NKA NORDIC LIAISON COMMITTEE FOR ATOMIC ENERGY

NKA/AO (81) 5
August 1981

ENLARGED NORDIC COOPERATIVE PROGRAM ON NUCLEAR SAFETY

NORDIC STUDY ON REACTOR WASTE

Technical Part III
Product Characteristics

A Joint Scandinavian Research Project
Sponsored by

The Nordic Council of Ministers

Organization of the Nordic Study on Reactor Waste

Project Board

Chairman: F. Marcus, Nordic Liaison Committee for Atomic Energy

Members:
- R. Boge, State Radiation Protection Institute, Sweden
- M. Bonnevie-Svendsen, Institute for Energy Technology, Norway
- K. Brodersen, Risø National Laboratory, Denmark
- H. Jensen, Nuclear Installation Inspectory, Denmark
- M. Kuuskoski*, Imatran Power Company, Finland
- O. Paakkola, Radiation Protection Institute, Finland
- N. Rydell, Swedish National Council for Radioactive Waste

Project coordinator: H. Reijonen**, Technical Research Centre of Finland

Project leaders:
- J.P. Aittola, Studsvik Energiteknik AB, Sweden: Product Characteristics
- P. Linder, Studsvik Energiteknik AB, Sweden: Disposal
- P.O. Nielsen, Scandpower, Norway: System- and safety analysis

---

Author/editor of final report: U. Tveten, Institute for Energy Technology, Norway

---

Author of Technical Part I: P.O. Nielsen

Author of Technical Part II: U. Tveten

Author of Technical Part III: M. Bonnevie-Svendsen

---

* replaced Mr. J. Heinonen in 1980

** replaced Mr. B. Berlin in 1979

NORDIC STUDY ON REACTOR WASTE

TECHNICAL PART III

PRODUCT CHARACTERISTICS

LIST OF CONTENTS

1 INTRODUCTION

Studies on product characteristics have been closely connected to the system analysis. They furnish input data for the safety analysis, which, as a feed-back, should direct the experimental work towards the study of those properties which can be important for safe waste management.

A certain steering mechanism is needed even for an intelligent adaption of published data. Much work has been published about the characteristics of cementized and bituminized wastes. Methods have been described to measure important characteristics such as stability, mechanical strength, leach and radiation resistance. Only a small fraction of this information deals with ion exchange incorporation products. Also, the main emphasis has been on products for sea dumping or disposal in salt mines, where the impact of product characteristics is hardly the same as in the ground disposal alternatives examined in the Nordic study. Experimental conditions are often poorly defined, which may be one reason for the great deviations between results from different sources.

There can be no doubt that techniques are available to meet even very strict requirements on low and intermediate level waste solidification products. The problem is that the very strict requirements may be unnecessary and counterproductive.

The goal of this study is to approach the establishment of relevant product specifications which can be adapted to the safety analysis of the entire waste handling sequence. Such product specifications would in turn influence the choice of incorporation techniques and may enable an optimization of the process.

The main questions encountered in this study were, that only a few of the many product properties seemed relevant to the safety assessment. It appeared that results of small-scale laboratory tests performed during relatively short time periods could not easily be interpreted with respect to the long-term performance of full-scale products. The properties of the solidified products will also be influenced in a rather unknown manner by a number of process variables and by the characteristics of the waste itself and the matrix material.

These questions have been examined from various sides:

- through qualitative evaluations of the relevance of product properties for normal and abnormal events during storage, transport and disposal

- attempts to quantify the relevance of different properties, i.e. their influence on radiation doses from different stages of well specified waste management systems

- assessments of available laboratory tests and of correlations between results from such tests and the long-term performance of full-scale technical products

- studies of reaction mechanisms and parameters that can affect the long-term performance of disposed products

- laboratory incorporation experiments to study impacts of process variables on the fixation of ion exchange wastes in cement and bitumen

- full-scale tests to study product performance under simulated accident conditions.

This approach was also intended to furnish guidelines for the assembly of a method catalogue with relevant tests for the important product properties. The laboratory studies on process variables give a broad spectrum of products, and these are well suited for checking the relevance of available and suggested tests.

Joint Nordic studies about the compatibility of cement and bitumen with ion exchange resins were started in 1974 /1, 2/. Meanwhile Swedish and Finnish reactor industries and authorities have sponsored extensive technical R&D work in connection with the adaptation of cement and bitumen processes for spent resins from Swedish and Finnish power reactors, references /3/ to and including /8/.

To facilitate the identification of systematic trends and critical variables, this study covers more extreme conditions and higher waste loadings than have been employed for the design of a specific technical process. This should also contribute to a wider basis for future process assessments, independent of the present Nordic practice.

2 RELEVANT PRODUCT PROPERTIES

Properties and tests considered as relevant for safe waste management are listed in table 2.1. Their relevance will differ for the different stages of waste management, and must be evaluated in relation to the whole system, contained radionuclides, man-made and natural barriers.

During the first 5-50 years the solidification product or at least product plus container must remain intact under normal storage and transport conditions. They should also meet the requirements imposed by specified accident conditions, described in Tech. Part II, such as fall, collisions and fire. Depending on their possible consequences even events with very low probabilities may have to be taken into account.

In connection with major accidents, fire resistance and burning characteristics can be important. Mechanical stability, fall and impact resistance will be required to avoid spreading of radioactivity in case of severe road collisions. Water resistance is relevant in the case of a so called "fall-in-water" accident.

Normal events during storage and transport can hardly result in dose commitments to non-occupational groups, but can nevertheless impose some requirements on product qualities. Chemical and dimensional stability can be necessary to prevent internal degradation and damage to the containers. Mechanical strength, fall and impact resistance can be relevant in connection with minor handling and transport accidents. The products should also withstand normal temperature variations. In a Nordic climate this can even involve several freezing - thawing cycles. Radiation resistance is relevant in the case of high waste loadings and where the waste is solidified before the majority of short-lived nuclides (half-life < ca. 100 d) have decayed.

Table 2.1 Relevant properties of resin-bitumen (B) and resin-cement (C) products.
Relevance for storage (S), transport (T), disposal (D), processing (P) /2/.

Property	Relevance				Test	Matrix	Requirement	Remarks
	S	T	D	P				
1. Water resistance	+	+	++	+	Immersion in distilled water	B C	Not swell Not decompose	Screening test
2. Leach resistance	+	+	++	+	Leaching of Cs, Co in water	B C		IAEA-standard
3. Mechanical strength	+	++	+	+	Compressive strength tensile strength	C		Cement standard
4. Fall resistance	+	++			Fall from 9-14 m height	C (B)	Not break 9 m	IAEA transport accident
5. Formstability viscosity	++	+	+	+	Ring-ball, penetration, break point, cylinder bending, hole migration "sag test"	B		Asphalt standard suggested Danish-Norwegian, Brit.std.
6. Heat resistance	+	++			Controlled heating Flash point	C B	800°C ½ h	IAEA transport accident
7. Frost resistance	+		+		Freezer, cycle, long-term	B C	-20 - 40°C	
8. Structure homogeneity				++	Optical E-microsc. X-ray diffr., autorad. chem. analysis	C B		
9. Long term stab. radiation corrosive chem. bacteria			++		Structure changes radiological gas evolution			

Damages to the products will not lead to a spreading of radioactivity as long as the container remains intact, but they can have delayed effects on the longterm performance in the repository. Requirements for resistance to normal storage and transport events will therefore partially be governed by those for the longterm product performance.

After disposal the multibarrier system: radwaste product - container - repository, should keep the radioactive waste components isolated from the biosphere to an extent as defined by the safety analysis. Longterm risks connected with environmental attack, aging of barriers, intrusion and use of land and water resources must be taken into account. The leaching of radionuclides in contact with water is the main means for radioactivity release from the repository provided a direct intrusion can be eliminated. In this connection the longterm water- and leach resistance properties are of primary importance. Other properties such as mechanical strength, resistance against bacteriological degradation and other natural events are important for the maintenance of the leach resistance.

How the burden of safety requirements should be distributed between the different barriers is a matter of optimization. Also for such optimization a certain knowledge and quantification of the relevance and impact of defined product properties is needed.

Table 2.-2 lists abnormal and normal events, which can affect the requirements for different product properties. To quantify these requirements and their relative importance, they must be related to thoroughly specified waste management systems, as has been done in the safety analyses, Tech. Part II.

Table 2.2 Waste matrix. Parameters of interest at different abnormal and normal events.
B = bitumen, C = cement
x = effect
– = minor effect
blank = irrelevant

PROPERTIES	Mechanical stability		Impact resistance		Temperature resistance						Water resistance and leach properties		Effect of micro org.		Radiation resistance	
					Low T		Elevated T		Burning prop.							
	B	C	B	C	B	C	B	C	B	C	B	C	B	C	B	C
ABNORMAL EVENTS																
1. Collision, drop	x	x	x	x	x	–	x	–	x	x						
2. Fall in water accident	x	x	x	x	–	–					x	x			–	–
3. Fire	–	–	x	x			x	x	x	x					x	–
4. Damage of container	x	x	x	x	–	–	–	–					–	–	–	–
5. Admin. errors	x	x	x	x	–	–	–	–	–	–	x	x	x	x	–	–
6. Retrieval	x	x	x	x	–	–	x	x	–	–	x	x	–	–	–	–
NORMAL EVENTS																
1. Stacking, storage	x	x	x	x	x	–	x	–	–	–	–	–	–	–	–	–
2. Transp., handl.	x	x	x	x	–	–	–	–	–	–	x	x	–	–	–	–
3. Degrad. of barr.	–	–	–	–	–	–	–	–	–	–	x	x	x	x	x	x
4. Disposal	–	–	–	–							x	x	x	x	x	x

3 PRODUCT CHARACTERISTICS AND SAFETY ANALYSIS

3.1 INPUT DATA FOR THE SAFETY ANALYSIS

The selection of proper input data for the safety analysis is complicated due to uncertainties connected with:

- the empirical character of most tests used for product characterisations

- the question of how far results from such tests are representative for the performance of technical waste products in the different stages of waste management

- actual variations in product qualities caused by varying technical process conditions, waste and matrix characteristics.

As a consequence, the applied input data (Techn. Part I, chapter 2) vary considerably with regard to documentary validity, degree of realism or conservatism, respectively.

Experimental assessments of these problems are presented in the following chapters. They were carried out in parallel to the safety analysis, and not all results were available to guide the initial choice of input data but are taken into account in later parameter studies.

The data for short term performance - mechanical strength, fall - and impact resistance, burning behaviour and particle size distributions - are mainly based on large scale tests, described in chapter 6. These should give representative or conservative results for average products from the bituminization and cementization processes applied or foreseen in the Nordic countries.

Fire: The data for the burning properties of bituminized wastes are conservative. A better fire resistance has been reported for products from the ASEA-ATOM bitumenization process, where burnable degradation products are removed by a pyrolytic pretreatment of the ion exchange resin /37/.

Release fractions are based on worst estimates. Recent results from small scale Danish tests /9/ indicate that they are considerably overestimated. Accurate predictions can so far not be made since the nuclide distributions are affected by scale factors, chemical state, oxygen access, burning rates and temperature gradients. There are, however, strong indications that the main fraction of radionuclides, even of Cs (≥75% of Cs) will remain in the slag residue. Similar conclusions can be drawn from recent pilot scale KBS fire studies /10/.

Water resistance: Recent results from extended water resistance tests (fig. 5.3 and 5.4) indicate that the swelling of bitumenized ion exchange wastes on uptake of water can be considerably higher than the assumed 5%. The swelling is influenced by small variations in process conditions, by the accessible amount of water and probably also by the water chemistry. It was highest for irradiated samples. It is difficult to judge how far such a high swelling can even occur under real waste management conditions, but the results emphasize the need for proper control of swelling properties.

Long-term leach properties: The applied leach data are based on the assumption that the leaching of radionuclides from the repository is only governed by diffusion and can be characterized by diffusion (D) or leach (L) coefficients (where D = L). Effects of chemical states and retarding reactions are not taken into account. The use of simplified conservative assumptions may be justified considering the many uncertainties involved in the prediction of long-term leach reactions.

The applied leach tests - even so called long term environmental tests - are of short duration. Experimental conditions are not directly comparable with real leach situations.

In the study it was attempted to standardize a "typical Nordic" water and to check leach rates both in de-ionized water and "Nordic" water. However, it appeared that even a "typical Nordic" water could hardly be representative for the water chemistry in a repository. The latter will be dominated by varying amounts of decomposition products from structural materials, canning and waste matrix, all of which can have significant effects on leach rates and distribution coefficients. Dissolution of alkaline compounds from a cement matrix and even from concrete moulds and bunker structures will strongly increase the pH of ground waters in and near the repository. In the first phase leached alkali hydroxides can raise the pH up to 13-14. A subsequent dissolution of "free" calcium hydroxide and finally of calcium aluminates and silicates can stabilize the pH at about 12-13 and 10, respectively /11/.

The leaching of radionuclides from cement products will probably follow a similar pattern. With some delay the Cs isotopes will follow the lighter alkali elements, most Sr-90 will be released together with calcium hydroxide, while Co-60 and other chemically bound nuclides will eventually be dissolved together with aluminates and silicates.

The high pH and saturation with decomposition compounds will delay the release of macro and micro compounds from cement products. Real leach rates will probably be lower than in leach tests with a large excess of distilled water. The same cannot be said for bitumen ion exchange products, where leach rates can be strongly enhanced by a variety of dissolved salts, including concrete degradation products /12/.

Leach rates could increase significantly in case of mechanical damages and deterioration of cement products. A swelling of bitumen products can also accelerate the leaching. The maintenance of a high water resistance, together with the possibility of chemical fixation of main radionuclides, are important guards against such unpredictable leach enhancements.

To allow for the involved uncertainties and to control the system's sensitivity towards inferior leach properties, the safety analysis must be based on conservative data and take worst estimates into account. Even these should, however, be as realistic as possible. This does not apply for all leach data used in the present safety analysis. The applied models and the neglect of chemical states and retarding reactions have introduced some unrealistically pessimistic values, in particular for C-14 and I-129 (Techn. Part I, table 2.11).

Even the values for the leaching of cesium from cement and bitumen are higher than generally anticipated for these nuclides. They correspond to present results for deteriorating samples and are 10-100 times higher than those for average product qualities, 100-10000 times higher than for optimally stabilized compositions. They can be characterized as realistic worst estimates, relevant for an examination of minimal acceptable leach properties.

The same or even higher values have been used for C-14 and I-129. The fraction of these nuclides contained in ion exchange wastes will be dominated by ionic species (CO_3^{2-}, HCO_3^-, I^-) /13/. It should be expected that such species are efficiently retained in a cement matrix. This has been verified by recent leach experiments. The resultant leach coefficients (table 4.2) were 1000-10000 times lower than the diffusion coefficients used in the safety analysis, 100-1000 times lower than experimental values for cesium ions. The bitumen data may be more representative. When experimental data is lacking, it should be permissible to assume that bitumen leach rates will not be essentially higher than those for cement. The values for Ni, Co and Sr are probably more realistic and somewhat less conservative than those for Cs.

Thus for a realistic-conservative approach with a comparable degree of conservatism for all elements, it can be appropriate to maintain the conservative values for Cs and to adjust the data for other elements as specified in table 3.1. For a more realistic approach these values can probably be reduced by a factor 10. The leaching of Cs, at least from cement, might be further reduced by a factor 10 or more where optimally stabilized compositions (st) are utilized. The consequence of such modifications of the leach coefficients is shown in Techn. Part II, chapter 7.2.

Table 3.1 Leach (diffusion) coefficients

Nuclide	Matrix	Leach coefficient (m^2/a)		
		Safety analysis x)	Recommended conservative	More realistic
Cs-137, Cs-135	Cement	3×10^{-4}	3×10^{-4}	3×10^{-5} (10^{-6})st
	Bitumen	1×10^{-6}	1×10^{-6}	1×10^{-7}
C-14	Cement	3×10^{-4}	3×10^{-6}	3×10^{-7}
	Bitumen	2×10^{-6}	3×10^{-6}	?
I-129	Cement	6×10^{-4}	6×10^{-6}	6×10^{-7}
	Bitumen	2×10^{-6}	6×10^{-6}	?
Ni-63, Co-60	Cement	4×10^{-9}	4×10^{-8}	4×10^{-9}
	Bitumen	4×10^{-9}	4×10^{-8}	4×10^{-9}
Sr-90	Cement	7×10^{-6}	7×10^{-5}	7×10^{-6}
	Bitumen	3×10^{-9}	3×10^{-7}	3×10^{-9}

x) Techn. Part II

3.2 EVALUATION OF RESULTS AS A GUIDELINE FOR PRODUCT CONTROL AND DEVELOPMENT

The safety analysis has not provided the antipicated guidelines for a quantification or mutual weighing of demands on product properties. Only few of the many product properties seemed relevant to the safety analysis.

Some effects of leach properties on radiation doses from disposed waste products were quantified. But in spite of the conservative high leach coefficients, radiation doses from leached main waste nuclides (Cs-137, Sr-90, Co-60) were in most cases insignificant (zero). Only in the case of a well drilled directly outside the repository were doses from Cs-137 high. In all other cases dose contributions were exclusively from long-lived nuclides (C-14, I-129, Cs-135) and - in spite of the low concentration in the reference waste - mainly from C-14 and I-129.

The relatively high doses from C-14 and I-129 are probably a consequence of an accumulation of worst estimates, i.e. use of unrealistically conservative leach rates and neglect of retarding effects such as of chemical reactions, isotope exchange reactions and dispersion. Thus for reactor wastes containing only a minor fraction of the total amount of C-14 and I-129 the results appear to be mainly of theoretical interest. They might, however, have practical interest in connection with an IAEA proposal /14/ for fixation of the main lot of C-14 as carbonates incorporated in cement. This could encourage the development of products with superior carbonate retention, e.g. by means of specific stabilizers (e.g. barium compounds).

