetted surfaces

Based on the available experience, the average quantity of residual sodium on sodium wetted surfaces after bulk sodium draining is typically 30 to 100 micrometers on vertical surfaces and 1 mm on horizontal surfaces. Japanese data show 0.2 mg/cm^2 (about 2 micrometers) in the sodium coolant region, and 14 mg/cm^2 (about 140 micrometers) in the cover gas region. PFR data indicates a sodium thickness of 2 to 5 micrometers on wetted surfaces.

For SuperPhenix reactor, the estimated quantity of sodium residue on wetted surfaces of the primary vessel is about 3500 kg in comparison with 3300 metric tonnes contained originally in the primary circuit.

A SuperPhenix steam generator represents about two thirds of the wetted surface of a secondary loop (not including the intermediate heat exchanger) and retains about 100 kg of residual sodium compared with about 135 metric tonnes of sodium in the secondary circuit.

For the German reactor KNK II, sodium left on the wetted surfaces of the primary vessel is estimated to be 10 kg compared with about 20 metric tonnes of total sodium.

3.2.2.2. Residual sodium pools

The SuperPhenix primary vessel is expected to retain about 35 metric tonnes of sodium if no special effort is made to improve bulk sodium draining. However, the current scenario will retrieve the sodium retained inside the core support and feeding structure (diagrid) and will drill holes in the core catcher before draining. Other pools will be drained or pumped out using adapted flexible nozzles. Finally, only about 1400 kg of sodium is expected to remain in the vessel at the end of the draining phase.

Residual sodium in the PFR primary vessel after bulk sodium draining would be about 32 metric tonnes, located mainly in core support structures and high pressure piping areas. Additional engineering work will be carried out to assist draining. This will lead to a residual sodium inventory of approximately 5 metric tonnes depending on possible plugging of small orifices.

Concerning secondary circuits, an estimate of the residual sodium (other than sodium film on the walls) for one of the four SuperPhenix loops is as follows:

- About 120 kg in the steam generator, divided into small quantities at numerous locations; and
- About 50 kg at various locations in the loop; the biggest individual portion does not exceed 4 kg.

For EBR II the figures are less than 1300 kg in the primary vessel and less than 400 kg in the secondary circuits.

3.2.3. Radiological aspects

3.2.3.1. Primary circuit

Distribution of particular radionuclides between various phases is important for decommissioning planning.

Cobalt radionuclides tend to concentrate on hot sodium wetted surfaces, whereas caesium isotopes concentrate in gas plenums. However, concentration factors could differ from one nuclide to another by several orders of magnitude. Non-gamma emitter isotopes, such as ^{63}Ni or ^{55}Fe, also generally accumulate in the residual sodium film.

Major actinides are generally in the form of heavy aggregated particles in bulk sodium and may be deposited during operation in lower regions of the vessel where the sodium velocity is low. After bulk draining, the concentration of actinides can be higher in bottom residual sodium pools than in bulk sodium.

Tritium generally accumulates in the thin film of residual sodium after bulk sodium draining. The residual sodium can be enriched in tritium by factors ranging from tens to thousands compared with tritium measured in bulk sodium. A significant quantity of tritium produced during operation may also remain trapped in steel structures.

3.2.3.2. Secondary circuit

Similar to its behaviour in the primary circuit, tritium contained in the secondary circuit accumulates in the residual sodium film.

3.2.4. Main waste management problems

Sodium vessels, components, and circuits are generally large, complex designs, and the radioactive contamination level may be high. Treatment of residual sodium or NaK of the LMFR main circuits must be performed in-situ with subsequent conditioning of reaction products. The main reasons are:

- Eliminate the potential hazard due to alkali metal chemical reactivity;
- Reduce surveillance requirements associated with the decommissioning strategy to keep the circuits or vessels under a care and maintenance scheme in order to take advantage of radionuclide decay or to defer the dismantling effort; and
- Facilitate dismantling operations of large and complex circuits by decreasing the dose rate and allowing air operations without sodium fire and caustic hazards.

3.3. REMOVABLE COMPONENTS FROM MAIN CIRCUITS

Removable components are those that can normally be removed for maintenance during reactor operations. These components include primary pumps, intermediate heat exchangers, control rod mechanisms, fuel handling machines, and secondary pumps. During the decommissioning phase, removable components become waste and the residual sodium must be eliminated before delivery to a final storage/disposal place.

Facilities used to clean the components during reactor operations are also generally used for decommissioning purposes. If the components should be treated by an in situ process, they may be left in place and treated together with the circuit. However, further dismantling and cleaning of the components may be necessary to eliminate sodium in areas where access is difficult, such as crevices.

Components such as control rods are highly activated and would, therefore, require shielding for sodium removal and dismantling operations.

The amount of sodium retained within the removable components is generally low because of the strong design requirement for self-draining, which is an incentive to facilitate maintenance. However, the presence of unexpected and unpredictable sodium retention is always possible, depending on geometry and sodium quality. The sodium film thickness on wetted component surfaces can be evaluated similarly to the circuits themselves: an average of 2 to 30 micrometers on vertical surfaces and 1 mm on horizontal ones.

Estimated mass of residual sodium in primary circuit components is as follows:

– Phenix intermediate heat exchanger:	about 40 kg
– BN 600 primary pump:	about 10 kg
– Superphenix control rod mechanism:	about 0.5 kg
– Superphenix fuel handling machine:	about 1.5 kg

Radioactive contamination of the sodium removed from primary circuit components is generally higher than that of bulk sodium because radioactive products accumulate on component surfaces, depending on material, ambient conditions, and physical/chemical properties of the equipment.

3.4. OTHER SODIUM WETTED METALLIC ITEMS FROM CIRCUITS

Components that are not normally removable from main circuits must be considered as a specific category of waste because their removal and treatment occur when the reactor is at the dismantling stage or during replacement or modification of components.

Items to include in this category are sodium valves, pipes, steel structures, small vessels, heat exchangers, sodium vapour traps, and other specific components, including some pipework which can not be treated in situ due to the small diameter or because it is plugged.

These items must generally be modified to make sodium removal possible. This preparation phase frequently includes disassembling or cutting work, either to gain access to residual sodium or to divide the item into subsections of acceptable dimensions for cleaning.

This type of waste may require specific cleaning processes or facilities. This is especially true with large quantities of steel, such as the main circuit of a large prototype or a commercial sized reactor. Even in the case of in situ treatment of the main piping and structures, many items need to be removed and treated separately.

For SuperPhenix reactor, the secondary loops represent about 1500 tonnes of steel. Consequently, there is a strong incentive to neutralize residual sodium in situ before dismantling. However, depending on technical options that are under consideration, several tens or hundreds of tonnes of steel could require processing in a dedicated facility.

Residual sodium trapped in these items is similar to that contained in removable components and the circuits from which they come. In other words, there is a higher concentration of radioactive products in residual sodium compared with bulk sodium.

3.5. COLD TRAPS

Among the various types of sodium wastes arising from LMFR operation and decommissioning, cold traps may be difficult to manage for the following reasons:

- Design complexity; internal structures are generally composed of curved shape deflectors to force the sodium flow through metallic mesh sections or other devices able to increase the surface on which oxide and hydride will deposit;
- Presence of internal or external devices to cool down the incoming sodium, in some cases using a thermal medium such as NaK or organic liquid;
- Presence of significant quantities of impurities, mainly oxides and hydrides, trapped inside in solid form, making the cold trap very difficult to drain;
- Cold traps are in most cases not designed to be self draining and are typically situated at the lowest point of the circuit;
- Selection of treatment process must take into account that sodium hydrides are more reactive than metallic sodium; moreover, the presence of hydride leads to possible release of hydrogen;
- Risk of violent reaction is more serious when NaK is concerned; and
- Due to its trapping function, the cold trap tends to concentrate radioactive products along with the sodium; thus, the radioactive inventory is generally substantial and leads to high dose rates.

Some examples of cold trap characteristics are given in Table III.

TABLE III. EXAMPLES OF COLD TRAP CHARACTERISTICS

	Outer height (m)	Outer diameter (m)	Metallic Na (kg)	Oxide (kg)	Hydride (kg)	^{3}H activity (Bq)	Gamma activity (Bq)
Phenix secondary cold trap [11]	~3.6	~1.5	4000	30	200	1.1 10^{13} (1979)	-
BOR-60 primary cold traps [12]	3	0.8	900	40	12	4 10^{12} (1995)	2 10^{12} (1995)

3.6. CAESIUM TRAPS

Given that caesium traps are dedicated to retrieval of radioactive caesium isotopes from sodium coolants, the caesium traps contain high levels of ^{137}Cs radioactivity accumulated in a small compact volume (up to 10^{13} – 10^{14} Bq in 1–10 litres of trap volume) and in sodium residues deposited on surfaces from carbon materials.

To treat caesium traps for ultimate disposal, it is necessary to fix sodium residues in a form that will not cause interaction with water and air or to provide for complete sodium removal from traps. During treatment, it is important to ensure the minimum release of caesium from the trap. Cleaning in lead and filling of the traps with lead was tested in Russia. Obtained results demonstrate that filling caesium traps with lead provides for safe ultimate disposal of highly active traps [13].

3.7. SECONDARY (DRUMMED) SODIUM WASTE

Maintenance or dismantling operations on sodium equipment, components or circuits generate sodium-contaminated waste, such as plastic gloves, tissues, vinyl envelopes, and small metallic items or tools, together with small pieces of metallic sodium. This waste is generally put into drums by the operators and covered with an inert powder or gas that isolates the sodium from ambient air. In Japan, paper towels and radiation protection equipment, such as clothes and gloves, are stored in metal cans and are cleaned in a special facility using water to remove possible sodium adhered to the cleaned equipment.

Another type of waste is generated in R&D activities on fast reactors and often referred to as 'historical waste.' Although similar to the technological waste, this type of waste presents another issue. Given the poor documentation associated with it and long periods between packaging and treatment, accurate knowledge on the package contents may be greatly reduced. This brings additional challenges for the re-opening, treatment and management of historical waste.

4. SODIUM WASTE TREATMENT PROCESSES

4.1. INTRODUCTION

The following review concerns the processes that have been developed beyond the laboratory and applied in the context of nuclear activities or that have good potential for successful industrial applications.

The objective of this section is to review the most common proven approaches for sodium and NaK treatment. It is not intended to make an exhaustive review of all treatment processes that can be conceived from physical and chemical properties of alkali metals nor to comment on existing patents that have been issued all over the world.

4.2. BULK SODIUM PRETREATMENT

4.2.1. Caesium removal

Experiments have shown that carbon and carbonaceous materials have efficient caesium trapping properties. Specific processes have been developed to trap caesium from sodium metal and were used to reduce the radioactive caesium inventory in primary circuits of operating fast reactors, especially in the USA. Similar procedures can be also used to facilitate handling and treatment of primary sodium or wastes coming out of reactor circuits during decommissioning. In France, they were used to purify waste sodium from Rapsodie circuits and sodium from test facilities, such as the CABRI/SCARABEE loop of CEA. At the BN-350 reactor in Kazakhstan, caesium was trapped from primary sodium prior to its draining for treatment.

The process [14] is based on circulating liquid sodium through caesium traps loaded with Reticulated Vitreous Carbon material (RVC). RVC is rigid carbon foam of very low apparent density, with a honeycomb-type structure and an excellent resistance to liquid sodium. Its implementation as a trapping device is generally without difficulty.

Granulated carbon materials (low ash reactor grade graphite and adsorbent 'carbonizate') are also used for caesium pretreatment in expendable and stationary traps in Russian design reactors [15].

Operating temperature is between 180°C and 300°C, and liquid sodium linear speed within the trap is on the order of a few mm/s.

Using this process, caesium concentration of the RAPSODIE primary sodium was decreased in 1985 from 42 kBq/g to 5.8 kBq/g. This means that about 2.0×10^{12} Bq of ^{137}Cs were trapped. The 15 metric tonnes of CABRI/SCARABEE sodium were then purified in 1997 by a factor of 13; the total amount of trapped caesium was estimated to be 2.6×10^{12} Bq (see Fig. 1).

For the BN 350 reactor, the caesium activity was reduced from 2.9×10^{5} Bq/g to about 370 Bq/g. The trapping activities at BN 350 surpassed the ultimate goal by about 500 Bq/g.

