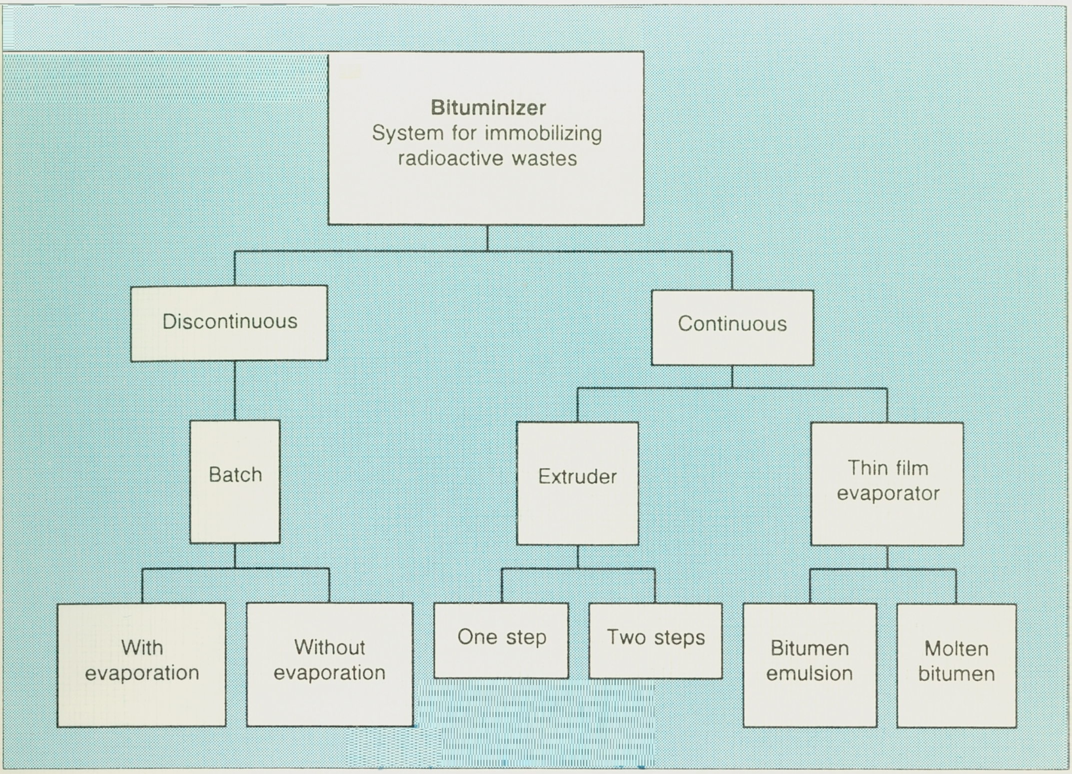

TECHNICAL REPORTS SERIES No. 352

Bituminization Processes to Condition Radioactive Wastes

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1993

BITUMINIZATION PROCESSES
TO CONDITION RADIOACTIVE WASTES

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FOREWORD

The application of bituminization for the conditioning of low and intermediate level radioactive wastes was described in the IAEA Technical Reports Series No. 116, Bituminization of Radioactive Wastes (1970).

Since this publication, bituminization of radioactive wastes has become a widely used method for conditioning radioactive wastes generated in the nuclear industry, research centres and radionuclide applications. Many full scale processing units have been operated in several IAEA Member States. The aim of this report is to review and evaluate the accumulated experience in the use of bituminization techniques for the immobilization of radioactive wastes and give an assessment on the role of the bituminization processes in the strategy for radioactive waste management.

To review and collect information on the current state of the bituminization of radioactive wastes, the International Atomic Energy Agency convened a Technical Committee Meeting (TCM) on the Evaluation of Bituminization Processes to Condition Radioactive Wastes in Vienna from 16 to 19 May 1989. The meeting was attended by 15 participants from eight countries and two international organizations. The TCM participants reviewed and completed the draft report on the above subject, which was prepared by the IAEA Secretariat and two Consultants, L.P. Buckley (Canada) and J. Claes (Belgium).

After the TCM the report was revised and rearranged in a series of Consultants Meetings. The final modification of the report was prepared by the IAEA Secretariat with the assistance of three consultants: C. Courtois (France), W. Hild (Germany) and L. Mergan (Belgium).

The officers responsible at the IAEA were V.M. Efremenkov and A.F. Tsarenko from the Waste Management Section of the Division of Nuclear Fuel Cycle and Waste Management.

CONTENTS

1. INTRODUCTION

Bituminization of radioactive wastes has been a technique used by the nuclear industry for nearly 30 years and it has attracted interest in more than 20 Member States. Large funds have been committed to build and operate industrial scale bituminization facilities to treat a wide variety of wastes generated from the nuclear fuel cycle and the accompanying research and development programmes.

Management of low and intermediate level radioactive wastes strives to use a strategy that incorporates a number of technologies to convert wastes into suitable forms for handling, storage, transport and disposal [1]. Among the conditioning techniques, bituminization is one that can, for some wastes, provide a form that is mechanically, physically, chemically and radiologically stable for the subsequent stages of radioactive waste management, including disposal.

This technical report is an update of Bituminization of Radioactive Wastes, Technical Reports Series No. 116 (1970) [2]. The initial report focused on an emerging technology and the underlying optimism that bitumen was a universal matrix. With the experience gained from the operation of full scale industrial facilities and from research into the performance of bituminized products, an assessment on how bituminization processes can now fit into an overall strategy dealing with nuclear wastes is presented here.

This report is intended to describe the major processes that are operational and to clarify which liquid and solid wastes are suitably matched to the physical, chemical and radiological properties of bitumen. This is not an exhaustive compendium of all the literature published on bituminization, but is an attempt to cover the current bituminization processes and describe their basic features, including their limitations, which, however, also exist for any other solidification technique.

In its form of presentation and with its extensive bibliography, this report may be of assistance to Member States in comparing the advantages and the drawbacks of the various processes, with the aim of meeting their specific needs in the field of the conditioning of low and intermediate level radioactive wastes.

In the Annex characteristic data from a number of bituminization facilities in some Member States are tabulated. These facilities may be taken as representative of the current practice, as they are built and operated to cover, each in part, a wide range of wastes from different sources, e.g. nuclear power plants, reprocessing plants and research establishments.

2. CHARACTERIZATION OF BITUMENS USED FOR WASTE IMMOBILIZATION

2.1. ORIGIN AND TYPES OF BITUMENS

In the context of this report, bitumen is a term used for a thermoplastic organic material, semisolid or solid at room temperature and composed of a wide variety of mixtures of high molecular weight hydrocarbons, which is soluble in carbon disulphide.

Although naturally occurring bitumens are known, the commercially available bitumens are almost exclusively obtained from asphaltic crude oil after separation of the light fractions. According to the mode of their preparation the bitumens used for the immobilization of radioactive wastes can be subdivided into the following types:

(a) Straight-run distillation (distilled) bitumen, obtained as the bottom product after the distillation of asphaltic crude oils;
(b) Blown or oxidized bitumen, obtained by blowing air through bitumen at temperatures between 200 and 260°C;
(c) Emulsified bitumen (liquefied bitumen), obtained by addition of anionic (alkaline soap), cationic (amine salt) or non-ionic aqueous solutions (emulsifiers) to distilled bitumen.

Detailed information about the production processes for the various types of bitumens as well as about the complex chemistry of bitumens is available in the literature [3, 4]. For the purpose of this Technical Report, a more complete description of bitumen manufacturing processes is not considered to be relevant. Applicable standards in some countries for the measurement of bitumen properties are given in Table I.

2.2. PHYSICOCHEMICAL PROPERTIES

When bitumens are considered as matrix materials for the embedding of radioactive wastes, a number of physicochemical properties of bitumens are important as they relate to:

(a) The storage and transfer conditions of molten bitumen,
(b) The operating conditions of the process,
(c) The compatibility with the waste material,
(d) The packaging requirements for the final product,
(e) The shipment and storage conditions of the packages,
(f) The final disposal of the bituminized wastes.

TABLE I. APPLICABLE STANDARDS FOR THE MEASUREMENT OF BITUMEN PROPERTIES

Property	Test		
	ASTM[a]	AFNOR[b]	DIN[c]
Softening point (R&B)[d]	D36	T66.008	52011
Hardness (penetration)	D5	T66.004	52010
Viscosity	D2171		
Flashpoint	D92	T60.118	DIN ISO 2592
Density	D70	T66.007	52004
Loss of weight on heating	D70	T66.011	52016
Ductility	D113	T66.066	52013

[a] ASTM: American Society for Testing of Materials.

[b] AFNOR: Association française de normalisation.

[c] DIN: Deutsches Institut für Normung e.V.

[d] R&B: ring and ball test.

In the following sections, typical properties of bitumens and methods of determining these are summarized. Examples of some physical properties are given in Table II [4].

2.2.1. Chemical composition

Bitumens are composed of hydrocarbons with small quantities of sulphur, nitrogen and oxygen compounds and traces of other elements, such as metals. The elementary analysis of bitumens shows that they consist of hydrocarbons, and derivatives originating from the condensation and oxidation of hydrocarbons with the substitution of carbon by sulphur and nitrogen. The molecular structure is complex and still partially unknown. The main components can be divided into:

(i) Asphaltenes, which are highly aromatic and have high molecular weights.
(ii) Maltenes, which constitute the fraction of high boiling point substances, containing resins and oils. The resins are amorphous solids with chemical structures comparable with asphaltenes. A typical feature of the resins is their change in viscosity with temperature. The oils comprise aromatic, cycloparaffinic and aliphatic fractions.

A typical composition of bitumen is given in Table III.

TABLE II. PHYSICAL PROPERTIES OF BITUMEN — MEAN VALUES [4]

Property	Value
Specific density	1.04 ± 0.03 kg/L (at 25°C)
Coefficient of cubical expansion	6.1×10^{-4} $°C^{-1}$ (in the range 15–200°C)
Specific heat	$1.88\ J \cdot g^{-1} \cdot °C^{-1}$
Thermal conductivity	$0.54\ kJ \cdot m^{-1} \cdot °C^{-1} \cdot h^{-1}$
Permeability of H_2O vapour	$9.75 \times 10^{-11}\ g \cdot h^{-1} \cdot cm^{-1} \cdot Pa^{-1}$ (at 25°C)
Surface tension	$(29 \pm 1) \times 10^{-5}$ N/cm (at 100°C)
Total surface energy	$51 \pm 0.1\ \mu J/cm^2$
Resistivity/conductivity	$10^{14}\ \Omega \cdot cm$ (at 30°C)
Dielectric strength	20–30 kV/mm (at 20°C; flat electrodes)
Dielectric constant	2.7 (at 20°C)
Dielectric loss	0.015 tan δ (50 Hz; 20°C)
Viscosity	10^3–10^{20} P (in the range 50–0°C)
Heat of combustion	4.2×10^4 J/g
Compressibility	$\approx 4 \times 10^{-5}\ cm^2/kg$
Permeability to H_2 diffusivity	$\approx 3 \times 10^{-12}\ g \cdot h^{-1} \cdot cm^{-1} \cdot Pa^{-1}$ (at 25°C)

The major difference in the chemical composition between oxidized and distilled bitumens is the higher fraction of asphaltenes found in oxidized bitumens.

2.2.2. Softening point

Since bitumens are mixtures of complex molecules, they have no well defined melting points, which indicate the transition temperature from the solid to the liquid state. Instead, bitumens are characterized by a progressive transition from solid to liquid that covers a rather large temperature range. The ring and ball test is a normalized procedure by which the softening point is determined as the temperature at which the bitumen reaches an established level of softening under standard conditions.

For the bitumens used to embed radioactive wastes, the softening point varies between 35 and 95°C. The lower end of the range applies to distilled bitumens and the higher end to blown (oxidized) bitumens.

TABLE III. TYPICAL COMPOSITION OF BITUMEN

Main compounds [5]	(wt%)
Aromatics and naphtenoaromatics	38.3
Asphaltenes	15.6
Saturated *i*- and cyclo-olefins	16.1
Neutral heterocompounds	14.2
Basic heterocompounds	8.5
Acid heterocompounds	7.2
Saturated *n*-olefins	<0.1
Main elements [6]	(wt%)
Carbon	84
Hydrogen	10.3
Sulphur	4.1
Oxygen	1.2
Nitrogen	0.4
Aluminium	~ppm
Silicon, vanadium, nickel	~ppm

2.2.3. Hardness (penetration)

A standard test that determines the penetration depth (penetrability), in tenths of millimetres, of a needle under a given loading (100 g) at a given temperature (25°C) during a given time (5 s) in a bitumen sample of a given size is commonly used as a measure of the mechanical resistance to deformation. The penetration depth may vary between 10 for the hardest bitumens and 110 for the softest type. The higher the asphaltene content, the lower the penetration depth.

2.2.4. Viscosity

Both the softening point and the penetration depth are related to the mechanical and rheological properties of bitumens. These characteristics depend upon the asphaltene content of the bitumen. Increasing the temperature lowers the viscosity exponentially and heating is therefore used for liquefying bitumens, with the exception of emulsified bitumens, which are fluid at room temperatures.

TABLE IV. EQUIVISCOUS TEMPERATURES (°C) [4]

Mexphalt grade	Viscosity (10^{-6} m^2/s)						
	20 000	5000	2000	1000	200	100	50
180/200 ('Spramex')	70	85	97	108	138	156	176
80/100	78	94	106	117	149	166	187
60/70	85	101	113	123	155	172	193
50/60	88	104	116	126	158	175	197
40/50	91	107	119	130	162	179	201
30/40	95	111	124	135	168	185	208
20/30	101	117	130	142	175	193	216
10/20	111	128	141	153	186	205	228
H80/90	133	150	163	172	206	224	246
H100/100	154	170	184	195	227	245	—
R85/25	126	144	157	169	205	225	248
R85/40	127	144	157	168	201	220	243
R95/15	143	161	176	188	225	245	—
R115/15	166	186	202	216	(256)	—	—
R135/10	190	210	225	240	—	—	—

Since precautions during heating of the bitumen are also linked to the flashpoint (Section 2.2.5), it is important that the real conditions of bitumen applications are known in order to predetermine the optimum process temperature (for pumping, mixing, blending, drum filling, etc.). The relations between temperature, viscosity and type of bitumen are given in Table IV.

The viscosity for blown bitumen at room temperature is much less dependent on time than that for distilled bitumen. This characteristic is also valid at higher temperatures (e.g. 60°C).

2.2.5. Flashpoint

The lowest temperature at which the volatile components of bitumens start burning with an open flame under standard conditions is referred to as the flashpoint.

The test indicates the temperature that must not be reached during processing for safety reasons. The bitumens chosen as matrix materials usually have high flash-points, typically in the range of 250 to 300°C, with some exceptions as low as 220°C.

2.2.6. Density

The density at 25°C of most bitumens is slightly above 1000 kg/m^3 and increases with the asphaltene content. Therefore, the density slightly increases with decreasing penetration depth.

2.2.7. Loss of weight by heating

When bitumen is heated for a sufficiently long time, volatilization of the constituents with the lowest boiling points takes place and this influences the properties of the bitumen, for instance the hardness and brittleness are increased.

The loss of weight by heating is a measure of the magnitude of the modification of these properties. It also identifies the amount of volatile components that can be released from the bitumen during the hot stages in the bituminization processes. Standard tests are carried out at 163°C for a duration of 5 h. Weight losses of 0.2 wt% for oxidized bitumens to 2 wt% for distilled bitumens are reported.

2.2.8. Ductility

The ductility of bitumen is closely related to its rheological properties. In the standard ductility tests, bitumen samples are stretched and the elongation is measured.

In general, the ductility of blown bitumens is low compared with that of distilled bitumens. This phenomenon is due to the oxidation of blown bitumen, leading to dehydrogenation and polymerization. The same phenomenon can occur as a result of ageing and irradiation. Typical values for the ductility at 25°C are 1 to 5 cm for blown bitumens and 45 to over 100 cm for distilled bitumens.

When the temperatures to which the bitumen is exposed decrease, the ductility decreases and the bitumen becomes brittle. Usually at temperatures of -20 to -30°C, bitumens show an increased tendency to fracture.

2.2.9. Other physical properties

The mean values of the other typical properties and constants are summarized in Table II. Among these, attention should be paid to the low thermal conductivity. The design of heating equipment, in particular the potential for carbonization on heating surfaces, should be addressed when considering bituminization of a waste.

TABLE V. RESISTANCE OF BITUMEN TO THE EFFECTS OF CHEMICALS AT ROOM TEMPERATURE[a] [4]

		Mexphalt 40/50,20/30,10/20				Mexphalt R85/25,R85/40,R115/15			
Time (a)		0.5	1.0	1.5	2.0	0.75	1.0	3.5	5.0
Inorganic acids									
Hydrochloric acid	≤10%	+	±		−				+
Hydrochloric acid	10–30%	±	±		−				+
Hydrofluoric acid	40%						+		
Nitric acid	≤10%	±	−						+
Nitric acid	10–25%	−							±
Nitric acid	25–50%	−							−
Phosphoric acid	5%					+			
Sulphuric acid	≤50%	+		±	−				+
Organic acids									
Acetic acid	20%					+			
Benzoic acid	1%						+		
Butyric acid	10%			−					+
Formic acid	85%					+			
Lactic acid	10%			−					+
Phenol solution	1%						+		
Picric acid	1%						+		
Salicylic acid	0.1%						+		
Inorganic alkalis									
Ammonia	25%						+		
Caustic soda	≤30%							+	
Soda solution	10%							+	
Soda solution (saturated)						+			
Salts									
Chlorine-containing brine								+	
Common salt solution (saturated)								+	
Formaldehyde solution	30%					+			
Magnesium chloride	14%					+			
Sea water									+
Sodium hydrosulphite solution (saturated)						+			
Sodium hypochlorite	5 g/L					+			
Sodium sulphite solution (saturated)						+			
'Teepol'								+	+
Waterglass						+			

[a] + Not affected, ± little to moderate attack, − strongly attacked.

2.2.10. Chemical stability

Bitumens are generally very resistant to many chemicals at ambient temperatures. They are therefore applied as coatings to protect materials that are more sensitive to chemical influences.

However, at higher temperatures, bitumen can react with various agents such as oxygen and sulphur. These reactions mainly cause the dehydrogenation of the bitumen and the formation of asphaltenes (Section 2.2.1). The reaction of bitumens with oxygen is important in the manufacture of blown bitumen.

Chemical changes may also occur when the bitumen, without being in contact with other substances, is exposed to high temperatures (≥300°C). These phenomena, which generally lead to a hardening, should be considered not only when producing bitumen by means of distillation but also in the bituminization of radioactive wastes.

In general, bitumens are less resistant towards attack by acidic solutions than that by alkaline solutions. Bitumens do not seem to be attacked by concentrated alkaline solutions at room temperature, although dilute alkaline solutions react with acidic bitumen constituents to form salts such as sodium naphthenates, which serve as excellent emulsifying agents for bitumen. This reaction is particularly noticeable in soft bitumens of high acid value and at a concentration of 0.1% sodium hydroxide.

The resistance of bitumens to acids depends on the concentration of the acids: in general, concentrated acids attack bitumens. Prolonged contact with dilute acids may cause a hardening of the bitumen, due to the formation of asphaltenes. Concentrated sulphuric acid (e.g. 96%) attacks the aromatic components of the bitumen (acid tar). The saturated hydrocarbons are not attacked even at 200°C. Bitumens are resistant to dilute sulphuric acid, and highly resistant to concentrated hydrochloric acid solutions at room temperature.

Bitumens are not resistant to attack by nitric acid. Concentrated nitric acid causes oxidation and nitration. Dilute nitric acid also attacks bitumens, even at low concentrations and at room temperature. Bitumens are therefore unsuitable for the protection of materials against the action of free nitric acid.

The resistance of bitumens towards various chemical reagents for different concentrations and periods of time is indicated qualitatively in Table V [4].

Finally, the high and fast solubility of bitumens in solvents, such as trichlorethane, is a favourable property with regard to the cleaning of bituminization process equipment.

TABLE VI. RESULTS OF INTERNAL ALPHA IRRADIATION OF BITUMINIZED REPROCESSING WASTES [12]

Composition (wt%)	Minimum and maximum integrated doses (MGy)	Minimum and maximum irradiation times (a)	Total radiolytic gas production, average values ($mL \cdot g^{-1} \cdot MGy^{-1}$)[a]							N_2/O_2 volume ratios, average and extreme values
			H_2	NO (10^2)	CO (10^3)	CH_4 (10^3)	C_2H_6 (10^3)	C_2H_4 (10^3)	C_3H_8 (10^3)	
80% Bitumen B15, 20% $NaNO_3$, 1.05 mg Cm_2O_3/100 g	1.0–2.0	1.2–2.3	1.2	3.8	6	0.32	1.0	1.0	0.3	23 (6–45)
60% Bitumen B15, 40% $NaNO_3$, 13.6 mg Cm_2O_3/100 g	13–24	1.2–2.2	0.8	3.8	3	0.46	0.13	<0.1	<0.1	12 (8–25)
60% Bitumen B15, 40% $NaNO_3$ 1.4 mg Cm_2O_3/100 g	1.2–2.3	1.0–2.1	1.4	5.5	10	0.7	<0.3	0.4	0.3	16 (8–20)
60% Bitumen R85/40, 40% $NaNO_3$, 1.5 mg Cm_2O_3/100 g	1.4–2.5	1.1–2.1	1.1	5.9	12	0.59	0.32	0.5	[b]	72 (20–110)
60% Bitumen R85/40, 35.8% slurry type A, 4.2% PuO_2	18–20	1.9–2.1	1.2	7.1	5	0.4	0.1	0.2	0.2	12 (5–30)
60% Bitumen R85/40, 35.8% $NaNO_3$ Pa 4.2% PuO_2	24	2.5	1.4	8.5	[b]	<0.02	[b]	[b]	[b]	76 (7–100)

[a] At 1.013 × 10^5 Pa and 25°C.

[b] Below detection limit.

2.3. RADIOLOGICAL PROPERTIES

The stability of bitumen with respect to alpha, beta or gamma radiations is an important property that defines:

- The maximum amount of radioactivity that can be incorporated in the bitumen matrix,
- The behaviour of the final product under storage and disposal conditions.

