KERNFORSCHUNGSZENTRUM

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Abteilung Dekontaminationsbetriebe

Fixing of Radioactive Residues in Bitumen

W. Kluger, H. Krause, O. Nentwich

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Contents

Introduction

In 1964, a batch operated bituminizing plant was started up at the Karlsruhe Nuclear Research Center. After satisfactory initial operating behavior there were some difficulties after prolonged operation (see Section 3.2.1). The experiments described below were performed to elucidate and remove these troubles.

The experiments were carried out primarily on simulated evaporator concentrate solutions because most of the radioactive waste water at the Karlsruhe Nuclear Research Center is decontaminated by evaporation. Since a large portion of the evaporator concentrates at Karlsruhe originates from the effluents of the equipment decontamination facility and from a small reprocessing plant, in the first line water of such a kind was investigated as is expected to come from those sources (high content of $NaNO_3$, Na_2CO_3, heavy metals, etc.). Difficulties due to the high nitrate content have been pointed out already by N. van de Voorde and P. Dejonghe [1]. Besides salt solutions, to a lesser extent also chemical sludges, plastics, organic ion exchangers and organic waste solutions have been stirred into bitumen. Corresponding to the design of the pilot plant the sojourn time of the products in the mixing vessel was set at about 1o hours.

1. Laboratory Experiments

1.1 Experimental

The apparatus shown in Fig. 1.1-1 was used for the experiments. The mixing vessels used were tin cans (diameter 1o cm, height 12.5 cm), the heater was a 2 kW annular boiler covered with an aluminium plate. The temperature in the mixing vessel was controlled through an immersed

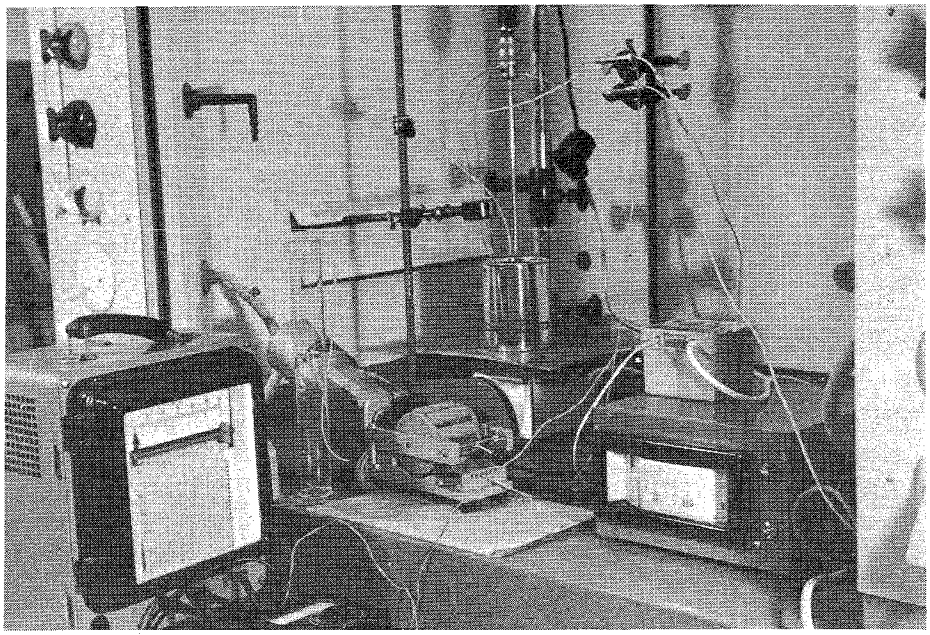


Fig. 1.1-1 Experimental device for stirring salt solutions into hot bitumen.

thermocouple via a temperature regulator. Another thermocouple was used to register the temperature on a recorder. Stirring was done with a propeller stirrer at a speed of 15o-2oo rpm. The salt solutions (mostly 2o percent) were metered with a hose pump. The time of continuous stirring and addition was about 1o hours, provided that the experiments did not have to be interrupted prematurely, e.g., because of excessive hardening of the products. In general, the laboratory scale experiments gave products of about 4o w/o salt [+] (or other solids to be fixed) and a volume of about 0.1 liter. The grade of bitumen used predominantly in the experiments was Mexphalt 15.

[+] The products consist of 8 parts by weight of bitumen and 5 parts by weight of salt. Products of this composition will be termed 8/5 products below.

1.2 Fixing of Chemical Sludges

In the experiments chemical sludges (water content up to some 9o w/o) were metered into hot bitumen batchwise until the composition of 8 parts by weight of bitumen and 5 parts by weight of dry sludge was reached. The investigations were performed at temperatures of 22o°C and 15o°C. When the chemical sludges were stirred in at 22o°C the final products could be poured out of the mixing vessel easier than at 15o°C. It was found that, contrary to salt solutions, there is no spraying even at temperatures around 22o°C, if chemical sludges are stirred.

Table 1.2-1 summarizes the results obtained for stirring of chemical sludges into bitumen at 22o°C.

When the chemical sludges contained the filter aid Fibra Flo 7c [+] the experiments had to be terminated prematurely because the stirring of such sludges is accompanied by strong felting of the products so that it is impossible to pour them out of the mixing vessel.

1.3 Fixing of Plastics and Organic Ion Exchangers

Of the plastics investigated, i.e. polyethylene, polyvinyl chloride and polystyrene, up to 3o w/o of plastic relative to the final product were stirred into hot bitumen. This requires the mixing process to take place at a temperature below the decomposition temperature of the corresponding plastic material. Metering of the plastics is carried out batchwise. Metering times were between 1/2 and 1 hour. The plastics were present as chips or granules.

[+] Fibra Flo 7c is an asbestos-type filter aid which has proved successful in filtering of chemical sludges.

Table 1.2-1

Fixation of sludges in bitumen

Components of the sludge	Method of precipitation (chemicals per 1 l of tap water) 16^{0} dH; 10^{0} kH	Water content of the filtered sludge (wt.-%)	Temperature of bitumen during mixing (^{0}C)	Time of mixing (h)	Quality of the hot final product	Quality of the solid final product		Result
						Wt.-ratio bitumen:dry sludge	Softening point (ring and ball) (^{0}C)	
Ferric-phosphate Ferric-hydroxide Calcium-phosphate Calcium-carbonate	$FeCl_3$ 50 mg/l Na_3PO_4 450 mg/l with 6 M NaOH adjusted to pH 11	88	220 - 245	8.5	homogeneous easy to pour	8/5	113	+
Ferric-phosphate Ferric-hydroxide Calcium-phosphate Calcium-carbonate	$FeCl_3$ 50 mg/l Na_3PO_4 450 mg/l with 6 M NaOH adjusted to pH 11	Lowered from 88 % to 53 % by pre-drying	180 - 230	1.75	homogeneous easy to pour	8/5	97	+
Calcium-carbonate	Addition of $Ca(OH)_2$ until 20^{0} dH, followed by sodiumcarbonate (50 % excess)	56	200 - 230	1.3	homogeneous easy to pour	8/5	87	+
$K_2Ni[Fe(CN)_6]$, $CaCO_3$	$K_4[Fe(CN)_6]$ 100 mg/l $NiSO_4$ 100 mg/l with 6 M NaOH adjusted to pH 9	82	120 - 230	2.75	homogeneous easy to pour	8/5	86	+

Fig. 1.3-1 shows products from a parallel experiment which were obtained by stirring PVC into bitumen at temperature between 160°C and 175°C. The products obtained at these temperatures (30 w/o PVC) are homogeneous and can be poured. The softening points are 105°C and 117°C, respectively. At a stirring temperature of 160°C - 175°C only a slight evolution of HCl was detected.

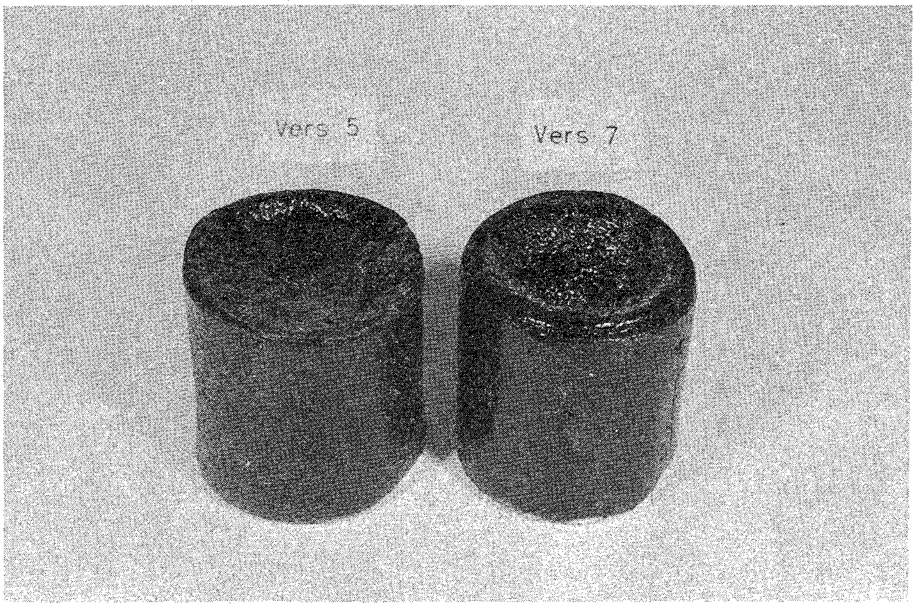


Fig. 1.3-1 PVC-bitumen mixtures with 30 w/o PVC made at 160 - 175°C. The products shown were made in parallel experiments.

In the attempt of stirring PVC into bitumen also at 210°C there was such a strong formation of bubbles of the mixture due to evolution of HCl that the product flowed out of the mixing vessel.

Fig. 1.3-2 shows products obtained by stirring polyethylene into bitumen at temperatures between 12o°C and 175°C. The mixture with 65 w/o polyethylene in the final product is not pourable. Moreover, it is not homogeneous. The product with 5o w/o polyethylene is homogeneous but difficult to pour, whereas the product containing 3o w/o polyethylene is homogeneous and pourable.

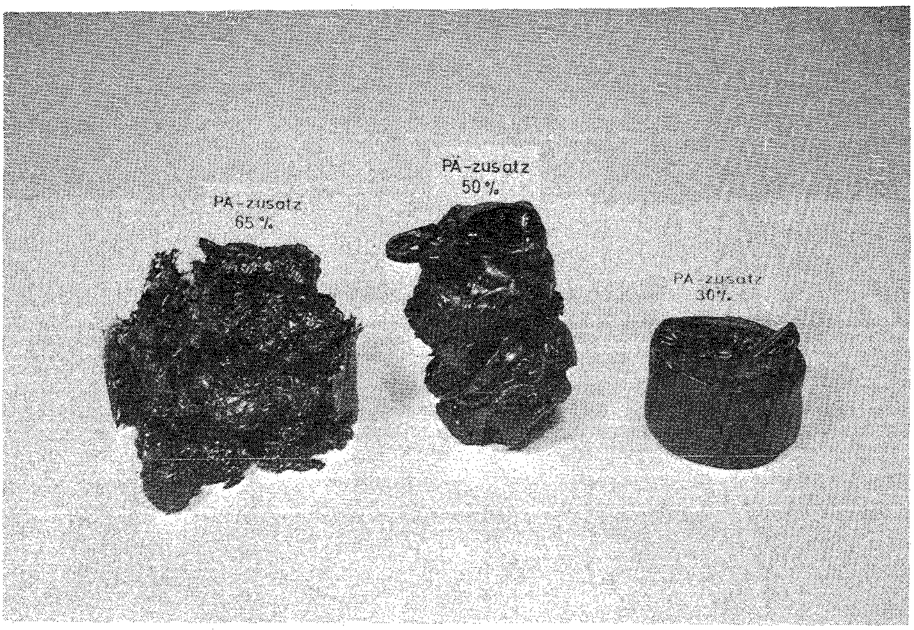


Fig. 1.3-2 Bitumen-polyethylene mixtures made at 12o - 175°C.

It was also possible to stir polystyrene granules into bitumen at temperatures between 12o°C and 135°C up to 3o w/o.

In other experiments, polyethylene and polyvinyl chloride, respectively, were stirred into finished bitumen-salt mixtures (8/5 products) at temperatures between 165°C and 175°C. This showed that the addition, after introduction of the salts, of 1o percent PVC or polyethylene, respectively, gives products which are still satisfactorily pourable.

Experiments to fix organic ion exchangers were carried out too. A mixed bed filter (volume ratio of strongly basic to strongly acid exchanger = 2:1) was loaded with tap water up to breakthrough and a sample of the loaded wet exchanger was stirred into bitumen at 175°C. This resulted in vigorous spraying in the mixing vessel. The final product of about 8o w/o bitumen and 2o w/o loaded dry exchanger was homogeneous and pourable. To avoid spraying, the exchangers should be dried before fixation.

1.4 Stirring of Organic Waste Solutions

The organic wastes produced in the reprocessing of spent nuclear fuels include

- TBP in hydrocarbons,
- aqueous solutions of the sodium salts of partially saponified TBP (in addition to inorganic salts, traces of butanol and hydrocarbons may be present).

For preliminary experiments pure TBP was stirred into bitumen. Metering was done batchwise at a temperature of 11o°C. Metering time was less than ten minutes.

Fig. 1.4-1 shows how the addition of TBP to bitumen reduces hardness. As far as they could still be determined, the softening points of the products are included too.

Another study has demonstrated that the alkali salts of dibutyl phosphoric acid can be precipitated out of an aqueous solution with Fe^{+++}ions [2]. Attempts to stir the precipitated ferric dibutyl phosphate into bitumen at 1oo°C - 14o°C, however, resulted in a product which was

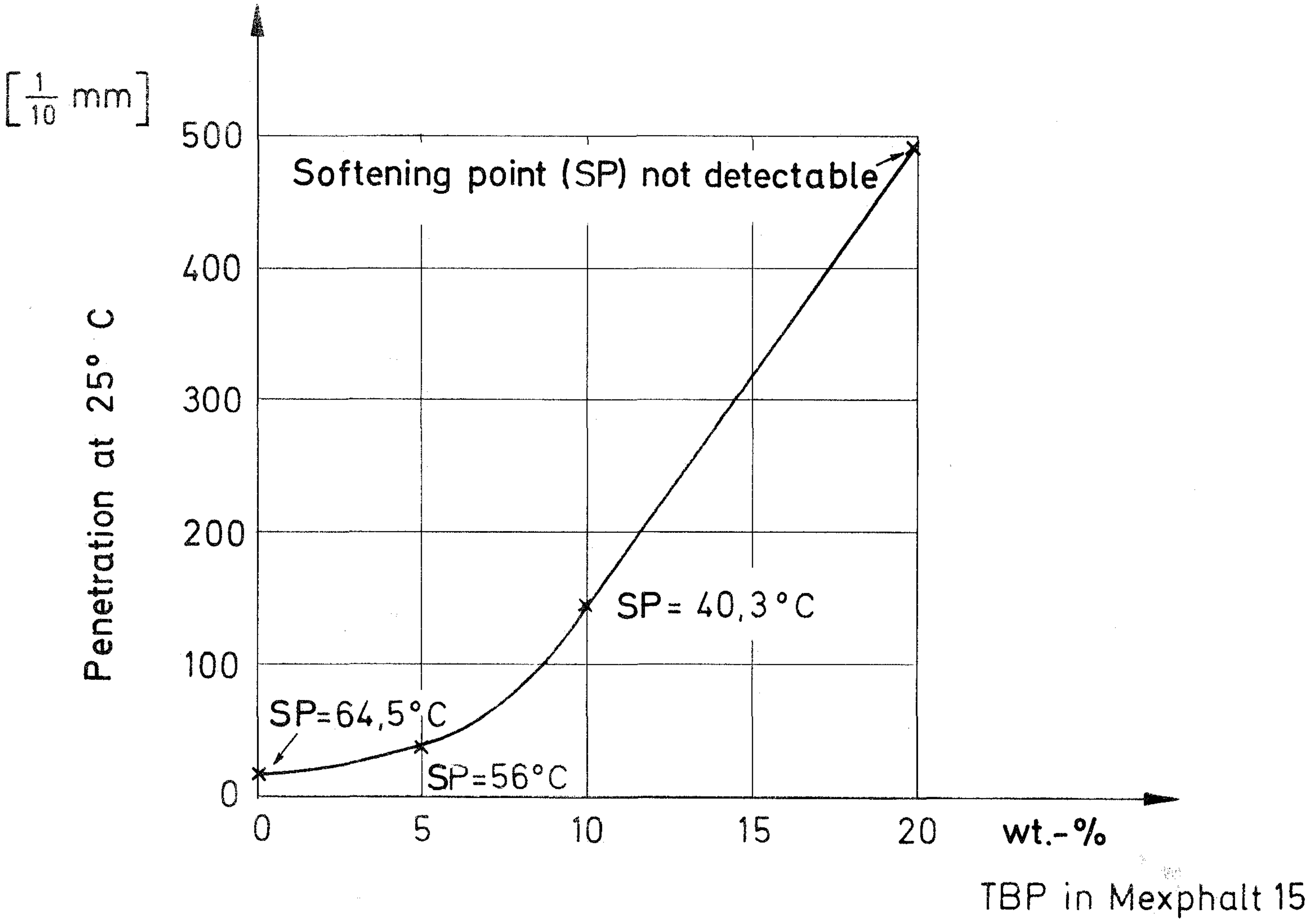


Fig. 1.4-1 Mixing of TBP into bitumen

no longer pourable and had a charred appearance. This is possibly due to a hardening of the bitumen by ferric compounds. A further disadvantage is that the product containing ferric dibutyl phosphate has a low burning point.