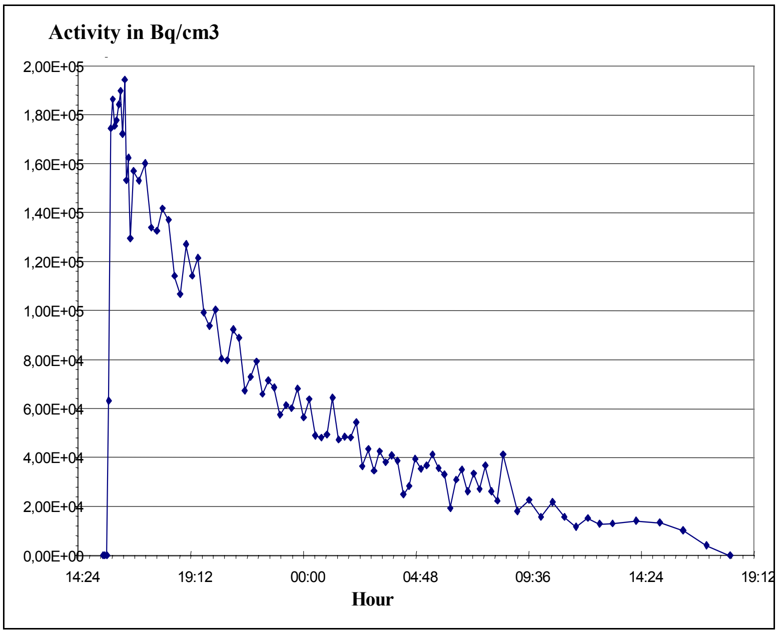

FIG. 1. Diminution of the residual activity of the primary sodium of CABRI/SCARABEE loop by caesium purification. [16]

For SuperPhenix primary sodium, the level of caesium activity was very low during reactor operation (estimated at less than 10 Bq/g). In addition, tests have been performed to check the potential for further caesium removal. Preliminary results were encouraging, showing that even for such a low concentration, it should be still possible to reduce the activity by a factor of ten at the minimum. Similar results were obtained at JOYO, where the concentration of Cs was reduced by a factor of ten in several days.

To control caesium removal efficiency, it is necessary to have rather precise methods of measuring caesium activity against a background of ^{22}Na activity (several kBq/g). The method of continual control of caesium activity in coolants during reactor operations in the presence of a high background of ^{24}Na developed in the Russian Federation can be adopted for this purpose. This method consists of reversible adsorption of caesium in graphite material and measurement of increased caesium concentration in the graphite samples.

4.2.2. Tritium removal

Although tritium release to the environment during sodium waste treatment is generally accepted and remains below authorized limits, tritium removal could represent an interest in some particular cases; for example, to achieve acceptable release limits for secondary sodium. Methods to extract tritium from sodium are the same as those used to extract hydrogen. Hydrogen and tritium are extracted simultaneously and in consistent proportion to the concentration ratio of hydrogen and tritium in the sodium.

Various physical principles can be used to extract tritiated hydrogen from sodium:

- Crystallization in the form of sodium hydride; this principle is used in cold trap systems;
- Diffusion through a membrane;
- Desorption through a gas / liquid interface; and
- Other less commonly applied principles (trapping by adsorption, etc.).

The principle behind another a possible process for tritium removal from sodium involves purifying the sodium of its hydrides by circulation through a cold trap. In order to trap tritium efficiently, it is necessary to maintain a high concentration of dissolved hydrogen in the sodium by continuously polluting the sodium with hydrogen (swamping principle). Tritium is then carried away together with excess hydrogen. A hydrogen concentration of less than 0.2 ppm is sufficient. This process is based on well-mastered physical and chemical principles. However, it has not been yet tested at a large industrial scale facility. Depending on the performance of the cold trap and purification systems used, a reduction factor of 10 for SuperPhenix secondary sodium activity is likely to be achieved using such a process over a 40 to 50 day period.

4.3. DRAINED RADIOACTIVE SODIUM TREATMENT

The bulk sodium treatment processes described below generally apply to both sodium and NaK. As indicated earlier, there is a relatively small inventory of NaK in sodium-cooled reactors. The most common practice is to dilute this NaK into bulk sodium before treatment. The physical and chemical properties of the sodium are not affected by the small addition of potassium.

For EBR II, NaK was mixed with sodium inside the primary vessel; at PFR it was mixed in a buffer tank or the primary vessel during sodium processing. Mixing is also planned at BN 350 and SuperPhenix.

4.3.1. Impact of impurities in sodium on its processing

Both the NOAH and Argonne processes are sensitive to impurities in sodium; therefore, sodium is mechanically filtered prior to injection to ensure that no particles are present that could potentially cause nozzle plugging. For filtration, a mechanical filter, such as a sintered metal filter rated at 20 microns, is sufficient and recommended. It is also recommended that the sodium be kept under inert cover gas prior to introduction into the process.

The sodium should be introduced into the system at a temperature greater than the plugging temperature of the sodium to assure the free flow of sodium.

Both processes use demineralized water for reaction with the sodium. This eliminates generation of crystalline compounds (admissions) in the sodium hydroxide product.

During the processing of the EBR-II sodium, the primary sodium contained 8 ppm lead. Lead is soluble in sodium but not in sodium hydroxide. Therefore the lead, precipitated from the sodium hydroxide in the caustic recirculation pump, made the pump inoperable.

4.3.2. Continuous processes

4.3.2.1. NOAH process

The principle of the NOAH process consists of injecting small amounts of liquid sodium by means of a dosing pump into a large flow of aqueous sodium hydroxide circulating in a closed vessel. Since the quantity of sodium reacting each time is low, the chemical reaction is moderate and continuously controllable.

The reaction is exothermic; therefore, continuous cooling through a liquid/liquid heat exchanger is required. The sodium hydroxide solution should be maintained at a temperature of about 60°C.

The sodium/water reaction results in sodium hydroxide and hydrogen formations. Aqueous sodium hydroxide concentration in the system should be kept at about 10 moles per litre by replacing part of the sodium hydroxide solution with water.

Exhaust hydrogen gas, contaminated by tritium, is released via the stack after passing through a mist eliminator and a dryer and subsequently via a very high efficiency filter in accordance with the applicable radioactive gaseous waste release limits.

The main advantages of the NOAH process are as follows:

- Sodium is transformed into sodium hydroxide in a single continuous operation;
- The quantity of sodium reacting at any given moment is very small.

The process was developed in France and successfully applied to processing the 37 metric tonnes of primary sodium at the Rapsodie reactor within a two-month time period (sodium flow rate of 40 kg/h).

Industrial verification of the NOAH process was the reason for its choice for processing of more than 1500 metric tonnes of contaminated sodium from PFR reactor in the UK. The main differences between this installation and the Rapsodie facility are:

- The sodium-processing rate is about four times higher at PFR than at Rapsodie. (This choice has been made on the basis of a technico-economical analysis, with the aim of limiting the risks related to the scaling factor);
- The facility is controlled through remote instrumentation and sensors. The valves are also operated remotely from the control room;
- Biological shielding is integral to the system structural frames; and
- The design has been optimized and improved using feedback from the Rapsodie facility and plant operating results.

The NOAH facility is expected to process the PFR sodium at an average rate of 2.5 metric tonnes per day based on an average plant availability factor of 80 per cent.

In France, a project is ongoing for the treatment of 5 500 metric tonnes of sodium from SuperPhenix. The plant is currently in the construction stage, based on a nominal sodium processing capacity of six metric tonnes per day.

The process is applicable also to NaK. However, conceptual modifications are necessary, considering that the solidification temperature is lower for NaK than for sodium.

A similar process was developed in the UK [17] to treat sodium from the German reactor KNK 2. A plant was constructed to treat 100 kg of sodium per hour. The plant was commissioned in 1996 for non-radioactive operation, but it failed to obtain approval for active operation from regulatory authorities.

4.3.2.2. Argonne process

This process, developed in the USA at Argonne National Laboratory West (ANL-W), was originally designed to transform sodium to sodium carbonate through two stages involving caustic and carbonate process steps. However, difficulties arising in operations of the carbonate process led to the abandonment of the second step, and a crystalline sodium hydroxide monohydrate product was subsequently chosen as a final product.

The carbonate process was initially designed to convert the hydroxide into a dry non-hazardous sodium carbonate waste acceptable for land disposal. The sodium hydroxide was transferred from the caustic facility to the carbonate facility, where hydroxide reacted with carbon dioxide in the variable temperature-controlled section of a thin film evaporator (TFE) to form sodium carbonate and water. The carbonate product was then heated to evaporate the residual water and finally dry the sodium carbonate to a powder. The powder was fed into a bulk cooler, where it was cooled from 150°C to less than 40°C and subsequently transferred to a drum filling station to be packaged in barrels. Testing operations showed, however, that the TFE device was inadequate for long term operation, because it was not able to dry the sodium carbonite sufficiently for transport of the product without system plugging.

Ultimately, a plant to process 680 metric tonnes of sodium from Fermi–1 and EBR-II reactors was built. This plant used a caustic process based on sodium reaction with aqueous sodium hydroxide solutions. The process flow diagram is illustrated in Fig. 2. The sodium is transferred by pressurization from a day tank into a reaction vessel at the rate of 140 litres of sodium per hour. In the reaction vessel, sodium reacts exothermically with water to form a caustic solution. Sodium is injected into the reaction vessel underneath the free level of liquid through one of two specially designed nozzles. The nozzles provide the capability to add steam or nitrogen gas for spraying sodium and have the ability of purging the nozzles to preclude plugging. The process is adjusted by controlling the atmospheric boiling point of the solution and by addition of water.

A caustic recirculation line provides for continuous recirculation of >70 wt % sodium hydroxide solution for homogeneous mixing. The sodium hydroxide solution is pumped from the reaction vessel into 270 litre barrels through a line that cools the product from 185°C to 95°C. When the product cools to less than 60°C, it solidifies into a concrete-like sodium hydroxide monohydrate crystal. This solid product could then be buried at a repository complex. However, it should be noted that this solid sodium hydroxide product is an acceptable-for-burial waste form only in certain jurisdictions.

The processing of the 680 metric tonnes of sodium to a solid sodium hydroxide product was successfully completed in March 2001 using the one step process.

The same method was used in the USA to transform NaK from EBR-I to hydroxides, acceptable for disposal. Some experience has also been gained in the UK with a similar caustic process used for processing 50 metric tonnes of NaK from the DFR secondary circuit.

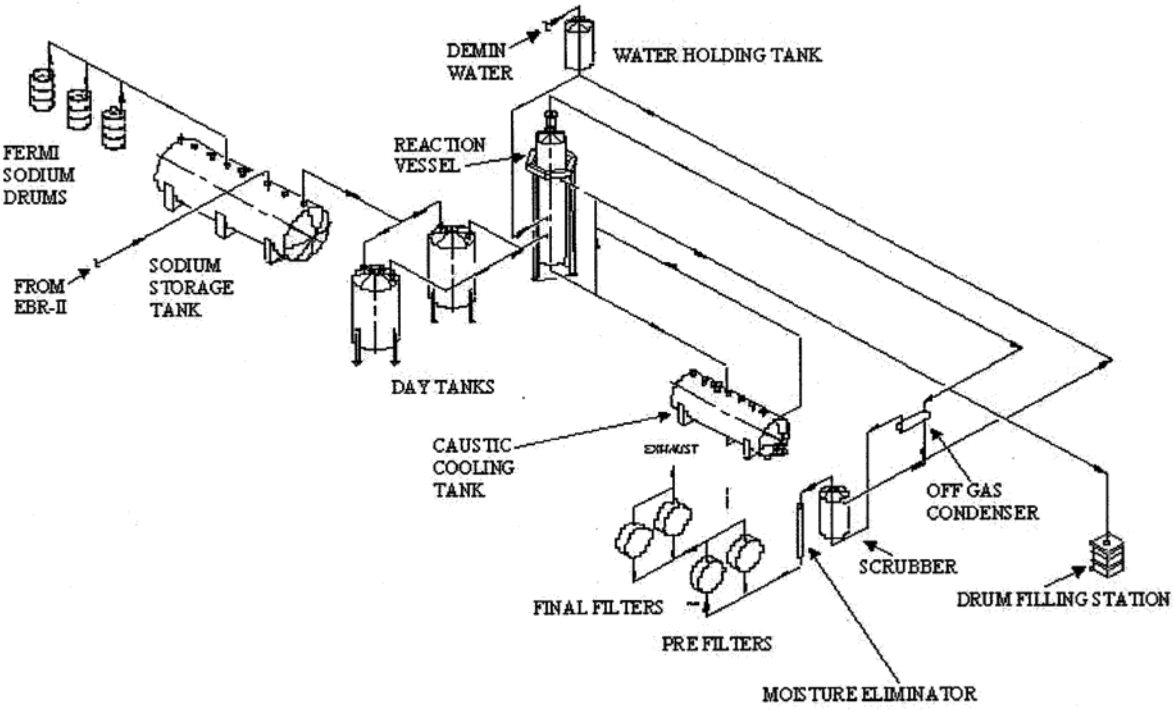

FIG. 2. Argonne Process.

4.3.3. Batch processes

The processes described below are based on principles that make them mainly suitable for processing limited quantities of alkali metal. However, they are very useful for processing highly radioactive sodium waste and/or waste containing a high proportion of oxides, hydrides, pollutants, reaction products or debris. The processes used for bulk sodium processing are, generally, not adapted for use in these particular cases.

Some batch processes have the potential to be scaled to allow treatment of larger volumes of alkali metals, such as bulk sodium coolant from reactors. However, they have not reached sufficient industrial qualification to be considered for such applications.

4.3.3.1. Autoclave reactor

In order to neutralize limited quantities of radioactive NaK, a process based on an autoclave reactor has been developed in France. The principle is to realize NaK-water reaction with a given quantity of NaK (less than 1 kg) and an excess of water.

