Advances in Technologies for the Treatment of Low and Intermediate Level Radioactive Liquid Wastes
ADVANCES IN TECHNOLOGIES FOR THE TREATMENT OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE LIQUID WASTES
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ADVANCES IN TECHNOLOGIES FOR THE TREATMENT OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE LIQUID WASTES

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The basic objective of radioactive liquid waste treatment is to remove radio- 
nuclides from the bulk of waste in order to meet the limits for release of radioactivity 
into the environment and to concentrate the radioactivity into a small volume for sub-
sequent conditioning and disposal. There is a rather stable trend in Member States 
to encourage radioactive waste producers to minimize radioactivity releases as low 
as reasonably achievable by further reducing the maximum permissible limits for 
radioactive liquid effluent discharges into the environment, as well as to limit the 
volume of waste to be disposed of. In addition, the cost of waste disposal is con-
tinuously increasing. For these reasons, intensive studies on methods of improving 
traditional treatment processes or developing new techniques are currently being 
carried out in many countries. These studies, based on a combination of chemical, 
physical and biological processes, aim first at improving the decontamination of 
effluents to be discharged into environment and secondly at decreasing the volume 
of waste to be conditioned and disposed of.

The following IAEA publications include technologies for the treatment of 
liquid low and intermediate level radioactive waste: Technical Reports Series (TRS) 
No. 236: Treatment of Low- and Intermediate-Level Liquid Radioactive Wastes 
(1984); TRS No. 287: Treatment of Alpha Bearing Wastes (1988); and TRS 
No. 294: Options for the Treatment and Solidification of Organic Radioactive 
Wastes (1989). However, these reports primarily describe well proven processes and 
only briefly novel processes. This report attempts to make up for this deficiency. A 
wide spectrum of treatment processes is considered in the document, beginning with 
upgraded traditional and well proven processes such as chemical precipitation, ion 
exchange and evaporation, which are described very briefly, in addition to rather 
new membrane and electrochemical processes and combinations of these processes. 
Methods based on the use of biological processes for the treatment of liquid radio-
active wastes are described in this report for the first time. The report describes both 
the advantages and disadvantages of different technologies and should be of interest 
to scientists and engineers involved in the research, development, design and opera-
tion of liquid waste treatment facilities.

The report was drafted by the Secretariat and the following consultants: 
L. Diels (Belgium), C. Courtois (France), Y. Hirose (Japan) and E.W. Hooper 
(United Kingdom). The draft was reviewed and revised by fourteen experts from 
eleven Member States and one international organization (CEC) at the Technical 
Committee Meeting held in March 1993 at IAEA Headquarters in Vienna. The final 
report was prepared by the Secretariat with assistance from the above consultants 
after consideration of comments and additional data received from meeting 
participants.
The IAEA wishes to express its appreciation to all those who took part in the preparation and publication of this report. The officer responsible for the report at the IAEA was A.F. Tsarenko of the Waste Management Section of the Division of Nuclear Fuel Cycle and Waste Management.

EDITORIAL NOTE

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1. INTRODUCTION

The various processes used in the nuclear fuel cycle and in the application of radionuclides in research, medicine and industry generate a range of low and intermediate level liquid waste streams needing treatment to isolate radioactive contaminants from the environment or to reduce their quantities to levels which allow safe discharge according to national regulations and in compliance with the ALARA principle.

At first, the treatment technologies employed in the nuclear industry were based on established processes used in conventional industries for the treatment of water and non-radioactive liquid wastes. These processes included chemical precipitation and, to a lesser extent, ion exchange and, sometimes, thermal evaporation.

In recent years the authorized maximum limits for radioactive discharges into the environment have been reduced considerably, and this, together with the requirement to minimize the volume of waste for storage or disposal and to declassify some wastes from intermediate to low level or to non-radioactive wastes, has initiated studies of ways in which improvements can be made to existing decontamination processes and also to the development of new processes. This work has led to the use of more specific precipitants and to the establishment of ion exchange treatment and evaporation techniques. Additionally, the use of combinations of some existing processes or of an existing process with a new technique such as membrane filtration is becoming current practice.

New biotechnological, solvent extraction and electrochemical methods are being examined and have been proven at laboratory scale to be useful for radioactive liquid waste treatment. These techniques have a potential for applications at industrial scale in the short or long term. Some techniques have already been applied to the treatment of non-radioactive waste.

The objective of radioactive waste management is to manage radioactive waste in a manner that ensures the protection of human health and the environment without imposing a burden on future generations. When considering a waste treatment process within a waste management system, a number of factors affect the choice, with economic considerations being very important. Capital and operational costs, plus the cost of disposing of secondary wastes, need to be minimized. The need for improved decontamination at low cost has also led to new or specific processes for waste streams being examined and developed.

In this report an attempt has been made to review the current research and development of mature and advanced technologies for the treatment of low and intermediate level radioactive liquid wastes, both aqueous and non-aqueous. Non-aqueous radioactive liquid wastes or organic liquid wastes typically consist of oils, reprocessing solvents, scintillation liquids and organic cleaning products. They could be a mixture of two or more of these products. It is pure organic waste if no aqueous
phase can be physically separated. If two phases exist, after separation an organic and an aqueous waste should be treated separately.

A brief state of the art of existing processes and their application is followed by the review of advances in technologies, covering chemical, physical and biological processes and combinations of different processes. The new processes can be considered either as alternatives to existing techniques or as an addition to existing facilities. With increasing maturity it can be envisaged that some of these processes could become routine operations in the not too distant future.

## 2. LARGE SCALE APPLICATIONS OF LIQUID WASTE TREATMENT TECHNOLOGIES

### 2.1. AQUEOUS WASTES

#### 2.1.1. Chemical precipitation

The objective of a chemical precipitation process is to remove radionuclides from a liquid waste by the use of an insoluble finely divided solid material. The insoluble material or floc is generally, but not necessarily, formed in situ in the waste stream as a result of a chemical reaction. Generally, radionuclides are removed from solution by one or more of the following mechanisms:

- co-precipitation with the carrier;
- sorption onto particulates present in the waste streams;
- sorption onto the floc (ion exchange, chemisorption, etc.).

The use of these processes concentrates the radioactivity present in a liquid waste stream into a small volume of wet solids that can be separated from the bulk liquid component.

Chemical precipitation processes are well established methods for the removal of radioactivity from low and intermediate level wastes and are in regular use at fuel reprocessing facilities, research establishments and some power stations [1–5].

The majority of precipitation methods use metal hydroxide flocs under neutral or alkaline conditions to remove the radionuclides. With this general process, a number of the radionuclides will be extensively hydrolysed and are likely to be either co-precipitated or sorbed onto the floc. Other treatments can be applied for specific radionuclides, for example, precipitation of barium sulphate for strontium removal, or nickel hexacyanoferrate for caesium removal.
The process may be affected by the presence of other components of the waste stream such as complexants, trace organics or particulates. In these cases, a pre-treatment may need to be added to the main process. When the waste stream composition is variable in nature, either in its radioactive or in its non-radioactive content, a single chemical precipitation process may be inadequate. A combination of specific treatments is frequently necessary to achieve the best overall decontamination factor (DF) for total alpha and/or total beta–gamma activity of the liquid waste. Combinations of processes can be used as a multistage batch process or as a continuous precipitation process and will produce one or several sludges for further conditioning and disposal.

The sludges usually have low solids contents and require further dewatering in order to reduce the final volume of the immobilized waste. The selection of a sludge treatment process must consider both chemical and radiation stability of the sludge. This treatment is sometimes associated with solidification of the sludges which confers on them mechanical resistance and long term stability to allow their disposal.

Precipitation processes are particularly suitable for the treatment of large volumes of liquid waste which contain relatively low concentrations of radioactive elements. These processes are fairly versatile and may be used to treat a wide variety of different waste streams, including those containing particulates or high concentrations of salts. The processes are economically attractive but achieve relatively low decontamination factors compared to other treatment methods, e.g. evaporation.

An example of a combination of specific treatments is the continuous precipitation process, STE 3, used in the Cogéma waste treatment facility at La Hague [2, 4] to treat low and intermediate level aqueous wastes at a throughput of 17 m$^3$/h. The addition of nickel hexacyanoferrate removes caesium, cobalt sulphide removes ruthenium and strontium is co-precipitated with barium sulphate. The decontamination factors achieved are:

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<td>Total alpha</td>
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<tr>
<td>Total beta–gamma</td>
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<td>Ruthenium</td>
<td>6–30</td>
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<tr>
<td>Strontium</td>
<td>100</td>
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<td>Caesium</td>
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A volume reduction factor of about 30 is obtained after decantation.

Another example is the new Enhanced Actinide Removal Plant (EARP) at the British Nuclear Fuels reprocessing site at Sellafield (UK). The total plant throughput exceeds 60 000 m$^3$/a. The treatment involves precipitation of ferric hydroxide using the iron component of the waste and sodium hydroxide to increase the pH value to 9–10.5. Addition of nickel hexacyanoferrate may be made after pH adjustment if required by the caesium loading of the waste. Liquid–solid separation is performed by primary and secondary cross-flow ultrafiltration stages [2, 5].
2.1.2. Ion exchange

The principle of ion exchange has been known for many years, and its application in water treatment processes was well developed before its use in the nuclear industry. Ion exchange processes are currently employed in a number of stages throughout the nuclear fuel cycle, from initial extraction of uranium from leach liquors arising from mining operations to the separation of actinides and the treatment of wastes arising from fuel reprocessing. For convenience, ion exchange processes will be considered in two groups: (a) those using organic exchange resins, and (b) those employing inorganic sorbents.

There are a number of extensive reviews of the applications of ion exchange processes in the nuclear industry [1, 6-8]; so discussion in this report will be confined to more recent developments.

2.1.2.1. Organic ion exchangers

Organic exchange resins have been well developed, and a wide range of both anion and cation exchangers is available. The resins are mainly based on polystyrene and phenol formaldehyde onto which active groups are added. The types available are strong acid, weak acid, strong base and weak base materials. By careful selection of the functional group on the resins it is sometimes possible to achieve a certain degree of selectivity for various ions. They are widely used in spent fuel storage pond water treatment.

The resins are used either in bead form in a packed bed arrangement or as a powder in conjunction with a filter. The packed bed processes usually involve elution of sorbed radionuclides into a smaller volume of solution followed by reuse of the exchangers, whereas the finely divided resin is used as a filter precoat on a once-through basis. The latter method has the advantages of providing removal of both ionic and colloidal material as well as avoiding pretreatment of the waste stream to remove any particulate material that could clog a packed bed.

Organic ion exchangers are prone to both thermal and radiation degradation, and certain chemical conditions can also cause degradation.

The immobilization of organic resins for disposal can be achieved but there is some concern over the long term stability of the waste form and over the possibility that their presence, even in very low amounts, in a repository may introduce a potential source of organic ligands that could enhance the mobility of radionuclides and affect the long term safety of the disposal.

2.1.2.2. Inorganic ion exchangers

The use of inorganic sorbents for treatment of a variety of aqueous radioactive wastes was originally made on the basis of their resistance to radiation, generally
good resistance to chemical attack and their compatibility with potential immobilization matrices.

Inorganic ion exchangers may be either naturally occurring minerals or synthetic materials. They perform the same basic exchange operations as those involved for organic exchangers.

The naturally occurring materials comprise aluminosilicate materials such as zeolites, clays, feldspars [9]. Synthetic ion exchangers generally fall into the following categories:

1. Hydrated metal oxides, e.g. hydrous titanium oxide, polyantimonic acid;
2. Insoluble salts of polyvalent metals, e.g. titanium phosphate;
3. Insoluble salts of heteropoly acids, e.g. ammonium molybdophosphate;
4. Complex salts based on insoluble hexacyanoferrates;
5. Synthetic zeolites.

The advantage of naturally occurring materials is their low cost but their industrial use is often difficult (impurities, bad physical properties for packed bed operations) and they sometimes need a chemical or thermal pretreatment.

Inorganic exchangers can be prepared as granular materials but they can also be used as finely divided materials in chemical precipitation processes to enhance the decontamination factor for some nuclides. Inorganic ion exchange is used at a number of nuclear plants but its application is usually confined to the removal of fission products, e.g. caesium and strontium, from waste effluents.

An example of a large scale application is the Site Ion Exchange Effluent Plant (SIXEP) at Sellafield (UK) [10]. The plant is used to treat the cooling water from fuel storage ponds. Typical decontamination factors achieved are 2000 for Cs and 500 for Sr, and the number of bed volumes treated between bed discharges is 20 000.

During the past few years, a wider application of inorganic ion exchangers in liquid waste treatment has been investigated for fission and activation product elimination and for alpha emitter removal. The use of small amounts of inorganic ion exchange materials in conjunction with ultrafiltration has been shown to be a very effective decontamination process. A wide range of exchangers exist, so the proper selection of appropriate inorganic exchangers could lead to good decontamination for the actinides, fission and activation products. These developments will be discussed in Section 3.

The large scale use of granular forms of inorganic exchangers might be difficult, because of poor mechanical stability. Some developments are in progress in this area.

2.1.3. Evaporation

Evaporation is a proven method for the treatment of liquid radioactive waste providing both good decontamination and high concentration. The technique is well developed and both its advantages and limitations are well understood [1, 11, 12].
With nitrate systems, evaporation is usually continued to a salt concentration of up to 400 g/L [1]. At the Paks Nuclear Power Plant in Hungary, concentration of boric acid up to 200 g/L is achieved with a volume reduction factor of 40 to 50 and a DF of $10^5$ [13]. The formation of solids during evaporation is generally avoided as these tend to cause problems; evaporator/dryer and wiped film evaporators are, however, designed to operate in the presence of solids, and concentration may continue until a 50 wt% salt content is obtained.

In spite of high operating costs, evaporation is at present almost invariably chosen when high decontamination factors are required ($>10^3$) or when very low radioactivity discharge is necessary in order to meet regulatory discharge requirements.

The presence of volatile nuclides such as tritium and some forms of iodine and ruthenium, particularly at high nitric acid concentration, will reduce the overall DF. By adding alkali to the feed solution, the volatility of iodine and ruthenium may be reduced but tritium is not affected. Operation at low evaporation temperature under a reduced pressure will decrease the volatility of ruthenium [14].

The condensate resulting from evaporation is an almost salt free solution of very low activity which may be subsequently ‘polished’ by ion exchange, reverse osmosis, or simply fed to another stage of evaporation, before it is discharged or recycled for use in the plant. The concentrate containing the radionuclides can be directly incorporated into a suitable matrix (e.g. cement, bitumen or plastics) or be dried to produce a salt cake for compaction into pellet form before immobilization [15].

Although evaporation may be considered a fairly simple operation which has been successfully applied in the conventional chemical industry for many years, its application in the treatment of radioactive waste may give rise to various problems such as corrosion, scaling or foaming [1].

Corrosion may be a severe problem in evaporators, mainly because of the elevated heat transfer surface temperature employed. Severe corrosion of stainless steel at a liquid–vapour interface has been encountered in a nitric acid solution containing substantial amounts of nitrate salts [16]. Corrosion of stainless steel, even at high nitric acid concentration, has been mitigated by using low temperature boiling under reduced pressure conditions [14].

Scaling is caused by the formation of solid deposits on the inner surface of the evaporator, particularly on the heat transfer surface, reducing the heat transfer efficiency and making it more expensive to operate; it may enhance corrosion.

Forced circulation evaporators are much less affected by scale formation than natural circulation evaporators [17].

Some consideration has been given to the application of various chemical precipitation processes for the removal of radioactivity from concentrated salt wastes arising from the evaporation process [18].
2.1.4. Membrane processes

This section is concerned with processes which enable radioactive contamination to be separated from a waste stream by selective passage of certain components of that stream through a membrane. The pressure driven transfer of material across a membrane is known as either reverse osmosis (RO), ultrafiltration (UF) or microfiltration (MF), depending on the pore size in the membrane. The pore size ranges are:

- RO < 1 nm
- UF 1-100 nm
- MF 0.1-1 μm

Details of these processes are presented in Ref. [18].

Radioactive waste treatment applications have been reported for the laundry wastes in nuclear power plants, of mixed laboratory wastes, and for cleanup of boric acid solutions for recycle. Figure 1 schematically shows a mixed aqueous waste processing plant at the Chalk River Laboratory of the Atomic Energy of Canada Ltd. [18]. A total of 80 m$^3$ of mixed aqueous waste is collected in tank
Tk. 1-1 every week. The fresh feed contains a gross beta-gamma activity of typically 10 000-30 000 Bq/mL. Suspended solids larger than a nominal 0.2 \( \mu m \) are rejected by the microfiltration unit (MFU). The filtrate from the MFU becomes the fresh feed to the spiral wound reverse osmosis (SWRO) system. The resulting clean water (permeate) is sentenced for discharge. Part of the concentrate stream (retentate) is recycled back to the feed tank. The retentate from the SWRO system undergoes further volume reduction in the tubular reverse osmosis (TRO) system. The backwash solution from the MFU is further volume reduced in a thin film evaporator. The retentate from the TRO system is immobilized in bitumen, also in a thin film evaporator. The TRO permeate is fed back for reprocessing with SWRO. The salt content in a product drum is about 35%. Membranes are manufactured in cellulose acetate polyamide and polyether amide polysulphone. Thin film composite polyamide membranes are the most commonly employed membranes in the industry. A 6.1 m vessel contains four modules, each 10.2 cm in diameter and 102 cm long. It also contains one shorter module (53.3 cm long) of the same diameter.

Ultrafiltration is used in two stages in the Enhanced Actinide Removal Plant at Sellafield. In this plant the primary separation stage produces a concentrate of a few weight per cent solids content which is then dewatered in a second stage.

In Hungary, at the Paks Nuclear Power Plant, an ultrafiltration plant is used for cleaning and recycling contaminated boric acid solutions. At the beginning of 1993, 983 m\(^3\) of solution had been treated by using polysulphone membranes giving a volume reduction factor of 45 and decontamination factors in the range 10-100 [19].

Good decontamination and high volume reduction is being achieved at the Harwell pilot plant using ultrafiltration to separate floc and liquid [20]. The high DFs from the pilot plant were achieved by the addition of a small quantity of titanium (IV) solution to form hydrous titanium oxide which is a good absorber for \( \alpha \) activity during precipitation of ferric floc. The pilot plant was successfully operated to give a volume reduction of about 200 and produce a concentrate containing about 1 wt\% solids [20].