1.5 Stirring of Salt Solutions

1.5.1 Influences of Temperature

Table 1.5.1-1 gives a survey of the quality of the final products obtained by stirring 2o percent solutions, such as NaCl, $NaNO_3$, and $Ca(NO_3)_2$, into bitumen at 15o°C and 25o°C. The products obtained by adding distilled water under identical conditions, are included for comparison. At 15o°C, products are obtained in all cases which are easily pourable and whose softening points are only slightly higher as compared to pure bitumen (Mexphalt 15). The process of mixing occurs smoothly at this temperature. Contrary to stirring at 25o°C, there is no spraying, not even at the beginning of the addition. At 25o°C, the products become so hard when $NaNO_3$ and $Ca(NO_3)_2$ solutions are used that the experiments had to be interrupted before the desired final concentration (4o w/o salt) had been reached. These products are no longer pourable.

Fig. 1.5.1-1 shows photographs of products obtained by stirring of sodium nitrate solutions into bitumen at 15o°C and 25o°C, respectively.

Table 1.5.1-1

Influence of Temperature on Stirring of Salt Solutions into Bitumen

Introduced at 15o°C						Introduced at 25o°C			
Solution	pH	Experiment No.	Result	Product (Bit./Salt)	Softening point (ring + ball) °C	Experiment No.	Result	Product (Bit./Salt)	Softening point (ring + ball °C
H_2O dist.	4.8	67	+	8/0	79	69	+	8/0	141
2o % NaCl	4.2	73	+	8/5	94	71	+	8/5	186
2o % $NaNO_3$	4.65	33	+	8/5	8o	39	-	8/2.1	> 2oo
2o % $Ca(NO_3)_2$	4.o	34	+	8/5	84	4o	-	8/2.9	> 2oo
		Introduced at 15o - 2oo°C							
7 % $Ca(NO_3)_2$ +) 13 % NaCl	3	28	+	8/5	89				

+) pH-value adjusted with o.5 M HNO_3 (1 drop/1oo ml solution)

Amount of bitumen (Mexphalt 15) 8o g, rate of addition of the solutions 25 ml/h, period of addition normally 1o h, unless the experiments had to be interrupted earlier.

Normally, an 8/5 product (8 parts by weight of bitumen/5 parts by weight of salt) is obtained.

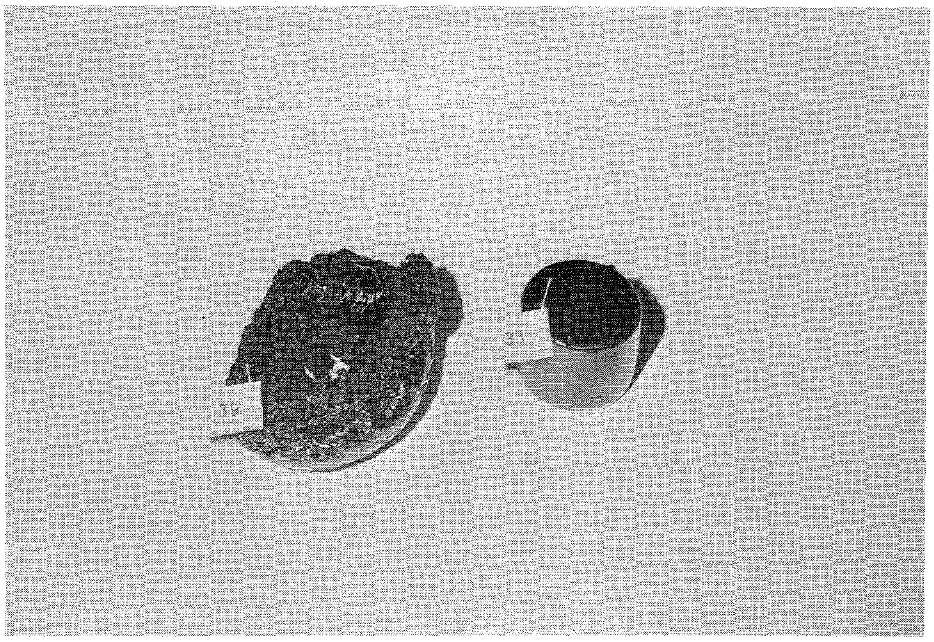


Fig. 1.5.1-1 Bitumen-NaNO$_3$ products
39 2o % NaNO$_3$ solution stirred into bitumen at 25o°C (8/2.1 product)
33 2o % NaNO$_3$ solution stirred into bitumen at 15o°C (8/5 Product)

1.5.2 Influences of Iron and Aluminum Salts

The influence of these salts on the hardening of bitumen was investigated because the effect of such materials (e.g., FeCl$_3$ or AlCl$_3$) is known from catalytic blowing processes in the bitumen industry and because iron is sometimes present in radioactive effluents in considerable quantities (e.g. in bath liquors from the decontamination of solid objects). To get a first impression of the process of hardening of bitumen through iron and aluminum salts, 2o % solutions of these salts were stirred into bitumen at 15o°C. The experimental results can be seen from the Fig. 1.5.2-1 and 1.5.2-2.

Amount of bitumen (Mexphalt 15) 80 g
Temperature approx. 150° C
Dosage rate of 20 % solutions approx. 25 ml/h

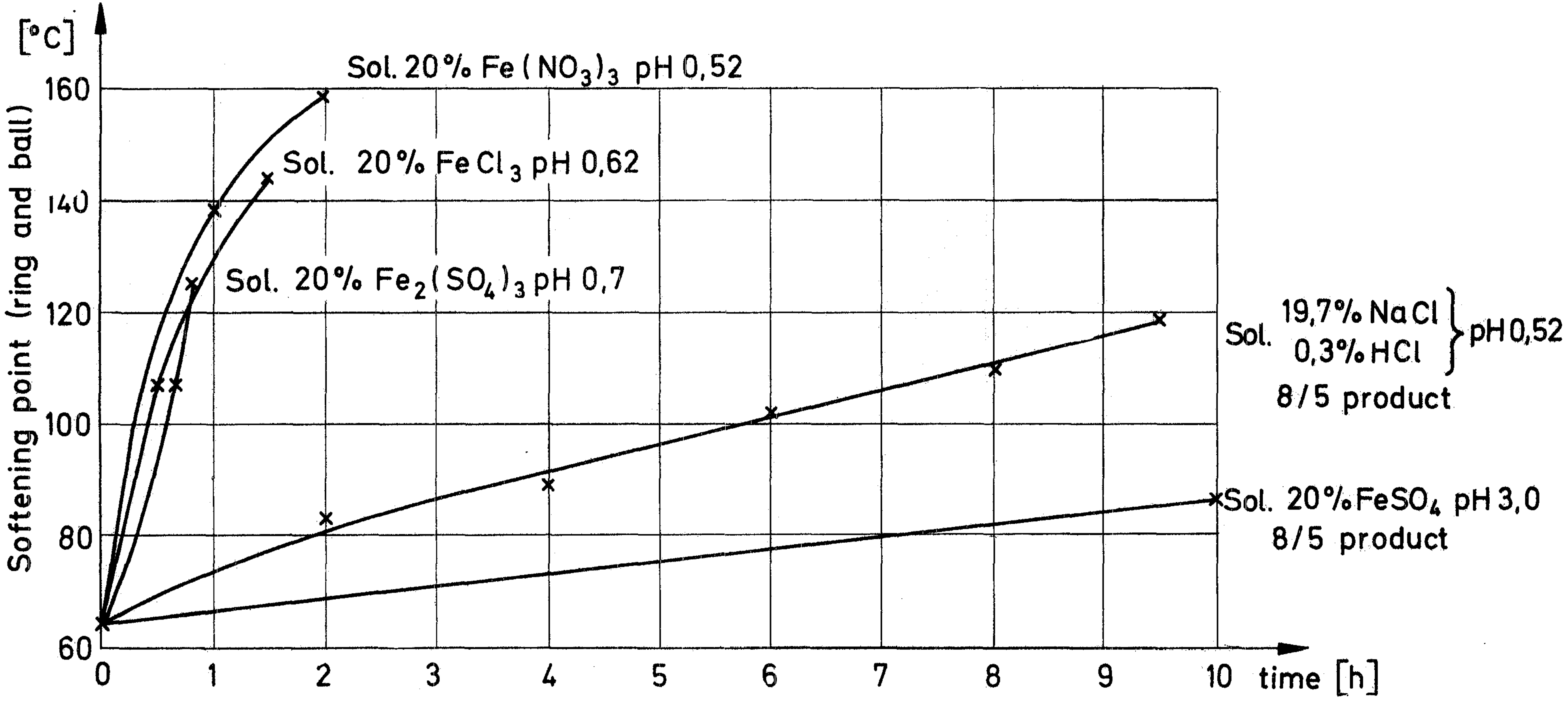


Fig. 1.5.2-1 Mixing of Fe-salt solutions into bitumen

Amount of bitumen (Mexphalt 15) 80 g
Temperature approx. 150° C
Dosage rate of 20 % solutions approx. 25 ml/h

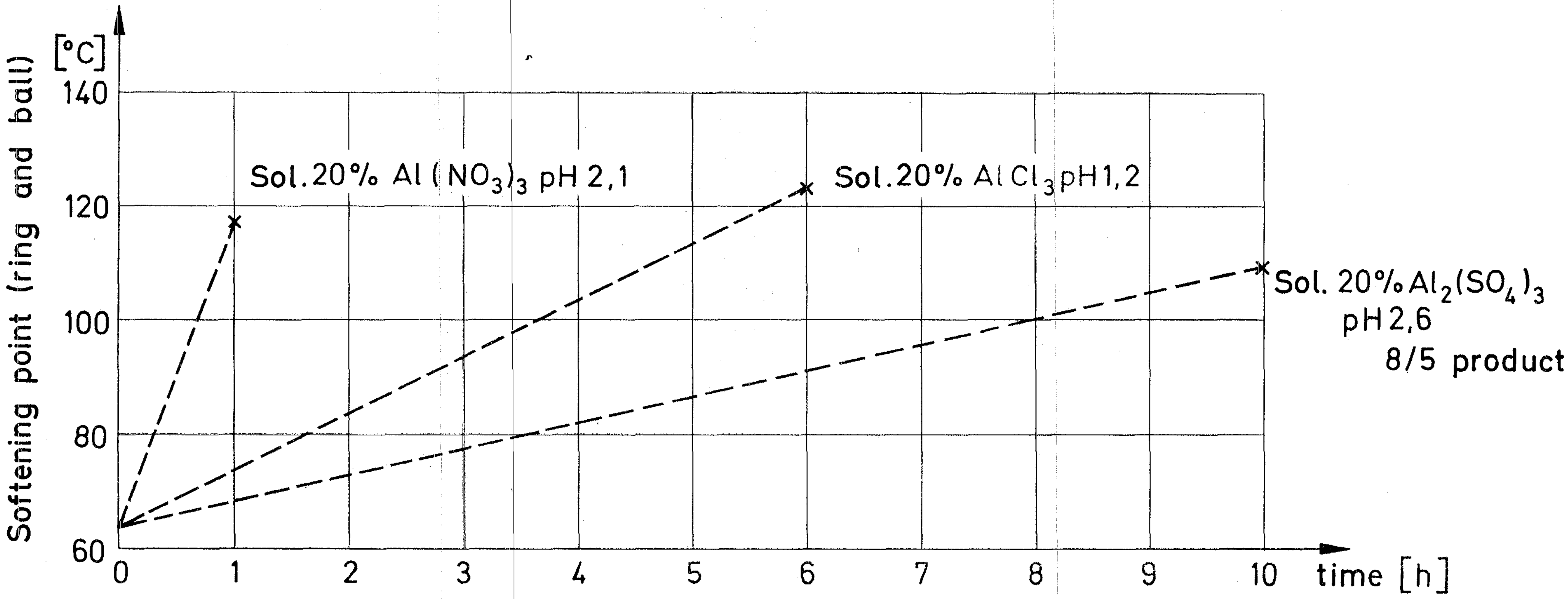


Fig. 1.5.2-2 Mixing of Al-salt solutions into bitumen

The results can be summarized as follows: When 2o % ferric salt solutions (chloride, nitrate, sulfate) were stirred in the experiments had to be terminated already after 1-2 hours because of excessive hardening of the products, while a 2o % ferrons sulfate solution could be completely added (for 1o hours) without difficulty.

In Fig. 1.5.2-3 products are shown which were obtained by stirring iron salt solutions into bitumen at 15o°C.

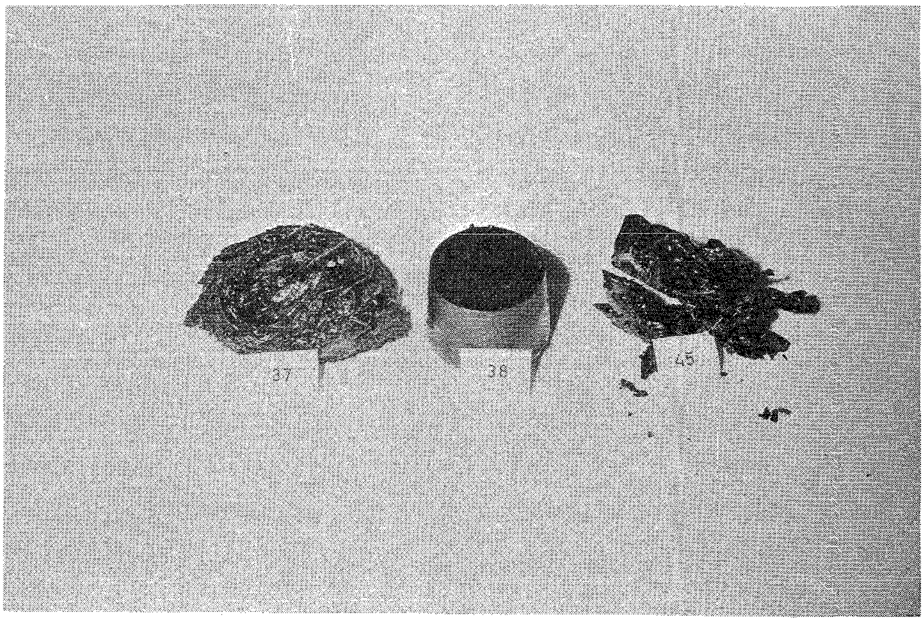


Fig. 1.5.2-3 Bitumen - iron salt products

37 $FeCl_3$ stirred into bitumen as a 2o % solution at 15o°C (8/o.75 product)

38 $FeSO_4$ stirred into bitumen as a 2o % solution at 15o°C (8/5 product)

45 $Fe_2(SO_4)_3$ stirred into bitumen as a 2o % solution at 15o°C (8/o.46 product).

Of the aluminium salt solutions (nitrate, chloride, sulfate) only the aluminium sulfate solution could be completely added under identical conditions.

