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Handling and treatment of radioactive aqueous wastes

Technical manual for the management of low and intermediate level wastes generated at small nuclear research centres and by radioisotope users in medicine, research and industry



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FOREWORD

The International Atomic Energy Agency (IAEA) has published Technical Reports Series and Safety Series documents on radioactive waste management over nearly three decades. These documents have served Member States presenting basic reference material and comprehensive surveys of the 'state-of-the-art' technologies applied to radioactive waste management.

The need for assistance in specific waste management problems facing many countries has been demonstrated in IAEA activities including technical assistance projects and Waste Management Advisory Programme (WAMAP) missions. Technical Reports Series and Safety Series documents usually reflect:

- technological solutions based on experience and resources normally available in countries managing nuclear fuel cycle wastes;
- volumes and activities of radioactive wastes of orders of magnitude greater than those generated in countries without nuclear power.

A new series of technical documents is being undertaken especially to fully meet the needs of Member States for straightforward and low cost solutions to waste management problems. These documents will:

- give guidance on making maximum practicable use of indigenous resources;
- provide step-by-step procedures for effective application of technology;
- recommend technological procedures which can be integrated into an overall national waste management programme.

The series entitled 'Technical Manuals for the Management of Low and Intermediate Level Wastes Generated at Small Nuclear Research Centres and by Radioisotope Users in Medicine, Research and Industry' will serve as reference material to experts on technical assistance missions and provide 'direct know-how' for technical staff in Member States. Currently, the following manuals have been identified:

- Minimization and Segregation of Radioactive Wastes
- Storage of Radioactive Wastes
- Handling, Conditioning and Disposal of Spent Sealed Sources
- Handling and Treatment of Radioactive Aqueous Wastes
- Treatment and Conditioning of Radioactive Solid Wastes
- Treatment and Conditioning of Carcasses and Biological Material
- Treatment and Conditioning of Radioactive Organic Liquids

- Treatment and Conditioning of Spent Ion Exchange Resins from Research Reactors, Precipitation Sludges and Other Radioactive Concentrates
- Design of a Centralized Waste Processing and Storage Facility.

The order of preparation of the manuals is based on priority needs of Member States and it is recognized that additional areas of technical need may be identified as this programme is implemented. In this regard the programme is flexible, should other manuals or modifications prove necessary.

The objective of this manual is to provide essential guidance to Member States without a nuclear power programme on selection, design and operation of cost-effective treatment and conditioning processes for radioactive aqueous liquids arising as effluents from institutions or small research centres.

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EDITORIAL NOTE

In preparing this material for the press, staff of the International Atomic Energy Agency have mounted and paginated the original manuscripts and given some attention to presentation.

The views expressed do not necessarily reflect those of the governments of the Member States or organizations under whose auspices the manuscripts were produced.

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1.1. Objectives

This report aims to provide essential guidance to developing Member States without a nuclear power programme regarding selection, design and operation of cost effective treatment processes for radioactive aqueous liquids arising as effluents from institutions or small research centres.

1.2. Background

The application of radionuclides in research institutions, hospitals and industries generates a range of aqueous waste streams needing treatment to reduce the quantities of radioactive contaminants to levels which allow safe discharge according to international conventions and national regulations. With short lived radionuclides, storage to allow the radioactivity to decay may be all that is required but with longer lived nuclides, processes will be needed which separate and concentrate the radioactivity from the aqueous phase.

The restricted quantities and low activity associated with the relevant wastes will generally permit contact-handling and avoid the need for shielding requirements. Exceptionally a small quantity of wastes from some radioisotope production cells and from reactor cooling water treatment may contain sufficient short lived activity from activated corrosion products to require some separate decay storage before contact-handling is suitable.

The selection of liquid waste treatment involves a set of decisions related to a number of factors. These can be grouped into five main categories:

- Characterization of arisings with the possibility of segregation;
- Discharge requirements for decontaminated liquors, both radioactive and non-radioactive;
- Available technologies and costs;
- Conditioning of the concentrates resulting from the treatment;
- Storage and disposal of the conditioned concentrates.

A technical manual entitled "Design of a Centralized Waste Processing and Storage Facility" (WPSF) is in preparation to cover the needs of developing countries [1]. As such, the design will be effectively limited to carefully chosen well-established and economic processes. In the area of liquid waste management, precipitation or flocculation processes will be the preferred option for the treatment of radioactive effluents.

1.3. Scope

The report will serve as a technical manual providing reference material and direct step-by-step know-how to staff in radioisotope user establishments and research centres in the developing Member States without nuclear power generation. Therefore emphasis is limited to the simpler treatment facilities, which will be included with only the robust, wellestablished waste management processes carefully chosen as appropriate to developing countries. An attempt has been made to provide detailed relevant data on existing experience. The specific composition of the waste stream, the subsequent efficiency of the processes, site-specific considerations (including the ability to segregate waste streams) and the availability of technology, however, must be taken into account when preferring a particular treatment system. It has been assumed in the document that sampling and analytical equipment is available at any point of effluent discharge to ensure that the levels of radioactive and toxic materials meet regulatory requirements.

2. WASTE ARISINGS AND CHARACTERISTICS

2.1. Specific activity of wastes

Radioactive liquid wastes are generated in all stages of nuclear reactor operations. They are also generated in other operations involving the application of radioisotopes (e.g. non-destructive testing, medicine, and research). The type of liquid waste produced depends upon the particular operation being conducted. The liquid wastes vary extensively in both chemical and radionuclide content. Most operations, particularly the larger ones, will also produce a variety of radioactive liquid wastes from activities such as showers, laundries, analytical laboratories, and decontamination services. The specific activity of the waste generated will depend upon the use of the radioactive materials. Users who produce the waste should be trained to provide segregation of wastes to keep the volumes of the high specific activity wastes as small as possible.

The various types of radioactive liquid wastes are normally classified according to specific activity. The specific activities defining the levels are often different in various countries.

The IAEA classification system [2], based upon specific activity, is shown in Table I. The treatment of liquid wastes of one category will normally result in two streams of other waste categories - a nearly equal volume of liquid waste of a lower specific activity and a much smaller volume of another category of waste (e.g. a solid from a precipitation process).

The composition of radioactive aqueous wastes covers a very wide range both with regard to activities and the presence of alpha-emitting and beta/gamma-emitting nuclides. Some streams will contain both. Many streams will contain specific groups of nuclides, other one or two. For streams containing mainly short lived beta/gamma activity, the effluents should be kept in storage. After decay to a specific activity within Category 1, they can generally be safely discharged to the environment.

2.2. Chemical nature of aqueous wastes

While specific activity and radiological safety are emphasized and are reasons that these wastes are regulated, it is the chemical and in some cases the biological characteristics of these wastes that can create problems in proper management. Failure to control the chemical nature of the aqueous wastes may result in inadequate decontamination and could even damage the waste processing facilities.

The treatment process selected can be based on conventional chemical treatment principles, but the individual sources of the waste and the following characteristics of each must be considered.

Category		Activity (m ⁻³) mixed β/γ emitters ^a	Remarks
	1	< 37 kBq	No treatment required; released after measuring ^b
Low level waste (LLW)	2	37 kBq to 37 MBq	Treated, no shielding required
	3	37 MBq to 3.7 GBq	Treated, shielding sometimes required according to radionuclide composition
Intermediate level waste (ILW)	4	3.7 GBq to 370 TBq	Treated, shielding necessary in all cases

^a Concentration of alpha activity is negligible.

^b Related to the release rates, licensed by the respective competent authority

2.2.1. pH value

The pH value is important in impacting on collection, storage and treatment facilities. Corrosion resistance limitations may necessitate neutralization of some waste streams and may result in precipitation of insoluble solids. Mixing of certain waste streams without adequate pH * control could release toxic or radioactive gases notably radioiodine or hydrogen cyanide.

2.2.2. Zeta potential

The Zeta potential is important in chemical treatment, where it is used to determine optimum coagulation and flocculation dosages. It is a measurement of the electro-kinetic charge surrounding solid particles suspended in the waste which must be neutralized before flocculation can occur.

2.2.3. Oxygen demand

The chemical oxygen demand of a liquid is the amount of oxygen necessary for the complete oxidation of all the inorganic and organic material in solution. This has to be satisfied before any chemical treatment involving coagulants etc. is carried out; thus it is sometimes an important consideration in chemical treatment methods.

2.2.4. Toxicity

Toxicity is the ability to cause harmful effects by a poisonous substance through physical contact with the human body by ingestion or inhalation. Therefore, the toxicity of a waste is of significance, since the safety of waste treatment personnel is of paramount importance. The presence of toxic organic compounds must be known, whatever the toxicity level. If the toxicity is high, a special treatment of the wastes must always be performed, preferably before being treated for radioactive decontamination. For compounds of lower toxicity, decontamination and/or dilution with other effluents may be sufficient to eliminate the potential hazard. Special precautionary measures have to be taken when dealing with cancer-causing labelled organic compounds. If the wastes are to be eventually discharged into sewers or waterways it may be necessary to meet requirements for chemical effluents.

2.2.5. Reactivity

The indiscriminate mixing of aqueous wastes from various sources can sometimes lead to undesirable chemical reactions. Examples include the release of toxic gases or radioactive iodine volatilization during changing redox or acidity conditions, and the production of gases and/or heat in a reaction to produce sufficient pressures to rupture containers. The presence of detergents and complexants is a decisive factor in selecting a treatment method. Some aqueous wastes could contain appreciable amounts of soluble (miscible) organic solvents (e.g. alcohol) which could also affect the decontamination process and create a fire.

2.2.6. Form of the impurities

The concentration of chemicals dissolved in the aqueous waste and the amount of suspended matter have a considerable influence on the performance of a decontamination process and in some cases, pretreatment is necessary before the main treatment can be applied. For example, filtration may be necessary to remove suspended solids before applying ion exchange processes or evaporation. Effluents containing corrosive, scale forming or foaming materials may have to be treated prior to evaporation.

2.3. Special considerations for aqueous wastes

Low level aqueous wastes may appear to be most straightforward to manage, as much knowledge exists on normal water purification processes and much of this can be applied to radioactive wastes. However, there are potentially some additional problems when using these water treatment processes to meet the specialized requirements of radioactive waste management.

The most obvious problem is the potential for the uncontrolled release of liquids with the creation of extensive contamination and therefore every effort must be made to avoid leaks, spills, or other unplanned releases. The integrity of containers is especially important when aqueous wastes are to be stored for decay. The management of corrosive aqueous wastes requires that the collection, storage, and treatment facilities withstand prolonged exposure to these wastes or the solutions must be conditioned directly without treatment.

Decontamination operations of research reactor systems or other nuclear installations very often are performed with chemicals. The classical chemical method is the APAC [3] (alkaline permanganate + ammonium citrate) which, together with its modifications, is a two-step method. The wastes produced are problematic to handle because of high concentrations of chemicals which, in many cases, cause difficulties in the treatment or solidification processes of the wastes. To avoid this problem, modern methods have been developed where a very low concentration of chemicals is used. The solution used contains citric acid, oxalic acid and EDTA. These complexing agents will have an adverse effect on the decontamination factors achieved by most chemical precipitation processes.

2.4. Characteristics of the waste arisings and sources

Many types of radioactive waste are generated through the use of radionuclides in research, medical, industrial and other institutional activities. Member States were classified as to the type and quantity of radioactive waste produced on the basis of the types of facilities and uses [4]:

•	Group A -	Member States which utilize radioisotopes at a few
		hospital locations with the waste containing only
		short lived radioisotopes. Only one institute
		utilizes long lived radioisotopes.
٠	Group B -	Member States which have multi-use of radioisotopes
		hospitals and other institutional areas and need a

- Group C Member States which have multi-use of radioisotopes and a nuclear research centre which is capable of
 - indigenous production of several radioisotopes.

The total estimated annual arisings are given in Table II [5]. In all cases the aqueous wastes account for an appreciable fraction of the waste volume. While grouping facilities and applications together has some value, for individuals responsible for the development and implementation of a systematic waste management approach it is also useful to consider the differences in the specific sources. Each type of application of radioactive materials is likely to result in aqueous wastes that have certain characteristics in terms of radioactive isotopes present and their chemical nature. The arisings from different types of applications are described in a qualitative way in Table III. It is important to recognize that those individuals responsible for the use of the radioactive materials (and hence the generation of the wastes) differ in terms of their training, understanding, and attitudes with regard to waste management. The following outlines the typical problems represented by each type of use or facility.

2.4.1. Nuclear research centres

In small nuclear research centres a number of radioisotopes are produced in research reactors or in particle accelerators. The desired isotopes are subsequently extracted or processed in nearby hot cells or laboratories. Most of the radioactive wastes, solid and liquid, are contaminated with short lived radioisotopes and should be managed to provide for decay, dilution and subsequent discharge. Wastes containing long lived fission products including transuranic nuclides, are not usually generated in the laboratories of small nuclear research centres in developing countries. Only a small part of the radioactive waste is contaminated with long lived radioisotopes e.g., ¹⁴C and ³H from limited laboratory experiments or uranium and thorium from processing investigations in laboratory and pilot plant scale. The volume of liquid and solid radioactive wastes produced by the individual users of radioactive materials is not likely to be large.

The aqueous wastes generated by the operation of a low power research reactor are usually treated by decay storage or ion exchange and then discharged to the environment. The spent ion exchange resins are low level solid wastes, unless they are regenerated, in which case a liquid waste

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TABLE II ANNUALLY ESTIMATED UNTREATED LIQUID RADIOACTIVE WASTE VOLUMES AND ACTIVITIES GENERATED IN COUNTRIES BELONGING TO GROUPS A, B, AND C [5]

Waste Volumes		L	iquid Effl	uents for	<u>, , , , , , , , , , , , , , , , , , , </u>	
	Decay, D Discharg		Treatm	ent	Direct C	onditioning
Categories	m ³ /a	Ci/a	m ³ /a	Ci/a	m ³ /a	Ci/a
Group A	5-10	1	_	-	-	-
Group B	10-50	5	1–5	0.1	0.1	0.01
Group C	100-400	10-50	100-200	510	0.5	0.1

	Source	Typical Isotopes	Chemical Characteristics	Recommended Disposal Method
1.	Nuclear Research Centres	(see Table V) Variable with long lived Fe-59,Co-60 Cs-137 etc. mixed with short lived Na-24 etc.	Generally uniform batches with nearly neutral pH from regeneration of ion exchange resins	Storage for decay and if necessary treat by precipitation
2.	Laboratories producing radioisotopes	Wide variety depending upon production and purity of targets	 a) Small volumes of high specific activity and high chemical concentrations b) Larger volumes of low specific activity 	Segregate a) and b) Store a) in hot cells for interim decay then remove for further storage and/o treatment along with Type b)
3.	Radiolabelling and radio- pharmaceuticals	C-14, H-3, P-32, S-35, I-125 (see Table IV)	Small volumes of variable but predictable chemical composition	Decay in storage, isolate low specific activity for disposal Treat or solidify hig specific activity ¹⁴ C wastes
4.	Medical diagnoses and treatment	Tc-99m, I-131, Sr-85 (see Table IV)	 a) Large volumes of urine from patients b) Small volumes from preparation and treatment 	a) Direct release to sanitary wasteb) Collection, decay and release
5.	Scientific research	Variable (see Table IV) with much C-14, H-3 I-125	Extremely variable	Researcher should segregate wastes by chemical classes, specific activity and radionuclide. Individual containers taken to central facility for direct release or storage for decay prior to release. Little requires treatment, but must be separated
6.	Industrial and pilot plants	Depends upon applications	Volumes could be large and chemical composition undefined	Storage for decay and release. U and Th may require processing .
7.	Laundry and decontamination	Wide variety likely	Volumes large with low specific activity but containing complexing agents	Storage for decay. If treatment is required chemical pretreatment may be necessary.