At Nukem, Hanau, the application of ultrafiltration to low level wastes arising from a fuel fabrication plant is being examined [21]. These wastes consist of general cleaning waters, laundry wastes and decontamination effluents from plant operations that contain small quantities of oil, grease and general dust; alpha activity is mainly due to uranium. Direct ultrafiltration of the laundry and cleaning waste gave a DF about ten, but was inadequate for the other wastes. However, pretreatment of these wastes by the precipitation of U(OH)\(_4\) after photochemical reduction of the uranium, or by the addition of a hexacyanoferrate, or co-precipitation with small quantities of calcium phosphate or ferric hydroxide flocs, gave DFs of about 100-200, provided no carbonate, oxalate or fluoride were present to form soluble complexes with uranium. The volume reduction achieved by ultrafiltration was 10-15 times greater than that obtained with precipitation methods.
2.1.5. Biotechnological processes

Nuclear waste water treatment by biological means is based on the use of biological specimens or bioproduced compounds for the concentration of radionuclides or the degradation of organics.

The concentration can be achieved by sorption or crystallization of radionuclides by multicellular or unicellular organisms (dead or alive) or by some of their products (enzymes or structural compounds). The passive uptake of metals or radionuclides which is based on the chemical composition of the cell or its components (such as the cell wall) is termed 'biosorption'. Biosorption can occur with higher and lower organisms. In case of biosorption dead biomass is generally used. Active uptake is the concentration of metallic species by living microbial cells and is termed bioaccumulation.

FIG. 2. Biological liquid waste treatment flowsheet.
Organics can be removed by complete degradation to CO₂ and H₂O and biomass production. Most of the degradations are done by bacteria. Degradation is done by cellular catabolism which uses the organics as a carbon source in the presence of nitrogen or phosphorus. Also cometabolism (degradation of an organic compound together with the catabolism of a given substrate) can be envisaged.

A combination between biosorption or bioaccumulation and biodegradation provides successful treatment of some types of radioactive waste. These processes are being engineered into complete systems or system components. Many potential bio-approaches will function well if they are not considered as stand alone processes but are interfaced with existing technologies. For example, bioprocessing of an organic/aqueous solution could render that solution free of the toxic organics with the radionuclides biosorbed to the biomass. A volume reduction could then be achieved by ultrafiltration to separate the biomass.
A biological treatment always needs an aqueous phase in order to keep the biological systems operable. Therefore, organics can only be treated after passing to an aqueous phase. All liquid wastes for biological treatment will therefore fall into one of the three following waste types: aqueous phase, aqueous phase containing inorganics (nitrates) or aqueous phase containing organics. Then one of the three possible biotechnological processes (biodegradation, biosorption or bioaccumulation) is used for further treatment (Fig. 2).

Existing biological liquid waste treatment systems will be presented below.

2.1.5.1. Biotreatment of uranium containing acid mine water

Highly acidic nitrate waste containing uranium and other toxic metals is biologically treated to remove the nitrate (Fig. 3). The waste stream is first neutralized with lime and subjected to microbiological action under anaerobic conditions in the presence of acetic acid (carbon source) and triethyl phosphate. The bacteria reduce nitrate to $\text{N}_2$. Carbon dioxide produced by microbial action reacts with calcium to form insoluble calcium carbonate which makes up a major part of the solids generated from this process. Effluent from the denitrification process is polished by lowering the pH of the waste by addition of sulphuric acid and soluble carbonates are removed as $\text{CO}_2$ in a degassifier. Ferric sulphate, a coagulant, is added to aid the co-precipitation of the heavy metals, including uranium. The solids generated are stored in 2000 m$^3$ storage tanks for appropriate disposal of the mixed wastes [22].

FIG. 4. Overview of different microbial processes in ARUM.
Test cell system for acid reduction using microbiology

Iron precipitation cells

Area: 131 m²
Volume: 128 m³
Retention time: 89 days

ARUM cell

Area: 123 m²
Volume: 114 m³
Retention time: 89 days

Retention time: 89 days

ARUM cell

Area: 93 m²
Volume: 86 m³
Retention time: 79 days

Retention time: 71 days

FIG. 5. General representation of ARUM processes concerning contaminant removal.
At the Oak Ridge Y12 plant a denitrification plant has been operational since 1987 with a capacity of 10,000 m$^3$/a and with an installation cost of US $11 M.

2.1.5.2. Biotreatment of high nitrate, uranium aqueous waste

In the USA and especially in Canada, methods are being developed to reduce the contamination of acid mine waters [23–25]. This ARUM (Acid Reduction Using Microbiology) process is also used to reduce the uranium content of uranium mine waters. The system is based on the combined use of plants and microorganisms living in wetlands and creating a natural situation of oxidizing and reducing conditions combined with biomass with an adsorptive capacity.

*Sphagnum* or *Sargassum* moss and cattails or *Typha* are planted in constructed wetlands and these plants bind a number of metals and radionuclides. The upper water layer is anaerobic which enhances biodegradation of organics. The anaerobic layer promotes biodegradation of organics, reduction of iron, chromium, uranium and precipitation of metals as metal sulphides because of sulphate reduction. Combination of physical, biochemical and biological processes will further reduce the toxic contaminants of the mine waters. The ARUM process is presented in Figs 4 and 5.

2.1.6. Other processes

The use of the electrochemical or electroflotation process and the solvent extraction process for radioactive waste treatment is under examination but no information is available on any operating plant that uses these techniques.

2.2. ORGANIC WASTES

Incineration is currently the most generally used method for the reduction of organic radioactive waste. The radioactive organic liquid wastes requiring treatment are [26]:

- Oils — lubricating, turbine, hydraulic fluids;
- Reprocessing solvents — mainly tributyl phosphate (TBP) diluted with a light, saturated hydrocarbon;
- Scintillation liquids — containing aqueous or non-aqueous solvents and non-polar solvents;
- Dry cleaning wastes — perchlorethylene, etc.;
- Decontamination liquids — eg. toluene, acetone, chlorinated hydrocarbons.
2.2.1. Incineration

Incineration of liquid organic wastes provides excellent volume reduction, particularly, if the liquid can be fed directly to the incinerator. Depending on the activity of the ash residue, it may be simply packaged for storage and/or disposal or a further immobilization step may be required.

A variety of incinerator types and concepts has been tried throughout the world.

A pilot plant incinerator is in operation at Cadarache for the destruction of organic wastes including chlorinated solvents, oils, scintillation liquids and TBP which arise from nuclear research centres, reprocessing plants and from institutes and hospitals. Between 1981 and 1985, 130 m$^3$ of solvent were incinerated during 5000 hours of operation with a volume reduction factor of 30 to 300 [27] (Fig. 6).

The fluidized bed incinerator at Rocky Flats [28] is being tested for incinerating organic liquids including TBP, naphtha solvents, trichloroethylene, waste oils, polychlorinated biphenyl (PCB) and solvent mixtures. The feed rate is limited by a
maximum heat output for the unit of 450 kW. The unit was designed to treat plutonium contaminated wastes at concentrations less than $10^{-3}$ g Pu/g waste. The unit has incinerated about 6 m$^3$ of low level power plant liquid wastes.

KfK Karlsruhe has a dedicated incinerator for organic liquid wastes which burns a feedstock of the following composition: 40% oil, 34% solvent, 10% scintillation liquid, and 16% water. By the end of 1983, 360 m$^3$ of radioactive liquid containing 18.5 GBq/m$^3$ of alpha and beta-gamma activity, respectively, had been incinerated [29]. The unit was designed to treat radioactive wastes containing less than $10^7$ Bq/m$^3$ of alpha emitters and $10^5$ Bq/m$^3$ beta-gamma emitters.

Radioactive waste incineration is a well developed though fairly complex technology. The equipment is sophisticated, particularly for off-gas systems which can include afterburners, heat exchangers, cold air injection, filter candles, bag houses, scrubbers and HEPA filters. This means that adoption of this process requires a substantial capital outlay, and operating and maintenance costs are likely to be high. Even though the technology is well developed, problems still arise with incomplete burning, component corrosion and off-gas filtration, suggesting that further design improvements are required to enable the technique to attain its full potential.

Any decision as to whether or not organic radioactive waste incineration should be adopted is likely to depend on the individual economics of each waste storage/disposal scenario and on political considerations. If the costs associated with waste storage or disposal are sufficiently high to make volume reduction attractive they may make incineration a preferred option despite its generally high cost.

2.2.2. Other processes

2.2.2.1. Hydrolysis

The alkaline hydrolysis process for destroying TBP was first investigated in Germany and subsequently extensively developed in the UK. The process can be effective for a wide range of TBP concentrations in odourless kerosene (OK) and other diluents, but has been most extensively studied in the range of 20–30 vol% TBP/OK.

For these solvents the optimum conditions are to partially reflux at about 125°C an approximately 3:1 molar ratio of NaOH:TBP (NaOH:7.5M). Distillation of part of the diluent removes the butanol formed and allows the reaction to be essentially complete in less than 3 h. On completion the reaction vessel contains three phases: a lower alkali layer which contains in excess of 90% of the fission products and heavy metal species, a middle aqueous sodium dibutyl phosphate layer which contains virtually all the remaining activity, and an upper OK/butanol layer which is virtually free of activity.
If a fairly active spent solvent is to be treated, it is first necessary to wash the solvent with a reagent, such as sodium carbonate, to remove the majority of the uranium present, otherwise the formation of a flocculent precipitate of sodium diuranate prevents phase separation after the hydrolysis.

The resulting OK/butanol is suitable for being fed to a comparatively simple combustor, and the spent caustic phase is a suitable feed for a chemical precipitation plant.

The aqueous solution of sodium dibutyl phosphate, particularly if the spent solvent has been prewashed, may be of sufficiently low activity to allow it to be discharged since it has been shown to have a low toxicity and to be biodegradable in seawater. However, if it is desirable to convert the NaDBP to inorganic phosphate, this has been shown to be possible by acidic hydrolysis, chemical oxidation or microbiological degradation.

Extensive development has been performed at up to 250 L scale of TBP/OK on clean materials and at 1 L scale with actual waste solvent from the reprocessing plant.

A plant with a design capacity of 750 m$^3$/a of 30% TBP/OK is currently under construction at BNFL Sellafield site in the UK, a flow diagram for which is shown in Fig. 7 [30].

FIG. 7. Block flow diagram of Sellafield solvent treatment plant current process.
2.2.2.2. Phase separation by adduct formation [31]

Phase separation by adduct formation has been considered as a pretreatment before destruction or disposal of TBP and diluent. This is done by contacting contaminated TBP/diluent with concentrated phosphoric acid at room temperature in conventional solvent extraction equipment, such as mixer-settlers or pulsed columns.

The TBP is solubilized quantitatively in the phosphoric acid. Almost all the radioactivity and the degradation products are transferred to the adduct phase which can be pyrolyzed.

In Germany, 300 m$^3$ of 2–30% TBP/dodecane from the WAK plant have been treated in this way. In Belgium, the Eurowatt process has been developed to a pilot scale plant in which 100 L of spent 16% TBP/diluent were treated at 1 L/h.

2.2.2.3. Distillation [31]

Simple distillation may be used for the pretreatment of scintillation fluids and miscellaneous solvent wastes. Substantial volume reduction is possible as the activity is generally concentrated in the residue.

The distillation of scintillation fluid has been practised in the USA and Brazil. Absorption and conditioning [31] have been extensively used, particularly in the USA, to convert the organic liquid to a solid form.

3. ADVANCES IN TECHNOLOGIES FOR THE TREATMENT OF AQUEOUS WASTES

Further research and development is in progress on chemical and physical processes, with many developments being made on combined processes which associate two or more techniques, for example the use of finely divided inorganic exchangers in combination with ultrafiltration.

The development of advanced combined processes will be reviewed in the sections relating to the main process used in the treatment, so the above example will be discussed in the paragraph on the membrane process.

In this section some indication will be given on developments, in particular, single processes which are not detailed elsewhere in this report.
3.1. CHEMICAL PRECIPITATION

An investigation into the removal of transuranic elements by oxalic acid from intermediate level liquid waste was made at the European Institute for Transuranium Elements in Karlsruhe [32], simulated ILLW as well as genuine ILLW from reprocessing were used. The parameters studied for optimization of the precipitation process were: type and amount of carrier, pH, time of digestion of the precipitate and the temperature of precipitation.

DF values of >5000 and >70 were found for americium and for plutonium, respectively, with calcium as the preferred carrier. No difference in performance between simulated and genuine ILLW was found.

Investigations have been made in Italy by ENEA [33] for the treatment of wastes from the EUREX plant. The waste (88 m$^3$) contains a large amount of aluminium together with Fe, Hg and NO$_3$. The selected process includes:

- pH adjustment with sodium hydroxide;
- removal of Sr and actinides by co-precipitation with ferric hydroxide;
- Cs removal using sodium tetraphenyl borate;
- two stages of solid–liquid separation by decantation.

The mean DFs achieved with this process are for Cs >1000, Sr = 100, TRU > 1000. From these experimental results, a total volume of 3–4.5 m$^3$ of sludge is expected.

3.2. ION EXCHANGE

3.2.1. Organic ion exchangers

The commercial availability of new organic ion exchangers is largely dependent on alternative uses since the expense involved in producing a new exchanger requires a larger industrial market than would be afforded by radioactive waste treatment alone.

An extensive investigation of the removal of Pu and Am from nitric acid waste streams using ion exchange processes has been carried out. At Rocky Flats, the waste streams contain Pu and Am at 1–10 mg/L and the aim is to recover the actinides, leaving effluents containing <10$^{-2}$ mg/L. The primary recovery stage in the process is a PUREX type solvent extraction and this is followed by a secondary plutonium recovery anion exchange process. Subsequent purification cycles for both Pu and Am also use anion and cation exchange processes [34, 35].

The Rocky Flats study has examined a wide range of different resins including microreticular (gel type) resins and the newer macroreticular or microporous resins. The sorption of Pu from 7M HNO$_3$ was found to be strongly influenced by the large
size of the extracted Pu(NO$_3$)$_5^{2-}$ complex, and loading kinetics were improved by adjusting the temperature of the feed to 60-70°C.

An ion exchange process has been developed for the separation of Am from sulphuric acid waste solutions arising from the acid digestion of plutonium contaminated materials [36]. A strongly basic anion exchange resin is employed, and Am is extracted from 2M H$_2$SO$_4$ solutions as the anionic sulphate complexes Am(SO$_4$)$_2$ and Am(SO$_4$)$_3^{-}$. An Am DF of $10^4$ was reported for the treatment of a waste containing between 0.5 and 5 mg/L Am.

At most nuclear plants the medium active waste streams are combined before treatment. However, at KfK, the alternative approach of decontaminating the individual waste streams has also been investigated. Ion exchange processes have been developed on a laboratory scale for the removal of actinides from three intermediate level waste streams [37, 38].

Each of the studies described in this section has considered the removal of actinides from medium active waste streams. There appears to be very little information on the application of ion exchange processes to the decontamination of low level alpha bearing waste streams. However, a wide range of radioanalytical procedures for the analysis of actinides in environmental samples is based on ion exchange reactions such as those described above. Therefore, it can be expected that these types of process could be used for the decontamination of low level wastes with low inactive salt contents.

For beta–gamma emitters, adsorption can be regarded as an extension of ion exchange techniques, particularly in the removal of undissociated or complexed species, which would not be absorbed on more conventional ion exchangers. Active charcoal will also remove activity such as $^{60}$Co.

Further developments will probably occur, particularly with the use of organic solvents held on an inert substrate, which offer the possibility of selective adsorption from active streams of individual species whose concentration is too low for economic treatment by normal solvent extraction. This can also relate to the development of solvent extraction processes which will be discussed in Section 3.5.

A caesium specific organic ion exchange resin has been tested at the Savannah River site [39, 40]. The resin is a condensation polymer made from resorcinol and formaldehyde. It has been shown to be stable to chemical and radiation attack in a highly concentrated alkaline waste. In tests on caesium removal it was superior to other available resins, with the distribution coefficient being limited primarily by competition from potassium and nearly independent of the sodium concentration. The optimum pH was approximately 12.5 in high NaNO$_3$ concentrations (>2M). The resin was much less effective for strontium removal, which was limited by competition from sodium.

In India, experiments made with a resorcinol–formaldehyde polycondensate resin show promising results for caesium removal from alkaline salt solutions. A DF of about 2000 was obtained during the test runs using actual waste solutions [41].
Some phenolic polymers were also found to show selective uptake of radiostrontium from such solutions [42].

The use of grafted cellulosics has been proposed to treat low level liquid wastes; polyelectrolytes were attached to the backbone polymers [43]. Industrial operating possibilities of these products have not yet been explored.

Laboratory scale experiments have been conducted with amine intercalation compounds of alpha tin hydrogen phosphate for the extraction of metals [44].

3.2.2. Inorganic ion exchangers

There is considerable interest in the development of further applications for inorganic ion exchange, and some full scale experiments have been conducted.

At Harwell, a generic study has been underway since 1982 to assess the application of inorganic absorbers to the treatment of low and intermediate level wastes. A programme of experimental work is currently investigating their performance. Information is being collected on the effectiveness of absorbers for the removal of fission products and actinides and the influence of process parameters such as pH and temperature, on their performance. The results are clearly showing the usefulness of these materials (Fig. 8).

Distribution coefficients ($K_d$) for the individual actinides, plutonium, americium and neptunium, over a range of conditions (4M HNO$_3$ — pH12), were measured in batch experiments, and the results obtained are summarized in Fig. 8 [45]. It is apparent from Fig. 8 that antimononic acid is very effective over a wide pH range, while other materials are more pH dependent. In general, the affinity series for the actinides is Pu$^{4+} >$ Am$^{3+} >$ NpO$_2^+$, and the rate of uptake is greater for americium and plutonium than for neptunium.

Further work has been carried out at Harwell, using column experiments to examine the loading, elution and exchange capacities of the inorganic absorbers. In addition, the physical properties of the sorbents are being examined.

Similar investigations are being undertaken by a number of other research groups. Particular interest has been focused on the application of hydrous titanium oxide (HTiO). Several more recent investigations of HTiO have been reported.