2.3.1. Radiolytic effects

Since bitumens are high molecular mixtures of aliphatic and aromatic hydrocarbons, they can easily give rise to radiolytic decomposition products as a result of a series of radiological and chemical processes.

Early experiments carried out in France [7], Czechoslovakia, the former Union of Soviet Socialist Republics [8, 9] and the United States of America [10] on different types of bitumens, using external gamma sources, have shown that the production of radiolytic gases (H_2, CH_4, CO_2) depends upon the type of bitumen, the dose rate and the absorbed dose.

The *G* values[1] for the total gas evolution from bitumen are between 0.4 to 0.5, i.e. relatively small values, so that part of the radiation energy seems to be absorbed by excitation without chemical transformation.

The radiolytic yield decreases by a factor of 100 as one shifts from saturated to unsaturated aliphatic hydrocarbons and to aromatic compounds. In fact, the saturated hydrocarbon fraction in bitumen is responsible for the intensity of the radiological reactions. Thus, as the level of bitumen oxidation increases, both the rate and the yield of the radiolytic products decrease, which establishes the fact that oxidized bitumens are generally more stable (radiation resistant) than the distilled varieties. However, irradiation experiments with some types of bitumen carried out in Germany showed practically no difference in the radiolytic stability of bitumen [11].

The alpha radiolysis of bitumen can only be studied after incorporating alpha emitting radionuclides. Such a study has been conducted in Germany [12] for the bituminization of concentrates from spent fuel reprocessing. Samples of bitumen–$NaNO_3$ doped with Cm_2O_3 or PuO_2 were exposed to internal alpha doses ranging from 10^6 to 2.4×10^7 Gy for 1 to 2.5 years. These alpha doses were calculated to be the total lifetime doses for the average waste composition (60 000 a). The yield of the H_2 production was 1.2 $mL \cdot g^{-1} \cdot MGy^{-1}$. Internal alpha irradiation increases the average H_2 formation yield by a factor of 2.7 compared with the external gamma irradiation or irradiation by 10 MeV electrons. The detailed results of these experiments are summarized in Table VI. Similar effects were experienced in the United Kingdom [13].

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[1] The *G* value is the number of molecules produced for 100 eV absorbed.

2.3.2. Alteration of physical properties

Experiments carried out in the UK [14] show the influence of the type of bitumen on the degree of swelling. When oxidized bitumen (Mexphalt R85/40) is gamma irradiated, the radiolytic gases cause mechanical tension resulting in pore formation or cracks and easier gas release. In samples of distilled bitumen (Mexphalt M35), the pore formation is more difficult and a bubble growth model, which considers gas formation, coalescence of gas into bubbles and gas escape, can be applied. The resulting swelling is plotted against the total dose in Fig. 1, whereas the visual effect of swelling for the two irradiated bitumens is shown in Fig. 2.

Further observations on the swelling tests conducted in the UK [15] confirm the validity of this bubble growth model and stress that the swelling is much less important on a full scale drum than with small samples, especially when oxidized bitumen is used. Similar French experiments [16] confirm that swelling is important for distilled bitumens when gamma doses exceed 2 × 10^6 Gy. However, oxidized bitumen does not show a volume increase for gamma doses up to 2 × 10^8 Gy.

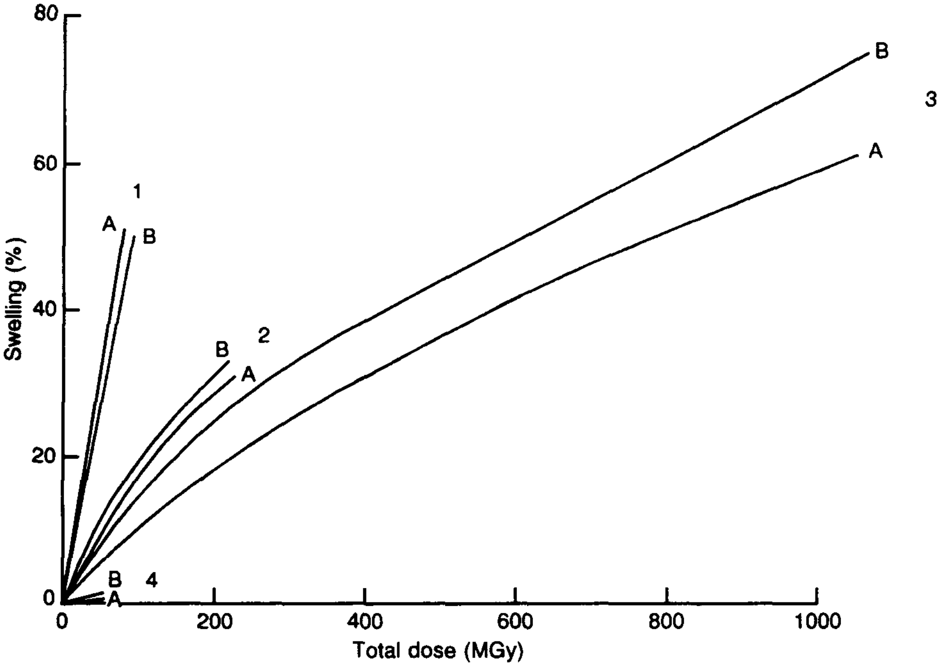

FIG. 1. Swelling of unfilled bitumens at different dose rates and with different specimen shapes and sizes. Curves A are for Mexphalt 35 and curves B are for Mexphalt R85/40. 1, material in 5.6 cm diameter open top canister at 5.5 kGy/h; 2, 2 cm diameter, uncontained, right cylinder at 4.4 kGy/h; 3, 3 cm, uncontained, right cylinder at 6.5 kGy/h; 4, 2 cm, uncontained, right cylinder at 0.93 kGy/h [14].

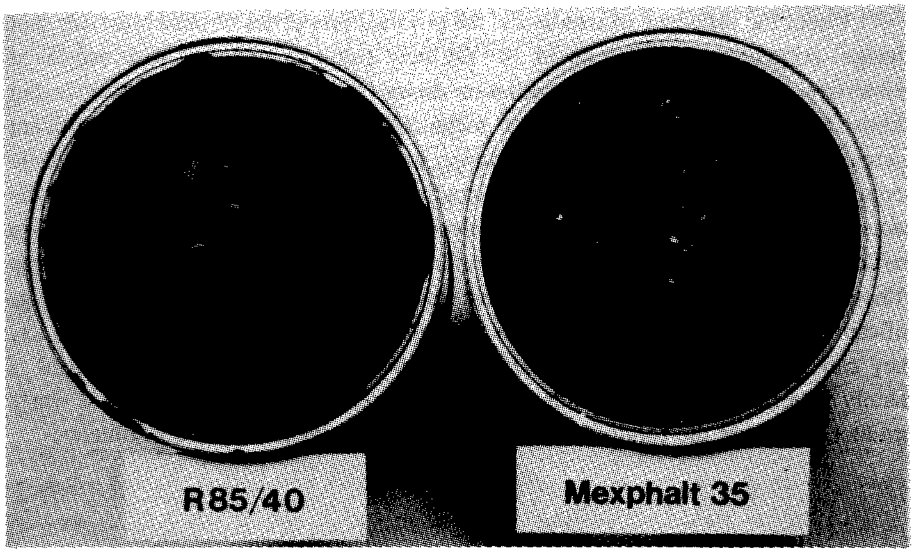

FIG. 2. The appearance of specimens of unfilled, (a), R85/40 and, (b), M35 after irradiation [14].

TABLE VII. EFFECT OF GAMMA RADIATION ON SOFTENING POINT AND HARDNESS OF MEXPHALT 35 AND R85/40 [14]

Bitumen	Mexphalt 35		Mexphalt R85/40	
	Softening point (°C)	Penetration[a]	Softening point (°C)	Penetration[a]
Manufacturer's specification	51–62	28–42	80–90	35–45
Unirradiated	55.5	37	95.5	31
Total dose, 0.54 MGy	59	29	101	31
Total dose, 2.16 MGy	60	23	109.5	28
Total dose, 10.50 MGy	91	15	124	14

[a] Penetration: 0.1 mm per 100 g and 5 s at 25°C.

Under the influence of irradiation the physical properties of pure bitumens will change. Irradiation of up to about 10^6 Gy may result in products with improved properties, whilst at very high irradiation doses ($>10^7$ Gy) not only bitumen but almost all polymers are converted to technically useless materials. A significant increase of the softening points of bitumen and consequently of their viscoelastic properties takes place at total integrated irradiation doses exceeding 0.5 MGy. At the same time a decrease of the penetration depth occurs, demonstrating an increase in hardness. Table VII presents experimental data demonstrating these radiation effects. The presence of solid or solidified inorganic waste components does not significantly worsen the radiation stability of bituminous materials nor improve it; i.e. they can act as a kind of inert diluent. The amount of radiolytic gas produced is mainly governed by the percentage of bitumen contained in the bituminized waste product, provided the product is free of water and organic waste constituents.

2.4. LONG TERM BEHAVIOUR OF BITUMENS

The tendency of bitumens to age under the influence of atmospheric conditions has been known for a long time. Ageing is influenced by several factors, such as the presence of impurities in the air or in the water in contact with the bitumen, the nature, state and amount of incorporated solids and the radiation effects. Two additional factors need to be considered:

(a) Reactions with materials coming into contact with bitumens (for instance aqueous solutions and backfill materials),
(b) Possible biodegradation of bitumens.

The general conclusion to be drawn from available data on the reactions of bitumens with materials that contact them under storage and disposal conditions, is that the important bitumen properties are affected only at and near the surface of the product and are not modified in a way that would endanger their functions as protective coating materials [4]. The ability of bitumens to resist attack from different chemical solutions suggests that they may show a good resistance against the less aggressive aqueous solutions and against the various solid materials occurring in nature and in waste repositories.

As to the possibility of biodegradation, the following relevant elements can be deduced from the available literature [3, 4, 17–20]:

(1) Microorganisms, which are widely present in nature, are capable of attacking bitumens under aerobic and most probably also anaerobic conditions.
(2) The speed at which microbes attack asphalt is very slow. Under optimum growth conditions a thickness of about only 0.025 mm of bitumen was found to be affected after 3 years.

TABLE VIII. IMPORTANT PROPERTIES OF BITUMEN–WASTE MIXTURES IN THE VARIOUS WASTE MANAGEMENT PHASES [4]

Property	Waste management phase[a]			
	Solidification process	Interim storage	Transportation	Long term storage
Ageing				++
Burning point	++	++	++	+
Burning rate	++	+	++	+
Cold resistance		++	++	++
Compressive strength				++
Content of solids	++	+	+	++
Density	+		+	
Dose rate	++	++	++	++
Effect of microorganisms				++
Flashpoint	++	++	++	+
Gas generation		++		++
Homogeneity	++	+	+	++
Ignition point	++	++	++	+
Leaching		+	+	++
Penetration		+	++	+
Phase separation during burning	++	+	++	+
Plasticity			++	+
Porosity		+	+	++
Radiation stability		++		++
Shock resistance		+	++	+
Softening point	++	++	++	++
Specific activity (α,β,γ)	++	++	++	++
Swelling (due to radiolysis)		+	+	++
Swelling (due to water)		+	+	++
Thermal conductivity	++	+	++	++
Thermal expansion	+	+	++	++
Viscosity	++	+		+
Water absorption		+	+	++
Water content	+	+	+	++

[a] +, important;
++, very important.

TABLE IX. PROPERTIES OF BITUMENS USED IN SOME BITUMINIZATION FACILITIES

Bitumen types	10/20	20/30	40/50	80/100	R85/40	40/60	BND 60/90	Pioneer 312
Application[a]	CH		B(Batch) F(Sa) S(Ba, Fo) SU	F(LH,M)	B(Ext) J(T)	J(M)	SU(TFE)	USA
Type	Distilled	Distilled	Distilled	Distilled	Oxidized	Oxidized	Oxidized	Oxidized
Softening point, (°C) (ring and ball)	67–72	59–69	52–60	41–51(M) 38–53 (LH)	80–90	53	47	88–93
Penetration 0.1 mm per 100 g and 5 s at 25°C	10–20	20–30	44–50	70–100(M, LH)	35–45	42	66	20–28
Flashpoint (°C)	>290	>275	>220	>230(M) 295–315 (LH)	>250	270	280	>288
Density (g/cm^3)	1.03–1.06	1.02–1.07	1.03	1(M) 1–1.05 (LH)	1–1.05			
Ignition point (°C)	>400			>300(M) 340–350 (LH)				

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[a] B, Belgium.
CH, Switzerland.
F, France:
LH, La Hague;
M, Marcoule;
Sa, Saclay.
J, Japan:
M, Mihama;
T, Tokai.
S, Sweden:
Ba, Barsebäck;
Fo, Forsmark 1,2,3.
SU, former Union of Soviet Socialist Republics
USA, United States of America.
Ext, extruder.
TFE, thin film evaporator.

(3) The exposure conditions would have to remain in the range of the optimum for a long time to produce any noticeable damage.

(4) The probability that microorganisms destroy bitumens appears extremely small. The demonstrated stability of naturally occurring bitumens over millions of years is the fact that corroborates this conclusion.

2.5. BITUMENS USED IN CONDITIONING PROCESSES OF RADIOACTIVE WASTES

When selecting the bitumen best suited to meet the requirements for a bituminization process, a series of bitumen properties are generally considered and assessed. As a guideline, to be appraised in relation with the applicable national rules, a compilation of such properties is presented in Table VIII, together with an initial assessment of their importance.

In general, the incorporation of solid matter into bitumen causes a considerable decrease of the penetration depth and of the ductility of the bitumen with increasing solids content. Furthermore, significant increases of the softening point and the flashpoint result from this incorporation. As these changes in physical properties affect both the operating conditions of the bituminization process and the product characteristics of the bituminized waste, a careful selection of an appropriate bitumen has to be made, which best meets the particular requirements. Representative incorporation tests and analytical measurements are mandatory to achieve this selection.

A large variety of bitumens are commercially available, which is reflected in the choice of bitumen types for radioactive waste bituminization in various technical facilities as can be concluded from Table IX.

3. TYPES OF RADIOACTIVE WASTES SUITABLE FOR IMMOBILIZATION IN BITUMEN

Radioactive wastes arise from all nuclear activities. Current practice indicates that some low and intermediate level wastes from nuclear power plants, fuel reprocessing plants and nuclear research establishments can be embedded in bitumen. However, this does not exclude the future use of bituminization for wastes that are diverse in their chemical composition from other nuclear activities and other types of waste from nuclear power plants, fuel reprocessing plants and nuclear research establishments. Several bituminization processes are available but not every waste type can be bituminized because of factors such as the form (solid waste), adverse chemical compositions affecting safety or the product quality as well as subsequent radiation damage to the matrix material.

TABLE X. CHARACTERISTICS OF TYPICAL CHEMICAL PRECIPITATION SLUDGES

Source	Physical characteristics			Chemical characteristics			Radioactivity content	
	Nature	Density	Dry solids content (wt%)	Composition	pH	Nuclides	β–γ (GBq/m^3)	α (GBq/m^3)
Nuclear power plants	Flocculated suspension	1.01–1.05	2–6	Metal oxides, hydroxides and filter aids	7–9	Activation products, fission products	20–100	negligible
Fuel reprocessing facilities	Thickened colloidal or flocculated suspension	1.1–1.2	10–20	Metal oxides, hydroxides, sulphates, ferrocyanides, etc.	7–9	Activation products, fission products, transuranics	500–30 000	3–200
Nuclear research establishments	Thickened colloidal or flocculated suspension	1.1–1.2	10–20	Metal oxides, hydroxides, sulphates, ferrocyanides	7–9	Activation products, fission products, transuranics	1–4 000	0.1–50

To minimize radiation damage it is desirable to limit the total radiation dose to 10^7 Gy. Waste streams for which this requirement is not a limitation include the arisings from power reactor purification processes, such as filtration, precipitation, ion exchange and evaporation, which result in sludges, slurries and concentrates. Nuclear power reactor wastes contain activation products like ^{60}Co and fission products such as ^{137}Cs.

Intermediate level liquid wastes from fuel reprocessing plants can have beta-gamma radioactivity concentrations of up to 4 TBq/m^3 with high salt contents (nitrates). These wastes are also alpha contaminated and may contain organic compounds such as tributyl phosphate (TBP) and its degradation products. Depending upon the research and development programmes carried out at nuclear research establishments, their wastes are a combination of the above mentioned waste types.

3.1. SLUDGES AND SLURRIES

Removal of the radioactivity from liquid waste streams by chemical precipitation and flocculation is a widely applied treatment process [21]. This process generates sludges with concentrated radioactivity contents and it has been practised at major European research establishments in Belgium, France and the UK, at reprocessing facilities in France, and at some nuclear power plants [22–24].

The purpose of this treatment is to process large volumes of radioactive liquids and to generate a small volume of waste concentrate. The treatment involves adding small quantities of non-radioactive chemicals to the waste volume to form insoluble precipitates with which the radionuclides can be fixed either by co-precipitation or adsorption. With the use of this treatment 90 to 98% of the radioactivity can be removed from the liquids. The sludge is then concentrated by filtration, centrifugation or settling. The dewatered sludges generated contain solids concentrations of between 1 and 20 wt%. Each treatment process depends upon the radioactivity level of the waste effluent stream, the type of radionuclides and the decontamination factor required.

In general, to fix radionuclides into insoluble compounds, preference is usually given to:

(a) Ferrocyanides (Ni, Co, Cu) for caesium and cerium;
(b) Barium sulphate for strontium;
(c) Metal hydroxides (Cu^{2+}, Fe^{2+}/Fe^{3+}, Ti^{4+}) for the alpha emitters ruthenium and antimony [21–23, 25].

Typical sludge characteristics are outlined in Table X.

While the radioactivity may be removed efficiently, the sludges produced are often gelatinous, or do not flow freely and may cause difficulties in transfer for the bituminization process. Steps have to be taken to make the transfer easier, by using

TABLE XI. CHARACTERISTICS OF SPENT ION EXCHANGE MATERIALS

Typical properties	Organic		Inorganic, granules
	Beads	Powder	
Particle size (mm)	0.6–1.8	<0.3	1–3
Particle density[a] (g/cm^3)	1.0–1.3	1.1–1.2	1.2–1.4
Water content after draining (wt%)	40–60	50–80	5–20
Type of ion exchanger	Mixed anion/cation or mixed bed	Mixed anion/cation	Cation
Typical contaminants			
Chemical	Corrosion products, borates, chlorides, carbonates	Corrosion products, chlorides	Carbonates, Na ions
Radioactive	Activation products, fission products	Activation products, fission products	Fission products (Cs, Sr)
Specific activity (GBq/m^3)	370–37 000	<400	3.7–37 000

[a] True density range: the effective density range is between 0.6 and 0.9 g/cm^3 and the pore volume about 40 vol.%.

specifically designed equipment, e.g. stirrers, agitators and air pulsing systems [26, 27].

A number of precautions should be taken to prepare sludges for bituminization:

(1) The pH of the water associated with the sludge should be neutral or slightly alkaline: the range of values should be between 7 and 9. High alkalinity facilitates oxidation of the bitumen and can cause hardening and product discharge difficulties [28].

(2) When sludges contain both sodium nitrate and unhydrolysed ferric nitrate the latter should not exceed 1 wt% in the sludge. Above this limit the thermostability of the bitumen product is lowered and, if ignited, can rapidly burn out. The iron has a catalytic effect on the burning rate [27].

(3) The concentration of TBP or of its decomposition products in the final sludges should be minimized and should not exceed 1 wt%. Excess amounts of TBP cause a lowering of the bituminized product flashpoint and can enhance oxidation reactions in combination with sodium nitrate; in general the recommended value is the solubility limit.

(4) Provisions should be taken to prevent the presence in the feed of strong oxidizing compounds, such as potassium permanganate or MnO_2 originating from this in decontamination solutions, which can give rise to spontaneous exothermic reactions; or to prevent these reactions by means of suitable chemicals and additives, such as oxalic acid, which destroy oxidants. Otherwise the product can become hard and thermal investigation and ignition tests indicate rapid and powerful exothermic reactions [4, 11].

(5) Granular filter aids (no fibrous materials, e.g. Fibre Floc) should be used for sludge filtration prior to incorporation into the bitumen. The fibrous material can become matted together and impede discharge from the bitumen equipment [4, 11].

(6) Appropriate mixing has to be provided to prevent high density solids (e.g. $BaSO_4$) from settling in the slurries.

3.2. ION EXCHANGE MATERIALS

The spent ion exchange materials generated throughout the nuclear industry are predominantly organic resins, either beads or powders, but there is some use of inorganic materials. Many applications are for coolant purification by ion exchange and for filtration of primary and secondary circuits of pressurized water reactors (PWR), of moderator and primary coolant circuits of pressurized heavy water reactors (PHWR) and feedwater and coolant purification for boiling water reactors (BWR). Some resins in use at power reactors are regenerated while others are used only once and then discarded. The characteristics of spent resins are provided in Table XI [1].

TABLE XII. CHARACTERISTICS OF TYPICAL LIQUID CONCENTRATES

Sources[a]	Physical characteristics		Chemical characteristics			Radioactivity	
	Density (g/cm^3)	Dry solids content (%)	Major cations	Major anions	Organic compounds	Beta-gamma specific activity (GBq/m^3)	Radionuclides
PWRs	1.1-1.35	5-25	Li^+, Na^+	BO_4^{3-}	Detergents, decontamination agents	3–400	$^{58-60}Co$, $^{134-137}Cs$, ^{125}Sb, ^{54}Mn, $^{110}Ag^m$
BWRs	1.1-1.30	10–30	Na^+, Cr^{3+} Fe^{3+}	SO_4^{2-}, Cl^-	Detergents, decontamination agents	3–40	$^{58-60}Co$, $^{134-137}Cs$, ^{125}Sb, ^{54}Mn, ^{55}Fe
Fuel reprocessing facilities	1.4	≤50	Na^+	NO_3^-, CO_3^{2-} SO_4^{2-}	TBP and degradation products	400–40 000	^{106}Ru-Rh, ^{144}Ce-Pr, $^{134-137}Cs$, ^{125}Sb, ^{60}Co, ^{90}Sr-Y, alpha trans-uranics, $^{239-241}Pu$
Nuclear research establishments	1.1-1.3	5-30	Na^+, Ca^{2+}, etc.	SO_4^{2-}, NO_3^{4-}, PO_4^{3-}	Citrates, oxalates, EDTA[b], complexing agents, detergents	40-1000	^{137}Cs, ^{54}Mn, ^{60}Co, ^{90}Sr-Y, alpha transuranics

[a] All concentrates are one mixture of solutions with suspended solids.