Since some of the salts investigated (e.g., $FeCl_3$) react acid in solution, the influence of free acids on the hardening of bitumen should be taken into account in an evaluation of the experimental results. However control experiments showed that, for instance, a solution of 19.7 % NaCl and o.3 % HCl could be stirred into bitumen without any difficulties (Fig. 1.5.2-1). Moreover, NaCl solutions with small amounts of ferric nitrate added were stirred into bitumen at 15o °C. This showed that an addition of ferric nitrate to sodium chloride causes a stronger hardening of the bitumen than the same addition to sodium nitrate does. The results of these experiments are listed in Table 1.5.2-1.

The hardening effects of ferric and aluminum salts on bituminizing can be overcome simply by alkalizing the solutions prior to stirring them into bitumen. Table 1.5.2-2 contains a summary of these experimental results.

Table 1.5.2-1

Stirring in Bitumen of NaCl and $NaNO_3$ Solutions with Ferric Nitrate Added

Exp. No.	Solution	pH	Product	Properties of product at 15o°C	Softening point (ring + ball) °C	Result
36	19 % NaCl 1 % $Fe(NO_3)_3$	1.8	8/2.8	inhomogeneous non pourable	114	-
132	19.5 % NaCl o.5 % $Fe(NO_3)_3$	1.9	8/4.4	inhomogeneous non pourable	1o7	-
134	19.75 % NaCl o.25 % $Fe(NO_3)_3$	2	8/5	homogeneous pourable	99	+
35	19 % $NaNO_3$ 1 % $Fe(NO_3)_3$	1.9	8/5	homogeneous, viscous, poorly pourable	129	almost positive
131	19.5 % $NaNO_3$ o.5 % $Fe(NO_3)_3$	1.8	8/5	homogeneous pourable	1o9	+

Amount of bitumen (Mexphalt 15) 8o g, rate of addition of the solutions 25 ml/h, period of addition normally 1o h, unless the experiments had to be interrupted earlier.
Normally, an 8/5 product (8 parts by weight of bitumen/5 parts by weight of salt) is obtained.

Table 1.5.2-2

Exclusion of Influence of Ferric and Aluminium Salts on the Hardening of Bitumen by Alkalinization of the Solutions Prior to Addition

Rate of addition of the solutions	25 ml/h
Temperature	150 °C
Amount of bitumen (Mexphalt 15)	80 g
Rate of Stirring	150 - 200 rpm

Exp. No.	Solution	pH	Product	Properties of Product at 150 °C	Softening point (ring+ball) °C	Result
79	19 % $NaNO_3$ 1 % $Fe(NO_3)_3$ 0.5 % NaOH	8	8/5	homogeneous viscous pourable	82	+
81	19 % NaCl 1 % $Fe(NO_3)_3$ 0.5 % NaOH	8	8/5	homogeneous pourable	87	+
129	13.2 % $Fe(NO_3)_3$ 6.8 % NaOH ($Fe(OH)_3$ in $NaNO_3$ sol.)	8	8/5	viscous homogeneous pourable	113	+
130	13.1 % $Al(NO_3)_3$ 6.9 % NaOH ($Al(OH)_3$ in $NaNO_3$ sol.)	8	8/5	homogeneous relatively low viscosity pourable	115	+
126	9.1 % $Al(NO_3)_3$ 10.9 % NaOH (clear solution $[Al(OH)_4]^-$ plus $NaNO_3$)	13.3	8/5	homogeneous relatively low viscosity well pourable	108	+

In addition to this, Fig. 1.5.2-4 shows products obtained by stirring NaCl solutions with additions of ferric nitrate into bitumen at different pH values.

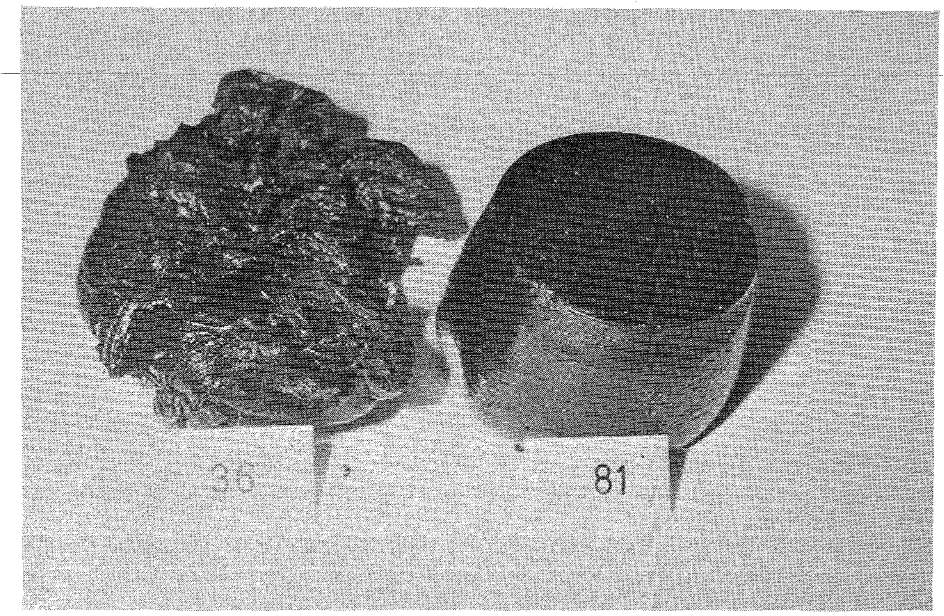


Fig. 1.5.2-4 Bitumen-NaCl-$Fe(NO_3)_3$ products
36 2o % solution (19 % NaCl, 1 % $Fe(NO_3)_3$) stirred into bitumen at pH 1.8 and 15o°C (8/2.8 product)
81 2o % solution (19 % NaCl, 1 % $Fe(NO_3)_3$) stirred into bitumen at pH 8 and 15o°C (8/5 product).

1.5.3 Influence of Sojourn Time

The experiments clearly show that short sojourn times of the products in the mixing vessel are favorable when salt solutions are stirred into bitumen.

To test the influence upon hardening of sojourn time of the product in the mixing vessel, a 2o % $FeCl_3$ solution was metered into bitumen at 15o°C for short periods of time (7.5 and 15 minutes, respectively). This resulted in products whose softening points are only slightly higher than those of pure bitumen. However, subsequent maintaining of these products at a constant temperature of 15o°C results in a distinct increase of hardening (curves 1 and 2 of Fig. 1.5.3-1). For comparison, the plot of hardening of pure bitumen without addition of ferric salt solution (curve 3) was included in Fig. 1.5.3-1.

1.5.4 Experiments with Simulated Evaporator Concentrate Solutions

To round off the experiments on stirring of salt solutions into bitumen, some thirty solutions of various compositions were stirred into bitumen at 15o°C. The investigations included simulated waste waters from the equipment decontamination, known as "exotic waste water" because of their chemical composition (nitrates, heavy metals, tensides, pickling pastes, complexing and chelating agents). Without going into the details of these experiments, the results can be summarized in this way: Even solutions of an extremely unfavorable composition gave suitable products at sojourn times of the bitumen in the mixing vessel of about 1o hours if a working temperature of about 15o°C was maintained and the waste solution had a weakly alkaline pH (8-1o).

1.5.5 Hardening of Different Grades and Constituents of Bitumen

In connection with the hardening of bitumen after addition of salt solutions the behavior of certain grades and constituents of bitumen may be of interest. For this reason, a 2o % $FeCl_3$ solution was stirred into different types

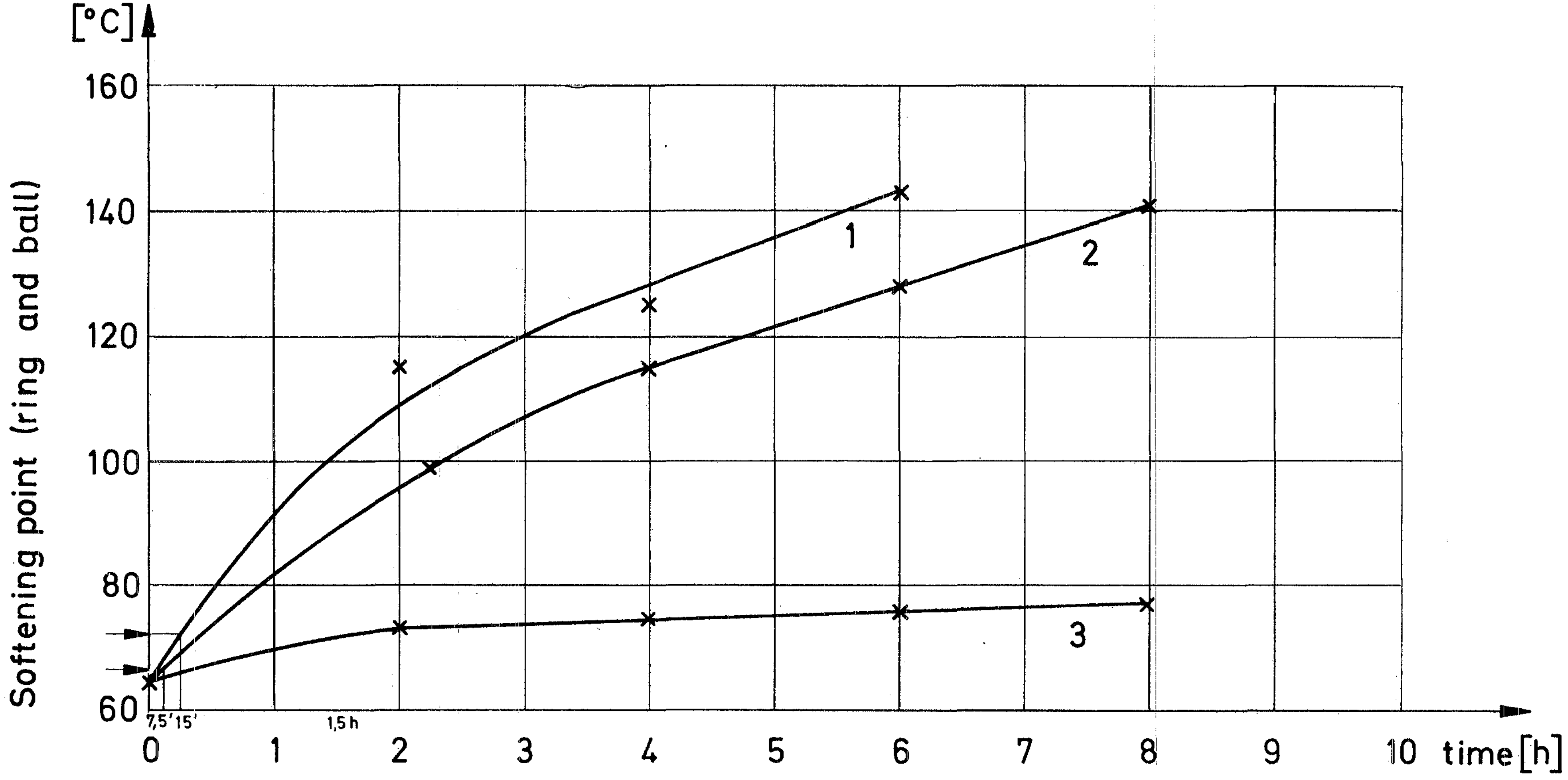


Fig. 1.5.3-1 Influence of sojourn time in the mixing vessel on the hardening of the product

1 = 20 % $FeCl_3$-solution mixed into 80 g Mexphalt 15 (rate 25 ml/h for 15 min) followed by stirring at constant temperature of 150° C

2 = Same as 1 (rate 25 ml/h for 7,5 min)

3 = Mexphalt 15 stirred at constant temperature of 150° C (rate of stirring in all cases 200 rpm)

of bitumen at 15o°C and hardening was determined through the softening points. The experimental results are indicated in Fig. 1.5.5-1. Although all these experiments had to be interrupted prematurely because of excessive hardening of the products, it is possible to detect gradual differences in the behavior of the various grades of bitumen. Thus, for instance, the bitumen grade PH 55/65 now in use at Mol is prefered to Mexphalt 15 under the aspect of hardening.

For practical purposes it would be worth knowing which constituents of bitumen are particularly sensitive with respect to hardening. For this reason, hardening experiments were carried out with the isolated maltenes of Mexphalt 15. Experiments aimed at investigating the behavior of the asphaltene constituents under the same condition were not feasible because the softening points of asphaltenes are above 2oo°C. For this reason, only the hardening of the maltenes of Mexphalt 15 was compared with that of unchanged Mexphalt 15.

2. Characteristics of the Products Obtained at the Stirring Experiments

2.1 Combustion Characteristics

The grade Mexphalt 15 used in most of the experiments has a relatively high flame and burning point. (The flame point determined according to Marcusson in the open crucible is near 35o°C. The burning point was determined by a non-standardized method to be around 43o°C.)

The experiments were to show if and how the combustion characteristics of the different final products change relative to pure Mexphalt 15. Besides the burning point, the period of combustion was determined for 1 g each of the specimen ignited at the burning point.

Amount of bitumen 80 g; in case of maltenes 65 g
Temperature 150° C
Dosage rate of 20 % $FeCl_3$ solutions approx. 25 ml/h
Rate of stirring 200 rpm

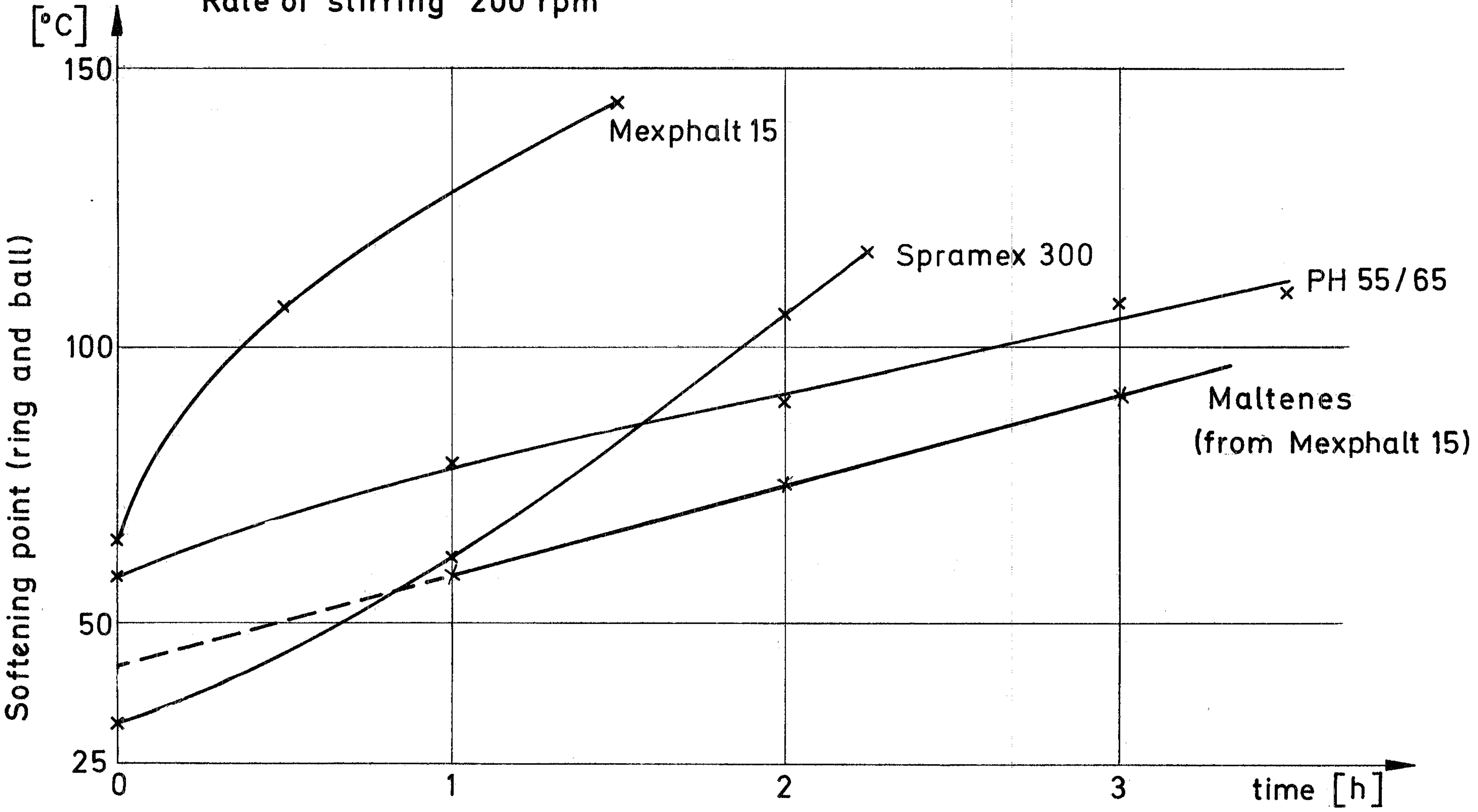


Fig. 1.5.5-1 Hardening of some types of bitumen

As has been mentioned in Section 1.4 above, the product obtained by stirring ferric dibutyl phosphate into bitumen has a burning point of only 190°C. In various experiments with organic materials it was noted that easily burnable constituents are destilled off during the introduction into bitumen. In such cases it might be advantageous to fix the respective substances in inorganic materials at normal temperature. Experiments of this type have been successful [3].