Hydrous titanium oxide has been selected for investigation at AGIP Nucleare within the framework of the CEC Research Programme [46]. In this work, the HTiO is prepared by a sol–gel process, and experiments using Cs$^+$, Sr$^{2+}$ and Eu$^{3+}$ show that the material has an exchange capacity of about 3-5 meq/g. The absorber is being investigated for the removal of americium from oxalate solutions arising during americium purification and for the treatment of intermediate level wastes containing plutonium and americium generated during the refabrication of MOX fast breeder reactor fuel. Results show that HTiO is capable of reducing americium activities in oxalate solutions from about $3.7 \times 10^9$ Bq/m$^3$ to about $1.5 \times 10^5$ Bq/m$^3$. The
FIG. 8. Total percentage of alpha removal.
second waste considered has been treated by a sol–gel HTiO co-precipitation process, and DFs of 50–100 were achieved for the actinides.

In China, sodium titanate (NaTiO) has been investigated for the treatment of liquid wastes containing alpha emitters and fission products [47]. The preparation, characterization and exchange capacity of the material was studied and it was shown to have high selectivity for polyvalent ions over monovalent ions in neutral and basic solutions. $K_d$ values for americium and plutonium in 0.6 M NaNO$_3$ solutions, measured by batch experiments, were $10^3$–$10^4$.

Finally, in Finland, HTiO has been investigated as a selective absorber for strontium [48]. The material used has an exchange capacity of 1.4 mmol Sr/g and was found to be effective for strontium removal from solutions containing 1M boric acid and 4M NaCl. DFs of about 100 were measured.

In addition to packed bed ion exchange, HTiO and other inorganic materials can be used in conjunction with ultrafiltration. In these applications the same exchange properties of the material are utilized but it is generally used as a finely divided powder to provide a large surface area improving absorption kinetics; this will be detailed in Section 3.4.

A number of studies on the use of other inorganic materials for waste stream treatment have also been reported. Some examples are given below.

The CEGB investigated the performance of several ion exchangers for fission product removal from AGR pond water [49]. Natural and synthetic zeolites and hexacyanoferrates were examined for the removal of caesium from a simulated pond water; a natural zeolite gave the best decontamination. Similar studies were conducted to find suitable absorbers for the treatment of a waste stream containing about 2g Mg/L arising from the carbonate dissolution of Magnox fuel debris. It was found that cobalt and strontium were most effectively removed by a form of manganese dioxide, caesium by Zeolon 900 and uranium by an organic anion exchange resin.

In India, pilot scale studies, using copper hexacyanoferrate loaded macro-porous anion exchange resins, were conducted for the polishing of spent fuel storage pool water. The tests indicated that a caesium DF of about 1000 could be achieved at flow rates up to 80 bed volumes per hour and a total throughput of 20 000 bed volumes [50].

The Duratek Corporation in the USA [51] has developed a series of inorganic exchangers specifically for radioactive waste applications. These ‘Durasil’ materials are based on glass or carbon which gives them good mechanical properties and a proprietary process is used to form active surface ion exchange sites.

In China [52], polyantimonic acid has been studied for the removal of cerium from various acidic waste streams to assess the potential application of this material.

All the absorbers considered above have been tested for the removal of cationic activity. Anionic species are also found in waste streams. For example, iodine and technetium are most likely to be present as I$^-$ and TcO$_4^-$, respectively. Other anionic species could result from the presence of complexants in the waste, forming com-
plexes such as \( \text{UO}_2(\text{CO}_3)_3^{3+} \). A study of the removal of anionic species by inorganic ion exchangers has been carried out at the University of Salford [53]. The uptake of iodine and technetium onto anionic hydrous oxide exchangers such as zirconium and titanium oxide has been investigated. The study includes examination of the thermal and radiation stability of the materials and a preliminary study of their encapsulation and leaching behaviour.

The effects of interfering cations and complexants have been reported in a number of studies reviewed. Generally, the amount of information available on the performance of absorbers in the presence of complexants is fairly limited, and further laboratory studies are required.

On a laboratory scale, the use of goethite modified with hydrophobic amines for the extraction of anions from alkaline solution has been recently reported [44].

The preparation and properties of complex hexacyanoferrates in robust granular form suitable for large scale use in packed columns for caesium removal has been recently reviewed [54]. The hexacyanoferrate compounds of Cr, Co, Cu, Ni, Sn, Tc, Zn and Sr appear to be promising. Several methods of preparation have been developed.

At the Loviisa Nuclear Power Plant, Cs is the dominating radionuclide in the evaporator concentrates. Since 1985, the use of inorganic hexacyanoferrate based materials for purification of caesium has been studied. A full scale system, called IVO-Cs Treat System, was constructed and commissioned in October 1991 (Fig. 9). A method of producing the ion exchanger in granular form on an industrial scale was developed and the facility to produce it was constructed. In the test run, 253 m\(^3\) of concentrate was purified by using three ion exchange columns of eight litres each. A volume reduction factor of over 10,000 was achieved, and the decontamination factor for caesium was about 2000 [55].

In the Czech Republic, some composite inorganic–organic ion exchangers using polyacrylonitrile as a binding polymer for the inorganic active component have been developed. The active components can be ammonium molybdophosphate, potassium–nickel hexacyanoferrate, sodium titanate, manganese dioxide, or barium sulphate. The kinetics of ion exchange is not affected by the binding polymer. The composite ion exchanger based on nickel hexacyanoferrate was used for the removal of \(^{137}\)Cs from long term fuel storage pond water. A decontamination factor of \(10^3\) was reached at pH = 8.0–8.3 for the treatment of 7500 bed volumes of pond water [56].

In the framework of a European Community contract the performance of about twenty inorganic ions exchangers has been compared in France to determine the pH range and concentrations where they can be used [57]. For Co and Sr, best results in neutral or alkali medium are obtained with sodium titanate, sodium zirconate and titanium oxide whereas in acidic medium polyantimonic acid alone has some efficiency. In acidic medium, ammonium phosphotungstate is efficient for caesium removal and plutonium is more readily removed than neptunium by polyantimonic
acid but for pH between 4 and 7 manganese and titanium oxides are best for plutonium and neptunium. The efficiency of all inorganic exchangers decreases with salt content increase and acidity increase of the waste. Treatment of real wastes has been tested with inorganic exchangers on laboratory scale, by using batch contacts. Inorganic ion exchange treatment alone has not been sufficient to reach the objectives of classifying the wastes from a geological repository to a subsurface disposal, according to French regulations.

The removal of $^{106}$Ru from alkaline intermediate level wastes was studied in India. A zinc–carbon system, with the waste adjusted to pH 2, was studied by batch equilibration and column operation. In columns, the cumulative DF, after passing 40 bed volumes of waste, was found to be 36.6 [58].

Some recent Japanese research studied the selectivity for Pu$^{4+}$, Am$^{3+}$ and NpO$_2^+$ of selected synthetic inorganic ion exchangers as a function of HNO$_3$ concentration at ambient temperature. A high selectivity toward Pu$^{4+}$ and Am$^{3+}$ was discovered on tin antimonate and titanium antimonate cation exchangers. The selectivity order was NpO$_2^+ <$ Am$^{3+} <$ Pu$^{4+}$. The ion exchange rate in the initial stage of adsorption was about the same as that of a commercial strong acid type organic cation exchange resin [59].
Recognizing the potential importance of these materials for the improvement of waste management technology, the IAEA initiated a co-ordinated research programme in 1987. This programme covered a wide range of natural and synthetic inorganic sorbents. Sorbents with high affinity for one or a few radionuclides (Cs, Sr) have already been identified. There are still a number of radionuclides for which no effective inorganic sorbents have been identified. Examples are ruthenium, technetium, radium and thorium. Further development is needed on these points [60].

Inorganic ion exchange is a promising process for low level waste treatment but it seems that the use of inorganic materials cannot be universal and that they probably have to be included in combined processes such as the use of finely divided materials associated with membrane solid–liquid separation.

3.3. EVAPORATION

Two objectives appear in the research on evaporation processes. The first is to reduce the cost of the process, thereby making it more competitive with alternative treatment methods. The greatest economy in operating evaporators can be achieved by minimizing energy consumption [3]. The second area of research is aimed at improving the extent of evaporation in the presence of solids. Evaporator/dryer and thin film evaporators are being studied and designed to operate in the presence of solids, and concentration in dryers may continue until a dry salt cake is obtained.

At AECL [61] studies have been made to evaluate the use of thin film evaporators for the treatment of liquid wastes. The objectives of drying operations are various and include:

— volume reduction, and
— in order to facilitate future disposal/stabilization of the waste, production of a solid dried waste that is easier to condition.

In these drying processes, a denitration step is sometimes used on evaporation concentrates with high nitrate or nitric acid content [62–65]. This denitration step achieves volume reduction of the liquid waste to be treated and disposed of, and nitrate removal makes any further conditioning for disposal easier. Also, addition of water to an evaporator concentrate containing high nitrate and nitric acid levels, and then removal of the extra volume by distillation can result in a significant reduction in nitric acid concentration.

On the Three Mile Island (TMI) site (USA), a process has been developed for the processing of radioactive water resulting from the 1979 accident. The contaminated water was produced by direct release of reactor coolant during the accident as well as primary coolant leakage and in-leakage of river water through the reactor
building air coolers. Additional water was generated during defuelling and de-contamination activities in the post-accident years (total anticipated volume about 10 000 m³). The method of management is proposed to process the water through a closed cycle evaporator, to redistil the condensate and to discharge it as a vapour containing essentially all tritium. The remaining particulate contamination will be concentrated in the evaporator bottoms and then dried to a solid waste form (Fig. 10). 190 tons of boric acid/sodium borate solids will be obtained. The volume reduction for this system is 56 because of the total evaporation and vaporization of the liquid [66].

A volume reduction technique has been examined at the Palo Verde Nuclear Generating Station (USA). A vacuum dryer system will reduce evaporator concentrates to a dry solid which is loaded into drums for disposal. Vacuum on the discontinuous blender/dryer is maintained at 30 kPa. The volume reduction factor obtained is five [67].

The IDAHO Chemical Processing Plant (ICPP) has for more than 30 years used the fluidized bed technique to dry various liquid wastes produced in the nuclear centre. A new installation has been designed and built which has been in operation since 1982 and can treat the liquid waste from a 3000 t/a reprocessing plant [63].
An experimental calciner is being operated in Tokai [64] treating liquid wastes from reprocessing operations. The pilot plant (reactor diameter 10 cm) can calcine one litre of liquid waste per hour.

In all these processes, it is necessary to add a chemical product such as iron or aluminium nitrate in order to avoid the buildup of sodium nitrate particles.

Sometimes the drying treatment of liquid wastes is carried out to facilitate further conditioning for disposal of wastes.

In Japan, research is in progress to dry the liquid waste (generally using a thin film evaporator) to produce a salt cake and then compact it into pellet form before immobilization into a container for disposal [62].

In France, a small pilot plant using a fluidized bed has been operated recently at a feed rate about 1 L/h with inactive solutions (4M NaNO₃, 1M HNO₃) with the double objective to denitrate the liquid waste (volume reduction) and, by addition of silica and alumina to the waste, to generate a product such as NaAlSiO₄, which, after thermal ceramic treatment, could be suitable for direct disposal [65].

For sites with favourable climatological conditions, a concept based on using solar energy for the concentration of low and intermediate level liquid radioactive wastes is being evolved in India. This approach, combined with conventional evaporation, is expected to provide an overall volume reduction of 300–400 and DF of about 10³ at much lower costs and space requirements than the conventional solar evaporator facility. A small pilot plant has been set up at the Rajasthan Atomic Power Station Site to generate design data for a larger facility [68].

3.4. MEMBRANE PROCESSES

It was stated in Section 2.1.4 that ultrafiltration and microfiltration are more selective than reverse osmosis and should be easier to apply to waste treatment because of less severe operating conditions.

The results of recent research and development of ultrafiltration for the treatment of radioactive waste streams indicate that the process has many attractive features [60, 69, 70] such as:

1. High DFs (>100) have been achieved for the actinides and for some fission products such as strontium and caesium.
2. Volume reduction factors of about 50 are obtained [71].
3. The process is capable of removing alpha activity to below the best detection limits from waste streams containing feed levels of about 2.0 Bq/mL.
4. The process is versatile and, when used in conjunction with small quantities of absorbers or flocs, may be tailored to treat a wide range of waste streams.
5. Smaller quantities of absorbers (<10 mg/L) are required than would be necessary in alternative processes such as ion exchange and precipitation; this gives
rise to smaller volumes of secondary wastes and, therefore, reduced disposal costs. The finely divided form of the additives also provides improved kinetics compared to ion exchange using packed beds of granular material.

(6) The process is relatively unaffected by the presence of suspended solids, foaming agents or high concentrations of inactive salts. Hence, it may be used when alternative processes such as evaporation or packed bed ion exchange are inapplicable.

(7) Ultrafiltration is more selective in its concentrating action than other membrane processes, e.g. reverse osmosis or electrodialysis. It is also operated at lower pressures than reverse osmosis.

(8) Excellent solid-liquid separation is achieved, including the removal of colloidal and polymeric species, making the process ideal for supernate polishing following precipitation processes.

(9) The process may be used to dewater and/or wash sludges arising from precipitation processes and can achieve solids contents of 30–40 wt%, which is higher than sedimentation or centrifugation.

(10) Ultrafiltration may also be used for direct cleaning of the primary coolant of PWRs, removing colloidal form activity using pH, temperature and radiation resistant inorganic membranes.

The extensive feasibility studies and pilot plant operations have indicated the following limitations in the use of ultrafiltration:

(1) The interruption to processing caused by membrane fouling and the need for regular cleaning operations although these can be minimized. About 1% of secondary wastes is produced by cleaning solutions [72].

(2) The plant required is relatively complex, operating at increased pressures and involving pumps. No plant has yet been operating for a long enough period of time to fully assess the lifetime of the individual plant components, although this is currently being tested at Harwell.

(3) The presence of complexants in waste streams may entail pretreatment before ultrafiltration but this may also be said of other processes.

The direct ultrafiltration of a radioactive waste stream can remove any activity present in colloidal or polymeric forms, or associated with particulates; in the case of actinides, this tends to be a large proportion of the activity present: ionic forms are not removed. The removal efficiency is a function of the membrane pore size.

Two effluent streams result from an ultrafiltration process: the clarified permeate stream which consists of the bulk of the liquid together with the dissolved ionic species, and a smaller volume of concentrated slurry containing the particulate and colloidal material rejected by the membrane. Volume reduction factors as high as 500 have been obtained [5], and, in general, the slurry can be concentrated to a considerably higher solids content.
Apart from direct treatment of feeds containing particulate or colloidal material, other areas of potential use can be identified:

(i) the polishing of supernates from floc processes, where it is possible to remove residual suspended matter — some of it in colloidal form — with its associated activity and thereby to increase the overall decontamination;

(ii) directly on active liquids by the addition of precipitating agents such as hydroxyl ion or floc formers such as hexacyanoferrate for caesium;

(iii) addition of preformed precipitates of finely divided forms of known absorbers;

(iv) a combination of (ii) and (iii).

In these ways ultrafiltration allows floc precipitation to be extended downwards to activity concentrations and effective partition coefficients where it is strongly competitive with ion exchange. The general limitations are:

(i) those of the chemical precipitants themselves — in streams of mixed activity it may not be feasible to find precipitating conditions which allow all the active species to be removed in one stage, e.g. in waste streams such as decontamination solutions containing complexing and sequestering agents.

(ii) deposition of some of the suspended solids on the membrane which then requires periodic backflushing or chemical cleaning which complicates the process. However, this membrane fouling can be overcome with some membranes (see Section 3.7.2).

Soluble species cannot be filtered directly, but if additives or seeds which absorb the species are added then even soluble radionuclides can be dealt with. Seeds specific to a number of radionuclides have been identified (e.g. nickel or copper hexacyanoferrate (II) for $^{137}$Cs) and optimum conditions of, for example, pH and concentration have been identified [60]. The use of a mixture or cocktail of seeds to remove a variety of radionuclides simultaneously is an obvious extension of the seeded ultrafiltration principle. The seed materials can enhance radionuclide removal by one of three basic mechanisms: precipitation, co-precipitation or adsorption. Precipitation and co-precipitation imply the generation of insoluble species in the aqueous waste either by pH change or addition of suitable chemicals in solution. With adsorption, however, preformed solid material or, more usefully, slurries of solid material can be added to the aqueous waste to be treated. The adsorption process is usually one of ion exchange (e.g. with surface hydroxyls), and this is generally the most versatile and useful of the three basic mechanisms. Seeded ultrafiltration is thus a novel way of utilizing ion exchange materials.

Current research and development work on waste treatment processes involving membrane technology is being directed towards development of the so-called seeded ultrafiltration procedure. Nickel hexacyanoferrate (II) and activated charcoal, in conjunction with ultrafiltration, are being used for the treatment of laundry liquid waste from the Cadarache nuclear research centre [69]. The performance of a number of inorganic sorbents, used singly or in combination, is being examined for
FIG. 12. Alpha removal for membrane plant.
the removal of activity from pressurized water reactor wastes at Harwell [70]. Some studies were also undertaken within the framework of the IAEA Co-ordinated Research Programme on the Use of Inorganic Absorbers for the Treatment of Aqueous Wastes and as Backfill [60].

Microfiltration has been used in Canada [73] for removal of dissolved contaminants. With the use of fine clinoptilolite (zeolite) it is possible to remove 99.9% of the $^{137}$Cs, $^{90}$Sr and $^{85}$Sr in the liquid waste. The addition of soda ash to the feed tank is used to preserve the clinoptilolite sites for $^{90}$Sr which would otherwise be exhausted by dissolved calcium. Ultrafiltration is also used in Canada in combination with polyelectrolyte additives, for removal of dissolved contaminants [74]. Microfiltration (MFU) in combination with spiral wound reverse osmosis (SWRO) and tubular reverse osmosis (TRO) has been used for the treatment of aqueous radioactive waste in Canada [75]. The process removes over 99% of the gross beta–gamma activity (Fig. 11) and about 99.9% of the alpha activity (Fig. 12). In 1992, 5 TBq of beta–gamma activity was brought into the plant; less than 37 GBq was released to the river.

At CRL a microfilter is used for the pretreatment of the feed stream. The turbidity is reduced from 200 NTU to less than 0.2 NTU in the MFU system. The backwash concentrate and TRO concentrate are fed to the wiped film bitumenizing evaporator for solidification with bitumen. The overall volume reduction of the plant is between 200 and 400. The plant currently treats a yearly volume of some 3000 m$^3$ [75,76].