[b] EDTA, ethylenediaminetetraacetate.

Inorganic resins are used in the water cleanup system of fuels and in fuel storage ponds, e.g. at Windscale [21]; they are generally aluminium silicate structures such as chabazite or clinoptinolite.

Anionic organic ion exchange resins release amines during the bituminization process [11, 29]. However, chemical or thermal adjustments to the operating procedures can minimize volatilization. Of greater importance is the damage reported to the product as a result of water uptake by dehydrated resins. Research has shown that the product swells as the resin reabsorbs water and expands [30]. Tests performed indicate that this is a problem only with fully dried resins with a loading in excess of 50% of the bituminized product weight [4]. It has been reported that when the resin is not fully dried that some residual water ($\simeq 5$ wt%) left in the beads prevents observable swelling in immersion tests. Bitumen product swelling with high resin loadings has raised concerns within a number of Member States, although loadings of up to 40 wt% do not appear to cause detrimental effects to the product [31]. Additional possibilities exist in the partial destruction of the resin or its loading with multivalent cations (Ba^{2+}, Ca^{2+}, etc.) before incorporation into bitumen to prevent subsequent water uptake [32]. Swelling is discussed in more detail in Section 5.3.4.2.

Density differences between ion exchange resins and bitumens as well as high water contents can cause severe mixing and foaming problems upon bituminization. In this respect, the extruder process offers more flexibility (Section 4.1.2.1).

3.3. LIQUID CONCENTRATES

Liquid waste concentrates resulting from effluent evaporation are generally characterized by large concentrations of inactive soluble salts and a low suspended solid content. Some concentrates are kept heated to prevent crystallization. New techniques to decontaminate large volumes of liquid waste resulting also in liquid waste concentrates include membrane applications in reverse osmosis, ultrafiltration and electrodialysis [22].

The primary waste sources for liquid concentrates arise from nuclear power plants, such as water from primary and secondary circuits, from fuel reprocessing facilities, such as solvent washing, acid recovery and decontamination processes, and from research centres, such as research reactor operations, laboratory facilities and auxiliary services. An example of the characteristics of the concentrates from these wastes is presented in Table XII.

For a concentrate to be suitable for bituminization, appropriate pretreatment steps are often needed to ensure the following:

(a) The pH of the concentrate should be in the range from 7 to 9 [26].

(b) Corrosive anions should be precipitated, e.g. fluoride as CaF_2 to prevent damage to the processing equipment [4].

(c) Compounds that decompose exothermically should be converted, e.g. ammonium nitrate to sodium nitrate [26].

(d) Loading of organics such as TBP or its degradation products should not exceed 1 wt% of the solubility limit; organic complexing agents and detergents can be destroyed by oxidation with H_2O_2 [1].

(e) The presence of significant amounts of hardening agents such as nitrates, chlorides and sulphates of aluminium and iron should be avoided. Precipitation as hydroxides is an adequate pretreatment.

(f) Catalytic agents, e.g. ferric chloride or aluminium chloride, should not exceed 1 wt% in the concentrate. Precipitation as hydroxides is an adequate pretreatment.

(g) The amount of hygroscopic substances such as sodium carbonate, sodium sulphate or sodium orthophosphate should be kept under 10 wt% in the bituminized waste product or converted with barium or calcium to non-hygroscopic insoluble compounds.

(h) Limits should be imposed on complexing agents in order to minimize their effect on the leaching rates.

Moreover, it is recommended that the waste feed be analysed for the detection of highly exothermic compounds by differential thermal analysis (DTA) and by differential scanning calorimetry (DSC). In the event that unstable compounds are registered, ignition tests should be carried out on bituminized products prepared in the laboratory [26]. This issue is discussed more thoroughly in Section 4.3.1.2.

3.4. INCINERATION ASHES

Solid waste arisings that can be incinerated from nuclear operations include:

(a) Bagging and sheeting materials;

(b) Protective clothing made of various plastics, rubbers, textiles, papers and leathers;

(c) Packinging materials of cardboard, paper, wood and plastic;

(d) Cleaning materials including rags, tissues and mops;

(e) Filters of textile, glass, cellulose or mineral fibre.

The burning of wastes in incinerators results in a significant reduction of the volume, an inert oxide product containing a few wt% of carbon, and concentration of the radioactivity in the ash [33]. Unless the wastes have been sorted prior to incineration, one of the difficulties with ash handling is the wide variability in size and the presence of metals. To prevent mechanical failures of the bituminization equipment, ash particle segregation must be applied. Encapsulation of incinerator ashes into bitumen has been contemplated [34]. At present no significant application of such methods has been reported.

3.5. OTHER SOLID MATERIALS

An example of solid materials that might be considered for embedding in bitumen are non-combustible wastes, which could be cut or shredded to provide some volume reduction. The limitations on the use of bitumen include:

(1) A total integrated dose to the bitumen not exceeding 10^7 Gy;
(2) Adequate embedding of the waste materials by the appropriate operating conditions (temperature, bitumen type, etc.) during the filling operation;
(3) Ensuring that materials are not pyrophoric or will not ignite when contacted with molten bitumen (120–160°C).

4. IMMOBILIZATION PROCESSES: OPERATIONAL AND SAFETY ASPECTS

Research and development efforts within a number of Member States have led to the construction and operation of full scale industrial plants for the incorporation of radioactive wastes into bitumen, some examples of which are presented in Table XIII [2,8, 35–39]. The objective of this section is to discuss in generic terms the processes available for the bituminization of both liquid and solid wastes. As a beginning, the various bituminization processes for solid and liquid wastes can be classified into batch and continuous processes (Fig. 3). A batch process is usually considered for processing an identified quantity of wastes to produce packages of conditioned wastes, within a given time period, while continuous processing suggests an operation to treat constant waste streams without stopping the process equipment. In any event the outcome of either type of processing is the same, to condition the waste and obtain a solid product suitable for long term storage and eventual disposal.

One of the critical areas in a bituminization system is the correct adjustment of the waste. As discussed in Section 3, there are a number of adjustments the waste solution may have to undergo before it can be added to the bitumen. Depending on the chemical composition of the waste, pretreatment may or may not be an extensive feature of the facility.

The choice when considering either a batch or continuous process depends on individual criteria such as the volume of wastes to be treated, time restrictions, limited waste storage capacities, space availability and process economics. In Section 4.1 bituminization of liquid and wet wastes is described, while bituminization of solid and predried wastes is covered in Section 4.2. In the subsequent sections of this report, generic system descriptions are provided giving guidelines for batch or continuous process applications. Examples of the facilities operated in some Member States are presented in the Annex.

TABLE XIII. BITUMINIZATION PROCESSES USED IN SOME COUNTRIES

Country	Origin of wastes	Type of process
Belgium (Mol)	Miscellaneous reprocessing	Batch Continuous extrusion
Germany (Karlsruhe)	Miscellaneous	Continuous extrusion
France (La Hague)	Reprocessing	Continuous extrusion
(Marcoule)	Reprocessing	Continuous extrusion
(Saclay)	Miscellaneous	Continuous thin film evaporation
Japan (Tokai)	Reprocessing	Continuous extrusion
(Mihama)	NPP[a]	Continuous thin film evaporation
(Tsuruga)	NPP	Continuous thin film evaporation
Sweden (Barseback)	NPP	Continuous thin film evaporation
(Forsmark-1, -2)	NPP	Batch
(Forsmark-3)	NPP	Batch
Switzerland (Goesgen)	NPP	Continuous extrusion
Former USSR	NPP	Continuous thin film evaporation

[a] NPP, nuclear power plant.

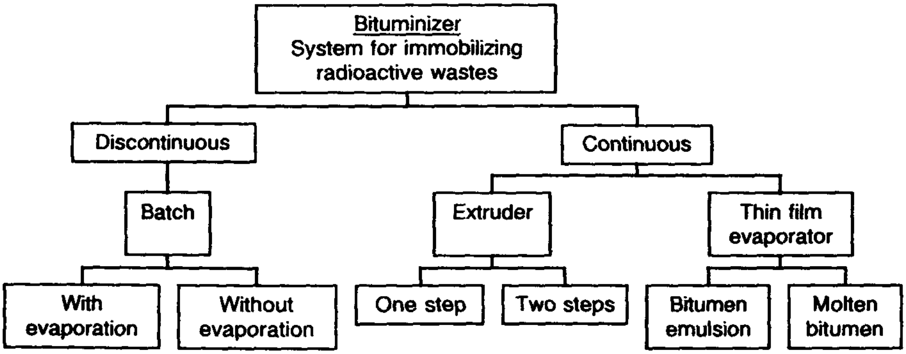

FIG. 3. Classification of bituminization systems.

4.1. BITUMINIZATION OF CONCENTRATES FROM LIQUID WASTES

Concentrates from aqueous wastes comprise evaporation concentrates, spent ion exchange resins, filtration sludges, sludges from chemical precipitation and concentrates from membrane processes. Bituminization of these wastes after appropriate pretreatment requires mixing with molten bitumen at elevated temperatures to evaporate water and to coat residual waste components with bitumen. The end product should be homogeneous as it cools and solidifies. Table XIII provides information about the bituminization processes used in various countries.

4.1.1. Discontinuous processes (batch processes)

Batch processes are applicable to various types of liquid wastes and sludges [40–43]. In general terms, wastes are continuously introduced into a known volume of molten bitumen with the mixture maintained at temperatures ranging from 180 to 200°C. The water is evaporated and the remaining solid particles are incorporated into the bitumen. After a predetermined amount of wastes have been added to achieve the required waste form composition, the feed is stopped. The process continues until the residual water has been evaporated and then the mixture is discharged into containers and allowed to cool. A general schematic diagram of this process is shown in Fig. 4.

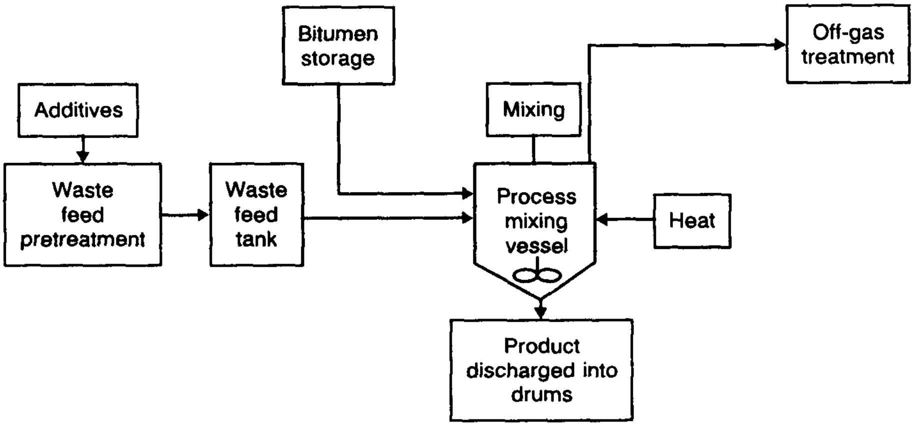

FIG. 4. Simplified diagram of a batch bituminization process.

General requirements for the waste pretreatment and/or feed tanks usually include the following equipment:

(a) A sampling system to ensure that feed quality is within set standards;
(b) An in-tank stirrer to ensure that a homogeneous sample can be extracted and to assure complete mixing of additives and slurry content as required to establish a homogeneous feed quality;
(c) Liquid level and temperature measuring systems;
(d) Connections from the chemical addition reservoirs to the ventilation system and to the process mixer.

Additional or optional functions are:

(e) To enhance mixing through the use of a recirculating pump;
(f) To transfer liquid to a backup tank in the event of leakage;
(g) To provide a preheated waste solution to the process mixer and reduce the heat transfer necessary to bring the slurry or sludge to dryness in the process mixer.

As the feed quality is of primary importance, and as the waste loadings must not be exceeded, both the bitumen feed rate (or the total volume introduced to the mixing vessel) and the waste solution feed rate must be well metered and controlled.

The bitumen storage tank should not be large. If it is unreasonably large, then either the cost to keep the bitumen molten may affect the economics, or the time to bring the bitumen from a cold solid to a pumpable liquid may be unreasonably long. In addition, a long residence time may adversely affect the quality of the bitumen (Section 2.2.7). The bitumen storage facility should be equipped with a recirculation and filtration system, a level indication and possibly an inert cover gas system to minimize the oxidation of the bitumen if it is maintained in a molten state.

The design of the heated feed line to the process is important in preventing blockage during transfer. If possible this line should drain into the process equipment and the number of valves should be limited. The line should be heated with steam or hot oil. Direct electrical heating may lead to local overheating and subsequent coke formation.

The heat supplied to the process mixing vessel must be limited to prevent the mixture temperature from approaching the flashpoint of bitumen. Control can be maintained by limiting the temperature of the heating medium (steam or hot oil systems). Direct electrical heating should not be applied.

The mixing of wastes and bitumens is critical for two reasons. First, sufficient agitation must be imparted to the mixture to release the water vapours. The thermal conductivities of bitumens are low and to ensure adequate heat transfer between wastes and bitumens, efficient mixing must take place to prevent localized cooling and poor product characteristics. Second, without sufficient agitation the mixture will become non-homogeneous. Sedimentation of waste particles can result in the coating of the inner wall of the vessel and in a further reduction of heat transfer.

Sedimentation also gives rise to a non-uniform distribution of waste particles throughout the bitumen. In this case, the waste product would not meet the expected quality objectives. The mixing device or stirrer must be capable of handling the increase in viscosity as the solids content increases in the bituminized wastes.

Waste particles of light density also result in mixing problems. Strong shearing forces providing vortex formation are recommended to overcome the flotation of, for example, ion exchange resins (Section 3.2). Possible foaming should also be taken care of through proper waste feed control and engineering provisions such as foam breakers in the mixing vessel.

The off-gas system removes evaporated water from the waste solution and also oil vapours released from partial distillation of the bitumen. The decontamination factors (DFs) realized for batch systems are dependent upon the evaporation rate, the use of de-entrainment devices in the vapour outlet and on the radionuclide composition. If the evaporation rate is high, usually through a combination of high operating temperatures and high feed rates, a significant release of entrained droplets can take place causing poor DFs. However, good design can bring the DFs of the system up to 100 or more [8]. Because there is partial distillation of the bitumen, oil is expected to be found in the condensate. Concentrations of up to 6000 mg of oil per kg of condensate have been reported [37] but, with proper separation equipment in the vapour discharge line, this concentration can be lowered to less than 1000 mg [44]. It should also be recalled that the correct choice of the bitumen type affects the fraction of distilled oil.

The mixing vessel should be designed to prevent local overheating and cold spots (e.g. crystallized waste salts on the off-gas exit point). This phenomenon is caused by temperature fluctuations. Incrustation may lead to lower evaporation rates and to a higher water content in the final product.

Although a large number of specific design criteria have to be considered, batch processes are generally of simple construction and satisfactory operability. Batch systems normally operate in the evaporation capacity range of 0.05 to 0.1 m^3/h [1, 2, 8, 37].

Batch bituminization systems for concentrates from aqueous wastes were the precursors of the continuously operated systems that will be described in Section 4.1.2. Some industrial batch facilities are installed in nuclear power plants, because of their efficiency and their capability for processing small amounts of different radioactive wastes.

4.1.2. Continuous processes

In this section, the main characteristics of continuous bituminization processes are described. The term 'continuous' refers to that part of the process where the waste stream at a constant flow rate is mixed with a constant flow rate of bitumen, resulting in a constant flow of final product to be poured into the appropriate containers.

The processes that are considered here are extrusion and thin film evaporation.

4.1.2.1. Extrusion

General process description. The extrusion process is applicable to a wide variety of wastes such as evaporator concentrates, sludges from precipitation, slurries of powdered or bead resins and diatomaceous earths from filtration. The essential components of extrusion processes are given in Fig. 5 and comprise:

(1) Waste feed equipment, including pretreatment units for, e.g., precipitation and insolubilization of radionuclides, to improve the chemical compatibility with the bitumen matrix and partially dewater the waste;
(2) Bitumen storage and feed equipment;
(3) The extruder itself, where the waste is mixed with the bitumen and the water is progressively evaporated;
(4) The off-gas cleaning to condense the water vapour and separate organic fractions that may volatilize from the bitumen during the residence time in the extruder. It also includes filtration of the non-condensable off-gas fraction;
(5) The filling station of the final product drums.

Extruders for bituminization have been developed from conventional plastic extrusion equipment. Since 1965, when the first extruder started up at the Commissariat à l'énergie atomique (CEA), Marcoule (France), numerous extruders have

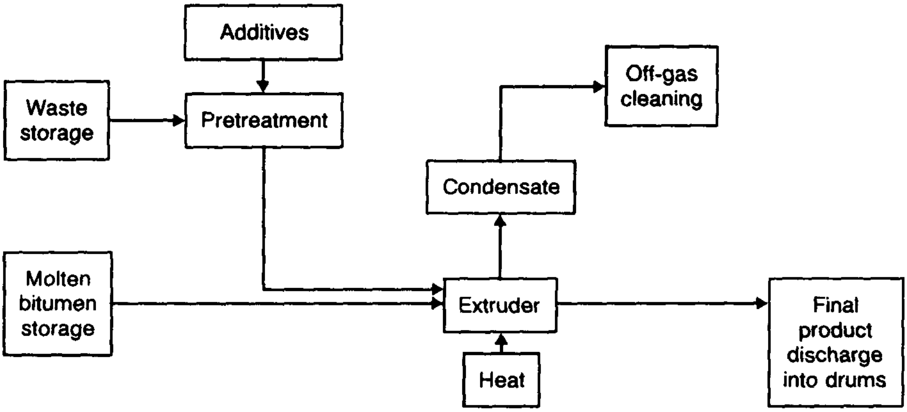

FIG. 5. Simplified diagram of an extrusion process.

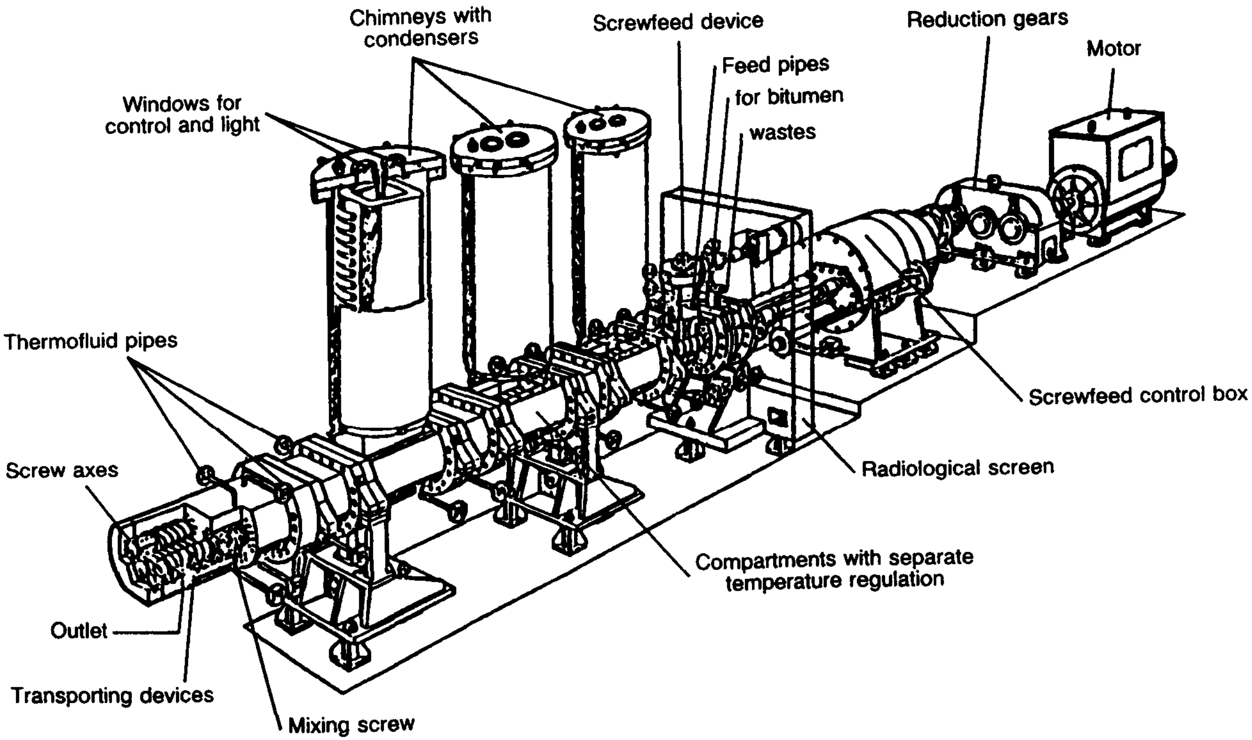

FIG. 6. General view of a typical extruder. (Courtesy of C. Courtois and A. Saas, Commissariat à l'énergie atomique, France.)

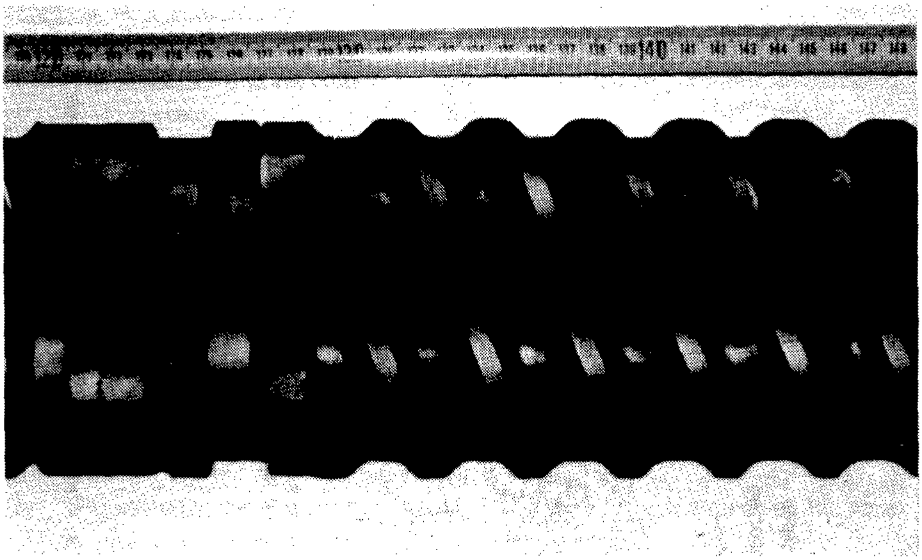

FIG. 7. Details of extruder screws. (Courtesy of C. Courtois and A. Saas, Commissariat à l'énergie atomique, France.)