The reaction occurs in an autoclave reactor (Fig. 3) specially designed to withstand the rapid rise of pressure caused by a NaK-water reaction. NaK alloy is introduced in a closed vessel, which is placed in the reactor. The reactor is then closed, and the inside atmosphere is removed with inert gas. Water is then introduced at the bottom of the reactor. The reactor is isolated, and the vessel containing NaK is opened by a mechanical device. The NaK is then immersed into water by a hydraulic jack. Reaction with NaK and water induces a pressure rise. When the pressure is stabilized, the autoclave reactor is decompressed, and all gases (mixtures of hydrogen, inert gas and steam) are diluted in an inert sweeping gas flow. The monitoring of various parameters (temperature, pressure, hydrogen release, etc.) allows verification of completeness of the reaction.

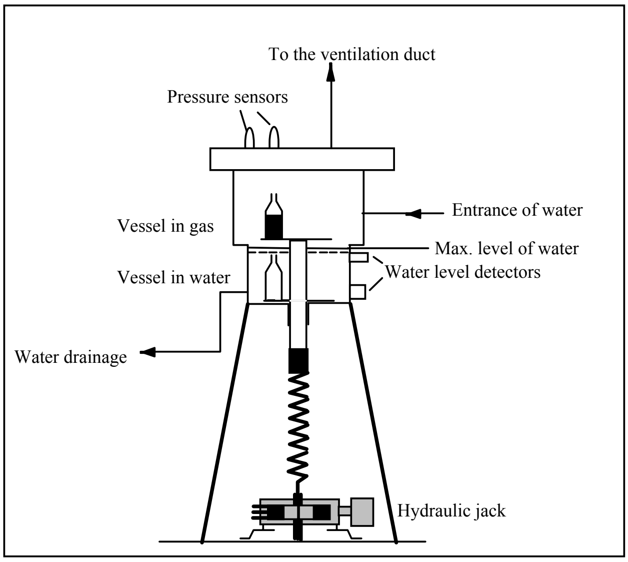

FIG. 3. Autoclave reactor. [18]

The main advantages of the process are safety and efficiency. It also minimizes the amount of liquid effluents produced. Safety is enhanced because there is no possibility of uncontrolled additional energy release. The objectives are to liberate all the possible energy during the reaction and to design the reactor to withstand this energy within significant margins. Furthermore, the system includes mechanical interlocks that prevent any possibility to introduce more NaK than the quantity for which the reactor is designed.

However, the system operates in batch mode and is, by principle, appropriate to process only limited amounts of NaK. At the present time, this process is used to treat radioactive NaK waste from the French experimental irradiation reactor Siloé run at CEA Grenoble.

Another advantage is that this principle can be applied to clean sodium waste and also to process polluted sodium, as well as various sodium contaminated items. Such an autoclave reactor is being developed in France. A prototype has been tested and an industrial application has been designed for a future sodium waste treatment facility called ATENA. This autoclave reactor will be able to treat various specific wastes; in particular, highly radioactive graphite cartridges from caesium traps.

4.3.3.2. Steam under vacuum process

This method of sodium neutralization was proposed at the Institute of Physics and Power Engineering at Obninsk in Russia and tested at Design Mechanical Engineering Bureau at Nizhny Novgorod and BOR-60 [19].

The process involves the injection of water into an evacuated vessel that contains items contaminated with metallic sodium. When sodium reacts with water under vacuum conditions, the energy released in the reaction is consumed in the evaporation of water at the reaction site. Investigations revealed that the reaction is stable if the pressure in the vessel is controlled below 10 kPa (absolute) and the temperature is kept below 25°C, producing a reaction rate not exceeding 1 g/min per 1 cm^2 of metallic sodium surface.

Wider operational limits were established for a smooth stable reaction using 25% (wt.) solution of sodium hydroxide in water. In this case, the solution temperature should not exceed 60°C and the pressure 70 kPa (absolute). In this regime, reaction rates not exceeding 2 g/min per 1 cm^2 of sodium surface have been observed.

This method has been successfully used at the Design Mechanical Engineering Bureau to convert approximately 7 tonnes of non-active sodium from reactor test rigs to hydroxide.

This process was also used at BOR-60 to dissolve small quantities of sodium (up to 4 kg), fixed on components from both primary and secondary circuits and for sodium conversion into hydroxide solutions inside decommissioned primary and secondary cold traps.

Successful tests on the BN-600 heat exchanger tube sheet mock-ups and the BOR-60 sodium vapour trap have also been carried out.

Operational experience shows that the process of water injection under vacuum is particularly good for removal of sodium in narrow gaps (less than 1mm) and small diameter tubes of 1 to 2mm.

4.3.3.3. Conversion into carbonates in a fluidized bed

This process is based on reacting sodium with oxygen in the presence of carbon dioxide, while avoiding the use of water or aqueous solutions, thus avoiding the production of hydrogen [20].

Reaction between sodium and oxygen produce oxides and peroxides:

$$4\ Na + O_2 \rightarrow 2Na_2O$$

$$2\ Na + O_2 \rightarrow Na_2O_{2r}$$

In the presence of carbon dioxide (CO_2), peroxides are unstable and decompose; oxides are transformed in carbonates:

$$Na_2O_2 + CO_2 \rightarrow Na_2CO_3 + \tfrac{1}{2}O_2$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$

For good efficiency and completeness of the reaction, turbulent conditions and tight contact between sprayed liquid metal and gas are created using the principle of fluidized bed. Moreover, the fluidized bed is a flame arrester and thus improves the overall safety of the process.

The reaction vessel is a vertical cylinder containing silica particles forming the inert matrix. The inlet of the main fluidizing gas (N_2 or Ar) and of the reaction gases CO_2 and O_2 is at the bottom of the reactor. Gas is circulated through the reactor in a closed circuit and creates the fluidized bed conditions. The gas circuit includes heat exchangers, thereby allowing temperature control.

Liquid sodium is injected in the fluidized bed using a spray system that disperses the metal in small drops. The reaction heat is removed by circulating oil inside a double containment of the reactor in order to maintain the average bed temperature between 350 and 450°C.

The process is batch operated. Adequate loading and unloading units are foreseen to take out the silica/carbonate mixture at the end of the reaction phase and to load fresh silica for a new cycle without necessarily opening the reactor.

The process is undergoing validation on a pilot plant. The estimated throughput of this pilot plant is 0.36 kg of sodium per hour. Values of up to 1 kg/h injection rate have also been tested successfully.

One of its main advantages is that there is no hydrogen production due to the chemical reactions on which it is based. Moreover, the silica/carbonate end product is ready to be conditioned in a glass or cement matrix, because silica is already a component of these types of matrices.

Considering the principle and the batch mode of operation, this process seems to be suitable for the treatment of limited quantities of sodium waste. In addition, incorporation in a glass matrix requires a proportion of 20% maximum of equivalent Na_2O in silica. The spraying nozzle principle for sodium admission in the reactor consequently limits the application of such a process to sodium with a low level of impurities or to a very good filtration system in place on the sodium injection line.

4.3.4. Other processes

Several other processes can be adapted to the neutralization of limited quantities of sodium and NaK waste, depending on their degree of radioactivity and content of impurities.

4.3.4.1. Processes developed by IPPE, Russia

Apart from the burning in the air process mentioned below in Section 4.3.4.2, three other processes are currently being developed in the Russian Federation in connection with BR10 decommissioning. They have reached an experimental stage, allowing the processing of 1 to 4 kilograms of alkali metal in a batch mode.

Burning in a vessel

The principle consists of introducing a load of alkali metal in a closed reaction vessel heated to about 350°C. Sodium is sprayed on a tray for burning. Pure oxygen is supplied until the absorption of oxygen by oxidation of alkali metal is complete (about 1.5 hour). Finally the chemical reactor is cooled down to 80°C, and water is supplied to the vessel. The reaction product, a caustic solution, is drained from the vessel. After washing and drying, the vessel is ready to treat a new batch.

Incorporation in a "geocement"

The principle is to react the alkali metal and transform the reaction products into a solid matrix in a single process [21]. There are three main stages:

- Dispersion of liquid alkali metal on a solid granulated carrier (blast furnace slag containing SiO_2, Al_2O_3, FeO and sand), which is inert to alkali metal and will constitute one of the main binding materials;
- Tempering by mixing with clay (bentonite or kaoline) mixed with a caustic solution (NaOH); and
- Hydration/solidification of the mixture and formation of a solid cement-like matrix.

The experimental facility is mainly composed of a dispersing unit (basically a cylindrical rattler mill), connected to a tempering/reacting drum fitted with a rotating mixer, which will house the final solid product. The operational sequences for treatment of 1kg of NaK are as follows:

- Loading of the solid granulated carrier (5 kg) into the dispersing unit;
- Loading of NaK into the dispersing unit under inert atmosphere;
- Dispersing of NaK by rotating the mill with temperature being controlled to 40°C;
- Loading of 1.7 kg of clay and 100 ml of 60% NaOH into the tempering unit;
- Batch supply of the mixture from the dispersing unit to the tempering unit and batch supply of water; the mixer being continuously operated. The temperature is controlled at about 100°C. Hydrogen production and release to atmosphere are monitored; and
- The drum containing the final compound is separated from the mixer and the compound is allowed to solidify.

The total duration of one treatment cycle is about four hours. Approximately 1 m^3 of final product can incorporate about 200 kg of alkali metal.

Solid phase oxidation

Solid phase oxidation using copper smelting slag is based on spontaneous exothermic interaction of alkali metal with copper slag [22]. The result is a solid mineral compound.

The core of the experimental rig (Fig. 4) is a 100 litre vessel in the form of a vertical cylindrical tube. The vessel has two sections separated by a flanged assembly and an isolating membrane. The upper section receives the slag, and the lower section is the reaction area.

The sequence of operation is as follows:

- Filling upper section with 70 litres of slag;
- Evacuation of the vessel;
- Supply of 23 kg of alkali metal into the reaction section from a supply unit;
- Inert gas supply to the facility;
- Heating of the vessel up to about 400°C by electric heaters;
- Initiating the reaction by breaking the membrane (using a rod passing through the vessel wall) and allowing the slag to fall on the alkali metal; and

- Cooling down of the vessel and disconnection of the lower part of the vessel containing the solid reaction product.

The total duration of the destruction cycle is about 10 minutes excluding the cooling down phase. The final volume of the formed compound is about two times the alkali metal volume.

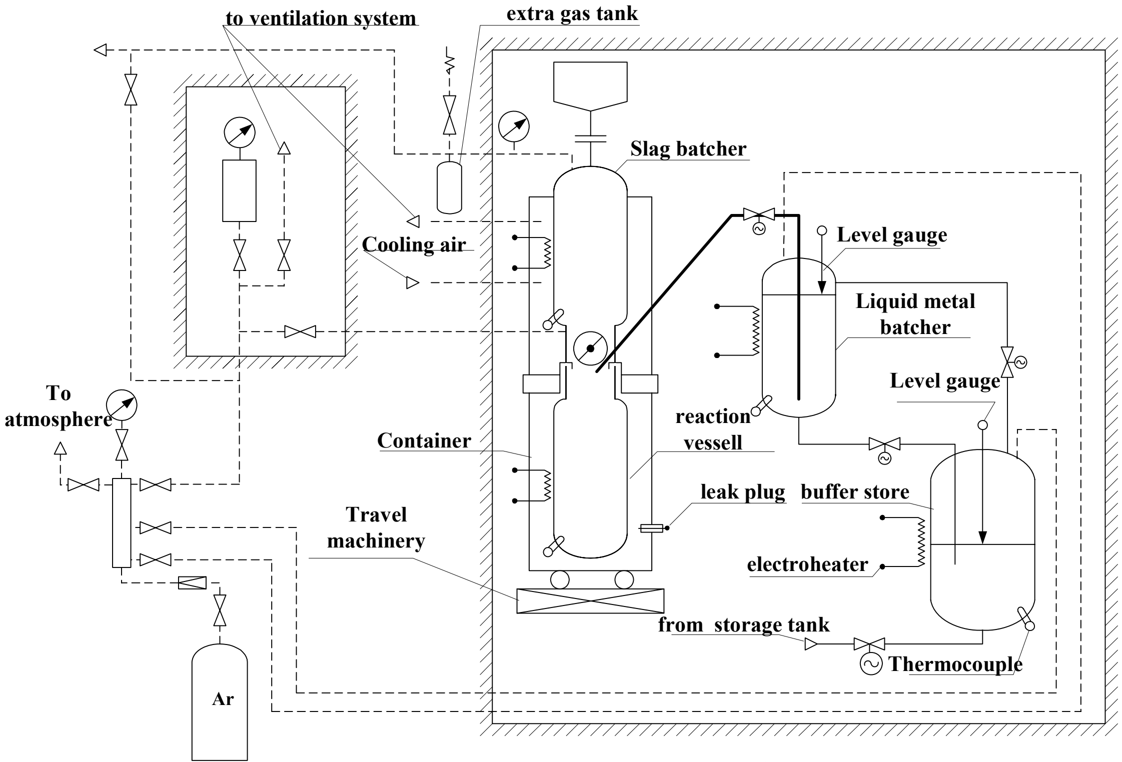

FIG.4. Solid-state oxidation method facility "Mineral" scheme

Gas phase oxidation

Fine granulated blast slag is used for alkali metal (Me) dispersion and a mixture of oxygen and carbon dioxide is used as an oxidizing agent. This process is realized at a constant pressure of oxidizing gas mixture and is initiated by heating the slag to 180°C. After initialization, the external heating is ceased and exothermic reactions run [21]:

$$2\,Me + O_2 \rightarrow Me_2O_2$$

$$Me_2O_2 + CO_2 \rightarrow Me_2CO_3 + 1/2O_2$$

$$2Me + 1/2O_2 + CO_2 \rightarrow Me_2CO_3.$$

The reaction product, the mixture of carbonate with slag, is mixed with water and cooled.