Since 1992, ultrafiltration has been successfully used in the Sellafield Enhanced Actinide Removal Plant for separation of ferric floc containing alpha bearing radionuclides co-precipitated from liquid.

3.5. SOLVENT EXTRACTION

Since the 1940s, solvent extraction has been extensively investigated for utilization in the nuclear industry [1, 4]. A wide range of different extractants has been used for the actinides, e.g. tributyl phosphate (TBP), thenoyltrifluoroacetone (TTA) and trioctyl phosphine oxide (TOPO).

The most important applications of solvent extraction processes are, at present, in nuclear fuel reprocessing and uranium ore processing plants. In fuel reprocessing, solvent extraction is used to separate Pu and U from fission products. A second extraction stage is used to separate plutonium from uranium. In the PUREX process, which is currently employed, TBP diluted with dodecane or kerosene is used as extractant.

Solvent extraction is also used on a smaller production scale for the recovery of americium and neptunium. These processes generally use organo-phosphorus reagents, e.g. TBP, dibutyl phosphonate, hexyldiethyl-hexylphosphonate (HDEHP).
The recovery of uranium from ore leachate by solvent extraction began in 1955 with the use of HDEHP in the DAPEX process, but since 1957 tertiary amines have been the favoured extractants.

A range of different solvent extraction contactors has been developed for plant operation, mixer-settlers, pulsed columns and centrifugal contactors which operate in a countercurrent mode.

Lastly, solvent extraction is routinely used in the nuclear industry on a laboratory scale for the chemical separations required before radiochemical analysis. A wide range of methods is applied in this case.

In principle, the selectivity achieved by solvent extraction processes suggests that they would be suitable for the separation of radioisotopes from waste streams.

In solvent extraction processes, the choice of extractant is determined by the chemistry of the species to be extracted and the composition of the feed solution, particularly with respect to other potentially extractable metal ions. In most cases the extractant is dissolved in a hydrocarbon diluent.

The organic phase in solvent extraction is usually recycled for further use. Sometimes it is necessary to remove any degradation products by a wash stage before recycle. In waste treatment applications, where the level of activity present is low, the extent of solvent degradation will be limited, and only occasional washing will be required although it would be necessary when treating reprocessing wastes as these will already contain solvent degradation products.

One of the main problems encountered with solvent extraction processes is the solubility of the solvent in the aqueous phase. This results both in the loss of solvent from the plant and the production of an aqueous waste stream containing low amounts of organic material.

The performance of a plant depends on the rates of flow of the aqueous and organic phases and the volume ratio of the two phases. The volume reduction obtained by a solvent extraction process depends on the ratio of the organic to the aqueous phase (both the feed and the strip solutions). In many cases the volume reduction factor is low (<10). For large volumes of low level or intermediate level radioactive wastes this will constitute a serious limitation and the treatment, due to the plant size, will be expensive.

With high level wastes, solvent extraction processes generally give good decontamination factors for actinides. With low and intermediate level wastes, the removal of actinides from solution has been very little investigated, and the lack of information and industrial experience is obvious. The removal of radioisotopes other than actinides has not been investigated until recently, either.

Many developments of solvent extraction processes refer to the reprocessing step or to high level wastes; some of these developments are nevertheless mentioned here because they could have potential practical application to intermediate level and transuranic wastes.
Research is being conducted to identify new extractants suitable for low concentrations of actinides and with new extraction techniques (extraction chromatography, liquid membrane, etc.) for their operation. Such separations could be used to reduce the quantity of actinide bearing wastes.

3.5.1. Extension of existing applications of solvent extractions to new types of waste

In Germany, a solvent extraction process has been developed for the recovery of plutonium from the highly active raffinate resulting from the PUREX process [77]. Real raffinates were used in a series of experimental investigations to determine the recovery of plutonium by extraction into 30% TBP/alkaline diluent in a mixer-settler. From the results, two flowsheets were devised, one for the extraction of plutonium from a neptunium containing raffinate and the other for a neptunium free raffinate. Typical distribution ratios were about ten, but crud formation during the process was found to be particularly troublesome.

A Talspeak type process has been developed in Sweden for the separation of americium and curium from trivalent lanthanides present in high level liquid wastes [78]. The actinides and lanthanides are extracted into HDEHP and then separated by selective stripping of the actinides using mixtures of diethyltriamine pentanecetic acid and lactic acid. The process is reported to separate 98.5% of the lanthanides from the trivalent actinides.

One of the most important areas of current development is the use of bidentate organophosphorus extractants such as dibutyl-N, N-diethyl carbamoyl methyl phosphonate (DBDECMP) and its dihexyl analogue (DHDECMP), instead of the mono-dentate extractants. The separation of lanthanides and actinides with these bifunctional extractants has been reviewed [79], and it was concluded that they are particularly well suited for the industrial scale solvent extraction of actinides from acidic nuclear waste streams. When these extractants were first investigated they were very expensive and commercially unavailable in a purified form; these problems are, however, being overcome by the development of effective purification procedures. DBDECMP and DHDECMP have strong affinity to the trivalent actinides and lanthanides and have an advantage over the more commonly used HDEHP in being less pH sensitive.

An application of solvent extraction with DHDECMP is reported by Los Alamos National Laboratory for recovery of actinides from moderate concentrations of nitric acid waste streams [80]. DHDECMP is used for extraction of actinides in their trivalent, tetravalent and hexavalent oxidation states. Comparative extraction data for Am(III) Pu(IV) and U(VI) has been obtained. Octyl(phenyl)-N, N-diisobutyl carbamoylmethylphosphine oxide (CMPO) is unquestionably a stronger extractant than DHDECMP; however, the stronger extraction from dilute acid makes stripping of actinides from CMPO into dilute acid more difficult. Am(III) readily backextracts
from DHDECMP into dilute nitrate solutions. Fluoride enhances the backextraction of Pu(IV); U(VI), however, does not easily backextract.

At the Argonne National Laboratory, the TRUEX process has been developed to extract and recover plutonium and americium from nitric acid waste streams [81]. Once again this process has been designed for the treatment of the highly active nitric acid raffinates arising from PUREX type processes, and the wastes generated in metallurgical scrap processing. These wastes generally contain the actinides at ppm levels, and the TRUEX process aims at reducing their transuranic content to <3700 Bq per gram, of disposed form, which in the USA defines the waste as non-transuranic. The process uses a mixture of two extractants, TBP and CMPO in carbon tetrachloride (0.25M CMPO-0.75M TBP). Use of CMPO enables the trivalent actinides to be extracted. A flowsheet was designed and tested in a countercurrent experiment performed in a 14 stage centrifugal contactor at the Argonne Laboratory (five extraction, two scrub, four Am strip and three Pu strip stages were used); high yields and good separation of plutonium and americium were achieved.

An extension of the TRUEX process to the treatment of specific acidic waste solutions at several USDOE sites has recently been reported [82, 83]. A solvent extraction process with DIDPA (diisodecyl phosphoric acid) and a stripping process with oxalic acid have been studied for the purpose of separating Np(V) from high level liquid wastes [84]. Using a miniature mixer-settler with continuous countercurrent extraction and stripping, more than 99.96% of Np(V) was extracted from simulated high level liquid waste by addition of hydrogen peroxide which accelerated the Np extraction. More than 99.94% of Np(V) was stripped from DIDPA by 0.8M oxalic acid.

Most research in the high level waste field has been, is, and will be conducted to improve the partitioning of plutonium in nuclear fuel reprocessing processes and to recover the minor actinides (Np, Am) in advanced fuel cycles, for further elimination through nuclear reactions. All this research is conducted in order to reduce the quantity of alpha bearing wastes for a geological repository.

3.5.2. New extractants and their applications to waste treatment

Some new extractants are potentially applicable to the processing of radioactive liquid wastes [85]. These extractants have generally been tested, or are under test, in laboratory scale experiments. Three kinds of extractant are being investigated: those usable for the improvement of present nuclear fuel reprocessing, those necessary for advanced fuel cycles which include the recovery of minor actinides and those concerning TRU wastes or mixed alpha-beta-gamma wastes. This report is only concerned with the last kind, but it is obvious that new extractants convenient for reprocessing will probably also be suitable for alpha bearing wastes. The use of more efficient extractants in reprocessing will also limit the amounts of nuclear waste produced.
For the improvement of fuel reprocessing, the mono- and diamides, as alternatives to the organophosphorus extractants TBP and polyfunctional phosphonates, show promising properties [86]. Three kinds of new solvent of this type have been tried [87]. The use of N, N-dialkylamides as an alternative to TBP can limit the amounts of nuclear waste produced in existing reprocessing plants. The N, N-tetraalkyl 2-alkyl propane diamide bidentate extractants are claimed to be able to remove actinide ions including the trivalent species (Am$^{3+}$, Cm$^{3+}$, ...) from various types of TRU wastes. Synergistic tripyridyl triazinedinonyl naphthalene sulphonate (TPTZ-HDNNS) has proved to be efficient in the selective extraction of trivalent actinides from nitric acidic solutions. These solvents are completely incinerable, which is important for the treatment of process secondary wastes, and do not produce harmful degradation products. Laboratory experiments, using countercurrent separations with a battery of mixer-settlers, have been conducted on real waste solutions [88].

FIG. 13. TESEO process reference flowsheet for the treatment of Casaccia liquid waste.
Many researches have shown that CMPO is a good extractant for actinides and can be used for the decontamination of aqueous wastes [82]. Improvements can be brought about by addition of tributyl phosphate (TBP). The CMPO extractant shows a very strong extracting power for actinides, independent of the valence state, over a wide range of acidities (0.5–6M).

A flowsheet for the treatment of alpha contaminated liquid wastes at CRE Casaccia, using liquid–liquid extraction with CMPO, is outlined in Fig. 13 [89, 90]. Tests on TRU separation from these liquid wastes were carried out by using both simulated solutions in batch experiments and real wastes with continuous countercurrent using laboratory scale mixer-settlers. This process enables the achievement of very high decontamination factors (>2000 for alpha emitters) as well as significant concentration factors (>25). A pilot plant has been designed and built (3 L/h) for treatment of the 10 m³ waste stored at Casaccia but is not yet commissioned.

CMPO-TBP mixture is also a good combination for the extraction of europium. It was used to compare the possibilities of metal extraction with CMPO containing gels [91].

When immersed in solubility consistent organic solvents, high polymers (e.g. polyvinyl chloride, polybutadiene, polystyrene etc.) can swell and form gels. The advantages of the liquid gel extraction process, in comparison with the liquid–liquid one, are to allow the extraction of metal cations from dilute aqueous solutions by using high aqueous-organic volume ratios. Europium extraction of 53% for [HNO₃] = 1M to 97% at pH 4 have been reported, dependent on pH, polymer used and aqueous to organic volume ratio in wastes with high nitrate contents (4M NaN₃). CMPO containing gels are promising systems for the extraction and concentration of radio elements (Eu, Pu, Am) from nitrate media but are not suitable for [HNO₃] ≥ 1M. The extraction is much slower than the liquid–liquid extraction. Improvements must be made to increase the interfacial area and therefore the rate of metal phase transfer.

Crown ethers (Fig. 14) were also used as extractants. These cyclic compounds, first synthesized in 1967, can form strong complexes with alkali metal or alkaline earth elements.

Research has been conducted on the removal of caesium and strontium by crown-ether extractants. The majority of studies deal with simple wastes with pH higher than 4. South Carolina University has studied caesium and strontium removal in a simulated fission product liquid waste with high nitric acid content (HNO₃ 3M) [92, 93]. Strontium extraction was also studied with three isomers of DC18C₆ in HNO₃ medium up to 4M [94].

For wastes with high nitric acid and sodium nitrate content, many crown ethers have been tested for caesium and strontium extraction on the laboratory scale. Best results were obtained with DC18C₆ for strontium [95]. For caesium, continuous laboratory solvent extraction (five stages) with DB 21C7/KsbC₁₆ diluted in
nitrobenzene on 12.5 L of a simulated intermediate level waste (0.5M NaNO₃ and 1M HNO₃) have given a DF of 90 [96].

Recent work at Argonne National Laboratory with a solution of di-t-butylcyclohexane-18-crown-6 (DtBuCH18C6) in 1-octanol gave good results for strontium extraction from 1M HNO₃ solution [97]. Tests conducted with this new process, called SREX, on a synthetic dissolved sludge waste solution show that only strontium, barium and technetium are appreciably extracted by the crown ether.

Recent work in France to remove Cs and Sr from evaporator acid concentrates with high sodium content has used solvent extraction in order to sharply decrease the volume of wastes to be disposed of in geological formations. With DC18C6, it
is possible to remove 80-90% of strontium from high sodium content acid concentrate.

Tert-butyl mono benzo 21 crown 7 (tBuB21C7) makes transfer of caesium possible but is far from being complete. Among several diluents studied, the best results were obtained with decanol diluted in hexylbenzene. These products were operated by using the liquid membrane technique and this will be reported later in Section 3.5.3 [98].

Cobalt (III) dicarbollide is a potentially superior reagent for extracting Cs, Sr and possibly other fission products from wastes. It has a high resistance to acids (up to 3M HNO₃). Workers in the Czech Republic and the former USSR have devoted extensive effort to studying this compound as an extractant. Technology based on the use of chlorinated cobalt dicarbolhyde in a polar diluent as extractant providing recovery Cs, rare earth (RE) and transplutonium elements (TPE) was developed. In the course of pilot trials at the reprocessing plant RT-1 in the Chelyabinsk region, this technology made it possible to obtain fractions of Cs, Sr, TPE and RE with a recovery degree above 99% [99].

Distribution ratios for caesium and strontium in HN0₃ medium have been reported [100].

Solvent extraction has also been investigated for the removal of plutonium from sulphuric acid waste solutions arising from the acid digestion of plutonium contaminated material [101]. Plutonium extraction has been demonstrated on a laboratory scale using HDEHP or HDEHP/TOPO in kerosene. The conditions for the extraction and stripping of plutonium were optimized by using a multistage mixer-settler, and the behaviour or uranium, thorium and americium was also investigated. The process was generally effective, with distribution coefficients between $10^2$ and $10^3$ being obtained for solutions initially containing about 4 g/L plutonium.

3.5.3. Extraction chromatography and liquid membrane processes

So far all the work described has used conventional solvent extraction; there have, however, been a number of studies undertaken to examine the use of the related extraction chromatography and liquid membrane processes.

3.5.3.1. Extraction chromatography

In extraction chromatography, the extractant is supported on an inert polymeric or inorganic substrate and used as a packed bed. For example, a commercially available resin consists of either TBP or HDEHP on a polymeric support. Operationally, the process resembles ion exchange but chemically it is similar to solvent extraction using undiluted extractants [102]. The feed solution is passed through the bed, the extractable species are absorbed onto the packing and then may subsequently
be eluted and the column reused. This column mode of operation makes extraction chromatography more compact than conventional solvent extraction processes.

The major operational problem encountered in extraction chromatography is the loss of organic extractant from the column, resulting in ppm levels of extractant in the aqueous solution. This loss may be overcome by presaturating the feed with the extractant, but still leaves a waste effluent containing low levels of organic material which may be unacceptable at the subsequent disposal stage.

A pilot scale investigation was undertaken to evaluate the use of extraction chromatography for the removal of neptunium, plutonium and americium from a nitric acid waste stream containing about 0.1 g/L of the actinides and about $4 \times 10^5$ Bq/L fission products. The actinides were co-extracted onto a column
filled with di-n-hexyloctoxyethyl phosphine oxide (POX.11) adsorbed on an inert silica gel support. The levels of actinides were successfully reduced to < 1 mg/L, by this process [103].

A commercially available resin was investigated for the removal of actinides from nitric acid solutions [104]. Actinides in the +IV oxidation state were strongly extracted, and in addition Np(V) was also removed at low pHs. This removal of neptunium in its most common oxidation state from a fairly dilute solution has been used in the design of a flowsheet for the treatment of a nuclear waste stream [105]. More recently, the use of several extraction chromatographic methods for the removal of uranium from phosphoric acid solutions has been presented. In each case, organophosphorus extractants were supported on, or impregnated into, polymeric resins. The uranium concentration was about 100-200 ppm, while the phosphoric acid concentration was up to 10M [106].

In Germany, for the decontamination of an intermediate level reprocessing concentrate, CMPO dissolved in TBP and fixed on an organic support inside a column was studied for the removal of lanthanides and possibly actinides (Fig. 15). Experiments were performed on 100 L batches of genuine evaporator concentrates with a feed rate between 0.6 and 1.2 L/h. After a filtration step, the waste solution passes through a column loaded with manganese dioxide to separate antimony. The active treatment campaign showed that the implementation of the CMPO column proved unnecessary on account of the high retention properties of manganese dioxide for lanthanides as well as antimony in acidic medium. The decontamination factor achieved for europium was 2000 [90].

The use of extraction chromatography is still limited by the stability of the resin both to chemical and radiolytic degradation and, in particular, the problem of solvent loss from the resin. Further study of these materials is required before the process can be adequately assessed for its application in waste treatment.

3.5.3.2. Liquid membrane processes

In liquid membrane processes, the aqueous phase is separated from the aqueous strip phase by a thin film of solvent instead of the solvent acting as the bulk transport medium, which is the case in conventional solvent extraction processes. Liquid membranes are usually formed by preparing an emulsion of the aqueous strip solution in the solvent and then dispersing large globules of this emulsion in the aqueous feed solution.

After extraction, the emulsion is separated from the feed solution, de-emulsified and the extracted species removed (Fig. 16). Alternatively, liquid membranes can be formed as a film of solvent supported on a solid porous membrane. In both cases the arrangement gives a large surface area for mass transfer which improves the rate of extraction. In addition, the film arrangement allows higher driving forces for mass transfer than for the equivalent solutions in normal
FIG. 16. Liquid membrane emulsion system.

solvent extraction and this enables lower concentrations of solute to be treated. The main problem with the technique, as in the case of extraction chromatography, is the loss of solvent during operation. Losses in the two processes are of comparable magnitude. A development of liquid membrane emulsion systems has been reported recently [107].

Researchers in ORNL have invented a device known as the emulsion phase contactor (EPC) [108]. When water droplets carrying the substance to be extracted are introduced into the EPC, they are shattered by electronic pulses that produce water particles in the 1 to 5 μm size range. These tiny particles enable the chemical solvent to extract more material from the water base. ORNL researchers initially tested the technology on a very small scale.

