SKBF KBS TEKNISK RAPPORT 81-13

Thermal stability of ion-exchange resins

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Studsvik Energiteknik AB, 1982-01-13

SVENSK KÄRNBRÄNSLEFÖRSÖRJNING AB / AVDELNING KBS

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Summary

The action of heat, radiation and oxidants on carbonchain polymers, such as ion-exchange resins, often cause irreversible chemical changes in macro molecules. These changes can be e g the rupture of the carbon-carbon single or double bond, and/or the degradation of the macro molecule. Ion-exchange materials also contain the far less stable bonds between functional groups and the polymer matrix. For this reason the thermal stability of ion-exchange materials is mainly based on the behaviour of the functional groups, which are responsible for the ion-exchange.

The solidification of the ion-exchange resin waste usually involves elevated temperatures. Bituminization is carried out at 130-160°C. Cementation is carried out at room temperature. However, cementation can generate temperatures of up to 100-120°C in the solidification product during the curing period.

In this study the swelling/shrinking properties of different ion-exchange materials have been studied in air and water as a function of the drying time and temperature. The air dried resins were used as the reference material. The effect of sodium sulphate as a possible additive to reduce swelling was studied. The experiments which were performed and results observed are discussed in detail in Appendices A-C. Appendix D is a special literature survey on the thermal properties of ion-exchange resins.

1 INTRODUCTION

The action of heat, radiation and oxidants on carbonchain polymers often causes irreversible chemical changes in macro molecules. These changes can be for example, the rupture of the carbon-carbon single or double bond, and/or the degradation of the macro molecule. Ion-exchange materials, resins and membranes, also contain the far less stable bonds between functional groups and the polymer matrix (carbon-nitrogen, carbon-sulphur, carbon-phosphorus, etc). For this reason the thermal stability of ion-exchange materials is mainly based on the behaviour of the functional groups, which are responsible for the ion-exchange.

Under industrial conditions ion-exchangers are often used at relatively high temperatures. In nuclear power plants ion-exchange resins are used for water purification in different systems, for example reactor water purification and the purification of waste water streams.

Exhausted ion-exchange resins removed from these systems usually contain considerable amount of radioactive nuclides, and must be specially conditioned (mixed with concrete, bitumen, etc) to obtain a final solid product suitable for interim storage and/or disposal.

The solidification of the ion-exchange resin waste usually involves elevated temperatures. Bituminization is carried out at 130-160^{o}C. Cementation is carried out at room temperature. However, cementation can generate temperatures of up to 100-120^{o}C in the block of waste during the curing period. Changes in the physical/chemical properties of ion-exchange materials, such as swelling and changes in the polymer chain, and suchlike, due to this thermal treatment during solidification are of vital importance in estimating the properties of the solidification products. Swelling of the ion-exchange particles in the solidification product, for example, can lead to a break down of the waste blocks and an increased leaching of radionuclides from the products.

In this study the swelling/shrinking properties of different ion-exchange materials have been studied in air and water as a function of the drying temperature and time. The effect of sodium sulphate as an additive was studied as well.

The main report gives a short summary of the results obtained in this study. The experiments and results are discussed in more detail in Appendices A-C. Appendix D is a literature survey made on the thermal properties of ion-exchange resins.

2 PURPOSE OF THE STUDY

The aim of this study was to determine the swelling properties of ion-exchange materials in water after different drying times at different drying temperatures. The results will be used to evaluate the long-term behaviour of bituminized ion-exchange resins after disposal.

The swelling of ion-exchange resins in water depends on many factors, such as the nature of the water, the presence or absence of an electrolyte (in this study Na_2SO_4) in the solution, the nature of the fixed and counter ions, the nature of the resin skeleton, and the degree of crosslinking.

3 MATERIALS

The ion-exchange materials used in this study are listed in Table 1. The materials (ion-exchange resins, additives) studied were chosen of the basis on the actual materials used in Swedish nuclear power plants. The range of drying times and drying temperatures was also chosen on the basis of the parameters used at the Barsebäck and Forsmark nuclear power plants.

Samples prepared in this study are listed in Table 2.

Table 1. Ion-exchange resins used in the study

A	Expended, powdered resin (microionex) from the Forsmark power plant
B	New, granular, cation resin (Duolite ARC 351)
C	New, granular, anion resin (Duolite ARA 366)
D	Expended, granular resin (60 % Duolite ARA 366, 40 % Duolite ARC 351) from the Forsmark power plant.

Part of the ion-exchange resin was treated with Na_2SO_4. 1 kg anhydrous Na_2SO_4 was added to 12.5 kg ion-exchange resin (even level).

This addition of Na_2SO_4 corresponds to the pretreatment of granular ion-exchange resins carried out at the Barsebäck power plant before mixing them in bitumen.

Table 2. Samples prepared in the study

Sample	1	A[x)]
"	2	A + Na_2SO_4
"	3	B
"	4	B + Na_2SO_4
"	5	C
"	6	C + Na_2SO_4
"	7	D
"	8	D + Na_2SO_4

[x)] Capital letters refer to ion-exchange resins as specified in Table 1.

4 EXPERIMENTAL DETAILS

4.1 General lay-out of the experiments

In order to investigate the effect of heat treatment on the ion-exchange resins three types of measurements were done:

- thermogravimetry (TG)
- particle size analysis
- swelling measurements in water.

TG was used to obtain a general impression of the behaviour of the resins at different temperatures. Sieving experiments give the overall picture of the effect of the thermal treatment on particle size. Swelling measurements in water give information on the volume changes after thermal treatment.

In these experiments both powdered and granular ion-exchange resins were used.

The materials used and the samples prepared are listed in Tables 1, 2 and C.1 (Table C.1, see Appendix C).

4.2 Thermal analysis

The thermal analysis technique used in this work is known as isothermal TG, in which the sample mass is recorded as a function of time at constant temperature.

All measurements were made in static air, starting with air dried resins, and were recorded until no further weight changes could be seen.

A typical diagram obtained in TG-analysis is presented in Figure 1.

4.3 Particle size analysis

The particle size distribution was analyzed by sieving through wire cloth sieves, Ø 8-in, (ASTM specifications E 11) with the following mesh sizes 1000, 710, 500, 355, 255, 177, 125, 90, 63 and 45 µm. the material retained on each sieve was weighed and recorded.

The analyses were carried out on all the samples in Table 2 first after drying them in air at 20°C to a constant weight, and also after a 24 h heat treatment at different temperatures. In the latter case the sieving was performed both immediately after the heat treatment, and again after they had been exposed to the atmosphere for 24 h.

Diagrams (Appendix B) were drawn showing the sieving results as cummulative distribution graphs. Some typical results are presented in Figures 2 and 3.

4.4 The swelling experiments

Ion-exchange resin, which had been air dried or heat treated was poured into a graduated cylinder which was dropped from a height of about 3 cm 100 times in about 2 min. The volume was read and the density calculated.

The ion-exchange resin was then poured into another graduated cylinder containing water. The volume of the ion-exchange resin in the cylinder was noted after different periods of time. On the basis of these values the swelling, in comparison to air dried resins, could be calculated.

The swelling was expressed in per cent (S %).

$$S\ \% = \frac{(\text{volume in water}) - (\text{dry volume after shaking})}{\text{dry volume after shaking}} \times 100\ \%$$

Some typical data of the changes in volume, weight, density and swelling of the ion-exchange material used in experiments is presented in Tables 3 and 4 and in Figures 4 and 5. In Table 5 the observed and calculated swelling in mixed bed resins is compared.

5 RESULTS

The experiments made and the results obtained are discussed in detail in Appendices A-C. Short overall conclusions of the results are presented in this chapter.

Thermogravimetry (Appendix A)

The weight losses observed during thermal treatment up to 140°C are mainly due to water being driven off. Treatment at 140°C and higher temperatures results in a degradation of the anionic resin. For the cationic resin the weight losses seem to be mainly due to water evaporation at all the temperatures which were studied.

At 140°C the cationic resin reaches a constant weight in 60 minutes. The time for the anionic resin to reach constant weight was 300 and 3000 minutes at 180 and 140°C respectively.

The addition of Na_2SO_4 reduces the weight loss during the thermal treatment to less than half.

The powdered resin behaves similarly to the granular resin. The differences between the total weight losses at different temperatures are, however, somewhat less.

A typical weight loss diagram, for granular new and used resins with and without the Na_2SO_4 treatment, is presented in Figure 1.

Particle size analysis (Appendix B)

The ion-exchange resin shrinks during the thermal treatment by about 15 %. The different treatment temperatures only have a minor effect.

The anionic and cationic resins shrink by the same amount. The particles of the cationic resin are, however, 100 µm larger than the anionic resin.

When exposed to air for 24 h and after drying at 80 and 105°C the particles return almost to their original size. After drying temperatures of 140 and 180°C this effect is not observed, see Figure 2. Measurements on new granular anion and cation resins, after heat treatment at 140°C, showed that this effect is based on the partial destruction of the anionic resin, which leads to a continued shrinkage during exposure to air. The cationic resin, however, returned to its original size during the exposure to air. The addition of Na_2SO_4 resulted in a shrinkage of the anionic resin by 100 µm; the cationic resin remained unchanged.

The heat treatment had very little effect on the particle sizes of the expended powdered resin.

The swelling of ion-exchange materials (Appendix C)

In the following, the swelling of ion-exchange resins, in water, after heat treatment, is discussed. The swelling of the corresponding air dried (non heat treated) ion-exchange resins are used as reference values. All the results are compared to these values.

The cationic resins behaved reversibly in the experiments, up to at least 140°C. Experiments with mixed bed resins indicated that, even after longer drying periods (1 week) at high drying temperatures (180°C), the behaviour of the cationic component was reversible, see Table 3.

The swelling of anionic resin after a thermal treatment (1 h and 1 d) at 105°C or 140°C (1 h) was considerable: 200 % and 140 % respectively. This swelling was reduced after prolonged drying at 140°C.

It is obvious that two mechanisms are involved in the behaviour of the anionic resin: first, at low temperatures and/or short drying times a process, that gives an increased swelling compared to air dried resins takes place. At higher temperatures another process, resulting in an almost total inhibition of the swelling takes place.

This indicates that the thermal treatment causes irreversible changes in the structure of the resin, probably as changes in the less stable bonds between the functional groups.