4.3.4.2. Burning in air

The burning of sodium in pure oxygen is very exothermic. The reaction enthalpy for reaction resulting in sodium peroxide is $\Delta H = -520.2$ kJ/mol.

The reaction can be controlled by diluting oxygen with an inert gas, for example, by burning in the air. The reaction scheme depends on carbon dioxide and humidity content in the air, and the individual reactions could be as follows:

$$4\ Na + O_2 \rightarrow 2Na_2O$$

$$Na_2O + H_2O \rightarrow 2\ NaOH$$

$$2Na + O_2 \rightarrow Na_2O_2;$$

$$Na_2O_2 + H_2O \rightarrow NaOH + H_2O_2$$

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}\ O_2$$

$$4\ Na + 2\ CO_2 \rightarrow Na_2CO_3 + C + Na_2O$$

The main advantage of this method of sodium processing is that burning in air does not produce hydrogen as occurs in a reaction with water.

The combustion of sodium can occur spontaneously in the air more easily when the temperature is high. Hydrogen peroxide, H_2O_2, is also a powerful oxidizing agent, but it is not generated when sodium burns in air with a relative humidity higher than 40%.

During sodium combustion in humid ambient air, a dense white smoke of sodium oxides is generated that subsequently decomposes into sodium hydroxide, sodium carbonates and water. This decomposition can be accelerated by scrubbing the gas in a water scrubber. Solid residues, which remain in a reaction vessel after combustion is complete and which are not carried out with exhausting gas, are mainly sodium oxides.

Burning has been used extensively in various countries for sodium waste processing in both open areas where the smoke was released to the environment and in closed furnaces where the smoke was removed by scrubbing. Existing facilities range from a simple booth for burning mixed waste with limited quantities of sodium to large furnaces equipped with complex scrubbing systems. However, current regulations strictly require efficient filtration of the off-gas stream generated in sodium combustion to assure that radioactive products are not released to the environment.

In France, an operating facility exists in the sodium production industry. A cubical metallic furnace of about 2.5 m is closed by a door and is fitted with air ingress orifices. Solid sodium waste to be burned is placed on a tray. The combustion is started by a gas-fuelled torch. Gaseous effluents are sucked from the furnace by a high capacity ventilation system (up to 10 000 m^3/h) and filtered in a water scrubber. The facility is operated in a batch mode and has a capacity of burning 150 kg of sodium in 8 hours. The solid residues remaining at the end of the burning phase are reacted with water in another facility.

Some experience on sodium burning and scrubbing of gaseous effluents has been also gained in France at the Esmeralda facility of CEA. This facility was built and operated in the 1990s to study large sodium fires that may accidentally occur in a commercial-sized LMFR.

In Russia, development work is in progress on the method for burning alkali metal in a closed vessel filled with air within the frame of BR10 decommissioning. The experimental rig is operating in batch mode and allows the dissolution of the remaining ashes in water directly inside the furnace vessel.

The main difficulty with processing a large amount of radioactive sodium by burning in the air is the risk of contaminating the whole plant by the gaseous effluents. In addition to that, the ‘nuclearization’ of the process should add complexity. The high-density smoke quickly deposits on the walls of the furnace and in the gas exhaust and treatment systems. Periodic cleaning is therefore required, leading to frequent shutdowns and complicated maintenance.

A continuous process appears to be feasible by feeding liquid sodium by spraying (in the case of pure sodium). Requirements for a sodium feeding facility are similar to that of aqueous processes. Continuous processing requires continuous elimination of remaining ashes and subsequent treatment.

4.3.4.3. Reaction with water

A water spraying process in a facility similar to one presented in Section 4.7 or used for cleaning reactor pits (Section 4.6) is also possible for processing small quantities of polluted radioactive sodium. It is a question of scaling down or adapting facility internals. Small items and parts of technological equipment containing various amounts of polluted radioactive sodium can also be treated in such facilities, provided they have been dismantled or cut to assure proper exposure of sodium to the water mist.

Such a process is used at ANL-W for limited quantities of sodium (up to 2 kg/batch). Sodium is placed in a water wash vessel that has an airflow of 85 m^3/min. Water is sprayed on the sodium to produce a complete reaction of the sodium to sodium hydroxide and hydrogen. The hydrogen generated is diluted in the flow stream of ventilation gas and exhausted to the atmosphere through a filtration system. The hydroxide product is removed from the vessel and disposed in accordance with local standards.

4.4. IN SITU TREATMENT OF RESIDUAL (NON-DRAINABLE) SODIUM

4.4.1. Removal of residual sodium from tanks and pools

As previously stated, following drainage of the primary circuit vessel, there are still pools of sodium at the bottom of the circuit that cannot be removed without additional work. The residual sodium is generally located in areas where it is difficult to gain access. Special techniques are usually required to reduce trapped volumes of sodium. These techniques belong to two categories:

- Pumping techniques; and
- Draining techniques aimed to create orifices, allowing the liquid metal to be collected at the bottom of the reactor vessel where it can be more easily drained or pumped out.

Pumping techniques are based on mechanical, pneumatic, vacuum, electromagnetic, hydraulic or capillary principles. Draining techniques are based on machining principles, such as drilling and punching, or cutting techniques such as sawing, high pressure jet, plasma or laser cutting. Filling with an inert liquid of higher density than the liquid metal has also been explored.

In addition to the difficulty of access and the distance from reactor top closure, the following constraints should also be considered:

- Specific chemical/physical properties of alkali metals;
- Sodium temperature in the range of 150 to 200°C to ensure liquid state;
- Avoiding debris production and its distribution with regard to further pumping difficulties; and
- Avoiding ingress of pollutants into the reactor vessel (together with air or process fluids), that may cause corrosion, especially if the containment must be maintained for a long period.

Experience has demonstrated that the most efficient and practical techniques are:

- Drilling and punching for draining operations; and
- Pumping with electromagnetic or pneumatic pumps put inside the vessel to minimize the suction head. Pumping with ejectors should be also considered.

Difficult access often requires pumping equipment fitted with specially developed devices such as flexible nozzles. This was the case with pumping the residual sodium during dismantling of the fuel storage vessel of SuperPhenix. In some cases, the nozzle must be first introduced in place with special handling equipment.

Some examples of special techniques developed in the frame of current LMFR decommissioning projects are as follows:

- Drilling machine, punching device and pneumatic pumping (flexible nozzle) for the primary vessel of PFR. The equipment has been designed and tested and is currently pending operation;
- Drilling machine, EM pumping (flexible nozzle) for Superphenix’s primary vessel. After a testing phase with prototypes, the drilling equipment has been successfully operated at the reactor;
- Drilling operations are envisaged for the primary vessel of FFTF in the USA. A prototype drill string, 12 m in length, has been successfully tested to drill through an 8 cm SS 304 wall; and
- Drilling operations were successfully used for the BN-350 primary vessel.

4.4.2. Water Vapor Nitrogen (WVN) process

The residual sodium from drained vessels or circuits can be reacted in situ using a process based on circulation of a nitrogen carrier gas containing a small proportion (1 to 6%) of water vapour (WVN process). The small amount of water allows a controlled reaction between sodium and water, resulting in generation of sodium hydroxide and hydrogen.

Hydrogen must be safely vented via an off-gas system, and hydroxide residues are removed by water rinsing. Reaction control is based on monitoring hydrogen concentrations and temperatures, then controlling the rate of moisture input to the system.

The technological equipment applied for in situ treatment is derived from well known sodium cleaning methods, which are the bases for cleaning facilities utilized for maintenance of reactor components.

This procedure is one of the best developed and proven ones for sodium residue removal. The liquid aqueous effluent arising has less environmental impact potential than gaseous or liquid alcohol effluent produced with other methods. It is also a convenient form for further treatment and disposal. The process is suitable for Na and NaK.

Although the WVN process is known as a reasonable technique for alkali residue removal from vessels or piping sections of relatively limited size and rather simple geometry, there is not much experience with cleaning large and complex vessels, such as the primary vessel of pool type reactors. In large and complex vessels, it is difficult to control the formation of liquid aqueous sodium hydroxide. This liquid can flow and collect on non-reacted sodium layers (for example, along the vertical walls of the vessel, then toward the bottom where puddles form) or accumulate on the surface of sodium pools and induce violent reactions and possibly uncontrolled situations.

In the USA, the Hallam reactor was decommissioned between 1966 and 1969. Primary vessel sodium residues were converted to sodium hydroxide by injection of a WVN gas mixture. Temperatures at the primary vessel reached as high as 150^{o}C, so the sodium was molten, and the reaction of sodium with the steam was initiated. The entire process of reacting the residual sodium in the reactor vessel and connecting piping involved a total of 82 hours of steaming, followed by a nitrogen purge to ensure removal of all hydrogen. The vessel was then dried by circulating dry nitrogen.

The NaK in the EBR-I reactor was cleaned using a WVN process in the 1970s.

At EBR-II, tests were conducted using a process similar to the Hallam process, and layers of sodium exceeding 4 cm were fully reacted. However, development of the process was abandoned due to schedule requirements, and the carbonation process described below in Section 4.4.4 was used in cleaning the EBR-II systems.

In the UK, residual sodium has been removed from PFR's primary vessel by using the WVN process. A test facility was built and operated for a comprehensive test program to define the operating envelope. Test results indicated temperature and pressure deviations, but these were well within the safety margins for the primary vessel. Similarly, DFR NaK was mixed with PFR Na and treated using the WVN process.

4.4.3. Superheated steam/nitrogen process

The superheated steam/nitrogen process has been used at Fermi 1 for reaction of the residual sodium in the secondary circuit and is planned to be used for its primary circuit. The NaK loops at EBR-II also used this process.

A steam generator (e.g. propane fired) is used to create steam that is then routed through an electric heater to superheat the steam. Superheated steam is then mixed with a hot nitrogen carrier gas and circulated through the systems to be treated. The gaseous products, including nitrogen, water vapour, hydrogen and caustic vapour are exhausted to the atmosphere. The exhaust gas line may contain a scrubber and HEPA filter.

The process uses hydrogen generation to indicate completion of the reaction. Hydrogen concentration is monitored, and as the concentration approaches zero, the sodium and/or NaK reaction is complete.

Oxygen in the system is also monitored. It is imperative that oxygen is not present in the system to avoid the possibility of a hydrogen ignition. In this process, even with no free oxygen present, rapid sodium oxidation and heat generation may occur due to the reaction of water with sodium.

The liquid waste stream generated by this process is sodium/potassium hydroxide. The systems are generally flushed with water to remove the caustic substance and to verify completion of the reaction. After neutralization and drying, the system can be removed or remain in place for ultimate dismantlement.

4.4.4. Carbonation process

Similar to the WVN process, the carbonation process derives from sodium cleaning methods for reactor components cleaning pits, and it is based on ’wet’ gas. The process consists of circulating carbon dioxide (or a gas mixture of carbon dioxide and nitrogen) inside the vessel or circuit with a very low amount of water vapour at a controlled dew point. Sodium reacts smoothly with the very low amount of humidity carried by the gas, producing anhydrous sodium hydroxide, which is immediately transformed into solid sodium carbonate or bicarbonate by reaction with CO_2 gas. By maintaining a sufficiently low concentration of water vapor, hydrogen production is continuously limited to a very low level (less than about 0.2% in the circulating gas).

The major advantage of the carbonation process, which is also its main difference from the WVN process, is that it avoids formation of liquid sodium hydroxide as the sodium is converted into solid carbonate. This prevents any reaction excursion and uncontrolled reactions between aqueous sodium hydroxide and non-reacted sodium.

Depending on operating conditions, the structure of the carbonate can be much more porous and cracked than hard and impermeable. In this case, the reaction is not inhibited by the diffusion limitation of treatment gas through the carbonate layer, and relatively deep pools of sodium can be treated. Experiments conducted at Argonne National Laboratory West showed that the impermeable carbonate was present when the carbonation process was conducted on molten sodium or at higher temperatures.

Carbonate residue can be evacuated by rinsing with water, or it can be acidified if necessary for better dissolution. Another advantage of this process is that dismantling operations can be carried out in an air atmosphere, given that carbonates are chemically stable and not harmful.

This process has already been applied with success in France for the internal cleaning of the spent fuel storage vessel of SuperPhenix in 1988 before its dismantling. In that case, the objective was to inert sodium films in large areas; localized thicker retention areas could then be removed by mechanical means.

Another successful application of this technique was carried out on several steam generator modules of the Phenix reactor. The aim of the treatment was to eliminate the residual sodium after drainage without damage to the structures. The three bends and the super-heater (22 to 25 meters long, 194 mm diameter) containing seven steam tubes were connected to each other, and a water vapour/CO_2 mixture was circulated inside. The quantity of sodium in each module was estimated to be 7 kg. In some locations the thickness of residual sodium reached 5 mm. The total duration of the treatment was seven days, resulting in a complete conversion of sodium metal into carbonate.