In general, a main conclusion from the safety analysis must be, that demands on waste solidification and product properties can be very modest. One question is of course whether the applied models and the data used in the models are relevant enough to serve as basis for such a conclusion. The presence of a more or less independent barrier in form of a high quality waste product may to some degree compensate for uncertainties in the documentation of the safety provided by the geological environment and other outer barriers.

Another question is the problem of public acceptance. Regardless of identified demands on product properties, the additional safety gained by a fixation of the radioactivity in well defined stable products will probably have to be maintained. It will prevent or retard the release of activity to the soil around the repository which by the public might be regarded as a positive factor in itself.

For these two reasons it is important that:

- all product properties are well defined and reproducible
- the solidification process has wide tolerance limits towards technical process variables, so that acceptable homogeneities can be ascertained
- physical and chemical reaction mechanisms are so far understood that reasonable evaluations of long term stabilities are possible

4 LABORATORY TEST METHODS

4.1 BACKGROUND AND AIM

A great variety of laboratory tests are available for the characterization of waste solidification products. Some of them are standard tests designed for control of "conventional" products (concrete, asphalt) and are not always directly usable for testing solidified radioactive ion exchange wastes. Others have been developed for relative studies and are not standardized to ascertain comparable results from different sources. In general the main questions is, how far are results from such short term laboratory tests representative for the long term performance of technical waste products.

The present assessment of test methods has been coupled with routine analyses for laboratory incorporation studies. Efforts have been made to adapt and improve existing tests and to develop "new" tests, especially for bitumenized ion exchange wastes. Due to the importance at present attached to leach properties and the prevailing controversy about their determination, a main emphasis has been on leach tests and leach mechanisms.

Main tests for the characterization of cement and bitumen ion exchange products are compiled in table 4.1. Additional tests can be imposed by local requirements. For some purposes it will be necessary to use rather lengthy sequences of coupled tests, for example to control the influence of freezing - thawing on mechanical properties and on water and leach resistance.

Since only few data for solidified ion exchange wastes have been reported, "typical values" for this waste category have been included in table 4.1. They are mainly based on average results from the present laboratory studies. The values can vary for different

Table 4.1 Tests for properties of solidification products
B = bitumen/ion-exchange resin
C = cement/ion-exchange resin

Properties	Test method
Mechanical strength	
compressive strength	ISO R 679
tensile strength	ISO
impact resistance	
- fall tests	IAEA
- particle size analysis	sieving
Form stability, ductility	
homogeneity	microscopy
sag test	BS-7147 11973 Appc.
ring and ball	ASTM
penetration	"
hole migration	
cylinder bending	
Thermal stability	
freeze/thaw cycling	deep freezer - water
break point	DIN
softening point	ASTM
melting point	ASTM
heating tests (eg. 105°C)	oven
flash point	ASTM
fire tests	oven, 30 min. at 800°C
particle size analysis in fire	microscope, Coulter counter
Radiation stability	
gas evolution	gas chromatography
effects on mech. properties, water- and leach resistance	
Water resistance and chemical stability	
water resistance	immersion tests }
water uptake	immersion, ASTM }
multielement analysis of leachant	plasma analyzer
water content in products	ASTM
Environmental effects	
biodegradation	growth of bacteria
contact zone chemistry	
Leach behaviour	"Longterm" leaching of radionuclides in deionized water and in representative ground waters (see chapter 4.2)

Typical value	Matrix	Origin of data
15-20 M Pa	C	A0(79)3, IAEA
3- 5 M Pa	C	"
1-20 m	B, C	A0(79)17
5 weight % < 10 μm	C	"
± 5% deviation	B, C	IAEA-SM-207/78
25^{o}C, 1 mm	B	British standards
Bitumen specific	B	IAEA-SM-207/78
" "	B	"
" "	B	"
" "	B	"
50 cycles	C	A0(79)3
±0^{o}C (bitumen spec.)	B	A0(79)30
70^{o}C (bitumen spec.)	B	"
(bitumen spec.)	B	"
7d, 105^{o}C	B	A0(79)3
>250^{o}C	B	A0(79)30
	B, C	A0(79)18
30% of part. >10μm	B	A0(79)21
0.2 - 1 dm^3/kg	B, C	IAEA /15/
	B, C	
no visual damage after 7d (100d)	C	IAEA-SM-207/78
no swelling after 7d (100d)	B	A0(80)26
	B, C	A0(80)13
< 1%	B	A0(79)30, IAEA
	B, C	
	B, C	
Cs $\sim 10^{-6}$ cm/d	B	IAEA-SM-207/78
Cs $\sim 10^{-3}$ cm/d	C	IAEA-SM-207/78
t = 100d		A0(80)26

bitumen and cement processes, and are influenced by waste and matrix characteristics. They will also vary with the applied test conditions. To compare values from different sources, a detailed specification of process and test conditions should be available.

4.2 LEACHING PROPERTIES

Leach tests are often used as the main measure for the fixation of radionuclides in the products. The tests are in principle very simple. A sample spiked with one or more tracer nuclides, mostly Cs-137, is immersed in water, and samples taken with adequate intervals are analyzed radiometrically to determine the release (leaching) of radioactivity to the water (leachant). Unfortunately, the leaching is strongly influenced by a variety of parameters, such as:

- water chemistry, water volume to sample surface area, temperature and possibly pressure
- sequence of sampling and renewal of leachant
- product (specimen) preparation, form and exposure

Consequently, there can be great differences between results from the many different static and kinetic, accelerated and "long term" tests, which are presently in use for leach measurements. They are all vulnerable towards minor variations in experimental conditions.

Considerable efforts have been devoted to the development of a universal (static) "long term" standard leach test to be used for all types of solidified wastes (IAEA-Hespe, ISO /17,18/). But there is still no satisfactory procedure to determine real long term leach properties, or even to ascertain comparable results from different laboratories.

Comparisons are further complicated by the many different modes of presentation, as:

- leached fraction $A_n = a_n/(a_o \cdot t_n) d^{-1}$ or $\Sigma a_n/a_o$
- leach rate $R_n = A_n \cdot V/F$ cm d^{-1} = $A_n \cdot W/F$ g $cm^{-2} d^{-1}$
- leach coefficient $L = \Sigma R_n^{\;2} \cdot \pi/4 \cdot t$ $cm^2 d^{-1}$

where:

a_o = initial activity in test sample
a_n = activity leached per test period (t_n)
V = sample volume
F = sample surface
W = sample weight

At present several combinations of different units are in use. Leach rates are for example given in $cm \cdot s^{-1}$, $m \cdot s^{-1}$, $m \cdot a^{-1}$.

In this study, plots of accumulated leached fractions (ΣA_n) or leach rates (ΣR_n) versus time (t) or $\sqrt{t}$ have been adopted as the most realistic and illustrative basis for relative product comparisons. The latter gives indications about reaction mechanisms and a basis for deriving leach coefficients (L) and extrapolated R_n values.

Reported leach rates are mostly based on the mean R_n values for a "virtually constant range". There can be doubts about the definition and even the long term existence of a constant range. To be consistent, even the reference time, e.g. 100-200 d, should be specified. For small samples with poor leach resistance, an initial depletion may result in too low final R_n values, which is not representative for leaching from full scale products.

Leach or diffusion coefficients L (or D) are used in the present safety analysis. This enables a parallel treatment of leaching from the waste product and diffusion through concrete and clay barriers. The presentation assumes that leaching is governed by diffusion, which may be acceptable as a conservative rough approximation. In reality, leaching is a more complicated process. It also involves dissolution of micro and macro compounds from waste and matrix and chemical reactions between such species and with the leachant. Leach mechanisms will change with time, and initial surface reactions will naturally be more dominant for small test specimens than for full scale products. Recent efforts concentrate upon the development of advanced mathematical models and computer programs to enable a better coverage of the involved mechanisms /19, 20, 21/.

Expressions which relate the leaching to the (geometric) surface involve another uncertainty, in so far as neither the real "leach surface" nor its changes with time are known. For porous cement products the leach surface is certainly much greater than the geometric reference surface. Reference to the ("real") BET surface /22/ is hardly more correct, since the whole pore surface available for inert gas condensation will hardly be accessible for an aqueous leachant. Different modes of presentation are illustrated by figure 4.1 and table 4.2.

Test conditions

Modified "ISO conditions" /18/ have been used for control of products from incorporation experiments. Exposure of the entire sample surface was adopted, because this gave more consistent results than the old IAEA standard /17/ where only one surface is exposed. Inadequate sealing of the other part of the surface may result in the calculation of too high leach rates, as may be the case in the results shown in figure 4.1.I and table 4.2.

Normally, the test specimens have been 100 cm^3 cylinders with a volume/surface ratio of 0.8 cm. But even 5000 cm^3 cement (figure 4.1.III) and 500 cm^3 bitumen products

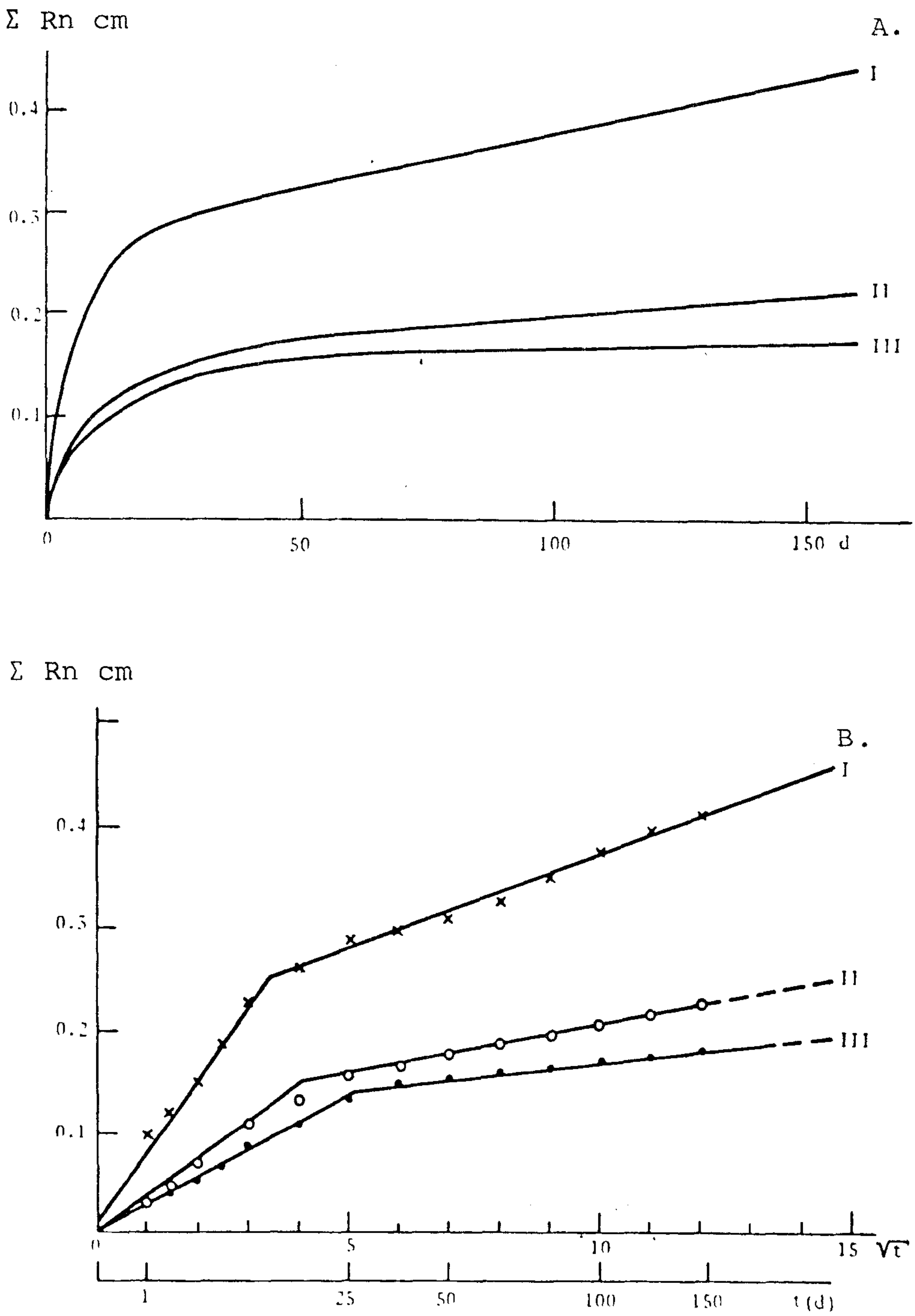

Figure 4.1 Typical leach plots for ion exchanger-cement products.

Leaching of Cs in distilled water /16/. Accumulated leach rates plotted A. aginst time, B. against √time.
I. Hespe test, one surface exposed. Sample volume ca. 100 cm^3.
II. Whole surface exposed (ISO). Sample volume as I.
III. As II, but sample volume increased to ca. 5000 cm^3.

Similar curves were obtained for the much lower leaching of Co from the same samples.

Table 4.2 Leach data, measured in distilled[x)] water. Typical modes of presentation

	Fig.	Leach rates, R_n			Leach coefficients, L				Remarks
		ΣR_n cm	R_n (100-200) cm/d		L_1		L_2 or L_a, resp.		$L_1 L_2$ from 2 different, L_a from
		after 150d	Measured	Extr.	cm^2/d	m^2/a	cm^2/d	m^2/a	average slopes
Cs-cement	4.1-I	0.42	-	$8 \cdot 10^{-4}$	$3.9 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$3.2 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$	Hespe
Cs-cement	4.1-II	0.23	-	$4 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	Wholebody, small
Cs-cement	4.1-III	0.19	-	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$1.8 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$7.5 \cdot 10^{-7}$	Wholebody, large
Cs-bitumen	4.2-I	0.024	$1 \cdot 10^{-4}$	-	-	-	$4 \cdot 10^{-7}$	$1.5 \cdot 10^{-8}$	L_a = average
Cs-bitumen	4.2-II	0.034	$1 \cdot 10^{-5}$	-	-	-	$4 \cdot 10^{-7}$	$1.5 \cdot 10^{-8}$	0 - 250 d
I^--cement		-	-	$6 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$7 \cdot 10^{-8}$	$1.3 \cdot 10^{-6}$	$5 \cdot 10^{-8}$	13% ion exch. SR-cement, no additives
CO_3^{2-} cement		-	-	$4 \cdot 10^{-5}$	$7 \cdot 10^{-7}$	$2.5 \cdot 10^{-8}$	$3 \cdot 10^{-7}$	$1 \cdot 10^{-8}$	

x) not typical for the leaching from disposed bitumen products, see even chapters 3.1 and 7.4.3.

have been assayed. The ratio between leachant volume and specimen surface has been 10 cm, and in special cases 1 cm. The leachant is renewed with each sampling according to a strictly maintained sequence, e.g. with intervals increasing from 1 day during the first week, to 1 week, 1 month and finally to 6 months.

Distilled water has been the main leachant. ISO prescriptions for excessive water purities and narrow pH limits were abandoned as irrelevant, since for cement products and salt containing bitumen samples the water chemistry will in any case be dominated by dissolved cement and salt compounds. Tests with "environmental waters" were omitted for similar reasons. Emphasis has instead been on control of pH and conductivity in the resultant leach solutions. Furthermore an ICP (inductive coupled plasma) spectrometric method has been developed for quantometric control of up to 25 leached inactive elements /24/. Selective effects of the water chemistry on the leach behaviour of bitumen products have been investigated in other experiments /12/.

Cs-137 and Co-60 and in some cases Sr-85 measured by gamma spectrometric analysis, have been used as main indicator (tracer) nuclides. The leach behaviour of Sr-90, I-125 (iodide) and C-14 (carbonate) was studied in separate tests, measured by beta counting and liquid scintillation analysis.

Under strictly comparable conditions the impact of process variables could be measured with a relative accuracy of $\pm$ 10-20%. Intercomparisons of cement and bitumen products are difficult to make, because essential variables have adverse effects on the two materials. "Absolute accuracies" are hard to specify (or even define) and may at the best be within a factor of 10.

To study the effect of mechanical damages and significantly increased leach surfaces, the activity release from a few thoroughly crushed cement samples was measured. Both the total crushed sample and separate fractions (lumps >3.35 mm, 3.35 - 0.85 mm, and < 0.85 mm) were assayed.

Trends and results

The results clearly illustrate that both the course of leaching and the influence of the water chemistry are fundamentally different for cement and bitumen products. Some representative results are shown in table 4.2 and figures 4.1 - 4.3.

Figure 4.1 is illustrative for the course of leaching from cement samples. The leach rates are initially relatively high, but they decrease significantly after a few weeks. The $\Sigma R_n/\sqrt{t}$ plots show two different slopes. The resultant L coefficients (L_1 and L_2 in table 4.2) can differ by a factor 10 or more. Such a course of leaching can either be due to depletion, to effects of the sampling frequency or to a decrease of the leach surface. Depletion would mainly affect the smaller samples, while in this case the L_1/L_2 ratio was highest for the large sample (4.1.III). The sampling sequence has certainly some effect, but is hardly the dominant cause. A decrease of the leach surface, for example a blockading of pores due to some redeposition of dissolved macro compounds, cannot be excluded. In this case, similar stabilizing effects should be expected for disposed waste products.

The leaching from bitumen products both in deionized water and in salt solutions is very slow during the first weeks, but is followed by irregular activity bursts or by gradually (sometimes apparently exponentially) increasing activity releases, as illustrated by figures 4.2, 4.3, 5.1 and 5.2. In some cases steady leach rates were approached after 200-300 days.

