IAEA-TECDOC-1579

New Developments and Improvements in Processing of ‘Problematic’ Radioactive Waste

Results of a coordinated research project
2003–2007

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FOREWORD

Radioactive waste, with widely varying characteristics, is generated from the operation and maintenance of nuclear power plants, nuclear fuel cycle facilities, research laboratories and medical facilities. These wastes must be treated and conditioned as necessary to provide waste-forms acceptable for safe storage and disposal. Of special interest in this regard, is a category of wastes termed “problematic wastes” - wastes for which safe, efficient and cost effective methods for processing are not readily available. For the purposes of this report, these “problematic wastes” are defined as those for which:

- the technologies for the treatment of the waste types had not been established for routine waste management, or

- the waste-type failed to meet criteria for acceptance for processing by technologies generally available at the local level.

In this report, processing options for a total of 27 problematic waste streams that were identified and addressed by the individual laboratories participating in the CRP are discussed. These waste streams covered an extremely broad spectrum, ranging from simple, one-component aqueous solutions originating from a research laboratory to very complex aqueous concentrates of waste resulting from reprocessing activities or reactor operation. These challenging wastes included: waste contaminated by tritium, wastes containing transuranic elements, and solid health care waste. The range of aqueous wastes included those contaminated by organic complexing agents and surfactants to pure organic waste such as contaminated oil. Correspondingly, the scale of approaches and technologies used to address these wastes is very broad.

Use of this report is likely to be most effective as an initial screening tool to identify technologies best able to meet specific waste management objectives in terms of the waste generated, the technical complexity, the available economic resources, the environmental impact considerations, and the desired end product (output) of the technology. The report should assist the user to compare technologies and to reach an informed decision based on safety, technological maturity, economics, and other local needs.

This report is the result of a CRP involving 15 organizations from 13 Member States, beginning with the first Research Co-ordination Meeting (RCM) in Prague in November 2003. Additional RCMs were held in the Ukraine (Kiev, May 2005) and India (Mumbai, November 2006). A Consultants Meeting was held in India (Mumbai, December 2006) to consolidate the results.

The IAEA wishes to express its appreciation to all those that took part in the research comprising the CRP, as well as in preparation and publication of this report. Organization, checking and consolidation of the TECDOC was the work of the consultants B.B. Verma, S.R. Samanata, J. John, G. Parsons, V. Avramenko, and V. Efremenkov. The IAEA officer responsible for this publication was Z. Drace of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

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APPENDIX III. INDIVIDUAL RESEARCH REPORTS (ON CD-ROM ONLY)

SUMMARY

This publication summarises results of an IAEA CRP which addresses the problem of treatment and conditioning of “problematic” radioactive waste, for which safe, efficient and cost effective methods for processing are not readily available. It offers a full range of technical solutions for the variety of “problematic” waste streams that were the subject of the CRP. The extent of progress evident on treatment methods examined varied considerably, from promising and scaleable results demonstrated at the laboratory level, through those with demonstrated performance at pilot plant scale, to fully developed commercial applications.

In the report, processing options for a total of 27 ‘problematic’ waste streams that were identified and addressed by the individual laboratories participating in this CRP are discussed. The general criteria used for deciding which wastes should be defined as ‘problematic’ were:

- the technologies for the treatment of the waste types had not been established for routine waste management,
- the waste-type failed to meet criteria for acceptance for processing by technologies generally available at the local level.

Following their origin and nature, these 27 identified waste streams covered an extremely broad spectrum, ranging from simple, one-component aqueous solutions originating from a research laboratory to very complex aqueous concentrates of waste resulting from reprocessing activities or reactor operation. These challenging wastes included waste contaminated by tritium, wastes containing transuranic elements, and even solid health care waste. The range of aqueous wastes included those contaminated by organic complexing agents and surfactants to pure organic waste such as waste tetraphenylborate or contaminated oil. Correspondingly, the scale of approaches and technologies used to address these wastes was very broad. To simplify presentation and provide an overview of the results achieved in the TECDOC, the waste streams addressed were grouped into four broad categories:

1. Aqueous waste.
2. Aqueous concentrates.
3. Spent resins and sludges.
4. Site specific and miscellaneous waste.

The main problems identified during the work on this project, and the approaches to their effective solution that can be generally recommended on the basis of the results achieved, are summarised below.

1. Aqueous waste

The main problems arise during management of decontamination solutions. Photodegradation of the organic complexing agents and/or surfactants followed by selective sorption can be considered as the most promising approach to these problems. In this respect, development of selective inorganic ion exchangers continues to be an important direction

2. Aqueous concentrates

The main problems within this category of waste are concerned with processing of concentrated waste containing complexants. The results obtained in this CRP indicate that solutions can be found through development of efficient forms of cobalt complexes, with

oxidation by the Fenton reaction, and/or hydrothermal oxidation. Separation of problematic inactive constituents, e.g. sulphate, before vitrification of high level waste is also very useful. Future work in the area of aqueous concentrates should include (i) the development of more effective processes for the removal of ruthenium and cobalt, (ii) the proper management of spent sorbents and secondary waste streams, (iii) the scale-up of promising processes and testing with actual waste (iv) recovery and recycle of chemicals (e.g. boric acid) wherever possible

3. Spent ion-exchange resins (SIER) and low-level sludges

The main problems in this waste category arise during upgrade from simple immobilization methods (involving cement, bitumen or polymer matrices) to volume reduction methods, namely high-temperature processing and oxidation of spent resins. The problems are related to release of radionuclides (e.g. ^{14}C) into the gaseous phase and the risk of spreading of these into the environment. The main results obtained within the scope of this CRP lead to the conclusion that successful management of SIER waste would involve a preliminary step for removal of ^{14}C (if present) followed by a suitable oxidative destruction method such as the photo-Fenton reaction or molten salt oxidation. A method for efficient trapping and immobilization of the separated ^{14}CO2 will also have to be developed.

4. Site-specific and miscellaneous waste

The main problems here are related to the tritium and ^{14}C-containing legacy waste from either health-care or research. The main achievement observed is progress in tritium waste management and the practice evolved during the selection of optimum technology for management of the legacy health-care waste will be very valuable for anyone facing a similar problem.

The report contains a review of processing for a variety of decommissioning wastes with complex compositions, processing of some specific liquid waste concentrates and treatment and conditioning of spent organic ion exchangers generated in the nuclear industry. There is no doubt that the issue of “problematic” waste will stay as an emerging issue, regardless of the wealth of research results presented within this CRP, considering that expected new developments in the application of nuclear energy will result in the generation of new (and not always easy to process) “problematic” waste streams. A key element to the approach to solving the issues of problematic wastes is in having a diversity of options available. This TECDOC brings these options together to enable fruitful discussions, the assessment of the options and lessons learned, and to serve as a generator of ideas for the future.

Probably the most important observation –and conclusion - that can be made on the basis of the studies performed is this: multistage processes, aimed at breaking down the issues associated with ‘problematic’ waste into ‘standard’ issues in the initial stages of the sequence, generally seem to offer the most versatile and effective solutions to the treatment of ‘problematic’ wastes. This approach enables the processing of such wastes, after a suitable waste-specific pre-treatment, by standard treatment technologies.”

There is one very pronounced commonality in the approach of several groups involved in this CRP – the emphasis on further minimising the volume of the waste to be finally disposed-of by partitioning radionuclides, regenerating media, and re-using as much of the waste as technically and economically feasible. This approach, emphasizing the reuse/recycling strategy, represents a robust waste treatment strategy for the 21st century and should be appropriately pursued.

1. INTRODUCTION/BACKGROUND

Operations in the nuclear power industry, application of radioactive materials in academic and industrial research, biomedical research and medical treatment produce a wide variety of radioactive wastes. Such wastes are generated in all sectors that handle radioactive materials, and include almost any process material or equipment used in that sector. These wastes may include small amounts of process chemicals, spent solutions for specific analysis, spent ion exchange resins and other sorbents, radioactive sludge, scintillation cocktails, discarded laboratory and process equipment, etc.

In many countries, especially with NPP operation, fuel reprocessing, nuclear research activities and diverse nuclear applications, the inventory of radioactive waste generated is very broad and includes several specific waste types, which require special care for handling, treatment and conditioning. The amounts of such wastes may be limited, but conventional treatment and conditioning methods may not be efficient for this type of waste; therefore special options maybe required to manage this waste. In addition, very large quantities and a broad variety of waste are generated from the decommissioning/dismantling of nuclear industry facilities and other facilities handling radioactive materials.

Radioactive waste processing technology is a subject that has received considerable attention in the Member States in recognition of its importance for the protection of human health and the environment from adverse effects of radiation associated with this waste. During the evolution of waste management practices, many processes achieved a high degree of acceptance and many of them are now regarded as technically mature. A large body of information is currently available on proven (conventional) waste, processing technologies. Most of the existing technologies have been developed for processing of large amounts of operational radioactive waste from such facilities as nuclear power plants and other nuclear fuel cycle facilities.

However, many specific and some routine wastes exist, which can be considered as “problematic” for treatment and conditioning by these “conventional” techniques. This, for example, includes waste containing different organic components, toxic or chemically aggressive constituents, radionuclides with specific properties (high mobility, high chemical activity, volatile elements, etc.), waste difficult for treatment and not appropriate for direct immobilization (e.g. spent organic ion exchange resins), etc. For such waste, application of conventional treatment and conditioning options may not be efficient and appropriate in terms of economy, safety and performance characteristics. In many cases, such wastes are stored awaiting an appropriate treatment and conditioning solution. Such wastes require the selection or adaptation of special processing techniques or a combination of different techniques to address properly their specific properties and characteristics.

Selection and/or adaptation of adequate waste processing techniques for such problematic radioactive waste is rather difficult and complicated. There are two main reasons for this: One is *the cost of waste processing*. Since waste management is not a direct pay-back process, consideration of cost in many cases is an important driving force for optimization of waste processing to keep the required level of quality and safety. Another reason for the complexity in this case may be *diverse waste characteristics*. For specific waste types development of special technologies may be required with appropriate validation and adaptation to these specific waste types.

Selection of waste processing technologies for specific waste streams should follow certain waste safety, quality and acceptance criteria. Most safety requirements and criteria are well developed and are generally applicable to almost all wastes management systems. Other criteria, e.g. waste acceptance criteria could be site- or country-specific. These requirements and criteria should be carefully considered in development and application of waste processing technologies, specifically for problematic waste streams.

Information collected during implementation of several previous IAEA CRPs (e.g. on "Combined methods for treatment of liquid radioactive waste", "Evaluation of radioactive waste forms and packages"), during technical missions to different waste management facilities in Member States and information presented at International Conferences shows that this problem exists in many countries. Many "problematic" waste streams need careful selection of appropriate technologies to meet established operational, safety and economic requirements. Increasing safety requirements may also stimulate searching of new efficient solutions for managing rather routine waste streams.

Several new emerging technologies are at different stages of development in different countries and institutions to address the problem of managing specific waste types, and to improve efficiency and economic performance of waste operation. Combining efforts and sharing the information and experience in this field would be of great benefit to Member States. The IAEA could play a key role in co-operation and co-ordination of this work in its Member States. The Co-ordinated Research Project is a well established instrument for such co-operation and co-ordination of common efforts in solution of specific waste management problems. The experience and knowledge gained by participating institutions during project implementation serves as a basis for improving existing waste management practices in these institutions and in participating countries, for improving existing practices or in proper planning of future waste management activities.

The CRP addressed the problem of treatment and conditioning of radioactive waste, for which efficient and cost effective methods for processing is not readily available. In many cases, these wastes (e.g. boric acid concentrates at PWRs, spent ion exchange resins, decontamination solutions containing organics, tritium and C-14 containing waste, some old legacy waste, etc.) are collected and stored pending future efficient solutions to meet specific disposal requirements. In some cases certain waste types could be considered "problematic" for specific site when its characteristic is different from routine waste streams and therefore appropriate technology for its processing is not directly available. Technical solutions for processing of such waste could be very site-specific.

Some waste can be considered as "problematic" for different reasons. This could be trade-off between specific waste characteristic and access to readily available technologies for waste processing. Problems associated with particular waste could not only be defined by waste characteristics, they could be facility-specific, site-specific or even country-specific. Problems with some waste may be associated with the existing regulatory framework or specific timeframe, existing waste management experience, available disposal option, etc. Taking this into account the "problematic" waste could be very diverse, and what is considered "problematic" now at one site may become more or less routine later or at another site or facility. This fact evidently defines a variety of wastes considered in this Project and the difficulties in generalization of the results achieved.

The objectives of the CRP were to encourage and to co-ordinate R&D work on management of specific and problematic waste types, to facilitate exchange of information and technological experiences on new developments in the area, to identify particular specific waste types which require special approaches and innovative technologies to be applied for conformity with modern safety and economic requirements. The execution of the CRP promoted the exchange of advanced information on the ongoing research and development activities and facilitated access to the practical results of their application for processing of specific waste types. Exchange of information and co-operation in resolving identical problems between different institutions in Member States contributed towards improving waste management practice its efficiency and general safety. Participation in the Project and its implementation is contributed towards transferring of new knowledge and practical experience among participating institutions, and contributed to the improvement of the general efficiency of waste management in participating Member States.

2. DESCRIPTION OF THE WORK DONE

A total of 27 'problematic' waste streams were identified and addressed by the individual laboratories participating in this CRP. The general criteria for deciding that the respective waste should be defined as 'problematic' were:

- the technologies for the treatment of these waste types had not been established, yet, in routine waste management
- the specific type of waste failed to meet the criteria for acceptance for processing by the locally available technologies.

2.1. WASTE STREAMS

Following their origin and nature, these wastes covered a wide range, e.g., simple one-component aqueous solutions originating from a research laboratory, complex aqueous concentrates resulting from reprocessing activities or reactor operation, waste contaminated by ^{3}H, waste containing transuranium elements, waste contaminated by organic complexing agents and surfactants to pure organic waste such as waste tetraphenylborate or contaminated oil, and including even solid health care waste. Correspondingly, a variety of approaches and technologies were used to address these wastes. To simplify the orientation in the overview of the work done and the results achieved, the waste streams addressed are grouped – for the purpose of this review – into four large groups:

- Aqueous waste.
- Aqueous concentrates.
- Spent resins and sludges.
- Site specific and miscelaneous waste.

An overview of the waste streams, together with their basic characteristics, and identification of the research group(s) involved in the work with these streams, is given in Table I below. The structure of this chapter then follows the classification suggested in this table.