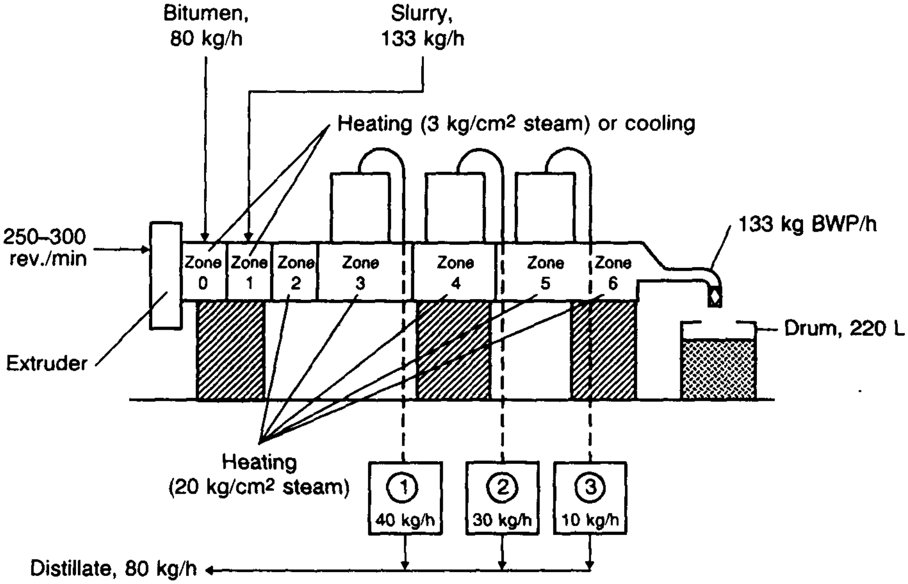

FIG. 8. Flow sheet showing an example of the extruder heating zones. The bitumen–waste product (BWP) has the following characteristics: bitumen, 60 wt%; solids, 40 wt%; water, ~0.5 wt%; density, ~1.35 t/m^3; radioactivity, <37 GBq/L; product volume, ~200 L. The distillate contains the following: oil, ~0.4 g/L; NO_3^-, 100 mg/L; NO_2^-, 50 mg/L; solids, 20 mg/L. (Courtesy of I. Mergan, Belgoprocess, Belgium.)

been installed worldwide for the bituminization of different concentrates from liquid waste treatment facilities at various nuclear power plants, in reprocessing facilities and different nuclear research establishments.

The extruder has two or four co-rotating horizontal screws, which consist of shafts fitted with kneading, mixing and conveying sections, that alternatively homogenize and convey the bitumens and the wastes through the extruder until the discharge point is reached. The feed materials (bitumens and wastes) enter the extruder, where they are immediately combined by the mixing action of the intermeshing screws. Figure 6 shows a general view of a typical extruder and Fig. 7 shows details of the extruder screws. The screws are housed in close fitting barrels, which make up the extruder housing.

The required heat to evaporate the free water in the waste feed and to maintain a sufficiently low viscosity of the bitumen is usually provided by steam through outer jackets located in the extruder body. Figure 8 presents a typical bituminization flow sheet showing an example of the particular heating zones of the extruder. A proper temperature profile along the length of the extruder is thereby maintained to provide adequate evaporative capacity and to yield a predetermined residual total moisture content in the product. Under normal operating conditions the moisture content is about 1 wt%. Depending on the required product quality, the highest acceptable moisture content reported is 5 wt%.

During the evaporation, water vapour and small amounts of the lightest oil fraction of the bitumen leave the extruder via steam domes and are strained in condensers. The distillate is returned to the liquid waste treatment system when it contains a trace of radioactivity, the amount of which depends upon the radiological and chemical compositions of the liquid waste and the pretreatments that have been applied to it.

A separation unit is generally installed to remove oil entrainment from the distillate. Non-condensible gases from the distillate receiver and ventilation air from the system are processed with a conventional high efficiency particulate air (HEPA) filter system. A Teflon coating of the evaporator domes and water spray devices may prevent incrustations of the steam domes.

Since the discharge of the liquid bituminized waste mixture is continuous, the filling station located at the end of the extruder must include a positioning system to allow for subsequent filling, cooling and closing of the final packages (usually steel drums). The filling of the drums is carried out in two or more steps to allow for shrinking and minimizing the inclusion of air bubbles. The drums are completely cooled (about 24 hours) before closing for transport and storage operations. Owing to a possible evolution of radiolytic gases, a non-gastight drum closure has to be provided.

Practical operating experience. The experience gained so far with extruders for the immobilization of radioactive wastes is based upon more than 150 000 operating hours and over 20 000 m^3 of wastes that have been processed [45]. Extruders are used especially in the following specific cases:

(a) Large volumes of effluents and wastes,
(b) High activity contents (more than 10 GBq/m^3),
(c) Large contents of soluble and insoluble salts in the concentrates.

Bituminized waste products resulting from extruder processes normally satisfy all the safety requirements for reprocessing facilities.

TABLE XIV. CHARACTERISTICS OF BITUMENS

Distilled or straight bitumen	
Softening point (°C)	38 to 72
Penetration	10 to 100 (0.1 mm per 100 g in 5 s at 25°C)
Flashpoint (°C)	220 to 315
Storage and transfer temperature (°C)	120 to 160
Blown or oxidized bitumen	
Softening point (°C)	80 to 90
Penetration	35 to 45 (0.1 mm per 100 g in 5 s at 25°C)
Flashpoint (°C)	>260
Storage and transfer temperature (°C)	140 to 160

TABLE XV. FIELD OF APPLICATION OF BITUMINIZATION IN EXTRUDERS

Nuclear installation	Waste type			
	Evaporator concentrates	Spent ion exchange resins	Filtration sludges	Precipitation sludges
Nuclear power plants	×	×	×	
Reprocessing plants	×		×	×
Research establishments	×			×

Two types of bitumen are commonly used for the bituminization in extruders, as can be derived from Table IX. The main characteristics of these bitumens are given in Table XIV.

The radioactive wastes that are currently processed in extruders are low and intermediate level wastes, the characteristics of which are described in Section 3.

The field of extruder applications to the various waste types is summarized in Table XV.

Most of the extruders in use today are one step units. In some particular cases, two units in series have been operated to increase the evaporation capacity. The same effect can be obtained by filtration or by partial water evaporation of sludges prior to feeding them to the extruder. A double stage extrusion process has been operated in Marcoule, France [6, 38], whereas a rotary dryer has been inserted upstream of the extruder in the former USSR [8].

The extruders are almost always installed as a fixed item of equipment, although a mobile bituminization plant using an extruder has been reported [46].

The throughput of the extruders is determined by the evaporation capacity. With the extruders available at present, the evaporation capacity ranges between a few tenths of a kg/h for small scale equipment up to 230 kg/h. The throughput of final product depends on the dry solids content in the slurry feed (see example shown in Fig. 8). The rotating speed of the screws is variable within the range of 30 to 300 rev./min.

The operational speed is usually between 100 and 250 rev./min. The bitumen feeding and bituminized waste discharging temperatures are generally kept below 175°C. As already indicated, appropriate temperature profiles can be adjusted along the extruder. The oil content of the off-gases is generally 0.05–0.1 wt% of the bitumen fed to the system [1].

The bitumen–waste mixture leaving the extruder normally has a residual water content of less than 2 wt%. This mixture is poured into the containers, which are usually 210 or 220 L drums [47]. The filling station of the drums often comprises a turntable system with four to nine drum positions, depending upon the sequence of filling and cooling.

Since the radioactivity concentrations of the various waste types that are currently being bituminized can be relatively high, especially in the case of concentrates or sludges from liquid reprocessing wastes, the extruders and the radioactive components of the auxiliary equipment need provisions for shielding. The external dose rates in contact with the final packages may range between 0.05 and 10 Gy/h. The existing extruder units are mostly remotely operated and are installed in shielded cells [26, 39].

The entrainment of radioactivity in the water vapour depends upon several parameters, among which the radionuclide composition and the applied pretreatment of the wastes are the most critical ones. The available operating experience shows that DFs of up to 6000 have been obtained [48].

Depending upon their hardness, the immobilization of salts and precipitated solids may lead to abrasion of the screw elements, particularly with high contents of diatomaceous earths. Wear of the screw elements due to abrasion has been measured at the EUROBITUM facility of the reprocessing plant at Mol in Belgium of the European Company for the Chemical Processing of Irradiated Fuels (EUROCHEMIC) after 5050 h of operation [49, 50]. Since the exchange of screw elements is an operation requiring direct contact of personnel with the equipment, a thorough decontamination of the extruder and surrounding equipment must be carried out to minimize the occupational doses [50]. Two factors facilitate this operation: the use of solvents and the fact that the holdup volume of bitumen-waste mixture in the extruder is limited to about 0.03 m^3.

4.1.2.2. Thin film evaporation

General process description. Thin film evaporation is the alternative bituminization process for the continuous immobilization of liquid wastes, i.e. concentrates, sludges, slurries and spent ion exchange resins (Fig. 9).

The five essential components of a thin film evaporation process for bituminization are identical to those given in Section 4.1.2.1 for extruders:

(1) The waste storage with chemical or physical pretreatment and feeding equipment;

(2) The bitumen storage and feed equipment;

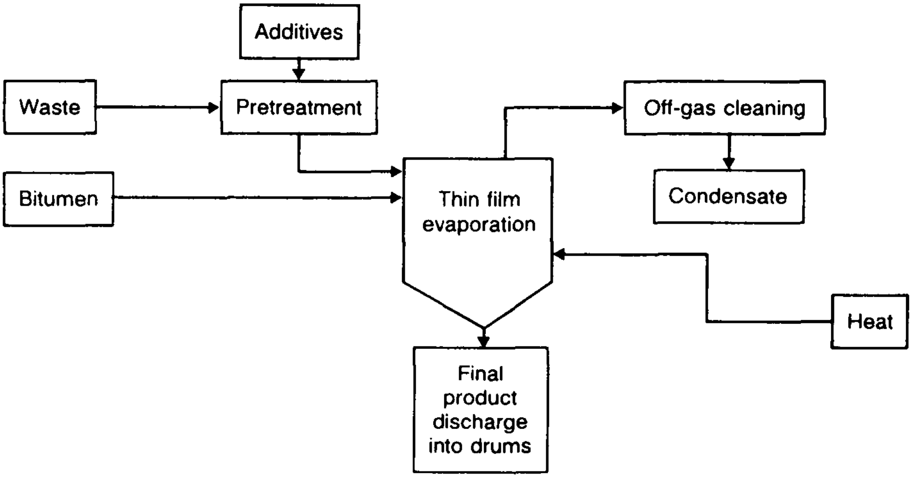

FIG. 9. Simplified diagram of a thin film evaporation process.

(3) The thin film evaporator, where the waste is mixed with bitumen while evaporating the water;
(4) The off-gas cleaning system for condensing the evaporated water together with the oil fraction and for processing any non-condensibles;
(5) The filling station for discharging the bituminized product into drums.

With the exception of known thin film evaporation processes in India [51] and the former USSR [52], all continuous thin film evaporation applications for the immobilization of wastes are based upon the use of LUWA thin film evaporators. This type of equipment was first applied in a bituminization process developed by the CEA at Saclay and Cadarache in France during the early 1970s.

There are fewer thin film evaporator units for the bituminization of liquid wastes than extruders; however this technology is commercially available and in use at both nuclear power stations and at nuclear research centres [8, 53–55].

The thin film evaporator is a heat transfer device consisting of:

(a) A vertical, cylindrical, heated surface to vaporize the water from the liquid waste feed;
(b) A high speed rotating set of blades.

The blade tips have a clearance with the inner wall of about 0.5 to 1 cm and rotate at speeds of up of 10 m/s. The rotational speed is between 600 and 1200 rev./min, depending upon the physical size of the evaporator. The speed decreases with increasing rotor diameter. The tight clearance between the blade tips and the heated surfaces permits the wastes and bitumen to be strongly agitated and provides a high heat transfer coefficient (1300 $W \cdot {}^{\circ}C^{-1} \cdot m^{-2}$).

The liquid wastes are fed at a controlled rate into the top section of the vertical evaporator. Liquid bitumen is simultaneously metered into the evaporator through a second feed nozzle located diametrically opposite the bitumen feed port. The evaporator is heated countercurrently by a heating medium, typically steam or hot oil, circulated through an external jacket. As both the waste and bitumen are fed into the evaporator, the blades of an internal rotor spread the two streams into a thin, turbulent film against the heated surface wall. The action of the rotor blades and gravity create a spiral flow of the waste–bitumen mixture. As the mixture flows downwards through the evaporator, water is evaporated and the vapour flows countercurrently upwards and leaves the top section through a mechanical entrainment separator.

Most entrained liquid droplets are removed from the vapour stream and are returned by gravity to the thermal processing section of the evaporator. The cleaned vapour passes to the condenser. Any non-condensibles from the condenser are discharged into the exhaust air system for further processing. The distillate will require further treatment to remove the oil carried over to the condenser, and the residual radioactivity carried through the separator, as liquid droplets from the evaporator. A schematic view of an LUWA thin film evaporator is presented in Fig. 10.

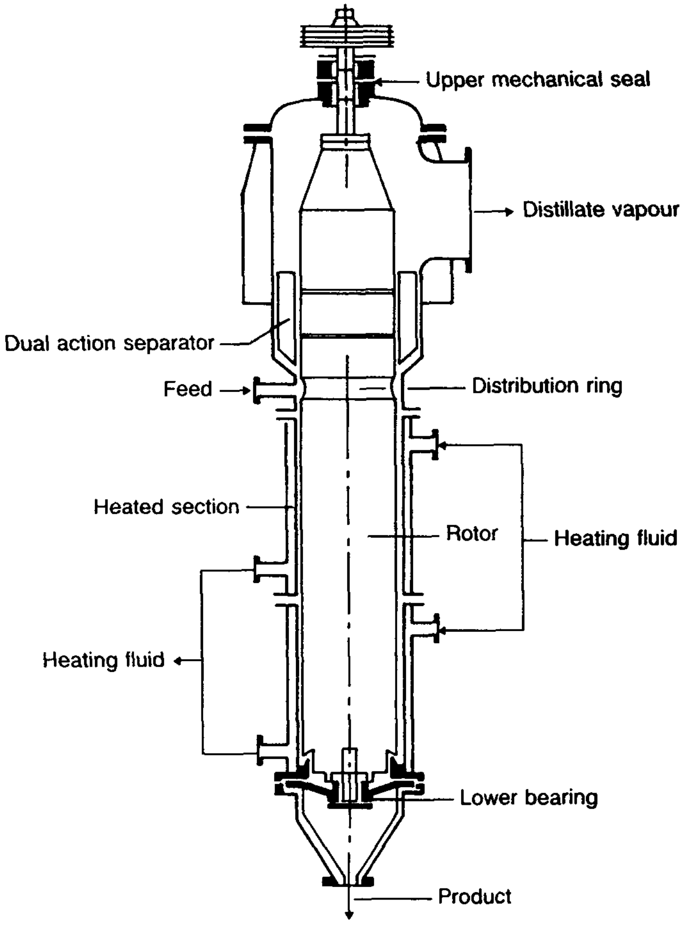

FIG. 10. Vertical LUWA evaporator. (Courtesy of C. Courtois and A. Saas, Commissariat à l'énergie atomique, France.)

At the bottom of the evaporator a discharge system allows the bituminized waste product to flow into containers, which are usually drums of 220 L capacity. Since the process is continuous the filling station must allow for the positioning of the drums to collect the bituminized waste product, to allow cooling and hardening of the product and to permit the non-gastight final closure of the drums.

While the above description applies to stationary applications, the thin film evaporation process can also be carried out with a mobile unit. An example of such a unit is presented in Ref. [56].

Practical operating experience. The first LUWA thin film evaporator system operation began in 1971 at the Cadarache Nuclear Research Centre, France, followed in 1975 by the first unit operating in a power station at the Swedish Barsebäck nuclear power station. Since then the process system has achieved about 500 000 operating hours and over 2000 m^3 of bituminized wastes have been produced in nine stationary units and in one mobile unit, that have been in operation since 1983.

The bitumens used in thin film evaporator units are:

(a) *Distilled bitumens,* with softening points between 45 and 65 °C and flashpoints between 220 and 280°C — storage temperatures of the bitumen are between 120 and 130°C;

(b) *Blown bitumens,* showing low softening points at about 60°C and flashpoints of 225°C;

(c) *Emulsified bitumens,* in which the bitumen feed is a mixture of straight distilled bitumen, containing 35 to 45 wt% water, and 1 to 2 wt% emulsifying agents.

The thin film evaporator process is basically applicable to waste types similar to those described in Section 3, provided the solids content in the feed is below 20 wt%. In the case of filtered precipitation sludges, resuspension is necessary to permit their introduction into the top of the thin film evaporator, otherwise thin film

TABLE XVI. TYPICAL THROUGHPUTS OF WASTES IN LUWA EVAPORATORS WITH HEAT EXCHANGE SURFACES OF 2.0 m^2

Waste type	Raw waste feed rate to evaporator (m^3/h)
Bead resin, dewatered	0.11
Powdered resin, dewatered	0.11
Filter sludge, dewatered	0.10
EDTA steam generator, cleanup waste	0.18
12% boric acid evaporator, concentrates	0.20
20% sodium sulphate evaporator, concentrates (untreated)	0.16
20% sodium sulphate evaporator, concentrates (treated for swelling)	0.07

evaporators can treat the same wastes as are at present being processed in extruders. As for other bituminization processes, attention has to be given to the feed homogeneity and to potential foaming in the thin film evaporator.

Thin film evaporator installation and operating characteristics. The throughputs of LUWA thin film evaporators depend upon their heat exchange surface areas. Current operating units have surface areas of 0.5, 1.0 and 2.0 m^2. For the largest LUWA evaporator, which has a height of about 2.5 m and a diameter of 0.3 m, typical process rates are given in Table XVI. The velocity of the rotor blade tips is 8 to 9 m/s. The evaporator is heated with a recirculating heating oil system with an adjustable inlet temperature of 250 to 300°C. The temperature of the bitumen waste product can vary between 140 and 190°C and the evaporation capacity between 0.05 and 0.2 m^3/h.

Thin film evaporators operated in the former USSR [52] are larger in size and use steam as a heating medium. The reported data on evaporators with an evaporative capacity of 0.2 m^3/h, which were considered in the reference design of the bituminization facility for a four unit nuclear power plant with WWER-1000 reactors, are:

(1) Steam temperature, 170°C;
(2) Total height of evaporator, 6.3 m, with a diameter of 0.8 m;
(3) Rotational speed of rotor blades, 64 rev./min.

The low rotational speed of the blades in contact with the bitumen waste mixture reduces the efficiency of the unit. This change in operation requires larger heat exchange surfaces to accomplish the same throughput as the smaller LUWA evaporators. The discharge temperature of the bituminized waste leaving the evaporator determines the water content of the final product. Above 125°C the water content is less than 1 wt%, while operating the evaporator with a discharge temperature of 115°C will increase the water content to 10 wt%.

Since the bitumen waste mixture is carried down the vertical length of the evaporator by gravity, the increase in solids content raises the viscosity and may cause discharge difficulties for solids contents in excess of 50 wt%. Typical product solids contents levels to maintain the smooth operation of the thin film evaporator are between 30 and 45 wt%. At higher levels buildup of material on the blades and on the heat transfer surfaces limit productivity.

The entrainment of radioactivity in the vapour released during evaporation of the liquid wastes is chiefly dependent on the nature of the radionuclides, the concentration of the waste feed and the waste feed rate. Typical DFs where entrainment devices have been used are in the range of a few thousands [57].

Minimal routine maintenance is required for thin film evaporators. The major maintenance and repair items are the upper mechanical seal, the lower bearings and the rotor blades (Fig. 10), which should be serviced at least once a year.

4.2. BITUMINIZATION OF SOLIDS OR PREDRIED WASTES

Basically there are few bituminization processes that are solely devoted to the embedding of solids; i.e. bituminization processes without evaporation [37, 58, 59]. The processes are relatively small scale batch operations in which solid or predried wastes are introduced into a vessel containing molten bitumen and the two components are mixed to create a homogeneous product that is subsequently discharged to a container and allowed to cool. The production rates are from two to five 210 L drums per day; one drum usually being prepared at a time.

The processes have been applied to dried sludges in Austria [59] and the former USSR [8] to dried ion exchange resins in Finland [58] and to incinerator ash in Canada [33]. In each case the equipment used is somewhat different, e.g. an extruder, a conical mixer or a ribbon blender. Only the Austrian process relies entirely on sedimentation of solids in molten bitumen to achieve solidification. In general, mixing is required to allow wetting of the solid material with molten bitumen and to achieve a homogeneous product. The processes rely on weight measurements to achieve the correct ratio of wastes to solids (generally 1:1), either by weighing the wastes as they are transferred to the mixing vessel or by weighing the content of the mixer. The processes are quite simple to operate. The products are discharged to 210 L drums for subsequent storage after the content cools and the drums are capped. The mixing operation can be accomplished in one to two hours.The processes are vented to normal HEPA filter systems to remove fine particles of waste that become airborne during the transfer operation. The mixers are closed systems and therefore releases are limited to the filter systems. The operations can be easily handled by manual or remote manipulation.

When dealing with special pieces of solid waste or scraps, the latter can be packed into a metallic drum in which all voids are thereafter filled with molten bitumen to ensure proper embedding of the waste.