It is obvious that no substances should be stirred into bitumen which decompose already at the working temperature. Thus, during the introduction of sodium citrate solutions containing complex bound heavy metals (Fe, Ni, Cr), there was such a strong development of smoke in bitumen at 180°C as to fog the hood. At 150°C, however, it was possible to stir the solution into bitumen without any difficulties. The product made at 150°C had a relatively low burning point (225 - 240°C).

However, primarily the combustion characteristics of bitumen specimens with a high content of nitrate were investigated because there are indications in the literature to the effect that the flame point of bitumen is reduced by fixed nitrates [4]. Table 2.1-1 contains some data on the burning points of the 8/5 products obtained in the stirring tests. For comparison, also the burning point of pure Mexphalt 15 is listed. The values indicated in parentheses refer to the temperature at which the salt solutions were stirred into bitumen.

Table 2.1-1

Burning Points of 8/5 Products Compared with Mexphalt 15

Product:	Burning Point °C: (Range)
1. Mexphalt 15	420 - 440
2. Mexphalt 15 - 38.5 % NaCl (230°C)	420 - 430
3. Mexphalt 15 - 38.5 % $Al_2(SO_4)_3$ (150°C)	420 - 430
4. Mexphalt 15 - 38.5 % $FeSO_4$ (150°C)	440 - 450
5. Mexphalt 15 - 38.5 % $NaNO_3$ (150°C)	400 - 430
6. Mexphalt 15 - 38.5 % $Ca(NO_3)_2$ (150°C)	370 - 380
7. Mexphalt 15 - 36.6 % $NaNO_3$ (150°C) 1.9 % $Fe(NO_3)_3$	330 - 340
8. Mexphalt 15 - 25.2 % $Al(NO_3)_3$ (150°C) 13.3 % NaOH (Note 1)	350 - 360
9. Mexphalt 15 - 17.5 % $Al(NO_3)_3$ (150°C) 21.0 % NaOH (Note 2)	260 - 270

Note 1: Suspension of $Al(OH)_3$ in $NaNO_3$ solution, pH = 8

Note 2: Optically clear solution of sodium aluminate and $NaNO_3$, pH = 13.3

The product listed under (9) of Table 2.1-1 exhibits a remarkably large reduction of the burning point.

For comparison, Table 2.1-2 contains the burning points of products made at 25o°C which could not be brought to a salt content of 4o % because of excessive hardening of the mixture.

Table 2.1-2 Burning Points of Strongly Hardened Bitumen/ Nitrate Products Compared with Mexphalt 15

Product	Burning point °C (Range)
1. Mexphalt 15	42o - 44o
2. Mexphalt 15 - 21 % $NaNO_3$ (25o°C)	32o
3. Mexphalt 15 - 26.5 % $Ca(NO_3)_2$ (25o°C)	27o - 28o

Despite their low nitrate content the products made at 25o°C exhibit a stronger reduction of the burning point than those obtained at 15o°C. Apart from the values of Table 2.1-2 which refer to excessively hardened and untypical final products, reductions of the burning point of up to 16o°C can be observed in bitumen specimens containing nitrate as compared to Mexphalt 15. Generally it can be said that bitumen specimens containing nitrate have a faster burning rate than pure bitumen. Some of the specimens burnt up to five times faster than Mexphalt 15. In some cases the burning was sizzling.

To find out whether the presence of large quantities of nitrates in bitumen increases the speed of burning considerably and makes the products shock sensitive, thus impairing the safety of production, transport and storage, some specimen were subjected to the following tests:[+]

(1) Temperature of ignition on heating (5°C/min.) in the deflagration apparatus

(2) Period of burning on injection into a red-hot steel dish (12o mm dia., 6o mm depth)

(3) Behavior during heating under inclusion in a steel shell (25 mm OD, 24 mm ID, 75 mm length) with the nozzle plate closed by welding

(4) Sensitivity to the shock wave of a Nitropenta No. 8 explosive capsule

    (a) with a metal plate of 1o mm between fuse and specimen

    (b) with the explosive capsule directly attached to the specimen (detonation shock)

(5) Sensitivity to the shock effect of an intensifier charge of 1o g tetryl through a steel plunger. The experiment was carried out in a steel shell of 25 mm OD x 24 mm ID x 75 mm.

Table 2.1-3 gives the composition of the bitumen-salt mixtures which have been used for these tests.

[+] These investigations were performed by the Institut für Chemie der Treib- und Explosivstoffe der Fraunhofer-Gesellschaft e.V., Berghausen

Table 2.1-3 Composition of the Bitumen-Salt Mixtures for Combustion and Shock Tests

Specimen No.	Composition
1o4	Kuwait 18o/2oo - 7o % $NaNO_3$ (introduced as a solid, 12o°C)
189	Mexphalt 15 - 38.5 % $NaNO_3$ (introduced as a solution 15o°C)
19o	Mexphalt 15 - 38.5 % $NaNO_3$ (introduced as a solid, 15o°C
191	Mexphalt 15 - 6o % $NaNO_3$ (introduced as a solid, 15o°C)
M 15	Mexphalt 15 - (control substance)

The results of the experiments carried out so far show that the bitumen specimens investigated can be handled without any hazard regarding shock sensitivity and burnability. Although the nitrate content facilitates and accelerates combustion, it is not sufficient to increase the rate of combustion significantly. Maximum values will possibly be obtained only with an even oxygen balance, i.e., a sodium nitrate content of about 85 %.

The specimens show a very inactive behavior when heated under inclusion in a steel shell. Even with the nozzle plate closed by welding there will be blast flames only after a relatively long period of heating without the combustion changing into an explosion. All the specimens investigated are completely insensitive to shock treatment.

The experiments are being continued with the aim of determining the upper concentration limit of nitrates up to which safety regarding burnability and shock sensitivity of the bitumen is guaranteed. The experiments are to be extended also to irradiated specimens. The preliminary experiments carried out so far have shown no major change of the burning points in irradiated specimens. Since heavy metal salts are capable of catalyzing the rate of combustion, investigations are planned with bitumen specimens containing heavy metal salts in addition to alkali and alkaline earth nitrates.

2.2 Stability against Radiation

Investigations at the Asphalt Laboratory of Esso AG have indicated that distillated as well as blown bitumen is merely hardened by gamma irradiation to $1o^9$rad. A surprising result of these tests has been deemed the fact that by irradiation the asphaltene content of the bitumen did not increase but rather slightly decrease [5].

From irradiation experiments in the United States it is known that there may also be swelling after irradiation of bitumen [6]. The formation of gas bubbles in the bitumen matrix is mentioned elsewhere [7].

In our own experiments, bitumen products were irradiated with 1o MeV electrons up to an absorbed radiation dose of $5 \times 1o^8$rad and the change of hardness, density and the formation of gas bubbles in the bitumen matrix were checked as a function of the absorbed dose of radiation. The irradiation was carried out with a linear electron accelerator Varian V 77o3. The specimens exposed were disk-shaped (diameter 4.5 cm, height 1-1.4 cm). The absorbed radiation dose per exposure was 2 x $1o^4$rad. After 2oo exposures (about 1/2 hours of irradiation corresponding to 4 x $1o^6$rad), the specimens had warmed up by 15°C to some 4o°C. To avoid further heating of the specimens during irradiation, intermissions of 1/2 h were made after every 2oo exposures.

As can be seen from Fig. 2.2-1, the hardening effects on bitumen-salt mixtures become apparent at radiation doses in excess of $1o^8$rad. A striking feature for the range $> 1o^8$rad is the relatively strong increase in hardness of a bitumen product containing calcium nitrate. In Table 2.2-1 the densities of irradiated and unirradiated bitumen specimens are listed for comparison. The densities were measured by weighing the specimens at room temperature in air and water (at densities below unity, alcohol was used instead of water). The ratio of density of the original specimen versus densities of the irradiated specimens is a standard for the swelling of the specimens as a result of irradiation. Again, the changes are most marked in the product containing calcium nitrate.

Investigations of an unirradiated specimen have shown that this product contains about 8 w/o of water, bound as water of crystallization, in addition to bitumen and calcium nitrate which is not removed completely at the stirring temperature of 15o°C. It is possible that the presence of water in the specimen is responsible for the greater sensitivity to radiation.

It is striking that irradiation of the bitumen grade PH 55/65 to 5 x $1o^8$rad shows but minor changes of density. Moreover the number of gas bubbles per cm^2 of fractured surface was counted in the irradiated bitumen and bitumen-salt specimen and their diameters were estimated. The result has been compiled in Table 2.2-2. (It should be mentioned that occasional gas bubbles can also be observed in unirradiated bitumen-salt specimens.)

Fig. 2.2-1 Hardening of bitumen and bitumen-salt mixtures at irradiation with 10 MeV-electrons. The values in brackets are the softening points of the non-irradiated samples.

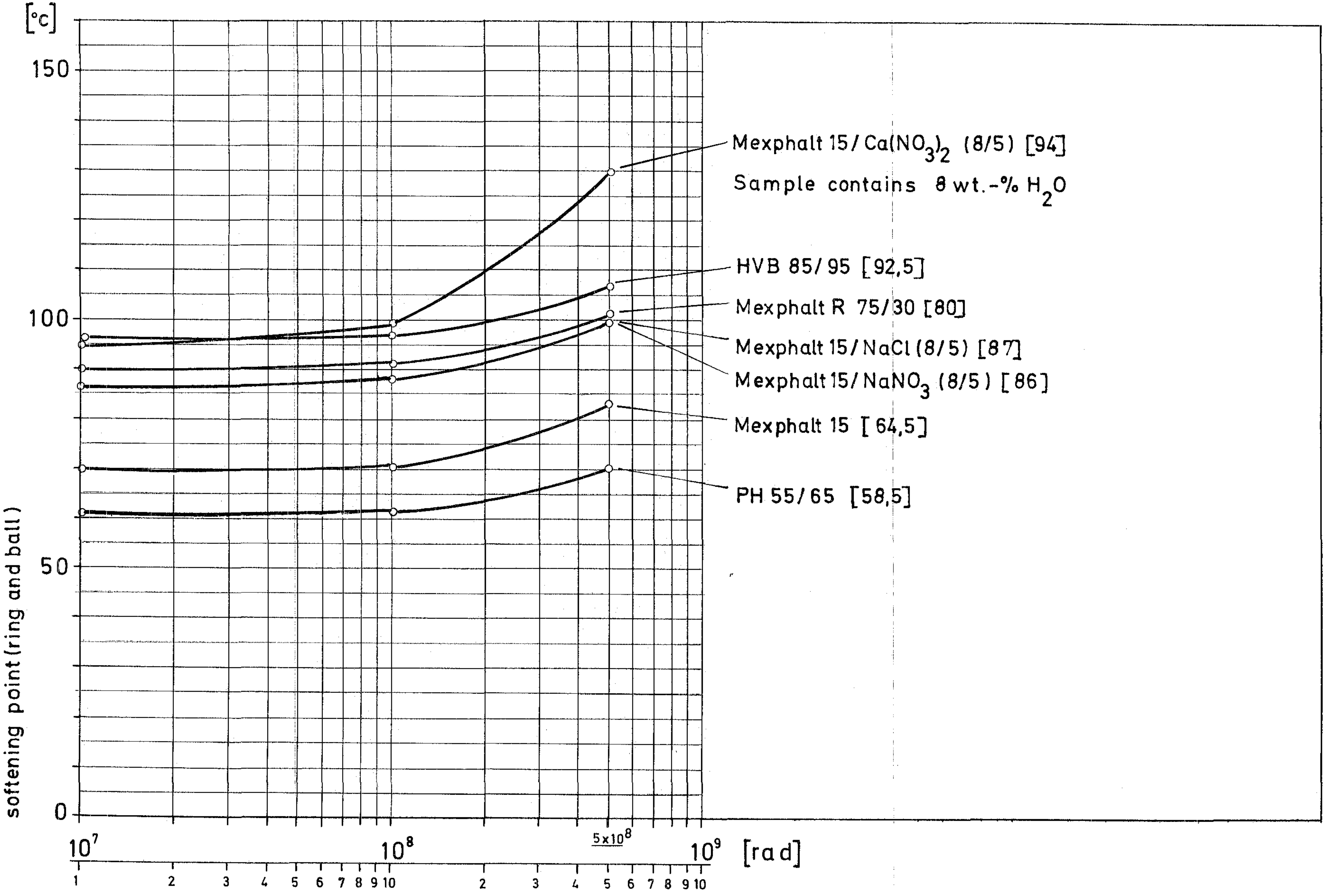


Table 2.2-1

Density of irradiated and unirradiated samples of bitumen
(irradiated with electrons of 10 MeV at a rate of ~ $4\cdot10^6$ rad per 33 min. at ambient temperature; overall dose $5\cdot10^8$ rad)

Number and species of sample	Density of original sample [g/cm^3]	Density of irradiated sample [g/cm^3]	ratio of densities original : irradiated
3.6 PH 55/65	1.070	1.057	1.01
3.8 Mexphalt 15	1.04	0.935	1.11
3.7 Mexphalt R 75/30	1.01	0.888	1.14
3.5 HVB 85/95	1.034	0.842	1.23
3.2 Mexphalt 15 $NaNO_3$ (8/5)	1.29	1.045	1.23
3.1 Mexphalt 15 NaCl (8/5)	1.25	1.005	1.24
3.3+) Mexphalt 15 $Ca(NO_3)_2$ (8/5)	1.29	0.902	1.43

+) After admixture of the salt solution the water content was determined by the KARL FISCHER method. 8 wt.% of water were found.

Table 2.2-2

Formation of gas bubbles at the irradiation of bitumen and bitumen-salt mixtures

1) Number of bubbles per sq. cm. after cutting (approx.)

Sample Dose [rad]	pH 55/65	HVB 85/95	Mex-phalt 15	Mex-phalt R 75/3o	Mex-phalt 15 -$NaNO_3$ 8/5	Mex-phalt 15 -NaCl 8/5	Mex-phalt 15 -$Ca(NO_3)_2$ 8/5 +)
$5 \cdot 1o^8$	2-4	1o	1o-15	1o-2o	4o	8o	14o
$1o^8$	2	3-4	1-2	4-5	5o	6o	16o
$1o^7$	0	0	0	0	0	4o	2o-4o
0 (origin.)	0	0	0	0	0	1o	25

+) This product contained 8 wt.-% of water

2) Diameter of the gas bubbles in mm (approx.)

$5 \cdot 1o^8$	1-4	1-7	1-5	1-4	up to 1.5	up to 1	up to 1
$1o^8$	1-4	1-4	1-3	o.5-3	up to o.5	up to o.4	up to o.5
$1o^7$	-	-	-	-	-	up to o.2	up to o.1
0 (origin.)	-	-	-	-	-	up to o.4	< o.1

Figures 2.2-2 and 2.2-3 show fractured surfaces of an unirradiated and an irradiated bitumen-salt specimen. The formation of gas bubbles in the irradiated specimen is clearly visible.