TABLE I. OVERVIEW OF THE TYPES OF WASTE ADDRESSED IN THE CRP

Group/Waste	**Country**	**Nuclide/ Composition**	**Matrix**	**Source**	**Type of work**	**Scale**	**Remark**
Aqueous waste							
Decontamination liquids	Belgium	FP, CP	sulphates, Ce(IV)	steel decontamination	spent MEDOC process liquids – coagulation / flocculation, filtration	pilot	demonstration (actual waste)
	Czechia	FP, CP	NTA	NPP	photodegradation, sorption	laboratory	simulant
	India	^{60}Co, ^{55}Fe	aqueous	NPP & NFC	photodegradation	pilot	demonstration (simulant)
	Finland	^{60}Co	complexants, acids	model solutions	^{60}Co sorption, Mn-antimonate	laboratory	model solutions
Waste containing oxoanionic contaminants	Finland	^{99}Tc, ^{125}Sb	aqueous	NPP	doped oxides - SnO_2	laboratory	actual waste
	Belarus	IO_3^-	aqueous	model solutions	hydroxocomplexes / membrane (dialysis)	laboratory	model solutions
Waste containing large amounts of suspended matter, oils and other organic substances	Russia (Radon)	FP, CP	aqueous	NPP & NFC	cross-flow ultrafiltration, sorption, reverse osmosis, ambient-temperature evaporation	full	actual waste
Acidic transuranium elements containing waste	Finland	^{241}Am, ^{236}Pu	dilute HNO_3	laboratory	Sorption on Quasar N (antimonysilicate - $SbSiO_2$)	laboratory	actual waste

Legend: FP – Fission Product, CP – Corrosion Product, NPP – Nuclear Power Plant, NFC – Nuclear Fuel Cycle, NTA – Nitrilotriacetic Acid, LSC – Liquid Scintillation Counting

TABLE I. CONTINUED

Group/Waste	**Country**	**Nuclide/ Composition**	**Matrix**	**Source**	**Type of work**	**Scale**	**Remark**
Aqueous concentrates							
Reactor operation concentrates	Czechia	^{60}Co	borates, organic, nitrates	NPP evaporator	Boron removal, photodegradation, sorption	laboratory	demonstration (actual waste)
	Russia (RAS)	^{137}Cs, ^{60}Co	borates, organic, nitrates/ chlorides	NPP evaporator	HydroThermal oxidation, sorption by highly selective sorbents	pilot	demonstration (actual waste)
Reprocessing concentrates	India	U, Pu	nitric acid, oxalates	reprocessing	photodegradation	laboratory	
	India	FPs, Ans	nitric acid, sulphates	reprocessing	neutralisation, sulphate separation, ^{137}Cs recovery, vitrification	pilot	demonstration (simulant)
	India	FPs, Ans	nitric acid, sulphates	reprocessing	direct immobilisation in barium-borosilicate glass	full	operating
	India	Ru-106	alkaline, nitrate	reprocessing	precipitation, sorption	pilot	demonstration (actual waste)
Decommissioning waste	Czechia	^{137}Cs, ^{60}Co, ^{90}Sr	nitrate, chloride	Dissolved Na, Na/K metallic coolant (decommissioning)	sorption on selective inorganic and inorganic-organic absorbers	laboratory	demonstration (simulant)
	Russia (RAS)	^{137}Cs, ^{60}Co, ^{90}Sr	organic, nitrates / chlorides	R/O concentrates	Sorption by highly selective sorption-reagent materials	full	operation (actual waste)
Isotope production waste	Australia	U, FP	uranium, acidic nitrate	^{99}Mo production	Synroc	full mock-up	cold runs

Legend: FP – Fission Product, CP – Corrosion Product, NPP – Nuclear Power Plant, NFC – Nuclear Fuel Cycle, NTA – Nitrilotriacetic Acid, LSC – Liquid Scintillation Counting

TABLE I. CONTINUED

Group/Waste	**Country**	**Nuclide/ Composition**	**Matrix**	**Source**	**Type of work**	**Scale**	**Remark**
Spent resins and sludges							
Low Level Sludges	Australia	FP	aqueous	active drain (research reactor)	separation, drying, storage	full	cold runs
Spent resins	Argentina	^{137}Cs, ^{60}Co, alpha	cationic and anionic resins	NPP	elution, electrochemical deposition	laboratory, pilot plant	demonstration (actual waste)
	China	^{137}Cs, ^{60}Co	spent resins	CIAE, various	immobilisation in high performance cement	pilot	demonstration
	India	^{60}Co, ^{137}Cs,		NPP & NFC	photodegradation	pilot	cold runs
	Korea (KHNP)	^{14}C, ^{60}Co, ^{134,137}Cs	spent resins	NPP	^{14}C removal	pilot	demonstration (actual waste)
	Korea (KAERI)	Cs, Sr, heavy metals	spent resins	NPP	MSO	pilot	cold runs
Site-specific and miscelaneous waste							
Tritiated waste	Belgium	^{3}H	liquid organic	research	catalytic detritiation, tritium separation	full	operation (actual waste)
Miscelaneous organic legacy waste	USA	TRU	Alakaline complexants solution, TPB, oil	legacy waste	MSO, Fenton, Mn(VII) oxidation	laboratory	cold runs
C-14 waste	South Africa	^{14}C, ^{3}H	solid, liquid	legacy medical waste	characterisation, sterilisation, supercompaction	laboratory	
LSC cocktail	Finland	^{241}Am	LSC cocktail	research	sorption, (MnO_2 or Quasar N - Sb-silicate).	demonstration	

Legend: FP – Fission Product, CP – Corrosion Product, NPP – Nuclear Power Plant, NFC – Nuclear Fuel Cycle, NTA – Nitrilotriacetic Acid, LSC – Liquid Scintillation Counting

2.1.1. Aqueous waste

In most cases, the general approach to the treatment of the wastes of this group was to develop a sequence of treatment steps that would in the first step(s) render the waste amenable to standard treatment technologies applied in the final stage(s) of the sequence. As an example of this approach, a three-stage process, developed for the treatment of WWER-type NPP evaporator concentrates, may be cited. It comprises boric acid removal and organic complexants degradation in the first two steps followed by a standard step of radionuclides separation by sorption onto inorganic ion exchange sorbents. Four categories of 'problematic' waste were identified in this group (see Table I). They comprise:

- decontamination liquids
- waste containing oxoanionic contaminants
- aqueous waste containing large amounts of suspended matter, oils and other organic substances
- acidic transuranium elements containing waste.

In the category of decontamination liquids, four specific waste streams were addressed by the individual research teams. Their origin and compositions were as follows, the major radioactive contaminants in all these streams were the activated corrosion and fission products.

- Liquid waste from the MEDOC© (Metal Decontamination by Oxidation with Cerium) process, based on the use of Ce(IV) as strong oxidizing species in sulphuric acid, and developed and used at the SCK•CEN for the decontamination of stainless or carbon steel pieces. The effluents of this process represent diluted sulphuric acid mixed with cerium IV sulphate and all the dissolved metallic elements coming from the corrosion of stainless steel material. The salt content of about 22 g/L gives a mixture of hydroxide sludge of about 40 g/L after neutralization with sodium hydroxide.
- Spent decontamination solution with novel composition based on the use of nitrilotriacetic acid (NTA) as a substitute for the corrosive oxalic acid. This solution was recently introduced in decontamination processes at the WWER-type NPP Temelín in the Czech Republic. The simulated spent solution used in this work contained various quantities of NTA, hydrazine, Fe^{3+}, Mn^{2+}, Ni^{2+} and Cr^{3+} ions.
- Spent decontamination formulations generated at different stages of the nuclear fuel cycle in India. The simulated spent solutions contained various organic complexants and/or anionic surfactants, e.g. EDTA, citric and ascorbic acids, sodium salt of dodecyl benzene sulfonate or sodium lauryl sulfate.
- Simulated acidic decontamination solutions based on oxalic, citric, formic, sulphuric or nitric acid that may also contain some reducing agents like hydrazine, Na-dithionite, or ascorbic acid.

In the category of oxoanionic contaminants containing waste, most of the work was done with simple solutions as a part of laboratory investigations. The only real waste stream addressed was the Fuel Pond water from Olkiluoto-1 BWR, Finland, that contained sulphates, oxalates and chlorides at μg/L level and that was contaminated by ^{125}Sb, ^{137}Cs and ^{60}Co at 10^1-10^2 Bq/L level.

The aqueous waste streams studied, that contain large amounts of suspended matter, oils and other organic substances, comprised both simulants (e.g. 5.85 g/L NaCl and 50 mg/L engine oil) and several real radioactive waste streams from the RADON site, Russia, containing tens of grams of salts or silts per litre.

The acidic transuranium elements containing waste stream was a simple diluted nitric acid solution (pH = 1.1) contaminated with ^{241}Am and ^{236}Pu. This stream was generated during the selective sorbents development and testing in the University of Helsinki, Finland, laboratory.

2.1.2. Aqueous concentrates

A variety of aqueous concentrates are generated during the operation of reactors and other nuclear fuel cycle facilities. Such solutions contain high concentration (10-500 g/L) of dissolved salts. The evaporation of low level effluents is a very common operation that gives rise to such waste in the form of evaporator concentrates. Reverse osmosis is another process which leads to the generation of a concentrated 'reject' stream. The aqueous raffinates generated during reprocessing operations contain substantial quantities of dissolved salts which get further concentrated in the evaporators. Though direct immobilization is possible and is practiced in some cases, it is desirable to have a management scheme which leads to substantial volume reduction. Implementation of such a scheme would depend on the availability of highly efficient processes for radionuclide separation from the concentrates. The difficulty of such an approach can be appreciated from the fact that many of the non-radioactive ions, present at high concentration levels, can compete with the radioactive ions which are present at much lower concentrations. The situation is further complicated when the concentrates also contain strong complexing agents which bind the radioactive ions and must be destroyed before separation can be achieved. A summary of the status of work and achievements in this area is given below.

Concentrated aqueous waste streams from a number of sources and having a variety of chemical/radiochemical composition were taken up for study by the participating member states. The radionuclides present in these streams included fission products (^{137}Cs, ^{90}Sr, ^{106}Ru, ^{125}Sb, ^{99}Mo, ^{99}Tc, etc), activation products (^{60}Co) and actinides (U, Pu). The development work was done with simulated waste and then tested/demonstrated with actual waste in many cases. The waste streams in this category belong to four groups depending on their origin, viz., reactor operation, reprocessing, decommissioning and isotope production.

- WWER-type NPP evaporator concentrate was simulated based on the composition of such waste at NPP Loviisa, Finland. This work was carried out by the Czech Republic in collaboration with Finland. The problem of removing ^{137}Cs and ^{90}Sr from such waste was solved earlier using selective inorganic sorbents like Cs-Treat and Sr-Treat developed in Finland. The present study was concerned with the removal of ^{60}Co. The simulant contained sodium tetraborate hexahydrate (95 g/L), potassium nitrate (20 g/L), sodium nitrate (127.5 g/L), sodium hydroxide (30 g/L) and various concentrations of EDTA. The isotope ^{57}Co was used as the tracer for radiocobalt.
- Alkaline evaporator concentrate of NPP (Dukovany, Czech Republic) origin contains alkali metal salts of borate, nitrate, citrate and oxalate ions. The waste is similar to the one noted above except that instead of EDTA one has citrate and oxalate resulting from the use of Citrox process for decontamination applications in this plant. Similar to the the above described waste, the problem of removing ^{137}Cs and ^{90}Sr from such waste was solved earlier; the process was based on the use of selective inorganic-organic sorbents with polyacrylonitrile (PAN) matrix and active components based on

ferrocyanides or sodium titanate, respectively, developed in the Czech Republic. In the current CRP, the target radionuclide was ^{60}Co and actual waste was used in the study.

- Acidic waste is generated during the recovery of ^{99}Mo from nitric acid solution resulting from the sissolution of irradiated low enriched UO_2 targets in Australia. The waste contains nitric acid (<1 M), uranyl nitrate (20-200 g/L) and fission products. Given that the waste has been produced and accumulated since the late 1960s, the activity in the stored liquid is dominated by ^{137}Cs and ^{90}Sr.
- A saline waste would result from the proposed dissolution of Na/K liquid metal coolant during decommissioning of fast reactors, e.g., experimental (60 MWt) and prototype (600 MWt) fast breeder reactors at Dounreay, U.K. The projected volume and compositions are 15000 m^3 of 4M NaCl + 0.15M KCl and 800 m^3 of 2.2M $NaNO_3$ + 0.7M KNO_3, respectively. The target radionuclides include ^{137}Cs, ^{90}Sr, ^{60}Co and Pu.
- Another WWER-type NPP evaporator concentrate was obtained from real waste of the Novovoronezhskaya NPP, Russia. The composition of such a waste includes 250-300 g/L of sodium-potassium metaborate, sodium nitrate (up to 75 g/L), substantial concentrations (up to 2-3 g/L) of Trilon B (disodium salt of ethylenediaminetetraacetic acid - EDTA) and up to 2 g/L of complex salts of iron, nickel and chromium, pH 9-12. The major problems of this waste were concerned with Cs and Co radionuclides.
- The decommissioning of nuclear submarines in Russia and associated decontamination activities resulted in a mixed saline (sea-water) waste containing oxalates and about 10^{-3} mCi/L of ^{137}Cs and ^{90}Sr. The salt content was 0.1 g/L and pH was 7-8. This waste was subjected to treatment using reverse osmosis unit (DalRAO, Primorsky Territory, Russia), resulting in a concentrated stream having 30-50 g/L salts, with calcium content more than 0.5 g/l. The activity was in the range of 10^{-1} mCi/L. The removal of ^{137}Cs from this waste was easily achieved with the application of composite ferrocyanide sorbents. The removal of ^{90}Sr was difficult and was addressed in this study.
- The use of ferrous sulphamate in the past in reprocessing operations based on the PUREX flowsheet resulted in high level waste containing substantial concentration of sulphate ions (up to 10 g/L). Problems associated with phase separation of sulphate-rich layer were encountered during vitrification of such sulphate-bearing stored HLW in lead borosilicate glass in India. Extensive work was carried out to overcome this problem by adopting two approaches, viz., direct immobilization in an alternative matrix without phase separation and chemical pre-treatment for removal of sulphate from the waste followed by vitrification.
- Ruthenium-bearing waste streams from reprocessing operations present a special challenge for treatment because ^{106}Ru is present as numerous nitrosyl complexes which are difficult to remove by conventional ion exchange or chemical precipitation methods. The presence of high concentration of dissolved salts further complicates the problem. In such streams generated in India, the activity of ^{106}Ru could vary from 10^{-3} to 1 mCi/L, depending on whether the source is intermediate level waste from reprocessing operations or from the pre-treatment of sulphate-bearing high level waste at waste immobilization plant.
- Plutonium reconversion operations at reprocessing plants in India result in oxalate-bearing acidic waste containing 0.01M oxalic acid, 3.0M nitric acid and traces of plutonium. The present practice of destruction of oxalic acid using $KMnO_4$ leads to additional salt loading in the solution. The possibility of an alternative improved technique for destruction of oxalic acid was addressed in this study.

2.1.3. Spent ion-exchange resins and radioactive sludges

The waste streams of this section can be divided into two categories – a major one including spent ion-exchange resins (SIER) and a small one related to low-level sludges of specific type.

The radioactively contaminated ion-exchange resins comprise a specific type of radioactive waste produced at different stages of nuclear power cycle. Most of the spent ion-exchange resins are produced at nuclear power plants (NPP) and spent nuclear fuel (SNF) reprocessing plants. During the NPP operation the contaminated spent ion-exchange resins emerge in the following processes:

- cleanup system for the primary coolant
- condensate decontamination of single-circuit reactor
- decontamination of water from SNF storages (cooling ponds)
- decontamination of deactivation, trap and other water in NPP special water decontamination systems

The estimated total volume of ion-exchange resins at NPP is 0.02 – 0.025 m^3/MW of nominal power for two-circuit reactors of WWER-type and 0.08 – 0.025 m^3/MW of nominal power for single-circuit reactors of RBMC type. The spent ion-exchange resins from other production cycles substantially differ on contamination degree and radionuclide composition. For example, the spent resins from the decontamination systems of primary circuit contain significant amounts of ^{14}C isotopes.

For interim storage, when short-lived radionuclides decay, the spent ion-exchange resins are usually sent to liquid waste storage facilities where they are kept underwater for some time period. Before transferring to long-term storage, these resins are subject to processing that consists in conditioning and volume reduction of radioactive waste sent for final disposal.