The results obtained in the experiments with powdered resins seems to differ from thos with granular resins: The absolute level of swelling is 50-90 % higher. This is due to the "extra water" which can be adsorbed in between the small particles of the powdered resins.

The degradation behaviour described above for granular resins is also found for the powdered resins. The time needed to reach the same degree of degradation is, however, much longer than for the granular resin.

The use of sodium sulphate (Na_2SO_4) as an additive only had a minor effect on the swelling behaviour of expended granular mixed-bed resins. For new anionic granular resin the Na_2SO_4 treatment inhibits the increased swelling found for untreated anionic resins after short treatment times. No effect of the Na_2SO_4 treatment was observed for new cationic resins.

The addition of sodium sulphate to powdered resins had, contrary to the case for granular resins, a dramatic effect. The influence of the heat treatment on the swelling properties is totally inhibited. The swelling is almost the same after heat treatment at all the different temperatures and times, see Table 4.

The Na_2SO_4-treatment of powdered resins also reduces the adsorption of "extra" water in between the particles, which has the effect that the swelling measured is lower than it is for untreated resins.

6 DISCUSSION AND CONCLUSIONS

The results obtained in this study can be summarized as follows:

- In this study three different analysis methods were used to study the swelling properties of different ion-exchange materials. All three methods gave the same type of results - the thermal treatment has an clear effect on these materials.
- The granular anionic resin is degraded after the thermal treatment at temperatures higher than 140°C, and simultaneously looses its capacity to swell. The cationic resin displays the opposite behaviour after thermal treatment.
- The behaviour of granular mixed-bed resin is the sum of its components: anion and cation resins.
- The swelling behaviour of powdered resin is probably partly due to water adsorption. The "true" swelling is probably much more moderate than the observed.
- The use of sodium sulphate as an additive had the effect of reducing the swelling of powdered resins. The swelling effect of the granular resins are not affected when Na_2SO_4 is used.

The observation, that the resins lost their swelling properties after treatment for longer periods at higher temperatures, indicates that of some irreversible physical/chemical processes occur in the resins. One explanation could be that the loosely bound functional groups (trimethyl amine, sulphonic acid groups) split off during heating, which leads to a decrease in the content of the hydrophilic groups, and a reduced capacity for re-swelling. Such losses of functional groups have been observed in the form of reduced ion-exchange capacity after heat treatment in other studies. The fact that the swelling increased when the resins were treated for a short period at low temperatures, could be explained by the reorientation in the polymer matrix of the functional groups, which can lead to an increase in moisture absorption. The behaviour of anion resins can be taken as an example. It is also obvious that anion resins are more vulnerable to the thermal treatment than cation resins.

In the literature survey made, Appendix D, information on the thermal stability and swelling properties of ion-exchange resins has been collected. This survey indicates that different ion-exchange materials can behave differently after a thermal treatment. Changes in the exchange capacity and swelling depends on many factors, such as the nature of the water and the solvent, the presence or absence of an electrolyte in the solution, the nature of the fixed and counter ions, etc. In some cases the results found in the literature deviated from the results obtained in this study.

Table 3 Granular resins

3.1 The swelling of mixed bed, anion and cation resins in water in comparison to the air dried resins

The volume of air dried resins $V_{1-3} = 1$

t=(h) T °C	MIXED BED - RESINS				CATION RESIN				ANION RESIN				REMARKS
	0.5	1	24	168	0.5	1	24	168	0.5	1	24	168	
20				1.84				1.56				1.71	V_1/m_1 = 133 ml/100g V_2/m_2 = 129 ml/100g V_3/m_3 = 152 ml/100g
80	3.01	2.52	2.31	2.16									
105	2.94	2.67	1.97	1.32		1.56	1.59	1.65		2.99	2.35	1.25	
140	2.54	2.07	1.01	0.97		1.55	1.50	1.55		2.36	0.70	0.65	
180	1.50	1.11	0.98	0.95									
	V_1				V_2				V_3				

3.2 The swelling of Na_2SO_4-treated resins

The volume of air dried resins $V_{4-6} = 1$

t=(h) T °C	0.5	1	24	168	0.5	1	24	168	0.5	1	24	168	REMARKS
20				2.12				1.50				1.97	V_4/m_4 = 132 ml/100g V_5/m_5 = 121 ml/100g V_6/m_6 = 143 ml/100g
80	2.49	2.70	2.68	2.37									
105	2.64	2.80	1.64	1.33		1.46	1.49	1.53		1.99	1.78	1.23	
140	2.48	1.78	1.17	1.19		1.50	1.43	1.47		1.84	0.86	0.73	
180	1.61	1.14	1.09	1.14									
	V_4				V_5				V_6				

Table 4 Powdered resins

The swelling of powdered resin in water in comparison to the air dried resins

The volume of air dried resins V_1* = 1 (164 ml)

T °C \ t = (h)	1/2	1	24	168
20				2.70
80	2.78	2.75	2.84	2.80
105	2.72	2.76	2.63	2.01
140	2.66	2.61	2.24	1.34
180	2.45	1.66	1.36	1.23

Na_2SO_4 - treated resins V_2* = 1

T °C t = (h)	1/2	1	24	168
20				1.83
80	1.71	1.79	1.82	1.79
105	1.72	1.72	1.78	1.72
140	1.66	1.79	1.79	1.87
180	1.74	1.74	1.74	1.66

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* V_1 = 164 ml

* V_2 = 143 ml

Table 5 Calculated swelling in the mixed bed resins on the basis of individual swelling of anionic and cationic components (mixed resin, an:cat = 60:40)

A comparison with the observed swelling in used mixed-bed resins.

	GRANULAR NEW RESINS				MIXED-BED RESINS	
	Anionic component		Cationic component		Volumes in water (ml)	
	swelling factor	volume (ml)	swelling factor	volume (ml)	calculated	observed average
20°C	$V_A = 80$ ml		$V_C = 53$ ml			
168 h	1.71	137	1.56	83	220	245
105°C						
1 h	2.99	239	1.56	83	322	355
24 h	2.53	202	1.59	84	286	262
168 h	1.25	100	1.65	87	187	175
140 °C						
1 h	2.36	189	1.55	82	271	275
24 h	0.70	56	1.50	80	136	134
168 h	0.65	52	1.55	82	134	129
Na_2SO_4 - treated resins						
20 °C	$V_A = 79$ ml		$V_C = 53$ ml			
168 h	1.97	156	1.50	80	235	275
105 °C						
1 h	1.99	157	1.46	77	235	370
24 h	1.78	141	1.49	79	220	216
168 h	1.23	97	1.53	81	178	176
140 °C						
1 h	1.84	145	1.50	80	225	235
24 h	0.86	68	1.43	76	144	154
168 h	0.73	56	1.47	78	136	157

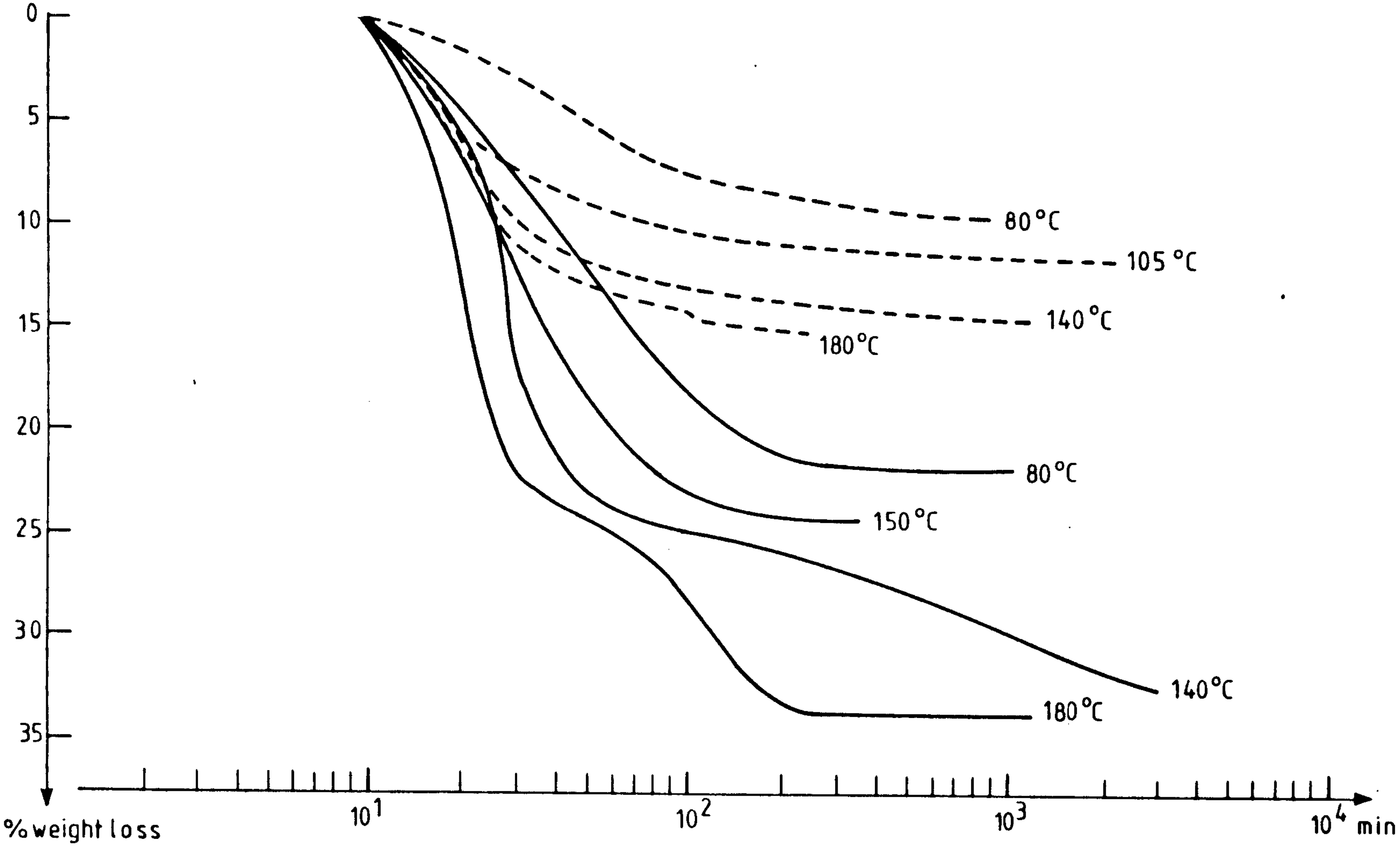


Figure 1. A typical weight loss diagram obtained in TG-analysis. Expended granular resin without and with sodium sulphate addition.