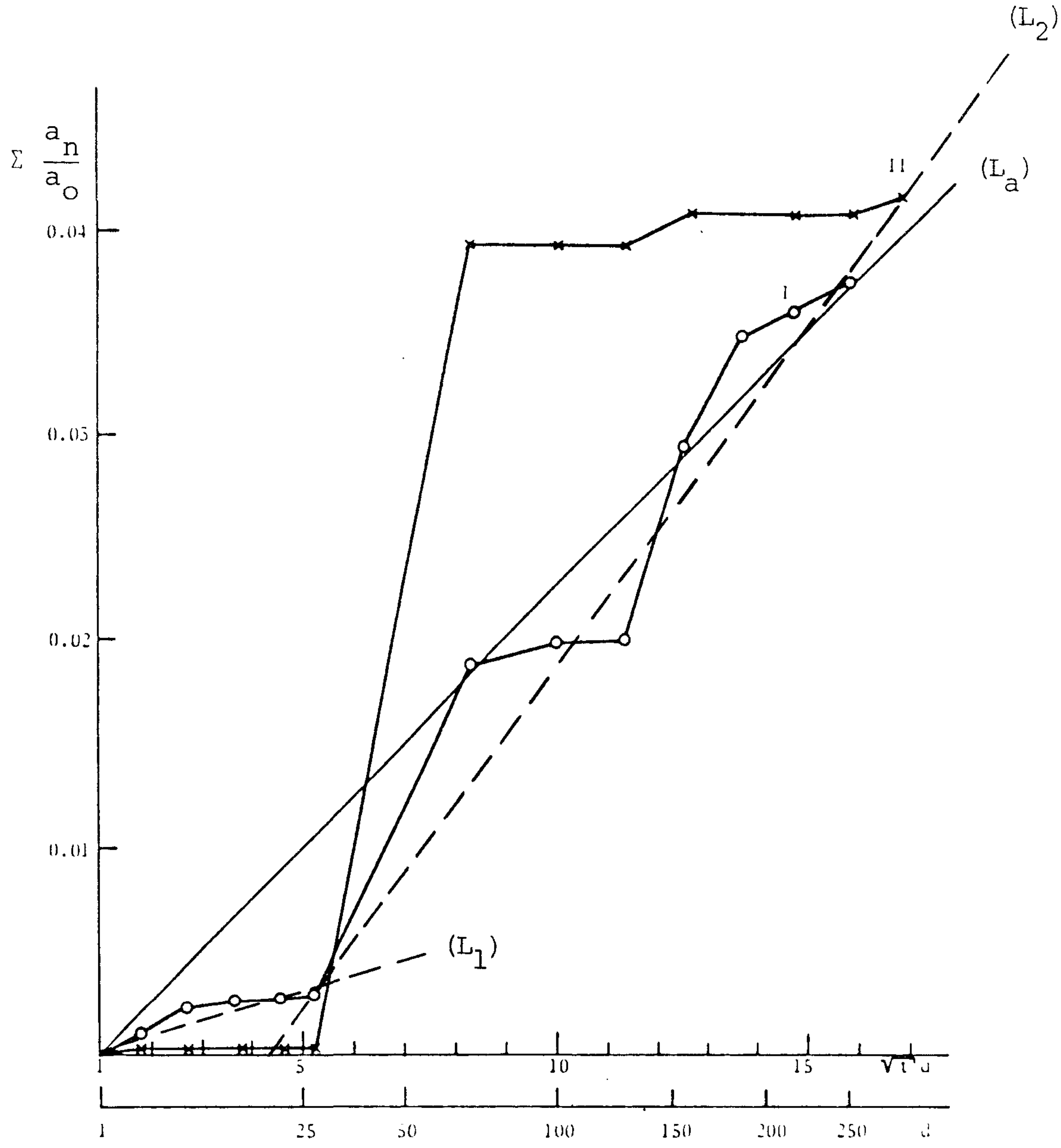

Figure 4.2. Typical stepwise leaching of Cs from ion exchanger-bitumen products in distilled water.

Whole surface exposed (ISO), sample volume ca. 100 cm^3.
Resin: bitumen I. 40:60, II. 50:50.

The leach rates are strongly influenced by the water chemistry. The leaching from bitumen is enhanced by most salts. Particular high leach rates were observed in the presence of magnesium salts and in contact with concrete /12/. For cement products most salts, including leached cement compounds have a stabilizing effect. Consequently, leach tests with excess of deionized water will give realistic conservative results for cement products, but such tests will give low results for bitumen and are hardly representative of the leach behaviour of disposed bitumen products.

Cesium together with other alkali elements /24/ is leached much faster than other waste nuclides, and much faster from cement than from bitumen. For cement the leach rates decrease in the order $Cs > Sr > I^- > CO_3^{2-} > Co$, with ratios of about 100:10:1 for Cs:Sr:Co. Leaching of I^- and CO_3^{2-} from bituminized products have not been measured. The sequence of the other isotopes tend to be the same as for concrete, but the ratios are smaller and strongly affected by experimental conditions. The difference tends to disappear when divalent cations such as Mg^{2+} or Ca^{2+} are present in the solution /12/.

Mechanical damages, cracks or a break down of the products would naturally give rise to increased release of radioactivity. In the tests with crushed cement samples the release was highest from the finest fraction (< 20 mesh), but did not always increase proportionally with the leach surface. The release of Co was not significantly affected. For samples stabilized with vermiculite and Corrocem even the release of Cs was only modestly enhanced (figure 5.6).

Both the Danish "DELTA tests" /12/ and tests with unprotected cylindrical specimen gave some indications that even deformations of bitumen products can have leach enhancing effects.

4.3 TESTS FOR WATER RESISTANCE

Prior to any leach testing the water resistance of a product should be ascertained. This is done by immersion of a cured specimen in distilled water and observation of its integrity and dimensional stability (after e.g. 1 and 7 days). Further periodical inspection for long term stability (e.g. after 100 and 200 days) is recommended. Water uptake and swelling are controlled by periodic weighing of the specimen and measuring of dimensional changes (see even figures 5.3, 5.4).

These tests are of special relevance for ion exchange solidification products where swelling can lead to severe damages of the waste package, even break down the whole product, and accelerate the leaching of incorporated radionuclides. The type of destruction is quite different for cement and bitumen products / 2 /, the former will crack and eventually pulverize, while the latter absorbs water under drastical dimensional changes. Bitumen samples containing 70-80 w% dry resin swelled even upon storage in air, while those with 50-60% resin swelled to twice their original volume after 2-3 months immersion in water. The water uptake in 40-50% mixtures depends on bitumen type and waste characteristics. Poor water resistance can even occur as a result of excessive residual water in the products.

The tests are rapid and well suited for screening purposes, but they also give valuable information about fundamental product properties and critical parameters. With some extensions they can even replace accelerated leach tests.

A so called "colour test" has been designed to make visible the course of water uptake and penetration in cement samples. Relative calibrations of the test have been initiated. Structural effects of water uptake and swelling - shrinking of resin particles have been examined by optical and electron microscopy.

4.4 MECHANICAL PROPERTIES

Radioactive materials can be released in connection with a dimensional break down of the product. For bitumen products shock resistance as well as plasticity are the most important properties, whereas in the case of cement products shock-proof and compressive strength are important.

Tests used to characterize the mechanical properties of bitumen waste products are penetration, break point and brittleness measurements. These tests are carefully defined in the ASTM standard test catalogue. In the case of cementized products compressive strength, tensile strength, shock and fall resistance have been measured. These tests have been described either by ISO or IAEA.

Not all of these standard tests are directly usable for testing radioactive waste products. Some of them can be adapted with small modifications, others could not be used at all, e.g. penetration of bitumenized ion exchange wastes. Instead some "new" tests, such as "cylinder bending" and "hole migration" /2/ have been introduced.

The tests are useful for relative product comparisons, but they cannot provide input data for the safety analysis. The latter must be based on more realistic waste handling conditions as described in chapter 6.

4.5 THERMAL RESISTANCE

Fire resistance and burning rates are the most important thermal properties. For radiological consequences release fractions for different radionuclides and particle size distributions of the burning products are important. Products in cement matrix are in general very resistant to fire, but some gasification of incorporated resins may occur and could even cause a certain activity release.

In a Nordic climate even the resistance against low temperatures must be considered. Both bitumen and cement products can behave surprisingly at temperatures below ca. 0°C. Bitumen is losing its plastic properties and becomes more glasslike (break point analyses). Residual water in cement may swell and waste blocks may crack /3 /. In both cases the result is particles of a wide size distribution as can be shown by size analysis. The thermal resistance of the products has been studied by freezing-thawing experiments, by making fire tests (bitumen, cement) and by standard tests for bitumens softening and melting points, ignition and flash points. Different heating tests (105-800°C) /2, 25/ with cement specimens were performed.

Even in these cases the small scale standard tests are mainly usable for relative studies and mechanism investigations. The input data for the safety analysis should preferably be provided by full scale tests, chapter 6.4.

4.6 RADIATION STABILITY

Changes caused by irradiation in the solidification product have effects on practically all the other properties. The effects are not sufficiently known, to predict exactly what will happen in a solidification product within a certain time with a certain specific activity and composition. Therefore a good safety margin should be ascertained.

Tests for radiation stability are discussed in chapter 6.5. Effects on water and leach resistance are shown in figure 5.4.

4.7 DEGRADATION BY NATURAL PROCESSES

The long term behaviour of different waste products is of importance for the safety assessment of the disposal systems.

Predictions about future performance or durability of materials should preferably be based upon:

- a description of the degradation factors influencing the material during its service life
- an estimate of the material's service life, as well as a description of its behaviour during the lifetime, including a description of maintenance possibilities, if relevant

Experience with the durability of "conventional" materials, e.g. from the building industry, can to some extent be utilized for such predictions /23,26/. Roughly speaking the main individual factors affecting the durability of materials are:

- water (moisture, moisture gradient)
- temperature (temperature gradients)
- mechanical stress
- corrosion (chemical and biological processes)
- radiation

In the study some accelerated tests for aging have been made such as irradiation of products, freezing-thawing cycles and elevated temperature tests. A few preliminary leach experiments with microbes in nutrient solutions indicated significant effects of growth of microbes, figure 4.3 /12/.

These tests, however, are difficult to compare with "real aging". The results are only indicative and mainly relevant for relative comparisons of different products.

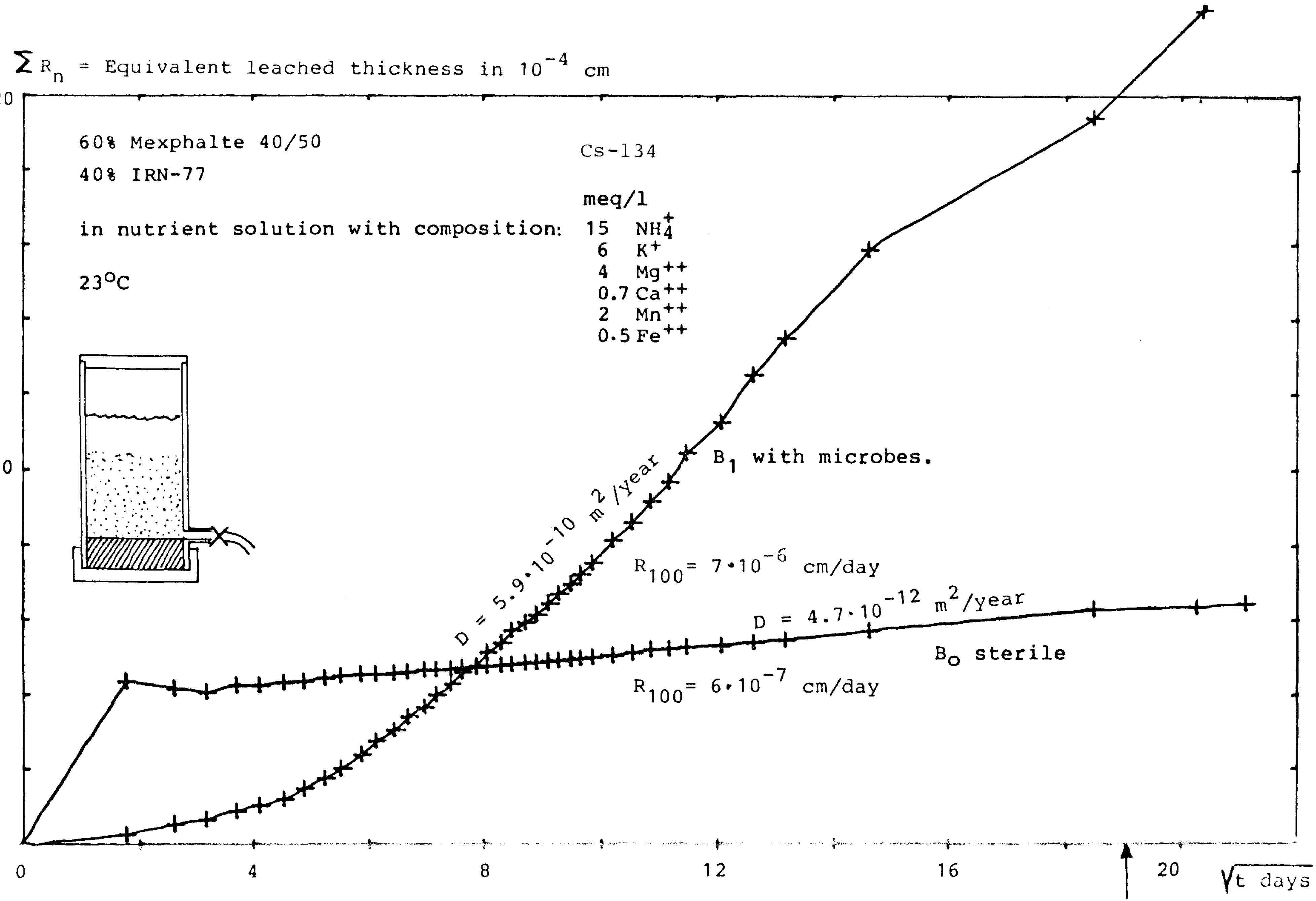

Figure 4.3 Cs-134 leaching [illegible] system as indicated.
With and without microbial growth (12).

5 LABORATORY STUDIES ABOUT THE IMPACT OF PROCESS VARIABLES

5.1 BACKGROUND AND AIM

Even with only modest demands on the stability of waste solidification products, it is essential that the product qualities are reasonably well defined and reproducible. For this purpose the impacts of main process variables must be known.

Both in Finland and Sweden incorporation studies have been performed to recommend processing conditions for the different technical plants. In this connection the Swedish Cement and Concrete Research Institute (CBI) has made an extensive study about the compatibility between resins and cement /3/.

The present investigations cover a wider range than the more process specific national projects. They have mainly been carried out as Norwegian/Finnish/Swedish co-operation efforts and have concentrated upon the identification of critical parameters and tolerance limits. The main emphasis has been on impacts of waste and matrix characteristics. A supplementary Danish study /12/ has mainly been concerned with bituminized products and leaching mechanisms.

Within the limits imposed on laboratory experiments, experimental variables have been adapted to those at existing and planned waste facilities in the Nordic countries. Some arbitrary simplifications and higher waste loading were employed to facilitate the identification of systematic trends and critical parameters.

Since earlier experiments /2/ indicated that, at least with cement, it was more difficult to achieve stable products with granular than with powdered resins, the present experiments concentrate upon typical granular resin wastes.

Effects of the resin type, of their saturation and exhaustion, of bound and free water, and of inactive salts have been examined. Several bitumen and cement qualities as well as a variety of cement additives have been tested.

5.2 WASTE AND MATRIX MATERIALS

5.2.1 WASTE

Both new (conditioned) and spent (inactive) strong acidic, strong basic ion exchangers - type Dowex 50W-21K, 20-50 mesh, Duolite and a corresponding Finnish resin - were assayed. Most experiments were performed with a spent Finnish resin from inactive test runs in the Loviisa power plant. The water content in the resins ("even level") /27/ has varied between 60% and 80% (referred to all water that can be removed by heating to 105°C). The waste loading is expressed in weight percent dried resin.

In some bitumen experiments 50% of the resin were replaced by a simulated evaporator concentrate (containing $NaNO_3$, $Ca_2C_2O_4$, $Na_2B_4O_7$, Na_2CO_3, NaOH, Fe_2O_3 and detergents). As a reference also the resin-salt mixture was assayed.

5.2.2 INCORPORATION MATRIX

Different types and qualities of blown and distilled bitumen, of Portland and slag cement, considered or used at Nordic waste facilities:

BITUMEN: BIT-15, BIT-45, BIP-85/40 from the Finnish Neste Oy, Mexphalt 40-50 and Mexphalt R-85/40

CEMENT: Different Portland cement qualities - ordinary (OC), sulphate resistant (SRC), low heat (LHC), in a few cases also rapid hardening (RHC) - and two blast furnace slag cements (Swedish and Finnish)

CEMENT ADDITIVES:

- Silix GP, a Ca soap forming concrete additive based on fatty acids, used to increase concrete densities
- Sika Aer, an air entraining agent, used to increase the frost resistance of concretes
- Corrocem, an anti-corrosion concrete additive developed for use in aggressive chemical environments, increases mechanical strength, resistance to water penetration and to attack by aggressive salts and acids
- Vermiculite (ball-milled, <30 mesh) used to bind Cs
- Water glass, various phosphates

5.3 PRODUCT CHARACTERISATIONS

The test program was rationalized by extensive use of simple screening tests:

- water resistance tests with visual observations of integrity and dimensional changes (swelling)
- compressive strength (cement samples)

Representative products were characterized by long term leach tests in deionized water mostly with 2 or 3 indicator nuclides (Cs, Co, Sr). For bitumen even the long term water uptake in the leached specimen was measured.

Selected samples were analysed according to tests listed in table 4.1.