Table III. LIQUID WASTE CHARACTERISTICS BY SOURCE AND APPLICATION

with concentrated radioactivity is produced. The other aqueous waste arisings could be from sumps and decontamination activities. As noted later, efforts should be made to isolate the aqueous decontamination wastes.

Cyclotrons can in general be built more cheaply than research reactors and have the advantage of not requiring a supply of nuclear fuel to produce a large number of radioisotopes by bombarding targets with atomic particles (mainly protons and electrons). For example, 57_{CO} , 67_{Ga} , 111_{In} , 20_{3}_{Hg} , 201_{T1} and 20_{3}_{Pb} are commonly produced by cyclotrons. Aqueous wastes are likely to be generated only by the processing and decontamination activities.

2.4.2. Laboratories producing radioisotopes

The radioisotopes produced in cyclotrons and research reactors are produced on targets and in capsules, respectively. Liquid radioactive wastes result from chemical processing, mainly the etching and dissolving of target materials. These wastes, although small in volume, are quite radioactive because of trace quantities of unwanted radioisotopic contaminants. It is therefore prudent to have storage capacity in the hot cell for waste from several targets and capsules. More than 50% of the wastes will be aqueous and should be stored in leakproof containers to allow for decay of the short half-life radionuclides.

Wastes containing incompatible chemicals should not be combined for storage. Depending upon the chemical processes used, the aqueous wastes may contain substantial concentrations of chemicals (e.g. acids) and can be very reactive. Less radioactive and less chemically contaminated wastes (e.g. from rinses and radiochemical analysis) should be stored separately to keep the volumes of the more difficult wastes (requiring storage and/or chemical treatment) to a minimum.

A special type of reactor-produced aqueous waste arises from radiochemical neutron activation analysis. These wastes can be extremely variable in chemical contamination and level of activity and often contain high concentrations of chemicals which can cause problems during storage or upon mixing (e.g. high acid or peroxide concentrations from dissolving irradiated samples prior to radiochemical separations).

In general, the personnel involved at a nuclear research centre appreciate the concerns for proper waste management, as they are familiar with all regulations regarding work in nuclear facilities. Nevertheless an effort should be made to educate the staff about the problems of waste disposal and the limitations of the facilities available. By being knowledgeable they are more likely to examine the consequences of the wastes (including the chemical nature of the aqueous wastes) which will result from new procedures and/or experiments.

2.4.3. Radiolabelling and radiopharmaceuticals

Table IV [6] details most of the radionuclides currently in use in medicine, research and industry. In many cases the isotopes are imported rather than being produced on site. The isotopes are incorporated into the desired molecules by chemical methods producing wastes which are variable in chemical composition. A significant fraction of the radioactivity employed should be expected in these wastes from the radiolabelling processes. Since these wastes may have relatively high specific activity they should generally be kept separated from lower activity wash solutions etc. The chemical composition will be variable (depending on the nature of the labelling process) but predictable. By using minimal quantities of radioactive materials in preplanned operations, well-prepared experiments and suitable segregation and monitoring, it should be possible for radiochemical laboratories to manage the wastes produced. Those responsible for the labelling laboratory should examine the options to achieve a specific objective, study the waste management implications of a chosen option and reconcile their intentions with site practices. Plans should be reviewed by a radioactive-materials co-ordinator responsible for the purchase and use of radioactive material and their subsequent disposal. Plans should be made to isolate and store short lived materials and maintain low volumes for high specific activity wastes containing carbon-14, tritium, or other long lived radionuclides.

Education of the individuals responsible for radiolabelling laboratories is critical. They are familiar with the chemical processes but may be less concerned about the care which must be taken with radioisotopes. This is especially true for those using carbon-14 and tritium where the radiological danger is perceived to be low and monitoring is difficult. To make those involved in the production of radiopharmaceuticals more aware of radiation safety and waste management, they should be given specific training. Attention should be given to the implications of the direct disposal to a sewer of a radioactive waste and the alternative of collecting and storing.

Special attention should be paid to any iodination process or wastes from this process. Iodine can easily be released during chemical procedures, the treatment of the waste, or during storage of the waste. The environmental release level for iodine radionuclides is extremely low because it concentrates so specifically in the thyroid. Workers using large amounts for labelling or those handling the wastes should be included in a bioassay programme.

2.4.4. Medical diagnostic procedures and treatment

In hospitals, the liquid waste arisings will depend on the kind of radiotherapeutic and diagnostic nuclear medicine techniques that are applied. Most of the radioisotopes used are very short lived and in most cases, the only waste treatment that is performed is the storage of the liquids for decay before they can be released to the environment.

The radionuclides in use for imaging work are dominated by technetium-99m, which is normally eluted in a sterile environment from a generator containing molybdenum-99.

The wastes arising from the preparation of technetium-labelled agents are potentially contaminated, but the contaminant decays rapidly. The half-life can be used for record or assessment purposes but there is rarely any justification for not allowing the immediate discharge of all such wastes into a drainage system, whether the patient is in hospital or at home. Although technetium-99m decays to the radionuclide technetium-99, the relative activity of the daughter is less than 10^{-8} that of the technetium-99m. The parent column containing molybdenum-99 can be treated as inactive after three to four weeks.

Other columns commercially available for radiopharmaceutical preparation are tin-113/indium-113m, tellurium-132/iodine-132. Other radionuclides used in scintigraphy include gallium-67, selenium-75, iodine-131, strontium-85, xenon-133, mercury-197 and mercury-203.

Radio- nuclide	Half-life	Principal application	Typical quantity per application	Waste characteristics
H-3	12.26 a	Clinical measurements Biological research Labelling on site		Solid, liquid Organic solvents
C-14	5960 a	Biological research Labelling	< 1 GBq Up to 10 MBq	Solid, liquid Solvent, exhaled ^{CO} 2
Na-22	2.6 a	Clinical measurements	Up to 50 kBq	Liquid effluents
Na-24	15 h	Clinical measurements	Up to 5 GBq	Liquid effluents
P-32	14.3 d	Clinical therapy Biological research	Up to 200 MBq Up to 50 MBq	Solid, liquid effluents
S–35	87.4 d	Clinical measurements Biological research	Up to 5 GBq	Solid, liquid effluents
C1-36	3.10 x 10 ⁵ a	Biological research	Up to 5 MBq	
Ca-45 Ca-47	164 d 4.5 d	Biological research Clinical measurements	Up to 100 MBq Up to 1 GBq	Mainly solid some liquid
Cr-51	27.7 d	Clinical measurements Biological research	Up to 5 MBq Up to 100 kBc	Mainly liquid effluents
Co-57	271.7 d	Clinical measurements and	Up to 50 kBq	Solid and liquid effluents
Co-58	70.8 đ	Biological research		
Fe-59	44.6 d	Clinical measurements Biological research	Up to 50 MBq	Mainly liquid effluents
Ga-67	78.26 h	Clinical measurements	Up to 200 MBg	Liquid effluents
Se-75	119.8 d	Clinical measurements	Up to 50 MBq	Mainly liquid

TABLE IV. PRINCIPAL RADIONUCLIDES USED IN MEDICINE, CLINICAL MEASUREMENTS AND BIOLOGICAL RESEARCH

Radio- nuclide	Half-life	Principal application		nt	al ity per cation	Waste characteristics
Sr-8 5	64.8 d	Clinical measurements Biological research	Up	to	50 MBq	Solid, liquid
Y-90	64.1 h	Clinical measurements Biological research	Up	to	1 MBq	Solid, liquid
Tc-99m	6.02 h	Clinical measurements Biological research	Up	to	500 MBq	Solid, liquid
In-111	2.8 d	Clinical measurements Biological research	Up	to	500 MBq	Solid, liquid
I-125	60 d	Clinical measurements Biological research				Solid, liquid Occasionally vapour
I–131	8.04 d	Clinical measurements Clinical therapy Biological research	Up	to	500 MBq 10 GBq 50 MBq	"
Xe-133	5.25 d	Clinical measurements	Up	to	200 MBq	;
Au-198	2.7 d	Clinical therapy	Up	to	10 GBq	Not significant
Hg-197 Hg-203	64.4 h 46.6 d	Clinical measurements	Up	to	50 MBq	Solid, liquid
T1-201	3 d	Clinical measurements	Up	to	200 MBq	Solid, liquid effluents

The most significant aspect to recognize about those persons involved with the medical use of radioisotopes is that their priorities do not include radioactive waste management. As physicians or technicians their concerns focus on patient care, sterility, and the speed with which patients can be diagnosed and/or treated. From a radiation protection point of view, contamination and misadministration are more important issues than waste management. However, since the wastes can be managed so well by decay in storage prior to environmental release, the procedures should be easy to implement as long as technicians are given appropriate training and procedures.

2.4.5. Scientific research

Users of radioactive materials in research establishments and universities are most commonly involved in monitoring the metabolic or environmental pathways associated with a large range of compounds as diverse as drugs, pesticides, fertilizers and minerals. The range of useful radionuclides is normally fairly restricted and the activity content of the labelled compounds low. In some cases the labelling of a chemical compound may involve complex synthetic procedures with low yields and the production of small volumes of waste with a relatively high concentration of radionuclides.

The volume of radioactive waste produced by each individual researcher is not likely to be large but may be quite variable in terms of its chemical nature. Both aqueous and organic liquid will be produced, and, unless an effort is made to segregate these, they will be mixed. Mixed organic/aqueous wastes create problems for disposal (whether the phases are separable or not). For example, if the wastes must be treated (e.g. by precipitation) then organic solvents, buffers, and complexing agents may reduce the decontamination factor.

The radionuclides most commonly employed in biochemical research are carbon-14 and tritium, as they can be incorporated into complex molecules with considerable uniformity. Products are expensive and this frequently provides control over quantities purchased. Individual purchases are normally up to 10 MBq. The labelling of compounds with tritium can produce intermediate level effluents, but fortunately the radiotoxicity of tritium is relatively low. The chemical form should be a part of the considerations for the disposal routes. For example disposals of tritiated thymidine may be a thousand times more significant than tritiated water for equivalent radioactive concentrations. If a problem occurs over the disposal of such chemicals, a solution may be to denature them.

Since iodine-125 has proved to be very valuable in the labelling of proteins, users should be aware of the possible loss of iodine during use and waste collection. Disposal sinks, pipework and disposal containers will inevitably become slightly contaminated. Routine monitoring of surfaces and wastes must be carried out with an instrument that can detect low energy gamma rays or X-rays.

In general, there are convenient radioisotopes available for the majority of the elements of interest and these may show up as part of the research waste stream. It is very unlikely that alpha-emitting radionuclides (other than uranium and thorium compounds) and long lived hard gamma emitters such as caesium-137 and cobalt-60 will need to be used.

Studies of metabolic pathways may use laboratory animals. The animals may be sacrificed at various stages of the work, resulting in active excreta, blood, carcasses and bedding. Some of this material may become part of the aqueous waste stream creating a potential biohazard. In some cases long lived radionuclides are used to label microspheres for such studies. While these microspheres are theoretically a solid, they can easily be suspended in the liquid waste. A special and growing research and medical use of radioisotopes is the <u>in vitro</u> radioassay procedures using commercially prepared radioimmunoassay (RIA) kits. In general the waste arising from these measurements is either liquid or adsorbed onto solid. For commercially available kits iodine-125 is the main radionuclide used and each assay involves small amounts (less than 50 kBq). Kits are usually sold in packages for 10-100 assays. After the stock expiration date they must be disposed of as waste, although only those parts containing the radionuclide material need to be treated as radioactive wastes. Storage for decay is the best disposal method.

Tritium-labelled compounds are also widely available for RIA use although they are not as commonly incorporated into kits. Assay will almost inevitably involve the use of liquid scintillation counters and give rise to contaminated solvents. Some measurements are in water based or water soluble solvents. Although the tritium content should generally not cause concern, the management of vials containing organic scintillation liquids has to be carefully planned. Among other radionuclides that are used for RIA are carbon-14, cobalt-57 and selenium-75.

As in the case of medical uses, the scientific researcher has priorities that do not include radioactive waste management. While the total amount of radioactivity is generally small, the chemical nature of the wastes are extremely variable and unless efforts are made to keep records, the chemical contents will be unknown. A good educational programme is necessary to provide researchers with the rationale to plan for their wastes.

Aqueous liquid waste contaminated with significant quantities of long lived radionuclides should be transported to a central place where receiving, treatment and conditioning are performed. The quantities of liquid wastes containing high specific activities of long lived isotopes as tritium, carbon-14 etc. can be kept small by proper planning and management.

Some regulatory authorities may have particular rules about the disposal of even small quantities of carbon-14 and tritium due to their significant half-lives. However, wastes at the levels in use in research laboratories can often be effectively dispersed through conventional waste disposal routes, as any subsequent reconcentration of these radionuclides in any exposure pathway is most unlikely and the collective effective dose equivalent resulting from minor discharges is likely to be regarded by regulatory authorities as insignificant. If the regulatory authority will not allow the discharge of the effluents containing carbon-14 and tritium, it is recommended that these effluents be solidified in drums using cement. The drums can be held in interim storage until a final repository is available.

Decisions about direct discharge to the sewers must include a determination of who will release the material. If researchers are to be allowed to make determinations on release then there needs to be education, procedures and some type of oversight (e.g. monitoring, records, quality assurance). If all wastes are to be collected for monitoring and release by radiation safety personnel then researchers must have appropriate waste containers and provide adequate information on the chemical as well as radiological nature of the wastes generated.

2.4.6. Industrial and pilot plant operations

Some industrial processes incorporate radioactive materials into the product. Apart from radiopharmaceuticals, the number of premises involved

in the manufacture of products, such as sealed radioactive sources, luminous devices and specialized electronic valves is small. Certain industrial premises use particular forms of radioactive material for scientific measurements, non-destructive testing, quality control, the evaluation of plant performance, and development and evaluation of their products and processes.