The method is being further developed in France to treat the residual sodium of the SuperPhenix primary vessel and main circuits. The results are very promising, showing that with appropriate choice of parameters, it is possible to react a significant thickness of sodium in a reasonable time. Recent tests have allowed treating a thickness of 2 cm of sodium in 100 hours, and there is no sign of slowing down of the reaction rate.

Carbonation has also been used at EBR-II for reaction of residual quantities of sodium in the secondary and primary circuits. Carbon dioxide gas with a relative humidity of 60 to 70% was circulated through the secondary circuit, with hydrogen generation monitored at the exhaust. The hydrogen concentration was maintained below 4%, and a decrease in the amount of hydrogen produced was an indicator that the process was complete. Oxygen was also monitored, and the process was temporary stopped if oxygen concentrations exceed 0.25%. The primary circuit tank was also subjected to the carbonation process, and the process was terminated when about 50% of estimated residual sodium was reacted. Estimates indicate that more than 80% of the original amount of primary residual sodium will be reacted using the carbonation technique. The Non-reacted sodium is generally located in deep pockets in areas not drainable using the immersion pump.

4.4.5. Alcohol treatment

Reaction of sodium with alcohol is less violent than with water, and there are no corrosion-associated issues, therefore, alcohol treatment has been used from the very beginning of LMFR history to clean sodium-contaminated items or to remove sodium residues. The principle is to circulate alcohol in the component to be cleaned in order to dissolve the sodium residue. The chemical reaction is:

$$\mathrm{R{-}OH + Na \rightarrow R{-}ONa + \tfrac{1}{2}\,H_2}$$

However, under conditions that are not well defined, the reaction can lead to uncontrolled complex chemical decompositions with production of large quantities of flammable gaseous byproducts. This risk exists particularly with heavy alcohol, such as ethyl-carbitol (2-(2-ethoxyethoxy) ethanol). The reasons for using heavy alcohol include low vapour pressure, high ignition point and mild reaction with sodium. At least two very serious accidents are known to have occurred in Europe using heavy alcohol:

- During cleaning of the residual sodium (about 100 kg) contained in a tank on Rapsodie reactor site (France, 1994), an explosion occurred. One operator died, four others were injured, and very serious damages were caused to the building housing the tank [23];

- During the cleanup of a small amount of sodium (about 3 kg) within a 500 litre storage tank of the test facility ILONA (Germany, 1996), an unexpected rapid decomposition of the compounds into ignitable gases, which were released through a safety valve into the building, caused an explosion. The personnel were evacuated from the building before the event happened, and nobody was injured. The building was seriously damaged [24].

This cleaning technique is therefore no longer permitted in France or in the United Kingdom.

In addition to the negative aspects of manipulating large quantities of flammable solvents and producing hydrogen (as in the aqueous methods), other disadvantages of this method should be highlighted:

- There is no convenient route identified for disposal of the sodium alcoholate produced;
- Sodium must be removed from resulting reaction mixtures in order to reuse the alcohol; and
- The reagent used is more expensive than those required by aqueous methods.

Ethanol was used for in situ treatment of SRE reactor in the USA during its decommissioning in the 1970s. No major accidental event has been reported; however, loud reaction noises were apparently generated by violent bubbling.

In France the process of using ethyl-carbitol was applied for cleaning of the Rapsodie primary circuit between 1988 and 1990, before the above mentioned accident. It allowed successful removal of 125 kg of residual sodium.

At Argonne National Laboratory West, a facility was used to clean primary coolant pumps and other primary and secondary components that required maintenance for reuse in the reactor. The system was sized to accept components as large as the intermediate heat exchanger. This facility used ethanol as the cleaning reagent and was operated safely for the whole duration of operations. Additionally, a system to remove the sodium from the alcohol was built and tested but has not yet been operated. (See Section 4.6.7.)

The alcohol treatment method is used in some countries for internal cleaning of components, such as heat exchangers and fuel handling equipment.

4.4.6. Other techniques

4.4.6.1. Sodium distillation

The principle is to create a vacuum in the vessel containing sodium residues to be removed and to maintain it at a sufficient temperature (350 – 550°C) to promote direct sodium sublimation. A condenser is placed between the vessel and the pumping system to collect the sodium.

The advantages are that no chemical reactant is required and no effluent is produced, although the recovered sodium must be further processed (neutralized) for disposal.

The main disadvantage is that the components to be treated must mechanically sustain the outer pressure due to vacuum. This is not generally the case for the LMFR with low-pressure designed structures, principally made of thin shells. The temperature must also be isothermal in the whole component to avoid sodium condensation in colder areas.

This method has been applied in the Russian Federation to remove sodium residues from cold traps. Although the process efficiently removes caesium, hydrogen and sodium, compounds of sodium as sodium oxides remain in the trap and impede sodium removal. The subsequent removal of residual sodium and oxides is performed using their reaction with steam under vacuum [13].

The same principle has been applied in the USA and the UK to clean reactor components placed in cleaning pits under a vacuum (see section 4.6). The process was subjected to an extensive R&D programme at the Hengelo test facility in the Netherlands during the 1970s on full-scale steam generator mock-ups of the German SNR 300 reactor.

Due to the required vacuum state, the method is easier to implement for relatively small sized vessels and circuits.

4.4.6.2. Reaction with steam under vacuum

The principle is similar to the WVN process. The vacuum reduces the risk related to formation of liquid aqueous phase, but it increases the risk of uncontrolled air ingress.

4.5. CUTTING OF ITEMS CONTAINING SODIUM AND NaK

4.5.1. General aspects

Cutting techniques are required for dismantling and further treatment of sodium waste items when draining is not possible and in situ treatment is not achievable for practical, economical or safety reasons. After cutting, the sodium is readily accessible and each piece of equipment can be treated in a common cleaning facility (see section 4.7). Various items such as valves, filters, cold traps, sodium aerosol traps, tanks, and portions of blocked pipes filled with solid sodium can be prepared for cleaning using cutting techniques.

The presence of sodium requires that techniques should be adapted to avoid any process fluid or material that could chemically react with sodium and to avoid any thermal or ambient condition that could lead to fire or uncontrolled reactions.

In France several cutting techniques have been tested on various sodium-containing items. The conclusion is that classical mechanical techniques have clear advantages over thermal processes or other techniques, such as laser and high pressure jet cutting. Advantages include the following:

- Low cost;
- No cooling required or possibility to use sodium compatible lubricants (e.g. synthetic oil);
- Low heat generation;
- Minimum risk of contamination spreading; and
- Safety of the cutting process.

The main disadvantage of mechanical cutting techniques is the need to apply high cutting forces, which generally limits the capability.

Thermal processes, such as plasma torch cutting have good productivity; however, generated heat can cause sodium fire and fume hazards. They also involve potential contamination spreading.

4.5.2. Cutting technique for sodium containing components

Significant experience in cutting of sodium containing components has been accumulated at KNK, where the decommissioning of the primary and secondary sodium circuits was done without any in situ treatment of the sodium before cutting. The process was based on experience gained from maintenance during operation.

Cutting was done using different kinds of saws and pipe cutters. Different techniques were used during and after dismantling.

In general, the temperature during cutting must be well below the melting point of sodium. At KNK, the temperature was always below 50ºC and cutting was performed in air. Only testing of the system was performed under the nitrogen atmosphere. The saw was cooled by paraffin and nitrogen.

The following techniques were used for cutting the circuits:

- Various kinds of band saws;
- Pipe cutter; and
- Orbital cutter for vessels.

Large band saws were used to cut components into small pieces for the washing plant. For cutting the intermediate heat exchanger bundles into small pieces, two saws that moved in different directions on a shielding wall were used. A band saw with paraffin cooling was used in KNK for cutting large components, such as pipelines, to prepare them for the washing plant.

The techniques of band saw or reciprocating saw cutting, portable milling, disk grinding, and hydraulic shears have been selected by CEA in France for various component disassembly.

To solve the problem of the treatment of cold traps and other non-drainable tanks, a cutting technique based on classical band saws has been tested in CEA (France). The cold trap is placed horizontally on a bench, and a **remotely operated** band saw cuts the trap into slices. The saw cuts the external envelope, internal structures including the mesh, and sodium altogether. Each slice is then treated in a dedicated washing facility (see section 4.7). These tests have demonstrated the feasibility of cutting cold traps full of sodium into slices without lubrication and with no risk of fire ignition by sodium.

Industrial application of this technique for the future sodium waste treatment facility of CEA will be assured using the facility called ATENA.

4.5.3 Cutting technique for NaK

Due to the high chemical reactivity of NaK in air at ambient temperatures, extreme care must be taken when breaching NaK contaminated circuits, especially when the presence of oxidized NaK is expected. All such breaches should be made under an inert gas atmosphere (nitrogen/argon) and within a glove or seal bag.

Cold cutting techniques should be employed, e.g. reciprocating saws, orbital pipe cutters, shears and band saws. A suggested methodology is to crimp the pipes flat and then cut through the flattened section, thus retaining containment on both sides of the cut.

Work is currently in progress to investigate the potential for freezing NaK using liquid nitrogen to allow size reduction operations of NaK contaminated components.

4.6. WASHING OF COMPONENTS AND SODIUM WETTED ITEMS

4.6.1. General

Given that eliminating sodium from components and fuel was one of the aspects to be solved from the very beginning of LMFR history, proven processes have been developed. Therefore, every LMFR has several cleaning facilities (cleaning pits) to allow the treatment of all removed components. Generally, LMFRs are equipped with three specific cleaning pits: one for the large components (intermediate heat exchangers, primary and secondary pumps), one for the small components (control rod mechanisms, fuel handling machines, miscellaneous in-reactor instruments), and a third for fuel subassemblies.

During the decommissioning phase, these facilities can be used to clean components for which they are designed, and they can also be used to clean other sodium wetted items generated in dismantling operations.

The main advantage of using these facilities for waste treatment is that they are proven and safe. However, they are generally designed to clean components which have small amounts of residual sodium or that have been dismantled to remove non-drainage sodium pools.

Although various principles are applicable (distillation under vacuum, reaction with alcohol, etc.), cleaning pits are mostly based on water processes. Water can be in the form of steam or water mist, the carrier gas being nitrogen or CO_2 or both, and the pit maintained under vacuum or pressure.

In general, the last phase of cleaning consists of rinsing with water, then filling the pit to immerse the component in order to eliminate sodium hydroxide and carbonates and small amounts of non-reacted metallic sodium in locations where it is difficult to gain access, such as bolted junctions. This final phase is avoided when possible, because it generates a large volume of radioactive liquid effluents.

4.6.2. Steam under vacuum process

The principle consists of making cold steam to react the sodium by heating a water reserve at the bottom of the pit to 60-80°C. A variant is based on partial vacuum and the presence of carbon dioxide to limit risk of corrosion, allowing constant transformation of sodium hydroxide into carbonates with no corrosive action.

This process is advantageous because the reaction with steam is efficient for removing sodium, particularly in areas where it is difficult to gain access.

However, the probability of uncontrolled air ingress and reaction with hydrogen is greater with a pit under vacuum. Another disadvantage is that the steam generation cannot be stopped immediately if required.

In France, the cleaning pits of Rapsodie and former versions of Phenix were based on such a process.

In Russia the cleaning pit of BOR-60 is based on water injection into evacuated vessels loaded with washed components. Vacuum is maintained by automatic vacuum pumps.

4.6.3. Carbon dioxide bubbling process

Since 1994 the process used in Phenix cleaning pits has been modified as follows to keep them always at positive pressure:

- A small quantity of water is introduced at the bottom of the pit;
- Carbon dioxide is injected at the lowest point of the pit and bubbles throughout the water; and
- The bubbling causes the gas to transport humidity that flows and reacts with the sodium adhering to the component wall.

Between 1994 and 1999, five intermediate heat exchangers and three primary pumps were cleaned at Phenix by this process for reuse or final disposal.

4.6.4. Water mist process

With this principle, a water mist is produced in the pit through nozzles placed on ramps along the pit wall. The carrier gas can be nitrogen, carbon dioxide or both. Sodium is progressively neutralized by reaction at ambient temperature with the mist made of a mixture of small water droplets and carrier gas. The chemical reaction of sodium and water mist is the following:

$$Na_{solid} + H_2O_{in\ excess} \rightarrow NaOH_{aqueous} + \tfrac{1}{2} H_2$$

When CO_2 is present, aqueous sodium hydroxide produced by this reaction is transformed to sodium carbonates. Hydrogen is released in the ventilation duct after filtration and dilution. During the chemical process, the cleaning pit is kept under inert gas (carbon dioxide or nitrogen). The process is controlled by adjusting the density of water in the mist as a function of the concentration of hydrogen released from the cleaning pit before dilution. In normal operation, the percentage of hydrogen is always lower than 1%.

During operation, the pit is always kept at a slightly positive pressure, and the temperature remains close to ambient. The mist injection is stopped as soon as the carrier gas admission is cut off, so the process is well controlled.