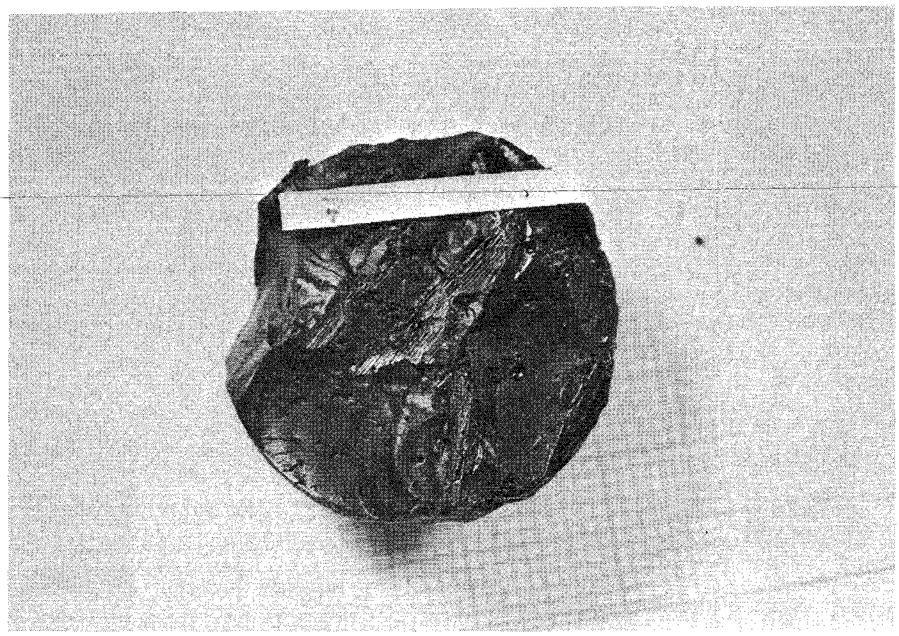


Fig. 2.2-2 Fractured surface of unirradiated 8/5 products (Mexphalt 15 - $Ca(NO_3)_2$)

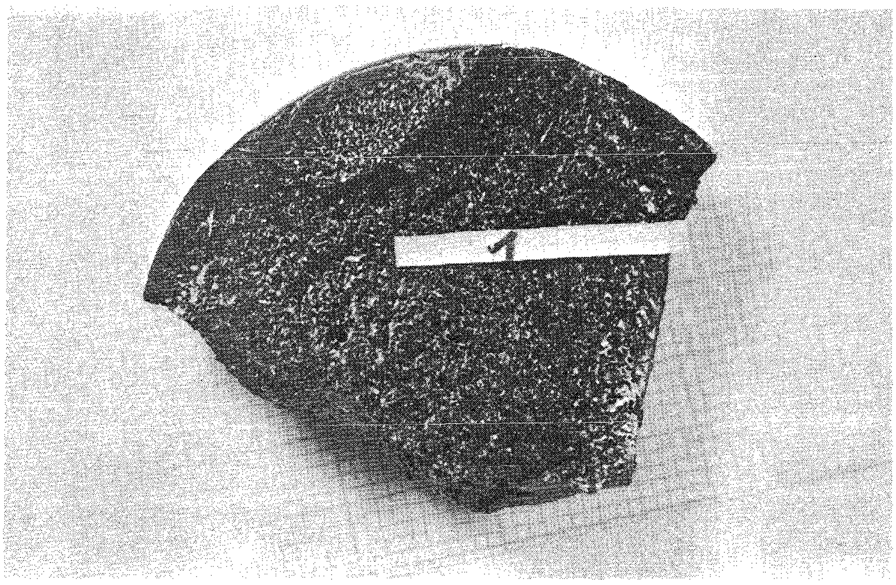


Fig. 2.2-3 Fractured surface of an irradiated 8/5 product (Mexphalt 15-$Ca(NO_3)_2$. Radiation source: 1o MeV electrons; absorbed radiation dose $1o^8$rad).

2.3 Leachability

Leaching tests were carried out on some of the products obtained in the laboratory experiments.

2.3.1 Experimental Method

For the leaching tests the products were put into 1 l plastic bottles containing o.5 l of distilled water. The water was not stirred; it was changed as follows: dayly during the first two weeks (except for the weekend); every other day during the following two weeks (except for the weekends); once every four weeks afterwards. Leaching was observed by determination of the sodium content of the leaching liquid. In a few samples, calcium and iron were determined in addition to sodium. The elements were determined by flame photometry with a Unicam Atom Absorption Spectralphotometer SP 9o by the emission method in the case of sodium and by the atom absorption method in the case of calcium and iron.

Up to now, leaching of most of the samples has been measured over a period of 255 days. Table 2.3.1-1 summarizes the experimental results. The table also contains data on the chemical composition and geometry of the samples used in the leaching tests.

2.3.2 Leaching Units

Diffusion Coefficient

Assuming that diffusion controls the leaching, equations of the following kind are mentioned in the literature to describe the mechanism of leaching of stable solids [8,9].

$$\frac{Q}{Q_o} = \frac{2\sqrt{Dt}\cdot F}{\sqrt{\pi}\cdot V_s} \qquad \text{(Equation 2.3.2-1)}$$

Table 2.3.1-1

Results of Leaching Tests of Bitumen Products

Sample No.	pH of introduced salt solutions	Chemical composition of the 8/5 products (wt.-%)	Concentration of indicating element in the products (Na unless otherwise noted) (g/cm^3)	mean leaching rate over 255 days ($f_L\cdot(\frac{cm^2}{g})^{-1}\cdot d^{-1}$)	Leaching rate at the end of the test period ($f_L\cdot(\frac{cm^2}{g})^{-1}\cdot d^{-1}$)	slope of lg Q/Qo vs. lg t	Remarks	Dimension of the samples for leaching tests		
								Volume (cm^3)	Surface:Volume (cm^{-1})	Density (g/cm^3)
146	6.6	19.25 $NaNO_3$ 19.25 $Ca(NO_3)_2$	0.066	$1\cdot10^{-5}$	$3\cdot10^{-5}$	0.33 1.- 13. d 0.05 13.-100. d 0.25 100.-255. d		46.8	1.54	1.26
162	7	31.65 H_3BO_3 5.7 Na_3BO_3	0.036	$5\cdot10^{-5}$	$2\cdot10^{-5}$	0.24 1.- 14. d 0.08 14.- 65. d 0.38 65.-255. d		40.7	1.61	1.18
164	7	38.25 $NaNO_3$ 0.25 NaF	0.14	$5\cdot10^{-5}$	$1\cdot10^{-5}$	0.14 1.- 10. d 0.06 10.- 95. d 0.33 95.-255. d		45.8	1.55	1.33
159	7	27.7 Na_2SO_4 2.2 $NaOH$ 6.1 $Fe(NO_3)_3$ 1.1 $Ni(NO_3)_2$ 1.0 $Ca(NO_3)_2$ 0.5 $CrCl_3$	0.137	$8\cdot10^{-5}$	$2\cdot10^{-5}$	0.34 1.- 14. d 0.18 14.-255. d		37.6	1.65	1.31
163	7	38.5 $Na_2C_2O_4$ 0.05 $NaOH$	0.172	$8\cdot10^{-5}$	$4\cdot10^{-5}$	0.17 1.- 53. d 0.67 53.-255. d		47.8	1.53	1.32
168	10	30.68 $NaNO_3$ 3.77 $NaOH$ 2.56 $Al_2(SO_4)_3$ 0.5 NH_4NO_3 0.2 NH_4Cl 0.2 $(NH_4)_2SO_4$	0.136	$1\cdot10^{-4}$	$4.5\cdot10^{-5}$	0.24 1.- 10. d 0.15 10.- 84. d 0.56 84.-255. d		47.8	1.53	1.32
167	12.8	29.1 $NaNO_3$ 6.08 $NaOH$ 0.22 $NaCl$ 0.21 Na_2SO_4 2.78 $Al_2(SO_4)_3$	0.143	$2\cdot10^{-4}$	$1\cdot10^{-4}$	0.35 1.- 53. d 0.63 53.-255. d		38.7	1.63	1.24
154	7	34.4 $NaNO_3$ 4.1 Na_2SO_4	0.145	$2\cdot10^{-4}$	$8\cdot10^{-5}$	0.25 1.- 10. d 0.15 10.- 73. d 0.96 73.-255. d		47.8	1.53	1.16
152	12.9	21.2 $NaNO_3$ 9.04 $NaOH$ 5.4 $Fe(NO_3)_3$ 2.08 $Al_2(SO_4)_3$ 0.39 NH_4NO_3 0.15 NH_4Cl 0.15 $(NH_4)_2SO_4$	0.131	$2.5\cdot10^{-4}$	$2\cdot10^{-4}$	0.28 1.- 10. d 0.37 10.- 84. d 0.46 84.-200. d 0.56 200.-255. d		27.5	1.85	1.23
169	8	15.2 $NaOH$ 1.76 $NaNO_3$ 21.6 $Al(NO_3)_3$ 0.26 $Fe_2(SO_4)_3$ 0.17 $Fe(NO_3)_3$	0.116	$3\cdot10^{-4}$	$1\cdot10^{-4}$	0.54 1.- 14. d 0.21 14.- 53. d 0.65 53.-255. d	swelling after 227 days water storage observed	47.8	1.53	1.25
143	7	28.7 $NaNO_3$ 1.12 Na_2MoO_4 3.6 $La(NO_3)_3$ 1.57 $Ni(NO_3)_2$ 0.84 $CsNO_3$ 0.76 ZrO_2 0.58 $Co(NO_3)_2$ 0.38 $Ba(NO_3)_2$ 0.26 MnO_2 0.19 $Y(NO_3)_3$ 0.17 $Sr(OH)_2$ 0.15 TeO_2 0.12 $Fe(NO_3)_3$ 0.02 Cr_2O_3	0.109	$3\cdot10^{-4}$	$2.5\cdot10^{-4}$	0.3 1.- 25. d 0.44 25.- 53. d 0.99 53.-255. d		44.8	1.56	1.26
158	7	27.0 $NaNO_3$ 2.5 $NaOH$ 6.4 $Fe(NO_3)_3$ 1.1 $Ni(NO_3)_2$ 1.0 $Ca(NO_3)_2$ 0.5 $CrCl_3$	0.114	$5.5\cdot10^{-4}$	$2\cdot10^{-4}$	0.38 1.- 53. d 0.47 53.-255. d		34.6	1.7	1.3
156	13.3	19.25 $NaNO_3$ 19.25 $NaOH$	0.201	$6\cdot10^{-4}$	$2\cdot10^{-4}$	0.56 1.- 20. d 0.26 20.-255. d		47.8	1.53	1.27
157	7	21 Na_3-citrate 3.43 $NaOH$ 10.0 $Fe(NO_3)_3$ 1.5 $Ca(NO_3)_2$ 1.8 $Ni(NO_3)_2$ 0.76 $CrCl_3$	0.094	$2\cdot10^{-3}$	$7\cdot10^{-4}$	0.55 1.- 10. d 0.49 10.-255. d	swelling after 170 days water storage observed	17.3	2.28	1.12
			Fe:0.028	$1\cdot10^{-3}$	$6\cdot10^{-4}$	0.51 1.- 10. d 0.44 10.- 57. d 0.51 57.-255. d				
			Ca:0.004	$9\cdot10^{-4}$	$6\cdot10^{-4}$	0.51 1.- 25. d 0.29 25.- 92. d 0.63 92.-255. d				

The symbols mean:

Q_o = amount of an element originally contained in the sample

Q = amount of an element migrating through the surface F in the time t

D = diffusion coefficient

F = surface of the solid sample

V_s = volume of the solid sample

t = time of storage in water (action period of water)

If leaching is controlled by diffusion, the diffusion coefficient could be used as the standard unit of leaching. According to Eq. 2.3.2-1 the quantity of the element leached is proportional to the square root of action period of water, i.e.

$$Q = \text{const.} \cdot t^{0.5}$$

or

$$\frac{Q}{Q_o} = \text{Const.} \cdot t^{0.5}$$

A plot of the $\frac{Q}{Q_o}$ -values obtained by leaching of bitumen samples versus the action period of water on a double logarithmic scale should result in a straight line of the direction constant o.5, if the leaching mechanism follows the equation mentioned above.

Table 2.3.1-1 contains the direction constants of the straight lines obtained by plotting Q/Q_o-time on double logarithmic scale. This shows that the leaching of bitumen-salt mixtures is often not proportional to $t^{0.5}$. Moreover, different direction constant values may be found for leaching of the same sample for different time intervals. Figure 2.3.2-1 shows some examples.

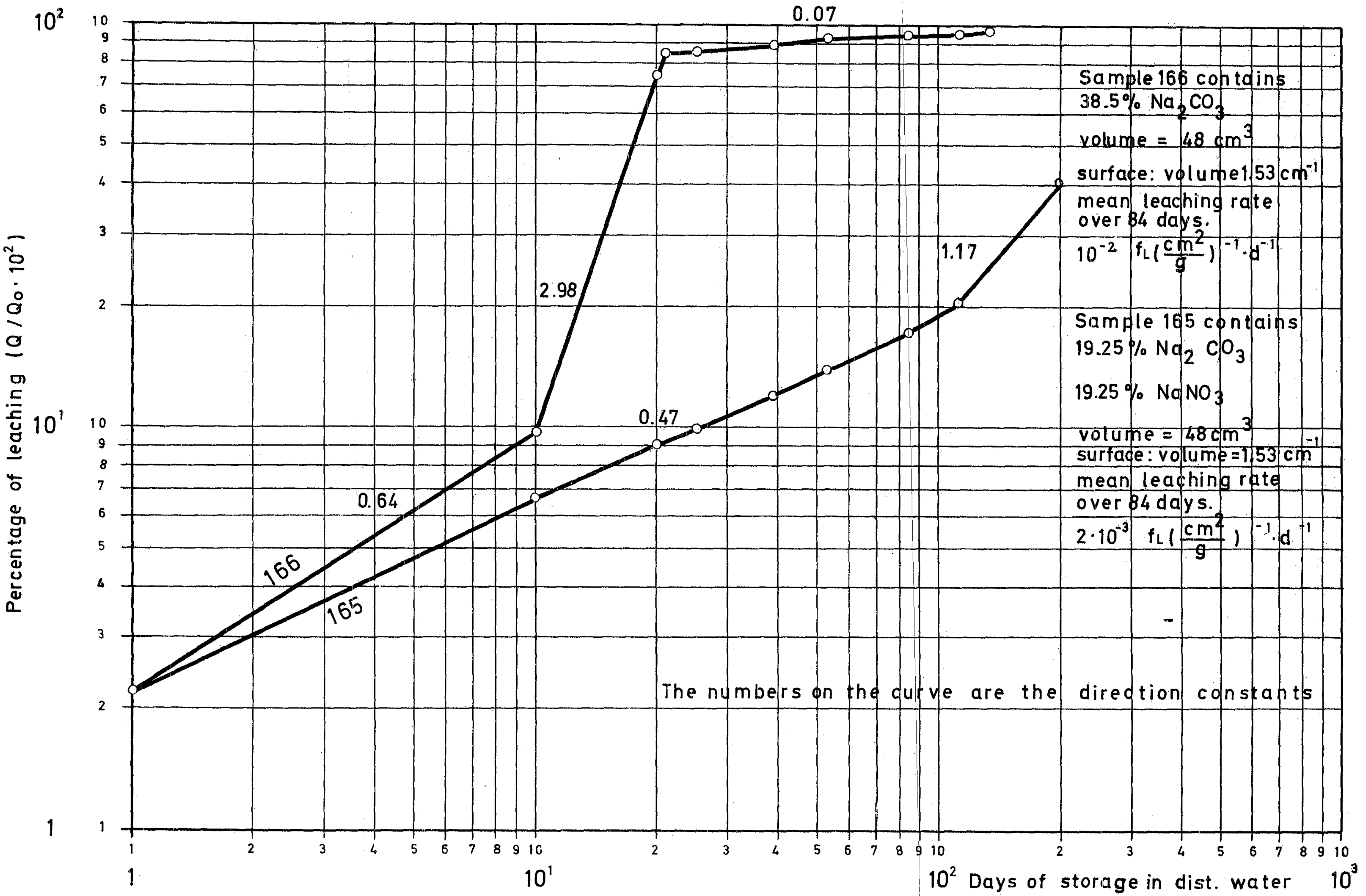


Fig.2.3.2-1 Leaching of bitumen samples. Inactive sodium was used for indication

Percentage of Leaching

The leachability of solids is often expressed by the total fraction of the indicator element leached within a standard period of time, i.e., by the quotient Q/Q_o. Often, the fraction of the element leached is indicated directly in percent. Since the quotient Q/Q_o thus determined depends on the surface/volume ratio of the specimens used in the leaching experiments, there must also be the indication of the geometry of the samples so that the experimental results of different laboratories may be intercompared. Unfortunately, this is not always done in practice.