As for the second category, the problem of managing low-active sludges produced at operation of NPP, reprocessing plants and research reactors is in a way similar to the SIER treatment problem. The concentration and transformation of sludges into a form suitable for disposal requires special research activities.

As regards the first category, the following real and simulated spent resins and respective storage facilities were studied and tested within the scopes of the present CRP:

- Radioactive spent resins of the primary circuit of HWRR in CIAE (China), specific activity: ^{137}Cs: 2.87×10^3Bq/g (dry); ^{60}Co:5.89×10^4Bq/g
- Radioactive spent resin storage at Wolsong NPP site (CANDU reactor, Republic of Korea), and in-station resin storage tank 2 at unit 1 (mixed cation exchanger and anion exchanger of the resin Amberlite IRN-150), activity of ^{14}C from 170 GBq/m^3 (0.78 Ci/m^3) up to 380 GBq/m^3 (1.73 Ci/m^3)
- Spent resins located in Atucha I NPP (Argentina) with the following activity inventory:: ^{60}Co: 6.7 x 10^{12} Bq; ^{137}Cs: 2.7 x 10^{13} Bq; c) total alpha: 3.5 x 10^{10} Bq
- Poly(styrene-divinylbenzene) resins – cation exchangers ($-SO_3H$) and anion exchangers ($CH_2N^+(CH_3)_3OH^-$) (India), activity from 0.1 mCi/l up to 10 mCi/l (radionuclides present: ^{60}Co, ^{137,134}Cs, ^{90}Sr, ^{106}Ru, ^{65}Zn, ^{54}Mn, ^{125}Sb)

- Amberite IRN 77 as a simulant of spent resins containing heavy metals and non-active caesium and strontium (Republic of Korea) for incineration in the MSO reactor

The second category waste – sludges were specially simulated to test a respective system at the effluent plant (Australia). The batch simulated test material had the following composition to test the most severe cases for the thickened sludge (total volume of the tank 3000 l):

- NaCl (11 kg), $NaNO_3$ (4.5 kg), Na_2SO_4 (3.3 kg), $Al(OH)_3$ (125 kg), Na_2CO_3 (1 kg), water (made up to 3000 l)

2.1.4. Site-specific and miscellaneous waste

Some problematic waste may be very site-specific, requiring consideration not only general, but some special properties or characteristics of this waste, taking into account some particular local conditions and options locally available for managing the concrete waste problem. Another specific and problematic waste may be the result of some combination of waste characteristics not typical for more common waste streams, which also may require "non-conventional" approaches or some special technologies for treatment and conditioning of this waste. Below are some examples of such waste streams investigated in the frame of the CRP.

- A variety of radioactive wastes generated in nuclear industry and at different nuclear applications contains substantial portion of different organic components, which may be flammable, toxic, chemically aggressive, etc., which make them difficult to handle and process by conventional treatment and conditioning technologies.
- In the existing installations and in future fusion devices, various categories of tritiated waste are and will be produced, which could be considered as problematic for conventional processing to reduce or eliminate potential impact on the environment and human health. In particular for *organic liquids containing tritium* the objective is to destroy organics and to separate and fix tritium for further immobilisation, storage or reuse.
- Substantial portion of historic or legacy wastes could now be considered as problematic for their relocation and reconditioning because of their complex composition, pure initial characterization, and inappropriate conditions for long-term storage or disposal. *Old biomedical waste contaminated with* ^{14}C, ^{3}H *and other radionuclides* is one example of such waste type. ^{14}C, ^{3}H isotopes found in the healthcare waste are mostly contained in a liquid solution. The contaminated liquid is either inside a syringe or still in the glass vial used for different medical tests. Some other materials used in these procedures are also discarded into the waste containers and can also be contaminated with these or other isotopes. The potential bio-hazardous nature of this waste proved to be additional complication in the development and implementation of appropriate characterization and conditioning methods for such waste.
- Spent liquid scintillation cocktails containing long lived alpha isotopes such as Am, Pu, etc. also could be classified as problematic waste for further processing both because of specific radioactive contamination and organic nature of this waste. Special options should be developed to address both these characteristics of this waste.

2.2. TECHNOLOGIES USED TO ADDRESS THE INDIVIDUAL STREAMS

2.2.1. Aqueous waste

2.2.1.1. Decontamination liquids

Two different types of spent decontamination liquids have been addressed by a total of four different groups in this project. The first type of this waste – spent decontamination liquids containing organic complexing agents and/or anionic surfactants – is a waste stream that is widely recognised to be 'problematic' because it is not amendable to standard high volume reduction waste treatment processes. This stream attracted the attention of three groups, two of which concentrated on the development of a two-stage process comprising photocatalytic degradation of the organic components of the waste followed by treatment of the resulting liquid by a standard method (e.g. sorption). The efforts of the third group concentrated on the development of highly selective inorganic ion exchangers that would allow direct separation of the radionuclides from the organic components containing waste.

The Bhabha Atomic Research Centre (BARC), Mumbai, India, and the Czech Technical University in Prague (CTU), Czech Republic, groups opted for the application of photocatalytic organics degradation process in the first stage of a two stage process for treatment of the spent decontamination liquids. In photocatalysis, degradation of organic compounds occurs mainly due to their reactions with $OH^\bullet$ radicals generated by interaction of UV radiation with a catalyst. In the presence of *heterogeneous photocatalysts* (e.g. TiO_2), the electron-hole pairs are formed that can then produce the $OH^\bullet$ radicals in reaction with the molecules of water adsorbed at catalyst's surface:

$$TiO_2 + h\nu \longrightarrow TiO_2\,(e^- + d^+) \qquad (1)$$

$$TiO_2\,(d^+) + H_2O_{ad} \longrightarrow TiO_2 + OH^\bullet{}_{ad} + H^+ \qquad (2)$$

The Fenton reagent belongs among prospective *homogeneous photocatalysts*. The mechanism of reactive radicals production can be, in this case, described as:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (3)$$

$$Fe^{3+} + OH^- \longleftrightarrow Fe(OH)^{2+} \qquad (4)$$

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + OH^\bullet \qquad (5)$$

At the CTU, treatment of spent decontamination solution based on nitrilotriacetic acid (NTA) has been studied. The results of a basic study of NTA photodegradation revealed that for pure NTA solutions, the effect of the photo-Fenton reagent is about four times higher than the effect of irradiation in presence of titanium dioxide. Even though this difference has been almost annulated in the simulated waste, that contains Fe^{3+}, Mn^{2+}, Ni^{2+} and Cr^{3+} ions, photo-Fenton catalyst has been recommended for the practical application because it avoids the need of heterogeneous catalyst separation and does not increase the amount of secondary waste significantly.

At BARC, degradation of EDTA, citric and ascorbic acids, sodium salt of dodecyl benzene sulphonate or sodium lauryl sulfate was found feasible at a pilot scale study with photo-Fenton catalyst. An important result of this study is the estimation of the influence of intensity of UV-light, estimation of the effect of radiation with longer wavelength (visible, infrared) and namely the study of the efficiency of various photoreactor types. Out of the selection of the Column Photo-reactor (CPR), Shallow Tank Photo-reactor (STR), Quartz Tubular Flow Photo-reactor (TFR) and Plug Flow Photo-reactor (PFR), the PFR showed most promising results for the industrial application. The reactor types used are shown in ANNEX I. As the second stage of the composed process for the treatment of the BARC waste, selection of conventional methods was proposed to be applicable. No specific testing or demonstration has been reported.

In the case of the spent decontamination solution containing NTA, the CTU group demonstrated that most radionuclides can be effectively removed from these solutions even in the presence of NTA, e.g. by means of a choice of inorganic absorbers or the Purolite NRW 160 resin. The two-stage process was needed only for efficient radiocobalt separation that was not satisfactory from the original spent solution. Laboratory-scale experiments, performed with a simulant of NPP Temelín solution, revealed that the efficiency of radiocobalt separation is significantly increased after NTA photodegradation, however, total degradation of NTA is mandatory. Purolite NRW 160 resin or sodium titanate inorganic ion exchanger display the highest distribution coefficients for radiocobalt uptake.

Another approach to the treatment of spent decontamination solutions was pursued at the University of Helsinki, Finland. There, a novel highly selective inorganic ion exchanger was developed and studied for direct radiocobalt separation from media containing organic complexing substances and/or acids commonly used in decontamination. The new manganese antimonate (MnSb) material belongs into the group of novel developmental mixed oxide materials with pyrochlore structure (see Figure 1). These materials allow varying the acidity and micropore size of the material by substitution of different metals in the pyrochlore structure thus affecting its ion exchange selectivity.

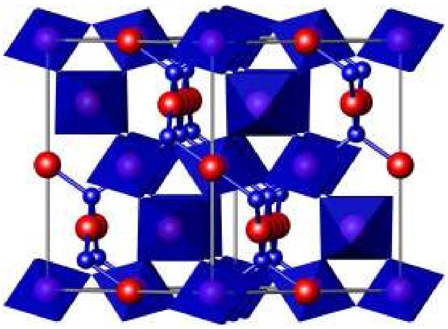

FIG. 1. Mixed metal oxides of pyrochlore structure have been found to be highly versatile ion exchange materials, the selectivity can be tuned by adjusting micropore sizes or the acidity of the framework metals by partial substitutions.

The results achieved demonstrated good prospects of these novel materials. In the experiments with oxalic, citric, formic, sulphuric and nitric acids, uptake of radiocobalt was more dependent on solution pH than type of acid. Picolinic acid decreased uptake of radiocobalt significantly, obviously due to strong complexation. Generally, the distribution coefficients of radiocobalt were high (5000-10000 mL/g) at pH 3-2 but decreased clearly as pH approached value of 1. In a test conducted at pH=2, reducing oxidising agents (hydrazine, Na-dithionite, ascorbic acid) did not decrease radiocobalt uptake.

In column test with oxalic acid, performance of the material was good (DF close to 20 at ~ 4000 bed volumes of treated solution) when even trace levels of EDTA were absent. This result indicates that selectivity of the material is not high enough to break the EDTA complex. Likewise, a decontamination factor of 20-50 was observed for radiocobalt in 0.01M HBF_4 solution simulant.

The second type of spent decontamination liquids represented a rather specific case of *liquid effluents from the MEDOC© process* developed and used at the SCK•CEN. The efforts in this field concentrated on developing an alternative to the current process of effluents treatment that involves a costly and energy and space-demanding freeze/thaw cycle easing the separation of the sludges. The studies performed aimed at the development of the optimal treatment technology including:

- Removal and recycling of the sulphuric acid
- Recuperation and recycling of cerium
- Coagulation and flocculation of colloidal sludges containing metal hydroxides
- Filtration of the sludges
- Cementation

The sulphuric acid could be removed from the solution by electrodialysis (ED) or electro-electrodialysis (EED), the latter allowing the removal of 90% of the 1M sulphuric acid present. More than 99% of the cerium IV, which is a high cost product, could be recuperated as $Ce_2(SO_4)_3$ with a very high selectivity (impurities <0.1%) after reduction of Ce(IV) to Ce(III) by H_2O_2.

An effective removal of sludges from the waste was achieved by optimising both the solids separation steps. For the reduction of the volume of settled sludge and easing the filtration, optimum coagulants-flocculants mixture and the conditions of their application were selected in extensive tests from the chemicals regularly used in the treatment of industrial waste water. The best results were obtained with EPIDMA (organic coagulant) and a mixture of coagulants-flocculants $FeCl_3.6H_2O$/C587/A370 L. As an alternative to freeze/thaw treatment, use of a precoat (perlite) was proposed to improve the performance of the filtration step. The use of such precoat could enhance the maximum load capacity on each filter cartridge by about a factor of two, further amelioration was achieved by addition of a coagulant (EPIDMA) during the filtration.

The individual steps of the procedure were tested on pilot scale with a real waste. In these tests, Ce(IV) was recovered from 4 L of the waste; the overall decontamination factor for ^{137}Cs and ^{60}Co achieved in the sludge separation steps was very high (between 1500-3000 for caesium and 700-1400 for cobalt). Currently plans exist to construct an industrial installation for the treatment of these effluents.

2.2.1.2. Waste containing oxoanionic contaminants

Two different technologies were proposed for the treatment of oxoanionic contaminants (e.g. ^{99}Tc or ^{125}Sb species) containing waste. The first technology, studied at the University in Helsinki, Finland, was based on the *development and application of novel highly selective inorganic ion exchange materials.*

The newly developed material is based on a tin dioxide modified by doping by other metal cations. In tests with simulated solutions, this material exhibited very high uptake for

^{99}Tc – the values of distribution coefficients (K_d) over 10^6 mL/g – in solutions with ionic strengths of 1 mol/L, and the uptake level remained high over a broad pH range from pH 2 to 11 (see Figure 2). Two different uptake mechanisms were identified for the technetium uptake in acidic and near neutral to basic solutions, however, the mechanism of uptake by ion exchange was questioned and the exact sorption process was still left open. The results of the column tests performed with 1 M $NaNO_3$ indicate that there is at first a rapid uptake in the surface of the material, followed by a slower process inside the granules of the material.

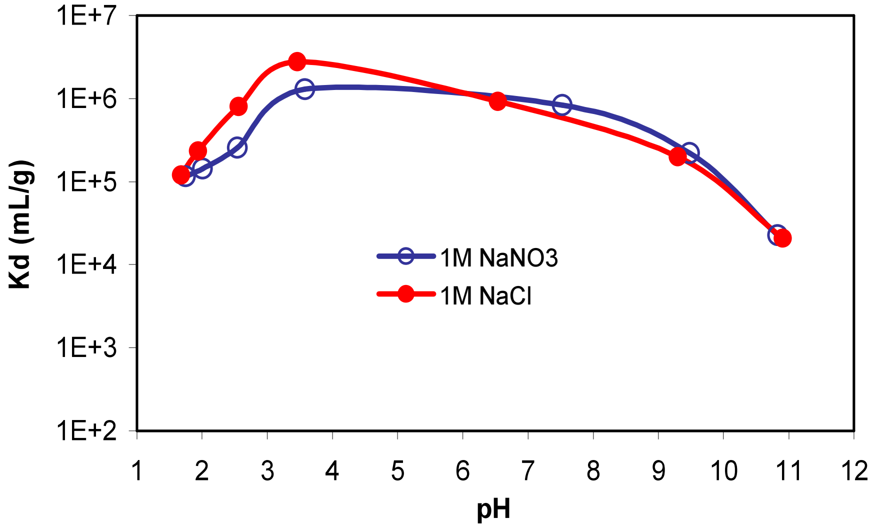

FIG. 2. Technetium uptake on modified tin dioxide distribution coefficients as function of pH from 1M sodium nitrate and chloride solutions.

Dynamic column experiments with another type of material showed efficient removal of ^{125}Sb (DF 300-600) from simulated BWR Floor Drain Water with no sign of column exhaustion when the test was discontinued at 2500 bed volumes. In a column test with real Fuel Pond Water from Olkiluoto-1 BWR, Finland, no ^{125}Sb was detected in the outlet solution after having treated 2000 BV of this water (decontamination factor for ^{125}Sb greater than 230).