Applications of radioactive tracer techniques are diverse and careful evaluation by both initiators and regulators are frequently different in magnitude from those on a laboratory scale. Particular materials incorporating radionuclides may have to be produced especially for the study, and the exact behaviour of the radioactive compounds may not be known. In all circumstances careful account must be taken of the forms in which radionuclides could be present in the products, as well as the waste streams. Assessments should include the radiological implications of the proposals as a whole.

One of the most valuable contributions of radioactive tracer techniques has been in the evaluation of wear and corrosion of key components in plant and machinery. In the majority of cases waste is produced as the radionuclide slowly wears with the component into the product or the waste stream. Storage for decay should be the primary means of disposal as volumes could be large.

Effluents contaminated mostly with long lived radioisotopes or uranium and thorium with their daughters can be generated from uranium and thorium processing in laboratory and pilot plant experiments. These will require special handling at a centralized treatment facility and planning is essential.

2.4.7. Laundry and decontamination effluents

All use of radioisotopes will result in production of marginally contaminated solid waste. In cases of equipment and facilities this contamination may be cleaned producing an aqueous waste which likely contains large amounts of complexing agents used to mobilize and solubilize the radioactive contaminant. These may end up in sumps where they are mixed with other waste material. Laundry facilities will generate large volumes of aqueous waste containing detergents. These factors are decisive in the selection of a treatment method as they will probably reduce the efficiency of any decontamination process.

Generally the volume of low-activity waste from these operations is too large to be conveniently handled by means of small containers. Thus a retention tank system may be employed. Two tanks should always be provided. When one tank is full, flow is diverted to the other, while the contents of the first are sampled and monitored for radioactivity level. It is also advisable to interconnect the tanks so that any overflow from one automatically spills over into the second. The volume of these tanks will be dictated by the waste-generation rate, time required for decay and analysis, and the rate at which the tank may be emptied, either to the sanitary drain system if permissible, or to treatment facilities.

3. WASTE MANAGEMENT STRATEGIES

3.1. Waste minimization

The first decision that must be made with regard to the management of aqueous low level radioactive wastes is whether there will by a systematic management approach using the appropriate disposal options or whether all wastes will be collected and treated by a process which is designed to be rugged enough to deal effectively with a wide range of chemical compositions, radioisotopes, and activity levels. The latter approach will mean larger volumes to treat. In addition the indiscriminate mixing of all wastes will most likely create problems since the applications and uses of materials will change with time.

Therefore Member States, especially those which have already established Nuclear Research Centres with indigenous production of radioisotopes for medical and research purposes need to have a systematic national waste management programme. A national waste management programme should consist of, but not be limited to, the following most important elements:

- education of the user and waste generator on the requirements for disposal;
- interaction with the generators to plan procedures;
- identification and documentation of waste by the generator;
- segregation and collection by activity level, half-life, and chemical nature;
- interim storage of the waste at the generator's site for decay;
- treatment (volume reduction systems) and conditioning (immobilizing) of the waste as appropriate (likely at a centralized facility);
- interim storage of conditioned wastes;
- disposal of waste in a repository.

Administrative measures should fix the rules from the very first steps of the waste management (i.e. segregation, collection and packaging for transport to buffer storage areas or directly to the treatment/conditioning facilities) and should include input from the generator. Emphasis must be placed on obtaining as much information as possible about the chemical as well as the radiological nature of the waste.

In order to facilitate subsequent handling, treatment and storage, it is strongly recommended to segregate wastes at the place of origin. It is essential to segregate inactive material from active wastes, so that the volume of active waste will be as small as possible.

It is also important to isolate low specific activity waste and those containing short half life radioisotopes from wastes that will require treatment. The chemical nature of the waste must be considered so as to avoid undesirable chemical reactions (which could result in releases and contamination) and to prevent problems during the treatment process.

3.2. Regulatory framework

3.2.1. Release to environment under authorization

Control of the disposal of radioactive wastes is normally exercised through the granting of permits, licences, or authorizations by a competent authority to the disposer. Such licences, etc. usually stipulate disposal routes for various waste forms, and the limits, in terms of specific and/or total activity, as conditions that the disposer must comply with. In granting an authorization the competent authority should consider the capability of the disposer to comply with its conditions which might include record keeping, arrangements for training, and maintaining administrative checks on disposal procedures.

Specific wastes may be exempted from the system of control described above, if, based on an analysis of the health hazards involved, the competent authority considers their inclusion in the system to be unnecessary. The competent authority shall also specify the conditions under which the exemption is authorized. This is discussed further in Section 3.2.2.

3.2.2. Release to the environment under exemption

There has long been a recognition that if every waste material that contains radionuclides had to be treated and disposed of as radioactive waste, the quantity of such materials would be large and the cost unnecessarily high. Many materials which contain small amounts of radionuclides can be shown to give rise to insignificantly small hazards. Their regulation achieves no benefit and it is usually considered to be more appropriate to segregate and exempt them from the requirements of regulatory control. Guidance has been given internationally on the principles for exemption from regulatory control [7] and also on the application of the principles to very low level radioactive waste disposal [8]. The responsibility for setting exemption levels is with the national competent authority.

Exemption is therefore an administrative procedure whereby wastes below a certain level of concentration or amount can be deregulated and treated just as if they were not radioactive. However, it has to be stressed that waste streams for consideration as exempt wastes must be shown to be below exempt concentrations. The exemption option must not be misused.

The Agency is currently developing guidance on the practical application of exemption principles to the wastes arising from the use of radionuclides in hospitals and research laboratories. In the meantime, and in the absence of specific national regulations governing exempt disposal, reference may be made to the guidance given in IAEA Safety Series No.70 [6]. The relevant parts of Safety Series No.70 relating to aqueous wastes are reproduced in the Annex.

3.3. Segregation and collection of aqueous wastes

Some of the reasons for keeping wastes segregated by the generators at the source have been stressed throughout this report. The nature of the wastes needs to be determined if unknown. At most establishments the types of waste arisings can be anticipated and a decision taken on whether storage for decay to exemption is required or direct disposal can take place. Another report in this series addresses the operational aspects of a storage facility used for decaying wastes [9]. When decay during storage is used as a part of the disposal system, waste containers need to be labelled and stored so that they are retrievable for disposal. Large tags tied securely to plastic containers have proven quite satisfactory. Besides giving the information, such as the isotope present and the date of storage, there should be a reference number that allows access to more detailed information on the chemical nature of the waste. Information on waste in storage as well as that disposed of can be kept using simple microcomputer database programes. With little effort these databases can do decay calculations and provide up-to-date information on the levels of the radionuclides present in a container.

The waste manager has several drainage systems, all arranged so that the minimum amount of effluent arising on-site requires treatment and can be segregated and that only a small proportion of the active liquors need to be diverted to the intermediate level waste treatment plant. The following system is often used.



FIG. 1. Tanker truck and pipe hanger gallery for the transport of low level liquid wastes

3.3.1. Sewage effluents

Liquids from all toilets and wash basins in non-active areas could be discharged directly to the sewage treatment works. These wastes should contain no radioactivity and may therefore be discharged after monitoring and conventional treatment.

3.3.2. Trace waste effluents (Category 1)

This water arises from laboratories and workshops where only 'trace' level solutions are used. It can also include liquids from secondary cooling systems of nuclear facilities (e.g. experimental assembly cooling and decontamination waste streams of the higher category). It normally contains virtually no activity and can be discharged well within the authorized limits. However, such effluents usually contain non-active contaminants such as suspended matter, grease or oils. After removal of the former by filtration or settlement and the latter by a grease trap and/or skimmer, the effluent can be collected, sampled and discharged without any further treatment. Concentrates produced in treatment of such liquids are usually handled as radioactive material.

3.3.3. Low level liquid wastes (Categories 2 and 3)

These wastes arise at laboratories and other areas where radioactive work is carried out, or as cleaning waters or decontaminated waste streams of the higher category. In laboratories they are normally discharged into a piping system inside the building or drained into tanks outside. When the tank is full, the liquid can be mixed, sampled and analysed and, if satisfactory, discharged to the main low level treatment plant. If the activity level is too high, the liquor can be diverted to the intermediate level treatment either by tanker or a special drain (see Figure 1).

The use of mild steel tanks lined with plastic or chemically resistant coatings or large filter glass tanks has been proven to be practical for larger facilities.

Water from cooling ponds can go by normal drainage directly to the low level treatment plant or, if considered too high, be diverted to the intermediate level plant.

The bulk of the active arisings in nearly every establishment should be in this category.

3.3.4. Intermediate level liquid wastes (Category 4)

These streams are segregated in a variety of ways. They can be collected at source in small containers (See Figure 2) and transported to the intermediate level waste treatment plant, especially in research establishments, or even have their own separate drainage system. Intermediate level liquors usually have their own special treatment facilities.

Although this system of classifying liquid waste arisings into a few broad classes appropriate to the existing facilities at the central treatment plant has been successfully applied for many years at many places and will probably continue, the separation of more specific streams, for which special treatments are and will be devised, has to increase.





FIG 2 Liquid waste collection containers

3.4. Monitoring of discharges

Before aqueous wastes are released into the environment after decay, or after treatment, representing exempt quantities (as defined by the national standards) they must be monitored to ensure compliance. Records can be used to predict activity but, since many generators are involved, the activity levels for each batch discharged should be measured. Simple β/γ activity can be monitored by appropriate survey meters. Carbon-14, tritium, and α -emitters will require sampling and measurement by liquid scintillation counting.

Chemical analysis of the effluents should at least include pH. The wastes should be nearly neutral (e.g. pH 6-9) before being put into drains, to prevent corrosion of pipes. Monitoring for metals will be necessary if there are discharge standards, and records of the chemical compositions suggest that these metals are present. Atomic absorption or ICP emission spectrophotometric analysis is most appropriate.

3.5. Considerations for a cost effective system

The sources of radioactive aqueous wastes will vary widely depending upon what programmes exist in each Member State or institution. The management that involves only collection and treatment may be the easiest system for the user and generator of the wastes. This is however the most difficult type of management system as the great variability of the aqueous wastes (in chemical content, specific activity, and radionuclides present) places nearly impossible demands on a simple general effluent treatment process. For the purposes of this report we assume that each institution and/or Member State will have a waste management system which seeks to minimize the wastes requiring treatment. It also assumes that one obtains sufficient information from the generators to avoid chemical problems during storage, conditioning, and treatment. The flow chart shown in Figure 3 summarizes the assumptions made when planning for the treatment processes described in Section 4 of this report. If managed properly from the point of generation the amounts requiring treatment should be small.

Note: Comments on aqueous waste flow chart (Figure 3):

- 1. Segregation by generators requires that they be trained and are aware of disposal processes to be used. New procedures and experiments should be evaluated to plan for the wastes and what solutions to segregate. Good records of wastes put into each container should be maintained and used to determine how wastes will be managed.
- 2. The half lives suitable for decay storage will depend upon the storage space available and the total volume of waste anticipated. Extra effort should be made to retain iodine isotopes for decay as the accepted environmental release levels are generally very low.
- 3. Generally aqueous wastes should be stored in heavy plastic containers of limited size (5 gallons)¹ or for larger operations (like a nuclear reactor centre) in tanks. Highly corrosive solutions should be neutralized with care to avoid excessive heat (from reactor) or the release of dangerous vapours (e.g. cyanide or radioiodine). When aqueous solutions contain substantial amounts of organic solvents, glass storage containers can be used. In all cases provisions should be made for periodic monitoring of the container's condition and for the collection of liquids accidently released.

¹ 1 gallon (US) = 3.785 litres.

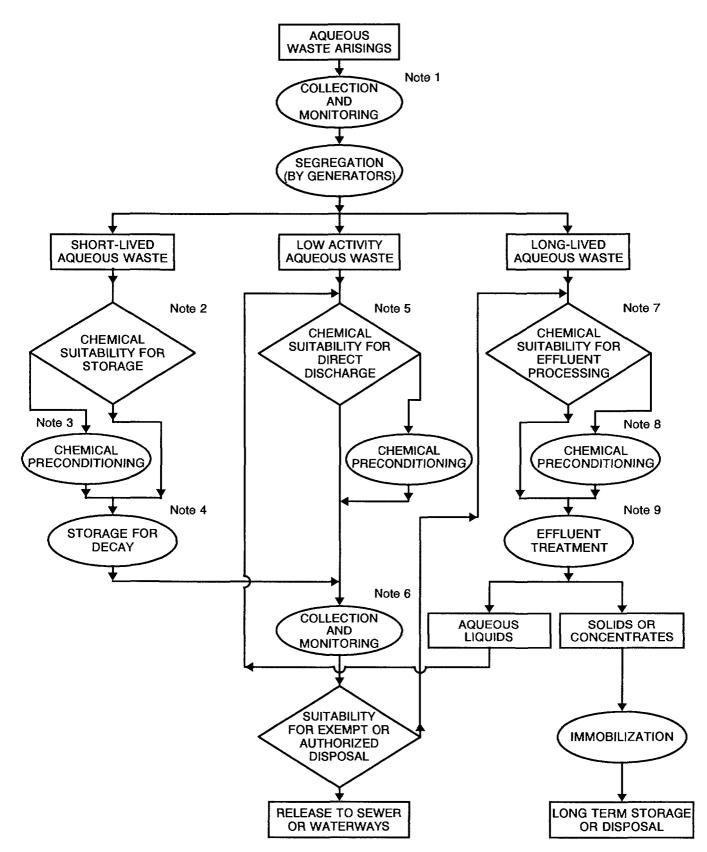


FIG. 3. Flow chart summarizing the assumptions for the treatment processes.

- 4. Containers should be carefully labelled and records kept to determine when the material is suitable for release.
- 5. Limitations will be based on national policy set for waste water discharges.
- 6. Monitoring by suitable instrumentation and records of releases provide safeguards to the entire system. All wastes that have been stored long enough for decay must be checked carefully following a specific procedure. In the case of aqueous liquids, the levels of radioactivity are calculated, and samples from each container are taken and counted. If the radioactivity is low enough, the material is checked to ensure that it is not a hazardous waste. Periodically the wastes are gathered and poured into the sewer. A special drain equipped with dilution water is desirable. The total activities and the concentrations must be recorded to ensure compliance with release requirements. If individual users are allowed to release aqueous solutions directly to the sewer system they should have a formal process of monitoring and recording these releases.
- 7. If the processing and treatment takes place at a centralized facility, transportation may be necessary. The waste containers must be suitably protected for transportation, shielded if necessary, and clearly labelled. Some type of manifest system should be used to keep track of the wastes and ensure their delivery to the central facility. So-called "overpack" drums and sorbent may be used for transportation to prevent loss of liquids in the event of an accident.
- 8. It should be recognized that some preconditioning could adversely impact the effluent treatment process. For example neutralization could add excessive ions, cause precipitation or cause the speciation of the radionuclide. These all have a significant effect upon a treatment process like ion exchange.
- 9. It is feasible to utilize batch chemical treatment where the volumes are small and where the nature of the wastes points to chemical treatment as the best method. It is suitable for application where the required reduction of activity in waste is small.