5.4 BITUMINIZATION

5.4.1 PROCEDURE

The waste slurry is mixed in a special mixer kneading equipment manufactured by Werner & Pfleiderer. The water in the waste is evaporated and evacuated during the process. The machine is supplied with a discharge screw and has also been used for casting of samples

- waste loading, 40-90 weight % dry resin, typically 40-60% (ca. 400-600 kg/m^3)
- water content in slurries 60-80%
- mixing temperature 120-180°C, typically 140°C
- sample size 100 cm^3 and 500 cm^3

5.4.2 OBSERVATIONS AND RESULTS

Both the leach behaviour and water uptake of bitumen products were found to vary significantly with the waste type, loading and bitumen quality.

Effects of the bitumen quality (BIT-15, BIT-45 and BIP-85/45) and waste loading (40 and 50%) on the leach behaviour of bituminized ion exchange products are shown in figures 5.1 and 5.2.

The water uptake (swelling) proceeds in a similar way as the leaching of Cs, figure 5.3 and 5.4. It is initially low but increases with time and has been considerably higher than anticipated, 10-25% after 540 days for the 40:60 resin/bitumen products, up to 40% for the 50:50 products. The harder bitumen qualities with low waste contents tend to swell less than the softer types.

It is difficult to evaluate whether the water is mainly taken up by the resin particles or if, once they have started to swell, even the stressed bitumen matrix will contribute essentially to the water uptake.

Swelling of bituminized wastes is not exclusively an ion exchange phenomenon. As shown in figure 5.4, the water uptake was even higher in mixed salt-resin and in pure (resin free) salt bitumen products. Even the leaching, particularly of Co, was considerably enhanced in the salt containing products.

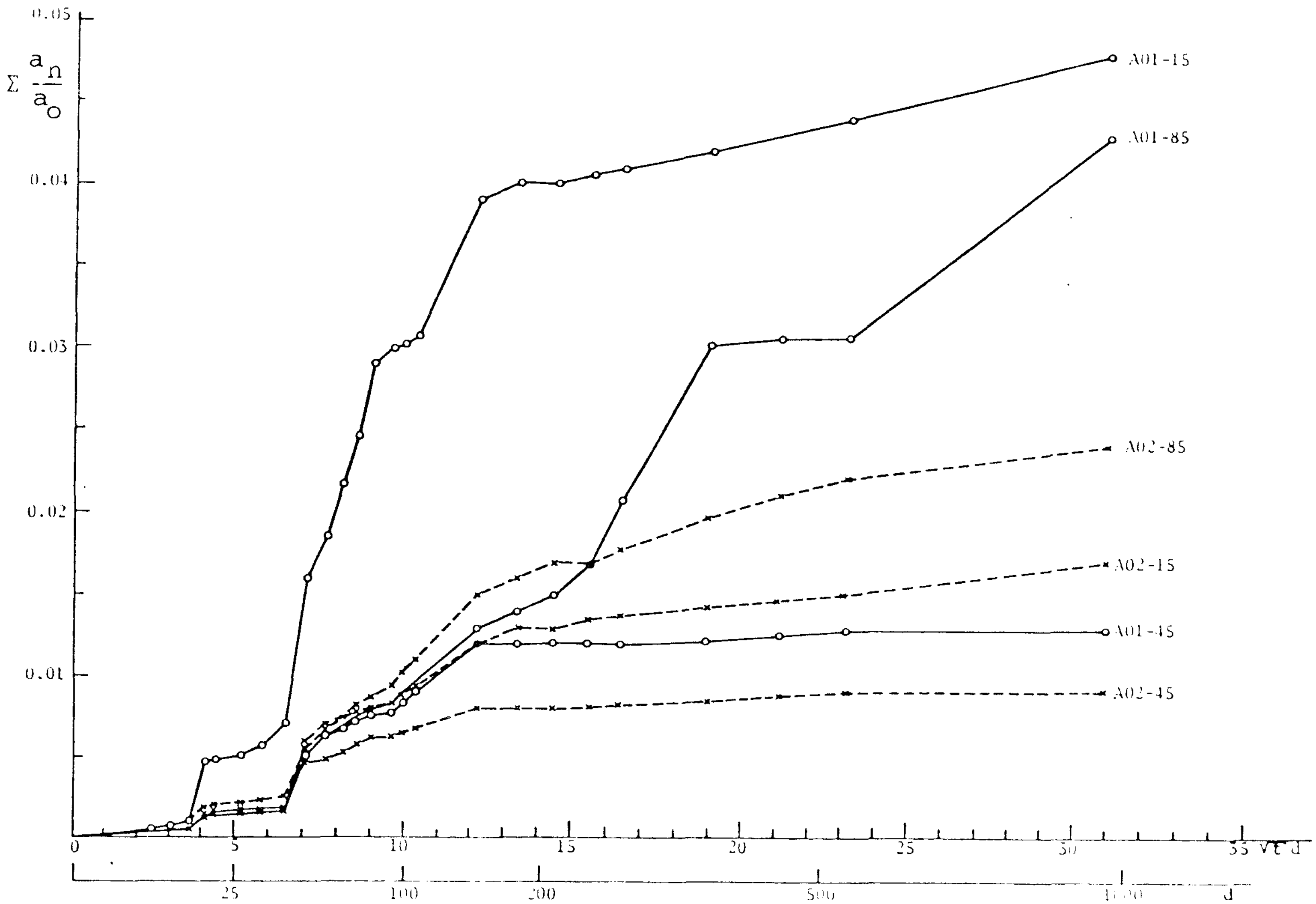

Figure 5.1 Longterm (900 days) leaching of Cs from ion exchange-bitumen products with distilled water.

Ion exchanger:bitumen = 50:50 (A01) and 40:60 (A02), respectively.
Bitumen qualities: BIT 15, BIT 45 and BIP 85/40.

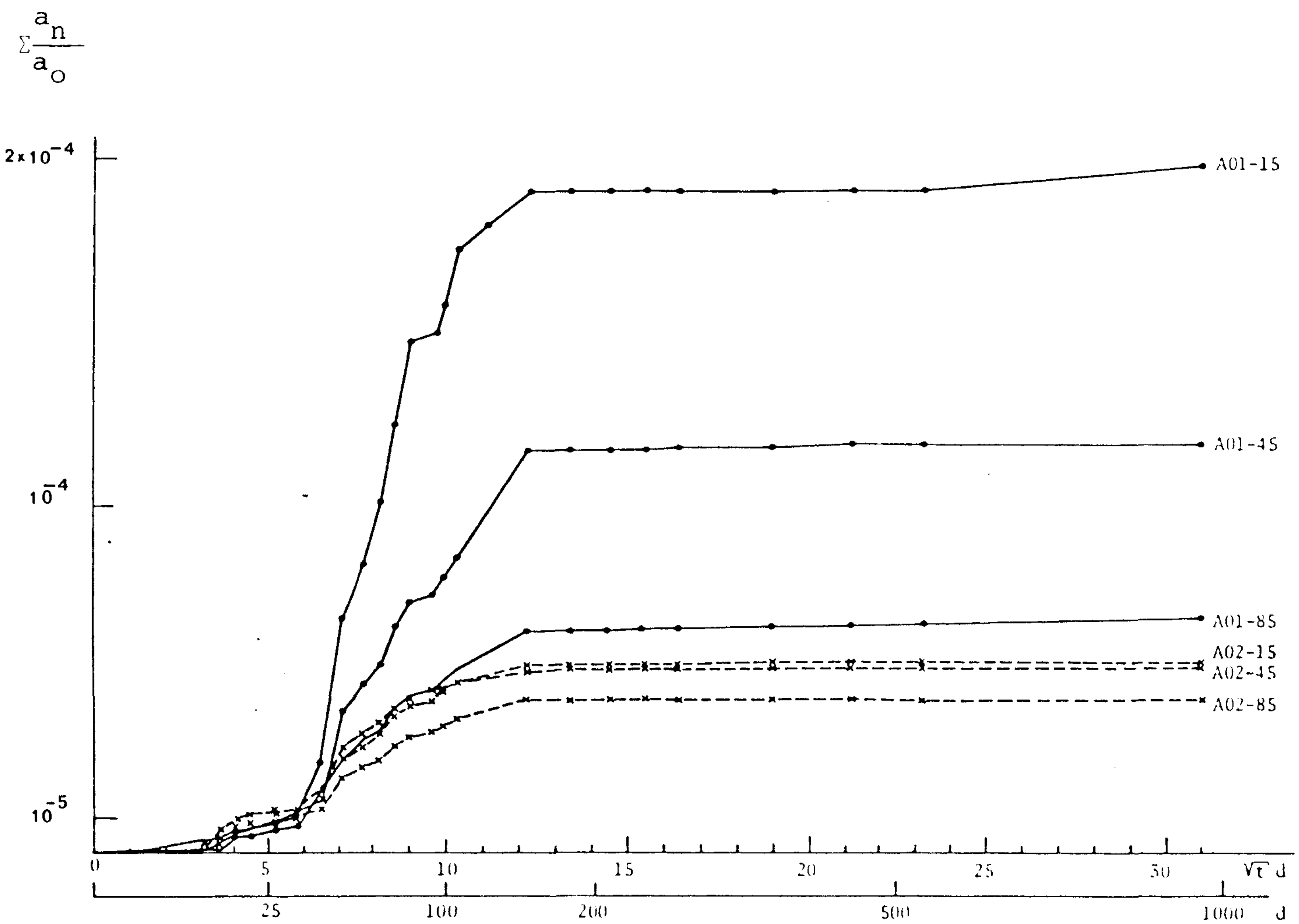

Figure 5.2 Longterm leaching of Co from ion exchanger-bitumen products with distilled water. Same samples as in fig. 5.1.

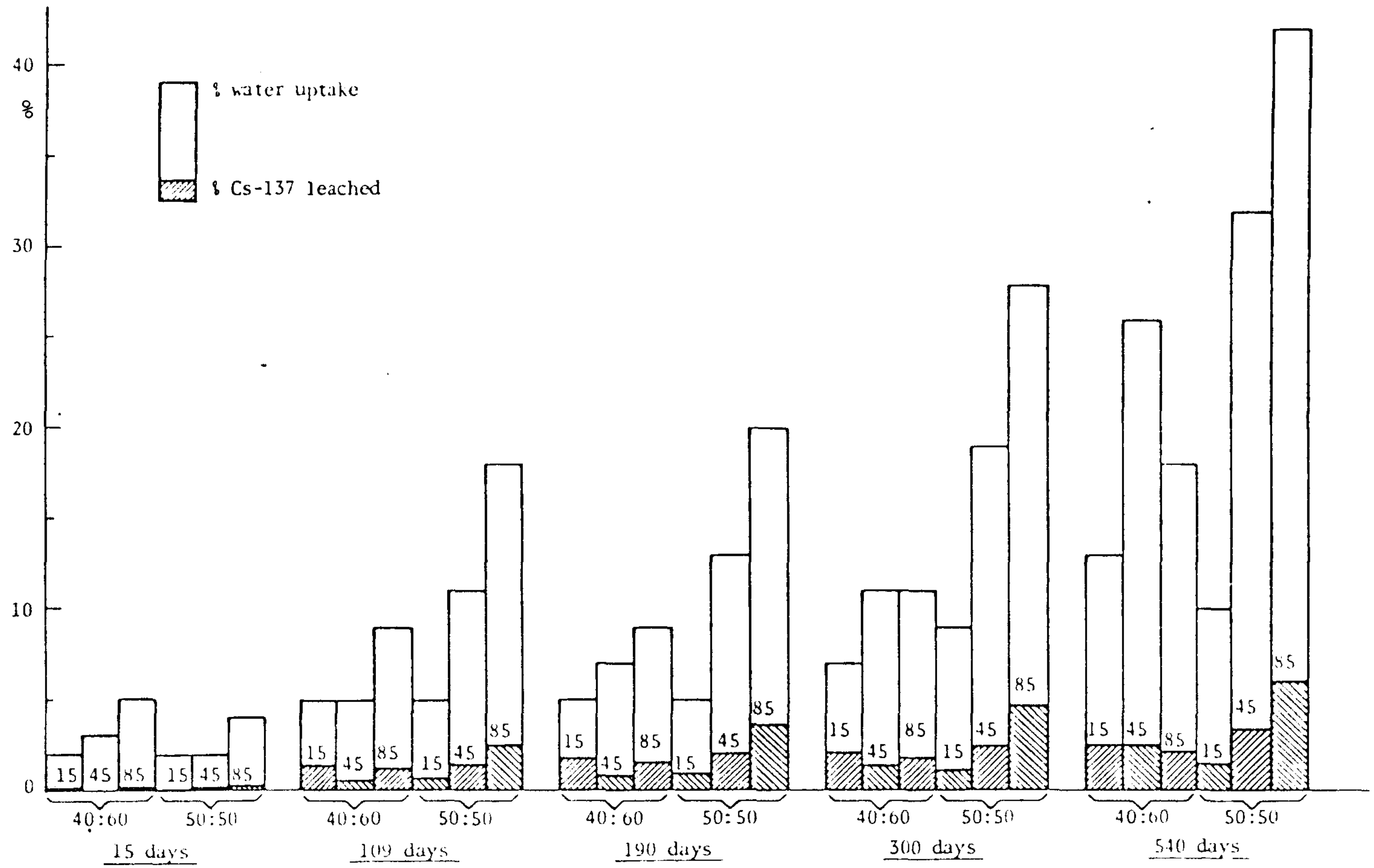

Figure 5.3 Comparison of the time dependent water uptake and Cs leaching for ion exchanger/bitumen products. Ratios 40:60 and 50:50. 3 bitumen types (BIT 15, 45, BIP 85/40).

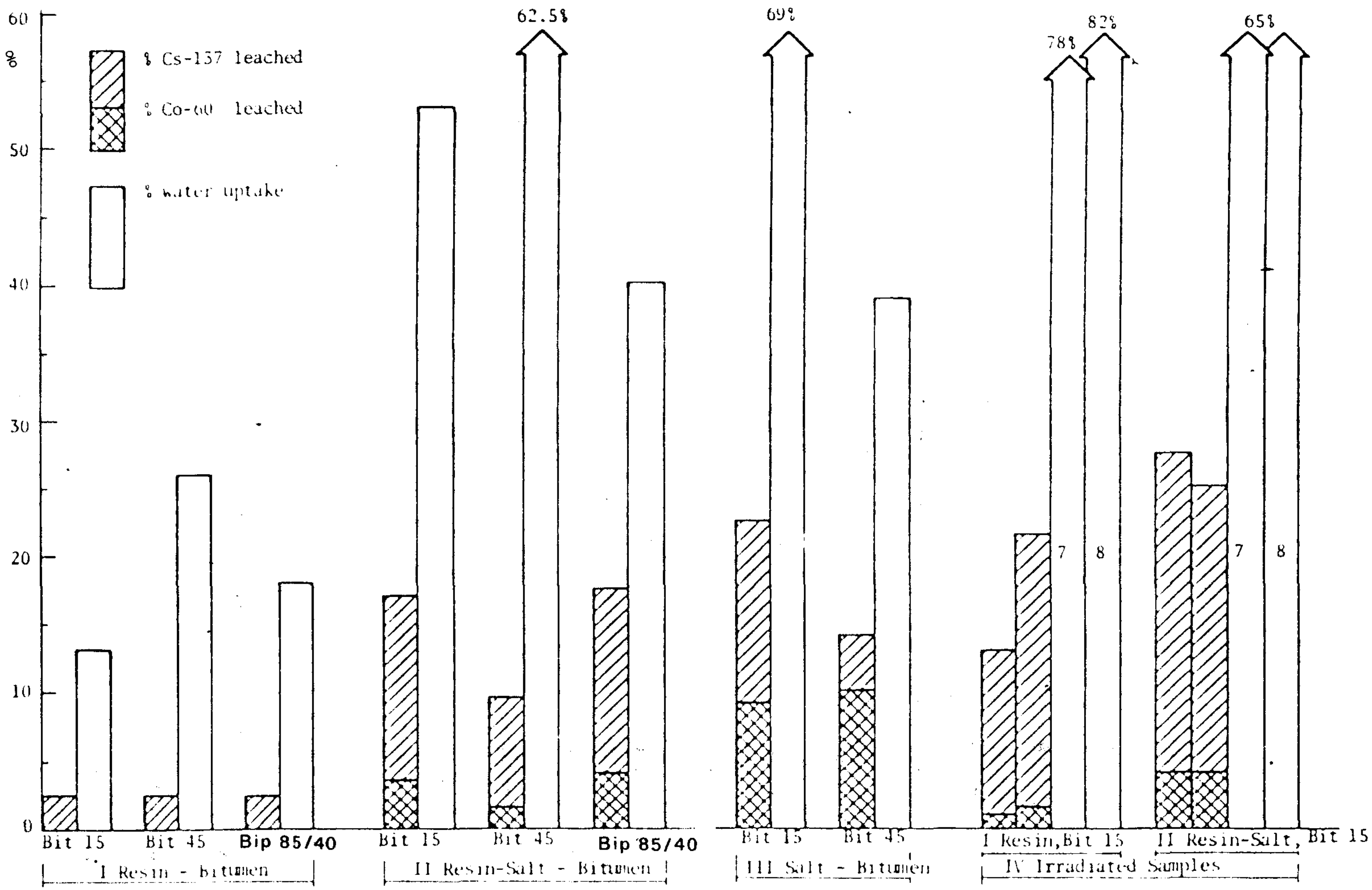

Figure 5.4 Water-uptake, Cs- and Co leaching after 540 days for bitumen products with 40% (40:60 products) of I. ion exchange resin II. resin+salt, III salt. IV. Irradiated samples exposed to /7/ 10^7 and /8/ 10^8 rad.