The second technology, proposed at the Joint Institute for Power and Nuclear Research, Belorussian Academy of Sciences, Sosny, Minsk, was based on the exploitation of the *interaction of some anions with polynuclear hydroxo-complexes of polyvalent metals.*

The basic part of the research performed demonstrated that the anions investigated can be sorted according to their ability to influence formation and state of iron(III), chromium(III) and thorium(IV) polynuclear hydroxocomplexes as

- Anions with low complexing ability (Cl^-, NO_3^-, ClO_4^-, I^-) that do not form any firm bonds with the polynuclear hydroxocomplexes, though their presence can increase the abundance of polynuclear species in solution.
- Anions with medium complexing ability (SO_4^{2-}, PO_4^{3-}, IO_3^-) that can join the polynuclear hydroxo-complexes, and as a result be separated from solution. Some of them at higher concentration can also hinder formation of polynuclear hydroxocomplexes (SO_4^{2-}).

- Anions with high complexing ability, the presence of which results in destruction of iron polynuclear hydroxo-species in a solution. As a result, they can hinder removal of other anions from solution.

Based on these results, a novel method for removal of radioactive anions with medium complexing ability (e.g. IO_3^- or PO_4^{3-}) from contaminated solutions was proposed. In a simple two-compartment set-up, the contaminated solution is placed into one compartment and contacted with the polynuclear species containing solution in the second compartment. Both compartments being separated by a dialysis membrane, the anions that pass the membrane and join the polynuclear complexes are rejected by the membrane and thus removed from the contaminated solution. This principle has been demonstrated on simple aqueous solutions contaminated with IO_3^- anions in laboratory scale. It has been also proposed for the removal of iodide anions, after applying additional oxidation stage for the conversion of iodide to iodate.

2.2.1.3. Aqueous waste containing large amounts of suspended matter, oils and other organic substances

For this type of waste, a multistage process consisting of three basic steps has been developed and demonstrated:

- removal of suspensions, mineral oils emulsions, or colloid particles with their simultaneous concentration to the highest achievable level in secondary waste;
- separation of radionuclides and other toxic impurities by membrane and/or sorption technologies;
- concentration of the aqueous secondary waste producing concentrates with salt content up to 300 – 350 g/L.

The principal scheme of this process is shown in Figure 3.

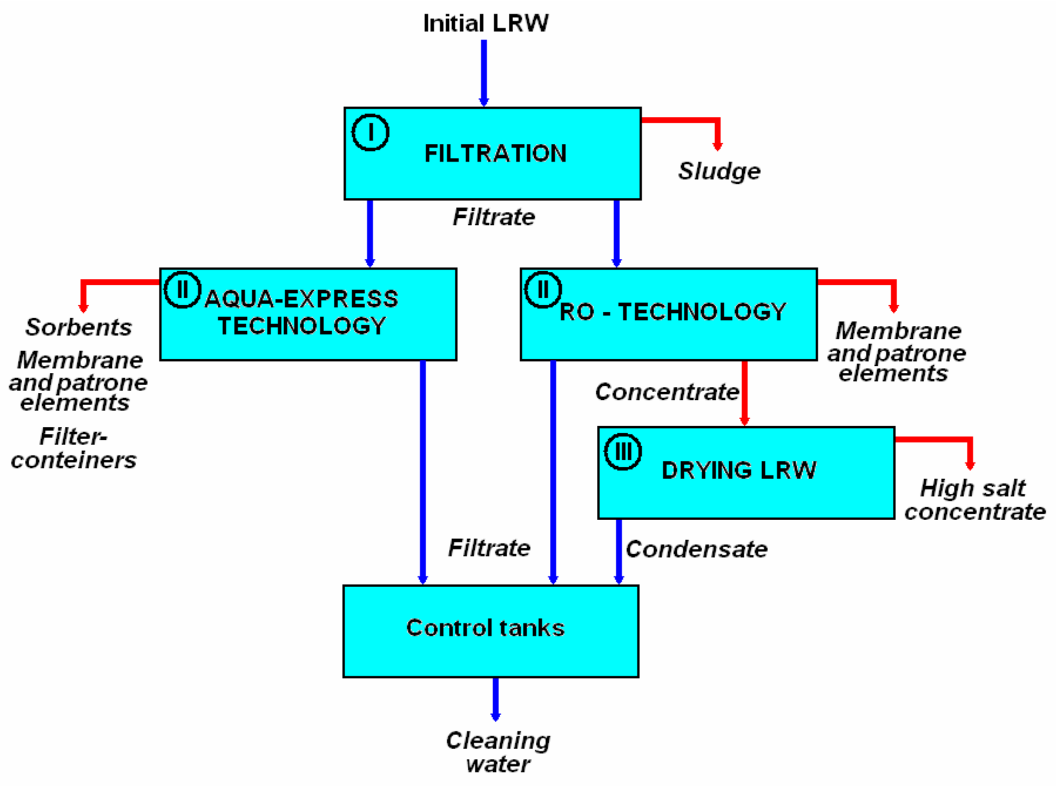

FIG. 3. The basic block diagram of a process for treatment of aqueous waste containing large amounts of suspended matter, oils and other organic substances.

As can bee seen from this scheme, the process has been proposed in two basic set-ups that differ by the technology used for the treatment of the liquid waste after separation of the particulates, colloids and/or emulsions. These options are:

- AQUA-EXPRESS technology using a cascade of sorption filters with various inorganic sorbents, which have selectivity to different radionuclides, and a polishing stage of ultrafiltration. This set-up is suitable for cleaning of liquid waste with a chemical composition similar with natural waters, and limited set of radionuclides (for example, ^{137}Cs, ^{90}Sr, ^{60}Co).
- RO-technology that makes use of reverse osmosis with a subsequent additional treatment of the permeate on selective inorganic sorbents. In comparison with the AQUA-EXPRESS, this technology is characterised by smaller volume reduction of the waste but it allows cleaning ot the waters with complex chemical and radionuclide composition.

The new developments pertain to the first and the third of the above specified stages of this new process. The efficiency of the filtration stage could have been significantly improved by:

- Replacement of standard filtration devices with cross-flow micro- or ultrafiltration. For this purpose, “DISKVIKIG” and “CYLINDERVIKIG” devices equipped with rotating disk- or cylinder-shaped ceramic, cermet or metallic filtration membranes were developed.

— Introduction of strong oxidising agents (e.g. ozone, hydrogen peroxide, oxochlorides) into the filtered waste. By this addition, reduced membrane clogging is achieved by organic substances decomposition that is further facilitated by the prolonged contact of the organics with the oxidising agents in the cross-flow filtration reject stream. In addition, some contaminants (e.g. Fe^{2+}) will precipitate after the oxidation and will be filtered off.

For the concentration of the aqueous secondary waste, an original method of evaporation of water from the wastes at ambient temperature (+15 to +45 °C) in a filter - press device with porous polymeric plates has been developed and tested on a real waste. The pilot device used had productivity of up to 10 L of evaporated water per hour.

The above-described set-up has been optimised and applied for the treatment of several real waste streams in full scale.

2.2.1.4. Acidic transuranium elements containing waste

This is an example of the waste that has been defined 'problematic' because the presence of alpha-nuclides in this waste disqualified it for acceptance for processing with other liquid waste by the locally available technologies. For the removal of ^{241}Am and ^{236}Pu from this simple solution, a commercial highly selective inorganic ion exchange material, Quasar N (antimonysilicate - $SbSiO_2$), was proposed. In two 10 mL columns, two batches of the waste with the total volumes of 5 L and 1 L, contaminated up to ~ 8 or 71 kBq/L, respectively, were treated. The total decontamination factors reached in these runs were about 30 or 73, respectively. The decontaminated acidic solution was released into the sewer after neutralisation.

2.2.2. Aqueous concentrates

A number of processes including selective ion exchange, chemical precipitation, advanced oxidation methods, etc. were developed for the effective treatment of the various 'problematic' concentrated waste streams described above. The scale of work ranged from laboratory scale using simulated waste spiked with radiotracers to full scale plant operation with actual waste. The following is a brief account of the work carried out by the participating member states and the results obtained.

2.2.2.1. Reactor operation

For WWER-type evaporator concentrate of composition similar to that from NPP Loviisa, Finland, a three-step process was developed in the Czech Republic and demonstrated in laboratory scale using simulants in collaboration with Finland. The first step deals with the boric acid removal from the solution. On decreasing the pH value of the solution from 12.5 to about 9 by addition of concentrated nitric acid, the vast majority of boric acid is separated due to solubility limits and is filtered off. The separated boric acid can be purified and reused in the nuclear fuel cycle. The second step aims at limiting the negative influence of the presence of EDTA in the solution to radiocobalt sorption on inorganic ion-exchangers. Photocatalytic degradation of EDTA using photo-Fenton system was carried out in a small immersion well photocatalytic reactor of 100 mL capacity. A 6 W low pressure mercury lamp was used for irradiating the samples by the short-UV range (254 nm) radiation. The method was shown to be promising for destruction of EDTA. After removal of both boric acid and EDTA, the last step is the removal of radiocobalt. This was tested using Co-Treat (titanium oxide-based inorganic absorber supplied by Fortum Nuclear Services Oy, Finland). The result showed that sorption of radiocobalt improved after EDTA removal by photocatalytic degradation. However, better sorption performance is required for practical application of this process. It is possible that further optimization of EDTA degradation process would lead to total EDTA removal and more effective separation of radiocobalt by sorption process.

The above study also showed that the removal of boric acid does not have pronounced effect on cobalt separation by sorption process. Tests were carried out using actual alkaline evaporator concentrate of NPP (Dukovany, Czech Republic) to determine if effective removal of ^{60}Co could be accomplished without removal of boric acid but after destruction of complexing agents like citric and oxalic acids by radiolysis. A number of inorganic absorbers and charcoals were tested in batch and column experiments. It was found that radiolysis at 300 kGy resulted in only partial destruction of the complexing acids and the removal of ^{60}Co by the sorption agents was insufficient for practical application.

In work carried out in Russia on NPP evaporator concentrates, specially designed carbon fiber sorbents with impregnated ferrocyanides were used for the removal of caesium. The destruction of Co-EDTA complexes in the waste appeared to be the most challenging task. Application of dithiocarbamate complexes for Co-EDTA precipitation showed good results. However, the obtained polynuclear complexes were difficult to remove completely from resulting solutions that does not allow obtaining concentrate decontamination factor more than 100. The hydrothermal treatment of such a waste appeared to be the most efficient way to destruct extremely stable Co-EDTA complexes. In this process, the organic portion in the waste is destroyed at 180-250°C, 50-150 bar pressure in the presence of a catalyst. The reaction was found to be completed in a few minutes (<10 minutes). Cobalt could be separated efficiently using a filter column after EDTA destruction. This process was tested successfully on a pilot scale in a 20 L/h flow-type reactor using actual waste at the Novovoronezhskaya NPP.

2.2.2.2. Reprocessing

For the sulphate-bearing high level waste of reprocessing origin in India, barium borosilicate was found to be a suitable matrix which did not result in phase separation. Full scale operations have been carried out in an induction-heated metallic melter at WIP Trombay to vitrify nearly 20 M^3 of HLW, producing nine ton of vitrified product so far. However, waste loading in the direct vitrification process is limited on account of the limited solubility of sulphate (≤ 1.5% w/w) in glass. Hence, an alternative approach leading to sulphate separation from HLW was also studied in laboratory scale using simulated and actual waste and in pilot scale using inactive simulated waste. In this process, acidic HLW is made alkaline by addition of sodium hydroxide. This leads to the precipitation of a sludge which carries down a number of waste constituents, viz., uranium, plutonium, lanthanides, strontium and substantial quantities of ruthenium. The alkaline supernatant stream contains most of the Cs activity, some portion of ^{106}Ru as well as sulphate and aluminate. A process flowsheet was developed to manage the sulphate-free sludge and alkaline supernatant and verified experimentally at pilot scale using simulated solutions. The sludge could be dissolved in concentrated nitric acid and vitrified in conventional sodium borosilicate matrix. The removal of uranium also from this solution by solvent extraction using TBP in hydrocarbon diluent was found to lead to increased waste loading. The alkaline sulphate-bearing supernatant can be decontaminated and converted to low level waste by removing ^{137}Cs using Resorcinol Formaldehyde Polycondensate Resin (RFPR) column and ^{106}Ru using zinc-charcoal column. The recovered ^{137}Cs can be utilized as a radiation source. Scaling up of the process to engineering scale has been completed. Processing of actual HLW is expected to start in the next two years.

Two promising ^{106}Ru removal methods were tested, viz., (i) chemical treatment involving precipitation of ferrous hydroxide and (ii) sorption in a fixed bed column of zinc-charcoal mixture. Different waste streams of reprocessing origin, including highly salt-loaded alkaline intermediate level wastes and sulphate-bearing alkaline supernatant streams resulting from the pre-treatment of HLW, were tested for removal of ^{106}Ru (initial activity was 10^{-3} to 1 mCi/l). These methods require adjustment of the feed pH to ~2.0. Under optimum conditions, a DF of 8-10 could be obtained in the chemical treatment process. The zinc-charcoal column method was found to be effective in bringing down the activity to very low levels.

Photo-Fenton mineralization was studied for destruction of problematic oxalic acid waste resulting from plutonium reconversion operations in India using simulated solutions at pilot scale in Tubular Flow Photoreactor. The results showed quantitative mineralization of oxalic acid. Visible light was also found useful besides ultraviolet light for the photo-Fenton reactions.

2.2.2.3. Decommissioning

For the treatment of highly saline wastes that would result from the dissolution of Na/K liquid metal coolant after decommissioning of the Fast Reactors at Dounreay, U.K., tests were conducted using a broad range of commercial inorganic and proprietary composite absorbers. These tests were conducted on simulated wastes. Cs-Treat (Finland) was confirmed to be good for Cs removal, KNiFC-PAN (Czech Republic) was proposed as an even more efficient alternative. Three absorbers, viz., IONSIV IE-910, sodium titanate and hydrous titanium dioxide were identified as prospective candidates for Sr and Co removal. Integrated system performance is to be improved further. These results will be used by the UKAEA, Dounreay, U.K. for the final selection of the technology for full-scale treatment.

Several sorption materials were tested for Cs and Sr separation from concentrates arising from reverse osmosis treatment of waste generated from decontamination and decommissioning of Russian nuclear submarines. If the caesium sorption was not a major problem due to application of composite ferrocyanide sorbents, the removal of strontium was a complicated task due to low Sr/Ca selectivity coefficients characterizing virtually all conventionally used sorbents. Application of sorbent-reagent materials comprising microcrystalline sorbents formed in porous matrix (for example, barium silicate) provided a dramatic increase of the strontium sorption selectivity. In this study ^{90}Sr was the main target radionuclide. The full-scale application of respective technology was performed on real solutions produced by a reverse-osmosis unit and 5000 M^{3} of concentrate was treated.

2.2.2.4. Isotope production

The acidic intermediate level waste resulting from the processing of ^{99}Mo in Australia has been processed since 1999 to a crystalline hydrated uranyl nitrate solid form by a combined evaporation-chemical process. This solidification process leads to a 97% reduction in volume but is an interim step only as the solid crystalline product is unsuitable for long term disposal due its solubility in water. Therefore, incorporation of the waste into a titanate based ceramic waste form (SYNROC) was identified as an appropriate strategy for immobilization of the waste before ultimate disposal. The process involves liquid impregnation into a precursor, drying and subsequent calcination for canning and hot isostatic pressing. Cold trials were conducted in a mock-up facility constructed for this purpose.

2.2.3. Spent ion-exchange resins and radioactive sludges

The methods of spent ion-exchange resins (SIER) processing for long-term storage can be divided into non-destructive methods, in which SIER undergo minimum destruction in some preliminary procedures and are immobilized into inorganic or organic matrix, and destructive methods concerned with complete or partial destruction of organic ion-exchange resins.