4.3. SAFETY ASPECTS OF BITUMINIZATION PROCESS OPERATIONS

4.3.1. Conventional safety

4.3.1.1. Storage of bitumen

As described in the previous subsections of this section, bituminization facilities use liquid bitumen as the matrix material for the embedding process. In the case the bitumen is not emulsified, the storage of significant quantities of bitumen requires heating the bitumen at temperatures that ensure a sufficiently low viscosity while still remaining sufficiently far below the flashpoint.

In practice the storage of heated bitumen is carried out in vented fully insulated carbon steel vessels with capacities ranging from 5 to 30 m^3. Heating bitumen to temperatures between 120 and 160°C (depending upon the viscosity and flashpoint) is done by means of steam or low power density electric coils. Because of the low thermal conductivity of bitumen, appropriate control provisions must be available to avoid local overheating of the coils and the formation of coke, which has even worse heat transfer characteristics.

A recirculation circuit with a filtration capacity, as well as an inert gas blanketing system, is highly recommended for the improvement of the storage conditions of the molten bitumen. The bitumen storage tank is usually installed separately from the components of the facility containing radioactivity and is equipped with an adequate fire protection system, e.g. CO_2 and heavy foam.

Fire fighting with water systems should not normally be considered. However, a well designed and controlled sequential water spraying system may provide, in successive steps with properly limited water volumes, the required cooling effect, avoiding undesirable foaming and scattering of the bitumen.

At the storage temperatures currently used and with the routine process control equipment, the conventional risks associated with the storage of bitumen are considered to be negligible.

A simplified diagram of a bitumen feed system is given in Fig. 11.

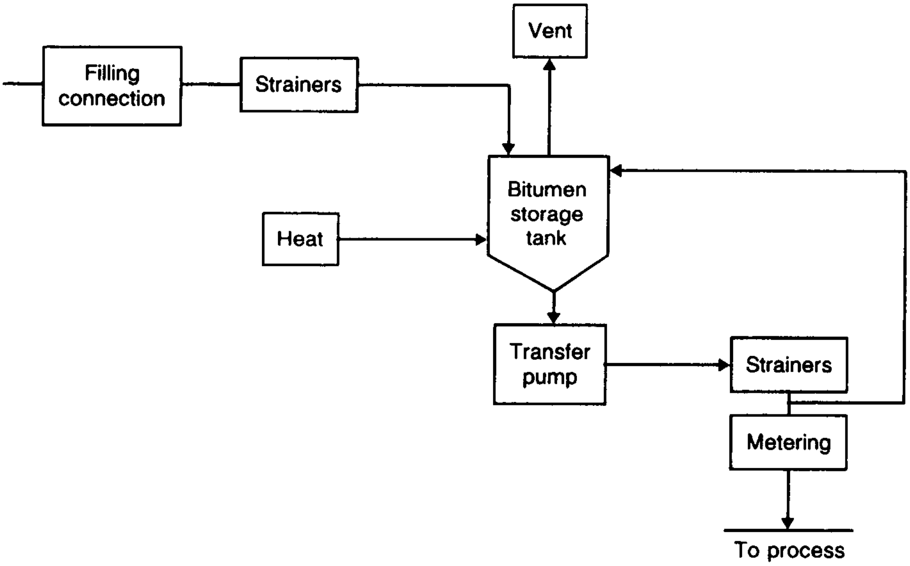

FIG. 11. Simplified diagram of a bitumen storage and feed system.

4.3.1.2. Analytical programme before processing wastes

As the immobilization of certain types of wastes into bitumen may not only involve the danger of ignition but also of explosion-like reactions, much attention has to be paid to the monitoring and the control of the concentration of these chemicals for the safe operation of bituminization processes.

In this respect, the waste concentrates from reprocessing plants, especially those containing nitrates and thermally unstable or volatile organic compounds, can be identified as a critical type of waste as well as concentrates of changing composition resulting from the evaporation of different effluents produced in nuclear research installations. In addition to $NaNO_3$, there are other chemicals giving rise to redox reactions such as MnO_2 and CoS_2, which can enhance the oxidation of bitumen with vigorous exothermic reactions. Moreover, compounds tending to decompose at elevated temperatures in exothermic reactions should be monitored.

Analytical methods such as DTA combined with evolved gas analysis (EGA) and DSC are considered to be reliable means for the detection of such compounds and/or the risk of corresponding uncontrolled exothermic reactions. These analyses are carried out on dried samples of batches that are to be bituminized. In this way the thermal behaviour of the sample residue is determined. Each recorded important exothermic deviation below 250°C is an indication of a heat producing reaction that can constitute a hazard when incorporating the investigated residue into bitumen. From the numerous investigations that have been performed on bituminized products prepared from pure $NaNO_3$ and $NaNO_2$ with blown bitumen (Mexphalt R90/40 or R85/40), one can conclude [26] that there exists no risk of a spontaneous exothermic reaction, provided that the bitumen–salt mixture contains at least 40 wt% bitumen, that the different salt constituents are homogeneously dispersed and that the temperature throughout the mixture is kept below 280°C. If the homogeneous dispersion of the salts cannot be assured, a minimum content of 50 wt% bitumen is required and the temperature at any point of the mixture should not exceed the flashpoint.

Similar thermal analyses on waste–bitumen mixtures may also be recommended — at least when the analytical results on the waste residues above reveal exothermic deviations below 250°C. The results will determine the appropriate bituminization conditions, e.g. the waste-to-bitumen ratio, and the operating temperature or the specification of an adequate pretreatment that has to be performed to eliminate the hazardous compounds (Section 3) and assure a safe bituminization of the waste batch.

The application of DTA in combination with EGA and/or DSC has been shown to be an effective and sufficient analytical programme to determine the feasibility of bituminization for non-routine wastes, especially those from reprocessing operations [26, 60].

Alternative analytical procedures to verify the chemical compatibility between bitumens and wastes are the determination of the flashpoint and ignition point on prepared samples [60, 61]. The lowering of these temperatures compared with those relative to pure bitumen indicates the level of hazard at the operating temperature of the bituminization process.

A valid analytical investigation programme before starting each bituminization campaign with new or undefined waste streams is therefore mandatory as an important safety provision and often a supposition for the acceptance of the bituminized waste product.

4.3.1.3. Temperature control and process interlocks

There is sufficient scientific evidence from all investigations, carried out on fire and explosion risks associated with bituminization processes, that at temperatures lower than the flashpoint these processes can be operated safely, provided that reasonable waste-to-matrix ratios are maintained and that uncontrolled exothermic reactions are excluded because of the appropriate waste pretreatment. In combination with the analytical programme described in Section 4.3.1.2, adequate temperature controls throughout the bituminization process and redundant process interlocks are important aspects when designing, constructing and operating bituminization facilities.

Typical equipment components that need to be interlocked are the metering pumps for the waste components and those for the bitumen. Other interlocks are to be installed between several temperature sensors and the heating system, in particular in the drum filling and cooling station.

4.3.1.4. Fire protection programme

The main objectives of a fire protection programme comprise at least the following:

(a) Fire prevention,
(b) Early and reliable fire detection,
(c) Efficient fire fighting,
(d) Limitation of fire extension,
(e) Limitation of consequent damage,
(f) Maintained operability of safety functions,
(g) No unacceptable radioactivity release or exposure.

Bituminization processes may involve the following combustibles [62]: the bitumen, the bituminized product, the decontamination liquids and, in some cases, the heating fluid.

The maximum operating temperature of the bituminization process should be set at least 50°C below the flashpoint of the bitumen being used. This temperature difference is adequate to prevent fires under most foreseeable operating conditions.

Ventilation is required not only for nuclear safety reasons but also to ensure the removal of any combustible volatiles that may be released from the bituminized products. In this respect, the most critical points are at the bituminized product outlet and at the drum filling and cooling stations, where extensive ventilation has to be provided. Other locations about which there is concern are the processing area where the mixing of wastes with bitumens occurs, and the venting system where volatiles may be collected.

At all the above locations, efficient fire detection systems have to be installed (smoke, temperature and flame detectors). Typical fire suppression involves [62] the deployment of the following systems:

(a) Carbon dioxide,
(b) Heavy foams,
(c) Halogen foam,
(d) Water sprays.

As already mentioned in Section 4.3.1.1 concerning water spraying, sequential sprays of properly limited water volumes have proven to be an efficient method of cooling and extinguishing that avoids undesirable mass foaming and spreading of the bituminized product, which would occur with large amounts of water. Furthermore, external cooling of the drum wall by water sprays has also been shown to be effective in abating exothermic reactions in the bituminized product contained in a drum [60].

4.3.1.5. Solvent cleaning precautions

In cases where decontamination of the equipment is required (maintenance, repair, etc.), appropriate procedures have to be strictly applied. An initial decontamination can be achieved by feeding pure water and/or bitumen to the process equipment.

When bitumen or bituminized products have to be removed, it is recommended to use non-flammable organic solvents. An example of a thorough decontamination and cleaning process of a screw extruder facility is presented in Ref. [50].

4.3.1.6. Reported incidents

Literature reviews have indicated information on only five operational incidents [57]. Three incidents have occurred at the Karlsruhe Nuclear Research Centre, Germany [29, 63, 64], in relation to a twin screw extruder process, two of them causing a fire.

The first incident occurred when vapours were ignited while a drum was being filled. Organic solvents in the waste concentrate caused the fire. Only one drum caught fire.

In the second incident, the evaporator concentrate had a pH of 13.8 and the agitation facility in the feed tank was not in operation, allowing organic components in the waste (TBP, degradation products, antifoaming agents) to separate. In this incident two drums caught fire and fumes, which were noticed to be escaping from the drums, ignited.

In the third reported incident, a newly filled drum was immediately sent to the storage cell, rather than first being cooled. Escaping fumes, later determined to be HCl from polyvinyl chloride (PVC) powder trapped in the bitumen product, triggered alarms. The result of packaging the 175 L drum in a reinforced 200 L shipping container before the drum had cooled down allowed the product to remain at an elevated temperature continuing the decomposition of PVC and the release of HCl, but no fire occurred.

Another installation that reported a fire was the bitumen plant at the United Kingdom Atomic Energy Authority at Harwell, which was decommissioned in the early 1970s [65]. The incident took place during commissioning of a batch bitumen–waste mixing unit provided with electric immersion heaters. When the fire occurred there was not sufficient bitumen to cover the electrical heaters completely and the agitator had tripped out. The temperature of the bitumen at the immersion heaters rose rapidly and the bitumen ignited. The surface fire on the bitumen only blistered the paint in the ventilation duct connected to the tank. The fire extinguishing system (CO_2) worked effectively and prevented further damage.

A fire on 15 December 1981 at the EUROBITUM facility of the EUROCHEMIC plant at Mol in Belgium was reported in Refs [66, 67]. The following facts associated with the incident are characterized and are described in Ref. [60]:

(a) Three drums of 220 L partially filled with bituminized waste product caught fire 8 h after being filled at intervals of 1 to 1.5 h. By means of CO_2 injection, light foam injection and water spraying, the fire was extinguished within a few minutes.

(b) The waste concentrate being processed was a non-standard mixture of bottom residues from a storage tank for evaporation concentrates containing TBP and its degradation products, decontamination liquors and recycled extruder distillate, containing bituminous oil and other volatile substances.

(c) The non-standard waste mixture, which had to be bituminized, was insufficiently known regarding its composition and thermal stability, because the prescribed analytical programme had not been carried out. Analytical controls performed thereafter on the waste mixture have demonstrated that the reference analytical programme (DTA, DSC) would have been able to identify the exothermic behaviour and avoid the incident.

With the exception of the Harwell incident, which was the result of a lack of equipment interlocks and the use of electric immersion heaters, all other known incidents were caused by the presence of organic materials in nitrate–nitrite concentrates and the incomplete analytical knowledge of the waste composition and its thermal behaviour. This underlines once again the importance of analytical investigations on the waste streams to define the appropriate process conditions guaranteeing a safe bituminization.

4.3.2. Radiation safety

4.3.2.1. General considerations

The radiation safety aspects that are of particular concern when dealing with bituminization plants are:

(1) Shielding and monitoring provisions to minimize occupational doses,
(2) Radiation monitoring,
(3) Prevention of contamination spreading in the process building,
(4) Protection against unacceptable activity releases under incident conditions.

Personnel radiation protection and radiation monitoring measures are comparable with those taken at all nuclear facilities. Contamination and unacceptable release aspects have to be examined taking into account the specific conditions of the bituminization processes. Additional requirements concerning alpha emitters also need to be carefully assessed.

4.3.2.2. Shielding

Since bitumen has a low density compared with cement or cement based matrix materials, the self-shielding effect of bituminized waste products is poor. On the other hand, the relatively high waste loading factors that can be achieved with bituminization may result in a considerable radioactivity concentration in the final product and significant radiation levels. The operating experience gained with waste concentrates and sludges from reprocessing plants shows that 220 L drums with contact dose rates in the range 2 to 10 Gy/h may be produced.

In the case of wastes from nuclear power plants, the activity levels are lower and the waste packages may have contact dose rates up to 0.5 Gy/h.

It is therefore important that a bituminization facility be designed and constructed to provide sufficient shielding of the different plant components. In the normal plant layouts, the waste storage and feeding components, the proper bitumen–waste mixing unit and the drum filling and cooling station are installed in separate cells to allow for maintenance without interference from adjacent radiation sources. For instance, concrete wall thicknesses of up to 105 cm have been provided at the EUROBITUM facility in Mol, Belgium [39], between the filling station and

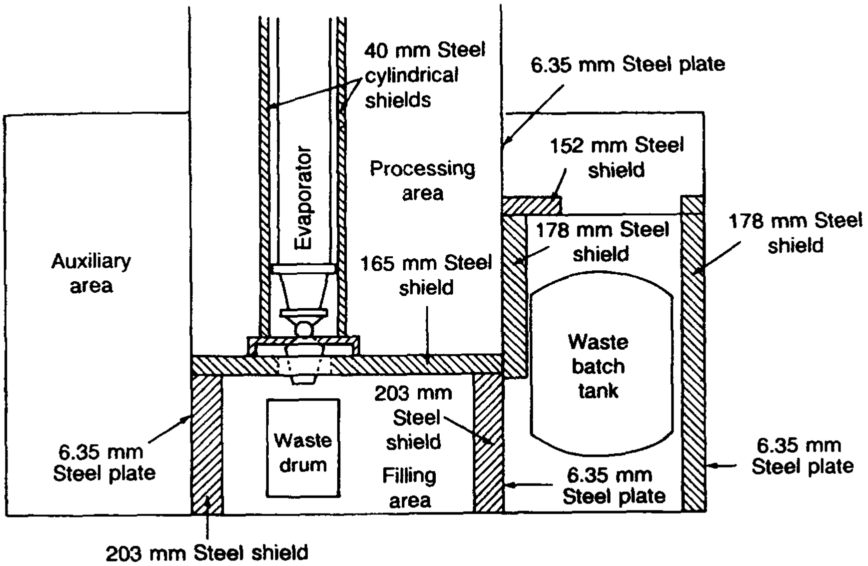

FIG. 12. Typical example of shielding arrangement (TVR-III) at Mol-Dessel in Belgium [53]. Shielding not shown to scale.

the control room. In the case of mobile bituminization plants, the shielding requirements depend upon the radiological characteristics of the waste to be processed in each individual campaign. The transportable volume reduction system TVR-III is equipped with shielding that is designed to allow for the processing of typical PWR and BWR waste types [53]. This shielding consists of steel plates, which are located around the waste feed tank, as well as the drum filling and loadout areas. This shielding is removed when transporting the system. In addition, the design allows incremental installation steps to cope with the activity level of the waste being processed. Figure 12 shows a typical shielding arrangement for the TVR-III system.

4.3.2.3. Contamination protection

The spread of airborne contamination is avoided by increasing the negative pressure levels inside the contaminated equipment and by a room ventilation system that ensures a draft from the areas with a lower contamination hazard to areas with a higher contamination hazard.

Vessel venting has to be provided for the waste concentrate storage vessel, the waste pretreatment system, the waste feed tank and the bituminization equipment.

A special venting system at the outlet of the bituminized waste products and the drums under filling conditions must also be provided.

Under normal operating conditions the risk of contamination in the cells housing the bituminization equipment and the drum filling and cooling station is negligible.

Possible contamination risks consequent to a fire incident have to be evaluated and adequate provisions made, e.g.:

(a) Efficient fire fighting means producing as little secondary wastes as possible,
(b) Provision of drip trays to collect sprayed or escaped liquids and bituminized waste products,
(c) Surface materials or coatings that are easy to decontaminate.

4.3.3. Conclusions on the safety aspects

From the above considerations the following conclusions can be drawn:

(1) Provided that the measures described on defined analytical controls of the wastes, on process controls and interlocks, on ventilation as well as on fire prevention are taken, the probability of occurrence of a fire during bituminization is extremely low and does not justify the level of apprehension associated with bitumen flammability.
(2) However, appropriate technical measures can be integrated into the facility at reasonable costs so as to minimize the possible consequences of incidents from the conventional as well as from the nuclear safety standpoints.
(3) All subject items dealt with in this section have to be assessed in the safety analysis of any bituminization facility.

5. PROPERTIES OF BITUMINIZED WASTE FORMS

As this report is a presentation of the state of the art and of good practice with respect to the bituminization processes in the management of radioactive wastes, it may also provide some guidance in preparing good performance specifications for all bituminized waste forms. The criteria can be qualified by suitable tests.

To begin the quantification of the quality control of bituminization processes, bituminized waste products must be subjected to specific tests that determine the ability of bitumen to provide a product suitable for disposal. It is essential that the products perform adequately during all phases of handling, storage, transportation and disposal.

In addition to the safety aspects, the effect of various wastes, and of the radioactivity contained in the wastes, on the properties of the bitumens is an important factor in determining if a bitumen is a logical choice as a matrix material. Of course, the requirements imposed by the storage facilities and by the disposal site shall influence the choice of the matrix material, the composition of the final waste form and its packaging.

To understand and control the bituminization process and to attempt to optimize the packaging, transportation, handling, storage and disposal options require knowledge of the safety issues and of the physical, chemical, physicochemical and radiological properties of the final waste form. Each of these topics is discussed below as it relates to bituminized products.

5.1. REQUIREMENTS FOR STORAGE, TRANSPORTATION AND DISPOSAL

The bituminization processes described in Section 4 result in final packages that are mostly metallic 220 L drums. After cooling, closure, radiation and contamination monitoring and identification, these final packages are ready for the subsequent steps in the management scheme: storage, transportation and disposal.

Depending upon the status of development of the radioactive waste management strategy in individual countries, on-site or off-site storage may be required while awaiting the availability of a disposal site. When the disposal site is available the packaged waste can be shipped directly to it.

A number of requirements, which relate to storage, transportation and/or disposal, need further consideration because of some of the typical characteristics of bituminized waste products. The purpose of this section is to identify these characteristics, which are described in more detail in Sections 5.1.1, 5.1.2 and 5.1.3, and to comment on the specific safety measures that they may require.

5.1.1. Storage of bituminized wastes

The mixing of wastes with bitumen causes an increase in the softening point and a decrease of the penetration and ductility of the bitumen. The mechanical stability of the end product, however, requires a containment vessel, that will maintain its integrity and quality during the expected storage period. The use of metallic drums, either galvanized carbon steel or stainless steel, with wall thicknesses of 1.0 mm or more, responds to this requirement and allows remote stacking of drums five to six high. Vertical storage of drums is mandatory to avoid any possible flow of the bituminized product outside of the drum.

During storage, swelling of the bituminized waste can be caused by the formation and accumulation of radiolytic gases, by retarded or low speed chemical reactions or by water uptake by salts. While in most cases the natural shrinkage of the bituminized waste after cooling allows sufficient space for such swelling, in particular cases, where a significant swelling may be expected owing to the characteristics of the waste, a reduction of the extent to which the drums are filled should be considered. Pouring a thin layer of pure bitumen on top of the bituminized waste product is also practised as a mean of coating and preventing water uptake.

The presence of radiolytic gases requires two specific actions. Firstly, the drums must not be closed tightly in order to avoid pressure buildup; in practice the cover lids are mechanically fitted to the drums by bolting or crimping the lid at a distinct number of points. Secondly, the buildup of hydrogen in the storage confinement (building or container) needs to be limited below the lower explosion limit for hydrogen in air (e.g. 4 vol.%). The rates of hydrogen generation under high radiation doses, however, are so low that the natural ventilation of civil engineering constructions due to atmospheric pressure variations is usually sufficient to evacuate the hydrogen. Forced ventilation can be installed so as to be almost certain of safe conditions [68].

Bituminized waste products containing up to 60 wt% wastes from the operation of reactor and reprocessing plants do not explode or detonate under storage conditions, nor do they burn if they are not heated above 300°C and an external ignition source is absent. These conclusions from relevant investigations, carried out in Germany, the former USSR and the USA [69–71], clearly indicate that bituminized waste products cannot be considered as the main fire hazard. Even at the usual maximum specific radioactivity levels, the decay energy cannot heat the bituminized waste product to such temperatures in a 200 L drum.

As discussed in Section 4.3 the bituminized low and intermediate level wastes require shielding provisions as a result of the low self-shielding capacities of bitumens (60% of the value of cemented wastes) and because of the high waste loading factors obtained. The retrievable storage concepts are complemented either by engineered constructions on or near the ground surface, or by shielded concrete casks, housing one or more drums, which can be placed in a light structure building. Examples of both practices are described in Ref. [1], showing that these techniques are well known and widely used.

5.1.2. Transportation of bituminized wastes

The basic requirements applicable to the transport of radioactive wastes are given in the IAEA Safety Standard, Regulations for the Safe Transport of Radioactive Material [72]. In implementing the provisions of these regulations, it may be necessary for Member States to issue complementary national regulations.

Available technology is adequate to meet the transportation requirements for low and intermediate level wastes. These wastes, including bituminized wastes, have been packaged and shipped routinely throughout the world for many years.

Typical safety aspects that relate to the transportation of bituminized wastes are:

(a) Presence of a sufficient amount of shielding to meet transport requirements,
(b) Requirements on dose rate and surface contamination limitations,
(c) Mechanical stability of the containment for the bituminized waste product,
(d) Behaviour of the conditioned wastes when incidents occur involving fire and/or explosion risks.

For bituminized waste drums with dose rates at contact exceeding the established limits on radiation levels, transportation in overpacks with capacities for one or more drums is currently carried out. Examples of typical arrangements for reusable transport casks are described in Ref. [72].