Leaching Rate

Another factor used to characterize the leaching is the so-called leaching rate (R_L) [6]. The definition can be seen from this equation:

$$R_L = \frac{\text{Fraction leached}}{(\text{Surface of sample/weight of sample})\ (\text{Time})}$$

The dimension of R_L is $f_L \cdot (\frac{cm^2}{g})^{-1} \cdot d^{-1}$, where f_L indicates the fraction of element leached.

It is customary to present the leaching rate in a diagram as a function of time from the experimental values. For bitumen leaching such diagrams have been published [6]. They show that the leaching rate of certain bitumen products becomes independent of time, i.e. constant, after less than 18o days of storage in water. On the basis of this fact a stationary state was assumed to establish itself for the leaching of bitumen and the leaching rate was quoted for this state.

The leaching tests we have carried out on bitumen specimens have indicated that for some 5o % of the investigated cases the conditions of the stationary state were not fulfilled. Examples of the two types of behavior are shown in the Figure 2.3.2-2 (samples No. 165, 166, 167).

In Table 2.3.1-1 also the mean leaching rates for the entire duration of the experiment of 255 days are compared with the leaching rates at the end of that period. In general it is found that the mean leaching rates are higher.

2.3.3 Swelling of Bitumen Products

From investigations at Marcoule it is known that a swelling of the samples was observed in some cases where bitumen products had been stored in water [1o]. In our leaching tests this behavior was found also in some samples. Example are the two bitumen specimens 165 and 166 whose leaching behavior has been presented already in Fig. 2.3.2-2. While in specimen 165, which contained 19.25 % each of sodium nitrate and sodium carbonate, visible changes could be recognized only after prolonged storage in water, the bitumen specimen 166, which contained 38.5 % of sodium carbonate, had been swollen to twice its original volume already after 15 days.

Fig. 2.3.3-1 and 2.3.3-2 show the swollen specimen of bitumen after 132 days of storage in water.

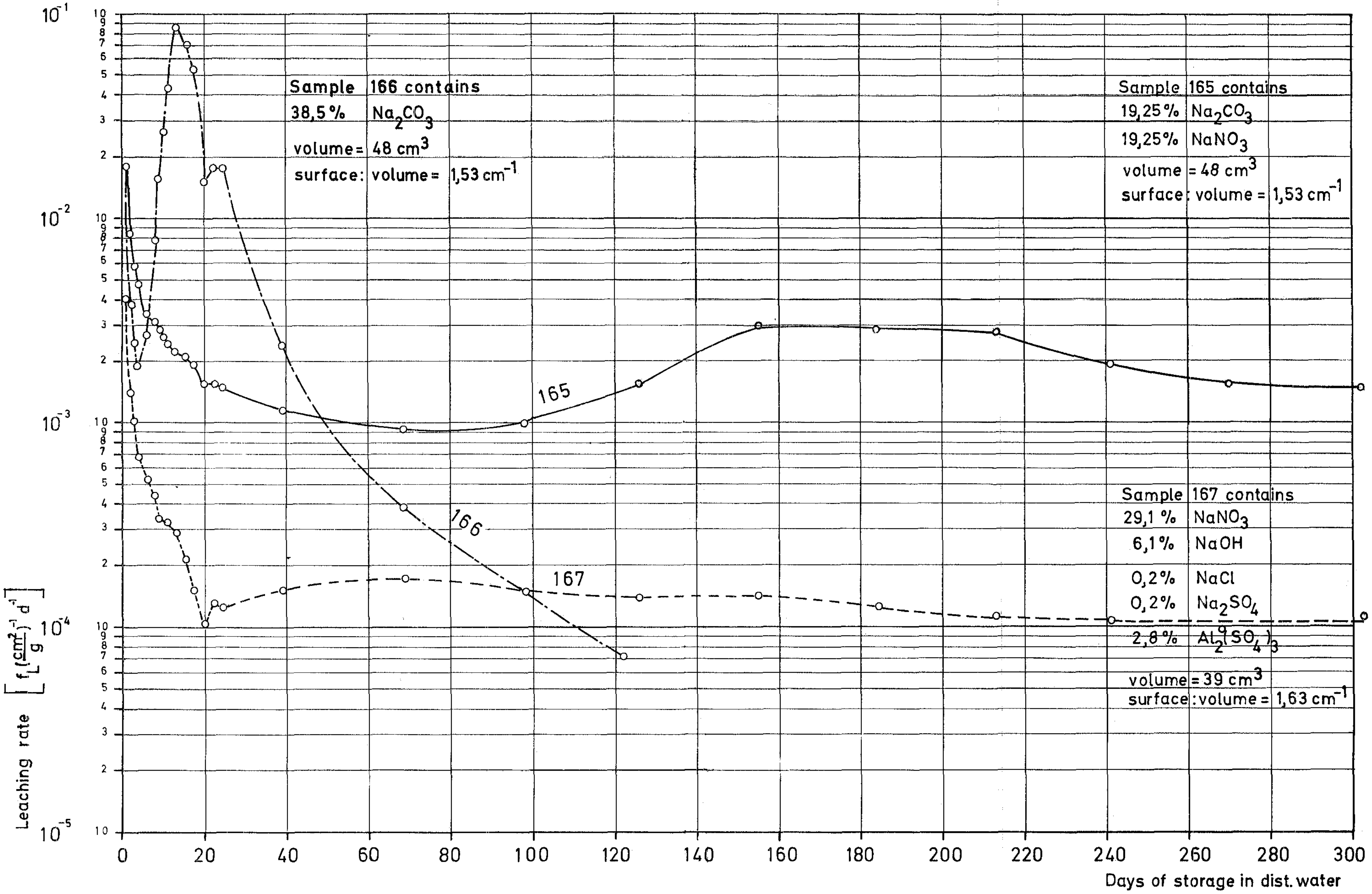


Fig. 2.3.2 -2 Leaching of bitumen samples. Inactive sodium was used for indication.

Fig. 2.3.3-1 Swelling of bitumen specimen 165 (19.25 % sodium carbonate, 19.25 % sodium nitrate in Mexphalt 15) after storage in distilled water (132 d). The water was changed corresponding to the leaching tests

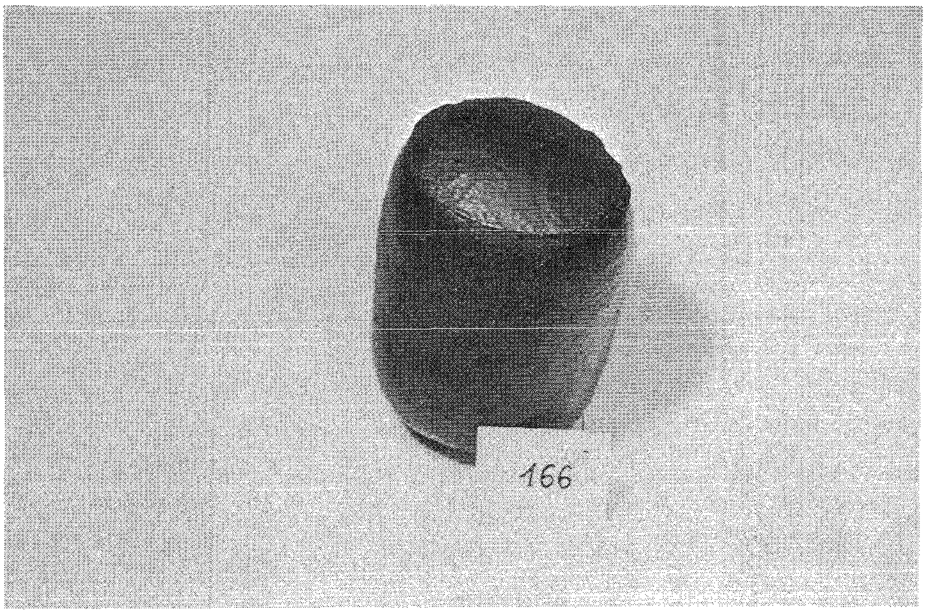


Fig. 2.3.3-2 Swelling of bitumen specimen 166 (38.5 % sodium carbonate in Mexphalt 15) after storage in distilled water (132 d). The water was changed corresponding to the leaching tests

Fig. 2.3.3-3 shows a section through bitumen specimen 166 in water. The cut surface touched like wet graphite.

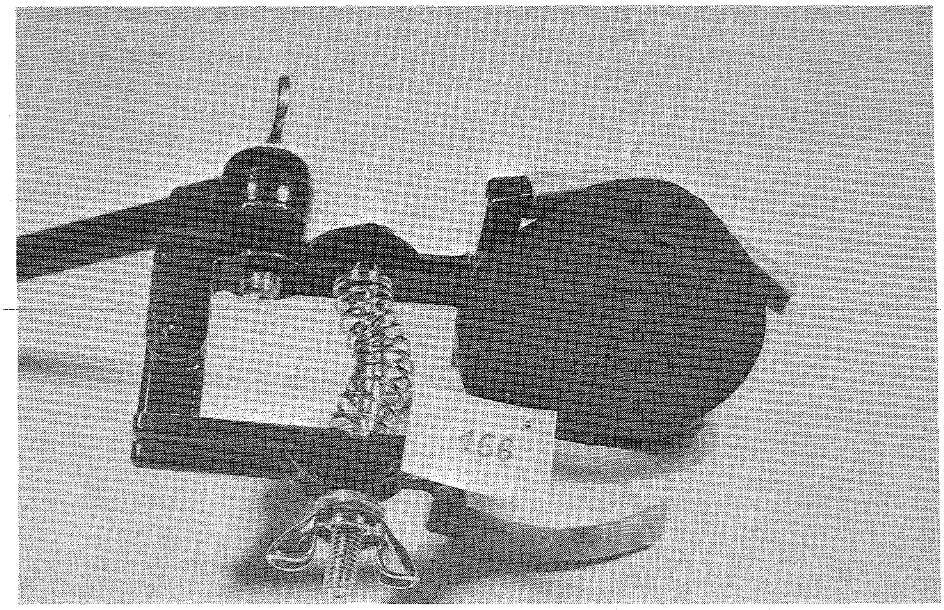


Fig. 2.3.3-3 Section through bitumen specimen 166 stored in water (38.5 % sodium carbonate in Mexphalt 15) after 132 days of storage in water

When this specimen was pressed together by the clamp, the water taken up during storage was driven out and appeared as droplets on the surface of the bitumen matrix (Fig. 2.3.3-4).

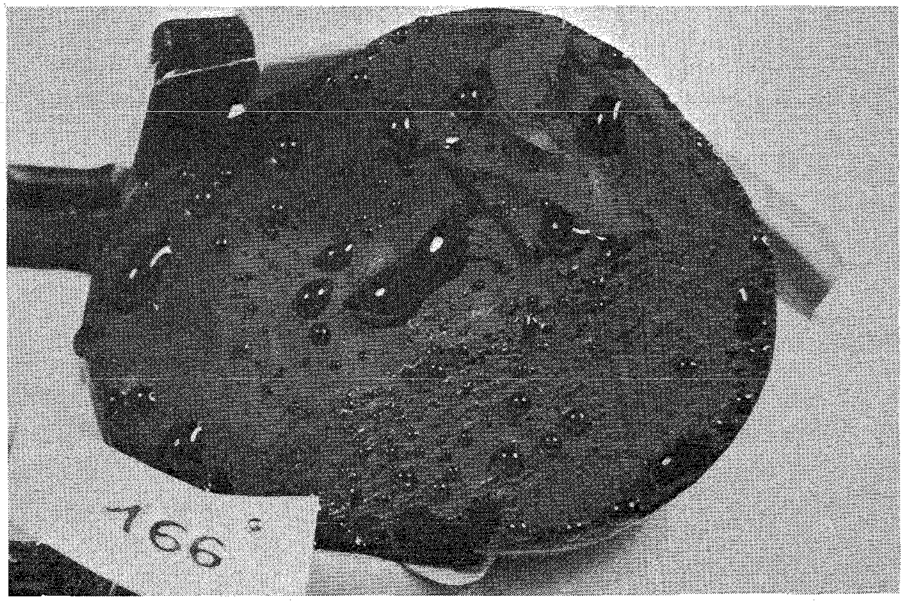


Fig. 2.3.3-4 Droplets of water driven out when bitumen specimen 166 is pressed.

It is interesting to note that on release of the pressure the water was taken up again by the bitumen matrix like a sponge. For comparison Fig. 2.3.3-5 shows another bitumen specimen which has been stored in water for 309 days without swelling.

In an attempt to determine the swelling of a few bitumen specimen quantitatively as a function of time (Fig. 2.3.3-6) it turned out that products of the same composition may exhibit a different swelling behavior in parallel tests. In these specimens, also different values of leaching were found.

In the leaching tests the result of other authors was confirmed that the radioactive concentrates fixed in bitumen are more resistant to leaching by about 1-2 orders of magnitude than those fixed in cement. However, some specimens were found whose leaching rates are comparable with those of cement specimens.

The leaching tests are being continued. It is planned to keep the bitumen specimens stored in water for at least one year. Since the wastes produced in the Federal Republic will be stored in the future either in salt mines or salt caverns, additional leaching tests with saturated salt solutions are planned.

Fig. 2.3.3-5 Bitumen specimen 156 (19.25 % $NaNO_3$, 19.25 % NaOH) after storage in water for 3o9 days (no swelling).

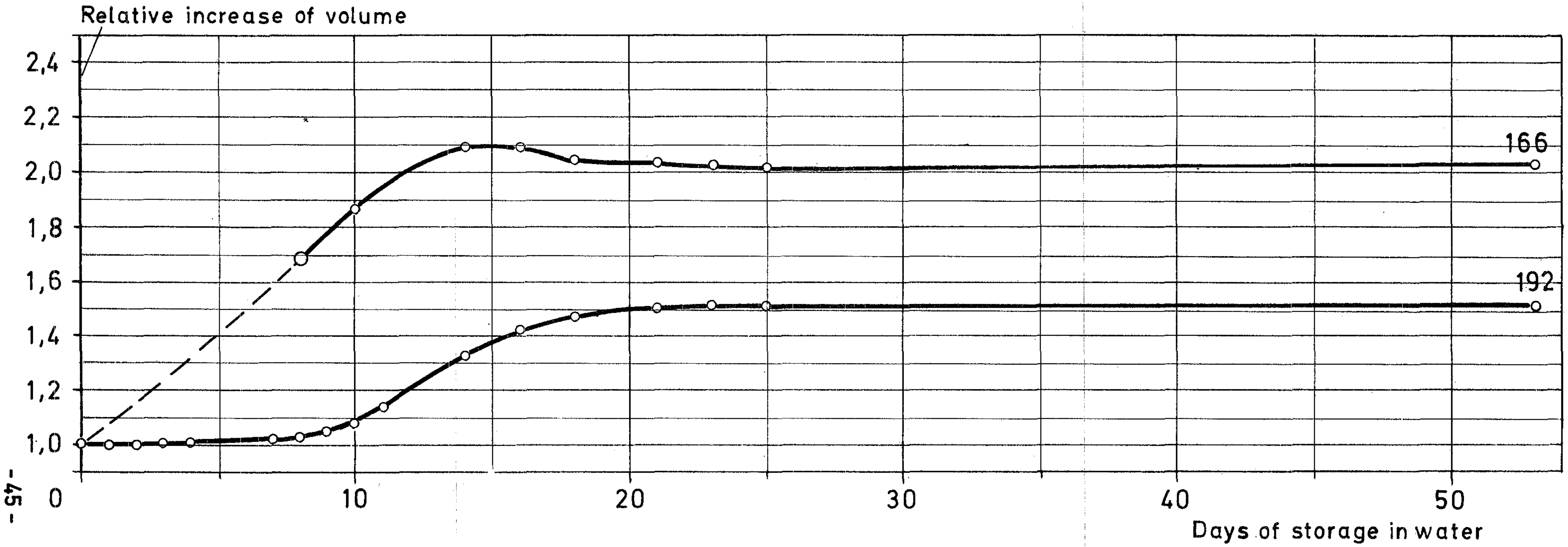


Fig. 2.3.3-**6** Swelling of bitumen-sodium carbonate mixtures (8:5) during storage in dist. water. The water was changed corresponding to the leaching tests.

Sample 166 original volume = 48 ml

Sample 192 original volume = 46 ml

3. Technical-Scale Experiments

Radioactive sludges and concentrates containing water can be introduced into bitumen basically intwo different ways:

- by drying of the products containing water and subsequent mixing of the dry residues with hot bitumen
- by introduction of the aqueous product into the hot bitumen under stirring and evaporation of the water from the mixture.