This process was applied at Rapsodie during its operational time and during its decommissioning. The SuperPhenix cleaning pits are based on this process. They will be employed during reactor decommissioning, especially to treat unloaded core subassemblies and primary components before dismantling and final disposal.

4.6.5. Steam cleaning

At PFR there are two sodium decontamination facilities. The larger of these can accommodate primary circuit components such sodium pumps, intermediate heat exchangers, pump valves and the fuel charge machine.

The cylindrical vessel dimensions are 2.5 m diameter by 10 m deep. Steam and nitrogen are introduced to the vessel by means of concentric arrays of nozzles that can be positioned to direct steam appropriate to the item being decontaminated. Following the steam-cleaning phase, the item is then water washed and the effluent discharged to the active effluent treatment plant, where it is conditioned prior to disposal.

The small facility is a stainless steel booth approximately 3 m x 2 m x 2.5 m. In this facility, smaller items may be decontaminated using a conventional steel lance.

In JOYO, small components, such as small valves and small diameter pipes, control rods and pumps, are cleaned by the mixture of steam and nitrogen gas.

4.6.6. Superheated steam/nitrogen process

The superheated steam/nitrogen process has been used at Fermi-1 for reaction of the residual sodium in the secondary circuit and will also be used for its primary loops. Superheated steam is injected into the systems using nitrogen as the carrier gas. The systems are at ambient temperatures when the process is initiated, but the steam and the exothermic reaction of the steam with sodium heats the system above the melting point of sodium. The molten sodium then reacts with the steam, forming a solution of sodium hydroxide. Fermi-1 has been successful in reacting the entire amount of residual sodium in the secondary circuit, and a water flush of the system has been performed after the steam/nitrogen process. This decontamination process of the secondary system was completed in 2001.

This process has also been used on components removed from the systems at Fermi-1. Sodium wetted components have been placed in a vessel where the superheated steam/ nitrogen mixture has been introduced. Similar successful results have been achieved.

KNK has installed a steam/nitrogen process in the washing plant. Steam is injected at 200ºC into a stream of nitrogen.

4.6.7. Ethanol process

At EBR-II, a Sodium Components Maintenance Shop (SCMS) has been constructed to remove sodium from reactor components that will be reused. Sodium removal is accomplished by the use of denatured ethyl alcohol to clean components that may be damaged if cleaned with steam or water. This cleaning system is capable of cleaning small components, such as valves and traps, and has the capability of cleaning large components, such as primary coolant pumps and intermediate heat exchangers. Fig. 5 shows a simplified cleaning system flow diagram. Both of the EBR-II primary pumps have been cleaned in this facility prior to maintenance and reinstallation into the reactor. The reaction of the sodium with alcohol produces sodium ethoxide and hydrogen.

A process for recovery and reuse of the alcohol also exists at the SCMS. This process uses thin film evaporator technology and produces a sodium carbonate slurry waste form. During the process, ethyl alcohol is evaporated, condensed, and reclaimed for reuse in the system. Fig. 6 provides a sodium carbonate process flow diagram for reclaiming the ethanol.

In JOYO, the fuel gripper of the fuel handling machine is cleaned by a mixture of ethanol and isopropyl alcohol.

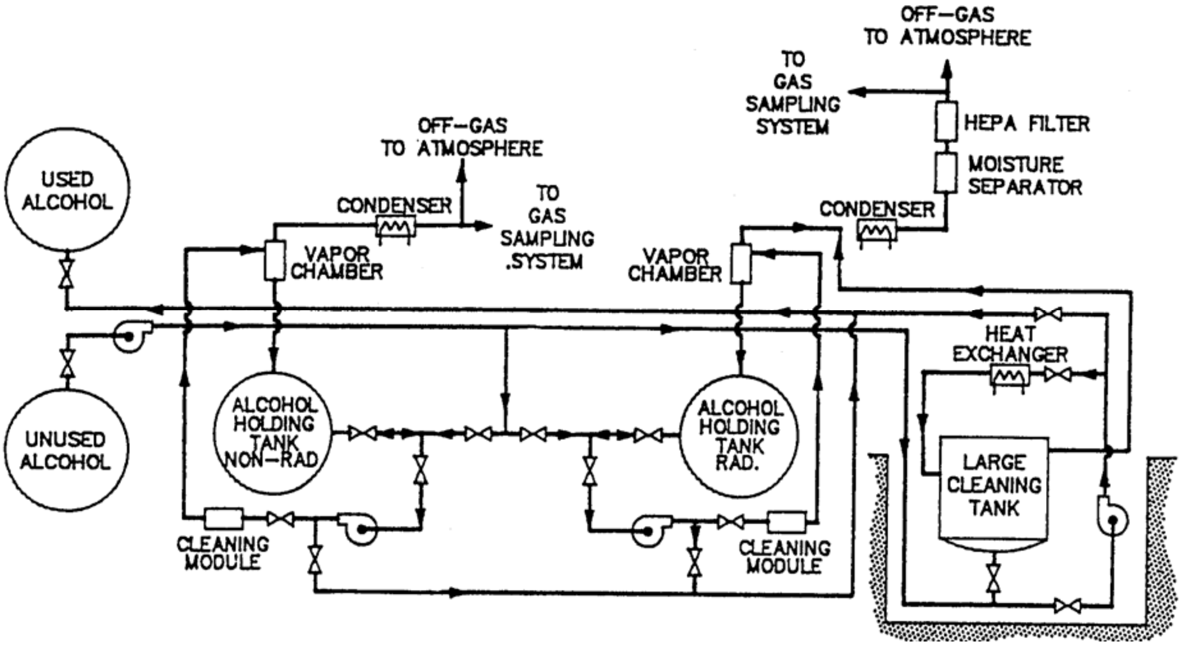

FIG. 5. Ethanol process sodium removal system flow diagram.

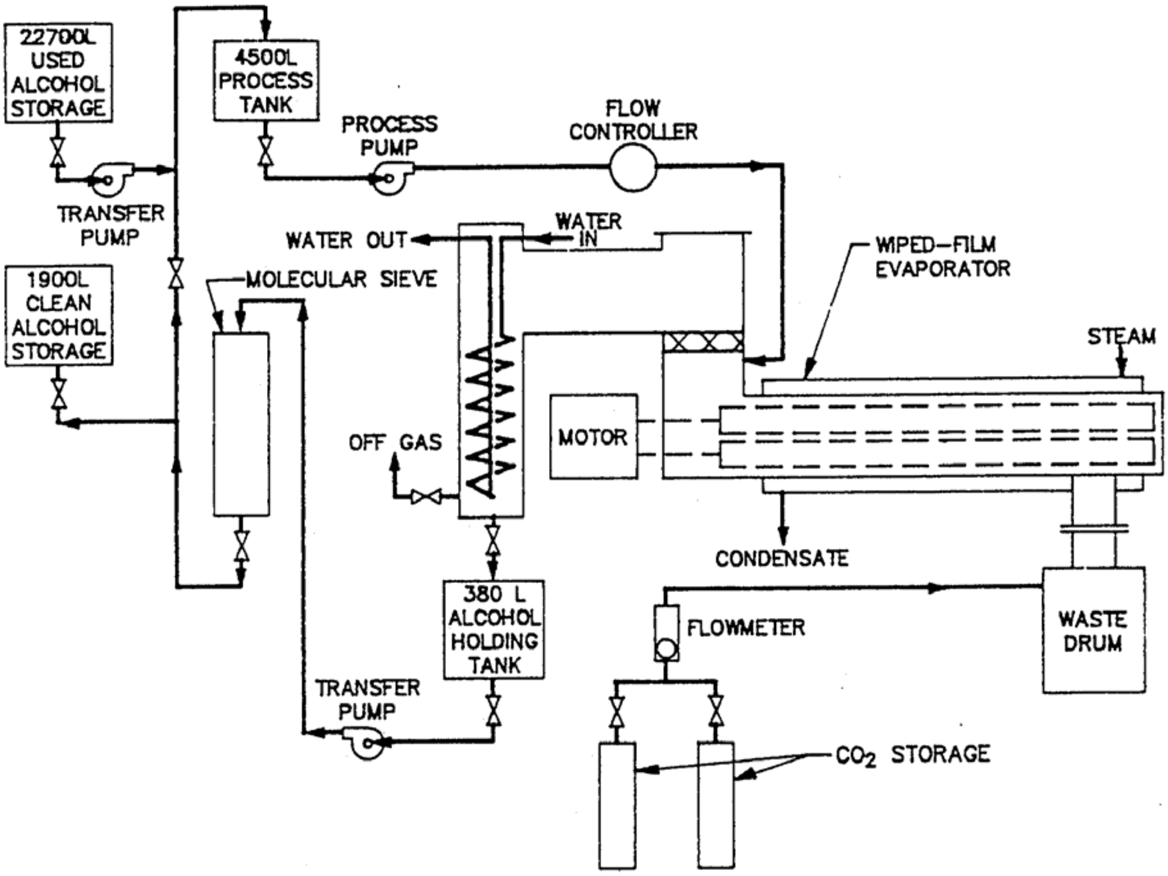

FIG. 6. Alcohol recovery process flow diagram.

4.6.8. Other techniques

4.6.8.1. Development of the Melt Drain Evaporate Carbonate (MEDEC) process

Argonne National Laboratory West (ANL-W) has been involved in the development of the MEDEC (Melt Drain Evaporate Carbonate) process for sodium removal since the late 1970s. This MEDEC technology has proven to be effective for removing sodium, including sodium lodged in crevices or annular chimneys. Two similar studies, produced by Westinghouse in 1979 and Rockwell International in 1980, corroborated Argonne's assessment, namely that MEDEC is an effective technology for sodium cleaning [25, 26].

The development of the MEDEC technology was formally initiated in 1979 with the inception of the Sodium Process Demonstration. The early MEDEC tests optimized the vessel design, heating requirements, seal design, and vacuum requirements. The process cycle involved loading the sodium-containing component into a vessel and heating the vessel to 200°C at ambient pressure to allow the sodium to melt and drain. Next, the temperature of the vessel was raised to 500°C, and a vacuum was applied to vaporize the remaining sodium. The recovered sodium was then treated. Several test campaigns, performed in the early 1980s [27], demonstrated that the MEDEC process was capable of removing sodium from crevices 20 cm deep and from a slot 5 cm long and 0.1 mm wide. Sodium was also effectively removed from mating bolt and nut threads. Sodium vapour conductance tests were performed that demonstrated MEDEC was capable of removing sodium from internal pockets through channels several feet long. The processing of non-irradiated blanket elements followed these tests. Blanket elements were examined in an analytical laboratory before and after processing and were found to be free of sodium. An EBR-II, a cold trap was also successfully cleaned.

With completion of the test campaigns, full production scale operations were initiated. During the course of production operations, sodium was removed from nearly 3500 fuel elements.

More recently, ANL-W has been involved in evaluation of the MEDEC process for treatment of 34 metric tonnes of Fermi-1 blanket fuel. During the first year of this study, a testing campaign was completed that demonstrated the MEDEC process was very effective in removing the elemental sodium from both radial and axial blanket fuel elements.

4.7. TREATMENT OF SODIUM MIXED WITH OTHER WASTE

Special processes have been developed for treatment of sodium mixed with other waste material:

- Metallic items containing significant quantities of non-drained sodium, which can be directly exposed to process reagents; for example, after being cut or dismantled;
- Sodium waste containing oxides, hydrides, various reaction products or pollutants, and debris;
- Drummed sodium and mixed waste; and
- Caesium traps.

4.7.1. Water spraying process

The principle of the water spraying process is similar to processes used in some cleaning pits of LMFR. Sodium or sodium containing waste is sprayed by water, reacting with sodium.

The reaction should be performed in a closed vessel that can be opened for introduction of a batch of waste. Wastes are placed in a basket made of perforated metallic sheets to give access to sprayed water. The spray system consists of ramps of upward-orientated nozzles located at the bottom of the vessel underneath the basket. Wastes are arranged and clamped in the basket in such a way that sodium faces the nozzles as much as possible. Such an arrangement, together with locating the nozzles underneath the basket, facilitates sodium hydroxide evacuation and avoids formation of retained pools and strong reactions between water and sodium. In addition to water injection, the nozzles allow inert gas injection, resulting in local cooling and effective sweeping of the reaction area.

The resulting sodium hydroxide solution is drained into a separate collection tank for further processing. Generated hydrogen is vented via an off-gas line. The control of the reaction is done by on-line measuring of hydrogen concentration in gas release and controlling the water flow rate. Inert gas is partly vented together with an off-gas and partly filtered and recirculated.

A facility based on the water spraying process has been realized in France and is operated by CEA to process sodium containing waste resulting from sodium fire experiments. Similar equipment will be a part of the future radioactive sodium waste treatment facility of the CEA called ATENA.

4.7.2. Other techniques

Some of the processes or techniques applicable to neutralization of sodium or to washing of components are also applicable to the treatment of sodium mixed with other waste. Such are the cases of burning sodium in air in a special furnace, described in section 4.3.4.2, or using the water–vacuum method or superheated/nitrogen process described in Subsections 4.6.2 and 4.6.4 respectively.

4.8. POTENTIAL REUSE OF SODIUM

The potential for reuse of sodium from reactors is limited. The most likely utilization would be as a reactor coolant, but there are currently no LMFRs being constructed in countries where sodium waste is available. Transport of radioactive sodium across international borders raises regulatory issues, often making such transports unfeasible.