4. EFFLUENT TREATMENT PROCESSES

4.1. Process options

The selection of a liquid waste treatment system involves a set of decisions related to a number of factors [5]. These can be grouped into five main categories:

- Characterization of arisings with the possibility of segregation
- Discharge requirements for decontaminated liquors
- Available technologies and their costs
- Conditioning of the concentrates resulting from the treatment
- Storage and disposal of the conditioned concentrates.

The selection of a treatment process for liquid wastes depends to a large extent upon their radiological and physico-chemical properties and the quantity of arisings. It is therefore important to know these

Basic treatment processes	Chemical precipitation	lon exchange	Evaporation
Liquid radwaste charac- teristics	 not sensitive to highly salt-laden solutions Possible negative effects when oils, detergents and com- plexing agents are present 	 Suitable for: Low suspended solids content Low salt content Absence of non-ionic active species 	 Low detergent content required (foaming problems)
Decontami- nation factor (DF)	<10-100(β,γ), 10 ³ (α) exceptional >10 ³ (α)	$<10 \text{ to } >10^4$ average 10^2 to 10^3	10 ⁴ -10 ⁵
Volume reduction factor (VRF)	10–100 (wet sludge) 200–10 ⁴ (dried solid)	500 to 10 ⁴	Depends on the salt content in the solution
Conventional combination with other	Possible with evapora- tion and ultrafiltration	Possible with evaporation	Condensate can be subsequently treated by ion exchange
Process drawbacks	Volume of flocs may be important. Dewatering system needed for sludges	 Limited radiation stability Limited heat resistance 	Sensitive to scaling, foaming, salt precipitation and corrosion
Application types	 Concentration of active species 	 Demineralization of effluent when salt content <1 g/L Separation of active species 	 Concentration of the solution (active and non- active species)
Scope of the application	 Utility liquid wastes from nuclear power plants LL and IL streams in reprocessing operations Nuclear Research Centres' liquid wastes 	 Maintenance of pond water quality Water conditioning in reactor circuits Various treatments in reprocessing operations Post-treatment for all other operations 	 Primary coolant cleanup Utility liquid wastes from nuclear power plants Various uses in reprocessing operations
Maintenance	Possible blockage of feed lines and corrosion	Possible blockage of ion-exchange beds	Possible foaming, scaling and salt precipitation problems, corrosion
Cost	Relatively cheap	Relatively expensive mainly for synthetic ion exchangers	Expensive (energy consuming)

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properties, not only based on the reference plant design but also with respect to the actual operational conditions in a plant.

The processes available for treatment of liquid radioactive wastes fall generally into three main categories: ion exchange, chemical precipitation, and evaporation. Other processes are being used but not extensively. Table V is a general guide showing the main features of the three basic treatment processes [2].

The decontamination factors (DFs) that can be obtained by each of these processes are generally -

evaporation $10^4 - 10^5$ ion exchange up to -10^4 precipitation 10 - 100 but can be >10³

The decontamination factor is defined as -

 $DF = \frac{\text{total activity in feed}}{\text{total activity in effluent}} = \frac{a_f v_f}{a_e v_e}$

where a_f and a_e = activity per unit volume of feed and effluent, respectively, v_f and v_e = volume of feed and effluent, respectively. The same expression can be used to calculate the DF for specific radionuclides, total alpha activity and total beta-gamma activity.

Since the DF is dimensionless, it is advisable to quote the specific activity of either the feed or the effluent since, with precipitation processes, the effluent concentration may be solubility controlled and therefore the DF will vary with the concentration in the feed.

The waste streams that are presented for treatment in the waste processing facility will have a range of compositions and may not be fully characterized with respect to chemical composition. They may contain organic compounds, oxidizing agents and suspended solids. In determining which treatment process will be best for a simple, small scale treatment plant, the following points have been taken into account:

4.1.1. Evaporation

Evaporation is a well established process, widely used in the nuclear industry. It is capable of giving high decontamination and large volume reductions and is currently being used in the treatment of high, intermediate, and low level waste effluents. On cost considerations, evaporation is a relatively expensive process and is therefore more attractive for the treatment of small volumes of highly active effluents than for the treatment of large volumes of low level wastes; although it is used for low level waste concentration at some sites with high volumes generated and contaminated with fission and corrosion products. When compared with other effluent treatment processes, the evaporation process is in principle relatively simple. Essentially it involves distillation of the solvent from a waste effluent, leaving a smaller volume of residue containing both the radionuclides and the inactive salts. In practice, evaporation gives very good decontamination for all non-volatile radionuclides (up to 10^4 in a single stage evaporator) and can result in very large volume reductions provided that the inactive salt content of the stream is relatively low.

The condensate resulting from evaporation is an almost salt-free solution of very low activity which may be subsequently 'polished' by ion exchange, before it is discharged or recycled for use in the nuclear plant. The concentrate containing the radionuclides can either be dried to produce a salt cake or be incorporated into a suitable matrix (e.g. cement) for disposal.

Evaporation processes are prone to three quite serious problems: corrosion, scaling and foaming. Most effluents treated could give rise to at least one of these problems, and it is often necessary to pretreat the feed.

All of those problems should be considered as potential limitation of the process. The performance of evaporators is strongly influenced by these factors, in terms of decontamination factor, costs and the lifetime of the facility. From these points of view, the process designer requires a good knowledge of the chemical and physical properties of the waste requiring treatment.

- Advantages and limitations of evaporation

The main advantages of evaporation are:

- (a) Large volume reduction for a range of effluents;
- (b) Good decontamination for non-volatile radionuclides (DFs of 10^4-10^5 are frequently achieved in a single stage);
- (c) It is unaffected by the presence of complexants in a waste effluent, unlike many of the alternative treatment processes.

There are several limitations to the application of evaporative processes:

- (a) They are unsuitable for waste effluents containing large concentrations of inactive salts, since the extent of volume reduction is determined by the dissolved solids content;
- (b) They are <u>expensive</u> compared to other treatment processes (e.g. 20-50 times higher than a floc process) due to their large energy requirement. Recently, the increasing cost of energy has actually led to the investigation of alternative processes to replace evaporation for the treatment of large volumes of effluents containing relatively low activity.
- (c) The problems caused by corrosion, scaling and foam formation may prevent the successful evaporation of some wastes;
- (d) The presence of some organics can result in explosions during evaporation, e.g. Tri-butyl phosphate (TBP) in nitric acid, and appropriate pretreatment is required, such as steam stripping.

For developing countries operating a small nuclear research centre and producing exclusively short lived radioisotopes, it is recommended not to use evaporation for treatment of radioactive effluents.

4.1.2. Ion exchange

The use of ion exchange procedures in chemical processing, water and waste water treatment was well developed at the time the technique was

first applied in the nuclear industry. Since then much progress has been made in improving the technology and ion exchange methods have been widely used to remove soluble radionuclides from liquid wastes.

The process involves exchange of ionic species between the liquid and solid matrix containing ionizable polar groups. When exchangers become fully loaded they are removed from service and treated as radioactive waste. Alternatively, many organic ion exchange materials may be regenerated by strong acids or bases, yielding radioactive liquid waste with a high salt content.

Ion exchange methods have extensive application in nuclear fuel cycle operations and other activities involving radioactive materials. Examples of these include the cleanup of primary and secondary coolant circuits in nuclear power plants, treatment of fuel storage pond water at nuclear power plants and reprocessing plants, cleanup of active drain water and treatment of liquid wastes arising in isotope production and research facilities.

Decontamination factors can range between perhaps 10 to 10^7 for very sophisticated systems; however, values of 10^2 to 10^3 are relatively common. Generally, the lower DFs are based on gross activity and the higher figures are nearly always for specific radionuclides for which the system has been designed.

Ion exchange procedures have been applied to the treatment of liquid wastes for many years. The technique is well established and its value has been widely demonstrated.

The application of ion exchange resins in a small nuclear research centre as a main method for decontamination of radioactive effluents is not recommended. Based on the experience gained from existing ion exchange processes and the more recent results from development studies, the application of ion exchange resins to remove activity from radioactive effluents offers a number of disadvantages.

- The resins show very low capacity for effluents with high inactive salt content (>1 g/L)
- regeneration gives rise to secondary wastes;
- non electrolytes, colloids, suspended and dissolved organics, detergents, complexing agents, cause difficulties and are the reasons to exclude ion exchange resins as a method for the decontamination of aqueous effluents generated in a small nuclear research centre.

4.1.3. Chemical precipitation

Chemical precipitation processes are well established methods for the removal of radioactivity from low and intermediate level liquid wastes and are in regular use at fuel reprocessing facilities, research establishments and, more recently, at several power stations. A wide range of different precipitates are now in use (e.g. metal hydroxides, oxalates and phosphates). Often small quantities of selected absorbers are added during a floc process to improve or provide decontamination from specific radioelements.

Chemical precipitation methods are particularly suitable for the treatment of large volumes of liquid effluents which contain relatively low concentrations of active species. They are fairly versatile and may be used to treat a wide variety of different waste streams, including those containing large amounts of particulates and high concentrations of inactive salts. The processes usually use readily available chemical reagents and are therefore relatively cheap when compared to the cost of some alternative processes, e.g. evaporation, which are 20-50 times higher.

Comparison of the three processes indicates that a chemical precipitation process will be the most suitable for waste treatment (see Table V) in developing countries for the following reasons:

- relatively low cost;
- ability to handle a large variety of radionuclides as well as non-radioactive salts in solution and solid matter in suspension;
- treatment procedures are based on well-proven, conventional plant and equipment;
- relatively easy to change the chemical precipitants, at least in batch processes, in order to accommodate changes in the composition of the liquid feed;
- large liquid flows can be handled economically;
- process allows for the separation of activity from inactive solutes which may have a larger bulk.

4.2. Chemical precipitation, detailed process considerations

4.2.1. General principles

The objective of a chemical precipitation process is to use an insoluble finely divided solid material to remove radionuclides from a liquid waste. The insoluble material or floc is generally, but not necessarily, formed in-situ in the waste stream as a result of a chemical reaction. A typical chemical precipitation method involves four main stages:

- (1) the addition of reagents and/or adjustment of pH to form the precipitate
- (2) flocculation
- (3) sedimentation
- (4) solid-liquid separation

Vigorous agitation is applied during the first stage of the process to ensure rapid mixing of added reagents and to disperse the precipitate in the waste. The length of time used for this initial mixing is a compromise: long times tend to favour increased sorption of radionuclides but can also cause the formation of collodial suspensions which cannot subsequently be flocculated.

Flocculation is usually achieved by slowly stirring the mixture, this helps the particles of precipitate to agglomerate to produce larger particles that will settle or can be removed by a separation process such as filtration. Laboratory tests using real samples of the radioactive waste to be treated are necessary to establish the correct conditions for operation. Simulated wastes or computer models may be used in initial studies but they are unlikely to include all the trace components present in the real waste which may affect the performance of the process.

The waste volume reduction and the decontamination factors achieved with a precipitation process are very dependent on the method of solid/liquid separation used. Gravitational settling is usually rather slow, so the resultant volume of floc, and hence overall decontamination factor, depends on the settling time. The physical nature of some flocs (e.g. gelatinous metal hydroxide flocs) will limit the extent to which they can settle under gravity. In these cases, secondary processes are necessary to dewater the floc and make it suitable for subsequent treatment or storage/disposal.

The decontamination achieved by a floc process will depend both on the particular precipitate, the chemistry of the radionuclide concerned and the degree of separation of the precipitate from the liquid. It may also be affected by the presence of other components of the waste stream such as complexants, trace organics or particulates. It should be noted that since a chemical precipitation process involves addition of precipitates or precipitate forming reagents, some of these may raise the level of a toxic material in the treated effluent to above the local discharge authorization. Generally, radionuclides are removed from solution by one or more of the following mechanisms.

- (a) Co-precipitation or isomorphous precipitation with the carrier, where the radionuclide precipitates under the conditions of the process and is subsequently swept out of solution by the bulk (or scavenging) precipitate, or where the radionuclide is incorporated into the crystal structure of an analogous precipitate, e.g. radiostrontium removal by barium sulphate precipitate;
- (b) Removal of radionuclides already sorbed onto particulates present in the waste effluent, which will be scavenged from solution;
- (c) Adsorption onto the floc or on added absorbers, e.g. by ion exchange, chemisorption, physical adsorption, etc.

The majority of precipitation methods use metal hydroxide flocs under neutral or alkaline conditions to remove the radionuclides. In these processes, a number of the radionuclides will be extensively hydrolysed and are likely to be either co-precipitated or sorbed onto the floc.

For some treatments it may be necessary to include a stage to remove entrained effluent from the sludge, which is particularly necessary when the effluent contains high levels of inactive salts or ions known to interfere in a subsequent immobilization process, e.g. a high ammonium ion concentration cannot be tolerated in cementation processes. At present only limited information is available about the effects of a washing process on both the floc and the adsorbed radionuclides. The ionic strength of the aqueous phase, and sometimes the pH, will change during washing, which could lead to resolubilization of radionuclides with the consequent generation of a new radioactive waste. Reduction in ionic strength of the aqueous phase associated with the floc can also lead to peptization or formation of colloids of the precipitated material which will, in turn, reduce the efficiency of the solid-liquid separation stage except possibly in the case of ultrafiltration.

4.2.2. Pretreatment

This section describes processes that may be used prior to the formation of a precipitate in order to improve the decontamination achieved by the precipitation stage. These processes may be carried out to oxidize organic contaminants, decompose complexed species or residual complexing agents, alter the valency state of elements or adjust the ionic species in solution to those with a greater affinity for the precipitate.

Some waste streams may require physical pretreatment prior to chemical treatment. Such pretreatment may include coarse filtering and oil/solvent removal. For example, floor drain wastes may contain general debris which could damage pumps, clog pipes and otherwise interfere with subsequent treatment steps.

When considering pH adjustment, oxidation or reduction processes for pretreatment of a radioactive waste stream it must be appreciated that a particular treatment may produce both desirable and undesirable effects. For example, the use of a reducing agent can often improve decontamination for a particular metal in the precipitation stage but may have an adverse effect on the removal of other radionuclides by converting them to a lower or more soluble valency state.