Recent developments in radioactive liquid waste treatment with supported liquid membranes have been reported [109–113].

A supported liquid membrane (SLM) consists of an organic liquid absorbed into the pores of a microporous support, separating two aqueous solutions: the first
one containing the permeating ions (feed solution), the second one free of these ions (receiving solution). For most of the laboratory experiments, a flat sheet membrane was used (Fig. 17).

For industrial purposes, hollow fibre modules are used to provide high surface area/volume ratios up to 10 000 m²/m³. Because of the small inventory associated with the membrane and to the non-volatile nature of the organic phase used, small amounts of extractant are necessary; thus, expensive extractants such as CMPO or the more expensive crown ethers can be used (Fig. 18).

The transport of ions through the membrane occurs when a chemical potential gradient is established between the two aqueous solutions. The chemical gradient is due to the differences in concentration of the chemical species present.

To be transported through the membrane, the ion must possess a high distribution coefficient in the organic phase and a low distribution coefficient in the stripping solution. To improve backextraction, some complexing organic compounds — formic acid, tartaric acid, sodium citrate, etc. — can be added to the strip solution.

Nitric acid is transported by CMPO and TBP through the membrane, the buildup of nitrate ions in the strip solution decreases the driving force, the permeation of actinides slows down and even stops. To avoid the buildup of nitrate it has been proposed to remove the excess nitrate by using a second SLM; nitric acid and

![FIG. 17. SLM (thin sheet membrane). 1 — feed solution; 2 — receiving solution; 3 — membrane; 4 — grip collar; 5 — magnetic stirrers.](image-url)
actinides are transported through the first membrane, and nitric acid only is transported in the alkaline strip solution through the second membrane impregnated with a long chain primary amine.

Liquid membrane processes are in relatively early stages of development, although they have already found several potential applications in the mineral mining industry [109], and, more recently, in the extraction of uranium from seawater. The removal of U(VI) was examined by using a liquid membrane comprising 7-dodecenyl-8-quinolinol supported on a 80 μm thick polytetrafluoroethylene film.
The uranium (about $10^{-6}$M) was extracted directly from spiked seawater, via the membrane, into the 0.1M HNO$_3$ strip solution. The advantage of such a method is its relative simplicity; however, the rate of extraction is slow since transfer across the membrane is diffusion controlled and it took about 20 h to achieve 99% extraction [110].

Recently, the use of supported liquid membrane for the treatment of evaporator concentrates has been examined by CEA, France. Reprocessing operations produce
intermediate level liquid wastes in which the main components are sodium nitrate and nitric acid. These wastes are treated by evaporation, the distillate is discharged into the environment and all active and inactive salts are concentrated, leading to a large volume of secondary wastes. The overall objective of research is to concentrate long lived radionuclides (actinides and Cs-Sr) from the large volume of the evaporator concentrate. CMPO and crown compounds (DC18 C6—B21 C7) are able to extract actinides and strontium/caesium, respectively, from these high salinity solutions. The SLM renders the use of expensive tailor made extractant molecules such as CMPO or crown ethers possible. A flowsheet for the process proposed for the evaporation concentrates treatment is indicated in Fig. 19 [112].

Experiments have been conducted in a hot cell with a few litres of genuine concentrate from the Marcoule reprocessing plant [114]. CMPO (0.25M) and TBP (0.75M) diluted in decalin were used for actinides and the mixture DC18C6/decanol/hexylbenzene was used for strontium. With these two membranes the total decontamination factor for actinides is higher than 400; by destroying the stripping solutions with hydrogen peroxide the actinides are precipitated. The separation of actinides by filtration allows concentration factors higher than 160 to be achieved. The results for strontium are not so good as those for actinides; the decontamination factor and the concentration factor are, respectively, about 50 and 32. The crown ether compound chosen for the complexation of caesium was not selective enough to allow separation between sodium and caesium.

The major drawback associated with the use of SLMs is their lack of stability due to the loss of solvent. This has been overcome with two of the membranes used that have proved to be stable for more than 350 h. However, improvements are still needed on this point. Moreover, for any desired extraction, it is necessary to identify a suitable combination of solvent and strip phases, which may require a considerable number of sorting tests.

3.6. BIOTECHNOLOGICAL PROCESSES

Many ecological studies have shown the metal and radionuclide accumulation capacity of biological specimens. Seawater organisms such as mussels can concentrate metals and radionuclides up to 1000 times [115]. Crustacea may also have high radionuclide contents when they are sampled in the neighbourhood of nuclear plants or estuaries.

High concentrations of metals have been found in mosses, some grasses and higher plants and in worms [116]. Many species of bacteria, fungi and algae have been shown to concentrate metal ions both by active and passive mechanisms. In waste water and sewage treatment, microorganisms are used in the form of activated sludges to remove the inorganics and to degrade the organics [117].
3.6.1. Biosorption

3.6.1.1. Use of unicellular organisms

Some dead organisms concentrate metals and radionuclides [117] whilst others are affected by the toxicity of the metals. Single compounds (polymers, chelators) of cells or organisms can be used to enhance the specific absorption capacity of the system.

Most biosorption processes will involve the following stages (see Fig. 20):

- cell growth,
- cell harvesting,
- metal cell contacting (in a batch or continuous process),
- metal recovery-elution or ashing of loaded cells,
- waste disposal.

Bacterial metal sorption can in general be described by the linearized Freundlich adsorption isotherm [118].

The choice of organism and the pretreatment it requires will depend on the metal to be recovered and the type of contactor to be used. Many of the initial laboratory studies have used batch contactors but a continuous process would be more appropriate for larger scale operation; at present, the results obtained by using fluidized bed systems look most encouraging. These require the microorganisms to be immobilized in a suitable particulate form for column use, and several methods

![FIG. 20. Metal recovery and decontamination using microorganisms.](image-url)
for their preparation are being investigated including pellet formation [119] and immobilization in a polyacrylamide gel [120]. Metal sequestering by different parts of dead microbial cells can occur by any one or a combination of mechanisms. Surface adsorption as a defence against heavy metal poisoning by restricted ion permeability into the cell is often attained by a protective layer of excreted polymer [121]. A number of anionic ligands participate in binding the metal: phosphoryl, carboxyl, sulphydryl and hydroxyl groups can all be active to various degrees in immobilizing the metal [120].

Microorganisms, exhibiting a remarkably high uptake of metals, sequester them within the cell wall via two mechanisms. The first is a stoichiometric interaction, either ion exchange or complexation, between the metal ions and active groups such as phosphodiester (teichoic acid), phosphate, carboxyl (glycosides) and amine (amino- and peptidoglycosides and bound protein) on the polymers making up the cell wall. Secondly, uptake is the result of inorganic deposition via adsorption or inorganic precipitation [122].

Fungi have walls that can bind high concentrations of heavy metals or radio-nuclides. *Rhizopus arrhizus* biomass was used for the recovery of $^{226}$Ra [123], U [124] and Th [125, 126]. In these cases chitin, a structural acetylated aminopolysaccharide, is the most important cell wall component with respect to the observed uranium uptake.

In order to use the biomass in a reactor it is necessary to modify the biomass so that it has a particle size in the range of other commercial adsorbents (for example, 0.5–1.5 mm). Further, increased mechanical strength, high particle porosity, hydrophilic and increased resistance to aggressive chemical environments are necessary. Such a modification of the native biomass properties is usually achieved by immobilizing the microbial biomass. At McMaster University, the immobilization was done with polymeric materials [124]. The immobilized biomass particles have up to 15 wt% inactive material content. The sorbed material can be eluted with 0.1M Na$_2$CO$_3$ or 0.1 M NaHCO$_3$. The *Rhizopus arrhizus* system can bind up to 180 mg U/g dry cell weight (DCW) and the bacterial cell biomass of *Pseudomonas fluorescens* about 10 mg U/g DCW.

At several plants, biosorbents are used at pilot scale. For example, a plant in the Czech Republic is examining the fungal waste mycelium of *Penicillium chrysogenum*. The sorption capacity is between 80–110 mg U/g DCW when the concentration of uranium in the liquid phase is about 1 g U/L. *Penicillium chrysogenum* is a waste biomass from penicillin production, and the only cost involved is the hardening of the mycelium [127].

The biosorption of caesium, plutonium and uranium by immobilized microorganisms is being studied in India. In the case of uranium, tests with industrial yeast samples immobilized in polyacrylamide showed significant capacity (60–100 mg/gm DCW) [128]. Immobilized *Saccharomyces cerevisiae* also showed promising results.
Bullman et al. [129] have noted that physicochemical treatment of bacterial biomass by heating, drying or ultrasound influences the sorption capacity of biomass. The benefit of such treatments was demonstrated for La sorption. *Arthrobacter* could bind 100 mg La/g DCW after freeze drying but only 40 mg La/g DCW after thermal drying [130].

A commercial example of the use of microbial biomass for metal and radionuclide removal is the AMT-BIOCLAIM product [131].

Another commercial product is BIO-FIX [132]. It consists of blended, thermally killed biomass immobilized in small porous polysulphone beads. Calcium and magnesium ions are initially sorbed by the BIO-FIX beads but are displaced by heavy metal ions. Elution can be done with a small volume of mineral acid (0.1M H$_2$SO$_4$, 0.05M HN$_O_3$ or 0.1M HCl).

### TABLE I. COMPARABLE URANIUM RECOVERY BY MICROBIALS OR MICROBIAL CELL PRODUCTS

<table>
<thead>
<tr>
<th>Organism</th>
<th>Method of U uptake</th>
<th>Accumulation (per mg dry weight)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Rizopus arrhizus</em> (f)</td>
<td>Adsorption to cell wall</td>
<td>180</td>
<td>[124]</td>
</tr>
<tr>
<td><em>Arthrobacter RAG</em> (b)</td>
<td>Binding to extracellular polymer</td>
<td>800</td>
<td>[153]</td>
</tr>
<tr>
<td><em>Penicillum digitatum</em> (f)</td>
<td>Adsorption to cell wall</td>
<td>5–7</td>
<td>[155]</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em> (b)</td>
<td>Intracellular</td>
<td>150</td>
<td>[156]</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em> (y)</td>
<td>Adsorption to cell wall</td>
<td>150</td>
<td>[156]</td>
</tr>
<tr>
<td><em>Zooloea ramigera</em> (b)</td>
<td>Binding to extracellular polysaccharide</td>
<td>500–200</td>
<td>[157]</td>
</tr>
<tr>
<td><em>Streptomyces viride</em> chromogenes (b)</td>
<td>Adsorption to cell wall</td>
<td>312</td>
<td>[154]</td>
</tr>
<tr>
<td><em>Chlorella regularis</em> (a)</td>
<td>Adsorption to cell wall</td>
<td>159</td>
<td>[154]</td>
</tr>
<tr>
<td><em>Citrobacter sp.</em> (b)</td>
<td>Binding to cell surface via enzyme action</td>
<td>9000</td>
<td>[142]</td>
</tr>
<tr>
<td><em>Streptomyces longwoodensis</em></td>
<td>Binding to phosphodiester residues</td>
<td>440</td>
<td>[8]</td>
</tr>
<tr>
<td><em>Aspergillus niger</em></td>
<td>General sorption</td>
<td>n.m.</td>
<td>[159]</td>
</tr>
</tbody>
</table>

*a* = alga; *b* = bacterium; *f* = fungus (filamentous); n.m. = not measured; y = yeast.

From Ashley et al. 1990 [135].
TABLE II. COMPARISON OF BIOMASS WITH TRADITIONAL SORBENTS AS RADIUS ADSORBENT MATERIAL

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Radium uptake capacity (pCi/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolite</td>
<td>2 800</td>
</tr>
<tr>
<td>Manganese zeolite</td>
<td>2 100</td>
</tr>
<tr>
<td>Zirconium salts</td>
<td>2 750</td>
</tr>
<tr>
<td>Bio-rex ion exchange resin</td>
<td>2 900</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>3 500</td>
</tr>
<tr>
<td>Biomass A (sludge)</td>
<td>40 000</td>
</tr>
<tr>
<td>Biomass B (sludge)</td>
<td>75 000</td>
</tr>
</tbody>
</table>

Data from Ref. [160].

Bioaccumulation of radionuclides is also reported for $^{60}$Co, $^{137}$Cs, $^{85}$Sr, U, Th, Ra, Am and Pu [133]. Usually, $^{226}$Ra is co-precipitated as a barium–radium sulphate sludge by addition of BaCl$_2$ to the sulphate rich effluent. The resulting precipitate settles very slowly. Effluents from these settling ponds often result in substantial releases of suspended $^{226}$Ra to surface water courses. Sulphate reduction by sulphate reducing bacteria (SRB) releases the radium back into solution under anaerobic conditions.

Organisms excreting negatively charged polysaccharides form a matrix around the cells [134]. Zoogloea ramigera, common in sewage plants, produces substantial amounts of extracellular polysaccharide when cultivated on a medium containing a carbon source in excess. The organism is sensitive to low concentrations of heavy metals; it has, however, successfully been used for metal adsorption.

Some examples of uranium recovery by microorganisms are given in Table I. Table II compares traditional sorbents with biomass as adsorbers for Ra.

3.6.1.3. Spent biomass management

Although biomass offers the potential to act as an efficient sorbent of radionuclides contained in waste streams, the process can generate large quantities of biodegradable and radioactive biomass. A number of workers have demonstrated that
adsorbed nuclides can be removed from biosorbents by using a variety of treatments with reagents such as sodium or ammonium carbonate solutions (notably for uranium cation removal). Thus there is the basis for setting up a biosorbent recycling process where nuclides may be removed from waste streams, recovered, and the biosorbent used to treat further waste streams [135].

The spent biomass can eventually be sterilized and immobilized for final disposal.

3.6.2. Bioaccumulation

A Citrobacter sp. accumulates heavy metals via precipitation with enzymically liberated inorganic phosphate [136]. This reaction has been harnessed to a biotechnological process for the treatment of metal bearing streams [137, 138], with potential also for nuclear waste decontamination [139], facilitated by the high radiotolerance of the cell bound, phosphate releasing enzyme (phosphatase) [140]. Immobilized whole cell biocatalyst tolerates loads of up to 9 g U/g DCW over several weeks without apparent ill-effect [138]. Previous studies have established the participation of the Citrobacter phosphatase in heavy metal bioaccumulation [141]. Cells challenged in suspension with uranyl nitrate and phosphatase substrate for 12 h accumulated uranium [142].

After the successful accumulation of the uranyl (UO₂²⁺) ion, La³⁺ and Th⁴⁺ ions were used as analogues for the chemically equivalent actinide oxidation states and their removal by the Citrobacter system was demonstrated. Preliminary experiments using americium (almost entirely in the 3⁺ oxidation state) and plutonium (almost entirely in the 4⁺ oxidation state) concentrations similar to those found in low level aqueous nuclear waste have shown sustained phosphatase mediated removal efficiencies of 90% and 45%, respectively [143]. Pu removal needs high concentrations of glycerol 2-phosphate. Np removal has so far only realized about 10% [144]. It appears that the pentavalent forms of actinides are recalcitrant to biological removal. The methods and reactors used are shown in Fig. 21.

With Alcaligenes eutrophus non mettalotolerans, a biomineralization process can be induced which results in a metal/dry biomass ratio between 0.5 and 2.0. The bacterium is used in a continuous tubular membrane reactor (CTMR) for removal of a number of cations [145, 146].

3.6.3. Metals reduction by enzymatic action

In many cases the reduction of radionuclides is a necessary condition for their removal from liquid waste. Reduction of uranium by iron reducing bacteria, resting cell suspensions of sulphate reducing bacteria [147] or cell free extracts of Micrococcus lactilyticus [148] and by mixed culture of anaerobic bacteria has been reported [149, 150].
1. Grow cells on support

2. Put loaded supports in column (bioreactor)

3. Diagrammatic representation of loaded support

4. Schematic representation of events at the cell surface

**FIG. 21. Heavy metal uptake by a Citrobacter sp. Growth of cells on a support. Use of the biofilm loaded supports in a column.**

In the same way, biological reduction of high valence forms of Tc and Pu to lower valence forms that are more amenable to biological desolubilization should be important for waste treatment.

3.6.4. Removal and recovery of radionuclides and metals from chelating compounds

A process has been developed at Brookhaven National Laboratory for removal of radionuclides and toxic metals from aqueous and solid wastes (Fig. 22). In this process, citric acid is used to extract metals such as Ba, Cd, Cr, Ni, Zn, Co, Sr,
Th and U by formation of bidentate, tridentate, binuclear, or polynuclear complex species [151]. The citric acid extract containing the metals is then subjected to microbiological degradation followed by photochemical degradation under aerobic conditions [152]. Some metal citrate complexes are biodegraded, and the metals are recovered in a concentrated form with the bacterial biomass. Uranium forms a binuclear complex with citric acid and is not biodegraded. The supernatant containing the uranium citrate complex is separated and, upon exposure to light, undergoes

FIG. 22. Recovery of radionuclides and metals from liquid waste.
rapid degradation resulting in the formation of an insoluble stable polymeric form of uranium. Uranium is recovered as a precipitate (polyuranate) in a concentrated form for recycling or for appropriate disposal [152, 153]. This process has significant potential for treatment of nuclear wastes because:

(a) it can be applied to a variety of waste forms, including liquids, solids, and soils;
(b) it does not generate secondary waste streams;
(c) environmentally and economically important radionuclides and metals are recovered in a concentrated form for disposal or recycling.

3.7. ELECTROCHEMICAL PROCESSES

Although electrochemical processes are currently less well known than the more traditional waste treatment processes, they do have a number of advantages and hence benefits. These include the minimization of secondary waste, mild operating conditions, an extra process control variable and savings in both capital and running costs.

An extensive literature review of electrical processes has been carried out, which describes a wide range of techniques and considers their applicability to radioactive waste treatment [161]. Further extensive experimental work has since been carried out, and the technological scope has been widened.

3.7.1. Electroflotation/electroflocculation for removal of suspended solids

In the electroflotation process, gases are generated electrolytically (Fig. 23) [162]. The contaminated water flows slowly into the tanks and gas bubbles rising through it entrap any contaminant and lift it to the surface, where it may be skimmed off in concentrated form for disposal. The gas bubbles leaving the electrodes may carry charges which neutralize colloidal particles in suspension and cause them to coalesce. Two disadvantages of electroflotation are the relative high capital cost of the equipment and the hazards associated with H₂/O₂ mixtures that are generated. The latter situation can be controlled either by introduction of an air purge, to dilute the off-gases before venting from the cell, or by catalytic oxidation to water.