Non-destructive methods of processing SIER are characterized either by increase of total volume of radioactive waste (cementation) or by slight decrease of this volume (bituminization, polymerization). In this case there are no problems of decontamination of large amount of radioactively contaminated gases and spreading of decontamination of ^{14}C radionuclides that occurs with carbon oxides emitted during the resins incineration.

The problem of SIER cementation was focused in the work made at China Institute of Atomic Energy, Department of Radiochemistry that dealt with fixation of spent resins in composite cement materials containing high-efficiency cements (ASC) with fillers (zeolites) substantially reducing the radionuclide leachability from cement composites formed. Studies of composites properties with using high-efficiency cements were performed in comparison with regular Portland cements. Optimization of the cement mixture composition was performed in regard to composite mechanical properties and their changes in the process of many days' water immersion and freeze-thaw cycles. The obtained cement compositions showed good mechanical properties, performance stability and low diffusivity of ^{137}Cs and ^{60}Co radionuclides.

Destructive methods of SIER processing including various incineration methods, wet oxidation, pyrolysis, acidic and alkaline destruction are usually accompanied by substantial (sometimes tens-fold) reduction of the volume of conditioned solid radioactive waste (SRW) formed during processing. One of the possible ways of this volume reduction is the application of SIER incineration in molten salt – in so-called molten salt oxidation (MSO) reactors.

Such a method of complete destruction of spent ion-exchange resins was implemented by Nuclear Fuel Cycle R&D Group, Korea Atomic Energy Research Institute, Republic of Korea. The authors of this project studied accumulation of heavy metals, caesium and strontium as well as sulfates during oxidation of ion-exchange resin IRN-77 in the reactor. The setup comprising two MSO reactors was used: the primary reactor was heated up to 700-900^{0}C whiles the secondary reactor – up to 900-950^{0}C. The conditions of reactor operation in the process of destruction and accumulation of heavy metals, strontium and caesium in the system and their transformation into non-volatile carbonates were determined. It was shown that use of the secondary reactor allows reducing the carbon monoxide emission by up to 100 ppmv. Sulfur-containing compounds were retained in the reactors completely. In this case sulfur dioxide emission was not observed at all. This project was also focused on possibilities of using 'Brown's gase' obtained in electrochemical generator for regeneration of waste salt melts from accumulated chlorides that can be of interest in processing of chlorine-containing ion-exchange resins.

In the project performed by the Nuclear Recycle Group, Bhabha Atomic Research Centre, Government of India, Trombay, Mumbai, India one of the objectives was the development of the methods of wet destruction of spent ion-exchange resins – such an approach would enable one to make safer the process of SIER management in regard to radioactive gas emissions. The project dealt with the photocatalytic degradation of SIER using the Fenton reaction. Hydrogen peroxide and ozone were used as oxidizers. The results obtained at pilot-plant scale application have shown that photocatalytic oxidation of two-phase system solution – ion-exchanger is able to produce a homogeneous aqueous solution subject to conventional LRW treatment. Also, preliminary eluation of caesium from SIER to reduce SIER γ-irradiation dose and possibility of cementation of such eluates were examined within the scopes of this project. The caesium leachability from cement matrices containing substantial amounts of multivalent metals was estimated.

The problems of 'dry' destructive methods are related to noticeable emission of radioactively-contaminated gases and large content of ^{14}C radionuclides in carbon dioxide formed at spent resins incineration. The problem of ^{14}C is becoming more urgent due to stricter requirements on environmental protection. Thorough filtration and absorption of all the emitted carbon dioxide by alkaline absorbers with formation of insoluble carbonates reduces significantly total volume of SRW produced at the end of such processes. That is why recently the methods of preliminary deactivation of SIER have been developed intensively. This is especially crucial in regard to ^{14}C radionuclides, since the very necessity of localization of the whole amount of carbon dioxide emitted at destruction imposes limitations on applications of many oxidation methods.

In the work performed at Nuclear Engineering Technology Institute, KHNP and Korea Atomic Energy Research Institute, Republic of Korea the studies were conducted on removal of ^{14}C through preliminary treatment of spent ion-exchange resins by solutions that did not contain strong acids. The objective of this work was to determine the conditions of the highest possible removal of ^{14}C radionuclides combined with minimum removal of other radionuclides (^{60}Co, ^{137}Cs etc.). The work was focused on spent ion-exchange resins of a CANDU-reactor, in which maximum amount of ^{14}C radionuclide is formed. Resins processed in this way can be, according to national regulations, sent for final disposal. Studies were performed on non-active and real samples of mixed ion-exchange resins IRN-150. The results obtained using phosphoric acid and its acidic salts ($NH_4H_2PO_4$) allow concluding on a possibility of removing more than 96% of ^{14}C radionuclide from SIER. In this case ^{60}Co and ^{137}Cs are removed less than 1 and 5 per cent, respectively. The SIER processed by this method can be transferred for final disposal or treated by some oxidation method without problems concerned with spreading of ^{14}C radionuclides.

In principle, one can make a separate group of technologies dealing with **preliminary decontamination of SIER** and transferring of radionuclides into liquid phase from which they could be conditioned with using conventional methods. As an example, one can take the project implemented by the Comisión Nacional de Energía Atómica, Buenos Aires, Argentina where the radionuclide removal was carried out through consecutive treatment of a resin by sulfuric (10%) and, after washing with water, oxalic acid. The authors studied removal of metal radionuclides (^{60}Co, ^{137}Cs) and α – emitters from deactivation solutions by fixation in the process of electrolysis in aqueous (Co) and alcohol (^{137}Cs) media. The ^{14}C radionuclide emitted, after acidic treatment, as carbon dioxide, was fixated by gas infiltration through sodium hydroxide solution. Secondary decontamination from caesium and cobalt radionuclides was conducted by filtration of deactivation solutions through zeolites. The system with acidic decontamination of SIER through consecutive treatment by sulfuric and oxalic acids was tested on real SIER of NPP in a pilot-plant variant, and it was shown that less than 0.7% of initial caesium activity and less than 2% of initial cobalt activity remained after the treatment.

The problem of SIER treatment is similar to that of processing of radioactively contaminated sludges formed in a different waste management stream which is addressed in one part of the work done at ANSTO, Australia. The simulated waste containing aluminium hydroxide, sodium carbonate, nitrate, sulfate and chloride was prepared, and comprehensive tests of the approach were performed to estimate its applicability in management of the Effluent Plant-produced radioactive waste sludge. The optimal regimes of the drum dryer performance were found, and the approach will be commissioned for treatment of real waste.

2.2.4. Site-specific and miscellaneous waste

Some conventional technologies for processing of organic waste, as for example incineration, requires substantial investments, sophisticated off-gas cleaning and off-gas control systems, and now is hardly acceptable for the public. Thus, new methods, more tolerant to the environment, for organic waste destruction and conditioning are needed that can provide high-destruction efficiencies with low capital and operating costs for the safe treatment of these types of "problematic" radioactive wastes. New non-thermal methods for the destruction of organic components of radioactive waste are now being explored in the USA and elsewhere. A molten salt oxidation (MSO) process is being studied in Clemson University, USA for the safe and effective destruction of organic components of radioactive waste. This work involves a laboratory-scale molten salt oxidation system where solid or liquid organic waste is injected into a bed of molten carbonate salt in the presence of an oxidizing gas. The relatively simple MSO process with the carbonate salt completely destroys organic compounds, such as contaminated oils. A major advantage of the process is that any acid gases generated are neutralized, thus no off-gas scrubbing system is required. All radioactive contaminants are retained within the bed of molten salt. In the past, high melting point salts have been used with air oxidation. In these new studies, the use of low melting point salts is being investigated along with stronger oxidizing agents, such as Fenton's Reagent and manganese (VII), oxidant concentration and temperature. The use of lower melting point salt mixtures appears to be an effective improvement to the MSO process in order to lower consumption of energy required.

To process the tritiated organic liquid waste a thermal/catalytic oxidation technology has been developed and demonstrated at SCK•CEN, Belgium. The heart of the system is a two-stage high temperature Hastelloy reactor. Organic liquid is injected into a heated cavity using oxygen as the propellant. Oxidation products and excess oxygen are re-mixed in an alumina diffuser zone downstream of the cavity and passed over heated 0.5% platinum on alumina catalyst. Gases leave the reactor and are separated into condensable (water) and non-condensable (CO_2) fractions. Typically, the wall temperature of the cavity is set at 750 °C while the catalyst temperature is fixed at 700 °C. A nitrogen gas cooling circuit is installed under the cavity heater to remove reaction heat when the need arises. The installation can accept liquid flows of up to the order of 1 L/h with activities up to 0.2 TBq/L. The gases leaving the reactor are excess oxygen, carbon dioxide and water vapour. Tritium is exclusively present in the water phase as HTO. Condensed tritiated water could be conditioned and stored or its tritium content could be recovered for recycling.

Investigation was carried out at NECSA, South Africa to establish procedures for characterization and conditioning of old biomedical waste contaminated with ^{14}C, ^{3}H and other radionuclides. Three potential options for this waste characterization and conditioning were considered for evaluation of their efficiency, safety and cost.

(1) Evaluation of gamma nuclides content of the drums by the segmented gamma scanner. Sterilization of waste after recovery from drum by the Stericycle Electro Thermal Deactivation (ETD) process. This consists of the mechanical shredding and mixing of waste in a negative-pressure environment, after which it is transferred trough the ETD deactivation process. After deactivation waste is reloaded into the drum for further conditioning by super-compaction and cementation.

(2) Initial evaluation of gamma nuclides content in drum as above. Sterilization of drummed waste using a very high activity gamma source. Super-compaction, collection and analysis of released liquid phase (if any), followed by conditioning of compacted waste and released liquids into cement (in over pack container). Model experiments have shown that existing liquids in this case almost completely could be released from compacted waste. This method has an advantage, since ETD process requires shredding and repacking of waste.

(3) Evaluation of gamma nuclides content in drum as above. Placing the waste container inside an over pack and filling the voids with a water-absorbing material (calcium-bentonite clay), which has relatively low swelling characteristics and would therefore not damage the outer container. A conservative estimation of ^{14}C content in drums is made in this case, which could not exceed 8.3×10^{10} Bq per drum. This option does not require the waste drums to be opened and therefore no sterilization is required.

The pros and cons of each option are now under evaluation against the existing WAC for disposal, cost involvement and impact on the long term safety of the facility.

Treatment of spent liquid scintillation cocktails *Wallac HISafe 3* used for measurement of ^{241}Am was studied at the University of Helsinki, Finland. Large number of ion exchange materials were screened for the removal ^{241}Am from these scintillation cocktails. The aquatic phase in the cocktails was either 0.2-0.4 M $NaNO_3$ or HNO_3. These cocktails were studied as such or mixed with methanol, ethanol or propanol diluents. The tentative test comprised the measurement of the distribution coefficient K_d of the tracer batchwise in the various liquids for the different ion exchange materials. In general, the americium uptakes were low ($K_d <$ 500 ml/g) for all the ion exchangers studied for the HiSafe cocktail alone. However, addition of alcohols as a solvent increased the uptake dramatically. Especially ethanol produced a very high uptake ($K_d >$ 10,000,000 ml/g) for SrTreat material. Further work was carried out with best materials (SrTreat-titanate, antimonysilicate, manganese oxide) to optimize the amount of diluents and to conduct column experiments. It was found that a ^{241}Am uptake in the materials increased with increasing dilution until the dilution ratio reached about 1:2. Columns (10 mL) packed with MnO_2 and $SbSiO_2$ removed ^{241}Am efficiently from diluted HiSafe liquid with a maximum DF of 60-250. There was no sign of column exhaustion when 2.5 L (250 BV) of liquid had been processed. A total of 8 L of scintillation liquids were purified in the column tests. In addition, americium-bearing nitric acid waste liquids (pH = 1.1) were decontaminated successfully using $SbSiO_2$-columns and the purified acid solution was disposed of in the sewer after neutralization.

2.3. IMPORTANT DEVELOPMENTS AND OBSERVATIONS

2.3.1. Aqueous waste

The results achieved enabled design of several promising novel technologies for the treatment of ‘problematic’ aqueous waste types, some of which were brought up to the pilot-plant or even industrial-scale level. The general feature of most of these novel technologies is their multistage nature with the first stage(s) designed so as to declassify the waste from the ‘problematic’ into ‘standard’ category which renders it amenable to standard treatment technologies applied in the final stage(s) of the sequence.

The following (not exhaustive) list of the most important developments can be drawn on the basis of the results achieved within this project:

- Applicability of the photocatalytic degradation of organic components of the aqueous wastes was demonstrated for various decontamination liquids on pilot- to full scale. Photo-Fenton homogeneous catalyst was found preferable to heterogeneous catalysts for this type of tasks. If such step is introduced as a pre-treatment stage, the ‘problematic’ spent decontamination liquids may be subjected to treatment by standard high-volume-reduction technologies.
- Important new achievements were reached in the development of inorganic ion exchangers. A new developmental class of inorganic ion exchangers, comprising mixed oxide materials with pyrochlore structure, has been demonstrated to be efficient for radiocobalt removal from organic complexants containing liquors. However, the selectivity of the material is not high enough to break the EDTA complex. Even more prospect seems to be offered by the novel materials based on a tin dioxide modified by doping with other di-valent metal cations. These materials were demonstrated to exhibit very high uptake of oxoanionic contaminants (e.g. $Tc_2O_7^-$ or $Sb_2O_5^-$) with distribution coefficients over 10^6 mL/g in solutions with ionic strengths of 1 mol/L; the uptake level remaining high over a broad pH range from pH 2 to 11.
- New results were reached in the field of separation of suspended matter, oils and other organic components from aqueous waste. It has been demonstrated that by a careful selection of the combination of coagulants-flocculants and filter pre-coats, the load capacity of the filters can be more than doubled while achieving radionuclide decontamination factors of several thousands even in pilot-plant scale with real waste. Significant progress in this field represent namely the novel cross-flow micro- or ultrafiltration devices “DISKVIKIG” and “CYLINDERVIKIG” equipped with rotating disk- or cylinder-shaped ceramic, cermet or metallic filtration membranes. In combination with the demonstrated positive effect of the introduction of strong oxidising agents (e.g. ozone, hydrogen peroxide, oxochlorides) into the filtered waste, these devices enable dramatic improvement of the filtration rate and filter capacity. For the concentration of the aqueous secondary waste, an original method of evaporation of water from the wastes at ambient temperature in a filter - press device with porous polymeric plates has been developed.

There are several general conclusions and recommendations that follow from the results of the work done in this field. These can be summarised as follows:

- Multistage processes, aiming at the declassification of the ‘problematic’ waste into ‘standard’ category in the initial stages of the sequence, generally seem to offer the most versatile and effective solution to the treatment of many ‘problematic’ wastes.

This approach enables to submit such wastes, after a proper waste-specific pretreatment, to standard treatment technologies.

- Application of novel materials, such as developmental inorganic ion exchangers, or novel technologies for treatment of ‘problematic’ wastes may lead to huge reduction of the amount of final waste solids thus significantly decreasing the final disposal costs at not very highly increased process complexity and the treatment costs. For this type of wastes, „simplest is the best” approach may become rather cost ineffective. The results obtain suggest that there is a high probability of good return of money invested into the research of new approaches to treatment of such ‘problematic’ wastes.
- There is one very pronounced commonality in the approach of several groups involved in this part of the work – the efforts to further **minimise the volume of the waste to be finally disposed by recuperating and re-using as much of the waste components as possible and economically feasible**. This approach, together with the regeneration / recycling strategy, seems to unequivocally represent the waste treatment strategy for the 21st century and should be properly pursued, e.g. in the framework of a future IAEA supported CRP.