——— without Na_2SO_4

- - - - with Na_2SO_4

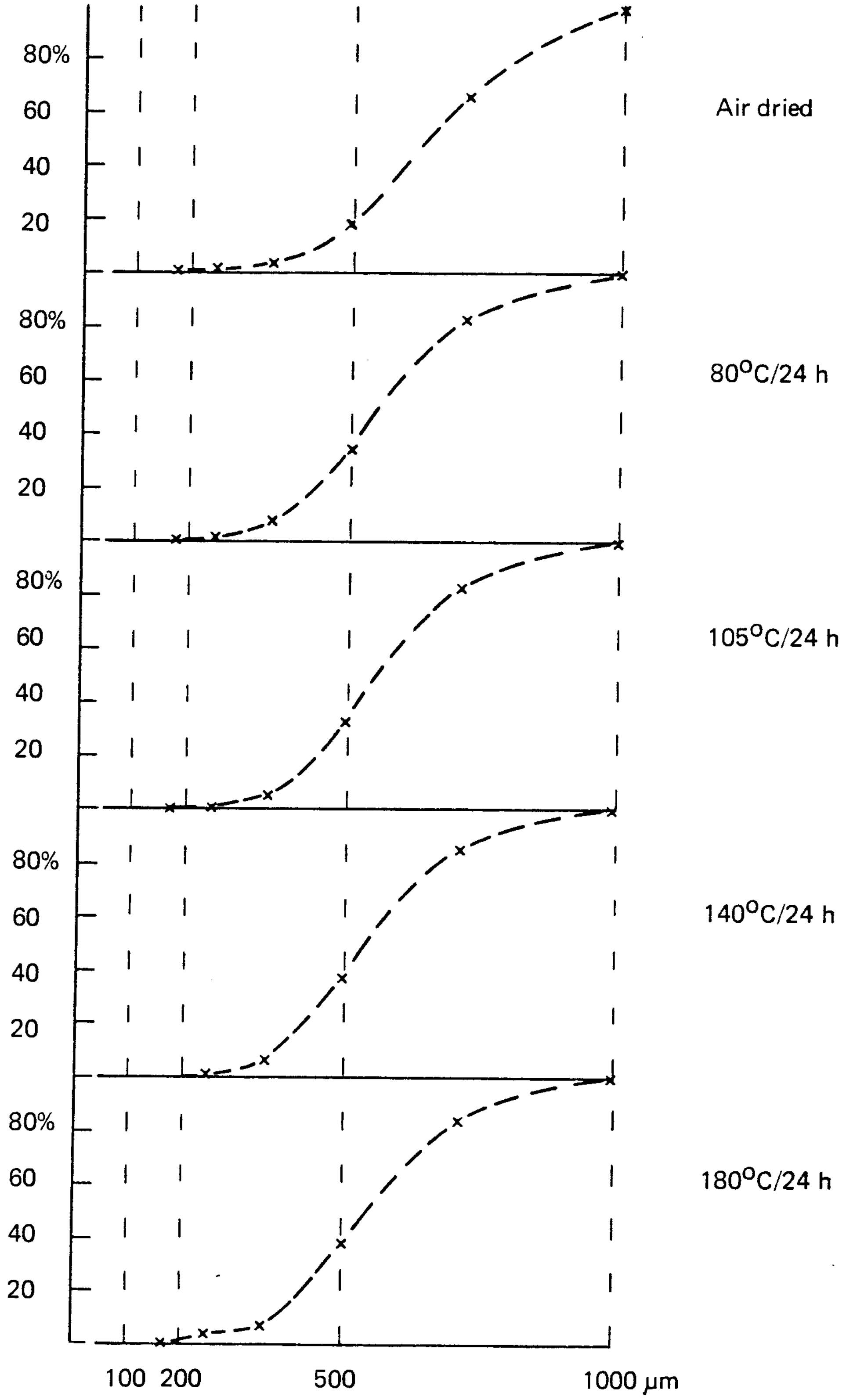


Figure 2. Sieving of expended granular resin (sample 7)

Drying temperatures 20, 80, 105, 140, 180°C.

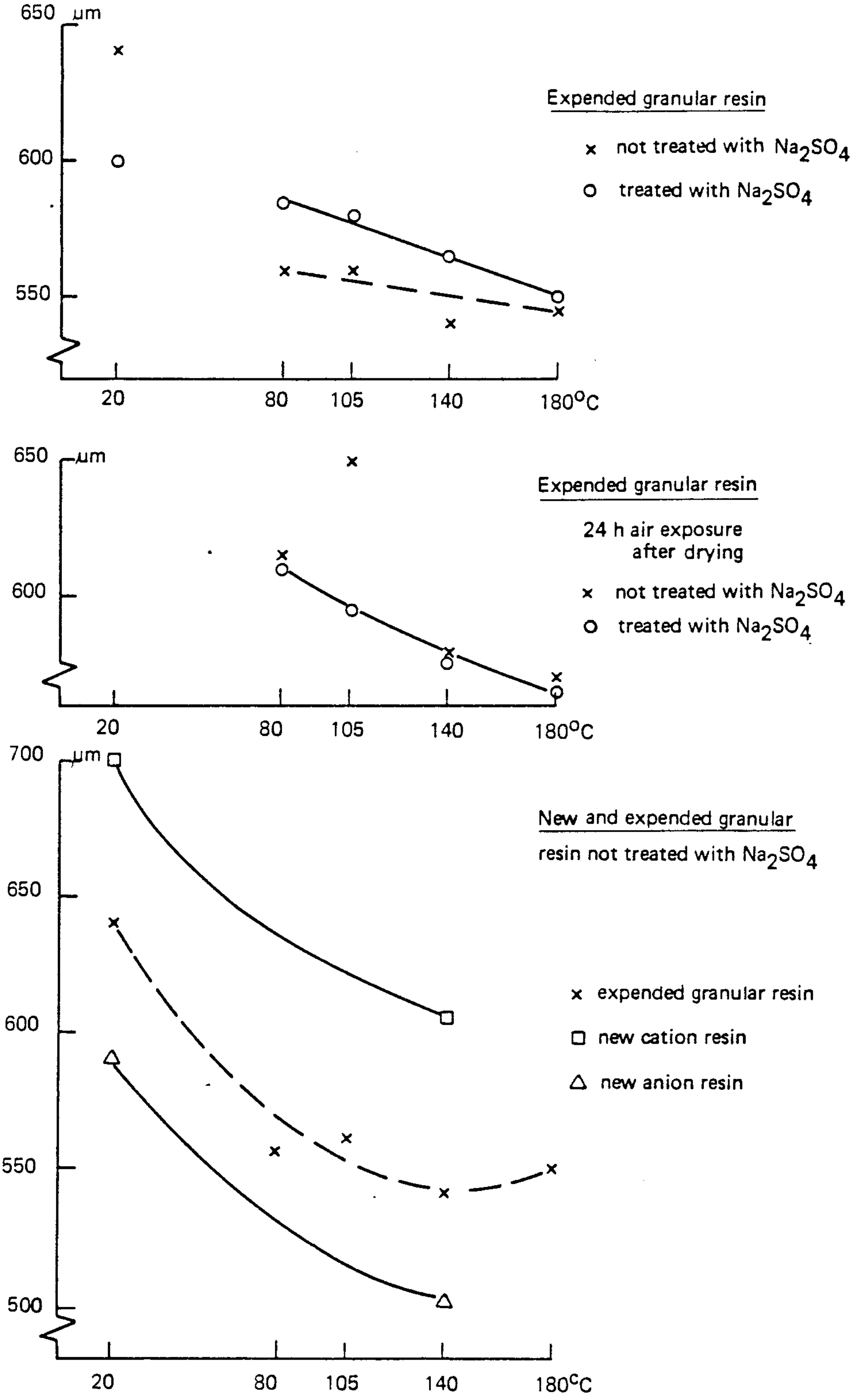


Figure 3. "Mean" particle size taken from the sieving curves. The values are the "50%" level values.