4.2.2.1. pH adjustment

The adjustment of solution pH can sometimes be advantageously employed in the treatment of wastes containing metal ion complexes, in order to form an undissociated acid or base. For example the precipitative removal of metals from EDTA complexes using calcium hydroxide appears in some cases to be improved by first lowering the pH to a value, e.g. 1-2, where the complex dissociates and the free ligand acid is formed, and then raising the pH to a high value such as 12 to gain maximum advantage from competitive mass action effects of OH⁻ and Ca²⁺. However, this treatment does not remove the complexing agent and so there is the possibility of further problems downstream if other waste streams are blended.

Complex formation is much more of a problem in waste treatment than is often realised. Inadequate stream segregation prior to treatment can create serious problems in plant performance. There are two ways of circumventing the problem (apart from avoiding the use of complexing agents), one is to isolate the stream for special treatment such as techniques to recover the complexing agent for re-use; the other is chemical destruction of the complexing reagent which generally involves oxidative or reductive attack.

Adjustment of the pH can be used to modify the ionic species present in the waste stream. This may influence the choice of precipitates and the operating conditions used in the treatment process.

4.2.2.2. Chemical oxidation

Chemical oxidation is used in liquid waste treatment to reduce odour, decolorize, destroying organic matter to improve precipitation and flocculation and to oxidize ions such as iron and manganese to a higher valence state and thereby improve the removal of these elements by the precipitation treatment. Common oxidants and their applications are:

Ozone is a very efficient sterilizing and oxidizing agent featuring several advantages over chlorination. In particular, it does not leave prejudicial decomposition products and allows destruction of complexing and chelating agents.

A number of organic compounds can be oxidized to carbon dioxide and water using ozone but often only partial degradation occurs. Metal-EDTA complexes appear to be more readily broken down (by an order of magnitude) than EDTA alone.

Unfortunately, most of the advantages of ozone are to some extent negated by the relatively high cost of ozone generation equipment and the inefficiencies associated with the low solubility of the gas in water.

<u>Chlorine</u> is a powerful oxidant and, like oxygen, can support combustion, thus presenting a potential fire risk. <u>Sodium hypochlorite</u> is a more acceptable form in which to store and dose chlorine.

In addition to destruction of bacteria and algae, and oxidation of many chemical compounds, the addition of chlorine or hypochlorite has a chemical action which can clarify some effluents by decolouration and deodorization through bleaching of organic matter. It is often advantageous to leave a small residual free chlorine content in the treated effluent to prevent further growth of bio-organisms.

Claims have been made in the patent literature for the alkaline oxidation of EDTA and unpublished work has shown that reaction does occur to some extent even at pH6. It was found that although EDTA or its sodium salt is susceptible to breakdown, heavy metal complexes appear to be resistant, so in order to make the process possible it is necessary to dissociate the complexes to release the EDTA. However, it appears that chlorination of EDTA at low pH values is slow and also incomplete, a pH in the region of 6 being towards optimum. Similarly, heavy metal tartrate and citrate complexes exert some chlorine demand, indicating some breakdown, but the demand is also variable with pH.

<u>Hydrogen peroxide</u> will oxidize many organic substances, particularly when there are unsaturated carbon bonds where attack can take place. The oxidation is often enhanced by the addition of a transition metal ion as catalyst. This catalytic oxidation process has been shown to oxidise EDTA present in solution as metal-EDTA but further work is necessary to optimize the process.

Hydrogen peroxide can be used to oxidise most sulphur containing compounds, nitrites and hydrazine and has the advantage of not adding to the dissolved solid concentration.

<u>Potassium permanganate</u> is a powerful oxidizing agent and will rapidly oxidize Fe^{2+} , Mn^{2+} , sulphides, and many organic substances. In the pH range commonly encountered in waste treatment (pH 3-11), MnO_2 is formed which is known to be a cation absorber.

4.2.2.3. Chemical reduction

Reduction reactions are employed in waste treatment with the objective of converting the pollutant to a solid form as in the reductive recovery of metals or through precipitation of an insoluble material.

Nuclides	Simple processes	рН	expected DF
Pu, Am	Hydroxides (especially Ferric) Oxalates	7 - 12 1	>1000
Cr	Ferrous hydroxide	≧8.5	>100
Mn	Manganese hydroxide Manganese dioxide	≧8.5	>100
Co Fe	Ferrous or ferric hydroxides	≧8.5	>100
Sr	Ferrous hydroxides Calcium or iron phosphate Calcium carbonate Manganese dioxide Barium sulphate Polyantimonic acid	7 - 13 >11 10.5 >11 ≥8.5 ~1	pH dependent >100 >100 >100 >100 >100 >100
Zr, Nb, Ce	Hydroxides (especially Ferric)	>8.5	100-1000
Sb	Ferrous hydroxides Titanium hydroxide Polyantimonic acid and Manganese dioxide Diuranate	5 - 8.5 5 - 8.5 ≃1 8.5 - 10.5	5 - 10 10 - 100 20 - 40 20 - 30
Ru	Ferrous hydroxide Copper + Ferrous hydroxides Cobalt sulphide Sodium borohydride	5 - 8.5 8.5 1 - 8.5 8.5	5 - 10 10 - 25 30 - 150 50
Cs	Ferrocyanide Zeolite Tetraphenylborate Phosphotungstic acid Ammonium phosphomolybdate	6 - 10 7 - 11 1-13 ≈ 1 0-9.5	>100 10 100-1000 >100 >10

Common reductants and their applications are:

<u>Sodium dithionite</u> $(Na_2S_2O_4)$. The potential for dithionite reduction in alkaline solution (+1.12 V) suggests that the reagent should be capable of reducing several types of metal ions to the metal. In practice, the metal when formed may be in a colloidal condition and so requires further treatment for separation. The reduction procedure can be useful when metal ions are bound with complexing agents which render normal pH adjustment for precipitation of the hydrous oxide inadequate for full treatment. In alkaline systems the rate of reduction may be slow when metal ions are complexed. Lowering the pH to dissociate the complexes may be necessary but at lower pH values the reducing power of dithionite is less, so a compromise has to be adopted.

The pertechnetate ion, TeO_4^- , is reduced to the insoluble TeO_2 by dithionite but reoxidation occurs readily and it is necessary to carry out operations in an inert atmosphere or maintain a level of reducing agent in the treated waste solution.

<u>Ferrous ion</u> is a well known reducing agent and is an intermediate reductant in terms of the more widely used reagents. It will reduce Cr(VI)to Cr(III) but in solutions with pH > 2 the ferric ion resulting from the reduction stage will precipitate and this may be an undesirable addition to the solids produced in the precipitation stage of the process.

<u>Hydrogen peroxide</u> (H_2O_2) although normally considered an oxidizing agent, is also a reducing agent. It will reduce Cr(VI) compounds providing the pH is slightly alkaline. Silver complexed with thiosulphate as in photographic fixing solutions, can be precipitated as a silver-silver oxide sludge.

4.3. Specific chemical reaction processes

In this section, the various processes which operate on the basis of a single or specific chemical reaction to form the precipitates are described.

Many of these processes have been widely used in the past for the treatment of low and intermediate level aqueous radioactive wastes. Advanced treatment processes now in use, or being developed, often combine these simple processes with other stages.

The pH of operation and the expected DFs for simple processes are summarized in Table VI.

4.3.1. General precipitation processes

A few precipitation processes are widely used; these basic treatments have shown decontamination efficiency for more than one radionuclide and can be considered as general treatments.

The most commonly used simple treatments are:

- Lime-soda process
- Phosphate precipitation
- Hydroxide processes
- Oxalate precipitation

Lime-soda process

This process removes 'hardness' from water and produces a precipitate of calcium carbonate:

 $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$

 $Ca(OH)_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaOH$

It was used in the past, primarily to remove strontium as an analogue of calcium, but has now been superseded by more efficient processes.

Phosphate precipitation

Soluble phosphates, especially tri-sodium phosphate, are added to the waste to form insoluble compounds with other ions.

$$3M^{n+} + nPO_4^{3-} \longrightarrow M_3(PO_4)_n$$

where M is Fe^{3+} , $A1^{3+}$, Ca^{2+} ... including radioactive strontium. Calcium ion is usually added as a bulk co-precipitant to enhance the removal of other cations.

The reaction is complex and some kind of hydroxyapatite is probably formed, whose structure can include strontium ions. The method also achieves good removal of metals, such as uranium, which have insoluble phosphates. In general, the higher the pH of the operation, the better the DF achieved. For strontium a DF of ≥ 100 is obtained at pH values > 11. Removal of caesium by this method is poor.

Currently barium sulphate precipitation, sometimes in combination with other precipitates, is more often used for strontium removal rather than the phosphate process.

Hydroxide processes

Many metal ions can be hydrolysed to form insoluble compounds, a number of which exhibit an affinity for sorption of other ions.

 $M^{n+} + nOH^{-} \longrightarrow M(OH)_{n}$

where M is Fe^{3+} , $A1^{3+}$, Ti^{4+} etc.

Although in conventional water treatment aluminium hydroxide precipitation is widely used, in the practice of radioactive waste management the use of ferric hydroxide precipitation is more common, partly because ferric ions may already be present in some waste stream due to plant corrosion. In general ferric hydroxide floc particles are larger and easier to settle than those of aluminium hydroxide.

Ferric hydroxide forms as a voluminous, gelatinous precipitate, which can be difficult to handle. Conventional filtration is not very effective, so gravity settling is usually favoured for the initial separation. There is also the possibility of carry-over of fine particles of floc suspended in the supernate. Generally, ferric flocs will require further dewatering prior to immobilization and the supernates often need to be polished in order to improve decontamination. The physical properties of the floc may be significantly improved by the presence of other precipitates (for example, calcium salts).

Ferric floc treatment can be affected by the presence in waste streams of other components such as carbonate ions or some complexants (e.g. EDTA and citric acid).

4.3.2. Treatment for specific nuclides

The treatments initially applied to radioactive wastes were those used to purify municipal and industrial waste water. In some cases, depending on the specific chemical and radiochemical composition of the waste, these treatments will not provide sufficient decontamination from certain nuclides and special treatments have therefore been developed, those for strontium and caesium are described as examples. Strontium is generally removed to a considerable extent by some of the general treatments described, such as precipitation of

- phosphate (calcium or iron)
- hydroxide (iron at pH between 7 and 13)
- carbonate (calcium)

A number of specific precipitation processes involving other absorbers, such as barium sulphate and hydrous oxides of manganese, titanium and antimony, have been employed when the treatment process does not involve any of these general treatments. Calcium and magnesium ions present at 'hard' water concentrations can affect strontium sorption.

The removal of strontium by in-situ precipitation of barium sulphate occurs by the isomorphous precipitation of the strontium. The removal of strontium increases when increasing the pH value of the stream; at pH 8.5 the decontamination factor is between 100 and 200.

The literature contains many reports presenting data on the sorption of strontium by inorganic sorbents such as polyantimonic acid, hydrous titanium oxide, sodium titanate and manganese dioxide. Recent investigations describe the use of finely divided precipitates of these materials either singly or in combination.

Caesium removal

A number of precipitation processes exist for the removal of caesium from aqueous waste streams:

- (i) use of transition metal ferrocyanides (Cu, Ni, Co)
- (ii) use of phosphotungstates or phosphomolybdates
- (iii) precipitation of the tetraphenylborate

Transition metal ferrocyanides are most commonly used and can be precipitated in-situ or added as a preformed slurry. Caesium adsorption appears to be effected by ion exchange. Decontamination factors higher than 100 are frequently observed. Different metal ferrocyanides provide maximum decontamination at specific pH values. The most commonly used are copper and nickel ferrocyanides which are effective over the pH range 2 to 10.5 and in the presence of high salt loadings (>5M Na⁺) but DFs decrease with increasing salt content.

At pH values greater than 11, decomposition of the transition metal ferrocyanides occurs, yielding the ferrocyanide ion and a precipitate of the transition metal hydroxide.

4.3.3. Combined processes

When the waste stream composition is variable in nature, either in radioactive or non-radioactive content, a single chemical precipitation process may be inadequate.

In order to provide good decontamination of the liquid waste a combination of the general or specific treatments previously described is frequently necessary. Often the final combined process is a compromise between the optimal conditions of each single process so that the best overall decontamination factor for specific nuclides or for total activity of the liquid waste is achieved. Combinations of the single processes described above can be used as multi-stage batch processes or as a continuous precipitation process. For example, phosphate treatment for strontium removal could follow a ferrocyanide treatment for caesium removal, the only requirement after the ferrocyanide precipitation being to raise the pH value before the next stage.

The use of these various techniques is strongly dependent on the requirements of each waste treatment site, on the local discharge authorizations for radiochemical and chemical components and on the intended solid waste treatment.

4.4. Process selection

The selection of a chemical treatment process for a liquid waste depends to a large extent upon the radiological and physico-chemical properties of the waste and the quantity of arisings.

It is therefore important to know these properties with respect to the actual operational conditions in a plant and also to the projected conditions for the near future.

The radiological properties of liquid wastes are much less restrictive in the selection of the chemical treatment process than the physico-chemical characteristics and the volume. This fact illustrates the importance of a thorough knowledge of the liquid wastes when designing a management scheme.

4.4.1. Solid/liquid separation

The precipitation process produces sludge as a result of the reactions taking place during chemical treatment steps and has always to be connected with physical methods for separation of sludges and liquids. Various possibilities include sedimentation and decantation, filtration or centrifugation. For treatments of up to 100 m³/year, the simple sedimentation and decantation technique will usually be the most suitable. Laboratory work may be required to determine optimum precipitation and separation conditions.

4.4.1.1. Sedimentation

The purpose of sedimentation is to ensure the settling by gravity of suspended solids contained in the floc and so to clear the carrying liquid as much as possible. The efficiency of this separation is the controlling element of the whole precipitation-flocculation-sedimentation process. In fact, because the radioactivity concentrates essentially within the sludge to be settled, traces of sludge swept along will have a direct effect on the decontamination obtained.

Phase separation generally uses a series of conical or sloping bottom tanks with an overflow line for decanted clear liquid and a bottom discharge for the thickened sludge. The process is generally used in a semi-continuous operation with periodic shutdowns to remove the accumulated sludge from the tank bottom.

4.4.1.2. Filtration

Filtration equipment is used to separate fine particulates that will not settle out in a "reasonable" length of time from supernatant fluid. It can also be used to pretreat influent waste to remove miscellaneous debris and to polish the supernatant liquid as a final processing step.