Another application for the reuse of sodium is the solvated electron technology (SET) process introduced by a firm in the USA for destruction of some halogenated compounds. Solvated electron is a strong reducing agent, generated in the process of dissolution of an alkali metal, such as sodium, in liquid ammonia. Although this process has been successfully demonstrated, its applications are limited and would consume only a small fraction of the sodium that exists in LMFRs. Moreover, only sodium with a low specific activity is considered for this process.

5. FINAL MANAGEMENT OF TREATED SODIUM WASTE

5.1. GENERAL ASPECTS

This section concerns only liquid and solid effluents arising from sodium waste treatment processes identified in section 4.

Gaseous effluents arising in sodium waste treatment processes are not a subject of this publication. They are generally filtered using classical filtration processes and released in accordance with applicable regulations. In some cases, gaseous effluents resulting from the treatment of waste containing a significant proportion of tritium, i.e., cold traps, are processed by water scrubbing or undergo catalytic oxidation, both resulting in tritiated water that is then stored or further processed.

A few processes are aimed at direct transformation of sodium waste in solid phase reactions to solid sodium compounds (e.g. section 4.3.4.1), which could be stored in a radioactive waste management facility or disposed, depending on the law in force in each country. However, they have not reached wider industrial application and, therefore, for a majority of sodium waste treatment processes, effluents are generally liquids or humid solid residues. They contain sodium hydroxide, carbonates, alkaline salts or a mixture of these compounds.

The disposal aspects of these wastes should be analyzed with care, given that no large-scale specific studies have been carried out yet. The environmental impact assessment, potential release to the biosphere, and impact on the disposal site performance will probably require specific studies, especially in the case of managing the large amount of sodium waste involved in the decommissioning project of large power reactors.

5.2. TYPICAL CHARACTERISTICS OF SODIUM WASTE TREATMENT PRODUCTS

The majority of alkali metal waste treatment processes include phases of neutralization and/or separation of alkali metal from its support (the metal surface). In these operations, liquid radioactive waste is generated.

This category of waste is in some aspects similar to those generally arising from decontamination or waste treatment operations in the nuclear industry. However, the caustic content of this waste is sometimes very high, and this causes difficulties in the further processing. Specific processes must sometimes be developed for its conditioning for final disposal.

The liquid wastes are generally aqueous, but in some countries where alcohol-based processes are permitted, alcohol-based effluents should also be considered.

It should be noted that the volume of generated liquid waste is generally much larger than the original volume of the metallic sodium. This is particularly relevant for bulk sodium processing when large quantities of metallic sodium are treated using aqueous processes. In some cases, concentration processes, such as evaporation, are used to reduce the volume of the ultimate waste.

For SuperPhenix bulk sodium processing, it is envisaged to neutralize about 5500 metric tonnes of sodium using a water based process. This will generate about 24.000 m^3 of 10 mol/L sodium hydroxide.

Treatment of 350 metric tonnes of sodium at EBR II using a water based process resulted in 900 m^3 of 30 mol/L sodium hydroxide.

The radionuclide inventory of these wastes is clearly linked to the initial radioactivity of the metallic sodium that has been treated.

For bulk sodium treatment by aqueous processes, the radioactive inventory in the liquid waste is determined by the dilution factor, except for tritium which is present in a large proportion (>70%) with the gaseous effluent.

Due to concentration effects, the radioactive inventory of the sodium retained on the reactor primary circuit components is generally higher than for bulk sodium. Moreover, the washing process can also have a selective decontamination effect for release of particular radionuclides from surface layers of the components. In some cases, decontamination of the components can also be considered simultaneously with washing of sodium layers. The aim is to decrease the activity level of the component to facilitate its further dismantling and final conditioning as metallic waste. Consequently, the radioactive inventory of liquid effluents generated during washing of sodium wetted primary components can be significantly higher than for the waste generated during treatment of the bulk metallic sodium.

For examples of the radioactive inventory in liquid effluents from washing of primary components and refuelling machines of selected LMFRs is in Table IV.

TABLE IV. EXAMPLES OF RADIOACTIVE INVENTORY IN LIQUID EFFLUENTS FROM WASHING OF PRIMARY COMPONENTS
(estimated activity concentrations in Bq/L)

Component	^{22}Na	^{54}Mn	^{60}Co	^{134}Cs	^{137}Cs	^{3}H	^{90}Sr
Phenix primary pump (at reactor shutdown date)	3.4 10^3	5.0 10^4	1.5 10^3	1.3 10^4	2.4 10^6	7.1 10^7	-
BN-600 primary pump (Waste volume 200 m^3)	2 10^2	1.5 10^6	7 10^2	3 10^4	3 10^5	5 10^2	1 10^2
PFR refuelling machine (Waste volume 22 m^3)	2.1 10^2	1.7 10^4	6.9 10^3	2.2 10^4	2.8 10^5	3.1 10^5	-

5.3. POTENTIAL REUSE OF TREATED SODIUM WASTE

An interesting and cost effective end destination for the caustic effluents from sodium waste treatment would be to find a reuse in the nuclear industry. There are two main potential routes for reuse:

- Neutralization of acidic effluents produced at the nuclear sites (electricity generation, fuel reprocessing, military and research facilities); and
- Decontamination of highly radioactive nuclear facilities during their dismantling.

Unfortunately the use of radioactive caustic solutions requires the nuclear site operators to adapt their caustic solution handling facilities to comply with nuclear specifications. For that reason, the operators are sometimes reluctant to accept the radioactive caustic solutions even if they are free of charge.

An additional issue is transport of the caustic solutions from one site to another. Special tank trucks or rail wagons must be used, and they must be approved for this application by the country's transportation regulatory department. Systems for the loading and off-loading of the caustic product from the vehicles require further design and testing. Therefore, the total cost for the transportation option could be high and prohibitive.

For example, some 180 m^3 of 10 mol/L sodium hydroxide, generated by treating 37 tonnes of primary sodium of reactor RAPSODIE were used to neutralize radioactive acidic effluents at LaHague reprocessing facility.

Another example is a proposal to use sodium hydroxide generated by treatment of primary and secondary sodium of FFTF to neutralize acidic wastes at the Hanford site. The Hanford site has identified the need for quantities of sodium hydroxide exceeding the amount to be produced by the FFTF sodium processing by greater than a factor of 10. A cost/benefit analysis was performed to determine the feasibility of building a facility at FFTF to react the sodium on-site versus transporting the sodium to Argonne National Laboratory West for processing. The analysis, including the costs of transporting the sodium and returning the sodium hydroxide product, showed favourable cost savings for processing the sodium at ANL-W.

5.4. MINIMIZATION OF TREATED SODIUM WASTE ACTIVITY

In some cases, decontamination of liquid effluents is required before their final processing. The reasons can be to simplify conditioning operations with regard to radiological protection measures or to decrease the activity of radionuclides to make the product acceptable with regard to the final repository specifications.

Another reason for implementing the decontamination process is to prevent the release of effluents to the environment. In this case, precise and demanding regulatory specifications must be respected. In addition, specific radionuclides may need to be removed from the effluents before release to the extent possible by available technologies.

Radionuclides present in effluents resulting from primary sodium waste treatment include caesium (especially ^{137}Cs), which is a major contributor to the gamma activity if it is not removed from the sodium metal before treatment. Caesium removal from sodium hydroxide effluents is difficult due to high concentration of sodium ions (10 mol/L and more). Classical techniques are not applicable due to the similar chemical behaviour of both caesium and sodium ions. There is strong competition between them, and they are difficult to separate. Processes based on iron-cyanide precipitate ($K_2NiFe(CN)_6$), inorganic ion exchangers, or organic ion exchange resins are not well adapted.

Various technologies and processes exist in the nuclear industry to remove radioactive elements from liquid effluents. They are based on filtration, chemical co-precipitation, ion exchange, and other principles.

5.4.1. Caesium removal from saline solutions

The most efficient process for caesium removal from neutralized saline solutions is based on ion exchange on selective ion exchange materials. The copper-iron-cyanide based exchangers are among the materials promising the best results. By circulating NaCl based effluent (approx. 5 mol/L, containing about 1.000 kBq/L of ^{137}Cs) through the column filled with the ion exchanger, the activity of ^{137}Cs was decreased to less than 2 kBq/L. The volume ratio of effluent to ion exchanger was about 1.000.

However some of the tested materials have a bad mechanical resistance, which may lead to plugging of the columns. In addition, the selective ion exchange material is very quickly saturated, and since the process is irreversible, it must be replaced. The volume of the produced waste is below 2% with regard to the effluent volume.

A caesium decontamination plant based on ion exchange principles has been constructed in the UK and is operational. The purpose is to treat saline effluents produced by the PFR sodium processing plant before release into the sea. The ion exchange media is potassium hexacyanocobalt (II) - ferrate (II). Some operational difficulties have been encountered due to flow constraints through the ion exchange media. This required the frequent (monthly) replacement of the ion exchange column. Early indications suggest that the flow restriction is caused by impurities in the neutralized effluent attributable to high levels of iron (approximately 360 ppm) in the bulk sodium and in the neutralizing hydrochloric acid (approximately 10 ppm). This has resulted in the deposition of between 200 and 1800 grams of ferric hydroxide in the ion exchange media per day. An experimental program has been commenced to solve this problem.

5.4.2. Caesium removal from sodium hydroxide solution

A process has been developed in several countries (e.g. in USA and France) and is based on liquid/liquid extraction techniques using a selective carrier. A selective carrier is a molecule that is able, due to its geometry and dimensions, to trap the targeted element (i.e. caesium) and extract it from the solution.

The extracting molecules (extractants) studied in France are mainly the ‘Calixarenes’. They are cyclic molecules formed by benzene cycles linked by methyl groups that can feature various dispositions, e.g. alternate, cone, crown. For the selective extraction of caesium from caustic solutions, a crown Calixarene molecule has been selected. It is composed of four benzene units. One of the main advantages of this extractant, is that it is produced industrially. Laboratory trials have shown an impressive effectiveness of this extractant, and the results are very promising.

Extracting technologies have been tested using centrifugal extractors and membrane techniques. The latter appears to be the most promising extraction technology.

In the case of the membrane technique, two aqueous phases circulate on each side of a membrane impregnated with selective extracting molecules (supported liquid membrane). On one side is the sodium hydroxide containing caesium and on the other side is demineralized water. The extracting molecule traps the caesium and moves it through the membrane due to the effect of chemical potential difference. Caesium is released at the demineralized water side, and the extractant molecule returns on the other side (its chemical potential has been modified) to trap caesium. In theory, the process does not consume the extractant. The demineralized water containing caesium is subsequently concentrated and processed as a high activity waste.

In the Russian Federation, natural zeolites (klinoptilolite) or artificial zeolites (molecular sieves) are used for ^{90}Sr and ^{137}Cs trapping in a dynamic column for a 1 to 10% hydroxide solution. Concentrated solutions should be diluted and neutralized before decontamination. About 3 kg of absorbent is needed to decrease the activity of 1 m^3 from 10^3 kBq/L to 10 kBq/L (radiation safe level). The maximum adsorption capacity is 0.3g of caesium per 1g of adsorbent. The dynamic decontamination factor in one adsorbing column is about 100-2000 for a 1 to 1.5% solution with an initial specific activity about 7.10^4 kBq/L [28]. Sorbent is then solidified along with astringent components forming 3 L of cement stones per cubic meter of decontaminated liquid wastes. Thus the efficiency factor of waste volume diminution is about 300. Components of astringent systems include slag, clay component, adsorbent, and alkali solutions. The most effective is sodium silicate solution, also called liquid glass.

5.4.3. Strontium removal

Chemically modified by sodium ions, natural zeolite (klinoptilolite) is used in Russia in adsorbing columns for ^{90}Sr separation from sodium waste solutions. Alkali solutions should be neutralized before sorption and diluted down to concentrations not exceeding 100 g/L of salts. Sorption is effectively increased by increasing the pH of solutions into the range 8 to 14.

Testing of ^{90}Sr sorption from solutions containing 13 g/L of salts, with pH 8 and specific activity 1.5×10^4 kBq/L reveals in three successive columns a summary decontamination factor of about 10^6 for an overall sorbent volume equal to about 1.3% of solution volume [28].

5.5. DISCHARGE OF TREATED SODIUM WASTE

When sodium waste effluents are of negligible radioactivity levels, a direct release through the site discharge system to the environment (sea or river) in accordance with authorized discharge limits can be envisaged. A minimum treatment could still be required, such as neutralization by acid to neutral pH (see section 5.6.3) or decontamination in accordance with the ALARA principle. This is the case in the UK, where effluents of the PFR sodium processing plant are neutralized and decontaminated before release into the sea.

Environmental impacts of the chemical components of discharged saline aqueous effluents must be also considered in accordance with statutory regulations. The choice of an appropriate acid for the neutralization offers flexibility in assuring minimal environmental impact, e.g. sulphates in rivers, chlorides in the sea. Carbonates have a very low impact, but their solubility is lower than that of other salts. They may also crystallize and make deposits, resulting in hot spots of radioactivity reaching unauthorized levels.