The mechanical resistance of the primary package with its contents against impacts has been studied in relation to transport safety. Tests have been carried out in Finland with 200 L drums filled with bitumen that have been dropped from heights of between 1.2 and 20 m [73]. From these tests it was concluded that reactor waste immobilized into bitumen and packaged into steel drums has a very high mechanical impact resistance. It is almost impossible to imagine an incident situation where a considerable part of the radioactive content could be released in dispersible form as a result of mechanical damage. The use of casks increases this mechanical resistance substantially.

Because of the relatively high flashpoint of bituminized waste products, it is impossible for a spontaneous fire to occur in a transport accident if an external fire source is absent. There exists no risk of explosion during transport. Experiments on the effects of fire on pure bitumen and simulated bituminized waste products in 200 L drums have been carried out. Other experiments have demonstrated that when concrete containers are used as shielding devices then protection against external fires [71, 74] is effective. Such a concrete overpack would be mandatory should the safety evaluation of an accident involving fire during transportation indicate that without such a shield, the release of contamination could exceed the tolerance level.

The safety assessments on the transportation by sea of bituminized waste products from Swedish nuclear power plants, [75], lead to the conclusion that the sea transportation system can be deemed to meet very high safety standards.

5.1.3. Disposal

The long term behaviour of bituminized waste products is of importance for the safety assessment of the disposal systems and the criteria for acceptance of the waste form in individual disposal sites.

Since bituminized radioactive wastes cover both alpha and beta-gamma emitters, the time span of concern may differ substantially between wastes from nuclear power plants and wastes from reprocessing or equivalent activities.

The bituminization of the wastes, aiming at the conversion of the wastes into a more stable form, their packaging and any additional engineering barriers used in the repository design, as well as the natural barriers of the actual disposal site, are important factors for isolating the wastes from the biosphere. The relative importance of the various barriers can be determined by a safety analysis of the total repository system and the pathways of the radionuclides back to man.

Depending upon the required quality of the source term, e.g. the bituminized waste radionuclides, other properties, which may need further consideration are:

(a) Radiation effects and stability,
(b) Thermal effects and stability,
(c) Dimensional and mechanical stability,
(d) Chemical stability,
(e) Long term sedimentation and homogeneity,
(f) Interaction with surrounding disposal media,
(g) Gas generation and effects,
(h) Leach resistance,
(i) Microbial stability.

5.2. PHYSICAL PROPERTIES

It has been suggested, and it is considered by a number of Member States, that the physical properties of an immobilized waste form are an integral part of a disposal system assessment. Some of the more important physical properties of bituminized waste forms that are relevant with regard to the bituminization process as well as to the storage and disposal are discussed in the following sections.

5.2.1. Waste-to-matrix ratio

Many references express the waste content in the final product as a weight percentage. It is to be remembered that several physical properties are influenced by the volume ratio between waste and matrix as well as by the size distribution of the waste particles. Since bituminization is a thermal process, most if not all of the water is removed leaving a dry waste in the final product. Solid particle loadings in a viscoelastic substance such as bitumen alter its viscosity. The viscosity will increase exponentially as the quantity of solid particles increases [76]. Waste loadings that are too high may have detrimental effects. First, an increase in viscosity could lead to discharge difficulties of the product by blocking the discharge. Second, and of more concern, are the difficulties expressed by a number of authors about the swelling of bituminized waste forms associated with water uptake, as noticed in leaching experiments [77–79]. This issue is described in more detail in Section 5.3.4.

5.2.2. Homogeneity

The homogeneity of a bitumen waste product is qualitatively defined by the absence of voids, bubbles, fissures and other product alterations as well as the absence of uncoated waste particles. Quantitatively, a bitumen waste product is homogeneous when the waste material and the radioactivity content are uniformly distributed, so that the results of chemical and radiochemical analyses of a random sample would not deviate from the required average chemical composition and reference radioactivity content in the specifications.

As an example, the specifications for near surface disposal in France [80] require that the deviation from the reference values should not exceed 25%. The level of homogeneity in the radioactivity can be measured by non-destructive gamma scanning of the packages or by destructive analysis of the samples. In the latter case, the sampling is carried out at a minimum of three levels in the package with three samples per level.

Homogeneity is dependent upon the intensity and duration of mixing, the ratio of waste to bitumen, the type of waste, the rate of water evaporation, the presence of emulsifiers, the scale of operation, the bituminization equipment, the type of bitumen and the process temperature. In general, inhomogeneity is caused by different sedimentation rates. The slower the mixing and the lower the evaporation rate, the larger is the size of the salt crystals and the probability of sedimentation. At high waste loadings or when there are more than two solid phases, e.g. cation and anion

TABLE XVII. CALCULATED MEAN SEDIMENTATION RATES FOR SALT PARTICLES EMBEDDED IN BITUMEN B15 [11]
(in units of mm/a)

Sample[a]	Temperature (°C)					
	30	40	50	60	70	90
1	4×10^{-4}	5×10^{-3}	3×10^{-2}	1×10^{-1}	6×10^{-1}	7.5
2	2×10^{-4}	3×10^{-3}	1×10^{-2}	5×10^{-2}	2×10^{-1}	4.3
3	3×10^{-4}	3×10^{-3}	2×10^{-2}	9×10^{-2}	3×10^{-1}	6.5

[a] Bitumen:salt weight ratio, 1:1; softening point range, 98°C — 100°C (ring and ball test); average salt particle diameter, 30 μm; salt particle density, 2.261 g/cm^3; bitumen density, 1.045 g/cm^3.

resin beads, which are different in density and size, inhomogeneity may result. It has been shown that, with the use of distilled bitumen, inhomogeneity will take place with a short mixing time [81].

For denser or larger particles, the downwards movement in molten bitumen may be accelerated with the use of a softer, less viscous bitumen. Since bitumen has a low thermal conductivity, it will take more than 24 h to cool a full 200 L drum (cooling rate is about 2°C/h). In this time period, phase separation could take place if the bitumen has a low viscosity. In general, this is one of the reasons that the high capacity bituminization units use drums mounted on a turntable and thus limit the amount of material poured into a container, allowing the product to cool down before adding more.

Inhomogeneity may lead to changes in various properties, such as increased leaching and modified microstructure of the waste bitumen product. These phenomena have been observed by comparing two products with different waste loadings, and with different homogeneities [82].

Taking into account the plastic behaviour of bitumens, the sedimentation phenomenon in the final products has been evaluated for storage and disposal conditions. Sedimentation rates can be calculated according to the Stokes formula [11, 71]:

$$W = \frac{(\delta_P - \delta_B)\, d_K^2 g}{18\eta}$$

where

W	is the mean sedimentation rate (cm/s);
δ_P	is the density of the incorporated particles (g/cm^3);
δ_B	is the density of the fluid phase, e.g. bitumen (g/cm^3);
d_K	is the diameter of the incorporated particles (cm);
η	is the temperature dependent dynamic viscosity (P), (g$\cdot$cm$^{-1}\cdot$s^{-1});
g	is the gravitational constant, 918 cm/s^2.

In Table XVII the mean sedimentation rates have been calculated as functions of the temperature for three simulated bituminized waste products containing 50 wt% bitumen B15 and salts (mainly $NaNO_3$) [11]. The viscosity of these products had been measured beneath the softening point as a function of the temperature at a low shearing stress. The bituminized waste products resulted from test campaigns in a screw extruder pilot unit, yielding homogeneously dispersed solid particles in the bitumen with a mean diameter of about 30 μm.

The results show that relatively low sedimentation rates were found; e.g. $W \leq 5 \times 10^{-3}$ mm/a for realistic storage temperatures up to 40°C. This corresponds to a sedimentation rate of at most 1 mm in 200 years, a rather small value. Experience shows that the calculated values agree reasonably well with the experimental findings [25, 71].

5.2.3. Density

The low density limits for final waste forms are usually prescribed with respect to final disposal.

The relative density of bituminized waste products varies from 1.06 to 1.1 for ion exchange resins, from 1.2 to 1.4 for concentrates and sludges, and from 1.4 to 1.6 for incinerator ashes.

5.2.4. Mechanical properties

The relevant mechanical properties are hardness and viscoelasticity. They are of importance during handling, transportation and storage of bituminized waste products to absorb mechanical impacts and to minimize loading stresses. These mechanical properties are influenced by the choice of bitumen, the type of waste and the waste loading factor. It has been observed that radiation can also alter the bitumen properties, generally making the material harder and less deformable [83].

The best known and most frequently applied procedure to determine hardness is the penetration test (Section 2.2.3). In general, the penetration value of a bituminized waste product decreases by a factor of 2 with respect to pure bitumen. As an example, the shallow land disposal requirements in France are for a maximum penetration limit of 6 mm [84]. For waste forms buried in shallow land in the USA the waste must exhibit a minimum unconfined compressive strength of 415 kPa as required by the appropriate specifications [85]. At this compressive strength, the deformation should not exceed 10% of the specimen height. An example of the change in compressive strength as a function of nitrate waste loading in oxidized bitumen is provided in Table XVIII [86].

Impact tests carried out involving free drops of 1.2 and 9 m indicate that bituminized waste products are resistant to deformation because of their plastic behaviour; packages dropped from 9 m did deform somewhat, but no dispersion took place. In addition to an application of a pressure of 70 MPa, hydrostatic pressure on properly manufactured bituminized waste products (40 to 50 wt% salts) indicates no damage. These tests were carried out in support of research on disposal at sea of low level radioactive wastes [83].

The bituminized waste product may in certain Member States be submitted to a wide range of temperatures, either during storage or transportation. The effects of thermal cycling could lead to a deterioration of the waste product performance or to possible dispersion in the event of a transport incident. At elevated temperatures some sedimentation might take place while at low temperatures the product might be brittle enough to break upon impact. Thermal cycling tests conducted to demonstrate that bituminized waste products are an acceptable waste form for disposal indicate that repeated cycling at temperatures between −40 and 60°C does not affect the waste form [86].

TABLE XVIII. COMPRESSIVE STRENGTH AT 10% DEFORMATION AS A FUNCTION OF WASTE LOADING IN BITUMINIZED WASTE PRODUCTS [86] *(bitumen: Pioneer 318; see Table IX)*

Sodium nitrate waste loading (wt%)	Compressive strength (kPa)
0	1720
41.6	2480
50.6	3520
60.2	4290

TABLE XIX. TYPICAL PROPERTIES OF BITUMINIZED WASTE PRODUCTS AT LA HAGUE, FRANCE [25]

Dry matter content in BWP[a]	40 ± 5%
Density at 25°C	1.33 to 1.45 g/cm^3
Penetrability at 25°C	40 to 60 (non-irradiated, see Section 2.2.3)
Softening point (°C)	45 to 60 (non-irradiated)
Flashpoint (°C)	260 to 270
Fire point (°C)	310 to 320
Flow threshold	1400 Pa at 40°C (non-irradiated), 50 Pa at 80°C
Viscosity for a flow speed gradient of 0.005 s^{-1}	2.7×10^6 Pa·s (20°C) 100 Pa·s (80°C, non-irradiated)
Specific heat at 30°C	1300 to 1400 J/kg
Thermal conductivity at 30°C	0.21 ± 0.01 W·m^{-1}·°C^{-1}

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[a] BWP, bituminized waste product.

5.2.5. Other physical properties

Other physical properties that may need consideration in one or more stages of the waste management scheme are:

(a) Ability to flow,
(b) Specific heat,
(c) Gas diffusion rate,
(d) Thermal conductivity,
(e) Softening point,
(f) Flashpoint and fire point,

Typical values for these properties of bituminized waste products from the La Hague bituminization facilities are listed in Table XIX [25].

5.3. CHEMICAL AND PHYSICOCHEMICAL PROPERTIES

This section deals with the most significant chemical and physicochemical properties required for the safe handling, transport, storage and disposal of bituminized waste products once they have been packaged and cooled. The compatibility of wastes with bitumens has been addressed in Section 2.2, but a complementary discussion is presented here in terms of the requirements for storage or disposal, since the product should remain stable for long periods to ensure the confinement of radionuclides.

5.3.1. Chemical compatibility of bitumens and wastes

Since volume reduction is a major concern in waste management, there is a tendency to maximize the waste loading without affecting the desirable properties of the final product. Evaluation of products should therefore be conducted to ensure that the quality limits are not exceeded, such as unacceptable leach rates, swelling and product stability.

It is well known that reprocessing wastes, containing sodium nitrates, can be easily mixed with bitumens to form homogeneous products. However, the potential of nitrates to oxidize organic materials at elevated temperatures has led to a limitation of the $NaNO_3$ loading in practical bituminization operations to about 40 wt%.

In addition to nitrates there are other chemicals that can enhance the oxidation of bitumens under certain conditions even in low concentrations, such as MnO_2, or which can adversely affect one or more of these properties. The concentration of such chemicals in the wastes must be known and controlled. Therefore, an appropriate analytical chemical programme must be applied before bituminizing the waste, as has been described in Section 4.3.1.2. This programme should lead to a valid definition of the waste loading limits as well as proper pretreatment and safe bituminization conditions.

In Table XX a survey of the main chemical components in radioactive wastes, their waste loading limits and their influence on the product characteristics are given. Limitations that apply to all wastes are as follows:

(a) pH range of 7 to 10 for liquid wastes before bituminization,
(b) Maximum temperature for processing equipment at most 180 to 190°C,
(c) Drum filling temperature in the range 115 to 140°C,
(d) Loading of containers at most 95% at room temperature.

Table XXI provides examples of practical requirements for the bituminization of reprocessing wastes in France [23].

5.3.2. Flammability

Data on the flammability of bituminized waste products are needed for safety assessments of possible fire incidents. Research efforts have mainly dealt with the consequences of a fire, and not with the mechanisms that could lead to an ignition. Bituminized waste products are flammable materials; however, the amount of external energy required to cause bituminized waste products to ignite or maintain a self-sustaining fire is the key issue for safety assessments in handling, transportation, storage and disposal.

Some bituminized waste products can be ignited below a temperature of 300°C [61, 71, 81, 87, 88]. If a fire is sustained, a substantial fraction of the radioactivity in the product container can be released [25, 89]. Nevertheless, once the bituminized waste product has been packaged and has cooled down it is incapable of self-ignition. Bituminized waste products are handled, transported and stored at ambient temperatures and, unless there is an external source of ignition, the waste product should not catch fire. For substantial external fires, it should be recognized, however, that the poor thermal conductivity of bitumens can lead to partial surface overheating and subsequent scattering of liquified bituminized waste products that might then be ignited. This possibility should be considered in the design and installation of fire protection equipment.

The fire risks must be placed in a proper perspective. Without the presence of flammable materials, fires will not arise in handling, transportation, storage or disposal. Perhaps the one scenario that must be considered is the event where there is a collision on a public road between a vehicle carrying a radioactive shipment and a vehicle having a large source of flammable material such as gasoline, diesel or propane. Otherwise, the risk of a flammable incident and loss of radioactivity can be considered unlikely. It should be recalled that transporting bituminized waste product drums in a concrete overpack provides an efficient protection against external fires (Section 5.1.2).

TABLE XX. CHEMICAL COMPATIBILITY OF WASTE COMPOUNDS WITH BITUMENS [25]

Waste material	Limit	Treatment or pretreatment required	Effects on BWP[a] in case of excessive loading
Sodium nitrate	Maximum loading 40 wt%	None	Salts released by leaching; swelling of BWP
Sodium sulphate	Maximum loading 40 wt%	Conversion to $CaSO_4$ is required when 40 wt% is exceeded	Swelling of BWP; excessive release of Na_2SO_4 by leaching
Borates	Soluble borates are not acceptable; maximum loading not to exceed 40–45 wt% as insoluble calcium borates	Conversion of soluble borates to insoluble Ca form	Swelling of BWP; excessive release of borates by leaching
Phosphates	Maximum loading 40–45 wt%	pH adjustment to slightly acidic conditions required, and/or conversion to insoluble alkaline earth forms	Swelling of BWP; excessive release of phosphates by leaching
Carbonates	Soluble carbonates are not acceptable; maximum loading not to exceed 40 wt% as $CaCO_3$	Conversion to $CaCO_3$	Swelling of BWP; excessive release of carbonates by leaching
Ammonium nitrate	Limit is not available as precautions are not allowed	Conversion to $NaNO_3$	Risk of exothermic reaction during bituminization if not destroyed
Oxidant accelerators	Limit should not exceed 1 wt% before conversion limit applicable for each conversion	Destruction of compounds by reduction in acid medium, etc.	Risk of exothermic reaction during bituminization if oxidants are not converted and accelerated oxidation of BWP without conversion

Reductants	Exact limit is not available: ≤1 wt%	Raise pH to 10, destroy by oxidation	Risk of exothermic reaction during bituminization without conversion and accelerated oxidation of BWP
Complexing agents	Not accepted by many storage requirements	Adjust pH from 8 to 9	Foaming during bituminization, radionuclide complex formation (excessive release by lixiviation)
Emulsifiers, soaps	Limit to 6 wt%	—	Foaming during bituminization (in case of effluent treatment, reduction of decontamination factors)
Organic liquids	Limit to 1 wt% or solubility limit	For non-water-soluble compounds (TBP, ...)	Causes lowering of flashpoint and viscosity; compressive strength reduction; risk of exothermic decomposition reaction
Sludges	Limit to 40–45 wt%	Adjust pH from 7 to 9	Operational difficulties (viscosity and homogeneity); possible swelling and separation of salts
Ion exchange resins	Limit to 40 wt%	Saturation of cationic and anionic exchangers, partial mechanical destruction	Swelling by hydration

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[a] BWP, bituminized waste product.

TABLE XXI. PRACTICAL REQUIREMENTS FOR BITUMINIZATION OF REPROCESSING WASTES IN FRANCE [23]

Parameters	Operating range
Ratio of bitumen to dry matter	≥1.00
Surfactant	1.5 to 2.5 wt% of dry matter
Nitrate content in liquid wastes	0.3 to 2N
Nitrite content in liquid wastes	0 to 200 mg/L
TBP	≤solubility limit
Hydrazine hydrate[a] (N_2H_5 mg/L)	0 to stoichiometric ratio + 10 mg/L
Sodium sulphide[a] (S^{2-} mg/L)	0 to 600
Cobalt sulphide[a] (Co^{2+} mg/L)	0 to 750
$Fe(CN)_6^{4-}$ (mg/L)[a]	0 to 600
Ni^{2+} (mg/L)[a]	0 to 200
Barium nitrate[a] (Ba^{2+} mg/L)	0 to 4500
Titanium sulphate[a] (Ti^{4+} mg/L)	0 to 300
Anionic flocculant[a] (mg/L)	0 to 30
pH	>7
Water content of slurry (wt%)	≥80
Diatomaceous earth content (wt% of dry matter)	0 to 15
Water content in the bituminized waste product (wt%)	<5

[a] To be applied per litre of liquid wastes.

5.3.3. Radionuclide releases by leaching

Leaching tests on bituminized waste products are performed to evaluate on a comparative basis how well the radionuclides are retained in the matrix and to provide information about source terms for the safety assessment of waste disposal systems. Since the publication of the last IAEA report on bituminization [2], there has been a concerted effort to standardize the leaching protocols to avoid using unique test procedures that make comparisons difficult. The Materials Characterization Centre [90] and the American Nuclear Society [91] have developed protocols that replace the leach tests proposed earlier [92, 93].

There are two additional aspects to be considered about leaching rate data in the literature:

(a) Different mechanisms, such as diffusion, dissolution or erosion, can proceed concurrently, so that their contributions to the overall release can change over time, at different temperatures, as a consequence of the chemical components encapsulated or possible chemical reactions, etc.

(b) The leaching test may not be indicative of the actual environmental conditions in the disposal facility (e.g. with regard to temperature and aqueous chemistry), nor does it take into account the role that other barriers may have to influence the rate of release of radionuclides from the package.

In general, the leaching tests developed are conservative in their approach and indicate the maximum release likely to occur in a disposal environment. The leaching rates may be considerably reduced in some specific site environments, such as those where there are saturated salt solutions or water that has been in contact, for instance, with clay or cement.

There is a significant amount of leaching data available in the literature on a variety of different bitumen waste products. Release rates span several orders of magnitude:

(1) From 10^{-8} to 10^{-5} $g \cdot cm^{-2} \cdot d^{-1}$ for actinides and rare earths,

(2) From 10^{-6} to 10^{-5} $g \cdot cm^{-2} \cdot d^{-1}$ for reprocessing waste radionuclides,

(3) From 5×10^{-6} to 5×10^{-3} $g \cdot cm^{-2} \cdot d^{-1}$ for alkali and alkaline earth metals [1, 94, 95].

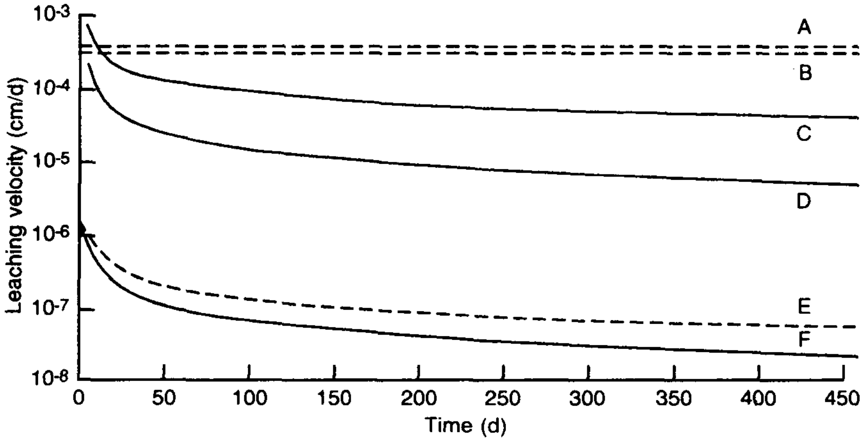

FIG. 13. Results of leach tests with BWP STE3 samples from La Hague with different sodium nitrate contents: ----, high $NaNO_3$ content, 2 mol/dm^3 BWP; ——, nominal $NaNO_3$ content, 0.5 mol/dm^3 BWP . A, D, Na; B, C, NO_3; E, F, Cs.