In the first case, expense and technological difficulties are concentrated mainly on the process of drying; for mixing of dry substances with bitumen there is a number of simple and very inexpensive devices. In the other case it is necessary to evaporate the water sufficiently quickly from the bitumen, which is not easy because of the poor heat transfer.

Before a decision was made regarding a large-scale facility, several semi-technical experiments were conducted to determine the advantages and disadvantages of those methods which appeared to be promising, as far as the suitable type of equipment was available.

3.1 Experiments on Drying the Evaporator Concentrates and Subsequent Introduction into Bitumen

3.1.1 Rotary Drier

9o kg of concentrate per hour were fed into a horizontal rotary drier with variable stirring paddles. The drier had a steam-operated heating jacket; moreover, it was penetrated by a hot air stream in continuous current flow. The material to be dried was spread over two series connected subsequent cyclones. The experiments were not satisfactory. Thick scale was formed on the walls and on the stirrer shaft causing the latter to be blocked.

3.1.2 Laboratory-Scale Rotary Drier

Small quantities of a granulate of polystyrene with an expanding agent were introduced into a horizontal rotary drier made of glass with slowly rotating stirring paddles to avoid incrustation and to enlarge the evaporation area. As a result of the heat in the drier the polystyrene particles expanded to 4o times their original volume. Although their melting temperature is around 12o°C, they retain their size also in a stream of dry air of 2oo°C as long as there is any water to be evaporated. Only at the end of the drying chamber, where the temperature of the material to be dried rises above 12o°C because of the low residual water content, (the danger of scale formation has ceased by that time) but in the stage of mixing with hot bitumen (about 15o°C) at the latest, the polystyrene foam particles melt down again to their original volume.

In subsequent experiments cubes of plastic foams of about 1 cm lateral length were used; their softening points were above 17o°C. This plastic foam was not introduced into the bitumen, but was continuously circulated in the drier, whereas the dried salt dropped through a grate into a discharge vessel at the end of the drier. In addition to the heating jacket, between 2.5 and 3 kg of air at 17o°C was blown through the apparatus per kg of water evaporated. Since the air was introduced in a countercurrent stream, passing throughthe wet zone at the end, the vapors were completely free of dust. The machine had an evaporation capacity of 1 kg of water per hour.

Since the experiments were carried out only on a laboratory scale as yet, it is not possible to transfer the experiences to a technical-scale plant.

3.1.3 Roller Drier

1-2 kg of concentrate per hour was fed on a double roller drier designed as a vacuum system. The rolls were internally heated. The material to be dried was removed by attached knives. The experiments proceeded satisfactorily, but this method was abandoned because regrinding of the knives and possible remilling of the rolls would require previous extensive decontamination work, and because the investment and operating costs are very high.

3.1.4 Spray Drier

The core of the system (Fig. 3.1.4-1) is a spray tower (1) of 8-9 m height. The concentrate is fed in by compressed air at the upper end of the tower. The dry material settles in the cyclone (2). The mixer (3) mixes the dry material with bitumen. At the injection level there is the inlet for the hot air which is led in circulation. Along with the water vapor generated it passes through the cyclone (2) and the scrubber (5). When the major quantity of steam has condensed, the air is fed via the circulator (12) through a heat exchanger (6) which is heated by the smoke gases of an oil burner (7). Then it re-enters the spray tower.

It was possible to carry out the experiments in a facility with a capacity of about 2oo l concentrate/h. They proceeded very satisfactorily. The results can be seen from the record (Table 3.1.4-1). Therefore, this process was included among those singled out for closer selection. The only minor disadvantages were the large space requirement (about 6 x 1o x 9 m) and the special tightness required for the system.

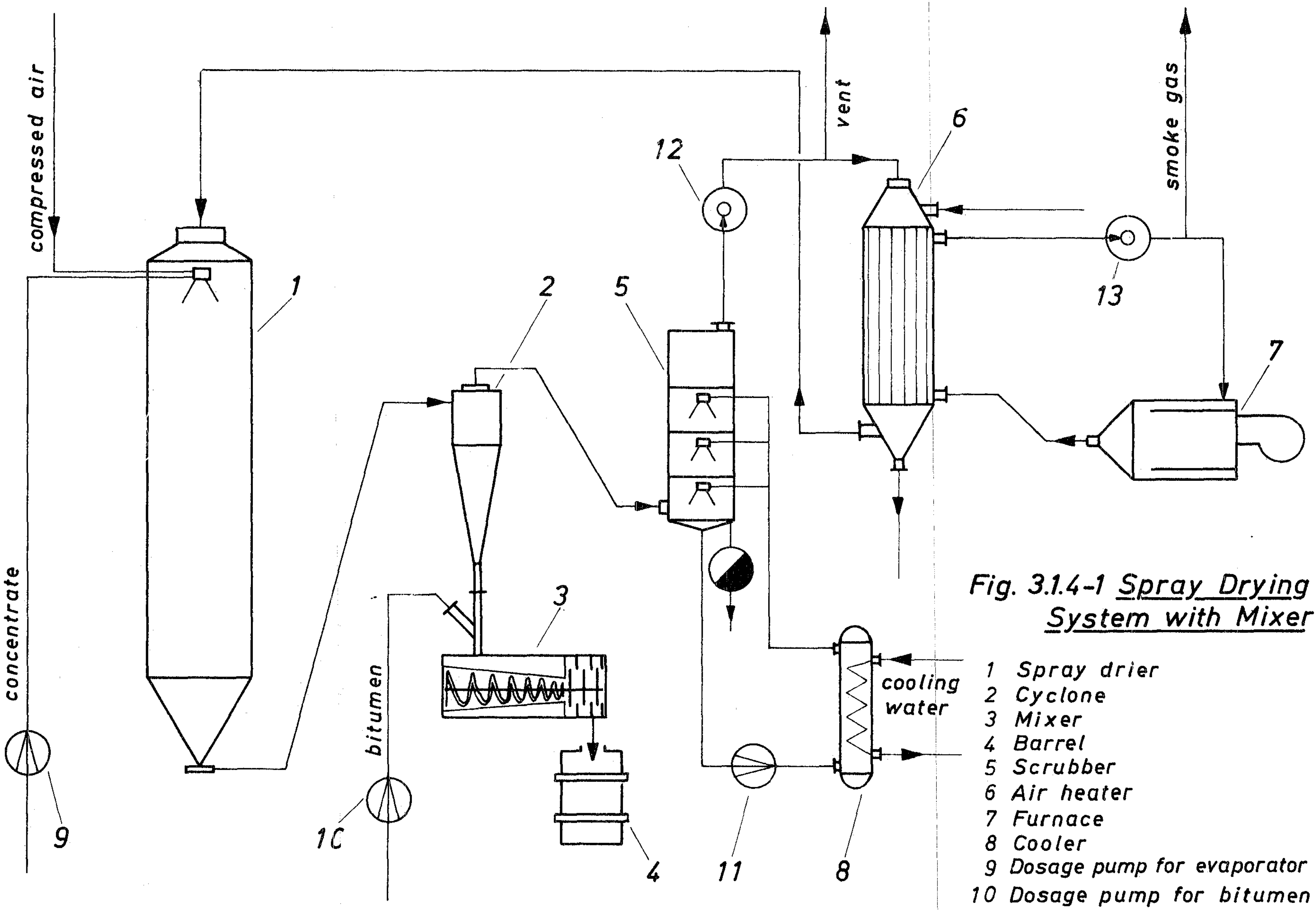


Fig. 3.1.4-1 Spray Drying System with Mixer

1 Spray drier
2 Cyclone
3 Mixer
4 Barrel
5 Scrubber
6 Air heater
7 Furnace
8 Cooler
9 Dosage pump for evaporator concentr.
10 Dosage pump for bitumen
11 Circulation pump
12 Circulation blower
13 Circulation blower for smoke gases

Table 3.1.4-1

Experimental Record
Spray Drier

Run No.	3
Evaporation residue of concentrate (w/o)	19.3
Specific weight (kg/l)	1.19
Composition of dry substance	40 % $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$ 50 % NaCl, $NaNO_3$, $NaSO_4$ 2 % $FeCl_3$, $Al_2(SO_4)_3$ 6 % other inorganic salts 2 % polyphosphate and detergents
Temperature of concentrate (°C)	18
Air temperature (drier) (°C)	320
Temperature, center of drier (°C)	148
Vapor oulet (°C)	122
Air flow (Nm^3/h)	1,500
Nozzle	Two components (compressed air)
Spray pressure (atm gauge)	2.5
Concentrate throughput (l/h)	212
Heating system	Indirect oil heating
Bulk weight of dry product (kg/l)	0.360 - 0.400
Residual moisture (w/o)	1.3
Temperature of powder (°C)	48 - 52

Mixing of the dry substance with bitumen was tested elsewhere by means of a mixing device which otherwise serves for the mixing of tar with filler material for the production of tar paper. Mixtures of 60 w/o dry powder with 40 w/o bitumen were produced.

The experiments proceeded without any disturbance.

3.2 Simultaneous Drying and Mixing in Hot Bitumen

3.2.1 Stirrer

Already in 1964, a small experimental apparatus for operation was started up (Fig.3.2.1-1).It consists of an electrically heated bitumen furnace with stirrer (1) with a capacity of 1oo l. The wall heating system is subdivided into two zones. The lower zone has a heating power of 25 kW, the upper one of 5 kW. The drain valve is heated with 1 kW.

The furnace is loaded with 8o kg of bitumen (Shell Mexphalt 15) per batch and is heated to a bitumen temperature of 22o°C. The concentrate (2o % salt content) is metered onto the surface of the stirred bitumen at a rate of 8 l/h until a mixture of about 4o w/o salt and 6o w/o bitumen is reached. Then the mixture is discharged into a drum of 2oo l volume.

The vapors pass through a column with wire mesh on which condensate is sprayed from the top. The condensate is circulated into a collection vessel (3) with an inclined bottom, from there through a pump (5) and a cooler (4) into the scrubber column. The noncondensable fractions are removed by a vacuum pump (8)through a baffle separator and a filter (7). The condensate collection vessel has an overflow. The condensate passes through a filter with Ecoperl (9) for separation of the volatile oils.

Originally, the vapors were scrubbed and condensed in a baffle separator and a double pipe cooler. However, after a few hours of operation the baffle separator used to be plugged up. Also the double pipe cooler became plugged with bitumen after prolonged operation. Therefore, the system was replaced by a wet precipitator (2) which worked without any disturbance.

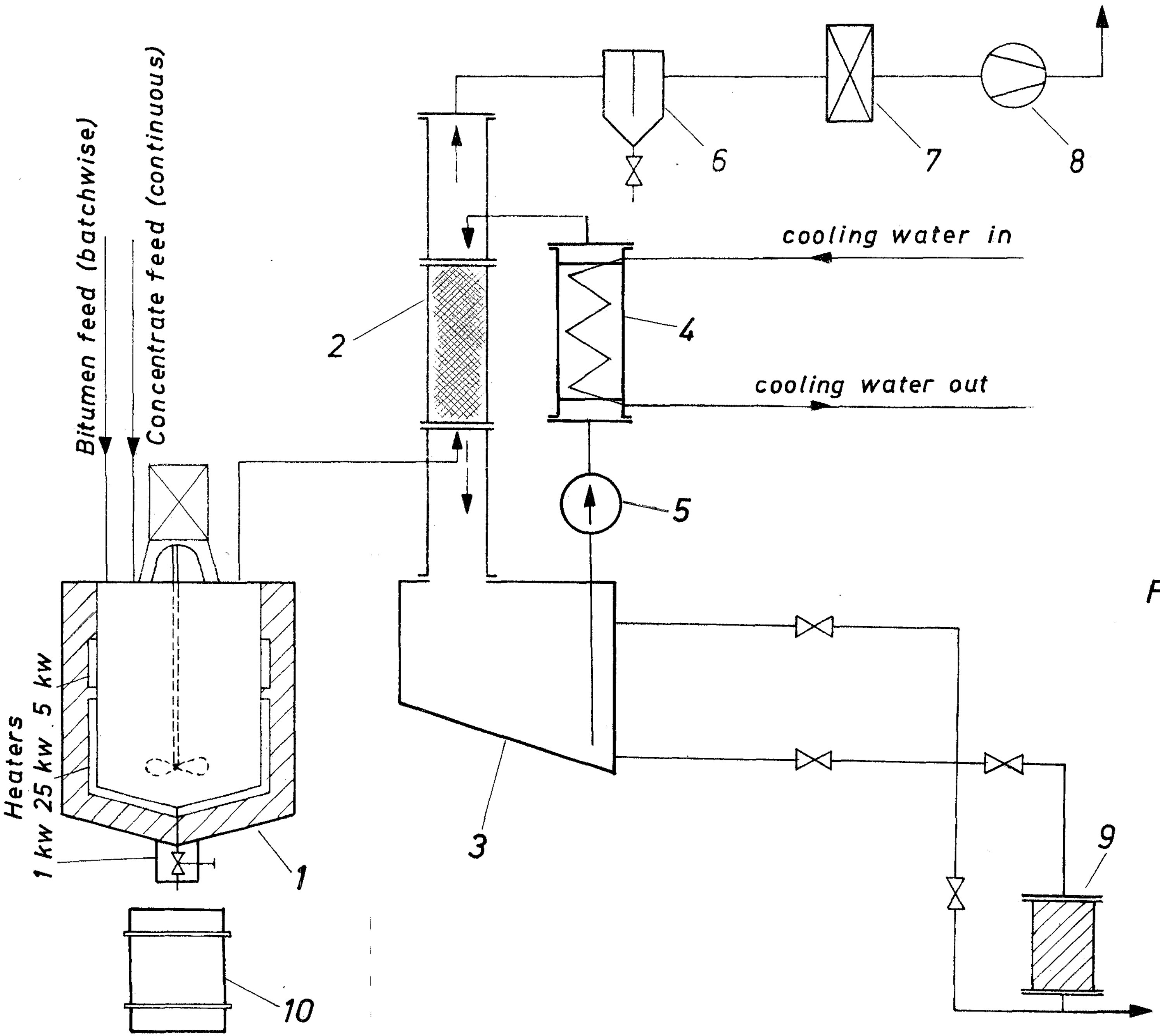


Fig. 3.2.1-1 <u>Bitumen Stirrer Vessel with Scrubber</u>

1	Bitumen furnace
2	Wire mesh
3	Condensate vessel
4	Cooler
5	Pump
6	Baffle separator
7	Filter
8	Blower
9	Oil separator
10	Barrel (200 l)

The advantage of the system lies in the relatively simple design and handling and the low price. The disavantages are

a) the long sojourn times under high temperatures of the mixtures. This can cause the bitumen to harden, especially in the presence of iron salts and nitrates;

b) the strong spurting; this causes thick incrustation along the walls of the vapor chamber and in the inlet line to the vapor scrubber;

c) the restriction of the salt content to a maximum of 4o w/o salt in the final mixture to safeguard the free discharge from the furnace;

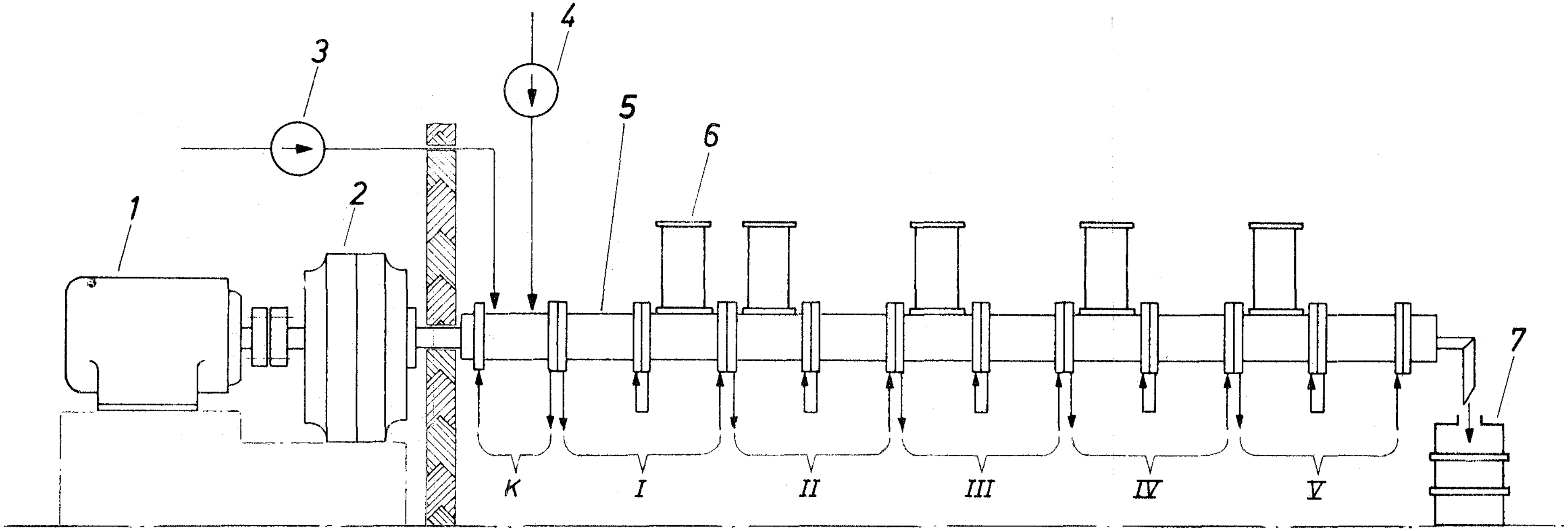
d) occasional violent shocks as a result of delayed boiling, etc.