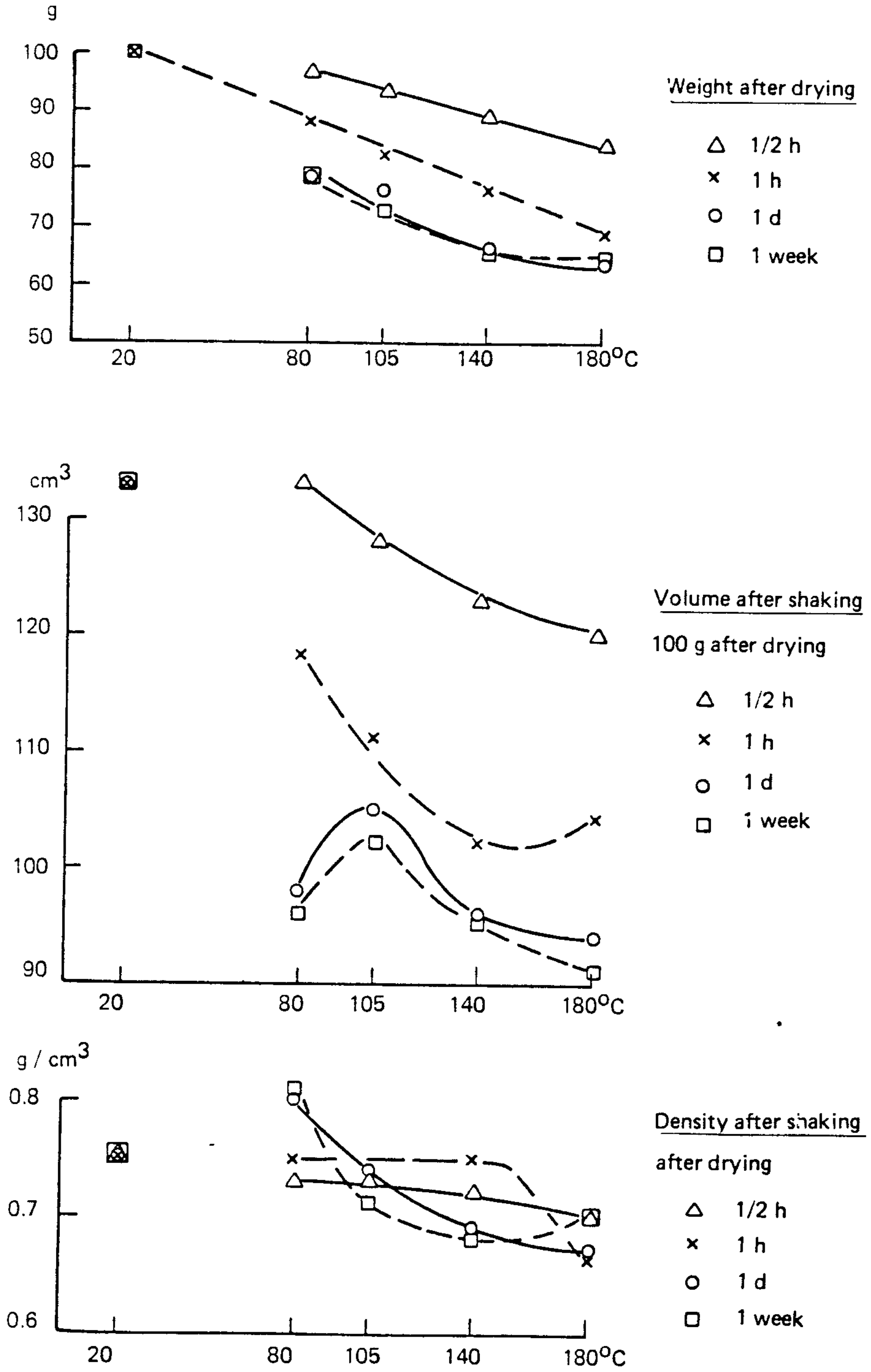
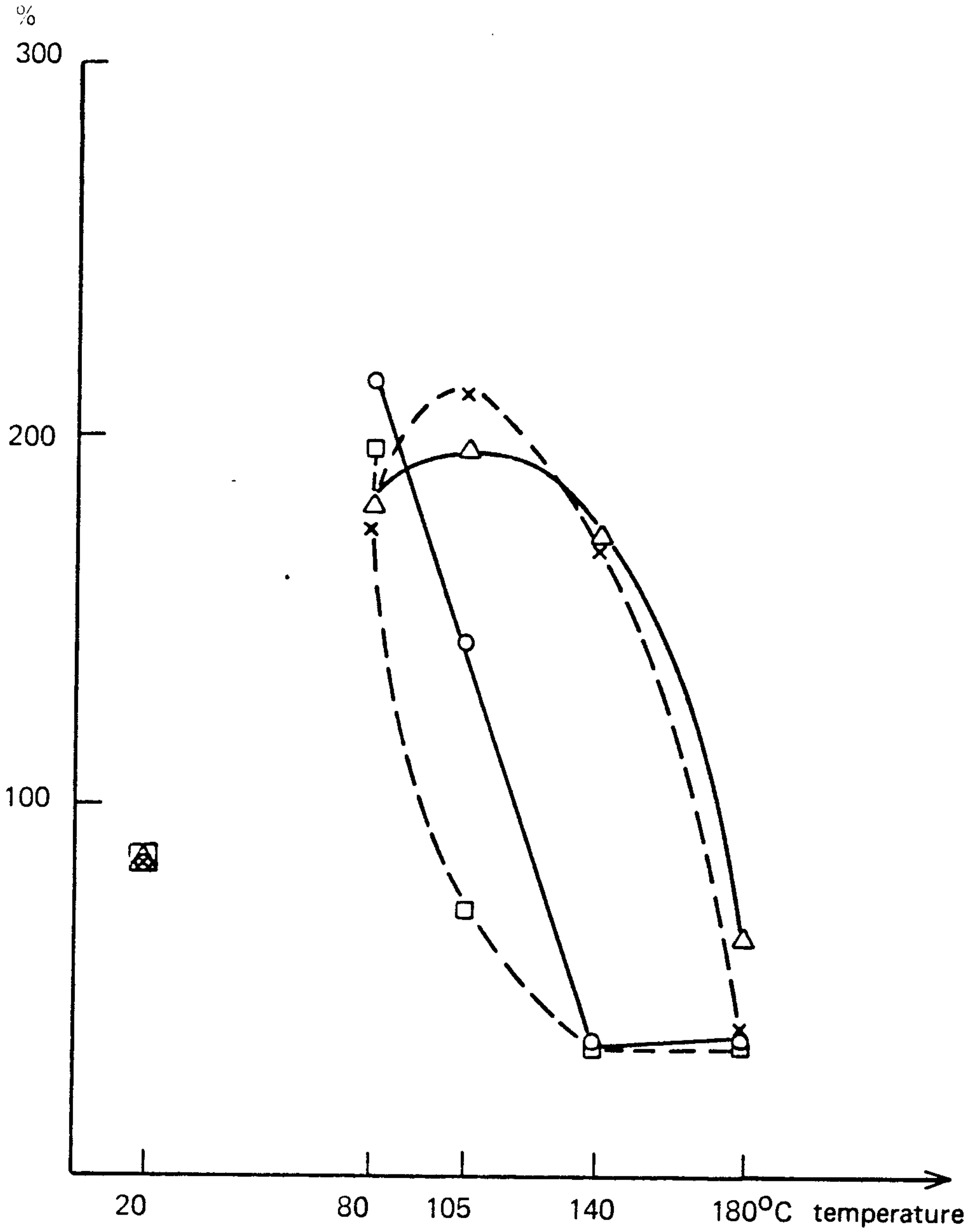


Figure 4. USED GRANULAR MIXED BED RESIN
Weight, volume and density after heat treatment.



$$^{*}\text{Swelling (\%)} = \frac{\text{volume in water} - \text{volume after shaking}}{\text{volume after shaking}} \times 100\%$$

Figure 5. EXPENDED GRANULAR MIXED BED RESIN Swelling* as a function of drying temperatures and time.

△ = 1/2 h ○ = 1 d
× = 1 h □ = 1 week

THERMOGRAVIMETRY (TG)

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1. EXPERIMENTAL CONDITIONS

The thermal analysis technique used in this work is isothermal thermogravimetry (TG), in which the sample mass is recorded as a function of time at constant temperature.

SETARAM type 1135 thermobalance was used, manufactured by SETARAM, Lyon, France.

All measurements were made in static air, and were recorded until no further weight changes could be seen.

Before the TG-measurments were started the samples, 1 - 8 described in paragraph 2, were dried in air at 20°C to a constant weight.

Samples 1; 2;7 and 8 were all analysed at 80; 105; 140 and 180°C.

Samples 3; 4; 5 and 6 were analysed only at 140°C.

The resulting isothermal weight-change curves are illustrated in Diagrams A.1 - A.4.

2. SAMPLES

2.1 Ion-exchange resins

A	Expended, powdered resin (Microionex) from Forsmark power plant
B	New, granular, cation resin (Duolite ARC-351)
C	New, granular, anion resin (Duolite ARA-366)
D	Expended, granular resin (60 % Duolite ARA-366, 40 % Duolite ARC-351) from Forsmark power plant

Part of the ion-exchange resin has been treated with Na_2SO_4. 1 kg anhydrous Na_2SO_4 was added to 12.5 kg ion-exchange resin ("even-level") .

2.2 Samples

Sample 1	A*
" 2	A + Na_2SO_4
" 3	B
" 4	B + Na_2SO_4
" 5	C
" 6	C + Na_2SO_4
" 7	D
" 8	D + Na_2SO_4

The Na_2SO_4 addition corresponds to the pretreatment of granular ion-exchange resins at Barsebäck power plant before solidification in bitumen.

3. RESULTS

3.1 Ion exchange resin without Na_2SO_4

3.1.1 Expended granular resin

From the measurements on Sample 7, Diagram A.1, the following conclusion can be drawn letters (a, b ...) refer to letters in Diagram A.1:

a The weight loss increases with increasing temperature. At 80°C the end point lies at 22 %, and at 180°C at 34 % weight loss.

b There are discontinuities in the weight loss curves at 140 and 180°C.

These discontinuities can also be seen on other diagrams. They can be explained as follows: the ion exchange materials used in this experiment are a mixture of anion and cation resins. Initially both anion and cation resins loose water. After some degree of drying, the water loss rate is qiote small and a plateau can be seen on the curves. (For 180°C after ~ 30 min and for 140°C after ~ 50 min.) After ~ 60 min at 180°C, and ~ 110 min at 140°C, the anion resin in the mixture begins its degradation and loose trimethyl amine; a further weight loss begins.

c The weight losses are almost completed after ~ 200 min drying, except the treatment at 140°C, in which the treatment had to be continued for ~ 3 000 min before a constant weight was obtained.

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* Capital letters refer to ion-exchange resins listed above.

3.1.2 New granular resin

From the measurements on samples 3 and 5 at 140°C, Diagram A.2, the following conclusions can be drawn (letters a, b... refer to letters in Diagram A.2):

a The difference in weight loss between anion and cation resins is 16 %.

b The weight loss from cation resins stabilized after ~ 60 min drying.

c The loss of weight from anion resins was a very slow process. It took more than four days to reach the end point, of constant weight, during drying.

On the basis of these experiments with new granular resins, it is obvious that the previously observed discontinuities in the drying profile of granular mixed bed resins are reflections from the degradation of anion resins. This degradation is mainly due to the evaporation of trimethyl amine groups from the resins.

3.1.3 Comparison between new and expended granular resin

By assuming that the expended granular resin is a mixture of 60 % Duolite ARA-366 and 40 % ARC-351, the resultant curves in Diagram A.3 were drawn on the basis of Diagram 2. The 140°C curves from Diagram A.1 (expended granular resin) were also drawn for comparison.

There is one difference between the new and expended resin. The new resin have not been stored in water and this might explain the observed differences in Diagram A.3.