The leachability and still more the water uptake were significantly enhanced for irradiated samples, which had been exposed to 10^7 /7/ and 10^8 /8/ rad, respectively, see figure 5.4.IV. It should be noticed that the effect of radiation was remarkably higher in products where the waste consisted only of ion exchange resins than in the salt containing products.

As a conclusion it can be stated that the initial leaching of ions from bitumen is relatively slow. The leached amounts, however, can be relatively large with time. Leaching of Co-6o was usually with factor 2-5 less than that of Cs-137. Bitumen quality and waste concentration had an effect on leaching, the best overall combination was BIT-45 and 40:60 (waste/bitumen) ratio. The mixing of bitumen with waste caused a viscosity increase compared to pure bitumen - this increase varied between 30-50%.

5.5 CEMENTATION

5.5.1 PROCEDURE

The waste slurry - wet ion exchange resin - was mixed into cement using ASTM standardized outfit and procedures specified for cement laboratories. To prevent an initial breakdown of the "resin concretes" the prescribed curing in water saturated atmosphere had to proceed in sealed plastic containers.

- waste loading 10-24%, weight % dry resin, typically 13-20% (ca. 220-320 kg/m^3)
- water/cement ratios (v/c), referred to the total amount of water in the mix, 0.35 - 1.0
- curing times 7 d, 28 d, 100 d, 180 d, 250 d
- sample size 0.15 - 0.2 kg and ca. 7 kg

5.5.2 TRENDS AND RESULTS

Product properties were strongly affected by waste and matrix characteristics and by water/cement ratios. In particular, for high waste loadings (>15-19%) it was often difficult to achieve products which passed the screening tests, i.e. did not deteriorate when they were immersed in water. The swelling - shrinking of the ion exchange particles tend to give rise to cracks. There were indications that under certain conditions these can develop into a system of communicating pores, which results in accelerated leaching and finally in a break down of the whole test specimen.

Water/cement tolerance ranges are often extremely narrow. Typical for ion exchange wastes, it is difficult to optimize and even define "true" water/cement ratios, because the fraction of bound water in the ion exchanger, which is available for cement setting tends to vary with resin and matrix characteristics. It can even be affected by the amount of added water /28/, probably also by the mode and time of curing.

Table 5.1 gives an extract of how waste and matrix characteristics tend to affect the water resistance (I), compressive strength (II), Cs and Sr leach rates (III). Effects on tolerance limits for maximal waste loading (A) and for water/cement (v/c) ratios (B) are indicated in the last columns.

RESIN CHARACTERISTICS had significant impacts on product integrities (I) and tolerable maximal loadings (A). Even nominally similar resins from different manufacturers behaved differently. Duolite resins were more compatible than corresponding Dowex resins. Spent resins were easier to incorporate than (conditioned) new resins, cation exchangers easier than anion exchangers. Na-, Cl- and particularly SiO_3 substituted ion exchangers were more compatible than those in H-OH form.

Table 5.1 Cement incorporation. Effects of process variables

PROCESS VARIABLES	PRODUCT CHARACTERISTICS				TOLERANCE		REMARKS
	I	II	III		A	B	
	Water re-sistance	Compr. strength	Leach ability Cs	Leach ability Sr	Max. loading	v/c tol. range	I. good-poor-decomposed II. 3-30 MPa III. 10^{-3} - 10^{-7} cm^2/d A. 10-35 w/w% B. max. 0.35 - 1.0
RESIN CHARACTERIST.	(x)	-	x	x	(x)	x	
Swelling⇄shrinking	(÷)	÷	÷	-	(÷)	(÷)	
Dowex→Duolite	+	-	-	-	+	+	
H → Na	+	-	-	-	+	+	
OH → Cl → SiO_3	+	-	-	-	+	+	
WASTE LOADING	(x)	(x)	x	x		x	1: linear (see fig. 6.1
<10 w/w%	v	1	-	-		x	v: dep. on other variables
10→15 "	÷v	÷1				-v	
15→25 "	÷v	÷1	-	-		-	
WATER/CEMENT	(x)	x	(x)	(x)	(x)		Nominal, incl. all water
0.4<v/c<0.6	+v	+v	+v	+v	+v		
CEMENT QUALITY	(x)	x	(x)	x	x	x	Adverse trend for powdered resins /2/
LHC→slag→OC→ →SRC (RHC)	+	-	+	+	+	v	
ADDITIVES	(x)	x	(x)	x	(x)	(x)	Varying effects
Silix-Sica	+	-	-	-	-	(+)	
Vermiculite (ver)	-	÷	(+)	-	-	+	Selective Cs-retention
Corrocem (cor)	(+)	+	+	+	(+)	+	
Cor + ver	(+)	+	(+)	+	(+)	(+)	

Effect: - insignificant, x some, (x) significant, + positive,
(+) significant improvement, ÷ negative, (÷) critical variable
1 linear v varies with other variables

WASTE LOADINGS approaching a critical upper limit (varying between ca. 15 and 22%) had strong effects on water resistance and leachabilities. The compressive strength decreased proportionally with the resin content.

THE CEMENT QUALITIES had marked effects on the leachability. Cs leach rates were relatively high for Finnish and Swedish slag cements, lowest for SRC (and RHC) qualities. Similar trends were also observed for resin-free cements.

THE CEMENT ADDITIVES affected compatibilities and product characteristics in various ways. Silix-Sika extended water/cement tolerance ranges. Water-glass gave initial improvement of all examined criteria, but the products deteriorated with time. This may be due to the introduction of excessive Na ions, and can probably be prevented by a better balancing of the composition. Vermiculite reduced the leaching of Cs significantly, provided the particle size was kept so low that essential impairment to mechanical properties was avoided. Attemtps to reduce the leaching of Sr by means of apatites and other phosphate systems failed. Corrocem improved all product characteristics and extended the tolerance range for water/cement ratios and for maximal waste loading. Best results were achieved with a combination of Corrocem and vermiculite (5-20% Corrocem + 2.5% vermiculite).

The effects of additives and waste loadings on the fixation of Cs-137 is illustrated by the leach plots in figure 5.5. Figure 5.6 shows the effects of stabilizing additives on the leaching from crushed samples. In this case the release of Cs-137 ($\Sigma a_n/a_o$) from a crushed SRC cement sample stabilized with Corrocem-vermiculite was actually lower than from a corresponding unstabilized slag cement sample. Whereas all Cs in the crushed unstabilized sample was released within a few days.

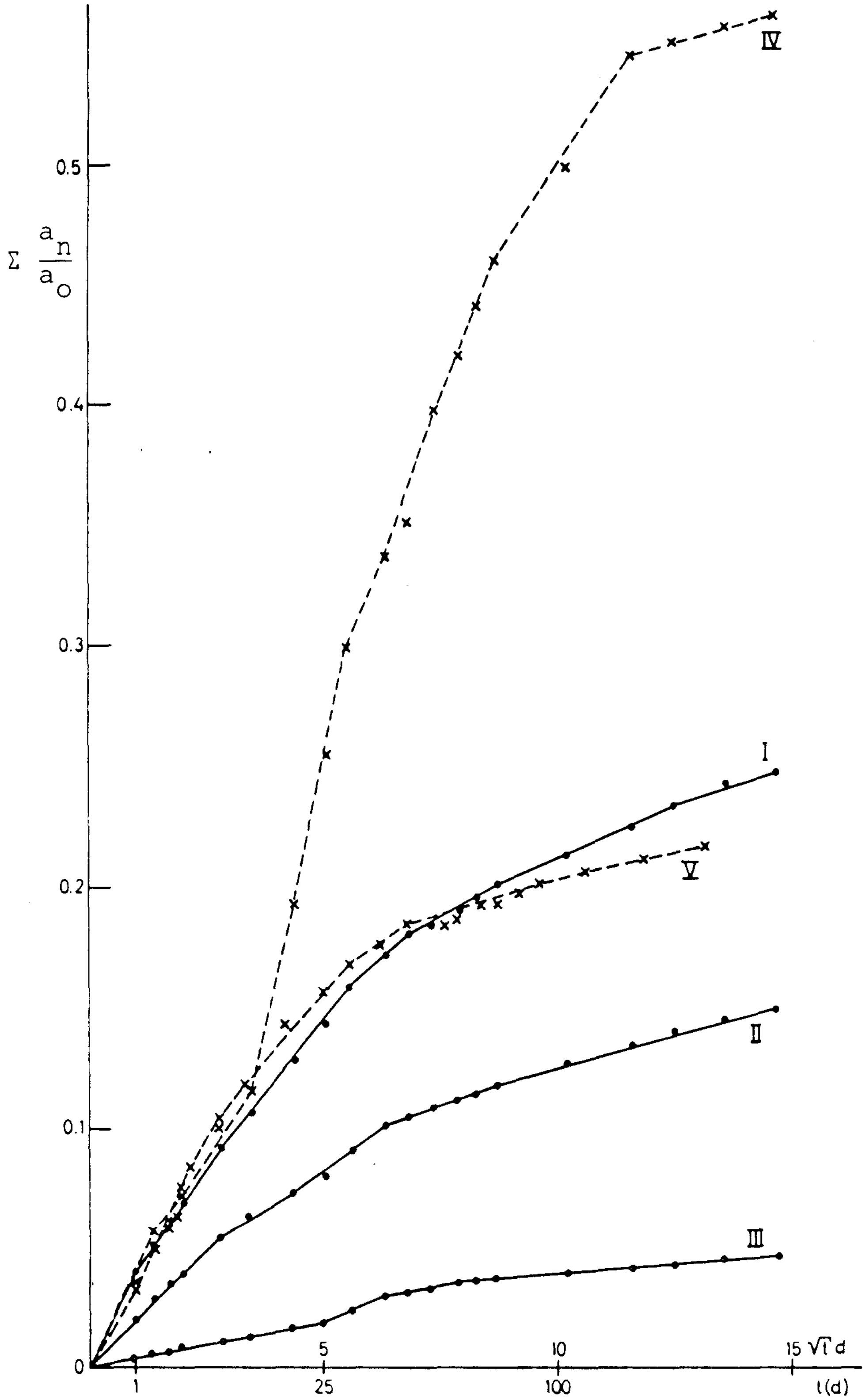

Figure 5.5 Leaching of Cs from slag cement - ion exchange products. Effects of waste loading and stabilizing additives.

I-III 13.4 weight % (dry) ion exchange resin
Additives: I Silix-sica, II 5% Corrocem,
III 5% Corrocem + 5% vermiculite
IV-V 19 and 18% resin, resp.
Additives: IV Silix-sica, V 10% Corrocem
+ 5% vermiculite

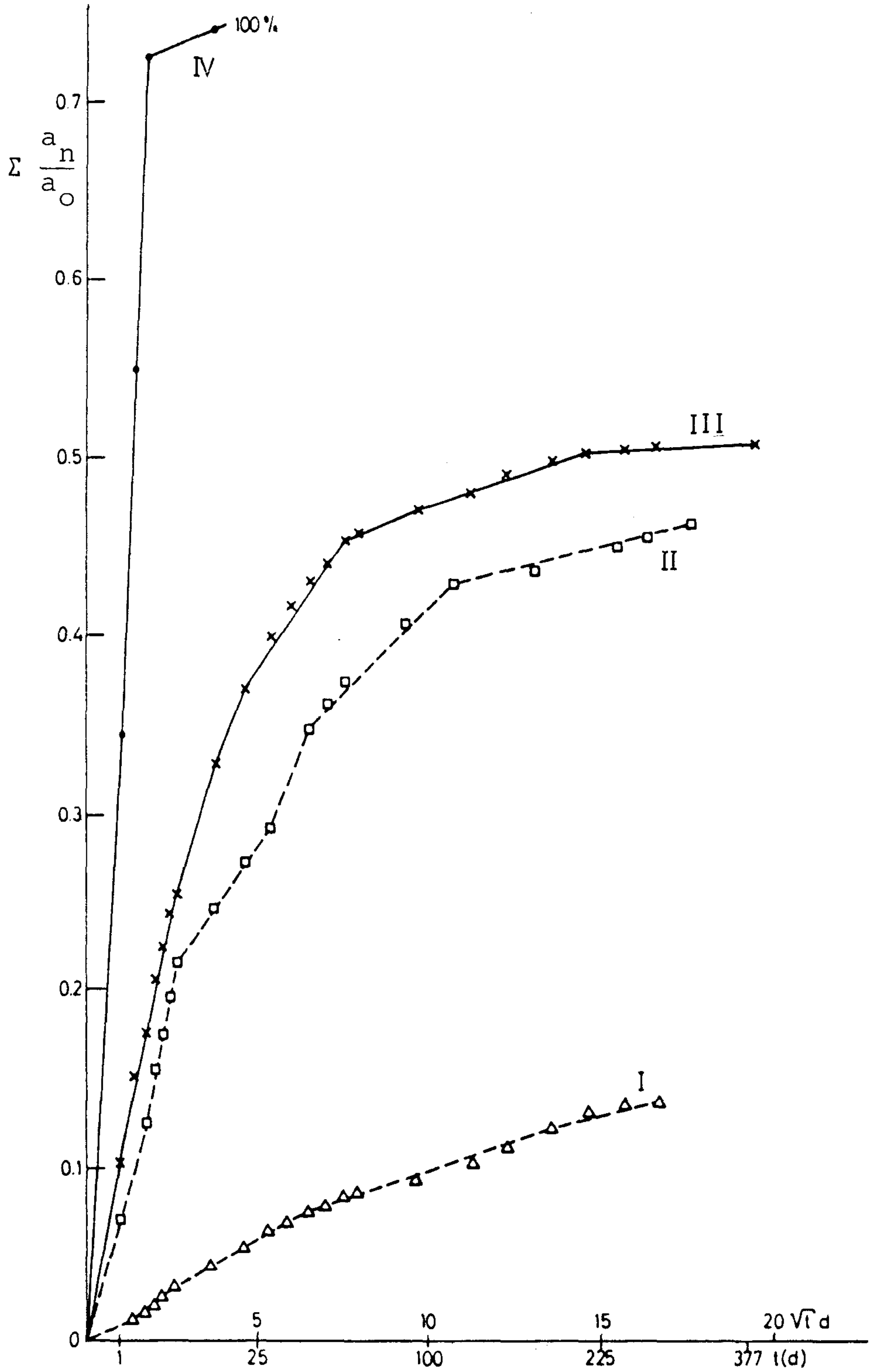

Figure 5.6 Leaching of Cs from crushed and intact cemented ion exchange products, 20% weight % (dry) ion exchange resin.
I-II SRC cement stabilized with 10% Corrocem + 5% vermiculite
I intact, II crushed
III-IV Unstablized Swedish slag cement
III intact, IV crushed

5.6 CONCLUSIONS

The tendency of the resin particles to swell is a main limiting factor for the amount of ion exchange waste that can be incorporated in cement and bitumen. Even variables which influence the pulsing (swelling - shrinking) of the resin particles can affect their incorporation and the properties of the resulting products. Product properties are also strongly affected by the matrix characteristics. The observed effects emphasize, that an adequate choice and control of raw materials is essential for the maintenance of stable and reproducible solidification products.

The applied relatively simple test routines provide an adequate product characterisation, in particular for cementation. Water resistance, controlled by simple immersion tests, is found to be a relevant criterium for product stabilities. Since poor water resistance - i.e. swelling of bitumen, cracking and disintegration of cement products - also affects the release of radioactivity, such tests can partly replace the tedious leach tests. A development of accelerated standardized tests would favour this approach and facilitate the control of the observed long term swelling of bitumen products. In case of bituminization additional tests for viscosity and form stability, e.g. "cylinder bending" /2/ or "sag" test could be desirable.

The most drastic impacts of process variables were observed in case of cementation. The sensitivity towards physico-chemical process variables even involves abundant possibilities to affect the system in a positive way. The present results give reason to believe that with further optimizations, very stringent specifications on product properties can be met. Even without such claims, the utilization of selective and unselective stabilizers - here represented by vermiculite and Corrocem, respectively -

has obvious advantages. The latter can significantly extend tolerance limits and lessen the vulnerability towards critical process variables. The former can selectively bind special nuclides, in this case the Cs isotopes, and thus significantly reduce their leachability, even from damaged products.

The study concentrates upon the identification of fundamental trends and critical variables. With an adequate adaptation to specified technical process conditions such incorporation tests can also be utilized as part of a technical process control. If appropriately calibrated and correlated, they would reduce the need for destructive analyses of technical waste products.

6 LARGE SCALE TESTS

6.1 INTRODUCTION

Correlations between laboratory and large scale product properties are seldom reported. These correlations are further complicated by uncertainties about the effects of sample preparation and even about the fundamental basis for extrapolations. To overcome these problems some inactive large scale tests have been made, based on the optimal process parameters identified in the laboratory scale studies. The results of these tests have been used in the system analysis, Techn. Part II.

6.2 LARGE SCALE SOLIDIFICATION STUDIES WITH PORTLAND CEMENT

To verify the earlier results from laboratory scale tests some large scale products (200 l drums) were assayed /29/. The aim of the study was:

- to clarify the overall process parameters in cementation
- to use the 200 l drums later in fall tests
- to study the temperature rise and profile in the drum due to hardening of the mixture
- to compare results between large scale (technical scale) and laboratory scale tests

As a result of these tests a correlation between the compressive strength, σ_m (MPa), and the weight percent of resin, W:

$$\sigma_m = 51 - 1.87\ W$$

was found, the index of determination being 95.3%, figure 6.1.

Figure 6.2 gives the centre point temperature due to heat generation in a styrox (0.5 m) insulated 200 l drum after pouring. The maximum temperature was ca. 120°C after about 2 days.

The laboratory scale tests and full scale tests had a very good correlation, even the water resistance of these 200 l products was comparable with laboratory scale samples.