However, even when the activity content is far below the authorized limits and the environmental impact is negligible, release to the environment still tends to be decreased because of the growing public concern with regard to any effluent release.

Apart from the treatment of bulk sodium coolant from reactors, the volume of operational sodium containing effluents is generally consistent with the capacity of the standard effluents treatment facility of the nuclear site where they are produced. In this case, the sodium treatment effluents often follow the same route as other liquid wastes produced on the site. As these wastes are mainly aqueous, they may be concentrated by evaporation and subsequently incorporated in cement or other classical matrix and before being to a repository.

Depending on the regulations applicable to the concerned country or state, it is sometimes possible to send effluents to another nuclear site with adequate treatment capacity and license.

5.6. CONDITIONING FOR STORAGE OR DISPOSAL

5.6.1. Conditioning of sodium hydroxide

5.6.1.1. Drying solidification

Hydrated sodium hydroxide is in a solid state below 60ºC when the concentration is more than 70 wt %. If sodium hydroxide is produced at concentrations below 70 wt %, it can be dried to increase its concentration so that it would form a solid at room temperature. In the USA, the sodium hydroxide from converting the 680 m^3 of sodium from the Fermi-1 and EBR-II reactors was produced at a concentration of 70 to 72 wt %. This caustic substance was loaded into 270 L barrels that were lined with a 2.5 mm layer of polyethylene. The barrels were sealed with a polyethylene plug and capped with a standard barrel cap and a V-groove clamp. When this product cooled, it formed a crystallized sodium hydroxide monohydrate and was shipped to a radioactive waste management complex for disposal.

Because of the water affinity of the solid product and the corrosive property of the product in aqueous form resulting in the potential for leakage of the corrosive product and spread of contamination, the envelope of the container must guarantee leak tightness for the long term to prevent any moisture ingress.

5.6.1.2. Cementation

The main advantage of the cementation process is that it can be implemented using cementation plants that already exist in numerous nuclear sites for radioactive waste conditioning. However, direct incorporation of sodium hydroxide in classical cement is not envisaged and has only been subjected to preliminary tests. Development of special cement composition still needs some R&D work.

The cementation of sodium hydroxide can be carried out using a cement that is rich in slag. The mixture obtained is highly viscous and difficult to pour. However after hardening, the mechanical strength is good and the method appears to be feasible [29]. A development plan is currently in progress with the aim to qualify a cement composition suitable for industrial application.

The degree of sodium incorporation in the cement varies between 80 and 150 g of Na/L depending on composition. For a conventional 400 litre drum, cementing allows incorporation of at least the equivalent of 32.4 kg of sodium. However, this would result in a net increase in waste volumes of up to a factor of ten.

Industrial application of cementation is envisaged in France for conditioning effluents from the future ATENA facility, which will process radioactive sodium waste of CEA, and also for cementation of effluents coming out of SuperPhenix reactor sodium treatment. The end product is often referred to as "sodacrete".

Japan is developing a solidification method for radioactive alkali waste, characterized by adding a granulated blast furnace slag to a radioactive alkali waste and solidifying it. Based on the small scale test, the maximum sodium in the 200 L drum will be about 50kg, or a net increase in waste volume of a factor of four.

5.6.1.3. Conditioning in a ceramic matrix

The principle of the ceramic matrix process developed in France involves transforming sodium hydroxide into a stable ceramic material called Nephelin (chemical composition $NaAlSiO_4$) by thermal treatment with mineral additives. Nephelin has a low solubility and, therefore, is suitable for disposal in a nuclear waste repository. Significant reduction in waste volume is achieved in the process.

The process is realized in four steps. In the first step, aluminum oxide (Al_2O_3) and silicon oxide (SiO_2) are mixed with a sodium hydroxide solution. In the second step, water is eliminated, and the product is calcinated at a temperature between 600 and 800°C. A powder mixture of amorphous oxides is obtained.

In the third step, the powder is pressed at about 1000 bar into pellets or slabs. Pellets are sintered in the fourth step at around 850°C. The resulting ceramic is a dense product composed of small crystals.

The Nephelin pellets can be loaded in drums and disposed of at the radioactive waste repository. Starting with a 400 g/L sodium hydroxide solution, the Nephelin process enables stabilization of the equivalent of 113.2 kg of sodium in a conventional 400 litre drum. The incorporation rate (waste volume efficiently) is about two to three times greater than incorporation in cement [29] and slightly greater than the maximum expected efficiency of Japan's slag solidification process.

Key steps of the Nephelin process have been tested and validated. However, this process has not yet been implemented on an industrial scale.

In addition, it should be noted that the process described in paragraph 4.3.4.1. is also fully applicable for conditioning of sodium hydroxide.

5.6.2. Conversion into dry carbonates

Theoretically it is possible to convert liquid effluents from sodium waste treatment into sodium carbonates as a final product. Since the main component of effluents generated in sodium waste treatment is aqueous sodium hydroxide, it can be converted into carbonates by reacting with CO_2. The reactions are:

$$NaOH + CO_2\ (+nH_2O) \rightarrow NaHCO_3\ (+nH_2O)$$

$$NaHCO_3 + NaOH\ (+nH_2O) \rightarrow Na_2CO_3 + H_2O\ (+nH_2O)$$

$$Na_2CO_3 + CO_2 + H_2O \leftrightarrow 2\ NaHCO_3$$

Carbonates are chemically stable, and they can be dried and poured directly into appropriate containers. If necessary, they can be conditioned using appropriate technology and then disposed in a repository. This is particularly interesting for large quantities of effluents, e.g. effluents resulting from bulk reactor coolant processing. The incorporation rate can be as high as 300 g of sodium equivalent per litre of final waste, representing a net waste increase factor of about 3.5. Nevertheless, carbonates are not accepted everywhere for disposition as an ultimate radioactive waste form, e.g. they are not accepted in some states of the USA.

However, difficulty appears in the full industrial scale application of this technology. A rotating thin film evaporator was tested at ANL-W without success (see section 4.3.2.2), and the carbonate route was finally abandoned. Other technologies could probably be envisaged but would also require an industrial validation.

Another disadvantage is that the carbonates produced by such processes are generally in the form of a light powder that could lead to radioactive contamination spreading.

5.6.3. Conversion into dry sodium salt

Aqueous sodium hydroxide produced by the treatment of sodium waste can be neutralized by mixing with an acid, yielding a saline solution of neutral pH. Neutralization of a base by an acid is commonly used in the chemical industry and does not need specific development. The operation is generally realized in two steps:

[1] Neutralization by an acid until the pH is between 10 and 13; and
[2] Adjustment of the neutral pH with diluted acid.

Several commonly available acids can be used for the neutralization. Typical examples are hydrochloric acid (37%), sulphuric acid (95%), phosphoric acid (80%), and nitric acid HNO_3 (63%).

Crystallization/drying of saline solutions is another classical industrial operation. A possible technology is based on two steps: evaporation with follow-up centrifugation. In this case the humidity content of the dry salt is on the order of 3%. Depending on the requirements for the final product, a lower humidity content can be reached with supplementary drying operations (calcination).

Conversion into dry salt offers the advantage of producing a final product with better chemical stability than sodium hydroxide. In addition, the incorporation rate of equivalent sodium metal in the final waste would be interesting, probably of the same order as with carbonate when compared to processes using a binding compound such as cement.

The choice of the acid depends on the ultimate destination of the salt. For long term storage in a radioactive waste repository, sodium chloride is not recommended and probably would not meet repository acceptance criteria because of its corrosive properties.

In spite of promising features of this technology, there is still no identified experience of acceptance of dry salt as an ultimate radioactive waste form for long-term storage or disposal. One option is to use special high integrity containers; however, long-term behaviour and properties of the container would have to be demonstrated.

5.6.4. Conditioning of sodium alcoholate

After alcohol treatment of radioactive sodium waste, a radioactive solution of sodium alcoholate is generated. This solution as an organic waste cannot be further processed at a standard effluent treatment facility, constructed for treatment of aqueous effluents.

A special facility should be constructed for processing of alcoholic (organic) waste. One of the most favourable options is incineration, resulting in carbon dioxide, water and ash containing most of radioactive components.

As described in section 4.6.7, ANL-W has a facility for removing sodium products from the alcohol stream using the conversion of the sodium-to-sodium hydroxide, reaction with carbon dioxide, and evaporation of the alcohol for recovery. The resulting slurry of sodium carbonate and alcohol is then processed for final disposal.

5.7. CONDITIONING OF CAESIUM TRAPS

The safe processing of caesium traps is related to the problem of managing residual sodium in the trap removed from the reactor. Preparing caesium traps for final disposal requires either fixing the sodium residuals in a form that will not cause vigorous interactions with water and air or completely removing sodium from the trap. In the latter case, it is important to assure the minimum release of adsorbed caesium from the trap.

Various procedures have been considered in preparing highly active caesium traps for disposal. If distillation of residual sodium and alcohol or water cleaning is implemented, significant caesium activity is lost from traps and new radioactive waste is generated, requiring further processing. Experimentally it was demonstrated that about 5 to 30% of caesium adsorbed on graphite in the trap was released together with sodium under vacuum distillation or was dissolved into a solution under alcohol cleaning.

Filling caesium traps with molten lead was found to be an appropriate conditioning technology. This method has advantages of smooth interaction of lead with sodium and the formation of alloys and chemical compounds of Na_nPb_m type. Lead is also characterized by corrosion neutrality toward steel at temperature up to 500°C. Experiments with filling traps in a container were performed at temperatures as high as 500°C. Molten lead lightly penetrates into the inter-granule volume of the graphite, and free space between graphite granules completely fills with solid lead. The release of caesium isotopes involved in the graphite granules was measured after saturation of lead with caesium and sodium after 90 minutes exposure at temperatures from 350 to 500°C. The amount of released caesium from graphite into molten lead was estimated to be 8 to 12 %. Caesium release from the surface of molten lead in aerosol form was found to be negligible. Filling with lead also decreases the gamma-radiation dose from high active traps and provides for the safe storage of graphite traps at the decommissioning site.

Thus, the following procedure for spent caesium trap conditioning may be considered: (1) After removing primary circuit sodium, the trap should be placed in the container with molten lead and then frozen. (2) After solidification, a lead plug should be provided to prevent release of sodium to the environment. (3) In this case, sealing the container is not required.

This method of filling caesium traps with lead was tested and used at the BOR-60 and BN-600 reactors. After primary sodium removal, the traps were installed in jackets designed for storage of spent fuel assemblies and filled with molten lead. Upon solidifying, the lead filled traps were placed in the pool with spent fuel assemblies. These caesium traps have been safely stored at BOR-60 and BN-600 since 1984 and 1986, respectively [13, 30].

6. CONCLUSIONS AND RECOMMENDATIONS

Management of radioactive alkaline metal waste (sodium and NaK eutectic) represents a specific challenge during the maintenance and decommissioning of LMFRs. Technologies are continuously developing and improving to respond to site-specific situations encountered at the particular LMFR sites. The treatment and conditioning methods presented in this report are not all encompassing but present the best available technologies at the time of issuance.

The following conclusions and embedded recommendations apply:

(1) Radioactive sodium waste treatment falls into three major categories: bulk sodium, residual sodium, and sodium containing mixed waste.

(2) Two proven technologies have been presented for the treatment of bulk sodium: the NOAH process used at Rhapsodie and PFR, and the Argonne process used for EBR-II and Fermi-1.

(3) Batch processes are generally preferred for treatment of relatively small quantities of sodium; they do not require the capital outlay of a continuous process.

(4) Residual sodium treatment has been successfully applied in many countries. The water vapour/nitrogen and superheated steam/nitrogen processes have been widely used, resulting in sodium hydroxide and hydrogen generation. Another technique being applied is the carbonation method, where residual quantities of sodium are reacted with moist carbon dioxide to produce a benign sodium carbonate compound along with hydrogen. Since hydrogen is generated during these processes, it must be carefully monitored in order to avoid hydrogen fire or explosion. Vacuum distillation process is also available, but the vessel containing sodium must be capable to withstand a vacuum applied in this process.

(5) Alcohol can be used to remove residual sodium from components. Alcohol has the advantage of not causing stress corrosion cracking of the components being cleaned, therefore it is generally applied to equipment that will be reused. Light alcohols, such as ethanol, are generally used for this process in the United States and Japan. The use of heavy alcohols has been banned in Europe due to accident events.

(6) Sodium and NaK wastes can be treated in several ways. The most common is to react the sodium with moisture in a controlled environment in order to avoid fire or explosion of the hydrogen generated during the treatment process.

(7) Storage of materials contaminated with sodium or NaK is not recommended. Removing the hazards associated with the alkali metal by using the treatment methods reviewed in this report may well eliminate risks of later reactions and hazardous substances.

(8) Special applications are still under development for handling various sodium contaminated items such as cold traps and caesium traps. These provide special challenges due to the elevated radiation levels associated with them and the difficulty of accessing the sodium or NaK contaminants.

(9) Conditioning of sodium waste for final storage or disposal depends on local regulations. Methods such as drying, solidification, and discharge after removal of the main radionuclides have been qualified and proven, but they are not universally accepted by regulatory authorities. Other methods, including conversion into carbonate and conditioning in cement, are still being developed.

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