From Diagram A.3 the following conclusions can be drawn (letters a, b... refer to letters in Diagram A.3):

a Expended granular resin looses more weight than new granular resin. The difference is ~ 7 % (probably due to a difference in the initial water content).

b Discontinuities can be seen on the curves for both the expended and new granular resins.

c The curves running roughly parallel to each other after about 60 min, showing that the weight loss rates are the same after this treatment.

3.1.4 Expended powdered resin

From the measurements on Sample 1, Diagram A.4, the following conclusions can be drawn (letters a, b... refer to letters in Diagram A.4):

a The weight loss increases with increasing temperature. At 80°C the end point lies at 20 % and at 180°C at 28 % weight loss.

b There is a disvontinuity on the weight loss curves at 140°C which can be explained analogueously to 3.1.1 (c).

c The time to reach a constant weight during drying at 140°C is somewhat shorter for the powdered resins than for the granular resins (Diagram 1).

d The major weight loss can be observed, in general, during the first 100 min, except at 140°C.

The time needed to reach constant weight at 140°C is ~ 1 000 min.

3.2 The effect of Na_2SO_4 as an additive

3.2.1 Expended granular resin

From the measurements on Sample 8, Diagram A.1, the following conclusions can be drawn (letters a, b... refer to letters in Diagram A.1):

a The weight loss increases with increasing temperature. At 80°C the end point lies at 10 % and at 180°C it lies at 15 %. This is about 50 % of the weight loss observed for untreated resins.

b There is one discontinuity on the weight loss curve in 180°C (trimethyl amine splits off). The discontinuity is not so apparent for Na_2SO_4-treated resins as for untreated resins.

c The time to reach a constant weight is about the same as for untreated resins.

3.2.2 New granular resin

The same conclusions are also valid for new granular resins as can be seen from the measurements on Samples 4 and 6 at 140°C, Diagram A.2.

3.2.3 Expended powdered resin

From the measurements on Sample 2, Diagram A.4, the following conclusions can be drawn (letters a, b... refer to letters in Diagram A.4):

a The weight loss increases with increasing temperature. At 80°C the end point lies at 7 % and at 180°C at 11 % weight loss. This is about 35 % of the weight loss observed for untreated resins.

b The time to reach constant weight at 140°C is quite short (~ 100 min) compared to other runs at 140°C.

c At higher temperatures (140 and 180°C) the major weight loss occurs during the first 30 min.

d The weight loss at 140°C with Na_2SO_4 starts almost instantaneously. Usually, depending on the experimental conditions it takes a few minutes before the systems are stabilized. However, in this special case the weight loss was recorded earlier than in other runs.

4. CONCLUSIONS

The drying of mixed ion exchange resins and the resulting weight loss is straight forward for the cation resin part. The cation resin reaches a constant weight at 140°C in ~ 60 min (Diagram A.2) and no degradation can be seen after that time. All the weight losses are thought to be water driven off from the cation resin.

The anion resin weight loss curve at 140°C (Diagram A.)2 is more complex. It takes very long time to reach a constant weight (more than four days). The weight losses here are a combination of water losses and losses of trimethyl amine, a degradation of the anion resin.

This degradation can also be seen in the mixed ion exchange resin (Diagrams 1 and 4) for temperatures of 140°C and higher.

Temperatures below 140°C are not sufficient to cause the degradation, and the weight loss at this temperature is due to the driving off of water.

The addition of Na_2SO_4 has the effect of reducing the weight loss at all temperatures studied. It also has the effect of reducing the degradation at higher treatment temperatures. However, a slight degradation can be seen at 180°C (Diagram A.1).

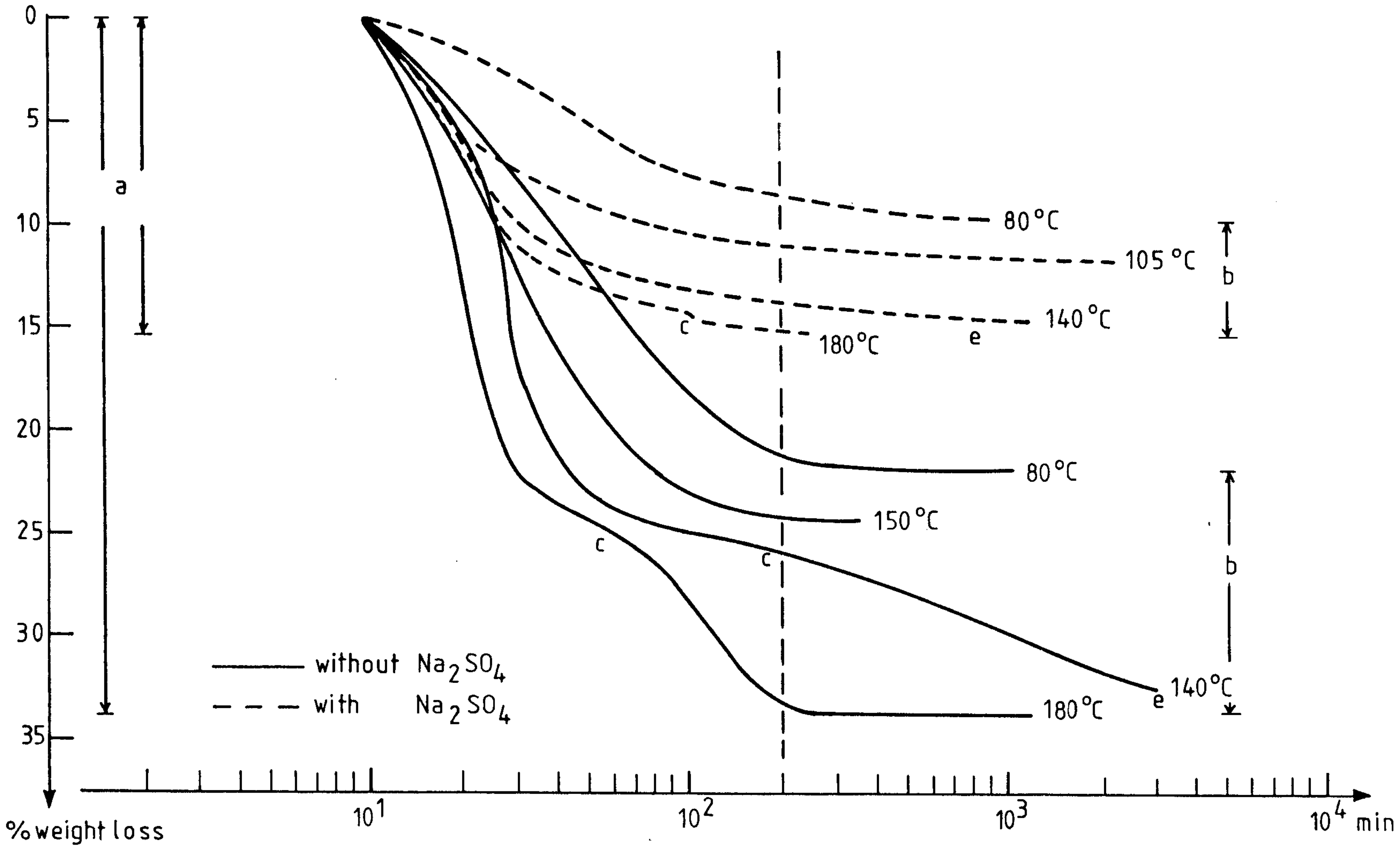

Diagram A.1. Weight loss diagram obtained in TG-analysis.
Expended granular resin with and without sodium sulphate.

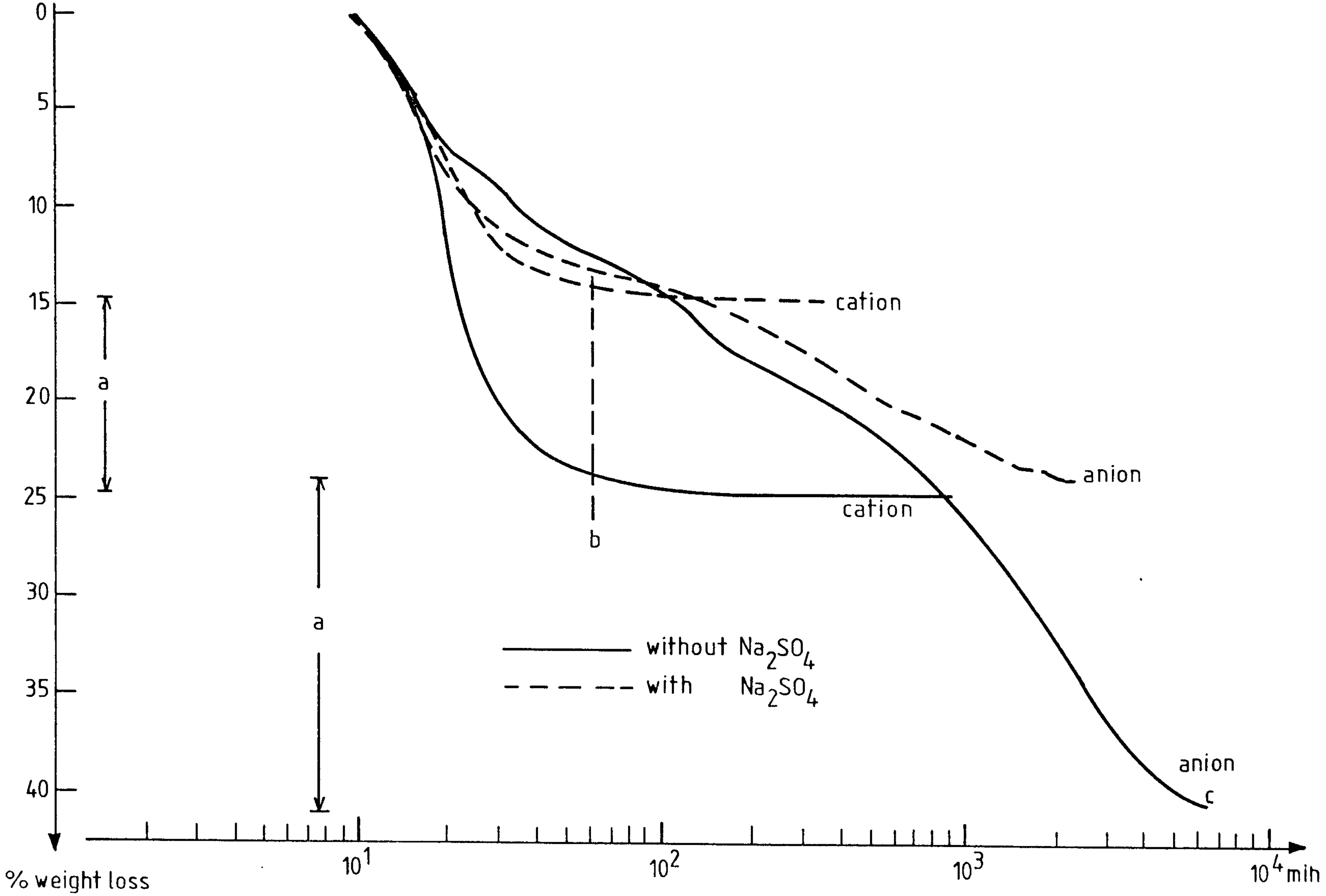

Diagram A.2. Weight loss diagram obtained in TG-analysis at 140°C. New granular resin.