Various filtration methods are used:

- Natural filtration, using gravity alone in a horizontal sand filter. Dried sludge is removed manually. This method requires large filtration surfaces, well formed and low activity sludges.
- Pressure filtration. By use of a horizontal tank, vertical leaf filter, cakes are formed under 2 to 3 kg/cm² pressure and dried by a compressed air flux. This flux, when reversed, allows easy removal of the cakes.
- Alternatively vertical candle filters are used, including precoat and cake removal by compressed air. The residual humidity of the cakes is among the lowest obtained. However, one disadvantage is the risk presented by the use of pressure, which may spread contamination in case of leakage.
- Vacuum filtration is the most frequently used technique. Generally, precoat type vacuum drum filters are used. The filter assembly is compact, hence easily protected and the use of vacuum improves safety. Residual moisture content of the cakes may reach 40 to 50%.

4.4.1.3. Ultrafiltration

An ultrafiltration (UF) system is capable of handling a wide range of feeds, with solids concentrations from less than 5 mg/l up to over 10,000 mg/l, and particle sizes from much less than 1 μ to over 50 μ . An ultrafiltration plant can be operated continuously with a steady bleed-off of the concentrated liquid sludge. Very high particulate concentrations (over 30% solids) can be obtained.

4.4.1.4. Centrifugation and hydrocyclone

Centrifugation and hydrocyclone devices use centrifugal forces, often thousands of times greater than gravity. They may be effective methods for separating liquid and solid streams and can be more economic and much smaller than gravity operated settling devices.

Centrifugation appears to be applicable only to precipitates which do not show any thixotropy, therefore excluding a number of colloidal suspensions. The difficulties in using the high speed complex devices in a radioactive environment are likely to outweigh the advantages for treatment of effluents considered in this report.

The hydrocyclone is not normally suitable when:

- solids of less than 5 µm are to be removed;
- the liquid in the slurry is of high viscosity;
- there is insufficient specific gravity differential between the liquid and the solid fractions.

The centrifuge and the hydrocyclone are not likely to be necessary or suitable for the flocculation treatment processes in the context of this report.

4.4.2. Further treatment

Before release or admission to another processing phase, the treated and filtered wastes are stored in holding or "sentencing" tanks. After their characteristics have been determined by various analyses, they are, according to the case and national regulations:

- (a) directly released to the environment with or without dilution. In the case of no dilution they are brought back to a pH ranging between 6 and 9 before release;
- (b) recycled through a new type of coagulation-flocculation treatment if the previous one did not give expected results;
- (c) sent to further finishing treatment.

4.4.3. Discharge requirements for decontaminated effluents

The restrictions or limits on release of the decontaminated liquors should be carefully considered. Determination of these limits is done differently in various countries but does in all cases require extensive analyses by both the waste producer and regulating authority to arrive at an agreement that the releases are acceptable. This limit will directly govern the decontamination factor required from the process and the activity limits of the liquid waste stream being treated.

Radiological requirements are not the only parameters that have to be taken into account. In the case of chemical waste treatment, physico-chemical considerations according to the regulating limits also need to be examined. The physico-chemical composition of the effluent depends on:

- arising waste streams;
- chemical reagents added during treatment;
- efficiency of solid/liquid separation.

5. EXAMPLES OF PLANT DESIGN FOR SPECIFIC TREATMENT VOLUMES [10]

The design of a radioactive waste decontamination plant for a coagulation-flocculation process is guided by the average daily or annual volume of product submitted to treatment.

Examination of units designed in various countries leads to four classifications of plants according to the specific throughputs: first, small treatment units which are not described in the literature, because of their small capacity; they have treatment capacities lower than 500 litres/d or 100 m³/year. Then, for capacities ranging between 2 and $3 m^3/d$ we find plants in nuclear research centres that possess reactors associated with various utilizations of the radioisotopes produced. Larger plants are industrial size units. The treatment stations of many nuclear research centres can process between 25 and 100 m³/d. Only a few centres, collecting their effluents through pipelines, process over 500 m³/d in plants, the treatment methods of which are very similar to those applied for producing drinking water.

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For small plants, operations are performed to treat in one working day (daytime) the contents of a tank of sufficient capacity to supply a volume equal to that of decontaminated waste. This leads to fewer controls and makes laboratory tests more able to predict the suitable coagulation treatment. This so-called "batch" method is often used in nuclear research centres when waste collection is controlled in the production areas and isolated for selective treatment.

For large plants, wastes are collected in large volumes in equalization basins and the treatment station operates continuously 24 h/d at a high rate.

Some examples of plants of various specific throughputs are described below. Where possible, these examples are based on existing plants.

5.1. Plants with throughput not exceeding 500 litres per day

For such units, wastes are collected in flasks, bottles or drums limited to 30 litres capacity for ease of handling. The treatment concept may be guided by two considerations:

- Accumulation of a large volume of effluent to be treated, the decontamination of which is not frequent; or
- Daily treatment of the volume produced per day.

In the first case, a higher investment cost will be balanced by savings on analyses, controls and tests for treatment orientation leading to an important labour decrease. In the second case, the argument is reversed. The choice between the two concepts depends both upon local conditions and the nature of the wastes (those that are non-miscible owing to risks of corrosion, toxicity, presence of foaming agents or chelatants, etc.) In these plants, the treatment is performed by the batch method.

Thus, in the Kjeller Institute [11], effluents to be submitted to a decontamination treatment are accumulated until they fill a 10 m^3 tank. This latter, designed as flocculator, receives reagents (alumina) allowing a coagulation-flocculation treatment. After the mixing action is stopped, the sedimented sludge is pumped and drained before being incorporated into concrete. Clear effluents are filtered and discharged after monitoring or further treated by ion exchange resins.

A plant may also be designed for a specific volume of 500 L/d to be treated (see Figure 4).

Bottles of wastes are emptied into a sink fitted with a strainer (to remove papers and various solid debris) and a device for washing these latter with tap water. Through a siphon in stainless steel, rigid PVC or other plastic piping the wastes are sent to a 500 litre capacity vessel (No.1) made of stainless steel or glass fibre reinforced polyester. This vessel, provided with a high level alarm and a cover, is fitted with a fast turbine mixer. It is first intended for homogenization of 500 litres of waste to allow sampling for control and laboratory tests. (A simple sampling device consists of a roller pump squeezing a plastic tube, the movement being manual.) Then coagulation reagents are added to the vessel, titrated in graduated test tubes sampled from a stock of solutions prepared in the laboratory and stored in plastic bottles.

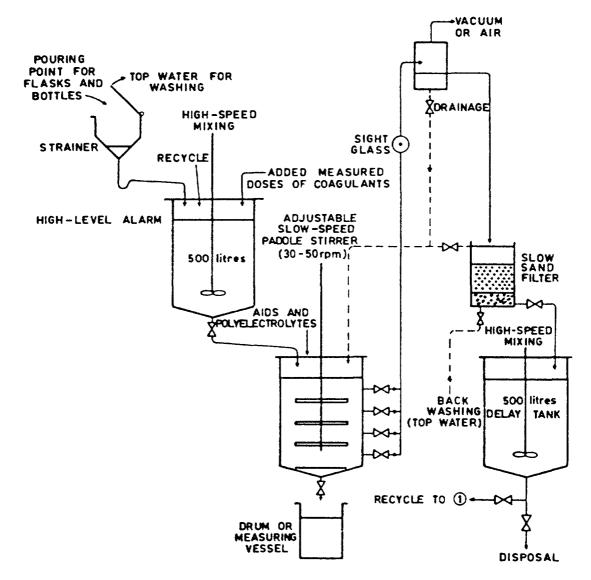
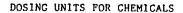


FIG. 4. Schematic design of proposed 500 litre batch treatment unit.

Mixing is stopped after 3 to 5 min; the waste is then quickly transferred by gravity to a vessel by means of a pipe of large cross-section. This vessel, the same size and material as the previous one, is provided with an adjustable low-speed paddle stirrer (30 to 50 rpm). In this vessel are added the necessary flocculation aids (activated silica, clays polyelectrolytes). Stirring is maintained during the period required to complete the floc formation (10 to 20 min); then it is stopped and the vessel is used as a settler.

After a few hours (e.g. 3 to 4), the clear liquid is sucked by vacuum from lateral piping of the vessel; it flows through a sight-glass and comes into a separation vessel, which serves as the gravity feed tank for a sand filter (containing if necessary other filtering material). This filter may be washed counter-currently with clear water, and water resulting from this washing overflows into another vessel.

Sedimentation sludges from this vessel are drained through the conical bottom fitted with a large cross-section valve, and sent to their final conditioning (incorporation into concrete or concrete + vermiculite).



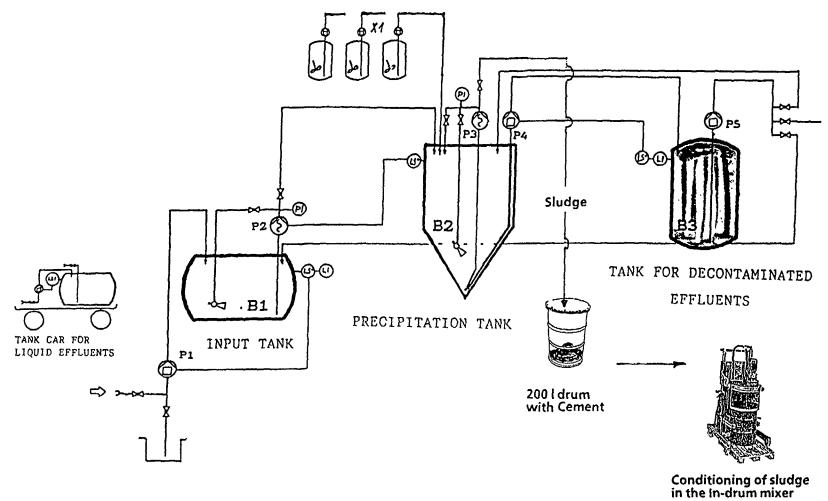


FIG. 5. Simplified flow diagram of the precipitation plant in Çekmece (Turkey).

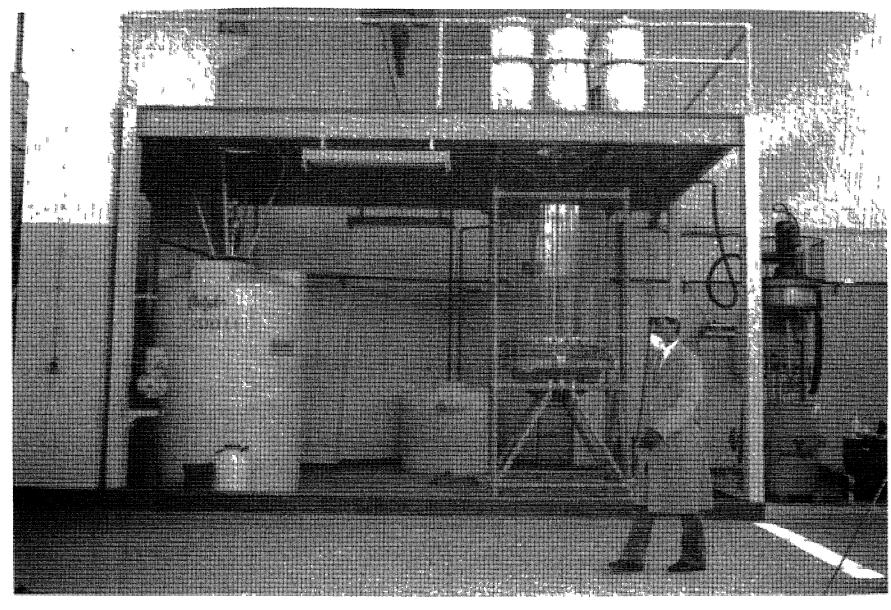


FIG 6 View of the precipitation plant in Çekmece (Turkey)

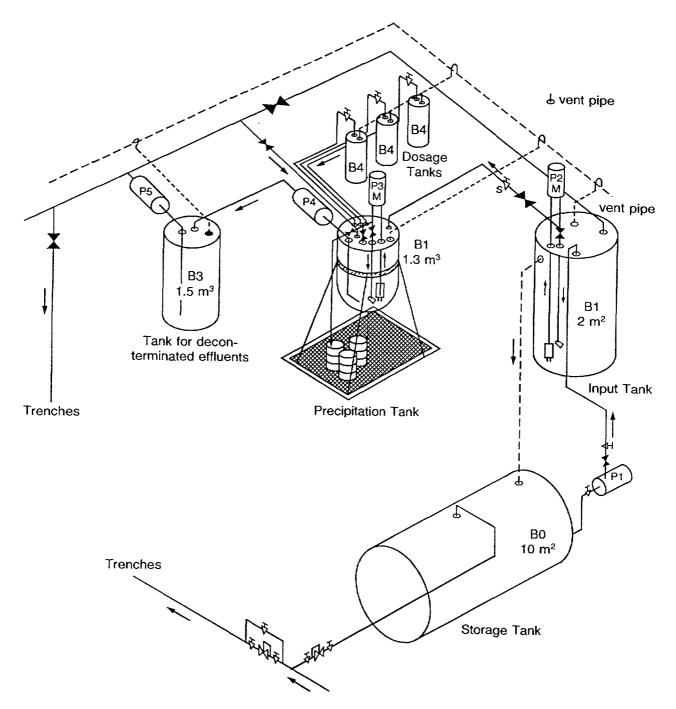


FIG. 7. Isometric drawing of the precipitation plant at the Nuclear Research Centre Huarangal (Peru).

Clear liquids from the filter are sent into a 500 litre vessel identical to the previous ones, in which the waste is checked before release or recycling through a new treatment.

Examples of $1 \text{ m}^3/\text{d}$ precipitation plants are located in Turkey and Peru. Figure 5 shows the simplified flow diagram of the precipitation plant in the Nuclear Research and Training Centre in Cekmece (Turkey) and Figure 6 a view on the installed completed plant in the waste treatment facility.

Figure 7 shows an isometric drawing of the precipitation plant in Peru planned and now under construction.

5.2. Plants with daily throughputs of $2-3 \text{ m}^3$

Here again, the wastes to be treated are collected mainly by means of special bottles and flasks. Hypotheses assumed in Section 5.1 remain applicable, although the plants are frequently oversized to cover any further extension of needs. In this case, the plant treats in a few hours the daily production of wastes.

Two designs are typical of these specific throughput levels:

(a) <u>Waste treatment pilot plant of J.E.N. at Madrid</u> [12]. This pilot plant includes a coagulation, flocculation and sedimentation chain preceding a battery of ion exchange columns. It allows decontamination of various wastes with a treatment capacity of 2.5 to 3 m³ during five effective working hours (see Figure 8).

Low activity wastes are received in tank (T-1) provided with remote control level and density detectors. They are removed by a pump through a flow-meter and directed to a flash mixer (A) where they receive coagulants (aluminium sulphate and activated silica).