A number of studies indicate that the release of salts is dependent upon the waste loading and nature of the wastes [11, 86, 96]. As shown in Fig. 13, the salt leaching rate increases with the waste loading [97]. At the same time, while the release of salts may be substantial, the release of radioactivity may not change or remain at low levels, especially for radionuclides that have been converted to insoluble species as demonstrated in the case of ^{137}Cs in Fig. 13.

With excessive waste loadings, e.g. soluble salts or ion exchange resins beyond 50 wt% in the bituminized waste product, high releases occur as anticipated. The mechanism for release is no longer diffusion, but is linked to dissolution, which occurs when the product surface expands and ruptures from the excessive amounts of material incorporated in the bitumen.

Finally, the leaching of full scale samples indicates that the leaching results compared with small samples may be lower by more than one order of magnitude [98]. Leaching tests on small samples allow an easy comparison of different bituminized waste compositions. They are, however, in most cases conservative and the use of the results to evaluate full scale product behaviour requires validation. Realistic information about the long term stability of bituminized waste forms in contact with the leachants that most probably occur in final disposal facilities should provide a better understanding of releases and how to extrapolate these to disposal conditions.

Future leaching studies must attempt to assess the leaching characteristics both on the laboratory scale and in full scale facilities, taking into account the particular near field disposal site environment in order to support the development of a mathematical model that gives a coherent picture of the long term release behaviour of radionuclides from bituminized wastes.

5.3.4. Swelling due to water uptake

Swelling is the result of water diffusion through the bitumen and water uptake by the incorporated material. Damage to the bitumen waste products, in the form of swelling or expansion of the product dimensions, has been observed during leach tests. Since this phenomenon may lead to damage to the integrity of the package containment, suitable provisions should be taken to prevent or limit this damage, and to account for its consequences. With some wastes the expansion is rapid, taking less than 24 h; with others, measurable changes in the product dimensions have only been observed after periods greater than six months [99] (see Table XXII).

The most rapid changes are reported for heavily loaded bitumen waste products, where the salt or resin loadings are in excess of 50 to 60 wt% dry solids. Three dimensional volume increases of 200 to 400% have been measured on small samples, which were fully immersed [77].

TABLE XXII. SWELLING OF BITUMINIZED WASTE PRODUCTS AFTER IMMERSION IN WATER [99]

Bituminized waste product	Type of water	Time (d)	Swelling (vol.%)
Sample dimensions: ϕ, 80 mm; height, 80 mm			
Ambolite ion exchanger, bitumen R90/40 : 60 wt%	Demineralized water	365	12.6
Chemical sludges, STE3/MA[a], bitumen 80/100 : 60 wt%	Tap water	730	0 to 2
Duolite ion exchanger beads, bitumen R90/40 : 60 wt%	Demineralized water	365	23
Microionex powder resins, bitumen R90/40 : 60 wt%	Demineralized water	365	8.2
Full scale samples: 200 L drums			
Chemical sludges, STE3/MA, bitumen 80/100 : 60 wt%	Tap water	365	0.5
Chemical sludges, STE3/MA, with TBP (solubility limit), bitumen 80/100 : 60 wt%	Tap water	365	1 to 1.5

[a] STE3, La Hague; MA, medium active (wastes).

5.3.4.1. Salts

Upon leaching bituminized waste products, swelling was observed with dehydrated salts, e.g. sodium sulphate and sodium carbonate, incorporated in the bitumen [11]. The increase in volume of the salt from the dehydrated to the hydrated form would give rise to a stretching of the bitumen membrane in place around the salt crystal. For bituminized waste products prepared with distilled bitumen the bitumen membranes remained mostly intact, but for the more viscous products resulting from oxidized bitumen the samples tended to disintegrate under the expansion forces when the samples were placed as free standing products in water. Similar effects due to low ductility can be expected with water at low temperatures [31, 100].

The volume increase in the formation of sodium sulphate decahydrate from unhydrated sodium sulphate calculated on the basis of the density difference is 200%.

However, sample measurements were in excess of these values, indicating the formation of open cracks and pores as well as the presence of osmotic forces. Recently, products with high loadings of sodium nitrate salts have been measured for volumetric changes and the conclusions of this work provide additional evidence for the high degree of swelling of dehydrated salts [86]. As an additional factor sodium nitrate is easily soluble, hygroscopic and absorbs water. The osmotic forces, considered to be possible contributors to swelling [78], were calculated on the basis of the dissolution of salt crystals in the aqueous phase. Theoretically, osmotic pressures of several hundred atmospheres can be calculated. The water in contact with the product moves into an area containing salt crystals. The water dissolves the crystals, causing the saturated solution to expand and form a cavity. The formation of many cavities provides interconnecting channels to the outer surface and allows the movement of salt solutions into the surrounding water.

The observations from heavily salt loaded bituminized waste products suggest that the process is time dependent, since the water must diffuse through the bitumen membrane before reaching the salt crystal. Thus, for lower loadings, with greater membrane thicknesses more time must pass before swelling begins [44]. The application of a pure bitumen coating could prevent swelling of bituminized waste products.

5.3.4.2. Ion exchange resins

The swelling from dehydrated ion exchange resins has been examined extensively [78, 101]. The water uptake results in a dimensional change to the resin bead that in turn thins the bitumen membrane and allows water to pass more quickly to the other dehydrated resins. The more resin in the product, the more rapid is the change in the product dimensions. The presence of residual water in the product will decrease the extent of maximum swelling [102]. Water uptake by bitumen-resin products is significantly reduced at lower loadings. Again, as with bituminized salts, water diffusion is the controlling factor. The thicker bitumen membrane has been shown to minimize the swelling during the observation periods. On the other hand, bituminized waste products containing cationic ion exchangers saturated with multivalent cations show considerably less tendency to swell.

5.3.4.3. Swelling pressures

There have been theoretical calculations made to establish the maximum pressure that could be developed from the swelling of bead resins and salts [102–104]. In each of these cases, the assumption made is that the products are incompressible solids. There are, however, results of measurements reported where extremely low pressures of a few tenths of an atmosphere have been found, in contrast with the hundreds of atmospheres calculated [105].

The experiments involved placing a sample of bituminized orthophosphate (60 wt%) in a confined space. A swelling pressure of only 21 to 28 kPa due to water uptake was observed, for a period of a few days. This waste loading would normally produce a doubling of the product volume for an unconfined sample within 24 h. The explanation given for the lack of pressure buildup in the confined sample is that the voids created by the dissolution of salts near the surface take up the volume expansion of the next crystal to dissolve. The product is elastic enough to deform into the void spaces created giving no further indication of pressure buildup.

Long term experiments have been conducted with bituminized ion exchange resins [78]. Observations indicated some significant delay for any pressure buildup from swelling.

With excessive waste loadings the swelling rate is apparently accelerated because of thinner membranes, punctures or cracks and pores in the membrane and matrix. Over the long term the buildup of high pressures may still have to be considered.

Proposals to minimize or eliminate swelling have been made for ion exchange resins and salts. Placing less resin in the product will give a greater bitumen membrane thickness and decrease both the rate and the extension of the volume expansion. When feasible, bituminization without fully drying the resins will reduce the possible change in dimensions upon rewetting, since the beads have not fully shrunk. Another solution for resins might be partial oxidization of the beads to prevent rehydration, or saturation of the cation exchange resins with multivalent metal ions. For salts, possible conversion to insoluble precipitates or to forms with less hydration water could also minimize swelling (Section 5.3.1, Table XX).

5.4. RADIOLOGICAL PROPERTIES

Since the initial work reported [2] on the influence of the absorbed radiation of the incorporated radionuclides on the stability of bituminized waste forms, there has been substantial progress in understanding radiation effects on swelling, radiolytic gas release, and changes in the leach rate and/or in other properties.

5.4.1. Radioactivity

Knowledge of the radioactivity content in the waste material and the final product is necessary in order to:

(a) Define the routing of the product packages for storage and disposal.
(b) Evaluate the influence of the radionuclides and their radioactivities on typical final product characteristics; e.g. swelling, radiolytic gas generation and leaching.

TABLE XXIII. GAS COMPOSITION AND PRODUCTION RATE (mL$\cdot$g$^{-1}\cdot$kGy^{-1} FOR GAMMA IRRADIATION OF BITUMINIZED WASTE) [13]

	Ref. [111]			Ref. [108]			Ref. [110]		Ref. [109]		Ref. [29]
Irrad. atm.	O_2	O_2	Ar	Ar	O_2	O_2	Air	Ar	Air	Ar	Air
Dose (Gy)	6.2×10^5	3.1×10^6	5×10^5	2.6×10^6	2×10^6	2×10^7	10^6	10^6	10^6	10^6	10^6
H_2	3.9×10^{-4}	3.9×10^{-4}	1.5×10^{-4}	2.2×10^{-4}	9×10^{-5}	9×10^{-5}	1×10^{-3}	1.1×10^{-3}	5×10^{-4}	5×10^{-4}	3.3×10^{-4}
CO	1.3×10^{-5}	3.5×10^{-5}	2.1×10^{-5}	1.8×10^{-5}	6.5×10^{-6}	1.5×10^{-5}	—	—	—	—	—
CO_2	2.6×10^{-5}	3.0×10^{-4}	1.1×10^{-5}	6.7×10^{-6}	5×10^{-5}	8×10^{-5}	—	—	—	—	—
CH_4	$< 10^{-6}$	10^{-6}	5.2×10^{-6}	7.5×10^{-6}	2.5×10^{-6}	2.5×10^{-6}	1.4×10^{-5}	4.9×10^{-5}	1×10^{-5}	4×10^{-5}	4×10^{-5}
C_2-C_5 hydrocarbons	$< 10^{-6}$	5×10^{-6}	1×10^{-6}	2.2×10^{-6}	10^{-6}		1.4×10^{-5}	4.9×10^{-5}	1×10^{-5}	4×10^{-5}	4×10^{-5}
O_2 consumed	4.4×10^{-3}	4.4×10^{-3}	1×10^{-6}	1×10^{-6}			—	—	—	—	—

In most Member States, the safety authorities require the measurement of the radioactivity content as a part of the classification system of radioactive wastes, prior to their treatment and conditioning. These results, in combination with similar measurements on final packages, allow verification of the compliance to upper radioactivity limits for disposal practices, such as 3.7 GBq/t for alpha emitters in France for near surface disposal.

In general, knowledge of the radioactivity content in each final package and the contribution of the most important radionuclides is required from the operator of a bituminization plant. This information can be obtained either by radioanalyses of samples of the input waste streams, that are usually stored in sufficiently large buffer tanks, or by a combination of input samples with samples from the bituminization process itself.

The following measuring techniques can be used:

(1) Destructive analysis (DA): mineralization of bitumen–waste samples, extraction of salts and radionuclides;

(2) Non-destructive analyses (NDA): use of scanning equipment, allowing NDA on full scale packages with radioactivity levels in the MBq to TBq range. Some of these items of equipment can also carry out gamma ray scanning to verify the homogeneity of the radioactivity within the packages.

Special measuring techniques have to be provided where alpha emitters are expected, to obtain the required sensitivity.

The determination of the radioactivity content and the contributions of the most important radionuclides permit the calculation of the following:

(i) The actual dose rate and its variation with time within the final product;

(ii) The contact or near contact dose rate of the packages;

(iii) The required biological protection for handling, transportation and storage.

In addition, the correct evaluation of the radioactivity content and the radionuclides is necessary to quantify the parameters that are used by the safety authorities in the modelling of the long term effects on the disposal conditions, such as:

- The dose rates as a function of time;
- The integrated dose as a function of time;
- The alpha, beta and gamma radiolytic gas generation.

These models aim at a better understanding and prediction of the swelling of bituminized products, gas release and alteration of physicochemical properties (hardness, penetration, etc.) that may influence the final product behaviour.

5.4.2. Radiolytic gas production and release

Experiments have generally been carried out using external gamma sources to irradiate bitumen-waste products [13, 101, 103–109]. The predominant gas is hydrogen with only minor contributions (up to 5% of the evolved volume of H_2) coming from carbon monoxide, carbon dioxide and low hydrocarbons. Related to the bitumen content of a bituminized waste product the G values for the radiolytic hydrogen production are typically 0.2 to 0.4, independent of dose [29, 107]. However, in oxygen [106] and at doses of 3.1×10^6 Gy [13, 109], the carbon dioxide release rate becomes comparable with the hydrogen release rate as shown in Table XXIII. The carbon dioxide production in pure bitumen is independent of the dose rate and lower than the hydrogen production [95, 98]. There is evidence to indicate that alpha radiation can increase the radiolytic gas production rate by a factor varying from 2 to 10 [12, 13] for equivalent total doses. However, it is unlikely that bitumen products contain more than 0.2 TBq/m^3 of alpha emitters.

When evaluating the radiolytic gas production of a bituminized waste product the presence of additional organic waste compounds and the residual water content have also to be assessed.

5.4.3. Swelling due to radiological causes

The swelling of bituminized waste products caused by irradiation is dependent on the dose rate, the total dose, the bitumen type, the nature of the waste, the loading, the final water content, the sample dimensions and the packaging.

There have been three models developed to explain the swelling observed. The IL^2 model predicts that for a given bituminized product in a right cylindrical configuration of equal diameter and height L, similar amounts of swelling will take place for the same total dose in cylinders of different sizes, L, at different dose rates, I, provided the value of IL^2 is the same. The model does not attempt to explain the mechanism of swelling and is only applicable to small samples [14].

The first bubble growth model [14, 15] has been developed from the theories that have been derived to explain and predict void swelling in neutron irradiated fuel elements. The complex model assumes spherical bubbles form and grow at existing sites such as trapped air bubbles, or waste particle surfaces in the bituminized waste product. The continued diffusion of gas into the nucleate bubbles allows them to grow against the viscous constraint of the bitumen matrix. Some of the gas produced escapes by diffusion or bubble permeation through open surfaces and/or can be redissolved from the bubbles into the matrix.

A second bubble growth model [97] has been developed for application to the irradiation swelling of full scale drums and has been validated by observations on actual drums containing immobilized reprocessing wastes. The model based on the diffusion of the hydrogen and radiolysis gases produced, and on the formation and growth of gas bubbles and their migration to the surface, confirms the swelling will level off as the gas escape rate matches the production rate. The experimental data collected over the years for a drum containing representative bituminized waste from the La Hague bituminization facility with 11.5 TBq (312 Ci) of beta-gamma and

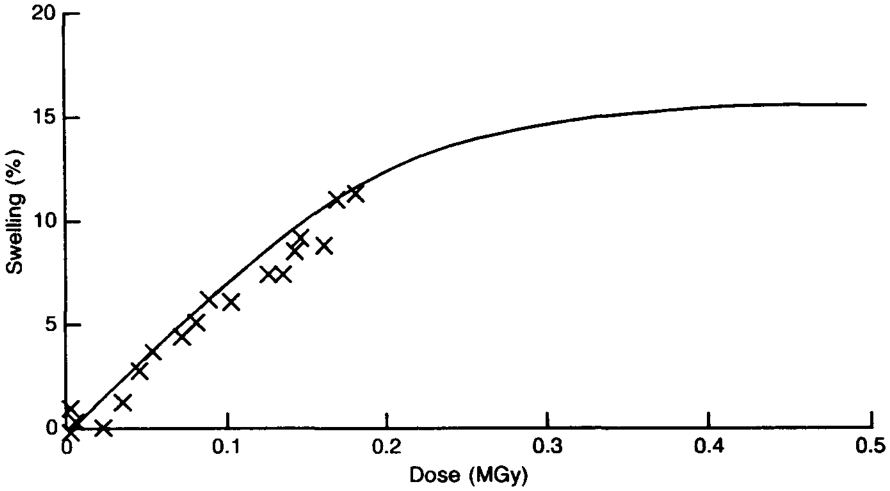

FIG. 14. Comparison of experimental data on swelling taken over six years (×) with model predictions (curve) for a full size drum containing bituminized reprocessing waste sludges from La Hague: 11.5 TBq (312 Ci), β–γ; 30 GBq (0.8 Ci), α; product viscosity, 1 MPa s; gas production, 0.6 L·kg^{-1}·MGy^{-1} [25].

30 GBq (0.8 Ci) of alpha activity, indicate an increase in volume of 16%, which seems to remain stable at present (Fig. 14). External accelerated irradiation experiments applying higher dose rates lead to a more significant swelling than that which results from actual internal sources. Studies indicate that lowering the dose rate by a factor of 10 from 1.2×10^3 to 10^2 Gy/h halves the swelling rate.

These models have been tested with a variety of waste forms [110]. The general conclusions concerning the IL^2 model are that large samples (180 L and 22 L) showed much smaller irradiation swelling than small samples (4 L) irradiated under the same IL^2 conditions. This demonstrates that the IL^2 model cannot be applied over a wide range of sample sizes and give reliable results. It is believed that this is a consequence of the fact that the model does not allow for those parameters that have an influence on the swelling mechanism. The first bubble growth model, which makes partial allowance for these parameters, has been applied with some success to data for which the IL^2 model is not accurate [15]. Application of the bubble growth model requires, however, the availability of a range of material parameters, some of which are difficult to quantify, such as the nature and behaviour of the bituminized waste product microstructure and its influence on the transport of gaseous molecules resulting from radiolysis.

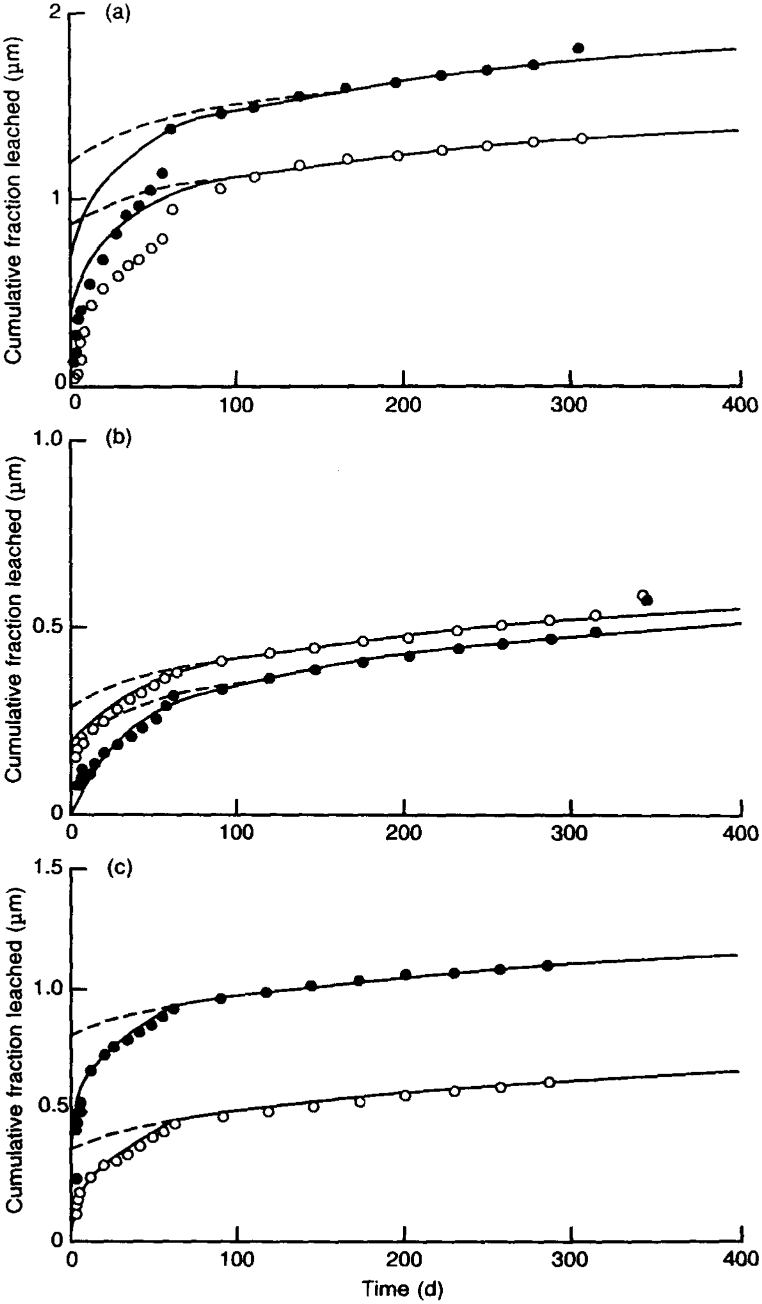

FIG. 15. Cumulative ^{137}Cs fraction leached from RWF7, unirradiated (a), and irradiated to 1 MGy (b) and 10 MGy (c) (RWF7: reprocessing waste concentrate incorporated into blown bitumen R85/40) [110]. The curves are for: ——, diffusion + sorption model; ----, diffusion model. The data (●, ○) are for duplicate models.

Nevertheless, both the theoretical and experimental work indicate that the bubble growth models provide versatile tools for assessing the radiolytic swelling of bituminized waste forms. For example, application of these models provides a valid theoretical basis for the assumption that it should be possible to produce bituminized waste forms that will not show significant swelling during the lifetime of the immobilized radionuclides. The composition of such waste products would probably be based on blown grades of bitumen with waste loadings not exceeding 40 wt% and specific activities of at most 37 GBq/L (1 Ci/L).

Both bubble models also predict that no significant swelling ($<1\%$) will be observed for alpha emitters at waste loadings of less than 37 TBq/m^3 [13, 109]. Taking into account the above mentioned radiolysis gas production rate in bitumen from alpha emitters, ranging up to a factor of ten higher than the corresponding production rate for beta-gamma emitters, this prediction should, however, be considered with prudence. In practice, bituminized reprocessing wastes will normally contain at most 0.2 TBq/m^3 of activity due to alpha emitters and so their contribution to the overall swelling of the bituminized waste product should be at least very limited if not completely negligible.