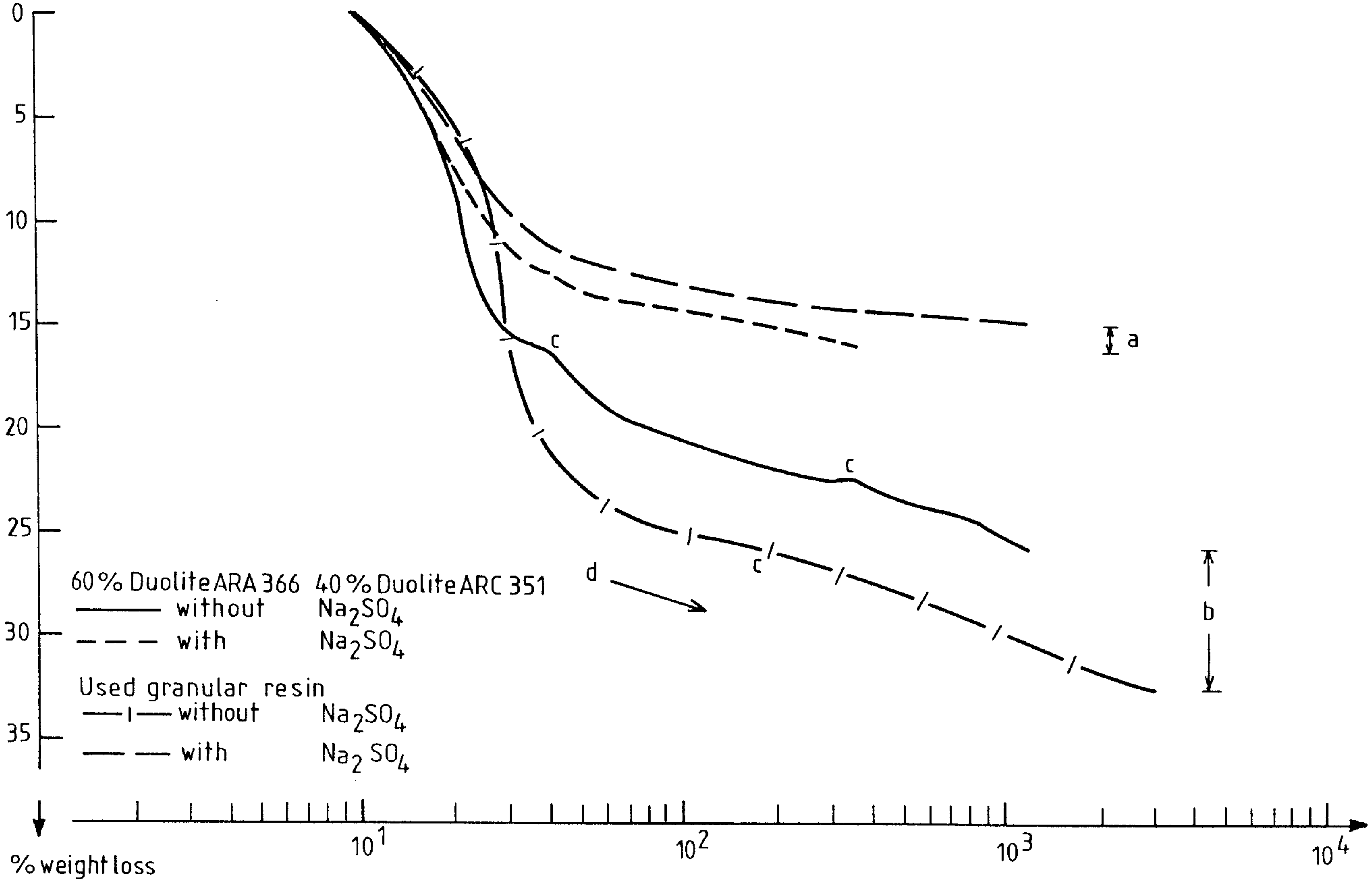

Diagram A.3. Weight loss diagram obtained in TG-analysis at 140°C
New and expended granular resins.

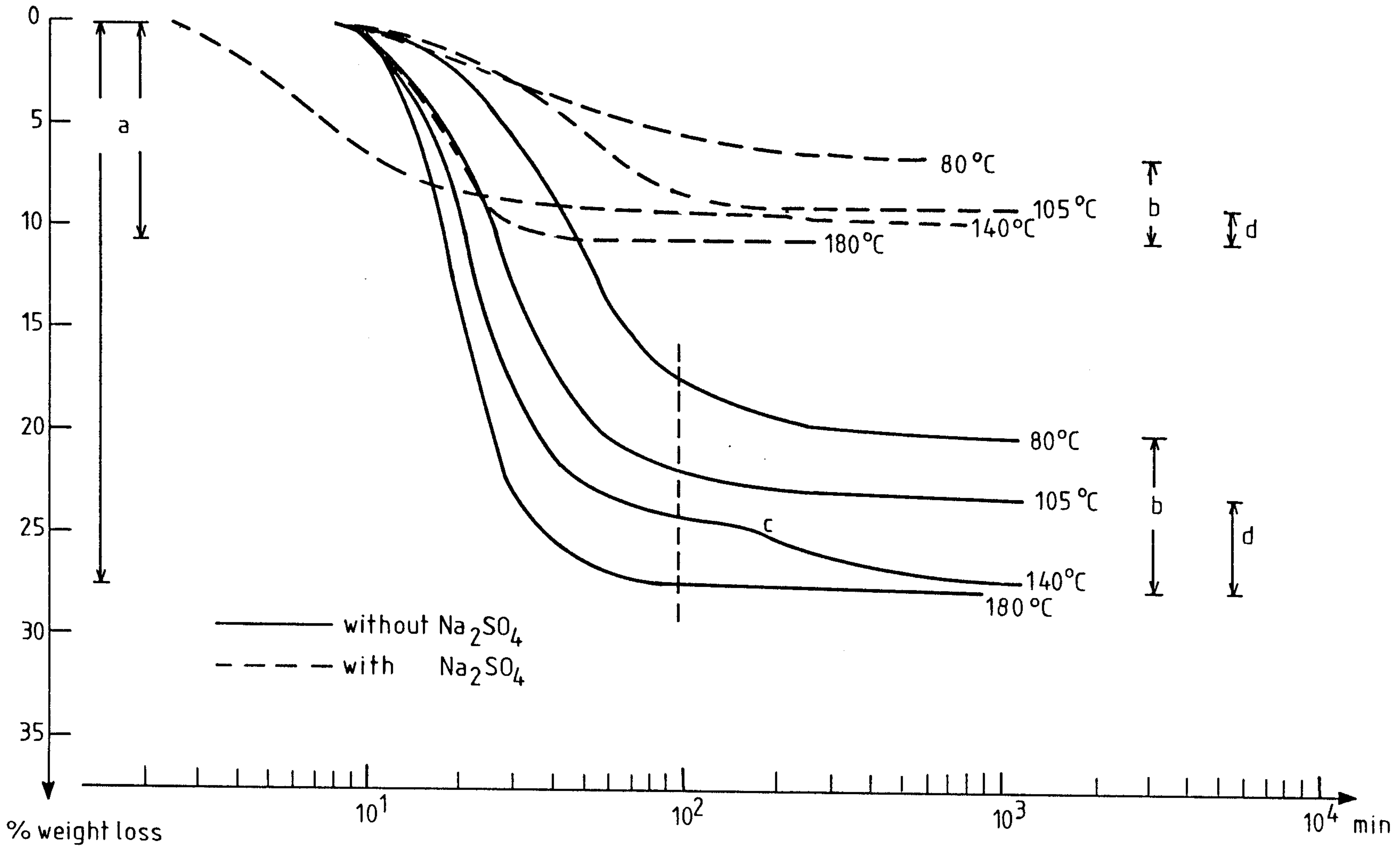

Diagram A.4. Weight loss diagram obtained in TG-analysis.
Expended powder resin.

1. EXPERIMENTAL CONDITIONS

The particle size distribution has been analysed by sieving. Wire cloth sieves, Ø 8-in, (ASTM specifications E11) with the mesh sizes 1 000, 710, 500, 355, 255, 177, 125, 90, 63 and 45 µm were used. The material retained on each sieve was weighed and recorded.

The analyses have been carried out on all the samples 1 - 8 described in paragraph 2, both on air dried resins and on resins after heat treatment. 100 g of air dried resin was used for each measurement.

The air dried resins were prepared by drying in air at 20°C until no further weight-loss was registered.

The complementary heat treatment was performed on an iron tray in a heating chamber, for 24 h. Samples 3 - 6 were treated only at 140°C, whilst the others were treated at the temperatures of 80, 105, 140 and 180°C.

The samples were weighed and sieved while they still were warm.

Afterwards the material was recombined and left in the open air for 24 h. After which it was sieved again. The sieving results are shown in Diagrams B.1 - B.12 as cumulative distribution graphs.

2. SAMPLES

2.1 Ion-exchange resins used

A	Expended, powdered resin (microionex) from Forsmark power plant
B	New, granular, cation resin (Duolite ARC-351)
C	New, granular, anion resin (Duolite ARA-366)
D	Expended, granular resin (60 % Duolite ARA-366, 40 % Duolite ARC-351) from Forsmark power plant

Part of the ion-exchange resin was treated with Na_2SO_4. 1 kg anhydrors Na_2SO_4 was added to 12.5 kg ion-exchange resin ("even-level").