6.3 FALL TESTS

The effects of mechanical impact and puncture forces on the reactor waste packages have been examined, using a 200 l drum as a packaging container /30/. Some preliminary mathematical strength calculations and small scale tests were conducted before carrying out the full scale test program. The cemented waste was simulated by inactive granular ion exchange resin solidified in cement, and the bitumenized waste by pure bitumen.

The small scale tests simulating accidents with reactor waste packages gave information about how different factors affect the accident resistance of the packages. The crushing of the cemented waste material expressed as the increase factor of the surface area (A/A_o) could be described by a linear regression model with the effective dropping height (h) and compressive strength (σ_m) as variables

$$A/A_o = 18.8 - 11.5\ \left(\frac{\sigma_m\ (\mathrm{MPa}) - 23.0}{18.7}\right) + 40.0\ \left(\frac{h\,(\mathrm{m}) - 17.6}{33.9}\right)$$

where the means and ranges have been separated. The index of determination was 89.5% while the 95% limit of significance was 24.8% /30/. Even better compatibility was achieved with the model:

$$A/A_o = 8.6\ (\sigma_m(\mathrm{MPa}))^{-0.71}\ h(\mathrm{m})$$

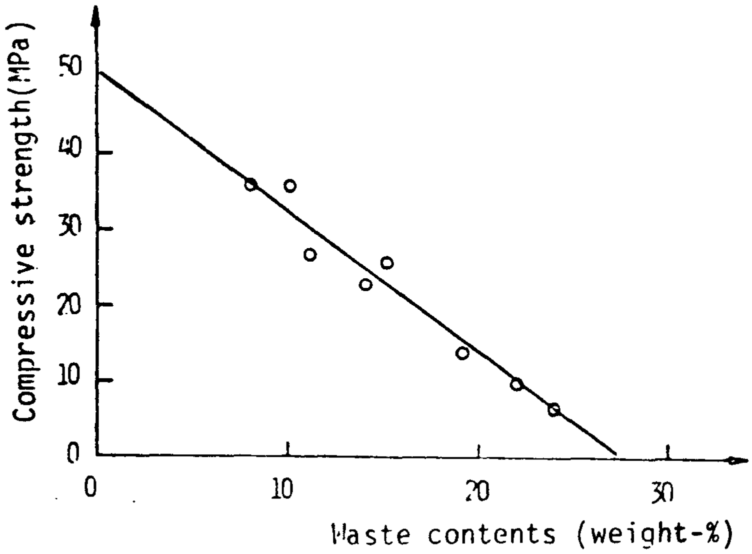

Figure 6.1 Correlation between resin contents and compressive strength of waste concrete /30/.

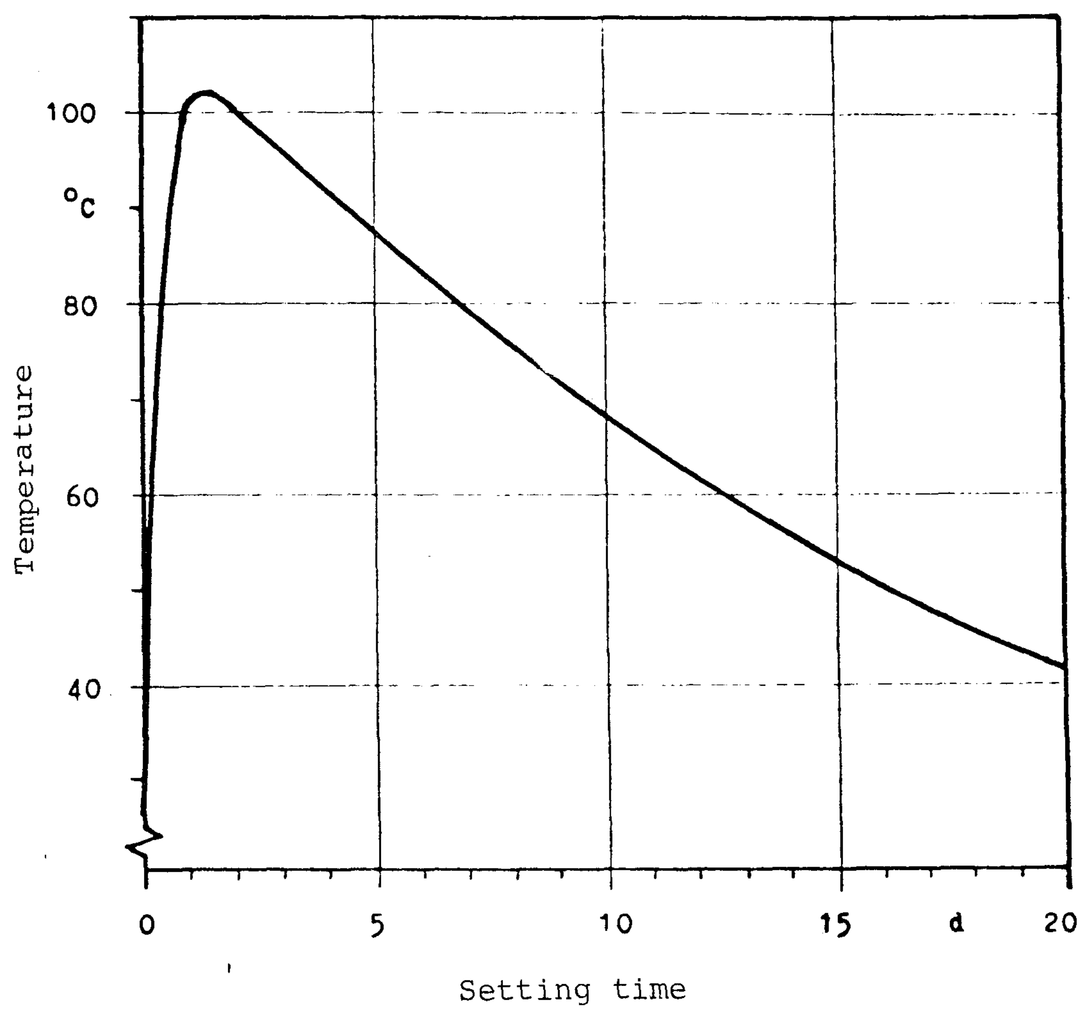

Figure 6.2 Centre-point temperature rise due to heat-generation in styrox (0.5 m) insulated 200 l barrel after pouring Portland Cement 1025 kg/m^3, water 445 kg/m^3, ion-exchange resin 260 kg/m^3 or 0.15 dry resin kg/concrete kg /29/.

As a conclusion it can be said that the observed increase of surface area and fraction of finest particles can be well explained as a function of compressive strength and dropping height. A similar regression model was formulated for steel covered blocks. The compatability of the latter model was, however, by far not so good as in the case of uncovered blocks. Obviously the steel cover caused indeterminism that could not be explained by any of the measured quantities and use of linear regression models /30/.

The steel canning decreased the crushing approximately to one third of the value for uncanned packages, and efficiently prevented the release of waste material. About 40% of the test blocks dropped at the maximum velocity 27.5 m/s were broken, the average release fraction being 1.1%. The dropping position did not have a determinant effect on the damage. Figure 6.3 presents the effect of dropping height on the particle size distribution in different waste mixtures. Small scale tests were not carried out with bitumenized waste.

In full scale tests the drums were subjected to impact and puncture forces. In the drops to a plane unyielding surface all the drums remained intact. Only the content was more or less crushed. The maximum dropping height was 20 m. The impact velocity was 19.8 m/s (71 km/h), which is approximately equal to the highest impact velocity that can be foreseen in truck transport accidents in Finland. In puncture tests the drums were dropped axially and radially on the top of a standard steel cylinder (ø 150 mm). In 1.2 m drop tests the damage was very small. The 9 m drop tests resulted in small failures of the steel cover, the release fraction of material being about 0.03%. The bitumen drums were dropped on their edge from 20 m resulting in small deformations of the drums without any release of the material, figure 6.4. The case of reinforced concrete containers was simulated by removing the steel cover from two concrete drums which were reinforced by iron net. In 9 and 20 m drops the inside part of concrete remained intact, figure 6.5.

The full scale tests show that reactor waste solidified in cement or bitumen and packaged into steel drums has very high mechanical impact resistance. It is almost impossible to imagine an accident situation where a considerable part of the contents could be release in a dispersable form as a result of mechanical damage.

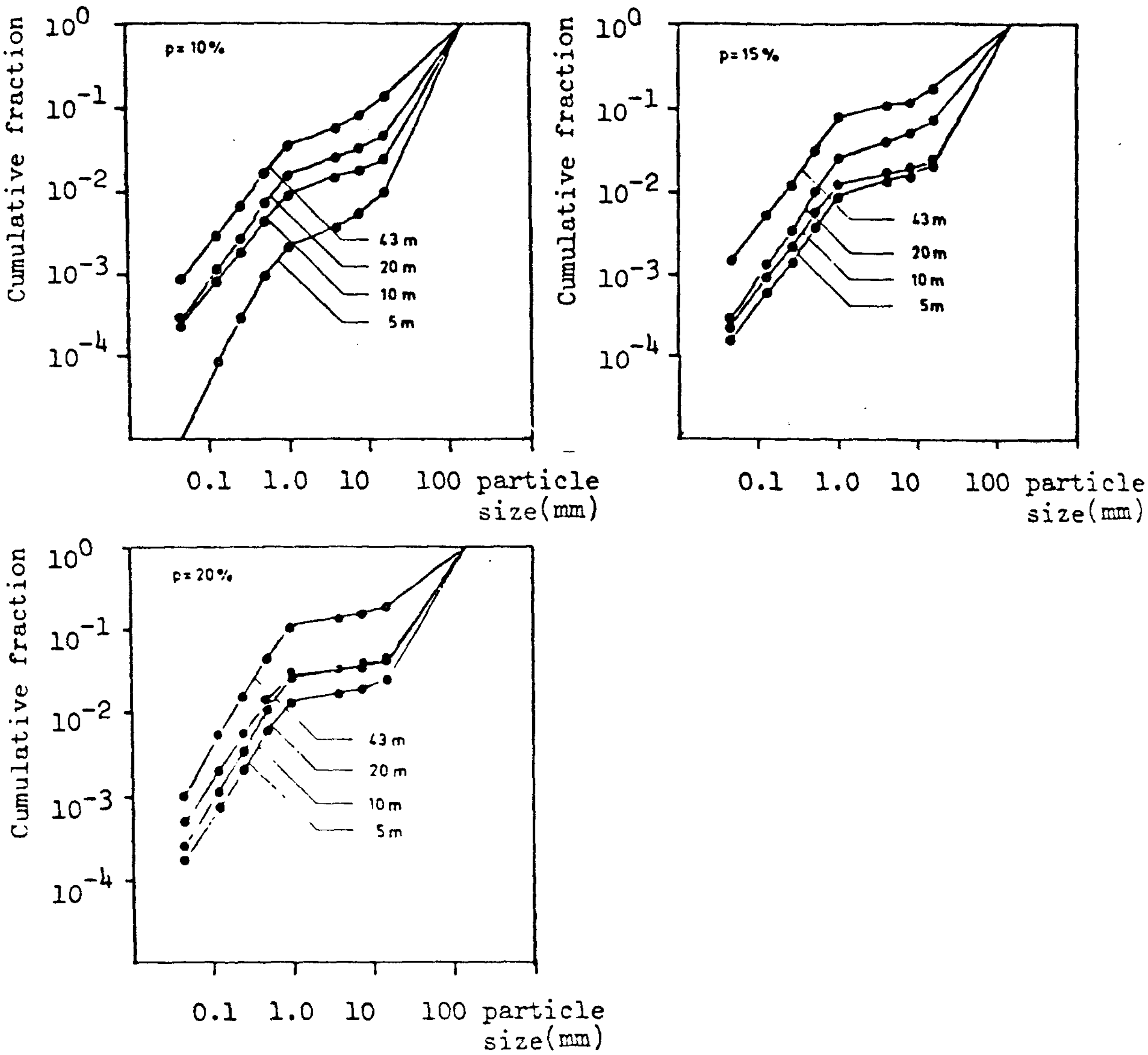

Figure 6.3 Effect of dropping height on the particle size distribution of damaged waste product in different waste mixtures /30/.

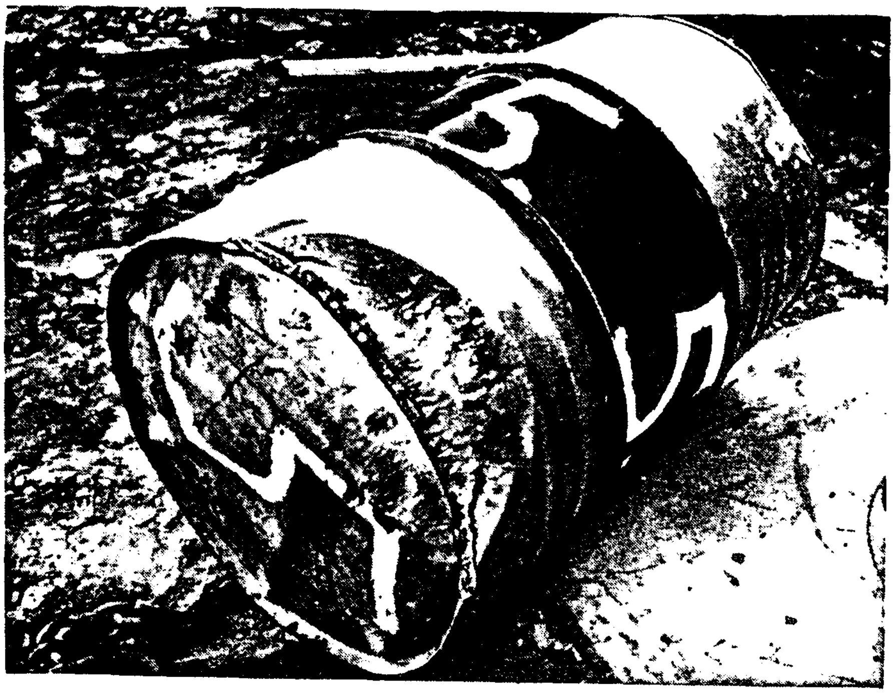

Figure 6.4 Corner drop onto plane surface from 20 m /30/.

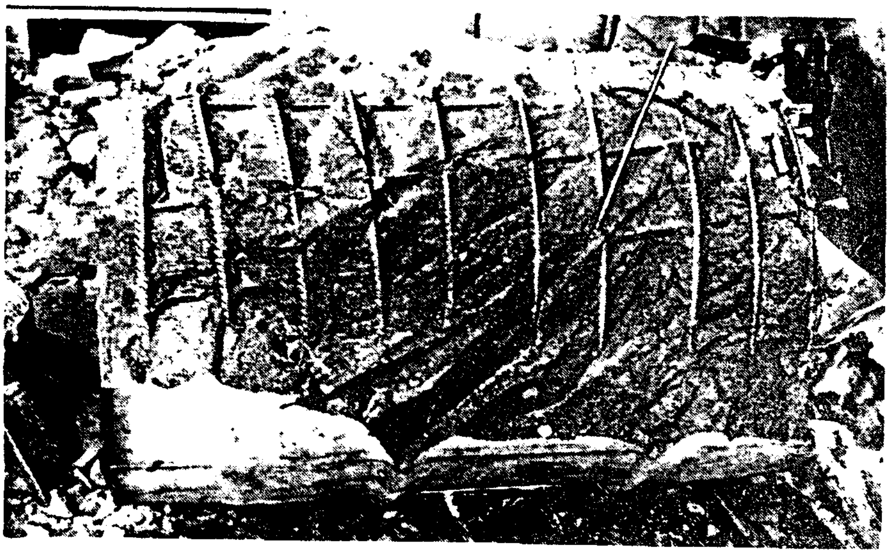

Figure 6.5 Side drop of the reinforced concrete block onto plane surface from 20 m /30/.

6.4 FIRE TESTS

Experiments were carried out at VTT, Finland, in order to have an insight into the response of solidified reactor waste packages to fire accidents /31, 32, 33/. Both cementized and bituminized waste were simulated. As could be expected the cementized waste was found to be very fire resistant. The maximum release fraction of activity after a 60 min fire of 800 $^{\circ}$C is estimated to be 13%. Pure bitumen (BIT-15) started to burn after 15 to 20 minutes heating time, and the release fraction of activity after 40 to 60 minutes fire is estimated to rise up to 85%, based on the assumption that all Cs follows the off-gases.

In the case of irradiated bitumen the start of the strong fire was a bit delayed but the burning was much more vigorous. 85% of the original amount of bitumen had burned after 37 minutes.

Figure 6.6 gives an assumed release fraction of total Cs activity versus burning time in a fire with a temperature of 800 $^{\circ}$C for both cementized and bituminized waste.

Thus in the case of a fire accident involving bituminized waste, the fire should be extinguished in about 15 minutes in order to avoid considerable activity releases. By using auxiliary shielding in transport and storage the fire resistance can be increased considerably.

To classify burning properties of ion exchange resins a study of their behaviour was also made. The specific heat of combustion for new ion exchangers is about 30 MJ/kg, the value decreasing with the increasing water content, figure 6.7.