While the method is used successfully for fixing precipitation sludges it is less suited to the processing of liquid concentrates.

3.2.2 Twin Helix Drier

The machine is essentially an extruder of the general type used for the processing of plastics (Fig. 3.2.2-1). The core of the system consists of two parallel helices of 5 m length with their threads meshing. The helices are supported in ten successive housings (5) each of which can be heated separately by steam. Concentrate and bitumen are dosed into the first housing simultaneously. The machine includes a heater with temperature control, drive (1) with a control gearbox (2) and an oil cooler, control console, and dosage pumps (3,4).

The mixture is distributed in a thin film in the threads and carried on at the same time. On the individual housings are pipes with coolers for condensation of the compression vapors. By the end of the helix the water has evaporated and the mixture of dry substance and bitumen is extruded



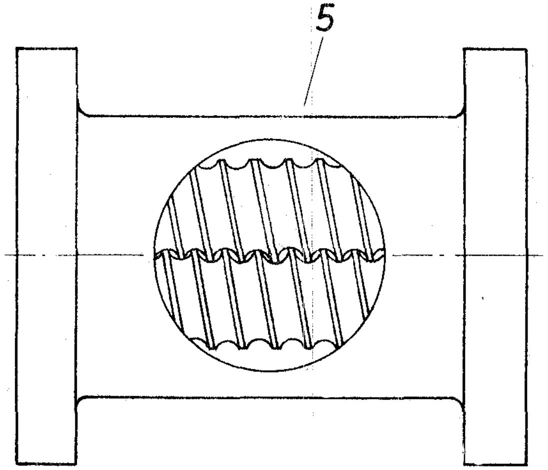


Fig. 3.2.2-1 Twin Helix Drier
for bituminizing radioactive concentrates

1	Driving motor
2	Adjustable gear, cooled by oil circulation
3	Dosage pump for bitumen
4	Dosage pump for concentrate
5	Housing of helices
6	Steam outlet with condenser
7	Barrel (200 l)
K	Cooling zone
I-V	Heating zones, increasing from 120 to 180 °C

into a drum of 2oo l volume as a viscous strand.

The experiments were carried out in an apparatus with a capacity of 8o - 9o kg of evaporator concentrate per hour. There were no disturbances. Mixtures of more than 6o w/o salt in bitumen were made without any difficulties. The residual water content of the final product was only o.1 w/o. A record of the experiment is included in Table 3.2.2-1.

The merits of the method are the following:

a) Drying and fixing are one operation
b) the machine requires but little space
c) the sojourn time of the bitumen in the machine is only 1.7 min; in this way, no hardening must be anticipated
d) the distribution of the mixture on a thin film excludes violent reactions as a result of delayed boiling etc.
e) the forced transport and discharge allow the production of mixtures with a high salt content; this results in major savings in bitumen, drums, transport, and storage costs.

The only recognizable disadvantage is the high purchasing price.

3.3 The New Facility Planned for the Karlsruhe Nuclear Research Center

On the basis of the semi-technical experiments outlined above, the anticipated operational safety, and the investment and operating costs the future operating facility selected was a twin helix drier as described under 3.2.2. The diameter of the helices is 12o mm, the capacity is 175 kg of concentrate/h. The plant is to become operational in early 197o.

Table 3.2.2-1

Experimental Record

Two-Component Drying Helix

Run No.		8
Evaporator residue of concentrate (w/o)		30
Specific weight (kg/l)		1.26
Composition of dry substance		40 % $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$ 50 % $NaCl$, $NaNO_3$, Na_2SO_4 2 % $FeCl_3$, $Al_2(SO_4)_3$ 6 % other inorganic salts 2 % polyphosphate and detergents
Helices rpm		300
Bitumen (kg/h)		15
Input concentrate (kg/h)		83
Output bitumen and salt (kg/h)		40 (bitumen 16 kg/h, 40 w/o), (salt 24 kg/h, 60 w/o)
Residual moisture (determined by toluene distillation) (w/o)		0.1
Feed temperature bitumen (°C)		126
Feed temperature concentrate (°C)		20
Discharge temperature of mixture (°C)		180
Temperatures of helix housings(°C)		
	t 1	120
	t 2	130
	t 3	135
	t 4	135
	t 5	140
	t 6	170
	t 7	170
	t 8	190
Heater	t 1-6	steam
	t 7-8	electrical
Specific weight of mixture 60 % salt / 40 % bitumen (kg/l)		1.45
Temperatures of mixture behind	t 8 (°C)	180

The experiments proceeded without any disturbance.

4. Cost Analysis of the Bituminization of Radioactive Concentrates

Fig. 4.-1 shows the total cost of solidification of a 2o w/o evaporator concentrate as a function of throughput (tonne of concentrate per year).

Table 4.-1 is a breakdown of the total costs into individual items. The costs have been determined for five different cases, namely:

1.) The planned bituminization in a twin helix drier, capacity 175 kg of concentrate/h
2.) Bituminization in a twin helix drier, capacity 7o kg of concentrate/h
3.) Bituminization in a twin helix drier, capacity 26 kg of concentrate/h
4.) Cementation of 2o w/o evaporator concentrate
5.) Evaporation of the 2o % concentrate to 4o w/o salt content and subsequent cementation

The operating costs shown refer only to the further treatment (fixation) of evaporator concentrate with a salt concentration of 2o w/o and thus do not include the costs of evaporation of the radioactive waste water proper. To calculate the costs of fixation of 1 tonne of original radioactive waste water the salt content of the waste water, which has a direct bearing on this figure, must be taken into account. For example the average salt content of low level radioactive waste waters in the Karlsruhe Nuclear Research Center is now o.2 percent. Evaporation to 2o % salt content results in a volume reduction of about 1oo. Hence, a price of fixation of DM 1,ooo per tonne of concentrate is reflected to the amount of DM 1o in the decontamination of 1 m^3 of waste water.

At the bituminization, the calculations are based on the processing of a 2o w/o evaporator concentrate into a product of 6o w/o salt and 4o w/o bitumen. For the cementation, a mixing ratio of 1oo kg of 2o % concentrate or 133 kg of 4o % concentrate with 2oo kg of cement is assumed. Moreover, it is supposed that the final products are discharged into 2oo l tin drums which have dose rates not exceeding 2oo mrem/h at the outside surface. Higher dose rates of the drums entail higher costs, especially for transport.

The cost survey shows that the direct operating costs of the fixation process (wages, energy, and material) constitute but a small fraction of the overall costs. The costs of ventilation alone, which are listed separately, including energy and filter consumption costs and costs of maintenance and depreciation, are a multiple of the direct operating costs at low loads. In the case of depreciations the following rates of amortization per annum have been assumed:

Processing section 13.3 % at 5o % loading
(minimum 1o %, maximum 2o %)

Construction 2 %

Heating, sanitary and electrical installations 5 %

Basic installations, minor equipment and furniture 2o %

The costs of maintenance are calculated to be 5o % of the costs of depreciation. They are lower at the beginning of the period of amortization, but they rise with the age of the plant.

The storage facility for radioactive wastes means the intermediate storage of residues at the Karlsruhe Nuclear Research Center. Costs of storage and overheads may differ greatly, depending upon the location. The costs of transport arise out of the transport of the residues to the final storage site (a distance of 6oo km).

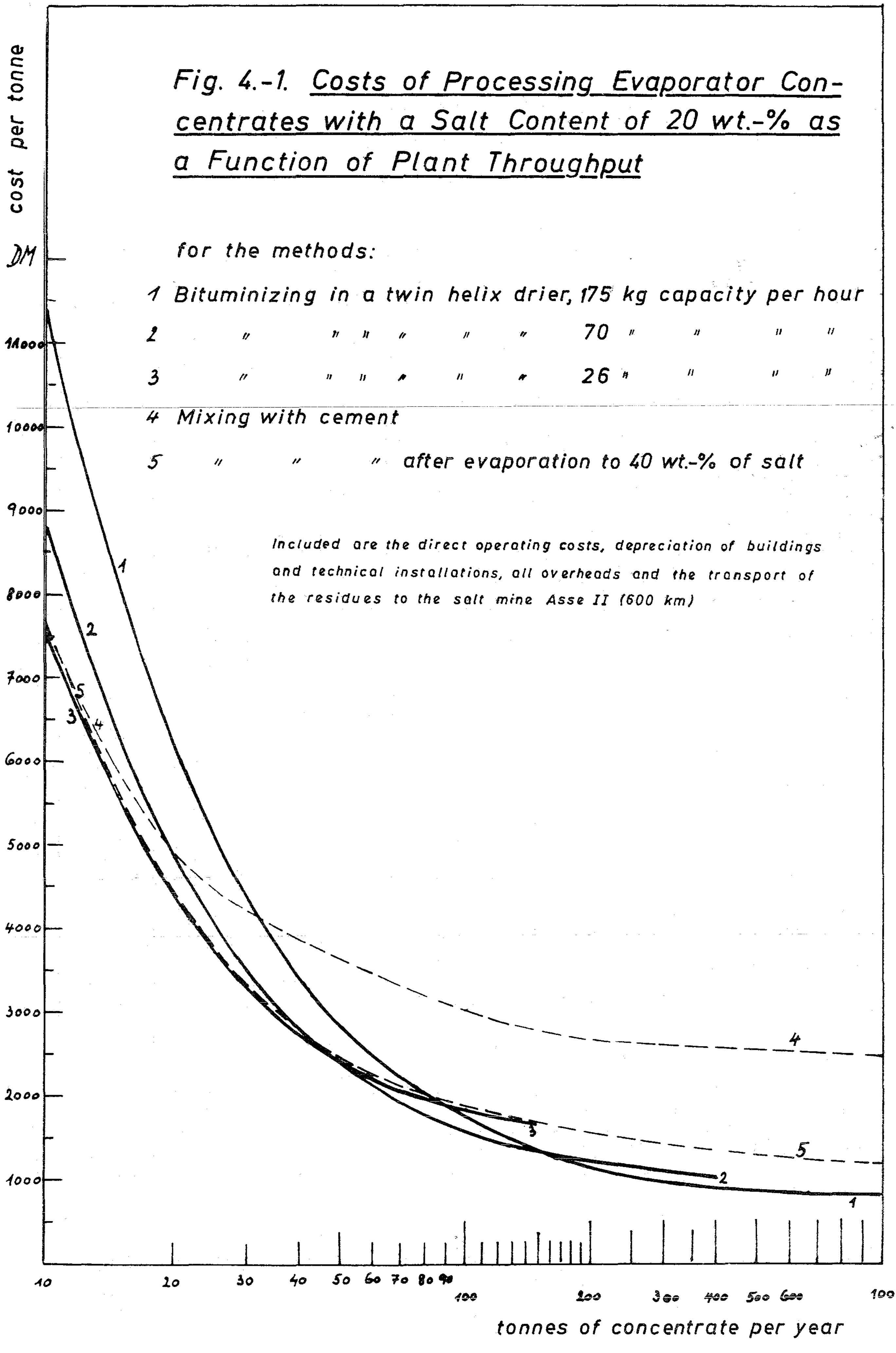


Fig. 4.-1. Costs of Processing Evaporator Concentrates with a Salt Content of 20 wt.-% as a Function of Plant Throughput

for the methods:

1 Bituminizing in a twin helix drier, 175 kg capacity per hour
2 " " " " " " 70 " " " "
3 " " " " " " 26 " " " "
4 Mixing with cement
5 " " " after evaporation to 40 wt.-% of salt

Included are the direct operating costs, depreciation of buildings and technical installations, all overheads and the transport of the residues to the salt mine Asse II (600 km)

Table 4.-1

Costs of Processing Evaporator Concentrates with a Salt Content of 20 w/o

Method 1: Twin helix drier, capacity 0.175 tonnes of concentrate per hour
2: " " " " 0.070 " " " " "
3: " " " " 0.026 " " " " "
4. Mixing of concentrate (20 %) with cement
5. Evaporation of the concentrate to a salt content of 40 %, mixing with cement

Breakdown of costs		Method				
		1	2	3	4	5
		DM per tonne concentrate				
Wages		59.00	148.00	400.00	25.00	41.00
Power		81.00	81.00	81.00	1.00	26.00
Material (barrels, bitumen or cement, resp., other materials)		57.00	57.00	57.00	405.00	155.00
Ventilation (incl. depreciation and maintenance)	Throughput 10 tonnes conc./a			2500.00	2500.00	2500.00
	20 " "		1250.00	1250.00	1250.00	1250.00
	50 " "	500.00	500.00	500.00	500.00	500.00
	100 " "	250.00	250.00	250.00	250.00	250.00
	500 " "	50.00	50.00		50.00	50.00
	1000 " "	25.00			25.00	25.00
Depreciation (operational equipment, buildings etc.)	10 tonnes conc./a			2765.00	1750.00	2750.00
	20 " "		1885.00	1413.00	875.00	1375.00
	50 " "	1100.00	775.00	615.00	493.00	554.00
	100 " "	557.00	442.00	361.00	248.00	350.00
	500 " "	155.00	157.00		53.00	74.00
	1000 " "	114.00			44.00	55.00
Maintenance	10 tonnes conc./a			1383.00	875.00	1375.00
	20 " "		943.00	707.00	438.00	688.00
	50 " "	550.00	388.00	308.00	247.00	277.00
	100 " "	279.00	221.00	181.00	124.00	175.00
	500 " "	78.00	79.00		27.00	37.00
	1000 " "	57.00			22.00	27.00
Storage of radioactive wastes (incl. depreciation and incidental costs)		184.00	184.00	184.00	1600.00	600.00
Overheads - staff-dependent (laundry, bus-service, medical service, cafeteria)		14.00	35.00	92.00	6.00	10.00
Overheads - other (fresh water, heating, disposal of sewage, rainwater, cooling water, cleaning, telephone, general store, guard, etc.) incl. alloted depreciation		100.00	100.00	100.00	100.00	100.00
Overheads - radiation protection service		90.00	90.00	90.00	90.00	90.00
Transport of residues to salt mine Asse II (600 km)		19.00	19.00	19.00	174.00	92.00
Total	Throughput 10 tonnes conc./a			7671.00	7526.00	7739.00
	20 " "		4792.00	4393.00	4964.00	4427.00
	50 " "	2754.00	2377.00	2446.00	3641.00	2445.00
	100 " "	1690.00	1627.00	1815.00	3023.00	1889.00
	500 " "	887.00	1000.00		2531.00	1275.00
	1000 " "	800.00			2492.00	1221.00

In bituminization the salt content of the final product is of special significance, and the possibility of producing salt-bitumen mixtures of 60 w/o salt content justifies the high investment cost of the installation which amounts to DM 450,000 for a capacity of 0.175 tonnes of concentrate/h. The operating costs for a final product of only 40 w/o salt, which could be produced in a less expensive plant, have not been included in Table 4.-2, because no reliable investment cost data were available for this case.

However, the savings in investment would be set off by the following additional operating costs per tonne of concentrate.

Drums and bitumen	DM 50.00
Storage costs	123.00
Transport costs	9.00
	DM 182.00

These additional costs will offset any savings in investment in a very short time.

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