2.3.2. Aqueous concentrates

A number of selective sorbents and ion exchangers were developed for the effective separation of radionuclides from concentrated aqueous waste streams. Many of these materials have been synthesized and even produced in bulk quantities using in-house facilities. In some cases, the production technology has been transferred to commercial organizations. The synthesis and production of most of these absorber materials were not discussed in detail in view of intellectual property rights issues. Hence the use of these materials is now limited to the original developers and their collaborators.

Tests carried out by some of the researchers with actual waste streams like evaporator concentrates, reverse osmosis reject streams and waste streams from reprocessing plants were found to give encouraging results in direct separation of radionuclides from these streams with the novel selective sorbents. Conducting more such tests with different types of actual concentrated aqueous wastes would lead to a better assessment of the possibility of using such materials in regular plant operation.

With the currently available separation technologies, the destruction of complexing agents like EDTA is essential for achieving efficient separation of cobalt. Two processes were found to be effective for the oxidative destruction of EDTA, viz., hydrothermal method and photo-Fenton method. The efficacy of the hydrothermal method was demonstrated in trials with actual waste using a flow-through reactor for oxidative destruction of EDTA followed by a filter column for removal of radiocobalt. The sorptive removal of cobalt was found to have improved after photo-Fenton treatment but further improvement in efficiency is required. This would require further work to ensure complete destruction of EDTA and its degradation products by this method and also to develop more effective sorbents for cobalt. For the treatment of oxalic acid-bearing waste streams, photo-Fenton mineralization of oxalic acid appears to be a promising clean method which should now be tested with actual waste.

The pre-treatment of sulphate-bearing high level waste by alkaline precipitation process for the removal of sulphate before vitrification was shown to lead to important benefits, including higher loading of the waste in glass matrix and the possibility to recover ^{137}Cs for utilization as a radiation source.

The removal of ^{106}Ru from waste streams is known to be very difficult because it is present as numerous complexes of nitrosylruthenium. It was demonstrated that removal of ruthenium can be best accomplished by a combination of chemical treatment involving ferrous hydroxide precipitation and sorption in fixed bed zinc-charcoal column from wastes with higher initial ^{106}Ru activity ($\geq 10^{-2}$ mCi/l). Treatment of streams with low ^{106}Ru activity can be accomplished directly by zinc-charcoal sorption.

Direct immobilization in a durable matrix like SYNROC, suitable for ultimate disposal, was also demonstrated in full-scale cold mock-up trials for waste streams resulting from ^{99}Mo production.

2.3.3. Spent ion-exchange resins and radioactive sludges

The work performed within the scope of this CRP that are concerned with development of destructive, non-destructive technologies and technologies including preliminary decontamination of SIER have shown the promising character for the chosen directions of development, and possibilities for their practical implementation. In particular for:

'destructive' technologies:

- Application of photocatalytic Fenton reaction in oxidation of spent ion-exchange resins and production of homogeneous aqueous solutions for treatment of LRW by conventional approaches.
- Application of two-reactor setup for management of spent ion-exchange resins in molten salt oxidation reactors.

'non-destructive' technologies:

- Application of compositions on the basis of cements with high aluminium content and zeolites for cementation of spent ion-exchange resins

technologies employing preliminary decontamination:

- Use of neutral and acidic phosphate solutions for removal of ^{14}C radionuclides from spent ion-exchange resins. The problem of ^{14}C in SIER of CANDU-reactors is at present a major ecological problem that requires immediate solution.
- Application of decontamination of spent ion-exchange resins by solutions of sulfuric and oxalic acids followed by fixation of radionuclides containing in eluent by means of electrochemical treatment and filtration through zeolites.

The development of novel safe and efficient methods for processing spent ion-exchange resins and low-level sludges into conditioned solid radioactive waste subject to long-term storage comprises one of the important tasks of management of radioactive waste generated in nuclear power fuel cycle. As follows from the results of the works performed within the scopes of the present CRP, the most prospective methods of managing spent ion-exchange resins will be those employing preliminary removal of ^{14}C isotope from the resin followed by its immobilization in small volumes of crystalline matrices characterized by minimal isotope exchange. Further, the resins containing fission radionuclides and α-emitters shall undergo oxidation destruction in condensed medium with minimum gas emissions. It could be a salty melt of MSO reactors or photo-Fenton oxidation. As a result of these operations, radionuclide localization will proceed in minimal volumes of media that can be easily vitrified or processed into crystalline matrices of Synroc-type. Such a processing will be optimal as from the ecological point of view as because of minimization of the volume of radioactive waste to be sent for final disposal.

2.3.4. Site-specific and miscellaneous waste

As indicated earlier, a molten salt oxidation process (MSO) is a promising method for treatment of variety of radioactive organic waste, many of which are considered as problematic for conventional handling, treatment and conditioning. For the destruction of organic components of radioactive waste high melting point salts have been used in MSO processes with air oxidation. In the present studies, the use of lower melting point salt mixtures together with stronger oxidizing agents appear to be an effective improvement to the MSO process in order to lower energy requirements. The methods were tested at laboratory conditions for simulated and real radioactive organic waste with promising results for full scale applications.

For processing of liquid organic tritiated waste the new technology has been developed at SCK•CEN, Belgium. The technology allows complete oxidation of different tritiated organic liquids into tritiated water and almost-complete capture of this product water followed by the discharge of the tritium-free off-gases. The technology can easily be adopted for destruction of different tritiated organic liquids with efficiencies exceed 99.99%. The installation is compact, leak-tight and tritium compatible. Based on the results of experiments and demonstrations for different waste types it could be concluded, that this technology is both technically feasible and safe and can be adapted for various categories of tritiated liquid organic waste.

Different possible options for processing of not well characterized waste, such as for example old not-processed biomedical radioactive waste should be carefully evaluated based on extended analysis of the waste and potential processing options. Factors to be considered in the decision making process are radiological and biological risks to workers, potential impact on the environment, waste acceptance criteria for disposal or extended storage, investments needed and operational cost, volume reduction alternatives, etc. Decision on particular option in most cases is waste- and site-specific considering existing safety and regulatory requirements. The radiological risks may be relatively low during the reconditioning process, and the main handling risk could be due to the bio-hazardous nature of waste. From this point of view, different options for characterization, handling and conditioning should be carefully evaluated considering potential risk, long term safety and compliance with the regulatory requirements.

When treating alpha-contaminated scintillation liquid special sorbents for alpha-contaminants removal could be efficient solution. Manganese oxide and antimonysilicate (Quasar N) were demonstrated as effective sorbents to treat organic Am-bearing liquid scintillation waste. These sorbents could be recommended for processing of Am-containing scintillation waste liquids followed by appropriate further processing of spent sorbents and decontaminated liquid phase. The investigation has shown that the efficiency of such treatment depend on several factors, in particular it could be substantially improved by addition of alcohols as a solvent to the scintillation liquids.

3. RECOMMENDATIONS

The main problems identified during the work on this project, and the approaches to their effective solutions that can be generally recommended on the basis of the results achieved, are as follows:

Aqueous waste

The main problems arise during management of decontamination solutions. Photodegradation of the organic complexing agents and/or surfactants followed by selective sorption can be considered as the most promising approach to these problems. In this respect, development of selective inorganic ion exchangers continues to be an important challenge

Aqueous concentrates

The main problems within this category of waste are concerned with processing of concentrated waste containing complexants. The results obtained in this CRP indicate that the solutions can be found through development of efficient methods of cobalt complexes oxidation by Fenton reaction and/or hydrothermal oxidation. Separation of problematic inactive constituents, e.g. sulphate, before vitrification of high level waste is very useful.

Future work in this area involving aqueous concentrates should include (i) the development of more effective processes for the removal of ruthenium and cobalt, (ii) the proper management of spent sorbents and secondary waste streams, (iii) the scale-up of promising processes and testing with actual waste (iii) recovery and recycle of chemicals (e.g. boric acid) wherever possible

Spent ion-exchange resins (SIER) and low-level sludges

The main problems in this waste category arise during upgrade from simple immobilization methods (into cement, bitumen or polymer matrices) to volume reduction methods, namely high-temperature processing and oxidation of spent resins by different methods. The problems are related to radionuclide release into gaseous phase and spreading of ^{14}C into environment. The main results obtained within the scope of this CRP lead to the conclusion that successful management of SIER waste would involve a preliminary step for removal of ^{14}C (if present) followed by a suitable oxidative destruction method such as photo-Fenton reaction or molten salt oxidation. A method for efficient trapping and immobilization of the separated $^{14}CO_2$ will also have to be developed.

Site-specific and miscellaneous waste

The main problems here are related to the tritium and ^{14}C containing legacy waste from either health-care or research. Even though the main achievement is a progress in tritium waste management the practice developed during the selection of optimum technology for management of the legacy health-care waste will be very valuable for anyone facing similar problem.

Probably the most important recommendation that can be made on the basis of the studies performed is that “Multistage processes, aiming at the declassification of the ‘problematic’ waste into ‘standard’ category in the initial sateges of the sequence, generally seem to offer the most versatile and effective solution to the treatment of many ‘problematic’ wastes. This approach enables to submit such wastes, after a proper waste-specific pretreatment, to standard treatment technologies.”

4. CONCLUSIONS

The CRP was successful in realizing its objective to address the problem of treatment and conditioning of radioactive waste, for which efficient and cost effective methods for processing are not readily available. A full range of technical solutions is offered for the variety of “problematic” waste streams that were the subject of the CRP. Additionally, the extent of progress varied considerably, starting from the consideration of scaling up of promising results demonstrated on the laboratory level or demonstrated performances on a pilot plant level to fully developed commercial applications.

There is no doubt that the issue of “problematic” waste will stay as an emerging issue, regardless of the wealth of research results presented within this CRP, considering that expected new developments in the application of nuclear energy will result in the generation of new and not always easy to process “problematic” waste streams. A key element to the approach to solving the issues of problematic wastes is in the diversity of options that may be available, which may or may not be site specific. The CRP brings these options or ideas together to enable fruitful discussions, assessment of options and lessons learned, and to serve as a generator of ideas for the future progress. The research in this particular field will not come to an end, so it could be recommended to the IAEA to consider continuing to support this coordinated research program.

Differences in national regulatory framework or in site-specific waste acceptance criteria, coming from site-specific safety assessment or simply because of different geographical, climatic or socio-economic conditions will continue to hinder the application of uniform solutions for “problematic” waste streams with similar characteristics. Availability of technological solutions is only one of the required pre-requisites, but very often not entirely sufficient to define the way forward. Furthermore, it is neither possible, nor economically feasible, to tackle all the possible research routes required to develop a technically correct, economically attractive and widely acceptable solution for a specific waste stream, whether for an individual waste stream, for a country or for an institution. Taking this fact into consideration it is worthwhile to encourage exchange of advanced information on the ongoing research and development activities in Member States and to facilitate access to the practical results of their application for processing of specific waste types, since that will contribute towards the implementing of novel ideas and for improving the efficiency and general safety of waste management practice in Member States.

This CRP is a prime example to the value of the information exchange among its participants and for the results achieved and offered to Member States. The full value of the IAEA CRP program approach will be reached with coordinated programs on either multilateral or bilateral research agreements/contracts bases among its participants, or wider. Although collaboration within this CRP resulted in a limited number of bilateral agreements between the participants, further efforts are required to promote the idea of legally binding contracts/agreements for the sharing of results of technology development programs.

Problematic areas emphasized in this CRP are processing of variety of decommissioning waste with complex compositions, processing of some specific liquid waste concentrates and treatment and conditioning of spent organic ion exchangers generated in the nuclear industry. Apart from these, many other site-specific or facility-specific waste are generated requiring special approaches to address their particular characteristics.

There is one very pronounced commonality in the approach of several groups involved in this CRP – the emphasis to further **minimise the volume of the waste to be finally disposed of, by partitioning radionuclides, regenerating media and re-using as much of the waste components as possible and economically feasible**. This approach, together with the reuse/recycling strategy, seems to represent a robust waste treatment strategy for the 21st century.

APPENDIX I. CO-OPERATION ACHIEVED

The CRP was initiated in 2002, based on evaluation of submitted research proposals and final selection of the participating institutions from the respective countries. The participants of the CRP holder of either research contracts or research agreements with the IAEA are as follows:

Argentina	Comisión Nacional de Energía Atómica
Australia	ANSTO
Belarus	IREP, National Academy of Sciences
Belgium	SCK/CEN
China	China Institute of Atomic Energy
Czech Republic	Technical University of Prague
Finland	University of Helsinki
India	Bhabha Atomic Research Center
Korea (Rep.of)	Nuclear Engineering Technology Institute, KHNP
Korea (Rep.of)	Nuclear Fuel Cycle R&D Group, KAERI
Russian Fed.	Institute of Chemistry, Far East Department, Academy of Sciences
Russian Fed.	CIA “Radon”
South Africa	NECSA
Ukraine	National Academy of Sciences
USA	Clemson University

The CRP had the following activities in regard to cooperation:

The 1st Research Co-ordination Meeting (RCM), November 2003, Prague, Czech Republic. The meeting resulted with identification of “problematic” wastes. Scope and preliminary results were discussed, and co-operation established. Formation of a network of institutions to realise the tasks identified in specific research objectives of the CRP. Discussion of working programmes and preliminary results was held, and bilateral and multilateral contacts were established.

The 2nd Research Co-ordination Meeting (RCM), July 2005, Kiev, Ukraine. The meeting resulted with discussion on progress in R&D work, results of bilateral and multilateral co-operation, and establishment of working plan for further research.

The 3rd Research Co-ordination Meeting (RCM), November 2006, Mumbai, India. Reports of final results of individual R&D work were submitted to the IAEA and presented during RCM. The discussion was held on achievements of the individual projects and on possibility for the implementation. Some novel ideas and approaches were presented and discussed among participants.

Consultants Meeting, December 2006, Mumbai, India.

Consultants meeting was held with an objective to provide integration, evaluation, validation and recommendations of technical solutions offered during CRP in the CRP Final Report. The secondary objective was to edit reports submitted by the individual participants to harmonize their presentations in the IAEA TECDOC.

This CRP is a prime example to the value of the information exchange among its participants and for the results achieved and offered to Member States. The full value of the

IAEA CRP program approach will be reached once coordinated program results in either multilateral or bilateral research agreements/contracts among its participants or wider. Although this CRP resulted in limited number of bilateral agreements between the participants, further efforts are required to promote the idea of legally binding contracts/agreements for the sharing of results of technology development programs.

The bilateral agreements were established between participants from Belarus, Czech Republic, Finland and Ukraine. The result was organization of a researcher exchange which was organized for more then 10 person-months. The same participants finding commonalities in their research programs have initiated project on “Novel methods for demanding radionuclide separations from nuclear waste liquids”, which was not accepted for funding by INTAS.

APPENDIX II. COUNTRY WORK SUMMARY

II.1. ARGENTINA

Approximately 70m3 of mixed spent ion exchange resins had been accumulated over the operational life of the Atucha I Nuclear Power Plant. Due the content of the alpha emitters in addition to other nuclides, principally Cs-137, Co-60, Sr-90, this waste is classified as intermediate level. Direct processing of this resin (by cementation) would therefore result in a significant volume increase to abide by the national policy. A laboratory test program was conducted on simulant and actual resin, followed by pilot scale evaluation on the actual resin to remove the activity to a small volume of product and leave a more barren resin.