The mixer speed is 1500 rpm. Coagulants are distributed by means of metering pumps from two storage drums, T12-T13. The wastes remain in the flash mixer for 2 min. From there they are sent to a flocculator (F) where they are kept for 1 h, the stirring speed being 1 rpm. Then, the flocculated liquids flow into the "sludge blanket" type purifier (CC). They remain in this purifier for 3 h and are stirred at an adjustable speed of 1, 2 or 3 rpm. The sludges, periodically drained, are sent to a bituminizing installation. Clear liquids overflowing from the purifier, flow into an intermediate storage tank (T4) from where they are pumped and filtered in an activated charcoal column (C1).

(b) <u>Treatment plant of Egyptian Atomic Energy Establishment</u> [13]. This plant has been designed to treat during the first 5 years 125 m^3/a , and during the next 5 years 250 m^3/a . The disposal of de-activated wastes is into the ground, the site conditions being favourable.

The coagulation-flocculation and sedimentation unit has been sized to allow treatment in 2 m³ batches with a maximum flow-rate of 500 litres/h. The treatment of the contents of one tank is thus performed in a normal working day (see Figure 9).

Wastes from storage tanks are received in one of two pretreatment tanks where their pH is adjusted. These tanks, of $2 m^3$ capacity each, are made of stainless steel. They are provided with a mixer, level gauges, high level alarm detectors and filtered vents. From these tanks, a pump raises wastes up to a constant feed head tank from which they flow by gravity to a flash mixer via a mixing flume with baffles. In this latter are added coagulation reagents (ferric chloride, calcium chloride, trisodium phosphate) delivered by metering pumps. From the flash mixer (20 litres) wastes flow into a flocculator (500 litres) with a low stirring speed adjustable from 10 to 60 rpm. Flocculation liquids overflow by gravity into a static settler (2300 litres) where sedimentation sludges are removed through a sludge measuring vessel into a concrete mixer. Clear effluents overflow by gravity from the settler, flow through a sand filter and are admitted into two post treatment storage tanks (identical to the pretreatment tanks). After monitoring, wastes are directed either to a disposal crib through a pipeline for injection into the ground or recycled to pretreatment tanks. A clear water storage tank allows the sand filter

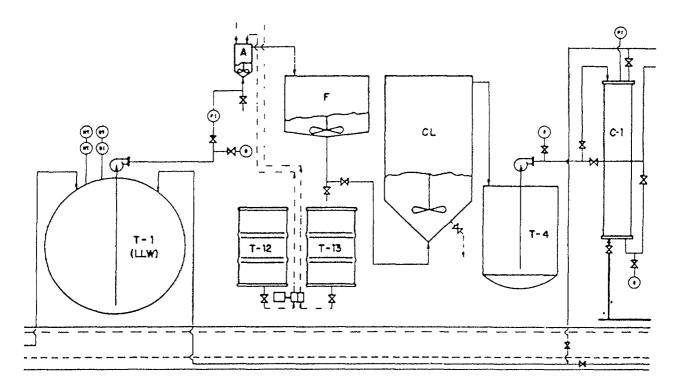


FIG. 8. Flocculation pretreatment pilot plant of JEN, Madrid [12].

to be washed countercurrently by a pump. Washing waters are sent to the settler. The plant is built over an impermeable tray forming a retention basin. Leaks are recovered in a sump and pumped back to the pretreatment storage tanks. Sampling devices are provided at each process stage. Piping and tanks are made of stainless steel; only those with a diameter smaller than 40 mm are made of rigid PVC.

5.3. Plants with daily throughputs of $25-100 \text{ m}^3$

This is the case for many nuclear research centres where waste collection is controlled at the production source to allow segregation. Contaminated liquids are transported mainly by means of tank-lorries, rarely through pipelines.

Two plants are described here: one performing a chemical treatment before ion exchange, the other performing only a chemical treatment.

(a) <u>Treatment of effluents at Karlsruhe</u> [14,15]. The decontamination chain is designed for discontinuous treatment of wastes by 10 m^3 successive operations. The average daily capacity is 25 m^3 . The main coagulation-flocculation processes used are: phosphate-ferric hydroxide, carbonate-ferric hydroxide and nickel ferrocyanide (see Figure 10).

The wastes received into a storage tank are pumped through an oil and grease separator to one of the conical precipitation vessels of 10 m^3 unit capacity. These cylindro-conical vessels are made of steel lined with rubber. They include a fast mixing zone in which are introduced coagulation reagents. Mixing action is stopped after 5 to 10 min and flocculation effluents settle during several hours. Clear liquids are then drawn off laterally through piping located at different levels and sent to the purifying filter. This latter, of precoat type and operating under high pressure, has a filtering surface of 7 m² formed by 12 graphite

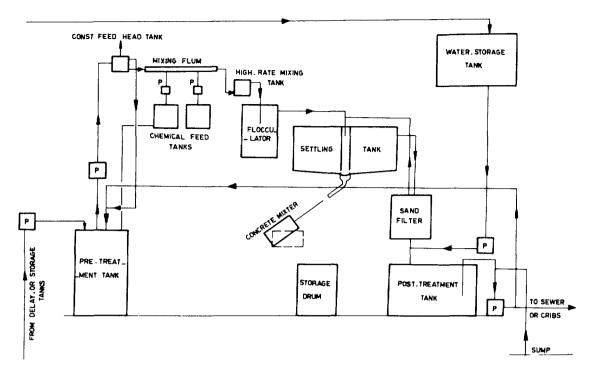


FIG. 9. Flow diagram of the radioactive liquid waste treatment plant of the Egyptian Atomic Energy Establishment [13].

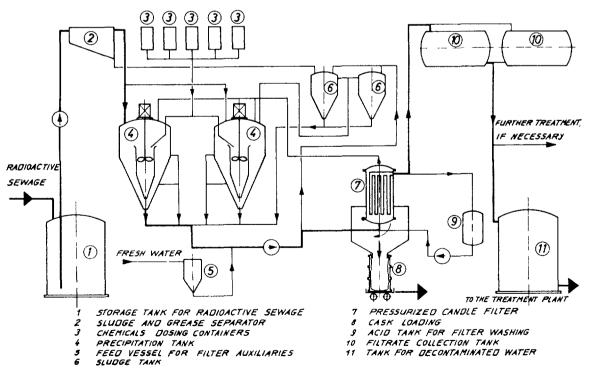
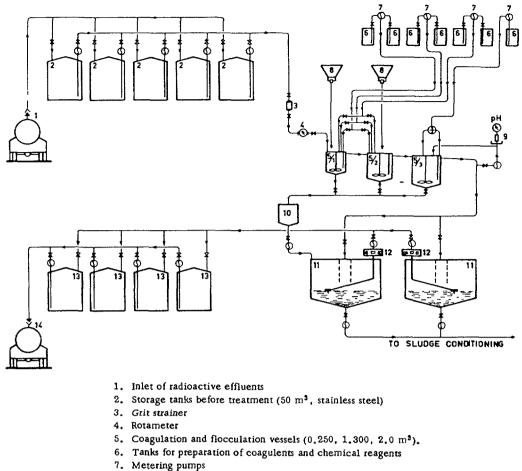
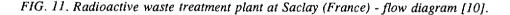


FIG. 10. Precipitation and filtration equipment at Karlsruhe (Germany) [14].



- 8. Dry hoppers
- 9. Measuring pot for pH
- 10. Drainage receiving tank
- 11. Static settlers
- 12. Turbidimeter
- 13. Storage tanks after treatment (50 m³, mild steel)
- 14. Unloading of treated effluents for disposal



candles. Sludges are removed from the flocculators only after every three or four operations. They are also sent through the filter. When the pressure drop becomes too high, the liquid is removed from the filter by means of compressed air, thus causing partial drying of the sludge; the air flow is then reversed, thus unclogging the filter. Sludges are drained at the filter base through a tilting movable bottom.

Clear liquids tested after sampling from one of the two post treatment tanks, are either recycled through a new chemical treatment, or sent to the ion exchange unit.

(b) Treatment of wastes at Saclay (See Figure 11). Wastes to be treated are received in 50 m³ capacity stainless steel tanks stirred by recirculation through pumps (self-priming type). These tanks are provided with remote control level gauges and high level alarm detectors. Treatment is carried out in 50 m³ daily batches at the rate of 3 to 6 m³/h. After the contents of one tank have been homogenized, a sample is taken for laboratory control and test purposes to determine the nature and doses of coagulants to be used. After a choice of treatment has been made, wastes

from the tank to be treated are pumped (stainless steel pumps and piping) through filters to remove debris. The flow rate is controlled by rotameter. Wastes are first adjusted in pH in two neutralizers where they also receive a part of the coagulants. These latter are distributed by means of dosing pumps or vibrated feeders according to whether they are in solution or powder form. The neutralizer (5/1) has a 200 litre capacity; mixing is ensured by an adjustable speed turbine from 0 to 1400 rpm. From this vessel, wastes are sent to a reactor (5/2) of 1500 litres capacity, mixing speed from 750 to 1500 rpm, where they receive the remaining coagulants. Then they overflow by gravity into the flocculator (5/3) of 3200 litres capacity, stirring speed 40 rpm. Addition of polyelectrolyte is partially done in this flocculator, as well as in the piping supplying one of the two 70 m³ capacity static settlers.

These circular settlers are 7 m in diameters; they are provided with a mechanical sludge-scraping device on the conical bottom and a sludge-removal system to rotary filters using diaphragm pumps. Operation of these settlers is alternate; while one is fed through the coagulation-flocculation chain, the second is drained or in the course of prolonged sedimentation. After complete settling (e.g. overnight), clear effluents are pumped from beneath the liquid surface through a hinged pipe to avoid pumping scums. A photo-electric turbidimeter installed in the liquid path allows the pumping action to stop as soon as the first sludge traces appear; rinsing of the piping is automatically ensured by the volume of clear liquid which flows back to the settler because of the slope effect.

Cleared liquids, not filtered (although the installation of a filter is foreseen) are stored in 50 m³ capacity tanks for monitoring before release or re-treatment.

After filtration in rotary filters without precoat (but this precoat may be applied), sludges are incorporated into the concrete.

5.4. Examples of higher flow rate plants

(a) <u>Chemical treatment plant for wastes at Trombay</u>

This is a treatment plant with a capacity of 225 m^3 for eight working hours. It includes mainly pretreatment storage tanks, a coagulation-flocculation section with mixer and clariflocculator, a filtration and ion exchange section and vacuum filtration of sludges before their incorporation in concrete (see Figure 12) [16].

After pH adjustment in pretreatment tanks, wastes are pumped to a mild-steel-lined concrete flash mixer where they receive coagulation reagents; the mixing speed is 60 rpm. After this addition, wastes flow to the clariflocculator. This latter includes a main cylindrical body, 7.30 m in diameter and 3.35 m high, made of mild-steel-lined reinforced concrete; the flocculation zone, hung concentrically, includes a cylindrical section 3.60 m in diameter and 1.80 m high, made of mild steel. Retention time for flocculation is 40 min approximately and 4 h 30 min for clarification.

Liquids issued from the clariflocculator are submitted to coninuous control to estimate the decontamination obtained; then they are passed through sand filters and, after pH readjustment, through ion exchange columns filled with vermiculite.

Sludges, pumped from the clariflocculator by diaphragm pumps, are stored and then filtered through a precoat-type vacuum drum filter. Filtrates are sent back to treatment. The cakes detached from the filter

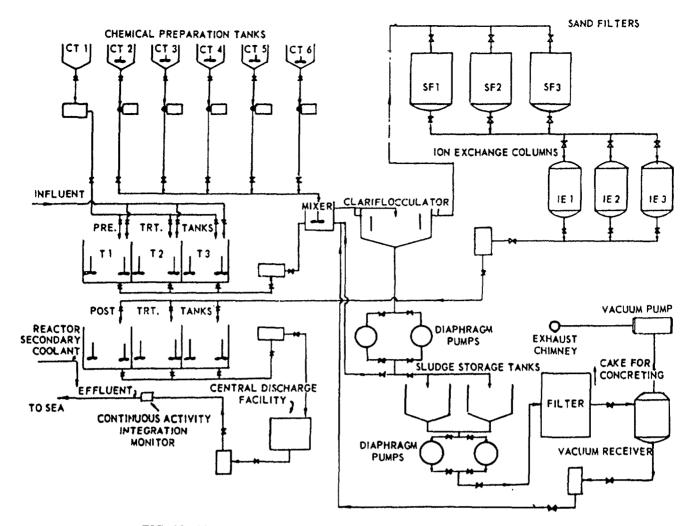


FIG. 12. Chemical treatment plant at Trombay (India) - flow sheet [16].

are received into mild-steel-lined concrete drums. Once filled, these drums are closed with a concrete lid and sent to storage above ground.

(b) Process waste treatment plant at Oak Ridge

This plant which has operated since 1957 has often been described [17, 18].

It is a conventional horizontal-flow water-softening plant using a lime-soda process, or alternatively, lime phosphate (for removal of 90 Sr) with clay addition (for removal of 137 Cs). The treatment capacity is 1900 m³/d.

Wastes, previously homogenized in an equalization basin of 3800 m^3 capacity, are pumped at a rate of $1.3 \text{ m}^3/\text{min}$ by centrifugal pumps, the flow rate of which is controlled by venturi flow meters. They are delivered into the flash-mixing basin where they receive coagulation reagents supplied by three gravimetric feeders (unit supply 90 kg/h). Contact time in the flash mixer is 1.3 min.

Then, the wastes cross the coagulation basin, which is divided into three sections by wooden baffles. Contact time is 31 min. Flocculated wastes leave this basin through perforated baffles and flow to the upper section of a settling basin where they are retained for an average of 129 min. These baffles are intended to slow down the waste flow and to supply them evenly at the end of the settling basin. The overflow rate is about 0.5 m/h.

Sludges are removed by means of an automatic Link-Belt collector and then temporarily stored in a 61 m^3 capacity concrete tank before discharge into a pit in a local shale formation.

Cleared liquids are then discharged, after control, into the environment, after having been previously submitted to an additonal settling in a 5700 m³ capacity basin. Feeding pipes from the equalization basin are made of rubber lined mild steel; pumps, venturi flow meters and valves are made of stainless steel. These latter, of plug-valve type, are fitted with rubber-faced plugs. Equipment of the unit (flash mixers, coagulators, sludge collectors, etc.) are lined with at least two coats of a protective thermoplastic material (polyethylene) after manufacture.

The general design of the unit offers a flexibility allowing recycling of treated waste and sludges as well as reagent addition at any time during the coagulation phase.

6. SAFETY ANALYSIS

Formal safety case reporting has generally not been carried out at the conditioning stages of design for a low level waste treatment plant due to low activity inventories and being low ranking for risks. At present, analysis of accident scenarios for selection of design features for non-reactor nuclear facilities is established as a regulatory requirement in only a few countries.

Appropriate safety analysis inclusive of risk estimation [19] is being made a feature in the generic design of the treatment and storage.