2.2 Samples

Sample	1	A*
"	2	A + Na_2SO_4
"	3	B
"	4	B + Na_2SO_4
"	5	C
"	6	C + Na_2SO_4
"	7	D
"	8	D + Na_2SO_4

The Na_2SO_4 addition corresponds to the pretreatment of granular ion-exchange resins at Barsebäck power plant, before solidification in bitumen.

3. RESULTS

The detailed results from the seiving analysis are presented in Diagrams B.1 - B.12. The particle sizes are illustrated as cummulative particle size distributions. In Diagram B.13 the main results of the experiments are presented as trend curves as a function of temperature. From the Diagrams the following conclusions can be drawn.

3.1 Ion-exchange resin without Na_2SO_4

3.1.1 Expended granular mixed-bed resin

The particles shrink by about 15 % during the heat treatment at all the treatment temperatures (Diagram B.1 and B.13). Particles from drying at 80 and 105°C re-swell to their original size during the subsequent 24 h exposure in air. Heating at temperatures 140°C and 180°C suppresses this effect (Diagrams B.1, B.2 and B.13).

3.1.2 New granular resin

Anion resin

The anion-exchange resin particles shrink by about 15 % during the drying process (Diagrams B.5 and B.6), the particles shrink by a further 5 % when exposed (24 h) in air. This shrinkage occurs in spite of a slight increase of weight (5 %).

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* Capital letters refer to ion-exchange resins listed above.

Cation resin

The cation-exchange resin particles shrink by about 15 % during the drying process (Diagrams B.7 and B.8). The exposure afterwards in air (24 h) has the effect that the ion-exchange resin almost returna to the particle size distribution it had before the heat treatment. There is also an increase in weight (~ 20 %).

Comparison between new resins

Particles of anion resin are, on the average, 100 μm smaller than particles of cation resin (Diagrams B.5, B.7 and B.13).

This difference in particle size is also seen after drying at 140°C.

The difference in particle size is further increased by the subsequent exposure in air (the anion resin shrinks further, the cation resin re-swells to its original size) the difference is ~ 200 - 300 μm (Diagrams B.6 and B.8).

Comparison between new and expended resins

By assuming that the expended granular resin is a mixture of 60 % anion and 40 % cation resin, the resultant "mean" particle size of this material can be calculated both after drying at room temperature, and at 140°C, on the basis of the "mean" particle sizes of anion and cation resins. This indicates that the particle size in mixed-bed resin before and after drying is in proportion to the behaviour of individual resin fractions.

3.1.3 Expended powdered resin

Drying has a very small effect on the particle size even after drying at 180°C (Diagram B.9).

The subsequent air exposure has no influence on the particle size (Diagram B.10).

3.2 The effect of Na_2SO_4 as an additive

3.2.1 Expended granular resin

The air dried particles shrink by ~ 50 μm (Diagram B.3) when treated with sodium sulphate.

The subsequent drying at elevated temperatures has a small effect on the particle size (< 8 %).

Particles dried at 80 and 105°C re-swell to their original size upon exposure 24 h in air particles dried at 140 and 180°C only re-swell partially (Diagram B.4).

3.2.2 New granular resin

Anion resin

By adding Na_2SO_4 to the anion-exchange resin, the air dried resin skrinks to ~ 100 μm smaller particle size in comparison with the resin not treated with Na_2SO_4 (Diagram B.13).

Drying does not change the particle size much, in spite of a decrease in weight of 25 %.

The subsequent air exposure (24 h) resulted in a slight increase in weight but no changes in particle size distributions.

Cation resin

The addition of Na_2SO_4 has no effect on the particle size in the air dried material (Diagram B.13).

Heat treatment at 140°C does not change the particle size. However, the decrease in weight is ~ 13 %.

The subsequent air exposure (24 h) resulted in an increase of ~ 18 % in the weight, but no change in the particle size distribution.

3.2.3 Expended powdered resin

Adding Na_2SO_4 has no influence on the particle size (Diagram B.11 and B.12).

Drying at various temperatures and the subsequent air exposure have no influence on the particle size.

4. CONCLUSIONS

The particle size distribution of granular resins changes on heat treatment or by adding Na_2SO_4 (smaller particles).

The granular anion resin and the granular cation resin shrink uniformly on drying. The "mean" particle size of the mixed-bed resin could be calculated on the basis of the "mean" particle sizes of the anion and cation resins.

The differences in particle size distribution at different drying temperatures (80 - 180°C) are quite small.

The addition of Na_2SO_4 to granular resins almost inhibits the shrinkage due to the heat treatment.

The particle size distribution of powdered mixed resins, with or without Na_2SO_4, is not affected by heat treatment (< 180°C).

The relative humidity of the air at the time of measurement influences the particle size distribution of the resin, and has resulted in a slight spread in the experimental results.

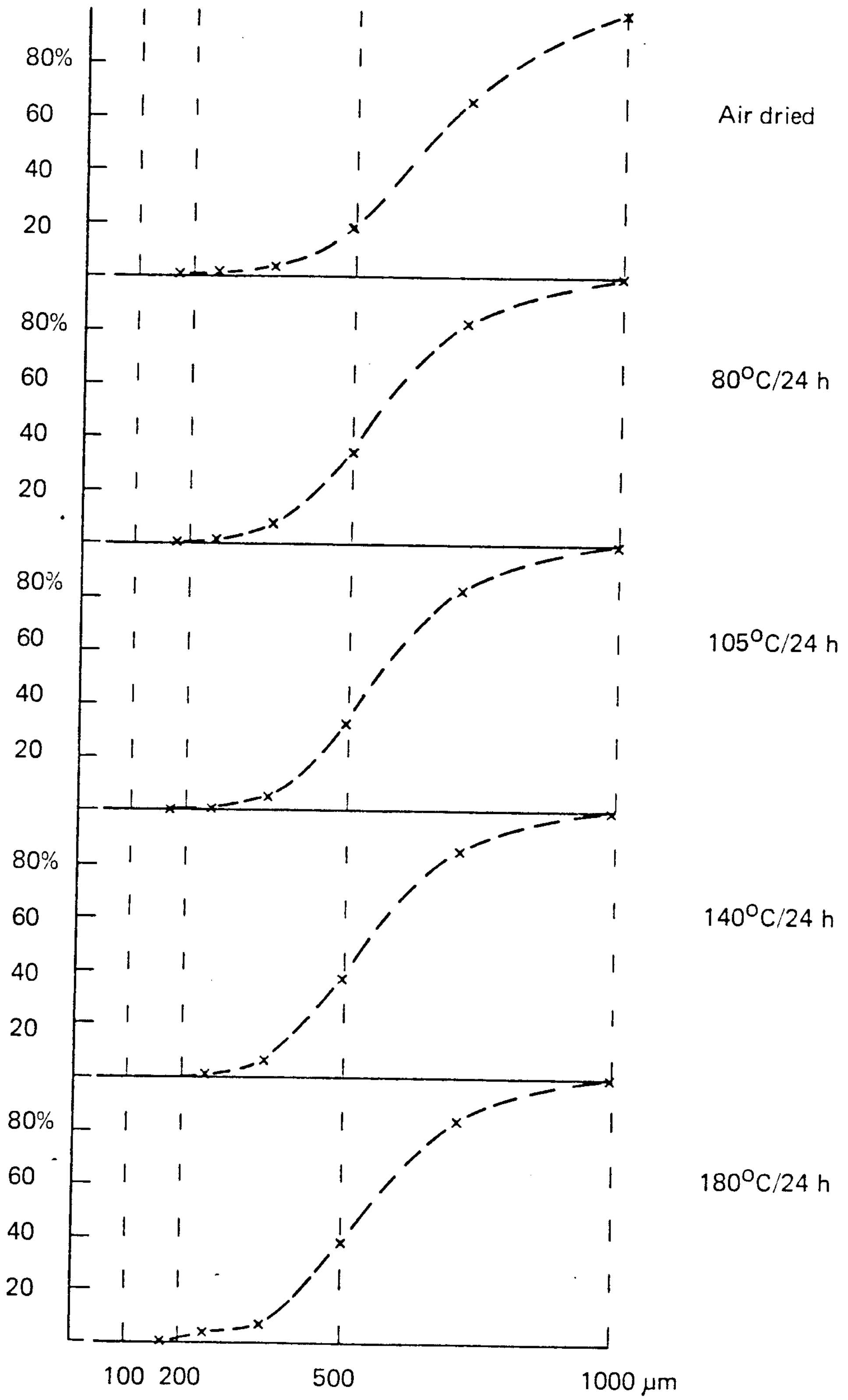


Diagram B.1

Sieving of expended granular resin (Sample 7).
Drying temperatues 20, 80, 105, 140 and 180°C.