The resin was treated with sulphuric acid solution to extract the nuclides and react with any remaining crud. The resulting solution was treated by an electrolysis cell to remove the cobalt and alpha emitters. It was also possible to retain the caesium in the electrolytic cell if alcohol is added to the solution. This step also enables the recovery of Li-7 from the solution as an insoluble sulphate to allow it to be recycled. Recovery of caesium (and cobalt) was possible on natural zeolite.

Laboratory tests produced superior extractions from the resin which were assessed to due to better liquid resin contact. Further pilot plant configurations and testing is required to optimize the process which has indicative significant cost benefits by volume reduction of waste classed as intermediate level.

II.2. AUSTRALIA

The work is divided in two main parts. The first part involved inactive tests for the drying of radioactive sludges produced in the Effluent Plant from liquid low-active waste streams. The simulated waste containing aluminium hydroxide, sodium carbonate, nitrate, sulfate and chloride was prepared, and comprehensive tests of the approach were performed to estimate its applicability in management of the Effluent Plant-produced radioactive waste. The optimal regimes of the drum dryer performance were found, and the approach will be commissioned for treatment of the actual thickened waste sludge. The tests concerning drum durability, stainless steel coupon corrosion testing and operating regime were conducted.

The second part of the work dealt with intermediate level liquid waste generated during Mo-99 radioisotope production that shall ultimately be sent for final disposal. The Synroc ANSTO technology was chosen as a preferable form for intermediate level solid waste disposal. The suggested technology comprises incorporation of the waste into ceramic matrix through liquid impregnation into a precursor; drying; and calcination followed by hot isostatic pressing. The resulting form represents the most durable one for ultimate disposal. The mock-up facility featuring all the above stages was constructed and operated to comprehensively test the impregnation, drying and calcinations in an integrated operation under non-active conditions. The results of the mock-up operation are presented.

II.3. BELARUS

The aim of the current research was the development of a novel method for removal of radioactive anions from contaminated solutions. The approach was based on the fact that polynuclear hydroxo complexes of polyvalent metals are able to interact with some anions to form non ionic species, which can be easily separated from solution. Polynuclear hydroxocomplexes are intermediate species between mononuclear hydroxocomplexes and hydroxide precipitates.

The effect of anions and cations on hydrolysis of chromium(III), iron(III) and thorium(IV) with formation of polynuclear hydroxocomplexes was investigated by applying a range of physico-chemical methods: dialysis, centrifugation, pH-metric titration, methods of radioactive indicators, and spectrophotometry.

The anion behaviour was broadly classified in three categories. Anions with low complexing ability (Cl-, NO3-, ClO4-, I-) do not form any firm bonds with the polynuclear hydroxocomplexes, though testing showed their presence can increase percent of polynuclear species in solution. Anions with medium complexing ability (SO42-, PO43-, IO3-) can join the polynuclear hydroxocomplexes, and as a result be separated from solution. Some of them at higher concentration (SO42-) can also hinder formation of polynuclear hydroxocomplexes. Presence of anions with high complexing ability in solution results in destruction of iron polynuclear hydroxo species, as a result they can hinder removal of other anions from solution.

The foreign metal ions hinder the process of cation polymerization when they are in a form of a hydrated cation and get attached to the polynuclear species when they are in a form of mononuclear hydroxocomplexes. The ability of PO43- and IO3- anions to join polynuclear hydroxocomplexes of iron can be used for their removal from solution by a membrane method.

The studies of these methods have shown that it can be effective use for the removal of anions with medium complexing ability.

II.4. BELGIUM

In the frame of this CRP was implemented two projects, "Experimental verification of detritiation techniques for liquid organic waste" and "Experimental evaluation of methods for processing secondary waste from decontamination activities".

A lot of efforts are devoting to the treatment of tritiated waste. In existing installations and in future fusion devices, various categories of problematic tritiated waste are and will be produced. The final goal is the reduction of tritiated waste and tritium discharges by treatments that allow trapping all tritium as tritiated water. This tritiated water could be conditioned and stored or its tritium content could be recovered for recycling. Since a few years SCK•CEN has been focusing on the treatment of tritiated organic liquids, tritiated metals, tritiated concrete, detritiation of molecular sieves, chemical purification of tritiated water, and water detritiation.

Over the past few years SCK•CEN investigated and has developed a process for the treatment of tritiated organic liquid waste. The method is a two-stage combustion with thermal and catalytic oxidation of organics into tritiated water for further treatment and tritium free off-gases for discharge. The first application of this thechnology was treatment of about 200 litres of tritiated organic solvent, with a total activity of around 17 TBq. The second one was a study to treat tritiated organic liquids from the Joint European Torus (JET) project. These solvents were treated completely with only limited discharges to the environment. It was concluded that this technology is both technically feasible and safe and can be adapted for the treatment of various categories of problematic tritiated liquid waste.

Another category of problematic waste studied is coming from the dismantling of existing nuclear plants. SCK•CEN has developed its own chemical decontamination process, so-called MEDOC© (Metal Decontamination by Oxidation with Cerium), based on the use of Ce(IV) as strong oxidizing species in sulphuric acid. It was designed to decontaminate stainless steel, later it was upgraded to allow decontamination of carbon steel. This produces a lot of various liquid radioactive wastes that need to be treated and conditioned for storage and final disposal.

Filtration techniques are widely used for removal of radioactive particles and sludge present in water. One recurrent problem is the removal by filtration of colloidal particles (mainly iron hydroxide and some iron oxides) to improve the efficiency of filtration. Well known techniques to improve the filtration of colloidal particles are freezing of sludge, use of filter aids and addition of coagulant-flocculants. The objective was to find an appropriate alternative for the currently used freezing of sludges and to increase the load of each filtration cartridge in order to minimize the volume of conditioned waste.

The use of coagulants-flocculants, to reduce the volume of settled sludge and to make the filtration easier has been investigated. Several tests like sedimentation, filtration under vacuum and filtration under pressure allow compare the use of different conventional coagulants-flocculants alone or in mixture together. It was shown that the use of coagulants-flocculants allows reducing the volume of settled sludge. The best results were obtained with EPIDMA (organic coagulant) and a mixture of coagulants-flocculants $FeCl_3.6H_2O$/C587/A370 L.

It was shown that the filtration of sludge without a cycle of freezing and defrosting is feasible using a precoat (perlite). The results show that it can enhance the maximum load capacity on each filter cartridge by about a factor of two. Moreover the addition of coagulant (EPIDMA) during the filtration over a precoat allows a further amelioration of the maximum load. Currently it is planed to construct an industrial installation for treatment of the MEDOC effluents.

II.5. CHINA

The option of direct encapsulation of the spent organic resins into cementitious materials was adopted in 2003, as a preferred method. In order to realize the end goal, the main work consisted of: the survey of the source terms; cementitious material formula investigation; and the process development. This work, which was undertaken in the following years, is addressed as follows.

Source terms of the spent resins in CIAE showed that a total of 24-29 m^3 of spent resins was generated and accumulated in the past 40 years. Spent resin arose from two research reactors (heavy water reactor and light water reactor), and from the waste management plant. The amount of the spent resins from the heavy water reactor was $1m^3$ or so, but its radioactive concentration was high to $\sim10^8$-$\sim10^9$ Bq/m^3.

Two kinds of cements, ASC and OPC cement selected, as solidifying matrix were investigated. In comparison, ASC was superior to OPC cement and it displayed preferable performances to encapsulate spent resins. The optimum formulation is:1) resin: .17(dry w/w);

and 2) ASC cement: .43; zeolite: .10; water: .30. The properties of the resulting resin-cement concrete mix met the national criterion and the process requirements. These properties included 104mm for the slump, 9.6(Mpa) for the 28-day compressive strength, 1.2% and 6.0% for the compressive strength loss after 42-day water immersion and 5 thaw-freeze circles, 2.72E-06(cm^2/d) and 1.63E-07 (cm^2/d) for ^{137}Cs and ^{60}Co diffusivities.

A scale-up demonstration of 200L was performed in batches directly in the final storage container, which was a 200L steel drum. Based on the recommended concrete formulation and on the determined operation conditions, the large volumes of resin-cement concretes were produced. The properties of the resin-cement concretes were examined by analysis of drilled cores. The results showed that homogeneous solidified forms were obtained under the given process parameters, and that mechanical performances and the peak temperature satisfied the regulatory requirements.

II.6. CZECH REPUBLIC

WWER-type NPP Evaporator concentrates

A three-step process was designed and tested for radiocobalt separation from NPP evaporator concentrates containing organic complexing agents(oxalic acid, citric acid, EDTA).

- The first step deals with the boric acid removal from the solution. After decreasing the pH value of the solution to the minimum of boric acid solubility (about 9.0-10.0), the vast majority of boric acid may be easily filtered-off. Moreover, the separated boric acid can be purified and reused in the nuclear fuel cycle.
- The second step of this process aims at limiting the negative influence of the presence of organic complexing agents in the solution to radiocobalt sorption on inorganic ion-exchangers. Homogeneous photo-Fenton system was confirmed to be most effective for such treatment of these solutions.
- Separation of radiocobalt from the resulting solution is the last step of the process. After boric acid removal and organic complexants degradation, efficient radiocobalt separation can be achieved by active carbons or some inorganic ion-exchangers, viz., Co-Treat and antimony silicate.

After a thorough study and optimisation of the basic parameters, performance of the three-step process was demonstrated with the simulant of NPP Loviisa (Finland) evaporator concentrates containing 95 g/l of sodium tetraborate hexahydrate, 20 g/l of potassium nitrate, 127.5 g/l of sodium nitrate, 30 g/l of sodium hydroxide, 300 mg/l of EDTA and spiked with ^{57}Co. This demonstration was done in collaboration with University of Helsinki. Results showed that cobalt separation by sorption on Co-Treat could be significantly improved after EDTA degradation by photo-Fenton reaction. However, total EDTA decomposition seems to be necessary to achieve effective cobalt separation.

Process for treatment of NTA-based decontamination solutions

The experiments performed revealed that most nuclides such as silver and strontium can be very effectively removed from the spent NTA-based decontamination solutions introduced recently in the Czech Republic, even in the presence of NTA, e.g. by means of a choice of inorganic absorbers (crystalline polyantimonic acid or sodium titanate) or the Purolite NRW 160 resin. Purolite NRW 160 resin was found to show good distribution coefficients (1770 ml/g) for problematic cobalt even in the presence of NTA. However, for very effective radiocobalt separation, a two-step process, analogous to the above-described process for radiocobalt separation from NPP evaporator concentrates, had to be designed and tested.

- In the first step of this process, negative influence of the presence of NTA in the solution to radiocobalt uptake is eliminated by NTA degradation. Photo-Fenton degradation was confirmed to be more effective for this purpose than the photocatalytic degradation with TiO_2 catalyst.
- In the second step, radiocobalt can then be separated from the resulting solution. Purolite NRW 160 resin or sodium titanate inorganic ion exchanger display the highest efficiency for radiocobalt uptake. However, total degradation of NTA is necessary for effective radiocobalt sorption.

After a study and optimisation of both the steps, the performance of the proposed process was demonstrated with the simulant of NPP Temelín (Czech Republic) NTA-containing spent decontamination solution.

PFR and DFR solutions

The liquid metal coolants from Dounreay Fast Reactor (DFR) and Prototype Fast reactor (PFR) at the UKAEA Dounreay, U.K. will be destroyed by dissolution thus producing highly saline solutions. The composition of DFR and PFR solutions are 4M NaCl+ 0.15M KCl and 2.2 M $NaNO_3$ + 0.7 M KNO_3, respectively, contaminated with radionuclides such as caesium, cobalt, strontium etc. which are to be separated.

In an extensive set of tests a broad series of commercial inorganic and proprietary composite absorbers and/or their set-ups were tested for the separation of radiocaesium, radiostrontium, radiocobalt and plutonium from a simulated liquid waste resulting from the destruction of bulk sodium (Dounreay Prototype Fast Reactor – PFR) or sodium / potassium (Dounreay Fast Reactor – DFR) liquid metal coolant.

The KNiFC–PAN inorganic organic composite absorber with polyacrylonitrile binding matrix was found to be more efficient for caesium separation and also more stable than the commercial Cs-Treat® material (Potassium hexacyano ferrate, FNS, Finland). The results obtained demonstrated that by using two columns of absorber in series, it would be possible to reduce significantly the total number of columns estimated to be required for caesium separation from these wastes if single columns were used.

Three absorbers, viz., Ionsiv IE-910, NaTiO and Hydrous titanium dioxide were identified as promising for Sr and Co removal form these streams. However, in an attempt to concurrently remove Cs, Sr, and Co, efficient strontium separation could not be achieved.

The results of these experiments will be used by the UKAEA, Dounreay, UK, for the final selection of the technology for full-scale treatment of the waste.

II.7. FINLAND

Novel highly selective inorganic IX materials have been studied for the removal of radionuclides from following “Problematic” liquid wastes.

Experiments were carried out in laboratory scale using simulated liquid wastes.

Alpha-bearing Scintillation cocktails

Tracer studies for removal of ^{241}Am (6-50,000 cpm) from Wallace HI safe liquid scintillation cocktails. The aqueous phase was either 0.2 – 0.4 M $NaNO_3$ or HNO_3. Batch studies were done on cocktail alone or after dilution with methanol, ethanol or propanol. ^{241}m uptakes were low (Kd < 500 ml/g) for several IX materials for cocktail alone. Addition of alcohols, especially ethanol produced a very high uptake (Kd : 10^7 ml/g) for Sr–Treat. Further column experiments using Sr-Treat-titanate, antimony silicate, manganese oxide sorbents showed that upto 1:2 dilution ^{241}Am uptake increased. Column packed with MnO_2 and antimony silicate removed ^{241}Am efficiently from diluted cocktail with DF_{max} ranging from 60 to 250. There was no sign of column exhaustion upto 250 BV.

Am – bearing nitric acid waste

Quasar N sorbent was studied for the removal of trace amounts of ^{241}Am and ^{236}Pu from 0.01-1 M nitric acid solutions. Kd > 100,000 of ^{236}Pu over the whole concentration range while uptake of ^{241}Am decreased at 1 M acid to about 1100 ml/g. Americium bearing liquids (8000-71000 Bq/l) was purified using column of Quasar N with DF of about 30-73.

^{57}Co removal from acidic decontamination solutions

Manganese antimonate sorbent was used for uptake of ^{57}Co. Uptake of cobalt was dependent more on solution pH than on type of acid (oxalic acid, citric acid, formic acid, H_2SO_4, HNO_3). Kd was high (5000-10,000 ml/g) at pH 2-3 but decreased gradually at pH ~ 1. In tests conducted at pH=2, hydrazine, ascorbic acid, Na – dithionite did not decrease cobalt uptake. In column experiments conducted on 10 mM oxalic acid solution traced with 0.1 mM EDTA (and 0.1 M iron) cobalt uptake was poor. However, when EDTA was excluded, DF ~ 20 was observed at ~ 4000 bed volumes of treated solution. DF of 20-50 was observed for cobalt in 0.01 M HBF_4 solution.

Removal of aquo-anions (pertechnetate and antimonate)

Modified tin dioxide (MOM) was very effective for ^{99}Tc removal. Kd was 10^6 ml/g in solution with 1 M ionic background and the uptake level remained high over wide range of pH (2 – 11). Normal organic resins gave Kd values of < 200 ml/g. Column tests were conducted on fuel pond water from Olkiluoto-1 NPP (BWR) of Finland containing 396 Bq/l of ^{125}Sb using MOM material. The result showed that no ^{125}Sb was detected in the effluent even after passing 2000 bed volumes of the feed. An overall DF of >230 was obtained.