For normal operation, detection of deviation from safe levels and consequent remedial measures by operators will need to be covered by essential process instructions. These instructions will have to be prepared for each type of waste stream being treated and will need to take account of any hazards associated with the waste and with the reagents that are used in the treatment process.

The preferred aqueous waste treatment process i.e. that of flocculation/precipitation is regarded as significantly safer than other viable alternatives. The process of evaporation is the most widely used in treating nuclear fuel cycle wastes, but the safety of the evaporator operation depends upon complex design and operational controls which are demanding on a developing countory.

Considerable documentation exists concerning explosions in evaporators or in evaporative environments in the nuclear industry [20]. The risk lies with elevated temperature of operation and the potential presence of oxidizing agents and organics in waste streams. The notable example is "red-oil" explosive reaction where nitrates (nitric acid or uranyl nitrate) have reacted with organic residues from solvent extraction processes. Safety in nuclear fuel reprocessing utilizing evaporation depends upon detailed evaporation design (e.g. vacuum operation, strictly limited heating, steam pressures, steam stripping of feed and other solvent removal measures such as feed treatment by diluent washing) matched with carefully controlled feed compositions.

The selection of a chemical precipitation process for the aqueous waste treatment and cementation for immobilization will mean that maloperation due to high temperatures is not a risk. Some other events could conceivably lead to the following abnormal conditions:

- 1. Gas generation gas generation can occur during pH adjustment of acid wastes, from heat generation and by radiolytic decomposition of water. The gases generated could be asphyxiating (CO₂), toxic (HCN,H₂S, NH₃) or explosive (H₂). Any associated activity release will be due to aerosol generation or radionuclide volatility except for explosion where solid or liquid dispersion will occur. It is probable that wastes arriving at the treatment facility will be near neutral and therefore gas evolution from pH adjustment or heat generation will only arise from unplanned reactions occurring because of insufficient waste characterization or segregation. The radiolytic generation of hydrogen will require forced ventilation of the storage area, the rate of generation in the precipitation plant should be very small and will be kept well below the explosive limit by the air circulation that will be necessary in the treatment area.
- Fire the source of flammable material in the area will have to be kept to a minimum. The plant design will need to take account of the consequences of a fire that originates in adjacent buildings and extensions.

The most probable source of flammable material in the aqueous waste treatment plant will be the waste being treated. If there is a requirement to process wastes containing flammable material, the plant will need to be designed to avoid sources of ignition by using, for example, flame proof electrical items.

The release of activity, that can cause a fire, will be due to rupture of plastic vessels and aerial dispersion from solution heating.

Segregation of all unnecessary flammable material and of radioactive material not being treated will minimize the impact of a fire.

Reasonable attention to waste characterization and a good definition of a precipitation process operation should mean that the above moderate risks are minimized. Operator training is essential to avoid maloperation.

ANNEX

(This annex is reproduced from Annex II of IAEA Safety Series No. 70 [6])

REGULATIONS ISSUED BY THE NATIONAL INSTITUTE OF RADIATION PROTECTION (SWEDEN) ON RADIOACTIVE WASTE NOT ASSOCIATED WITH NUCLEAR ENERGY

This is an English translation of the Swedish regulation (SSI FS 1983: 7) on radioactive waste not associated with nuclear energy, issued on 20 December 1983 by the National Swedish Institute of Radiation Protection.

The National Institute of Radiation Protection hereby issues the following regulations with the authority of §5 of the Radiation Protection Act (Swedish Code of Statutes 1958: 110).¹

§1. These regulations are applicable to the handling of solid and liquid wastes not associated with nuclear power. The activity limitations specified in §§3 and 8 for wastes apply to each of the laboratories (or corresponding entities) covered by licences issued by the National Institute of Radiation Protection for work with radioactive substances and at which the work results in the production of radioactive wastes.

Note. The handling of the waste may be controlled for reasons other than radiation protection, for example because of its toxicity or risks of infection or fire. In such cases, these regulations form a complement to other rules or regulations.

§2. If the conditions laid down in §§3-11 are complied with, the radioactive waste may be disposed of locally without specific permission from the National Institute of Radiation Protection. Local deposition means either release into the municipal sewage system or delivery to a municipal refuse disposal plant.

Liquid wastes

§3. The total activity released into the sewage system must not exceed 10 ALI_{min} per month per laboratory (or corresponding entity). On each occasion on which a release is made, the activity must not exceed 1 ALI_{min} and must not exceed 100 megabecquerel. On each release occasion flushing shall be carried out with considerable quantities of water.

The values for ALI_{min} which shall be applied are shown in Table A1 in Appendix 1. If the waste contains more than one radionuclide, the maximum permitted activity shall be calculated in accordance with Appendix 1.

Release of radioactive waste should be confined to one release point for each laboratory.

§ 5. At each release point there shall be a visible sign stating that radioactive waste may be released into the sewage system.

§6. Urine and facces from patients who have been administered radionuclides in connection with diagnosis or treatment may be released to the sewage system without the activity being included in the maximum permitted activity in accordance with §3.

§7. Liquid scintillation solutions need not be treated as radioactive wastes provided that:

- (1) the solution does not contain alpha-emitting radionuclides
- (2) the activity does not exceed 10 becquerel per millilitre or, if the solution contains only ³H or ¹⁴C, 100 becquerel per millilitre.

¹ Note. Indented paragraphs are not legally binding regulations.

Appendix 1

THE CONCEPT ALI_{min}

ALI (Annual Limit on Intake) is defined in ICRP Publication 30, 'Limits for Intakes of Radionuclides by Workers' and it constitutes limits for intakes of radioactive substances by persons employed in radiological work. The limits have been set paying regard to the ICRP annual dose limit (50 mSv). There are different ALI values for oral intake as opposed to inhalation. ALI_{min} for each nuclide means the lesser of these two values.

Table A1 shows the values for ALI_{min} for the most common radionuclides. For nuclides not included in the table, the National Institute of Radiation Protection specifies applicable values.

Wastes which contain more than one radionuclide

For wastes released into the sewage system or sent to a municipal refuse disposal plant the following shall apply to the total activity during one month:

$$\sum_{k} \frac{A_{k}}{ALI_{\min k}} \leq 10$$

For the activity in one individual package the following shall apply:

$$\sum_{k} \frac{A_{k}}{ALI_{\min k}} \leq 1$$

For each occasion on which a release is made to the municipal sewage system the following shall apply:

$$\sum_{k} \frac{A_{k}}{ALI_{\min k}} \leq 1$$

The total activity, however, must not exceed 100 megabecquerels.

 A_k is the activity of radionuclide k and $ALI_{min k}$ is the ALI_{min} value in the table for radionuclide k (see Table A1).

Nuclide	ALI _{min} (Bq)	Nuclide	ALI _{min} (Bq)
³ H water	3 × 10 ⁹	⁸⁵ Sr ^m	8 × 10 ⁹
¹⁴ C	3 × 10 ⁸	⁸⁵ Sr	6×10^{7}
¹⁸ F	2×10^{9}	⁸⁷ Sr ^m	1×10^{9}
²² Na	2×10^{7}	⁸⁹ Sr	$5 \times 10^{\circ}$
²⁴ Na	1×10^{8}	⁹⁰ Sr	1×10^{9}
³² P	1×10^{7}	90 Y	2×10^{7}
³³ P	1×10^8	⁹⁹ Tc ^m	3×10^{9}
³⁵ S	8 × 10 ⁷	⁹⁹ Mo	2×10^{8}
³⁶ Cl	9 × 10 ⁶	¹¹³ In ^m	2×10^{9}
³⁸ Cl	6 X 10 ⁸	¹²⁴ Sb	1×10^8
⁴² K	2×10^8	1231	1×10^{8}
⁴³ K	2×10^8	125	1×10^{6}
⁴⁵ Ca	3×10^{7}	1291	2×10^{5}
⁴⁷ Ca	3×10^{7}	130	1×10^{7}
⁵¹ Cr	7×10^8	131	1×10^{6}
⁵² Mn	3×10^{7}	¹³² 1	1×10^{8}
⁵² Mn ^m	1 × 10 ⁹	109Cd	1×10^{6}
⁵⁴ Mn	3×10^{7}	115 _{Cd}	3×10^7
⁵⁶ Mn	2 × 10 ⁸	¹¹¹ In	2×10^{8}
⁵² Fe	3 × 10 ⁷	129Cs	9 × 10 ⁸
55 Fe	7 × 10 ⁷	130 _{Cs}	2×10^{9}
⁵⁹ Fe	1×10^7	131	8×10^8
⁵⁶ Co	7 × 10 ⁶	134Cs	3×10^{6}
⁵⁷ Co	2×10^7	134 _{Ce} m	4×10^9
⁵⁸ Co	3 × 10 ⁷	¹³⁷ Cs	4×10^{6}
⁶⁰ Со	1 × 10 ⁶	¹³¹ Ba	1×10^8
⁶³ Ni	1×10^{8}	133Bam	9×10^{7}
⁶⁴ Cu	4×10^8	135 _{Do} m	1×10^{8}
67 Cu	2×10^8	¹⁴⁰ La	2×10^7
⁶² Zn	5 X 10 ⁷	169 Yb	2×10^7
⁶⁵ Zn	1×10^{7}	¹⁹² Ir	8 × 10 ⁶
⁶⁹ Zn ^m	2×10^8	198 A	4×10^7
⁶⁷ Ga	3×10^7	197 Hg	2×10^8
⁶⁸ Ga	6 X 10 ⁸	²⁰³ Hg	2×10^7
⁷³ As	8×10^8	201 TI	6 × 10 ⁸
74 A c	8×10^7	²⁰⁴ Tl	7×10^{7}
⁷⁵ Se	6×10^7	210Pb	9×10^3
⁷⁶ Br	1×10^8	212Pb	1 × 10 ⁶
77 Br	6×10^8	210Po	2 X 10 ⁴
⁸² Br	1 × 10 ⁸	²²⁶ Ra	2×10^4
⁸¹ Rb ^m	9 × 10 ⁹	²³² Th	4×10^{1}
⁸¹ Rb	1×10^9	²³⁸ U	2×10^3
⁸⁶ Rb	2×10^7	²⁴¹ Am	2×10^2 2×10^2
⁸⁸ Rb	7 × 10 ⁸	²⁴⁴ Cm	4×10^2
89 Rb	1 × 10 ⁹	252 Cf	1×10^3

TABLE A1. ALI_{min} VALUES FOR SOME COMMON RADIONUCLIDES

REFERENCES

- INTERNATIONAL ATOMIC ENERGY AGENCY, Design of a Centralized Waste Processing and Storage Facility, IAEA-TECDOC-Series, IAEA, Vienna (in preparation).
- [2] INTERNATIONAL ATOMIC ENERGY AGENCY, Treatment of Low- and Intermediate-Level Liquid Radioactive Wastes, Technical Reports Series No. 236, IAEA, Vienna (1984).
- [3] AYRES, J.A., PERRIGO, L.D., WEED, R.D., Decontamination of a PWR, Nucleonics (1967) 58-72.
- [4] BAEHR, W., "The IAEA's Programme of Technical Assistance for the Management of Radioactive Wastes in Developing Countries", IAEA Interregional Training Course on Management of Radioactive Wastes, Kernforschungszentrum Karlsruhe (1987).
- [5] BAEHR, W., The Management of Radioactive Wastes in Developing Countries: Technical Issues and Solutions, Kernforschungszentrum Karlsruhe, 1987.
- [6] INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Radioactive Wastes Produced by Users of Radioactive Materials, Safety Series No. 70, IAEA, Vienna (1985).
- [7] INTERNATIONAL ATOMIC ENERGY AGENCY, Principles for the Exemption of Radiation Sources and Practices from Regulatory Control, Safety Series No. 89, IAEA, Vienna (1988).
- [8] INTERNATIONAL ATOMIC ENERGY AGENCY, Exemption of Radiation Sources and Practices from Regulatory Control, IAEA-TECDOC-401, IAEA, Vienna (1987).
- [9] INTERNATIONAL ATOMIC ENERGY AGENCY, Storage of Radioactive Wastes, IAEA-TECDOC-653, IAEA, Vienna (1992).
- [10] INTERNATIONAL ATOMIC ENERGY AGENCY, Chemical Treatment of Radioactive Wastes, Technical Reports Series No. 89, IAEA, Vienna (1968).
- [11] GAUDERNACK, B., LUNDBY, J.E., "Waste treatment at the Institute for Atomic Energy, Kjeller", Practices in the Treatment of Low- and Intermediate- Level Radioactive Wastes (Proc. IAEA-NEA Symp. Vienna, 1965) IAEA, Vienna (1966) 147-160.
- [12] DE LORA SORIA, F., LOPEZ PEREZ, B., "The 'CIES' pilot plant for treating radioactive liquid wastes from the processing of irradiated fuel elements at the Junta de Energia Nuclear (Spain)", ibid., 403-410.
- [13] MAHMOUD, K.A. et al., "United Arab Republic programme for management and treatment of low- and intermediate-level radioactive wastes", ibid., 411-417.
- [14] KRAUSE, H., NENTWICH, O., "The treatment of low-level and mediumlevel liquid radioactive wastes at the Karlsruhe Nuclear Research Centre", ibid., 317-337.

- [15] BAEHR, W., HEMPELMANN, W., KRAUSE, H., NENTWICH, O., "Experiences in the treatment of low- and intermediate-level radioactive wastes in the Nuclear Research Centre, Karlsruhe", Management of Low- and Intermediate-Level Radioactive Wastes (Proc. Symp. Aix-en-Provence, 1970), IAEA, Vienna (1970) 461-484.
- [16] CHINOY, A.R., et al., 3rd Int. Conf. Peaceful Uses Atom. Energy (Proc. Conf. Geneva, 1964) <u>14</u>, UN, New York (1965) 264.
- [17] CULBREATH, M.C., Radioactive contaminant removal from waste water: engineering design features, J. Sanitary Engng Div., Proc. Amer. Soc. of Civil Engineers <u>85</u> SA3 (1959) 55.
- [18] COWSER, K.E., et al., "Operational experience in the treatment of radioactive waste at Oak Ridge National Laboratory and Brookhaven National Laboratory", Practices in the Treatment of Low- and Intermediate-Level Radioactive Wastes (Proc. IAEA/NEA Symp. Vienna, 1965) IAEA, Vienna (1966) 381-401.
- [19] HENSLEY, G., Application of probabilistic risk assessment in demonstrating adequacy of safety in design of nuclear chemical plants, EPRI-NP-3912SR, Vol.2.
- [20] INTERNATIONAL ATOMIC ENERGY AGENCY, Handling and Storage of High-Level Radioactive Liquid Wastes Requiring Cooling, Technical Reports Series No. 191, IAEA, Vienna (1979).