Particle size distribution in off-gases from a fire is an important factor in analysis of the consequences. This has been studied by burning ion exchange resin -

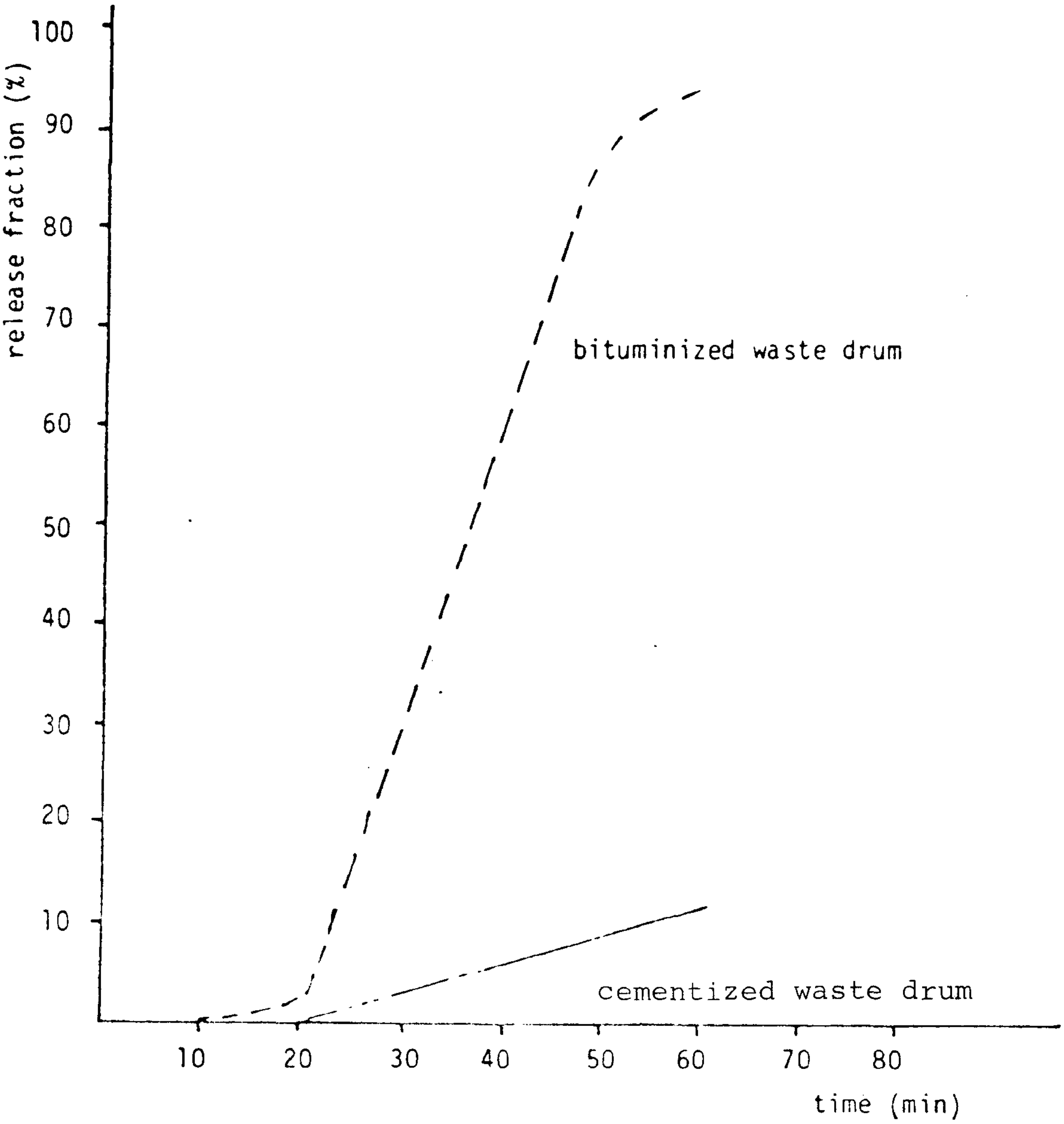

Figure 6.6 The assumed release fraction of total activity versus burning time in an 800°C fire for cementized and bituminized waste.

The estimated release fractions are based on full scale fire tests (external heating in 60 min., 800°C) with 200 l drums. The weight losses in experiments were 13% and 85% for cementized ion-exchange resin and bitumen respectively /31/.

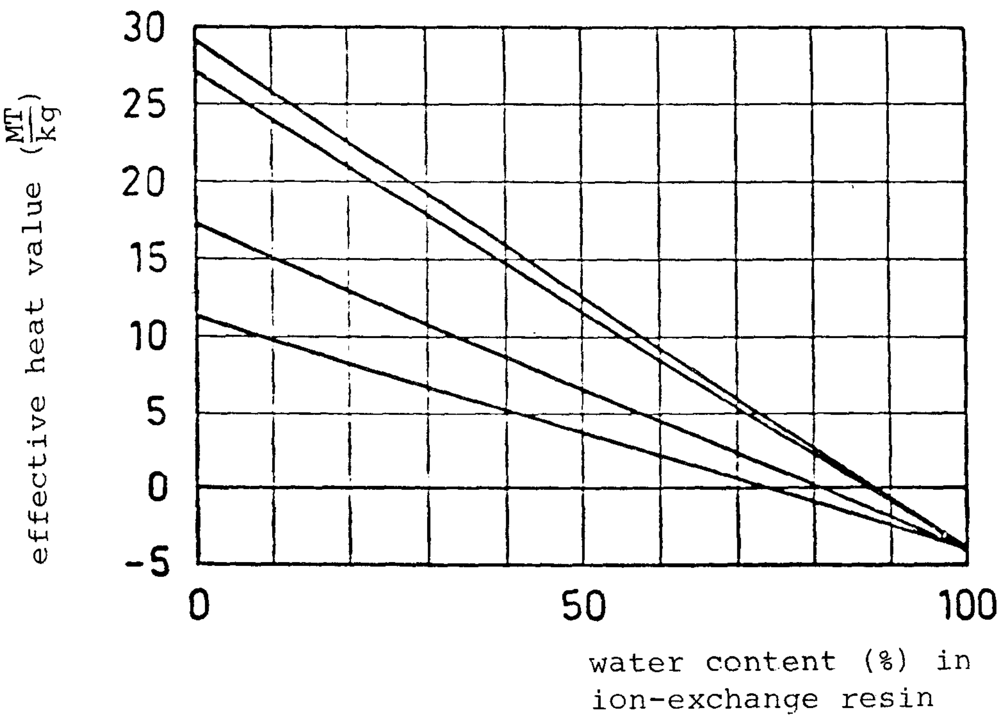

Figure 6.7 Thermal properties for ion-exchange resin/ water mixtures at incineration at 700°C /32/.

bitumen mixture in an open oven and analysing the size distribution of particles.

Analyses show that ca. 70% of particles are smaller than 10 μ and 30% smaller than 4 μ, figure 6.8. The experiments also showed that the fire in bitumen/resin mixtures was not selfsustaining - a gas flame was needed to maintain the fire.

The risk analysis performed within the Nordic study is based on assumptions directly drawn from the experiments discussed above. However, more recent experiments give reason to believe that these assumptions are very conservative.

Small scale fire tests with bituminized waste carried out at Risø /9/ indicate that even most of the cesium (>75%) will remain in the ashes. Accurate predictions can so far not be made since the nuclide distributions are affected by scale factors, chemical state, oxygen access, burning rates and temperature gradients.

The pilot scale study performed for KBS /10/ showed that the ignition temperature for bitumen samples was about 350^{o}C, and that it is difficult to ignite and maintain a fire in bitumen (use of a gas burner was necessary to maintain and complete the combustion). The fire temperature was about 500^{o}C. The slag rest was about 20% of the original sample weight and consisted mainly of unburned ion exchange resin rests. This study also included experiments with samples containing Co-60, Zn-65, Sr-90 and Cs-137. Results from these experiments indicated that more than 90% of the activity remained in the ashes.

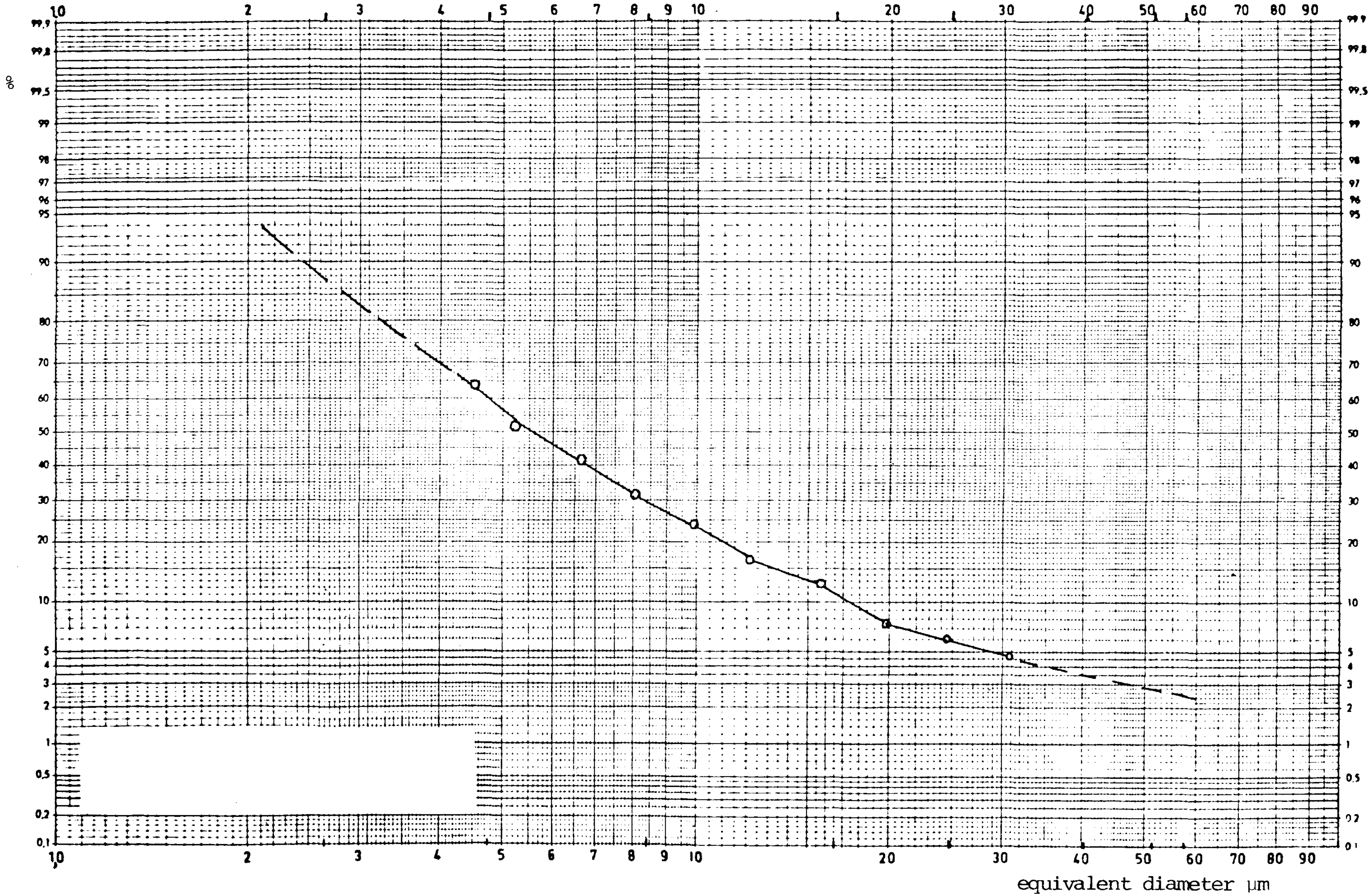

Figure 6.8 Particle size distribution (Coulter-Counter) /33/.

6.5 IRRADIATION TESTS WITH DIFFERENT BITUMEN TYPES

Irradiation causes in pure bitumen and in bituminized products following radiochemical processes:

- radical formation, partly gaseous
- reactions between waste materials, bitumen and formed radicals
- oxidation of bitumen and
- unfavourable polymerization reactions

As the result of these processes the waste products will swell and the properties of bitumen will change, sometimes drastically. The most important factors having an effect to the radiochemical processes in bitumen can be listed as follows:

- the type of bitumen
- the quality and quantity of the waste
- dose rate and absorbed dose

Also the experimental conditions, e.g. the way and the quality of irradiations and the atmosphere of the irradiation chamber will influence the changes in bitumen.

In this study external irradiation tests (37 GBq Co-60 source) with different bitumen types have been carried out for absorbed doses from 0.01 up to 5 MGy /34/. Radiolytic gas evolution, sample swelling, bubble formation and physical and chemical changes of bitumen material are the parameters being studied. Also the effect of the size of the sample has been followed. Studies to determine the most suitable tests for sample characterization have also been carried out.

The results of performed analyses are presented in table 6.1 and 6.2. Some photographs on the gas bubbles caused by irradiation are presented in figure 6.9.

Table 6.1 The changes in physico-chemical properties of bitumen types BIP-85/40, BIT-15 and BIT-45 as a function of absorbed doses of 10^4 and 5×10^6 Gy[x]

ANALYSES	BIP-85/40			BIT-15			BIT-45		
	0 Gy	10^4 Gy	$5x10^6$ Gy	0 Gy	10^4 Gy	$5x10^4$ Gy	0 Gy	10^4 Gy	$5x10^4$ Gy
Penetration 1/10 mm, 25°C	39	38	31	15	13	11	45	45	24
Softening point R&D, °C	80	80	93	75	75	82	57	56	65
Penetration indix	3.6	3.6	4.7	1.0	0.7	1.1	0	0	0.3
Ductility 25°C, cm	4	3	3	5	5	4	100	100	100
Break point Fraass, °C	-21	-25	-15	+5	+8	+23	-10	-9	-4

Table 6.2 The changes in chemical compositions (in per cent) of bitumen types BIP-85/40, BIT-15 and BIT-45 as a function of absorbed doses of 10^4 and 5×10^6 Gy[x]

ANALYSES	BIP-85/40		BIT-15		BIT-45	
	10^4 Gy	$5x10^6$ Gy	10^4 Gy	$5x10^6$ Gy	10^4 Gy	$5x10^6$ Gy
Asphaltenes, %	23	24	20	19	17	17
Oils, %	49	42	31	34	41	37
Resins, soft, %	19	23	35	31	28	33
Resins, hard, %	8	8	13	15	11	11
Σ, %	99	97	99	99	97	98

[x] 1 Gy = 100 rad

a) $5 \cdot 10^7$ rad ($5 \cdot 10^5$ Gy)   b) 10^8 rad (10^6 Gy)   c) $5 \cdot 10^8$ rad ($5 \cdot 10^6$ Gy)

Figure 6.9 as bubble structure in a 100 mm rod of BIT-15 a) after $5 \cdot 10^7$ rad b) 10^8 rad and c) $5 \cdot 10^8$ rad absorbed dose. Bubble diameters varied between 1-1.5 mm, 1.5-2.5 mm and 3-6 mm respectively /34/.
1 Gy = 100 rad

On the basis of the results the following conclusions can be drawn:

- The physico-chemical (structural-mechanical) properties of all the bitumen types are changing significantly after an absorbed dose of 5×10^5 Gy (= 5×10^7 rad), the most remarkable effect being the hardening of bitumen. However, in some cases the change is very slow.

- The changes in the chemical composition were marginal. The variation in the crude oil (from which the bitumen is produced) can easily mask out the changes caused by irradiation. However, a small polymerization effect was noticed.

- The form stability for BIT-15 and BIP-85/40 was good up to 10^6 Gy, for BIT-45 the "critical" dose was 5×10^5 Gy. After these absorbed doses the samples began to swell remarkably, because the amount and the size of gas bubbles inside the samples increased greatly.

- The size of the samples will obviously influence the form stability properties (e.g. swelling). An absorbed dose of ca. 1.5×10^5 Gy caused a swelling of about 15% for all the bitumen types, when using 20 l samples.

- The gas generation rates on the basis of gas pressure measurements were for BIT-15 0.95 cm^3/(kJ/kg) x kg and for BIP-85/40 1.12 cm^3/(kJ/kg) x kg. On the basis of the results taken from the linear part of the swelling test curve these values were 1.23, 1.13 and 1.26 cm^3/(kJ/kg) x kg for BIT-15, BIT-45 and BIP-85/40, respectively.

Also some 200 l drums filled with the bitumen types used in laboratory scale tests were irradiated with the Co-60 source. The aim of these tests was to confirm the earlier results: to follow the bubble formation and swelling and analyse the different characteristics of bitumen after irradiation.

The most remarkable difference between small, intermediate and fullscale test specimens was the difference in bubble dimensions: in the small specimens the max. bubble diameter was ca. 5 mm, in the intermediate ca. 20 mm and in the fullscale specimens ca. 50-60 mm.

6.6 CONCLUSIONS

Fullscale products were made and tested in order to scale up results obtained from laboratory studies and later compare respective results from product characterization.

In several cases the results from tests with the fullscale cementized waste products were comparable to those obtained in the laboratory. Correlations between fall resistance, compressive strength and waste loading were derived. Some dimensional effects were, however, noticed with bituminized wastes. These are probably most pronounced in the case of burning,where quantitative correlations are difficult to derive. Systematic scale effects were observed in irradiation tests, where the gas bubble size increased with increasing sample size.

Correlations between laboratory and fullscale products are seldom reported. These correlations are usually complicated to determine because of uncertainties about the effects of experimental conditions such as sample preparation. In these experiments, however, the properties of laboratory and fullscale products were comparable.

7 CORRELATION BETWEEN RESULTS FROM LABORATORY TESTS AND FULLSCALE PRODUCT CHARACTERISTICS

7.1 PROBLEMS

The laboratory tests, discussed in chapter 4 are useful for relative studies on product qualities and impacts of process variables. Unfortunately, there is a tendency to quote data from such studies as true values for long term product characteristics. It should be emphasized that most of these tests are of short duration and often so susceptible towards experimental conditions that results from different laboratories can vary considerably. For correlations with fullscale product properties even the following factors must be considered:

i Sample preparation
- process
- scale effects, e.g. temperature profiles

ii Test methods
- reproducibility, standardisation
- relevance for examined product properties
- involved reaction mechanisms and basis for extrapolation in scale and time

iii Relations to other barriers
- additional protection by steel drums, concrete moulds or other canning material
- possible interactions between waste products and canning, concrete structures, claylike compounds

A main question is, of course, whether the examined properties are relevant for safe waste management, i.e. the degree of the effect they may have on radiation doses from the different stages of the waste management cycle.