Commercial electroflotation cells are available up to a capacity of 50 m³, corresponding to a maximum throughput of 150 m³/h, and can be operated in either a batch or a continuous flow mode. Typical values of electrical energy consumption from experiments described in the literature [163–165] are in the range 0.5–20 kW·h/m³ of the emulsion treated.
Electroflocculation (also known as electrocoagulation) is the coagulation of colloidal material as the result of injection of flocculant ions directly into the waste at a controlled concentration to optimize their effect. Flocculant addition is achieved by means of electrolytic dissolution of a sacrificial anode (usually, Fe or Al) to form flocs, onto which particulates are preferentially adsorbed.

For an iron anode the simplified electrode reactions are:

\[
\text{Anode:} \quad \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \\
(4\text{Fe}^{2+} + O_2 + 2\text{H}_2\text{O}) \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^- \\
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 (s)
\]

\[
\text{Cathode:} \quad 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH} + \text{H}_2
\]

The cathode reaction is important for two reasons: first hydroxide ions are produced which help to maintain the local pH conditions sufficiently alkaline to enable the formation of ferric hydroxide flocs and, secondly, the cathode reaction provides gas microbubbles which assist solid–liquid separation.

As with bulk reagent addition, correct concentration/dosage of the reagent is required to produce effective coagulation/flocculation with minimal cost.

At Harwell Laboratory, a process has been developed for the removal of finely dispersed rape seed oil to less than 10 ppm from an oil in water emulsion [166].

Neither electrofloitation nor electroflocculation has been reported to be practically applied in the nuclear industry; these processes might, however, be useful to separate solid suspensions as well as oil emulsions from liquid wastes, such as floor drains, before final removal of radioactivity.
3.7.2. Electrically enhanced filtration (direct membrane cleaning)

It has been a goal of the filtration industry to develop membrane processes that do not suffer from the critical problem of membrane fouling. Crossflow (typically 3–5 m/s) can reduce the rate of solids deposition and hence the loss of performance, but still requires periodic backflush and chemical cleaning. These procedures are non-uniform since breakthrough at one point reduces the effectiveness elsewhere over the membrane surface.

Direct membrane cleaning (DMC) offers an alternative method of cleaning conductive membranes, such as stainless steel, graphite and conductive ceramics, and controlling filtration membrane fouling. The periodic in situ electrolytic generation of microscopic gas bubbles at conductive microfiltration or ultrafiltration membrane surfaces by short current pulses (1–5 s at 50–200 mA/cm$^2$) removes solid deposits without the need to interrupt the filtration [167, 168]. Electrical cleaning enables the crossflow velocity to be reduced significantly while still maintaining the target product solids content. In addition, transmembrane pressures can also be

---

**FIG. 24.** Permeation rate for 0.5 wt% Fe(OH)$_3$ suspension by direct membrane cleaning (DMC).

Transmembrane pressure 0.54 bar
Crossflow velocity 0.3 m/s
pH 10

10 V/100 A (195 mA·cm$^{-2}$) pulsed of approximately 5 seconds duration applied to the membrane after every litre of permeate was extracted

Restart membrane cleaning process

Normal crossflow filtration
Direct membrane cleaning

Total permeate extracted (L)
reduced without adversely affecting processing rates. Both factors have important implications in reducing plant wear and the degradation of the particles being separated and in minimizing the pump size and the associated pumping energy. DMC is attractive as a method of membrane cleaning when compared to backflushing as not only is it more uniform but also avoids interrupting filtration and therefore provides higher plant availability.

The process has been demonstrated on micro- and ultrafiltration membranes in both planar and tubular geometries. While DMC can concentrate feeds to greater than 25%, fluxes begin to decline beyond 5%. DMC is, therefore, principally suited to low solid content streams. Figure 24 demonstrates the ability of DMC to maintain high permeation rates during crossflow filtration of a Fe(OH)₃ floc [169].

DMC has been employed in a microfiltration system using a low level waste and an absorber mixture consisting of 44 ppm nickel hexacyanoferrate (Cs removal), 33 ppm zirconium phosphate (Sr removal) and 45 ppm hydrous titania (Ru, Ce and actinide removal). In addition to these, 100 ppm Fe(OH)₃ was precipitated in situ to assist in actinide and Cs removal as well as to act as a flocculant to trap fine particulate.

A 3 μm sintered stainless steel fibre membrane in the crossflow mode was judged to have the optimum properties of filtration and enhancement by DMC. Current densities in the range 100–300 mA/cm² were required for a maximum of 5 s duration at 15 min intervals to effectively clean the membrane. The effectiveness of DMC was further enhanced by transiently reducing the transmembrane pressure to zero and isolating the permeate outlet, particularly at higher solid contents.

After concentration of the mixed absorber to 5% by DMC microfiltration, they can be rinsed with 0.1mM NaOH to reduce the salt content to 0.02M NaN₃. This makes the resulting slurry suitable, in terms of conductivity, for subsequent electro-osmotic dewatering with virtually quantitative activity retention of up to 30% solids, which can then be immobilized by cement powder addition.

A disadvantage of this process is that it cannot be applied to an extremely low electrically conductive water.

### 3.7.3. Electro-osmotic dewatering for sludge thickening

Electro-osmotic dewatering (EOD) [170] can be used to dewater low conductivity slurries of intermediate solids contents (2–5 wt%) produced by crossflow filtration or gravity settling.

EOD operates by applying an electric field instead of a pressure gradient as the driving force across a microporous membrane (<50 μm), partitioning the solid and liquid components efficiently by charge separation (Fig. 25). It achieves an extremely high solids retention factor with minimal membrane fouling, even up to products of 40 wt% solids which are kept fluid by crossflow recirculation at 1 m/s.
The dewatering rate is proportional to the imposed current and the surface charge on the particulates being separated.

The most efficient separation is obtained under conditions of high particulate surface charge resulting from ionic adsorption (e.g. at higher pH). In addition to electro-osmosis, the dispersed particles in the feed are electrophoretically transported away from the membrane. Not only does this inhibit membrane fouling but also dramatically reduces the fraction of highly charged fine particles passing through. As a result, the process has a high DF with almost complete activity retention in the concentrate (>99.99%) as well as a high permeation flux.

The EOD rates are inversely proportional to the conductivity of the liquid. Typically, this restricts optimum operation to 0.01–1 S/m. This results in a limitation of the volume reduction factors achievable by EOD to ~10.

While this process has been demonstrated successfully to give virtually complete activity retention with low level radioactive liquid waste floc, intermediate level radioactive liquid waste trials have yet to be undertaken.
3.7.4. Electrodialysis

Electrodialysis (ED) is a membrane separation process achieved by the use of a differential driving force due to an electric potential across the membrane. Electrodialysis is a well-established technology [162] and is widely used today in various industries to perform several general types of separation, i.e. concentrating ionic solutions, deionizing salt solutions and separating ionic and non-ionic species.

In a typical electrodialysis cell to deionize a salt solution, anion and cation exchange membranes are arranged alternately in a stack and a potential field sufficient to force current through the stack is applied between two electrodes placed at each end of the stack. In order for current to pass between the electrodes, ions must be transported through each of the membranes and, by arranging the feeds to the various intermembrane compartments, it is possible to force ionic salts to pass from the dilute stream to the concentrated stream.

The energy consumption of an electrodialysis cell is determined effectively by the cell voltage and the current efficiency. The current efficiency is determined solely by the properties of the membrane, and the Faradaic processes occurring at the electrodes are unimportant. In practice, the cathode reaction is almost always hydrogen evolution and the anode reaction is the evolution of oxygen. The cathode reaction increases the pH of the solution in this compartment and the anode reaction decreases the pH.

The cell voltage required depends on the IR drop in the dilute streams, particularly towards the end of the process when the total ion concentration is very low. Hence, the cell must be designed to minimize this term, i.e. the gap between the membranes must be as small as possible.

The maximum useful current density through the membrane is normally determined by a phenomenon known as ‘polarization’ — in this context, depletion of the transported ion at the membrane surface. This is a mass transport problem, and it is therefore necessary to avoid stagnant layers at the membrane solution interfaces by operating the cell at a sufficiently high Reynolds number or with turbulence promoters.

Application of electrodialysis is usually limited by a low electric conductivity of a diluted stream due to a low concentration of electrolyte. 10 ppm of salt concentration is usually assumed as the limit.

Electrodialysis has been examined at the Japan Atomic Energy Research Institute (JAERI) for the removal of radioactive ions from low and intermediate level radioactive liquid waste using inactive coexisting salts as ionic carriers of very small amounts of radioactive ions [171, 172].

The first series of experiments was carried out in an electrodialysis cell using inactive coexisting salts such as NaCl, Na₂SO₄ or Ca(NO₃)₂. The volume of the dilute stream was 10 L and that of the concentrate stream 1 L, i.e. a concentration factor of 10 [171].
This study indicated that

1. differences in the coexistent salt species and their concentrations did not have any significant influence on the decontamination factor for radioactive ions, and

2. among the active nuclides tested, the efficiency of decontamination was in the order $\text{Cs}^+ > \text{Sr}^{2+} > \text{FPs} > \text{Ru}^{3+}$, which corresponds to the increasing order of ionic valency.

A second series of experiments used successive additions of coexisting inactive salt to the original feed waste stream containing $^{24}\text{Na}$, $^{42}\text{K}$, $^{137}\text{Cs}$ and $^{90}\text{Y}$. The test was made by using NaCl as the inactive salt, and successive additions of 1000 mg/L.
up to three steps. The concentration of monovalent ions was successfully reduced by a factor of $10^5$ by multistep treatment. However, the relative efficiency of removal of radioactivity gradually decreases in subsequent stages as shown in Fig. 26 [172]. The decontamination factor for multivalent ions such as $^{90}$Y was $10^2$, i.e. significantly lower than for monovalent ions.

A third series of experiments was carried out to demonstrate the multistep inactive salt addition process in a larger electrodialysis cell (190 dm$^2$ total effective area), using a genuine low level radioactive liquid waste containing 460 ppm of components such as Ca$^{2+}$, Na$^+$, Cl$, $ SO$_4^{2-}$, NO$^-$ and $10^{-3}$ $\mu$Ci/mL of $^{90}$Sr as tracer [172].

In the first step, where the total ionic concentration in the original feed solution was adjusted at 1060 ppm using Ca(NO$_3$)$_2$ as an inactive salt, a decontamination factor (DF) of 40.7 and a volume reduction factor (VRF) of 13.9 was achieved. In the second step, where no inactive salt was added, i.e. the salt concentration varied from 25.6 to 4.3 ppm, a DF of 6.0 and a VRF of 48.0 was achieved. In the third step, Ca(NO$_3$)$_2$ was added up to 1069 ppm, a DF of 45.0 and a VRF of 1.1 were achieved. The concentrated stream from the first step was finally fed to the diluted stream compartments of the same electrodialysis stack and produced 6.25 L of 1060 ppm diluted solution and 1.3 L of 77 000 ppm concentrated solution, i.e. a VRF of 13.4 was achieved.

Another example of electrodialysis applied in the nuclear industry is the recovery of NaOH and H$_2$SO$_4$ from the secondary liquid waste from the regeneration of ion exchange columns installed in LWR [173]. The study was carried out by the Chubu Electric Power Co., Ltd. (Japan) to demonstrate the process for reducing solidified waste volume by a factor of five by recycling of recovered reagents. The electrodialysis system consisted of two-compartment cells in bipolar mode. An anion exchange membrane was used to recover H$_2$SO$_4$, and a cation exchange membrane to recover NaOH.

The performance of the system was successfully demonstrated for simulated solutions using a plant scale system, i.e. recovery of 35 t/a H$_2$SO$_4$ and 28 t/a NaOH, as well as for genuine waste streams. Deposition of metals such as Cu, Fe, Ni on the cathode from the H$_2$SO$_4$ waste stream had to be overcome in this particular application. The effectiveness of polarity reversal, followed by washing by a mixture of air and water and finally by scrubbing by a rotating brush combined with ultrasonic cleaning, was demonstrated. A remote handling system was also developed for cleaning radioactively contaminated cathodes and membranes. No similar problems were experienced in the case of an NaOH stream. Long term life tests were also undertaken to determine the life of ion exchange membranes. The anion exchange membrane was observed to have a shorter life than a cation exchange membrane.

Salt splitting, i.e. the recovery of acid and alkali from a neutral salt solution, has been referred to in a text book [162]. For this process one pair of electrodes is
used for each pair of membranes, e.g. anion and cation exchange membranes; the acid is formed in the anode compartment, the alkali in the cathode compartment and the stream between the membranes is depleted in the neutral salt. However, another concept is to have a pair of electrodes with a cation exchange membrane separating the cell into two compartments; the alkali is formed in the cathode compartment and the mixture of acid and depleted salt in the anode compartment. The process has been reported to give 20% NaOH and 20% H$_2$SO$_4$ products directly from a 12–25% sodium sulphate feed solution [174].

3.7.5. Electrochemical ion exchange

An extension of ion exchange has been to introduce the reactive groups (e.g. –COOH, a weakly acid group) into an electrode structure. The electrochemical dimension increases the accessible sorption capacity and enhances the kinetics of the exchange reaction. The process has become known as electrochemical ion exchange (EIX).

EIX was first investigated as a process for brackish water desalination [175, 176]. In contrast to desalination, where pairs of cation and anion exchange electrodes are used, waste water treatment is concerned primarily with cation removal, and hence only a cation exchange electrode must be used. The other electrode can be an inert counter electrode and the most refined design, the ‘restricted electrode’ is described in greater detail in Refs [177–179].

Ion exchange can be induced electrochemically by a combination of field gradient and a local perturbation of the pH at the current feeder electrode coated with an ion exchanger. H$^+$ and OH$^-$ ions are electrochemically generated on the electrodes, which then interact with the ion exchanger via solid state diffusion.

The ion exchange process is thus under the control of an applied potential rather than the solution pH as in conventional ion exchange. The applied potential also induces migration in the ion exchange material, enhancing the kinetics of the processes and enabling high utilization of ion exchange capacity (75%). This leads to improved process limits and smaller plants with associated cost savings. The bed can be recycled many times; the regeneration step is often achieved without adding expensive chemical reagents and permits very large volume reductions.

The choice of absorber (organic/inorganic) and applied voltage control can be used to enhance the selectivity of a system for a particular ion. Long term cycling tests have shown this to be a robust system capable of making multiple use (>2000 cycles) of the exchanger capacity.

As part of an intercomparison exercise to test novel liquid waste treatment processes using real waste streams, some trials on EIX were carried out at the Tihange PWR station in Belgium. Figure 27 shows that the combined activity of the cobalt isotopes was initially 46.75 Bq/cm$^3$, approximately 71% of the total activity of the solution. The performance of the EIX cell was therefore quantified in terms
<table>
<thead>
<tr>
<th>Element</th>
<th>conc. ( \rho ) (moles·dm(^{-3} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{95})Zr</td>
<td>(2.65 \times 10^{-2})</td>
</tr>
<tr>
<td>(^{65})Zn</td>
<td>(2.82 \times 10^{-2})</td>
</tr>
<tr>
<td>(^{99})Tc (^{m})</td>
<td>961</td>
</tr>
<tr>
<td>(^{113})Sn</td>
<td>(4.05 \times 10^{-3})</td>
</tr>
<tr>
<td>(^{124})Sb</td>
<td>(2.83 \times 10^{-3})</td>
</tr>
<tr>
<td>(^{95})Nb</td>
<td>(2.09 \times 10^{-2})</td>
</tr>
<tr>
<td>(^{24})Na</td>
<td>(8.8 \times 10^{-4})</td>
</tr>
<tr>
<td>(^{54})Mn</td>
<td>(1.53 \times 10^{-1})</td>
</tr>
<tr>
<td>(^{51})Cr</td>
<td>(9.36 \times 10^{-3})</td>
</tr>
<tr>
<td>(^{60})Co</td>
<td>7.29</td>
</tr>
<tr>
<td>(^{58})Co</td>
<td>(4.16 \times 10^{-1})</td>
</tr>
<tr>
<td>(^{57})Co</td>
<td>(1.17 \times 10^{-2})</td>
</tr>
<tr>
<td>(^{110})Ag (^{m})</td>
<td>(9.26 \times 10^{-2})</td>
</tr>
</tbody>
</table>

**FIG. 27.** Concentration of radionuclides found in the PWR waste stream.
of the change in cobalt activity. The lowest combined cobalt activity measured following treatment was 0.93 Bq/cm$^3$, obtained by feeding samples of waste through a zirconium phosphate cation EIX unit, giving a decontamination factor of 50. A much improved performance was achieved by using a combination of exchanger materials optimized for the composition of this particular stream. The activity of the waste following treatment was then only 0.17 Bq/cm$^3$ (DF 275). The activity retained on the units could be eluted into a small volume for disposal, while Li and borate could be recovered separately for reuse if required.

A unit based on parallel anion and cation EIX electrodes has been successfully demonstrated for the treatment of high salt content wastes (>10 mM) containing beta–gamma activities and also for alpha activity from Harwell low level liquid waste.