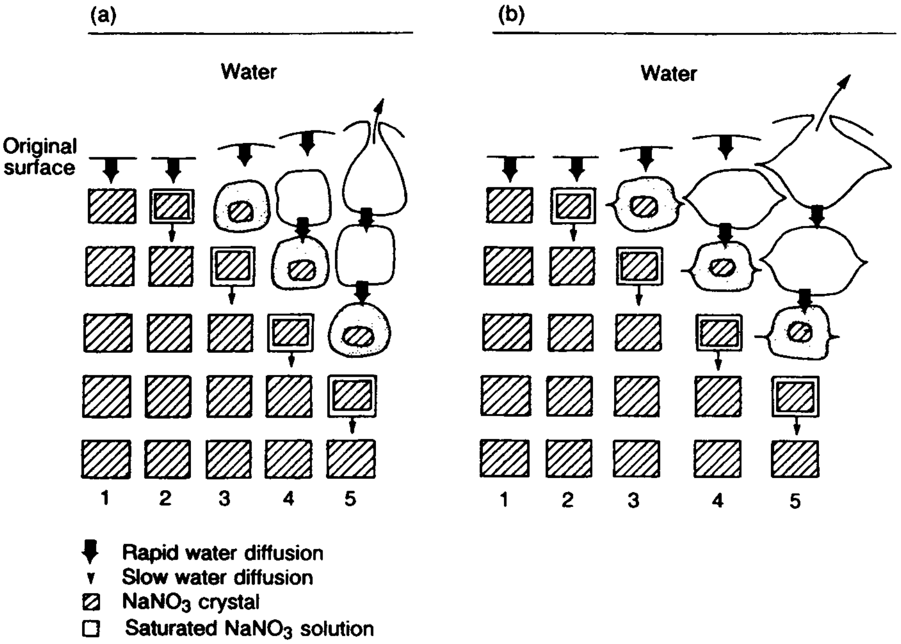

FIG. 16. Schematic model of leached zone development: (a), unirradiated RWF7; (b), α irradiated RWF7.

5.4.4. Radiation effects on leaching behaviour

A number of studies have examined the leaching behaviour of irradiated bituminized waste samples [25, 13, 109] and observed that there is little change with respect to unirradiated samples. One of the studies [13, 109] reports a lowering of ^{137}Cs release (Fig. 15), in spite of some swelling from irradiation and water uptake. This appears to be due to the sorption of the system, which tends to increase with increasing irradiation dose.

In general, releases are controlled by a diffusion mechanism, and there appears to be no difference between alpha and beta-gamma irradiation. The additional swelling from radiolytic gas production has practically no influence on the release of radioactivity from irradiated specimens as the schematic model shown in Fig. 16 suggests [13].

5.5. BIODEGRADATION

As many microorganisms are able to use hydrocarbons as their source of energy, bitumens are degradable by microbes (Section 2.4). The degradation is dependent on type and availability of the microbial community, on environmental factors that facilitate or impede microbial growth and on the chemical nature of the hydrocarbons present in the bitumen waste product. The disposal of bituminized wastes in geological deep underground repositories, and especially in near surface disposal facilities, requires consideration to be taken of microbial attack on bitumens, regarding their possible consequent degradation effects on the physical and chemical properties and in particular the enhanced release of radioactivity from the waste form.

Reviews in the literature describe bitumen degradation by microbes [111–117]. The rate of attack is influenced, for instance, by the environmental conditions, the chemical composition of the bitumen, its physical state and the microbial flora.

To establish the rate of biological degradation, one must examine environmental factors such as temperature, pH, the presence or absence of nutriments and oxygen, the salinity of water, the hydrocarbon state (solid, porous or even liquid) and radiation. Tests were performed to find the optimal conditions for biological attack of bituminized wastes and to measure the corresponding radionuclide leach rates [117]. The release rates were not statistically different from those for samples that were not contaminated with bacteria. The work also showed that the microbes were sensitive to radiation and that, after a dose of 500 Gy, there were few microbes surviving and none of the microbial cultures were capable of growth at doses exceeding 750 Gy. It was also concluded that a repository environment would not be conducive to microbial growth. Low temperatures, high salinity, high alkalinity, radiation and scarcity of oxygen would all contribute to restricting the aerobic and anaerobic growths of microorganisms.

Long term studies on the influence of microorganisms on the safety of disposal systems containing bituminized waste are under way at Cadarache [114]. Degradation rates for pure bitumen, and for bitumen and sodium nitrate products, are being measured. After nearly one year a thickness of about 3 μm of bitumen was removed from the inactive test samples under optimum conditions for microbial growth, much less than the reported equivalent value of 25 mm for pure bitumen over three years [18].

Investigations carried out in Switzerland both under aerobic and under anaerobic conditions using a variety of cultures established that long term bitumen degradation rates were essentially independent of the culture [17]. Under aerobic conditions microbial attack resulted in a bitumen loss of 20 to 50 $g \cdot m^{-2} \cdot a^{-1}$ and generated 15 to 40 $L \cdot m^{-2} \cdot a^{-1}$ CO_2 at standard temperature and pressure. Under anaerobic conditions the degradation rate was found to be about 1% of that for the aerobic rate. The study extrapolated the anaerobic conditions to a waste repository and estimated the loss of bitumen matrix from a 200 L drum to be 0.3 to 0.8% for a period of 1000 years.

A similar Swedish study [115] also concluded that bacterial degradation of bitumen can occur under aerobic and anaerobic conditions similar to those expected in a repository for conditioned reactor wastes. The maximum measured rate of CO_2 production was 2 $L \cdot m^{-2} \cdot a^{-1}$ for optimum aerobic conditions and about 0.57 $L \cdot m^{-2} \cdot a^{-1}$ for optimum anaerobic conditions.

It should be noted, however, that aerobic microbial activity can only take place in 'a deep geological repository' underground when oxygen is provided by appropriate ventilation. This condition is limited to the rather short period when disposal activities are taking place; after which aerobic microbial activity will come to an end and anaerobic microbial attack could possibly take over.

Investigations were carried out at Brookhaven National Laboratory on the biodegradation of blown bitumens (Pioneer 221) in the context of the shallow land burial of bituminized waste products [116]. Based on CO_2 production rates from aerobic microbial activity, a bitumen degradation of 1% was estimated from a 200 L drum with bituminized wastes after 300 years provided that ideal aerobic conditions prevailed throughout that time.

Taking into account the results of investigations on the long term stability of natural bitumens and natural bitumen analogues [19, 20], bitumens have demonstrated an excellent stability over periods of from more than 10^4 up to 10^7 years. A comparison of empirical natural bitumen stability data with degradation rates extrapolated from experimental microbial decomposition tests under idealized conditions reveals the extremely conservative approach of the latter. Consequently it appears up to now that the biological degradation of bituminized wastes takes place at rates that are low enough to be of no safety concern for the disposal facilities.

6. CONCLUSIONS

Since 1970, when information was first compiled by the IAEA on bituminized wastes in Ref. [2], there has been additional extensive research and development on bituminization processes and bitumen–waste product performance. The basic technologies available in the late 1960s were essentially batch or semicontinuous processes. Based on this early development work there are now full scale processing units operating in Member States. Continuous processes use either extruders or thin film evaporators. Batch processes handle smaller volumes of liquid or solid wastes and use relatively simple mixing vessels. The majority of the industrial scale units have been put in operation at nuclear power and reprocessing plants over the past twenty years. The quantities of bitumen waste products generated and either in storage or disposed off are greater than 20 000 m^3 and therefore substantial operational experience has been gained in several Member States.

The field of application of bitumens is the conditioning of low and intermediate level radioactive waste concentrates resulting mainly from processing liquid wastes. For this application bitumens have been well characterized. The physicochemical and radiological properties of bitumen are sufficiently well known.

Fire incidents during the operation of bituminization facilities are well understood and corrective actions and procedures have been established to eliminate or minimize the risk of reoccurrence. The corrective actions are concentrated on the engineering and technology of the heating systems, and on the instrumentation, process control and chemical analyses, so as to characterize the wastes and their compatibility with the bitumen fully. In addition efficient fire detection and fighting systems are provided in the bituminization installations. With the cumulative knowledge and the available operating experience, the probability of occurrence of a fire during bituminization is extremely low and does not justify the level of apprehension associated with the flammability of bitumens.

The wastes to be incorporated into the bitumens need to be quantitatively investigated to ensure that they do not detrimentally affect the bitumen properties to an unacceptable extent, and in particular that they will not cause a lowering of the flashpoint of the bitumen during processing or subsequent degradation of the waste form.

Many different wastes have been immobilized over the years and excellent waste forms have been produced. As is the case with all matrix materials, bitumen has its specific field of application. Poor performance is demonstrated when:

(a) The selection of bitumen as a waste incorporation matrix is on the basis of the unrealistic assumption that it is a universal matrix material for embedding all types of wastes;

(b) Overcharging the matrix by embedding wastes that cause a dose in excess of 10^7 Gy, bituminizing wastes at dry weight loadings above a reasonable limit or incorporating waste materials incompatible with the bitumen.

Much effort has been spent in evaluating bitumen performance. Radiation induces the production of radiolytic gases; however, only moderate swelling of 5 to 10 vol.% in 210 L drums is expected for doses at 10^7 Gy. The drum sealing should be permeable to gases, and adequate ventilation during storage must be considered to eliminate the buildup of hydrogen gas.

Bitumen waste products can support combustion, but they cannot self-ignite during handling, transportation, storage or disposal, e.g. large sources of energy are required to ignite bitumen waste products under these conditions.

Swelling due to the uptake of water is directly attributable either to poor pretreatment or to the overloading of bitumen with hygroscopic salts and ion exchange resins. Reasonable loading and pretreatment will still yield good volume reduction factors compared with other matrix materials, while obtaining satisfactory products for disposal.

Bitumens and bituminized waste products can be attacked by microbial activity. However, microbial degradation depends on the coincidence of suitable conditions to sustain the microbial activity. Even for ideal conditions the microbial degradation rates are sufficiently small to be of no serious safety concern for interim storage and final disposal, and this is much more marked when considering the rather hostile environment for microbial activity in a repository.

The investigation of natural bitumen deposits and natural analogues provides evidence for the excellent long term stability of bitumens. Combined with the available database on, and the demonstrated analytical test procedures for, the characterization of the bitumen and bituminized waste product properties, safety assessments and evaluations of the long term behaviour under disposal conditions are possible and are routinely performed for bituminized waste forms. This is not only the basis for the definition of the bituminized waste acceptance conditions, but also for the realization by the waste producers of the quality assessment and control measures. Thus, operational experience in bituminization facilities, together with supporting quality assessment and control efforts, have up to now guaranteed the successful production of a safe waste form.

Annex

APPLICATION OF BITUMINIZATION PROCESSES IN SOME MEMBER STATES

A-1. INTRODUCTION

This annex summarizes the information about the application of bituminization processes in the Member States that have participated in the preparation of this Technical Report. All the data presented in the annex were provided by experts nominated by Member States to participate in the development of this report. This annex provides some practical examples on the types and characteristics of the wastes incorporated into bitumens, the types of bitumens used for immobilization processes and gives some data on the bituminization facilities, together with a description of some

TABLE A-1. PHYSICAL PROPERTIES OF WASTES INCORPORATED INTO BITUMENS IN VARIOUS MEMBER STATES

Member State	Waste types				
	Slurry	Concentrate	Sludge	Spent ion exchange resins	Solids content (wt%)
Belgium (Mol)	×	×			23–40
France (La Hague)			×		9–16
(Marcoule)			×		23
Germany (Karlsruhe)		×			23
Japan (Tokai)		×			30
Sweden					
(Barsebäck)	×			×	20–25
(Forsmark-1, -2)	×			×	20–25
(Forsmark-3)	×			×	45
Switzerland (Goesgen)		×		×	15–30
Former USSR					
(Ignalina)	×	×			20–25
(Kalinin)	×	×			20–25
(Leningrad)	×	×			20–25

TABLE A-II. CHEMICAL PROPERTIES OF WASTES BITUMINIZED IN VARIOUS MEMBER STATES

Member State facility	pH	Organic substances (g/kg)	Major ions	Concentrations of major ions (g/kg or wt%)
Belgium (Mol)	1-2[a]	TBP + diluent[b] decontaminants	NO_3^-, SO_4^{2-}, F^-, $[Fe(CN_6)]^{4-}$, Na^+,	200, 41, 9, 1.4, 77,
			Ca^{2+}, Zr^{4+}, Fe^{3+}, Al^{3+},	39, 6.4, 4, 3.3,
			Cr^{3+}, Mg^{2+}, Ni^{2+}, K^{+}[c],	1, 0.8, 0.5, 0.3[c],
	8		Ba^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}	50, 2, —[d], —
France (La Hague)	6.5-9	TBP (<2.1)	Ni^{2+}, SO_4^{2-}	3-15 wt% PPNiF[e], —
(Marcoule)	8.5	5	Ba^{2+}, Fe^{2+}, S^{2-}, Cu^{2+},	51, 316, 9, 8,
			SO_4^{2-}, Ba^{2+},	18–70 wt% $BaSO_4$,
			Co^{2+}, SO_4^{2-}	3–15 wt% CoS
Germany (Karlsruhe)	8–10	Detergents, chelators (4.6)	Na^+, Ca^{2+}, NO_3^-, PO_4^{3-}	58, 4, 101, 52
Japan (Tokai)	8–10	TBP (<0.1)	Na^+, NO_3^-, CO_3^{2-}, PO_4^{3-}	130, 220, 51, 5
Sweden (Barsebäck)	5–7	Non-ionic		
(Forsmark-1, -2)	6–9	emulsifier		
(Forsmark-3)	6–9	(approximately 0.1)		
Switzerland (Goesgen)	7		Cl^-, SO_4^{2-}	0.1–4, 10–80
Former USSR (Leningrad)	10.3–11.4	0.015–0.03	Na^+, Cl^-, SO_4^{2-}, NO_3^-	80, 33, 8, 140

[a] Liquid waste concentrates before pretreatment; after pretreatment pH ≈ 9.

[b] Solubility limit.

[c] After pretreatment, average values.

[d] —, Not measured.

[e] Total dry waste compounds, wt%; PPNiF, preprecipitated nickel ferrocyanide.

TABLE A–III. RADIOCHEMICAL PROPERTIES OF WASTES BITUMINIZED IN VARIOUS MEMBER STATES

Member State	Radionuclide	Average activity concentrations (MBq/L)
Belgium (Mol):		
Batch process	β–γ, α	9, 0.2
Continuous process	β–γ, (fission products) α	$\leq 10^4$, $\leq 10^2$
France (La Hague)	Cs-134, Pu-238, Se-125, Ru-106, Ce-144, Cs-137, Pu-242, Sr-90, Co-60	8770, 8440, 2741, 2740, 2470, 1230, 121, 24, 16
(Marcoule)	Ru-106, Cs-137, Sr-90, Ce-144, Cs-134, α Pu-239	2000, 1400, 740, 670, 630, 7.4
Germany (Karlsruhe)	β–γ, α	1400, 55
Japan (Tokai)	Cs-137, Ru-106, Sr-90	140, 80, 50
Sweden (Barsebäck)	Co-60, Cs-137	100–200, 0.02–0.03
(Forsmark-1, -2)	Co-60, Cs-137	<250
(Forsmark-3)	Co-60, Cs-137	<300
Switzerland (Goesgen)		
Exclusive resins	Co-60, Co-58, Mn-54, Zn-65, Ag-110m, Sb-124	20, 0.5, 0.3, 0.01, 0.01, 0.01
Inclusive resins	Co-60, Co-58, Mn-54, Ag-110m, Sb-124, Zn-65	<20, <0.5, <0.3, <0.01, <0.01, <0.01
	Co-60, Cs-137, Fe-55, Cs-134, Ni-63	$<3 \times 10^3$, $<2 \times 10^3$, $<7 \times 10^3$, $<2 \times 10^3$, $<9 \times 10^2$
Former USSR (Leningrad)	Cs-137, Cs-134, Co-60, Co-58	8.28, 4.76, 0.08, 0.03

of the safety precautions applied in the bituminization processes. This is not a complete review of bituminization practice, since not all Member States utilizing bituminization techniques participated in the preparation of this report.

A-2. WASTE TYPES

A descriptive summary of the wastes produced in typical reactor operations and resulting from the reprocessing of irradiated nuclear fuel is compiled in Tables A-I, A-II and A-III.

The wastes are slurries, ion exchange resins, concentrates from evaporation or decontamination and sludges composed of flocculant materials or co-precipitants.

The wide range of chemicals and concentrations is more clearly shown in Table A-II for the complex waste streams arising in research and reprocessing centres. The radionuclide concentrations (Table A-III) are also highly variable. Alpha activity in measurable quantities is found in the reprocessing wastes. These wastes also contain the highest activities of fission products. These tables provide a demonstration of the versatility of bitumen to immobilize widely different waste streams.

A-3. TYPES OF BITUMEN

The information collected about the types of bitumen that are currently being used is summarized in Table IX (Section 2.5).

Both distilled and blown bitumens are used in continuous processes, whereas only distilled bitumen is used in the reported batch processes. The softening points of the different types of bitumen vary between 38 and 93°C, while the penetration varies from 10 to 10^2 mm (Section 2.2.3). The flashpoints of these bitumens are all above 220°C, in some cases even exceeding 250°C.

A-4. PROCESS DESCRIPTION

Among the twelve processes that have been reported, four are batch processes and eight are continuous processes.

A-4.1. Batch processes

The relevant information on batch processes is given in Table A-IV, showing that more than 3000 m^3 of bituminized waste products have been generated so far.

TABLE A–IV. BATCH BITUMINIZATION PROCESSES USED IN VARIOUS MEMBER STATES

Country Facility	Sweden Forsmark-2, -3	Sweden Forsmark-3	Sweden Barsebäck	Belgium Mol, Belgoprocess
Nuclear activity	NPP[a]	NPP	NPP	Various
Process type	With evaporation	With evaporation	With evaporation	With evaporation
Waste type	Slurry	Slurry	Slurry	Flocculation sludges
Pretreatment	—	—	pH adjustment	Freeze–thaw filtration
Bitumen type	40/50	40/50	40/50	20/30
Waste feed[b] (kg/h)	120–140	—	30–90	200
Evaporation rate (kg/h)	—	—	25–75	40
Batch temperature (°C)	115–125	120–150	140–180	180–200
Heating system	Steam	Steam	Oil	Electrical
First operational	1981	1986	1976	1960
Product density (kg/L)	1.15	1.1	1.08	1.3
Waste loading (wt%)	57	30–40	15–25	30–40
Residual water content (wt%)	<5–10	<1	<2	<2

[a] NPP, nuclear power plant.

[b] Prior to any pretreatment.

TABLE A-V. CONTINUOUS BITUMINIZATION PROCESSES

Country	Switzerland		France		Belgium	Japan	Germany	Former USSR
Facility	Goesgen		Marcoule	La Hague	Mol, Belgoprocess	Tokai	Karlsruhe	Leningrad, Ignalina
Nuclear activity	NPP		Various	Reprocessing	Various	Reprocessing	Various	NPP
Type	Extruder		Extruder	Extruder	Extruder	Extruder	Extruder	Thin film evaporator
Waste type and pretreatment	Evaporation concentrates, pH adjustment chemical	Ion exchange resins	Flocculation sludges, filtration	Flocculation sludges, filtration	Evaporation concentrates, chemical	Evaporation concentrates, chemical	Evaporation concentrates	Evaporation concentrates
Bitumen type	Ebano B15		Mexphalt R80/100		Mexphalt R85/40	Mexphalt R85/40	Mexphalt R15	BND 90/130 BND 60/90 BNK 45/80
Waste feed (kg/h)	100	10	250	250	133	240	170	400
Bitumen feed (kg/h)	20	20	60	60	80	90	30	40–60
Product rate (kg/h)	40	30	110	110	133	170	60	—
Evaporation rate (kg/h)	80	—	200	200	80	170	140	400
Bitumen temperature (°C)	150–160	120	160	140	160	175	140	125–135
Product temperature (°C)	120	120	140	115–135	180	160–180	175	100–120
Product density (kg/L)	1.1	1.1	1.45	1.3–1.4	1.3–1.4	1.3–1.4	1.32–1.43	—
Waste loading (wt%)	15	33	45	35–45	40	43	40–50	35–45
Residual water content (wt%)	1	1	2	≤5	0.5	<1	≤0.5	1
First operational	1986	1988	1966	1989	1978	1982	1972 (stand-by)	1984, 1987, 1989

TABLE A-VI. SAFETY PRECAUTIONS AT VARIOUS MEMBER STATE FACILITIES

Member State facility	Heating medium	Fire prevention medium, rate applied	Operator protection
Belgium (Mol)	Steam (extruder)	Fume–flame–temperature detectors	Shielded, separated cells for extruder
		Carbon dioxide (13 bottles of 50 kg, automatic and manual operation)	Drum filling and cooling station: limits doses to 0.005–0.025 mGy/h
		Cell flooding with light fumes	
		Consecutive water sprays of 1.7 L	
	Electrical (batch)	Nitrogen, direct contact for paddle mixer	
France (La Hague)	Steam	Carbon dioxide sprayed in cells	Shielded cell, <0.025 mSv/h
(Marcoule)	Steam	Water	Shielded cell, <0.025 mSv/h
Germany (Karlsruhe)	Steam	Fume and gas detectors: carbon dioxide sprayed at 13 kg/s (nozzle aimed at drums)	Shielded cell, <20 mSv/a
Sweden (Barsebäck)	Steam	Spray and flush 1–2 kg/s water	Shielded cell
(Forsmark-1, -2)	Steam		Shielded cell
(Forsmark-3)	Steam	Halogen foam	Shielded cell
Switzerland (Goesgen)	Steam	Carbon dioxide flushed into hot cell	Shielded cell
Former USSR (Leningrad)	Steam	Water and carbon dioxide sprayed at $0.36\ \mathrm{L \cdot m^{-3} \cdot s^{-1}}$	Shielded cell

A–4.2. Continuous processes

Continuous processes are, and have been, operated on an industrial scale, using both extruders and thin film evaporators. The waste feed rate varies between 100 and 500 kg/h, and the operating temperatures are well below the flashpoint of the corresponding bitumen.

The relevant data on the reported continuous processes are presented in Table A–V.

A–5. SAFETY PRECAUTIONS

All the processes surveyed in Table A–VI use steam or oil as the heating medium for the storage in bitumen of processing wastes. The only exception is the small batch unit at Mol in Belgium that uses electric heating for the process vessel. With steam as the preferred choice for the process heating, the process temperatures can be accurately and safely controlled.

Most of the processes have been installed with fire fighting systems that can use carbon dioxide alone or in combination with other fire fighting media such as light or heavy foams and consecutive water sprays of limited volume. Methods of fire detection include rate of temperature rise detectors and fume–flame or gas detectors.

All operations are carried out in shielded cells to provide operator protection and to minimize doses during the operation process.

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