Correlations between results from different sources are further complicated by the great variety of definitions and units used, e.g. for waste loading /35/, water content, water/cement ratios /3/ and test results.

7.2 EFFECTS OF SAMPLE PREPARATION

Without extensive cross checks it is difficult to predict how the deviating conditions applied for laboratory preparations and in a technical process will affect the product properties.

The need for such cross checks seems to be most exigent in the case of bituminization. The applied laboratory procedure deviates in several respects from the technical processes used in the Nordic countries. Thus for quantitative correlations, possible impacts of deviating process conditions should be controlled.

In the case of cementation, the preparation of test specimen is based on well established praxis from the cement industry. Still, the "ion exchange concretes" may be more sensitive towards scale effects than normal concretes. They appear to be more affected by the surface available for water uptake during setting, and they are probably more sensitive towards temperature variations. Elevated temperatures may give rise to gas evolution from the ion exchangers, especially from anion exchangers. This effect will be enhanced by the alkaline environment and will probably vary with resin characteristics. Temperature rises may even affect dehydration reactions and other interactions between resin and matrix. Due to the low heat conductivity of cement the sample size will have a great influence on the temperature profiles. In laboratory preparation, temperature rises during setting of cement are insignificant, while local temperature rises of 100°C or more are reported for technical processes.

7.3 ANALYTICAL MEASUREMENTS

Both random and systematic effects must be taken into account. Certain random deviations will result from poor reproducibilities for some of the applied methods, probably worst in case of leach measurements.

For standard tests adapted from conventional industries, the reproducibility may be good, but test conditions differ so much from actual waste management situations, that it is difficult to establish quantitative correlations with real fullscale product performance.

Main uncertainties are related to the extrapolation in time. Even the so called long term tests are mostly limited to a few hundred days, while 100-1000 years are considered for safety assessments. For such extrapolations some knowledge about fundamental reaction mechanisms is needed.

7.4 PRODUCT PROPERTIES SEEN IN RELATION TO OTHER BARRIERS

As shown by the safety analysis, Techn. Part II, the steel or concrete containers and finally the engineered and geological barriers in the repository provide the main protection against a spreading of radioactivity. Hereby the influence of product properties on possible dose commitment is essentially reduced. On the other hand, regard to possible interactions with other barriers can shift the emphasis towards other properties than those considered for unprotected products. Reactions to be considered in this connection include:

7.4.1 CORROSION

Corrosive compounds in waste (salts, acids) and matrix (e.g. sulphur compounds in bitumen) may lead to accelerated corrosion of the containers, in particular the steel drums, so that the assumed integrity during storage and transport cannot be maintained. A strict control with corrosive compounds can therefore be necessary.

7.4.2 DIMENSIONAL CHANGES

Excessive swelling of solidified ion exchange wastes can impair the integrity of the containers and concrete structures. In this connection the observed long term swelling of bituminized resins in contact with water, figure 5.3 and 5.4, deserves further attention, in particular with respect to how the swelling is affected by resin and bitumen characteristics and by irradiation. It can also be desirable to introduce accelerated tests and to establish quantitative correlations between results from standardized tests and possible effects on the containment. Possible specifications of maximal tolerable swelling will of course depend upon the type of containment.

7.4.3 EFFECTS OF STEEL AND CONCRETE DEGRADATION PRODUCTS ON THE LEACHING

As discussed in chapters 3.1 and 4.2, degradation products from containers and concrete structures, will to some extent govern the water chemistry and consequently also the leach conditions in the repository.

7.5 EFFORTS AND RECOMMENDATIONS TO IMPROVE CORRELATIONS

Quantitative correlations between results from the small scale laboratory tests and the actual performance of full scale products during storage and transport can be derived from statistical assessments of experimental data. For this purpose different types of parallel tests are needed:

i	Small scale laboratory tests both with laboratory test specimen and with corresponding small samples taken from full scale technical products, to control effects of the sample preparation. Can with advantage be combined with a statistical control of product homogeneities.

ii Large or preferably full scale tests parallel with corresponding laboratory tests to determine scale factors for the tests as such.

iii Simulated accident conditions parallel with laboratory tests for involved properties to quantify correlations between properties like mechanical strength and resistance against storage and transport accidents.

Extrapolations in time involve greater uncertainties. Both stabilizing and destructive mechanisms must be considered. The leach studies, chapter 4.2 and 5, give some guidelines for such extrapolations.

The observed course of leaching and selfstabilizing effects of dissolved cement compounds give reason to expect that the applied tests should provide a conservative basis for predicting the long term leach behaviour of intact cement products. As to mechanical damages, which increase the product surface, they would probably only have significant effects on the release of nuclides that are not chemically fixed in the matrix.

It is more difficult to make predictions about the long term leach behaviour of bitumen products. Both the rate and course of leaching are strongly affected by so many variables that it is hardly possible to prescribe representative test conditions. Tests with distilled water are certainly not representative, and will probably give far too low results. Still the leach rates are low enough to give considerably safety margins for unpredictable leach enhancing effects. Only major trends such as the observed /12/ drastical effects of certain salts and possible effects of microbial growth need to be taken into account.

8 RELEVANT TESTS FOR RELEVANT PRODUCT PROPERTIES

The study illustrates the relevance of different properties and test methods for different purposes, for

- safety assessments, incl. predictions of the long term product performance
- plant control and quality testing of technical products
- laboratory testing for control of tolerance ranges and impacts of process variables

8.1 SAFETY ASSESSMENTS

All properties which can affect the release and spreading of radioactivities should in principle be taken into account. In connection with possible storage and transport accidents these properties are mainly

- burning properties, release and distribution of contaminated gases and particles
- impact and shock resistance, particle sizes and distributions

The important properties for the long term performance of disposed solidification products are:

- resistance against disintegration and swelling in contact with water
- long term leach behaviour

Relevant tests for these properties should first of all be representative for actual waste management conditions. This implies that only few of the many laboratory tests listed in table 4.1 can be used to supply relevant data for safety assessments. Such data must as far as possible be based on large scale model tests and simulated accident conditions such as the fall and fire tests discussed in chapter 6. For predictions of the long term performance of disposed waste products, knowledge about the involved reaction mechanisms, including interactions with other barriers, is more important than the "accuracy" of the leach data.

8.2 PLANT CONTROL AND TESTING OF TECHNICAL PRODUCTS

A control is needed to ensure that the incorporation process is taking place satisfactorily and that the resulting products are suitable for further handling. The extent of the control programs and the choice of control methods will largely depend upon

- the expected range of process variables, in particular of waste composition and properties
- the impact of such variables on the properties of the resulting solidification products
- special conditions related to the design and operation of each specific plant
- demands on product properties

These factors will also determine whether the main emphasis should be on process control or on product analysis. In any case there will be a need for adequate control of all materials to be used in the solidification process.

8.2.1 CONTROL OF RAW MATERIALS

The observed impacts of matrix qualities emphasize the need for relevant tests for cement and bitumen characteristics. Specifications and tests designed for the "conventional" use of these materials cannot be assumed to cover their compatibility with radioactive ion exchange wastes. This can best be controlled by standardized incorporation tests (chapter 8.3) covering the relevant range of technical process variables. Such compatibility tests can also be relevant for the ion exchange resins and all other materials which will finally end up in the waste to be processed.

For bitumen it can also be relevant to control the radiation stability by tests for radiolytic gas evolution from the raw materials and for the degree of radiation-induced swelling of bitumen/ion exchange products in contact with water.

8.2.2 PROCESS CONTROL

The design of systems for supervision and control of the solidification process will largely be governed by plant specific factors, which are not within the scope of this study. Laboratory testings for control of tolerance ranges and impacts of process variables can, however, with advantage be utilized to provide basic data for the planning and optimization of such systems (chapter 8.3).

8.2.3 CONTROL OF THE TECHNICAL SOLIDIFICATION PRODUCTS

In principle two lines of tests are relevant

- simple non-destructive tests at the plant site
- destructive sampling for more extensive laboratory testing

The former can be carried out as part of the process control, and is mainly used to control homogeneities and reproducibilities. The results can be relative and need not even represent properties with relevance for safe waste management. They may be based on remote visual or microscopic inspection, on radiometric or ultrasonic scannings /36/ or on various thermal, viscosimetric or mechanical methods /35/.

Destructive testings would be of crucial importance in case of specified minimum demands for product acceptance. This would imply strict qualification tests and elaborate verification analyses for all specified characteristics. In the absence of such specifications, destructive testing of technical products can probably be limited to the minimum, which is needed to establish quantitative correlations with more or less relative process and laboratory control methods. The best approach would probably be to establish such correlations during the inactive or low active start-up phase of reactor and waste plant. Access to sufficient amounts of representative reference materials from technical plants would be a great help for the selection, calibration and standardization of relevant control and test methods.

8.3 LABORATORY TESTING FOR PARAMETER STUDIES, OPTIMIZATION AND DEVELOPMENT OF INCORPORATION TECHNIQUES

Laboratory testing for control of tolerance ranges and impacts of process parameters are relevant in connection with

- the assessment, optimization and development of solidification products and techniques
- compatibility testings of materials to be used in the solidification process (chapter 8.2.1)
- the planning and optimization of process control systems (chapter 8.2.2)

Considering the modest claims on product properties, extended efforts to develop products with superiour properties are hardly justified. Further product assessments and optimizations can be relevant in connection with the installation of new plants, evaluations of new incorporation techniques and possible demands for better volume reductions (cement).

The main demands for this type of testing will probably be connected with compatibility testings and process control. The latter may even be an incitament for further efforts to extend tolerance ranges, since this can reduce the demands and costs for control systems.

The testing can proceed in a similar way as the impact studies in chapter 5. To be relevant for plant control they must be adequately standardized and correlated with actual plant conditions. They can primarily be based on extended tests for water resistance, supported by simple relative tests for mechanical properties (compressive strength, formstability). In addition some checks for impacts on leach behaviour and thermal properties will be relevant.

8.4 METHOD CATALOGUE

It was originally intended to compile a method catalogue with standard tests for the purposes discussed above. The selection of methods and test conditions were to be based on demands identified by the safety analysis, Techn. Part II. One of the conclusions from the safety analysis must, however, be that demands on product properties are so modest that there is little or no need to specify strict product requirements and standardized qualification tests for product acceptance. On this background it appears that the most important guidelines for the selection of methods and test conditions might be how well they can be correlated with actual process conditions and with the actual conditions that the solidified waste products could be exposed to. This approach will, however, introduce a number of plant- and scenario-specific factors which complicates the establishment of standard procedures that are generally applicable. The availability of representative reference materials from full scale technical products appears to be a main condition for a relevant selection and standardization of test methods. It may possibly even be more useful to collect a broad spectrum of reference materials to be used for intercalibrations of methods, rather than to spend excessive time on detailed specifications of standard test methods. For these reasons work on the method catalogue has been postponed.

8.5 PRIORITIES FOR FURTHER R&D WORK

At present nearly all recommendations about further R&D work are primarily concerned with the standardization of test methods for product properties. It is certainly desirable to have standard tests which can ascertain comparable results from different laboratories. But such standardizations must be adapted to a realistic need. With modest claims on product properties, such elaborate standardizations as recommended in recent ISO drafts /18/ for long term tests are hardly relevant.

For all above discussed purposes it may be more relevant to concentrate further upon:

- the establishment of adequate correlations between results from laboratory tests and full scale product performance
- extended tests for the resistance against swelling and deterioration in contact with water
- extended relative tests for non-destructive control of technical products
- the establishment of realistic - not necessarily excessive - reproducibilities and validities for all applied tests
- fundamental studies about leach- and reaction mechanisms governing the long term leaching from disposed waste products and possible interactions with other barriers
- investigations about chemical and physical waste variables which can affect compatibilities with cement and bitumen, reproducibilities and homogeneities of the resulting products

Work on some of these items has already been initated. Hopefully this approach will contribute to make testing of radioactive waste products more realistic and closer connected to actual waste management conditions.

REFERENCES

1. Peltonen, E.K., Heinonen, J.U., Kuusi, J., Incorporation of radioactive wastes from nuclear power plants into concrete and bitumen. IAEA-SM-207/5.

2. Bonnevie-Svendsen, M., Tallberg, K., Aittola, J.P., Tollback, H., Studies on the incorporation of spent ionexchange resins from nuclear power plants into bitumen and cement. IAEA-SM-207/78.

3. Beijer, O., Casting granular ion exchange resins with medium-active waste in cement (in Swedish, separate summary in English), PRAV report 1.36, May 1980.

4. Harfors, C., Properties of bitumenized radioactive waste from the Barsebäck nuclear power plant (in Swedish). PRAV report 1.22, September 1979.

5. Christensen, H., Cement solidification of BWR and PWR radioactive waste at the Ringhals nuclear power plant. NEA/IAEA Symposium Zürich, March 1979.

6. Thegerström, C., Alternative solidification techniques for radioactive ionexchange resins and waste solutions (in Swedish), SKBF-KBS Technical Report 80-06, January 1980.

7. Eschrich, H., Properties and long-term behaviour of bitumen and radioactive waste-bitumen mixtures. SKBF-KBS Technical Report 80-14, October 1980.

8. Härkonen, H., Peltonen, E., Performance of reactor waste in repository.IVO/TVO Report YJT-79-05, November 1979.

9. Larsen, V.V., Vinther, A., Brodersen, K., Small-scale firetest of ion exchange resin solidified by bitumen or cement. NKA/AO(80)45, January 1981.

10. Aittola, J.P., Chyssler, J., Ringberg, H., Fire experiments with bituminized ion exchange resins. KBS Report. To be published.

11. Neretnieks, I., Andersson, K., Henstam, L., Leaking of Ni-59 from a repository in rocks (in Swedish). KBS Tech. Report 101, April 1978.

12. Brodersen, K., Winther, A., Leaching of bituminized radioactive cation exchanger resin. NKA/AO(80)46.

13. Salonen, L., Snellman, M., Carbon-14 determination from ion exchange resins. NKA/AO(80)42.

14. Radiological significance and management of tritium, carbon-14, krypton-85, iodine-129 arising from the nuclear fuel cycle. Annex B: Assessment of radionuclide capture, retention, storage and disposal technology, Section B.7. NEA, April 1980.

15. IAEA-TRS-116. Bituminization of radioactive wastes. Vienna 1970

16. Ollila, K., Rämö, E., Leach testing of simulated concrete products. NKA/AO(80)19.

17. Hespe, E.D., Leach testing of immobilized radioactive waste solids. Atomic Energy Review 9 (1971) 195.

18. Long-term leach testing of radioactive waste solidification products. ISO/TC 85/SV 5/WG 5 N 38.

19. Herrnberger, V., VH Ausbreitungsanalyse: Die mathematische Beschreibung des Auslaugprozesses verfestigter radioaktiver Abfälle. (Eine Literaturstudie). TM-PH-833, PrE-72, November 1979.

20. Herrnberger, V., Die mathematische Modellierung der Auslaugung verfestigter Abfälle. EIR-Bericht Nr. 416, November 1980.

21. Godbee, H.W., et al., Application of mass transport theory to the leaching of radionuclides from waste solids. Nuclear and Chemical Waste Management, Vol. 1, pp 29-35, 1980.

22. Chyssler, J., Grönroos, B., Aittola, J.P., Specific surface measurement (BET) of ionexchange resin and cementized ionexchange resin. NKA/AO(80)30, April 1980.

23. Brodersen, K., The significance of microorganisms for the leaching of activity from radioactive waste embedded in bitumen (in Danish). NKA/AO(79), May 1979.

24. Bonnevie-Svendsen, M., Multielementanalysis of leach-solutions (in Norwegian). NKA/AO(80)13.

25. Pihlajavaara, S.E., Aittola, J.P., Radwaste concrete: Solidification of nuclear wastes with Portland cement. NKA/AO(79)3, April 1978.

26. Pihlajavaara, S.E., An analysis of materials durability and its testing with reference to radwaste concrete. NKA/AO(79)2, January 1979.

27. Aittola, J.P., Kleveland, O., Tollbäck, H., Incorporation of granular ionexchange resin into cement - comparative tests with different types of cement (in Swedish). NKA/AO(80)26, May 1980.

28. Haighton, A.P., Central Electricity Generating Board. Private communication.

29. Pihlajavaara, S.E., A brief tentative review of the results of the research on radwaste concrete. Appendix to NKA/AO(79)2 (see reference 26).

30. Rämö, E., Pulkkinen, U., Aittola, J.P., Damage of reactor waste packages in transport accidents. NKA/AO(79)17, dated 1979.10.01.

31. Rämö, E. Effect of fire on solidified reactor waste packaged into steel drums. NKA/AO(79)18, dated 79.07.30.

32. Nykyri, M., Valkiainen, M., Incineration properties of ion exchange resin (in Finnish). NKA/AO(79)22, dated 1979.08.30.

33. Hahkala, M., Mehtonen, A., Aittola, J.P., Incineration of the ion exchanger resin/bitumen mixture. Particle size distribution in the off-gas. NKA/AO(79)21.

34 Aittola, J.P., Valkiainen, M., Autio, T., Gamma-radiation stability of different Finnish bitumen types. Paper presented at the 6th conference of Nordic society for radiation research and technology, Hirtshals, Denmark, August 1977.

35. NEA Workshop on intermediate level waste. London, May 1980.

36. Nikkari, K., Paroll, H., About the application of ultrasonic for evaluation of the contents of waste-resin and the compressive strength of the waste-resin-concrete (in Swedish). NKA/AO(80)11, January 1980.

37. Letter from ASEA-ATOM (T. Waltersten) to the Swedish Nuclear Power Inspectorate (in Swedish), 1981.04.16.