3.7.6. Electrodeposition of metallic elements on a cathode

Metal deposition is a well known large scale process as found in the electroplating industry. Metals that can be directly deposited from aqueous solutions are limited to those less electronegative than zinc, including Mn, Cr, Co, Fe, Ni, Ru, Te, Rh, Pd, Ag, Zn. Among the common fission products, Cs, Sr, Zr, and Nb are more electronegative than zinc and cannot be deposited so that a useful separation

![Proposed mechanism for the overall ruthenium deposition.](image)

**FIG. 28. Proposed mechanism for the overall ruthenium deposition.**
<table>
<thead>
<tr>
<th>Treatment processes</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| 1. Chemical precipitation| Suitable for large volumes and high salt content wastes  
Avoids salt contamination and concentration  
Easy industrial operations, not expensive | Generally lower DF than other processes  
($10 < DF < 10^{2} (\beta, \gamma), 10^{3} (\alpha)$)  
Salt discharge into the environment  
Efficiency dependent on solid-liquid separation step |
| 2a. Organic ion exchange | $DF$ good on low salt content wastes $> 10$ to $10^{3}$, average $10^{2}$  
Good mechanical strength and fairly easy to handle  
Regenerable | Radiation and chemical damage must be considered  
Resin costs important  
Conditioning may require chemical treatment |
| 2b. Inorganic ion exchange| Chemical, thermal and radiation stability better than organic ion exchangers  
Relatively easy disposal  
Large choice of products ensuring high selectivity  
$DF > 10$ to $> 10^{4}$, average $10^{2}$ to $10^{3}$ | Affected by high salt content and complexants but less than organic ion exchangers  
Bed blockage problems  
Possible high costs  
Regeneration and recycling often difficult |
| 3. Evaporation            | High decontamination can be achieved  
$DF$ $10^{4}$ to $10^{6}$  
Well established technology  
Possible high volume reduction factor | Process limitations (scaling, foaming, corrosion)  
High operation costs  
High capital costs |
<table>
<thead>
<tr>
<th>Treatment processes</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| 4a. Reverse osmosis | Removes dissolved salts  
DF 100-1000  
VRF\(^a\) 100-1000  
Economical  
Established for large scale operation | High pressure system, limited by osmotic pressure  
Non-backwashable, subject to fouling |
| 4b. Ultrafiltration | Separation of dissolved salts from particulate and colloidal material  
Inorganic membranes available with good chemical and radiation stability can also operate at elevated temperatures  
Pressure < 1 MPa | Fouling — need for chemical cleaning or backflushing  
Organic membranes subject to radiation damage |
| 4c. Microfiltration | Low pressure operation (100-150 kPa)  
High recovery (99%)  
Excellent pretreatment stage for RO  
Inorganic membranes available  
Low fouling when air backwash is employed | Backwash frequency can be quite high; depends on solids content of waste stream |
| 5a. Biotechnology | Suitable for large volumes  
Treatment of mixed hazardous waste (organic and inorganic)  
Denitrification of acidic high NO\(_3\) containing waste  
Biodegradation of metal chelating organic acids | Possible intermediate products  
Sludge with high radionuclide content |
<table>
<thead>
<tr>
<th>Treatment processes</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b. Biosorption</td>
<td>DF &lt; $10^3$ ([\text{metals}] / \text{[biomass]} = 0.05 - 0.2)</td>
<td>High sludge production</td>
</tr>
<tr>
<td>5c. Bioaccumulation</td>
<td>DF &gt; $10^3$ ([\text{metals}] / \text{[biomass]} = 0.5 - 10.0)</td>
<td>Steering of an active process is difficult</td>
</tr>
<tr>
<td>6. Solvent extraction</td>
<td>Established in the nuclear field Selectivity enables removal, recovery or recycle of actinides</td>
<td>Poor VRFs Sensitive to particulate in aqueous phase Organic material present in aqueous raffinate Generates aqueous and organic secondary wastes</td>
</tr>
<tr>
<td>7. Electrochemical</td>
<td>Provides an additional process parameter Can help minimize reagent usage Low energy consumption Enhances the effectiveness of reactions</td>
<td>Sensitive to impurities in waste stream Ionic strength of waste stream can affect performance Can produce gases which may be hazardous Fouling is a problem above 10 g/L total solids</td>
</tr>
</tbody>
</table>

* VRF stands for volume reduction factor.
might be obtained between some active and inactive components. As decontamination factors of the order \( >10^2 \) are required for the treatment of low and intermediate level radioactive liquid waste, the concentration of active ions will have to be reduced to very low levels. However, the lower the residual concentration of ions to be removed the slower is the deposition rate for a given mass transfer regime, and also parasitic reactions may assume dominant proportions.

Electrodeposition of metals on a cathode from secondary liquid waste produced from regeneration of chelate type ion exchangers had been studied [180]. Metallic species such a Co, Mn, Zn in the liquid waste were successfully deposited on a metal cathode in a metal plating bath. Inactive Ni\(^{2+}\) ions were found to be efficient carriers to fix ions from very dilute radioactive solutions. 95 to 99% of radioactive metallic ions were removed from the solution during 100 h of application of direct current. Repeated electrodepositions are feasible, and the process was demonstrated in the deposition range of up to 0.1 kg Ni metal on a squaremetre of cathode surface.

The feasibility of direct electrochemical reduction of Tc which is present in liquid wastes as pertechnetate was investigated at Harwell [181]. Using simple batch cell units, simulant solutions containing pertechnetate were treated to give decontamination factors in excess of 100. These experiments indicated the importance of utilizing cathodes with a large surface area when treating very dilute waste streams. A flow cell containing a stainless steel felt cathode was then manufactured and tested. Decontamination factors of \( \sim 10 \) were obtained in continuous use. This process gave the best overall performance of the methods studied for technetium removal from a very low level waste.

3.7.7. Electrochemical precipitation of RuO\(_2\)·H\(_2\)O

The goal of the process [182] was to remove Ru by converting RuNO(NO\(_3\))\(_3\) and RuO\(_4\) present in liquid wastes into an insoluble, non-volatile, non-corrosive oxide product. The transformation is achieved via sequential oxidation of a ruthenium nitrosyl complex at a Pt/Ti anode to RuO\(_4\)/RuO\(_4\) before reduction at a Pt/Ti cathode to a black precipitate of RuO\(_2\)·H\(_2\)O. The use of fixed potentials between the cell electrodes led to the deposition of some of the product on the cathode in addition to a dispersed phase, while periodic polarity reversal (20 s period square wave) formed only the latter.

The reaction is unique to a Pt electrode, and DFs \( > 100 \) can be achieved in minutes once operational parameters for the electrochemical cell have been optimized. The presence of interfering organics (50 ppm TBP) had no effect on either the electrochemistry or the nucleation steps involved in the conversion process. From filtration studies, the dispersed particulates are all \( > 11 \mu \text{m} \). The overall reaction kinetics were found to be independent of pH in the range of 3–12;
the process is, however, not likely to be applied to more acidic solutions. The proposed mechanism for the overall process is shown in Fig. 28.

The main advantages and disadvantages of treatment processes are briefly summarized in Table III.

4. ADVANCES IN TECHNOLOGIES FOR THE TREATMENT OF ORGANIC WASTES

Various techniques for the treatment of liquid organic wastes are being developed and evaluated in different countries. No one treatment appears to have an overriding advantage although incineration is attractive because it is applicable to both solids and liquids, organic wastes are easily combustible and high volume reduction factors can be obtained. However, incineration alone is not necessarily a satisfactory treatment for organic wastes as further immobilization of the ash may be required and also corrosive combustion products from some organic wastes could require special off-gas treatment systems to be fitted to the incinerator [26].

4.1. INCINERATION

Radioactive waste incineration is a well developed though fairly complex technology. The equipment is sophisticated, particularly for off-gas systems which can include afterburners, heat exchangers, cold air injection, filter candles, bag houses, scrubbers and HEPA filters. This means that adoption of this process requires a substantial capital outlay and operating and maintenance costs are likely to be high.

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

1. The fluidized bed incinerator at Rocky Flats, where sodium carbonate granules in the fluidized bed were used to fix the phosphorus from TBP [28].
2. The controlled air incinerator at Savannah River Laboratory, where only ~42% of the phosphorus was immobilized after slurrying the TBP with calcium hydroxide and feeding the slurry either in cartons or as a spray [183].
3. The controlled air incinerator at Los Alamos National Laboratory [184].

TBP/OK has also been burned experimentally in the cyclone incinerator at Mound [185] and, in small quantities, in liquid waste incinerators at KfK Karlsruhe [29] and at Cadarache where the phosphoric acid is neutralized by addition of a calcium salt to the feed [27].

For the chemical and thermal treatment of TBP in OK [186], NUKEM, Germany, has developed a special stirred bed reactor process which includes decomposition of TBP, neutralization of the phosphoric acid which is formed in the process by means of calcium hydroxide and incineration of the pyrolysis gases in an afterburner. The process has been demonstrated in inactive operation with a throughput of 15 kg/h TBP/OK mixture, and it is claimed that waste can be treated from a reprocessing plant with a capacity of 350 t/a. However, development work undertaken by NUKEM for British Nuclear Fuels plc. identified a number of problems including difficulties in obtaining a consistent solid product, encapsulation of the solid product and some concerns on meeting safety criteria [30].

4.2. OXIDATION PROCESSES

A number of oxidation processes are being investigated for the destruction of the organic component of radioactive liquid wastes. The objective of the waste treatment is to convert the organic material to CO₂ and water leaving an aqueous inorganic residue containing the radioactivity and which can be decontaminated in existing or planned aqueous waste treatment plants.

The processes being examined involve chemical, electrochemical and photochemical treatments.

4.2.1. Acid digestion

This process has been under development in a number of countries, though only Germany and the USA have any significant experience in the operation of an industrial scale plant [31]. The process requires the use of mixed nitric and sulphuric acids at ~250°C, with consequent need for expensive corrosion resistant materials
of construction. Extensive off-gas scrubbing is required since sulphur dioxide and nitrogen dioxide are generated during the process. Some organic liquids such as hexane and TBP can be treated effectively, though others, such as paraffins, only partly digest, with the balance being lost from the reaction vessel by distillation. Trichloroethane and toluene do not digest well unless they are dispersed by atomization.

4.2.2. Wet oxidation

In this process [187–189] the organic waste is reacted with hydrogen peroxide in the presence of a catalyst at 100°C with excess water and distilled or evaporated to leave a concentrated inorganic waste which contains the radioactivity. The main advantages of the process are low temperatures and an aqueous residue which is easy to treat. Early applications have been for polar materials including TBP and organic acid decontamination reagents, but more recently development has extended to the treatment of non-polar materials. Early reports during the development stage of the process indicated the need for high temperatures and pressures, implying the use of sophisticated process control. However, more recent developments have enabled operation at modest temperature and atmospheric pressure, thereby greatly simplifying process requirements. A plant has been constructed at Winfrith, UK, for treating up to 200 kg batches of waste.

The process has been extensively examined by BNF plc. Sellafield for the oxidation of TBP/OK using aqueous hydrogen peroxide with potassium dichromate as catalyst [30]. The TBP is totally destroyed when the reaction is carried out at reflux; however, there is no reaction with the diluent. The product is an aqueous solution containing the radionuclides and the spent catalyst, and a very low active diluent phase.

It is not currently intended to use this process for the TBP/OK, but its potential for treatment of organic wastes, including spent decontamination solutions, is currently being studied.

4.2.3. Electrochemical oxidation

Electrochemical oxidation [169, 190], developed at Dounreay (AEA Technology), is a radically new means of safely destroying organic based toxic or hazardous wastes. The process relies on the generation of a strongly oxidizing form of silver (Ag$^{2+}$), which breaks down the organic material to form carbon dioxide and water. It can operate at low temperature and pressures (Fig. 29).

At the heart of the system is an electrochemical cell, consisting of a platinized titanium or similar anode with a high overvoltage for oxygen evolution, a stainless steel cathode, and a membrane separating the cell into two compartments. The membrane consists of a sulphonated fluoropolymer and is selectively permeable to...
the cations which carry the current through the cell but prevents mixing of the contents of the compartments. This is necessary because the reduced species formed at the cathode would otherwise react with the Ag\(^{2+}\) formed at the anode and thereby reduce the cell efficiency. Electrolyte, consisting of a mixture of AgNO\(_3\) and HNO\(_3\), is pumped through the cathode and anode compartments and a voltage is applied.

At the anode, Ag(I) is oxidized to Ag(II), either by direct oxidation:

\[
\text{Ag}^+ \rightarrow \text{Ag}^{2+} + e^- 
\]

or via an intermediate and possibly adsorbed NO\(_3\) radical to form the brown AgNO\(_3\)\(^+\) complex. In the anolyte, the Ag(II) reacts with water to form species such as OH radicals:

\[
2\text{Ag}^{2+} + \text{H}_2\text{O} \rightarrow 2\text{Ag}^+ + 2\text{H}^+ + \text{OH}_{\text{rads}}
\]
The radicals react with the organics being fed to the anolyte, ultimately oxidizing them to carbon dioxide, some carbon monoxide, water and inorganic products arising from any halogens, nitrogen, phosphorus, sulphur, etc. present:

$$\text{Organics} + \text{OH}_{\text{rads}} \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} + \text{Inorganics}$$

The silver returns to the anode for reoxidation. The $\text{H}^+$ ions migrate across the membrane to the cathode compartment under the influence of the applied voltage and at the cathode react with the nitrate ions, forming nitrous acid:

$$\text{NO}_3^- + 3\text{H}^- + 2e^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O}$$

The nitrous acid can be further reduced to gasous nitrogen oxides if its concentration in the catholyte is allowed to build up. The catholyte is continuously passed through a regenerator where the nitric/nitrous acid mixture coming from the cell is heated, and air or oxygen is passed into the hot liquor to oxidize nitrous to nitric acid for recycle:

$$2\text{HNO}_2 + \text{O}_2 \rightarrow 2\text{HNO}_3$$

Overall, there is no consumption of either silver or nitric acid. Hydrogen ions are formed in the anolyte but are consumed in the catholyte. The only consumables are electric power and the oxygen used in the catholyte regenerator.

The required reaction temperature can vary, depending on the organic material being oxidized. The highest temperature studied to date has been $95^\circ\text{C}$, which is still below the boiling point of nitric acid, so that the process temperature is very low when compared to incineration.

The range of organic materials which can be destroyed is very wide. The process was initially developed for nuclear industry application and a variety of combustible waste types were found to be easily oxidizable. These include rubber, some plastics, polyurethane, ion exchange resins of various types, and hydraulic and lubricating oils. Recent tests have shown that this list is not exhaustive and additional organics amenable to treatment include aliphatic and aromatic compounds, and chlorinated aliphatic and aromatic compounds.

The process efficiency, as determined by measuring the $\text{CO}_2 + \text{CO}$ produced against the theoretical production calculated from the current passing through the cell, is very high and under optimum conditions often approaches or even exceeds 100%. In the latter case, a small amount of $\text{NO}_x$ is nearly always produced from the anolyte, suggestive of direct involvement of the nitric acid in the oxidation. Any nitric acid reduction products from direct reaction are reoxidized in the highly oxidizing anolyte environment, and little consumption of acid occurs other than through the slight loss of $\text{NO}_x$.  

73
When chlorinated material is destroyed, some AgCl, which has low solubility in nitric acid, is inevitably produced in the anolyte. However, not all chlorine ends up as AgCl since chlorine is evolved from the anolyte — from oxidation of chloride by one of the oxidizing species present. The presence of AgCl in the anolyte is not detrimental as commercial membrane cells can tolerate a considerable solid burden in the electrolyte. The formation of AgCl reduces the anolyte Ag concentration considerably but also has the beneficial effect of acting as a chloride buffer. It is possible to operate the process for the destruction of chlorinated species without significant precipitation of AgCl but usually at the expense of cell efficiency.

The power consumption for the process governs the economics of the process. Wastes such as kerosene, used for much of the initial development work, require the greatest amount of energy for their destruction, while chlorinated wastes require much less. For example, kerosene requires 35 kW·h/kg for complete oxidation to CO₂ and H₂O (assuming 100% efficiency and a cell voltage of 3 V) while carbon tetrachloride only requires 2 kW·h/kg for oxidation to CO₂ and Cl₂. This is the exact opposite to incineration, where flammable wastes such as kerosene offer an inexpensive route to destruction, whereas wastes such as carbon tetrachloride are non-flammable and require fuel additions.

4.2.4. Supercritical water oxidation

Supercritical water oxidation is a high temperature, high pressure, wet oxidation process. Above the critical point of water, 374°C and 22.1 MPa, organic materials and gases are completely miscible with water. In the supercritical oxidation process, organics, air and water are brought together in a mixture at 30 MPa and temperatures in the 400 to 600°C range, which provides for spontaneous combustion of the organics. Under these conditions, inorganic constituents precipitate out in the process effluent and organic destruction efficiencies in excess of 99.99% have been demonstrated.

Advantages of supercritical water oxidation include rapid oxidation rates, requiring short residence times, and inorganics are efficiently removed from the aqueous stream. Disadvantages include the need for high operating pressure which requires sophisticated equipment and techniques, and high temperature operation which increases corrosion.

The Los Alamos National Laboratory is investigating supercritical water oxidation [191].

4.2.5. Photochemical oxidation

At British Nuclear Fuels, photochemical oxidation is being studied as a process to destroy waste organic liquids and, in particular, to destroy relatively dilute
aqueous solutions of organic complexants in waste streams such as the spent liquors from decontamination operations.

Photo-oxidation, using ultraviolet (UV) light, is normally not a very efficient process. Hence, most research effort is directed at improving the efficiency either by the use of transition metal catalysts or by the addition of hydrogen peroxide or ozone to obtain a synergistic effect or by the simultaneous use of all three, i.e. UV light, hydrogen peroxide or ozone, and a metal catalyst [192, 193].

4.3. DISTILLATION

Simple distillation may be used for the pretreatment of scintillation fluids and miscellaneous solvent wastes [31]. Substantial volume reduction is possible as the activity is generally concentrated in the residue. The recovered organic solvent could be used as a technical grade solvent or as a fuel for an incinerator.

At IPEN, São Paulo, a 20 L/d unit has been operated. At 85°C the azeotropic mixture begins to distil and, when the water is exhausted, the temperature is raised to 110°C to distil off the balance of the organic solvent. The water/solvent distillate separates into two phases with any activity carry-over remaining in the aqueous phase. The organic solvent can be separated from the aqueous phase for reuse elsewhere. A waste volume reduction of 40%, a process yield of 80% and a 10 L batch operation time of 50 min are claimed [194].

In the USA, a type of steam distillation has been used to recover liquid scintillation counter solvents contained in plastic vials [195]. In this case the vials do not need to be emptied for processing. The process uses a steam sterilizer autoclave with a volume of 360 L. Disposable aluminium trays are placed in the bottom of the autoclave to collect the melted plastic vials. Each charge could accommodate approximately 400 vials. The autoclave is pressurized to about 500 kPa with steam for 1 h. The steam is released slowly into the coils of a cooling can to condense the water and solvent vapour, which is collected in a separatory funnel. The condensate consists of approximately one part water and three parts organic solvent. After separation into the two phases, the water phase is usually dilute enough in activity to allow discharge. The organic solvent can be reused as a technical grade solvent or as fuel. The melted plastic vials can be incinerated or treated as solid waste.