II.8. INDIA

Two broad methodologies were considered for the treatment of Indian 'Problematic' waste streams that included sulfate-bearing high level radioactive liquid waste, spent ion-exchange resins, oxalate-bearing acidic waste, decontamination waste containing organic complexants and surfactants, ^{106}Ru-bearing aqueous waste:

- Development of waste-specific solutions.
- Separation / destruction of the problematic species in the waste followed by adoption of conventional waste management practices.

Two alternatives were investigated for management of sulphate-bearing high level waste: (i) Direct vitrification in suitable glass matrix (ii) Separation of problematic sulphate from waste by alkaline precipitation and management of the resulting waste streams, viz., sludge and alkaline supernatant by conventional methods. Lead borosilicate and barium borosilicate glass matrices were subjected to systematic investigations using simulated and actual wastes. A full-scale plant based on induction-heated metallic melter, already available, was utilized for generation of data. Based on these studies, barium borosilicate matrix has been adopted for engineering scale operations on actual waste at Waste Immobilization Plant, Trombay. Nine tons of radioactive vitrified waste product have been produced successfully in 97 operations so far. In parallel, alkaline precipitation method was pursued as an alternative. The studies were conducted up to pilot scale using simulated wastes. A 15-litre precipitator was used for generation of engineering data. Experimental results showed that the problematic sulphate could be separated into the alkaline supernatant stream along with most of the Cs activity, some portion of the ^{106}Ru activity and aluminium as aluminate. The sludge retains other waste constituents, viz., uranium, plutonium, lanthanides and strontium. A process flow sheet was developed for management of sludge and alkaline supernatant and verified experimentally. The sludge can be dissolved in concentrated nitric acid and the resultant solution can be vitrified in conventional borosilicate matrix. In this way, the waste loading can be increased by a factor of nearly four compared to direct vitrification. Removal of uranium from the dissolved sludge and vitrification enhances the waste loading by a factor of about ten. The alkaline supernatant can be decontaminated to dischargeable levels by removing caesium activity using Resorcinol Formaldehyde Polycondensate Resin and ruthenium activity using zinc-charcoal column.

Destruction of organic matter by eco-friendly photo-Fenton advanced oxidation process was investigated as a method for treatment of problematic organic wastes, viz., spent ion-exchange resins, decontamination formulations, surfactants and oxalate-bearing acidic wastes. These studies were conducted using simulated wastes. A two-step process consisting of chemical degradation of resins into water-soluble products followed by photo-Fenton mineralization of the resultant resin solution was developed up to pilot scale in tubular flow photochemical reactor. Elution of radioactivity from spent resin facilitates its handling. Elution studies were conducted using multivalent metal ions (mainly ferric ion) as a pre-treatment step in batch and column modes. Immobilization of eluate in cement matrix was also demonstrated. Using different photochemical reactor types, degradation of EDTA, anionic surfactants (sodium salt of dodecyl benzene sulfonate and sodium lauryl sulfate) was also investigated at pilot scale. These results clearly demonstrated the efficacy of photo-Fenton reaction. Oxidative destruction of problematic organic constituents in the waste by photo-Fenton reaction results in the generation of aqueous waste that can be decontaminated by conventional methods like chemical treatment and ion exchange for achieving high volume reduction.

^{106}Ru is one of the most difficult radionuclides to remove from aqueous waste streams generated from reprocessing plants. Two promising ^{106}Ru removal methods were tested, viz., (i) chemical treatment involving precipitation of ferrous hydroxide and (ii) sorption in a fixed bed column of zinc-charcoal mixture. Both these methods require adjustment of the feed pH to about 2.0. Under optimum conditions, a DF of 8-10 could be obtained in the chemical treatment process. The removal of ^{106}Ru by zinc-charcoal column was found to give the best results. This was tested for removal of ^{106}Ru from different waste streams including highly salt loaded alkaline intermediate level wastes and sulphate-bearing alkaline supernatant streams. These experiments clearly demonstrated that the ^{106}Ru activity (10^{-3} –10^{-2} mCi/L) could be brought down to very low levels.

II.9. KOREA, REPUBLIC OF (KAERI, DAEJON)

Behavior of Hazardous Metals in a Molten Salt Oxidation Reactor during the Destruction of Chlorinated Plastics

Molten salt oxidation (MSO) is one of the promising alternatives to incineration for chlorinated organics without the emission of chlorinated organic pollutants. Research investigated behaviours of Cd, Pb and Cr and four radioactive metal surrogates Cs, Ce, Gd and Sm in a bench-scale molten Na_2CO_3 oxidation reactor during the destruction of PVC plastics. In the tested temperature ranges (870-950°C) and NaCl content (0-10%), the impact of the temperature on the retention of cadmium and lead in the MSO reactor was very small. Neither temperature increase nor chlorine accumulation in the MSO reactor reduced the retention of Cr, Ce, Gd and Sm. Over 99.98% of these metals remained in the reactor. The influence of the temperature on the caesium behaviour is relatively large for a chlorine addition, however, over 99.7% of caesium remained in the reactor throughout the entire test.

Molten Salt Oxidation of Ion-exchange Resins Doped with Toxic Metals and Radioactive Metal Surrogates

Ion-exchange resins doped with toxic metals and radioactive metal surrogates were test-burned in a two stage bench-scale MSO system. The purposes of this study are to confirm the destruction performance for the organic ion-exchange resin. The destruction of the organics is very efficient in the primary reactor. The primarily destroyed products such as carbon monoxide are completely oxidized in the secondary MSO reactor. Over 99.5% of all the fixed toxic metals (lead and cadmium) and radioactive metal surrogates (caesium, cobalt, strontium) remained in the MSO reactor bottom. Thermodynamic equilibrium calculations and the XRD patterns of the spent salt samples revealed that the collected metals existed in the form of each of their carbonates or oxides, which are non-volatile species at the MSO system operating conditions.

Influence of the Operating Behavior of Brown's Gas during the Thermal Treatment of an Incineration Ash and Waste Salt

In a burning of Brown's gas the reaction of the hydrogen molecule and the OH radical from the decomposition of the OH radical bonding produces gaseous water and hydrogen radicals. Hydrogen radical is very reactive and can react with NaCl, KCl or LiCl to produce HCl gas. High temperature steam does not react with NaCl, KCl or LiCl to produce HCl gas. Thus, Brown's gas can be used to remove chlorine from waste salt containing NaCl, KCl and/or LiCl.

II.10. KOREA, REPUBLIC OF (KHNP, DAEJEON)

An investigation program was initiated in 2004 to develop ^{14}C removal technology for the spent ion exchange resin currently stored at the Wolsong nuclear power plant site. The mixed ion exchange resin generated from various purification systems at the CANDU reactors was contaminated with relatively high activity of ^{14}C radionuclide, far exceeding the criteria for low level shallow disposal. Separation and analysis of samples of stored resin indicated about twice the concentration of ^{14}C on the anion exchange resin in comparison to the total. With consideration of the disadvantages associated with other acid stripping and thermal processing techniques various alkaline nitrate and phosphate leaching solutions were investigated for removal of ^{14}C.

Phosphate-type stripping solutions of $NH_4H_2PO_4$ or H_3PO_4 showed effective removal of ^{14}C from actual spent resin with three advantages. Once ^{14}C is removed from spent resin, the bicarbonate ion as HCO_3^- can simultaneously gasify to $^{14}CO_2$ gas without addition of an acidic solution. A high ^{14}C removal efficiency of over ^{14}C 99% could be obtained with ^{14}C trapped in a soda lime scrubber. The desorption characteristics of cationic nuclides from the cationic resin was low at less than 1% for Co and less than 5 % for Cs.

II.11. RUSSIAN FEDERATION (RAS, VLADIVOSTOK)

The present work aims at development and application of selective sorption materials in decontamination of problematic radioactive waste containing medium to high degree of salinity. Radionuclide concentrations are typically 10^5 – 10^6 Bq/l. The problem of conventional Cs selective ferrocyanide sorbents in LRW decontamination are mainly concerned with chemical and colloid instability that greatly hampers their real selectivity advantage. This problem was circumvented by developing new methods of synthesis of nickel ferrocyanide – active carbon fibre composite using thermolysis instead of conventional precipitation. This method of synthesis improves (upto two orders of magnitude) the composite material selectivity. These sorbents were applied for processing of solutions of different salinity and ~ 5000 m^3 of real waste was processed. New sorption-reagent materials on the basis of amorphous xerogels of barium silicate, titanate and zirconate were developed. These crystalline salts are allowed to be formed inside a suitable porous matrix. Selectivities of these sorbents for Sr removal are extremely high even in highly saline solutions (1M $CaCl_2$) with kd >> 1000. These materials were applied for decontamination of highly saline LRW formed during low saline LRW treatment by Reverse Osmosis. Approx. 5000 M^3 of LRW, including LRW with salinity > 30 gm/l was successfully treated using these novel sorbents.

Processing of NPP Evaporator Concentrates

Complex chemical composition of evaporator concentrate (EC) containing large amounts of complexing agents does not allow efficient removal of cobalt by conventional methods.

Composition of EC :

Na / K metaborate : upto 250 gm/l
EDTA Salt : 2 – 3 gm/l
Complex salts of Fe, Ni, Cr : upto 2 gm/l
pH : 9 – 12
^{60}Co : 10^6 Bq/l
^{137}Cs : 10^8 Bq/l

Some insoluble precipitates of dithiocarbamate [e.g. Mn (Et_2-N-CS_2)] remove Co-EDTA complexes selectively in alkaline medium giving Kd of ~ 1450 ml/g. However, due to the high colloid instability of the formed polynuclear complexes, precipitate separation is problematic.

Hydrothermal processing of evaporator concentrates emerged as the most attractive option for destroying Co-EDTA complexes. The process operates at 180-250°C and 50-150 bar under flowing conditions in the presence of a catalyst. The reaction completes in few minutes (<10 minutes). Destruction of EDTA facilitated cobalt removal by a filter column. These experiments were conducted upto pilot scale under flow conditions (20 L/h).

II.12. RUSSIAN FEDERATION (RADON, MOSCOW)

This report elaborates on the utilization of multi modular and multi functional technological facility for cleaning of LRW developed in MosNPO "Radon" that consists of three basic stages: 1)`cleaning of LRW from suspensions, emulsified mineral oils or colloid particles to allow for simultaneous concentrating of the specified impurity up to the greatest possible content in the secondary radioactive waste stream; 2) cleaning of LRW from radionuclides and other toxic impurities by the use of membrane and sorption technologies; and 3) producing of liquid salt concentrates with salt content up to 300 – 350 g/l.

Options for optimization of the membrane-sorption technological schemes for LRW cleaning are well-known [reference 1-3], therefore the basic attention of this research work has been given to the first and third stages of LRW cleaning or on the technical improvements of the facility cleaning stage and on new developments for production of liquid salts concentrates

The research work has proven that is possible to use a metal net or cermet porous diaphragms (the pore size 0.1÷10 μm) for LRW filtration with the large content of suspensions, emuslified oil and other organic substances. In addition it is also proven that use of some oxidizer (for example, hydrogen peroxide) in treated LWR, will destroy deposits of organic substances on a surface of a diaphragm, and hence increase efficiency and longevity of it. It is shown, that the rotation of a filtration element (disk or cylindrical) with a speed 1000÷3000 rpm increases speed of a filtration, prolongs the work cycle of a filtration element between two regenerations and allows regeneration of a filtration element surface to be carried out in a simple way. The device for high concentrating of slurries (the working area of disk filtration elements is 2 m^2) is developed and manufactured. The new feature of the device is a mechanical removal of deposits from surface of disk filtration elements, which slowly rotate with speeds of 1-3 rpm.

The original, novel method for evaporation of water from LRW at normal temperature (+15 to +45 °C) in the"AQUA-DRY" device with the filter - press type with porous polymeric plates has been tested with a real LRW. The design is developed and manufacturing of the pilot device for LRW drying with productivity up to 50 l/h of evaporated water has started.

II.13. SOUTH AFRICA

About 2500 drums of non-processed health care radioactive waste have been accumulated over the years at the Necsa site in South Africa. These waste drums contain unknown quantities of ^{14}C, some ^{3}H and bio-hazardous components. Before disposal this waste should be characterized and processed to meet the established acceptance requirement. The objective of the project was to investigate and assess options for characterization, treatment and conditioning of historically collected ^{14}C containing medical waste to satisfy regulatory requirements.

Several options for waste characterization with and without sterilization were studied. It was found and confirmed that ^{14}C is mainly contents in the liquid phase of waste. Reasonably accurate estimates of the ^{14}C contents of the waste packages may be obtained through compacting drums in a supercompactor and analysis of liquid released from the drum during compaction. Model experiments have shown that existing liquids in this case almost completely could be released from compacted waste. Super-compacted waste could be immobilized into cement in an over-pack drum. Collected liquids could be analyzed and conditioned into cement. In this way the waste volume to be disposed of was reduced by at least a factor of four.

The option to dispose of the waste without doing any quantification of the ^{14}C was also investigated. This option does not require the waste drums to be opened and therefore no sterilization is required. Characterization is in this case limited to assaying the drums for nuclides that can be measured with a gamma detector, and conditioning involves placing the drums in over packs and filling the voids with absorbing material.

The pros and cons of each option have been evaluated against the existing WAC for disposal, the cost involved and potential impact on the long term safety of the disposal facility.

II.14. USA

A variety of radioactive wastes are in storage around the world that contains organic compounds. These types of wastes can be difficult to treat, and complex and/or expensive systems are usually required to safely and effectively destroy the wastes. Conventional systems may not always be adequate for treatment. For example, the typical method for destruction of organic wastes is incineration, and this method has many drawbacks including public acceptance. Thus, new non-thermal methods are needed that can provide high-destruction efficiencies with low capital and operating costs for the safe treatment of these types of “problematic” radioactive wastes.

New non-thermal methods for the destruction of organic components of radioactive waste have been explored. The methods involve the use of strong inorganic oxidizers such as Fenton’s Reagent, manganese (VII), ozone, etc. The effect of oxidant, oxidant concentration, and temperature has being systematically investigated. Results of this work showed that samples with increasing sodium permanganate concentration gave a slower rate of post-precipitated solids formation. Also, temperature increases resulted in increased reaction rates and smaller lepidocrocite particle sizes. In preliminary scouting experiments, the possibility of TBP destruction by Fenton’s reagent was demonstrated.

A molten salt oxidation (MSO) process was also studied for the safe and effective destruction of organic components of radioactive waste. The work involved a laboratory-scale molten salt oxidation system where solid or liquid waste is injected into a bed of molten carbonate salt in the presence of an oxidizing gas. The relatively simple MSO process completely destroys organic compounds, and the carbonate salt neutralizes any generated acid gases and retains the radioactivity. In the past, high melting point salts have been used with air oxidation. In these studies, the use of lower melting point salt mixtures appears to be an effective improvement to the MSO process in order to lower energy requirements. The use of oxygen instead of air showed no improvement in oil destruction.

APPENDIX III. INDIVIDUAL RESEARCH REPORTS (ON CD-ROM ONLY)

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Research Coordination Meetings

Prague, Czech Republic, 17 – 21 November 2003
Kiev, Ukraine, 23 – 27 May 2005
Mumbai, India, 27 November – 1 December 2006

Consultants Meeting

Mumbai, India, 4 – 8 December 2006