Spent solvent from the Purex process is an organic waste, the volume of which must be minimized. It has been decided to provide a distillation facility to the UP3 plant at La Hague, France, in order to split this spent solvent into three parts: recovered diluent, concentrated TBP to be recycled and a residue which contains the radioactivity and most of the impurities. The distillation is performed at low pressure and temperature, using thin film evaporators in order to minimize the residence times in heated zones [196].
Work is also in progress on improving the efficiency by irradiating thin films of liquid, for example, as a falling film or on a spinning disc.

4.4. BIOTECHNOLOGICAL PROCESSES

Microorganisms have a diverse array of metabolic pathways which provide the catalysts (enzymes) to degrade/mineralize a myriad of natural and synthetic compounds. These metabolic functions are occurring in organisms that survive and grow in a wide spectrum of environmental conditions, e.g. aerobic, anaerobic, high and low temperature, pH or salt concentrations and in radiation fields. Some organisms have also been isolated that can live in two phase liquid solutions, for example, a Pseudomonas strain that grows under a layer of p-xylene was isolated by Wolfram et al. [197].

Today, bioprocesses are being engineered to optimize the living catalyst conditions and thereby improve the rates of decontamination of the material in question. The next generation of remediation systems employing bioprocesses can be envisaged to use contained waste which is highly concentrated in organic hazardous liquids. Although most of these efforts will be focussed on the manufacturing industries using chemicals in processes that generate waste or in the chemical production industries that also produce waste containing large quantities of organics, many other activities may also benefit.

The nuclear industry is unique in producing some wastes that contain both radioactive materials and toxic and hazardous organic liquids and solids such as turbine oils, scintillation liquids, resins, cutting oils, solvent extraction compounds, etc. These wastes, as they are generated, are not amenable to direct storage and must therefore undergo treatment for component disposal or radionuclide concentration and separation. At present, existing technologies cannot provide a satisfactory end product or process effluents. In some cases the treatment technology that is now proposed has either become very costly to engineer or does not meet specific regulatory limits. Bioprocessing offers some potential as a component in an overall treatment system that may render a mixed waste less toxic and in a form that is easier to treat further with existing technologies (Fig. 2 of Section 2.1.5).

Nowadays more and more bacteria that can degrade recalcitrant molecules such as aromatics (toluene, benzene, xylene, etc.) [198, 199], chloroaromatics [200], polyanaromatics [201], pesticides [202], herbicides [203], chlorinated polyanaromatics [204], etc. could be isolated. These bacteria can also be used for the treatment of organic contaminants in radioactive liquid wastes.

In the nuclear waste situation, biotechnology does not have many systems in operation, as yet. Although full scale systems do exist for denitrification, other pilot scale or demonstration tests are taking place, e.g. treatment of processing oils and scintillation waste.
Two case studies will be discussed, bioprocessing of cutting oils and the removal of aromatic solvents in liquid scintillation wastes. In the case of cutting oils, the work was done at Rocky Flats [205]. In these tests both batch and continuous process conditions were examined. Although the reaction rates were slow compared to incineration, it is likely that a timely processing of the stored waste could be achieved. The test was conducted under the influence of 100–1000 ppm of toxic and radioactive metals; these levels are considerably higher than anticipated in the contaminated cutting oils. The liquid effluents can be recycled for a period and then dewatered, sterilized and encapsulated for storage. This bioprocess was chosen as an alternative to incineration because of public opposition to thermal destruction (Fig. 30).

Liquid scintillation waste containing high levels of xylene, toluene, or pseudocumene has been drummed for interim storage. Treatment of this waste is under development, an outline of the proposed process is shown in Fig. 31. The uniqueness of the isolated organism is described by Cruden et al. [197, 206], and permits this contained waste to be fed at levels of 0.1 to 1% of the reactor volume. The system
has been continuously processing xylene for two years [207]. A demonstration project is now underway at the Mound facility to obtain data relevant for regulatory permission and engineering parametric studies for system scale-up. The system is a closed and continuously operating treatment, semi-automated. The liquid effluent will be used as the water requirement for cementation of other tritiated and plutonium low level waste of the facility. The gas stream will consist of carbon dioxide, oxygen and water vapour. If tritiated water vapour is encountered, a condensation step will be put into the off-gas stream.

Chitra et al. [207] have reported the degradation of laundry type waste from nuclear installations. In simulated effluents concentrations ranging from 5 to 100 mg/L in sodium dodecyl sulphate (SDS) were brought down to the level of 2 to 6 mg/L.

Lee and Donaldson have tested the decomposition of cellulosic waste by a 75 L digester [208]. The system operated in a once-through mode creating water as

![FIG. 31. Biotreatment of scintillation liquids.](image-url)
secondary waste. The results show that cellulose can be decomposed and total volume reduction of organic waste of 80–90% seems to be possible. The secondary waste arises from wet shredding of waste with a volume of ten times the volume of organic waste. Total volume reduction of waste after treatment of secondary waste was not reported either.

In Finland two different pilot plants have been operated for the decomposition of organic wastes [209, 210]. Figure 32 gives basic flow diagram of the system. Volume reduction factors from 10 to 20 have been reported for dry organic waste. No secondary waste is produced in the system. Volume reduction from 30 to 60 seems to be possible for spent resins when cementation is used as final treatment method [211] and no secondary waste is produced. Solidification tests for liquid occurring as a product of the bioreactor have been carried out [212, 213]. Achievement of high quality product seems to be possible.

5. FUTURE TRENDS IN PROCESS DEVELOPMENT

Future trends in process development for low and intermediate level radioactive wastes will be governed by:

(a) the necessity to reduce the radioactive discharge into the environment according to international conventions and national regulations with respect to the decreasing authorized maximum release limits and the ALARA principle.
(b) the aim to decrease the quantity of radioactive wastes for final disposal.
(c) the objective to minimize the radiation exposure to both workers and the public including long term effects from the final disposal.

Of course, the choice of a process must also consider other important items such as secondary wastes generated, operational simplicity and costs.

Future processes must achieve high volume reduction and decontamination factors, especially for alpha emitters, in order to change the waste category with respect to national regulations.

Liquid waste treatment must provide a solid or semisolid waste form so as to facilitate further conditioning or be sufficiently chemically and radiolytically stable to give a final disposal waste form with good long term properties — for example, avoiding organic material in the final waste form if necessary.

Owing to the variety of raw wastes produced, no single simple process can solve the whole problem. In the future, the use of combined processes will probably be the general rule. Sometimes a pretreatment is needed (destruction of organics, for example) in order to facilitate further treatment by means of an established process. This will reinforce the need for combined processes.

The minimization of raw wastes generated by the nuclear industry must be examined carefully before any waste treatment. For example, considering reprocessing wastes, the decrease of Na content is an objective which must be achieved by using other solvents or with solvent recycling inside the plant.

Partitioning of radioelements from high or intermediate level wastes in order to reduce the volume and the activity of wastes for geological repository is an option which is now being considered in the policy of some countries. The decrease of the content of alpha and long lived beta emitters in these wastes will reduce the potential hazards of a geological repository and make public acceptance easier. This partitioning must be considered in relation to transmutation studies or to conditioning studies of the separated radioelements in long term behaviour immobilization matrices. In view of the high volumes involved in the case of ILLW, an integral partitioning scheme for the long lived alpha and beta emitters should also include the treatment of these waste streams. This might induce important developments of new processes for intermediate level liquid wastes (solvent extraction, ion exchange and membrane processes could be concerned in the near future). A benefit in the medium term might be obtained by separating the actinides from ILLW and adding them to the stored HLLW, waiting for the transmutation concepts to mature, or for recycling.

According to these general considerations it is possible to briefly indicate future trends and the needs for research for the main processes discussed in this report.
5.1. CHEMICAL PRECIPITATION PROCESSES

Chemical precipitation has been widely studied and used. Decontamination factors cannot be greatly improved so that studies on chemical precipitation processes will be rather limited in the future. There is considerable potential for addition of specific reagents to enhance DFs for nuclides, and some developments are still needed or in progress on this point especially for ruthenium, antimony and technetium.

In the near future, chemical precipitation will remain an important part of some combined processes and developments or process adjustments at the industrial scale are needed.

Further development is necessary on the solid/liquid separation stage; the use of techniques such as ultrafiltration or electrically enhanced microfiltration in a combined process appears to be promising.

5.2. ION EXCHANGE PROCESSES

Development and use of organic polymers with radionuclide specific functional groups appear to be promising. New solvent extractants fixed on a polymeric support could be of value if the problems of solvent losses during process operation can be overcome. A useful application of these functional polymers could be in the area of partitioning ILW into a small volume of HLW and a large volume of decontaminated effluent. Development of new organic ion exchangers will be limited except for some specific radionuclides.

There is a great deal of promise in the area of inorganic sorbents and ion exchangers. It appears that development will proceed mainly in two areas. One is the use of finely divided inorganic sorbents in combination with cross-flow filtration, and the other will be granulation of these products or their incorporation into polymeric supports for use in column operation. One advantage with inorganic ion exchangers is the compatibility of many of these materials with subsequent immobilization matrices.

Many inorganic sorbents have been identified and show promising results for a limited range of conditions. More extensive characterization is required, preferably by an internationally agreed test procedure, to allow intercomparison.

5.3. EVAPORATION

Evaporation is a well known process which enables high decontamination factor and low discharge of radioactivity in the environment. Because of these advantages, evaporation will be more widely used in the near future. All salts and radio-
activity remain in the concentrate. The secondary waste generated is more often, especially in the case of TRU wastes, destined for a geological repository; therefore, volume reduction has to be improved by destruction of inactive salts or by concentration of radioactivity in order to declassify the greater part of the concentrate for subsurface disposal.

Evaporation must be combined with other processes to enhance distillate purification, for example by reverse osmosis or to achieve evaporator concentrate treatment, for example electrolytic destruction of salts. In this field, drying of concentrates, associated possibly with denitrification, appears to be promising but needs more development both from a technical point of view and for further immobilization needs.

The treatment of evaporator concentrates to separate and isolate long lived α emitters will also be a promising field of research in the context of partitioning policy.

5.4. MEMBRANE PROCESSES

Continuing development of membrane processes will be of considerable interest, particularly when combined with other waste treatment methods such as precipitation, ion exchange or evaporation. The combined processes will provide both improved decontamination and increased volume reduction factors when compared to the individual treatments.

Membrane cleaning and control of membrane fouling will need further development. Effective on-line cleaning techniques and chemical formulations for cleaning will be required, especially for polymeric membranes.

The effects of process conditions, such as feed composition (including scalable salts such as Ca₃(PO₄)₂, Na₂SO₄, Na₂CO₃ and NaHCO₃) and radiation, on operating equipment will need further examination.

With ultrafiltration and microfiltration, the use of inorganic membranes should be preferred in the presence of high radiation fields because of their wide operational range of pH and temperature and also their greater radiation resistance. Inorganic membranes are supplied in larger bore sizes (5-10 mm) than polymeric hollow fibres (0.5-1.2 mm) and are therefore able to handle much higher solids contents. However, their capital cost is much higher than that of organic membranes.

The application of seeded ultrafiltration is increasing in both nuclear and non-nuclear applications. The use of mixtures of absorbers that can be prepared by simple precipitation processes can provide a sorption stage tailored to a particular waste stream.

A new membrane separation technique known as nanofiltration uses membranes with pore diameters of about one nanometre, i.e. at the boundary of reverse osmosis and ultrafiltration. These new membranes act as a barrier to multivalent ions.
such as $\text{Ca}^{2+}$, $\text{Al}^{3+}$, $\text{SO}_4^{2-}$ and to non-ionic organic compounds of molecular weight greater than 300 Dalton, whilst allowing monovalent ions to pass through. There is very little published information at present but, in principle, nanofiltration could be a promising technique for separating multivalent radionuclide ions from inactive salts such as sodium nitrate.

5.5. SOLVENT EXTRACTION

Since large volumes of both organic and aqueous secondary wastes will be generated by any solvent conventional extraction treatment of LLW, a preliminary concentration stage will be necessary. The possibilities of liquid membranes in this field must be examined with special attention to kinetics studies.

The decontamination of evaporator concentrates by solvent extraction is a promising process but much more research is required to find good extractants and to industrialize, if possible, the use of liquid membrane techniques which reduce the volume of organic solvents necessary. Special developments are needed to solve the problem of membrane stability and to increase the kinetics of extraction.

A wide range of macrocyclic extractants have to be considered at the laboratory scale to evaluate their possibilities for separation of long lived alpha and beta emitters because their selective properties for some radioemitters are quite promising.

Fundamental research under progress in the solvent extraction field for partitioning of plutonium and other actinides is also promising in reducing the volume and radioactivity of reprocessing wastes. These studies need to continue, especially with respect to the minimization of secondary waste volumes generated.

5.6. BIOTECHNOLOGICAL PROCESSES

From the work performed to date relating to bioprocessing of nuclear waste and the existing applications of successful bioprocesses in other industries, there is a potential for the use of biological techniques in nuclear liquid waste treatment. In the future, bioprocesses can be envisaged to aid in separation, concentration, removal of toxic organics and conversion of organic degradable solid wastes. Although bioprocessing may not be an end itself, it may be a better system component for a particular step than existing techniques. One aspect that appears to have not been addressed is the stability or compatibility of biomass in the storage process (cementation) under the influence of a radiation field. A few possible future developments are presented below.

Many biopolymers display properties which make them very attractive as candidates for use in aqueous nuclear waste treatment. Many carry some degree of
charge, and in some cases the charge density is high. In addition, most biopolymers carry functional groups which have potential for co-ordination. The virtually infinite range of biopolymers found in nature displays a complete range of solubilities. Whole, unpurified biopolymers are insoluble and resemble conventional ion exchange resin systems. In addition, many biopolymers are highly hydrophilic and permeable which would permit the use of insoluble unpurified biopolymers in columns or fluidized beds or as an additive which can be removed by filtration or centrifugation in the treatment of aqueous nuclear waste.

Various microbial and other polymers, whole microorganisms and enzyme systems, having the capacity for radionuclide sorption or aiding such sorption via augmentation of other metal accumulation processes or able to degrade some organics, could be modified to provide improved performance by genetic and protein engineering techniques. Since the biomass would be killed by heat and/or chemical treatment before use, genetic modification would pose no threat with respect to 'release' of modified genetic material to the environment.

In the area of organic degradation, the main need is to take existing isolates or mixed populations and tailor a process to fit a specific nuclear waste. In some bioprocesses, the capital costs and the safety related areas are reduced in comparison with chemical and physical techniques. A main issue here is to achieve satisfactory, engineered systems and to adapt ancillary systems for handling the aqueous liquid effluents, minimizing the liquid volumes and concentrating the biomass and radio-nuclides, if needed, before storage. The advantage of biological treatment is that it removes toxic organic compounds or organic compounds that might interfere with long term storage.

5.7. ELECTROCHEMICAL PROCESSES

Despite substantial research and development for over a decade, electrochemical processes are still premature to be extensively applied to nuclear industry. However, judging from the successful application of electrochemical processes among a wide scope of non-nuclear industries, at the present there is no reason to deny their nuclear application provided the necessary development work is continued.

Since any sophisticated application of technology may encounter more complex problems, a combination of high performance, electrochemically induced liquid-solid separation processes with chemical precipitation and/or solid absorber processes might be an immediate application to the current needs of nuclear industries.

Figure 33 shows an example of an engineering flow diagram for optimized application of electrochemical processes in which direct membrane cleaning, filtration and electro-osmotic dewatering have been combined with sodium diuranate
FIG. 33. An example of electrochemical processes for low level liquid waste.
precipitation, electrochemical RuO$_2$ precipitation and seeded microfiltration to remove radioactivity from a hypothetical low level liquid waste stream from a spent fuel reprocessing plant, so as to discharge liquid effluent containing only NaNO$_3$.

The ultimate role of electrochemical processes will be not only to remove radioactive material from non-active material, but also providing procedures to decompose material to its component chemicals, as well as to recover and reuse the chemicals. In order to perform this role, more extensive and intensive uses of the reaction at electrodes and membranes are required. Thus, substantial development is needed to procure high performance functional materials to accommodate various electrochemical reactions.

Disadvantages of electrochemical processes are always associated with co-existent impurities in any waste streams, which may cause fouling and/or deposition on both membranes and electrodes. Thus, in order to take advantage of every aspect of electrochemical processes, it is necessary to tailor the process to a particular waste stream.

5.8. TREATMENT OF ORGANIC WASTES

Processes are now being established for the treatment of spent TBP/OK. Future work is likely to concentrate on dissolved organic materials such as spent decontamination liquors which will contain relatively low concentrations of complexing agents such as citric acid and EDTA. Another area for future work will be bulk organic liquids such as lubricating oils and scintillation liquids.

Oxidation processes of some form appear to be the most promising, with much interest centred on photo-oxidation and chemical oxidation with hydrogen peroxide and ozone, particularly by enhancing the efficiency of such processes by employing a mixture of photo and chemical oxidation, with enhancement by metal catalyst and possibly electrical means.

There is also some interest in high temperature and high pressure oxidation processes such as supercritical water oxidation; however, the high costs and possible safety problems mean that such processes will probably only be used if the atmospheric pressure and relatively low temperature processes described above are not found to be suitable.

6. CONCLUSIONS

In this report the principal methods under research and development for the treatment of low and intermediate level liquid wastes have been described.
For each method, the current state of the art and the potential use have been indicated. Some indications have been given on the necessary research work still needed.

Good decontamination factors and large volume reduction have been the main criteria according to which a particular process has been assessed. Other criteria, however, for example, operational feasibility, costs, minimization of secondary wastes and total policy for waste management, have also to be considered.

The present techniques for treatment of liquid wastes are based on industrial processes and have been able, up to now, to satisfy the international and national requirements. However, the ALARA principle defines objectives more and more ambitious for the efficiency of liquid waste treatments. It seems evident that these new goals cannot be achieved without bringing into question the principles of existing processes even if modifications to plant and equipment design can provide considerable improvement.

The newer processes described in this report illustrate the extent of research and development in progress. These processes are, of course, at different stages of maturity. Some of them appear to be very promising. Such new processes can be considered either as alternatives to existing techniques or as additions to improve the efficiency of current facilities.

It seems to be obvious that some of these new processes will become routine operations in the near future.
REFERENCES


[63] BINGHAM, C.E., Operating Performance of the New Waste Calcining Facility (NWCF), Cong. 870822, New York, American Institute of Chemical Engineers (1987).


DOZOL, J.F., CASAS, I., GARCIA, J., SASTRE, A.M., "Application of crown ethers to caesium and strontium removal from Marcoule reprocessing concentrate",


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