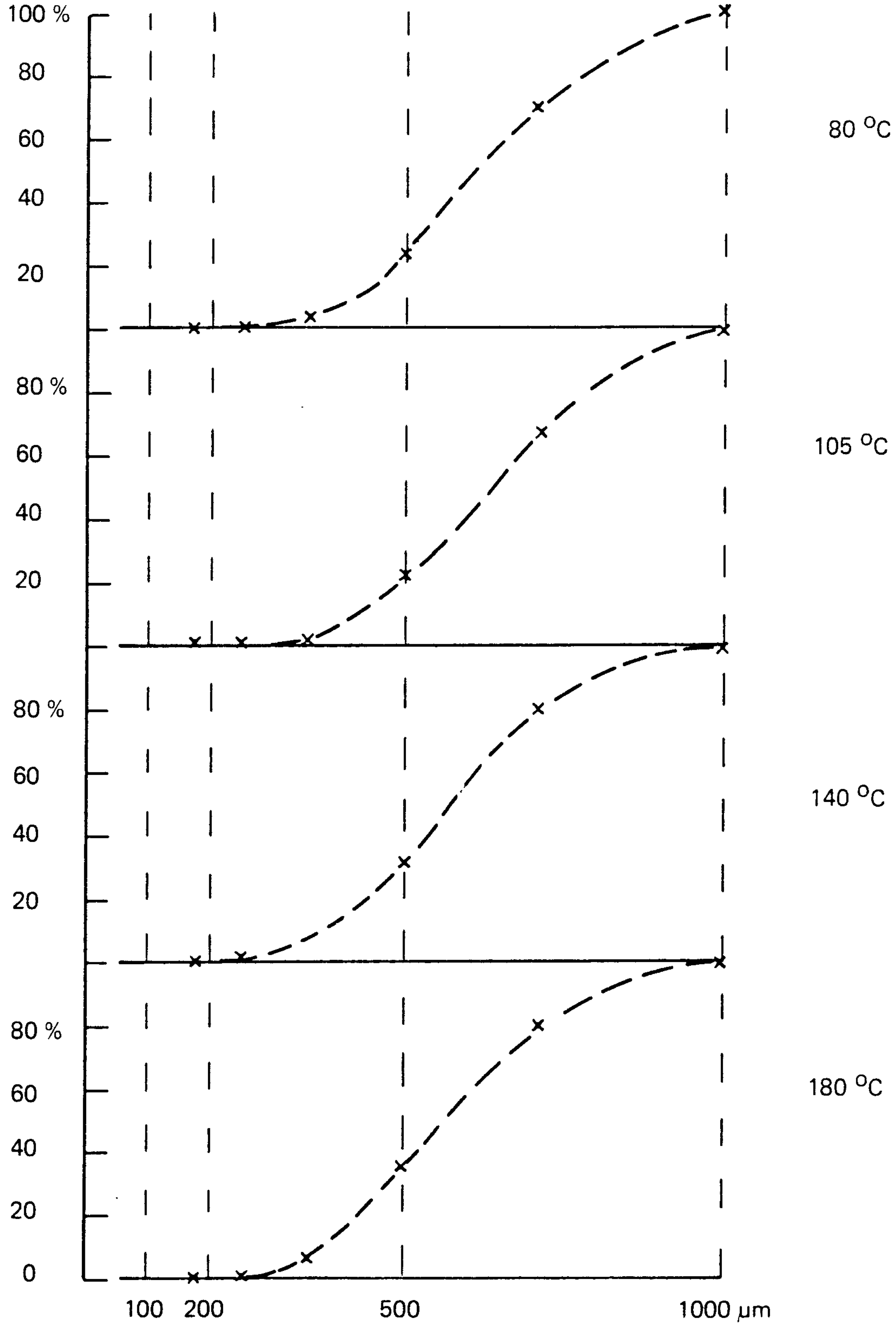


Diagram B.2

Sieving of expended granular resin (Sample 7). 24 h air exposure after drying at 80, 105, 140 and 180°C.

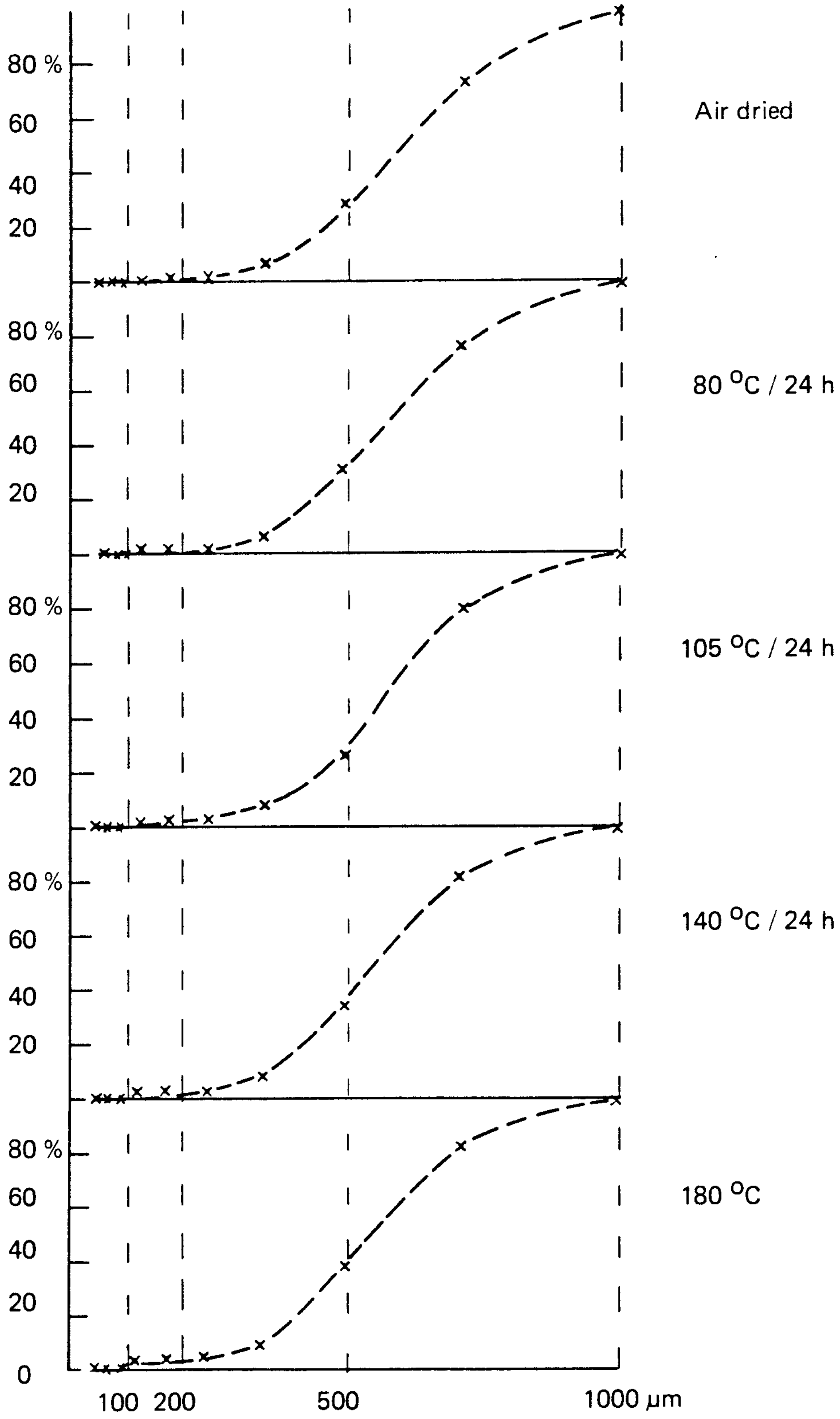


Diagram B.3

Sieving of expended granular resin treated with Na_2SO_4 (Sample 8). Drying temperatures 20, 80, 105, 140 and 180°C.

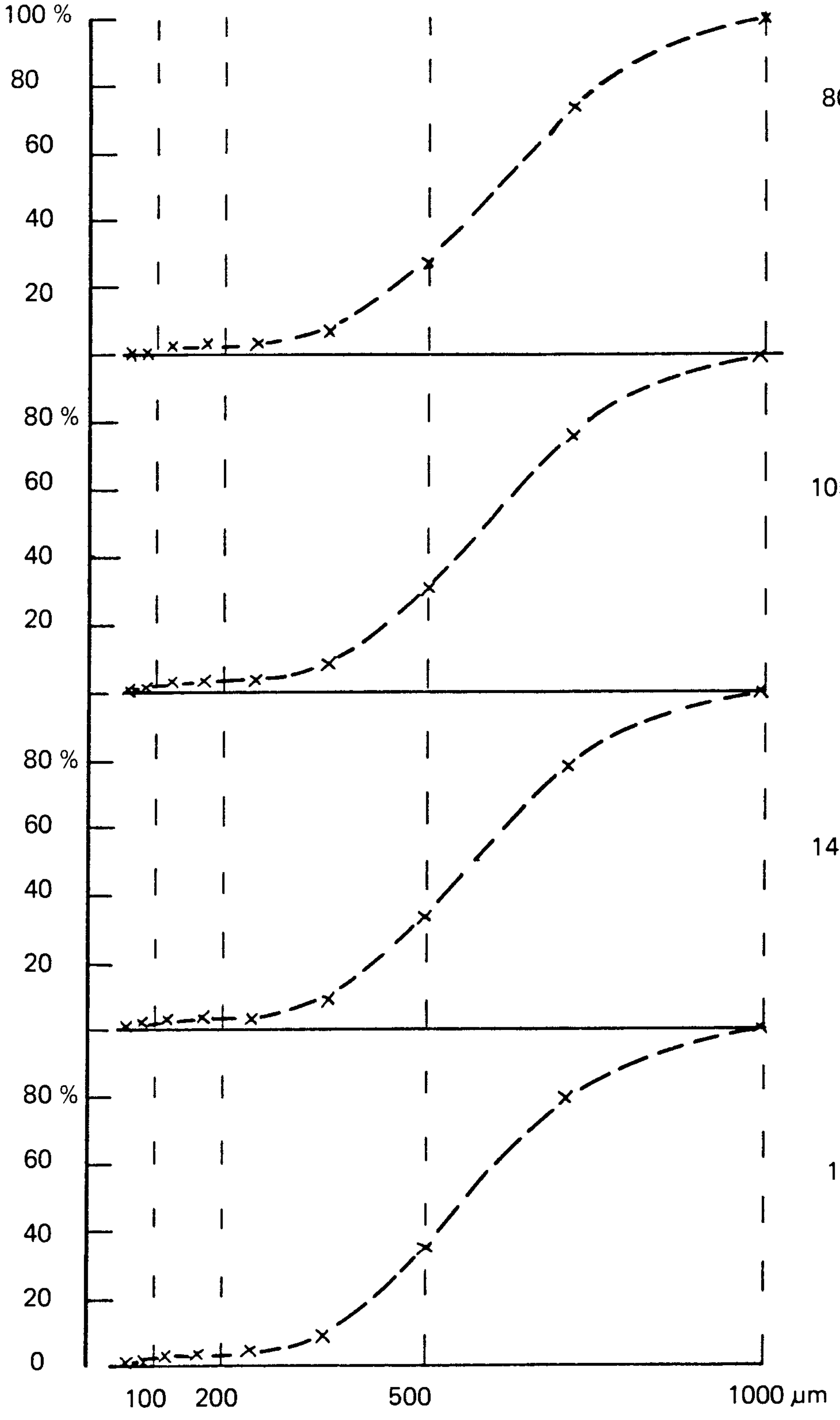
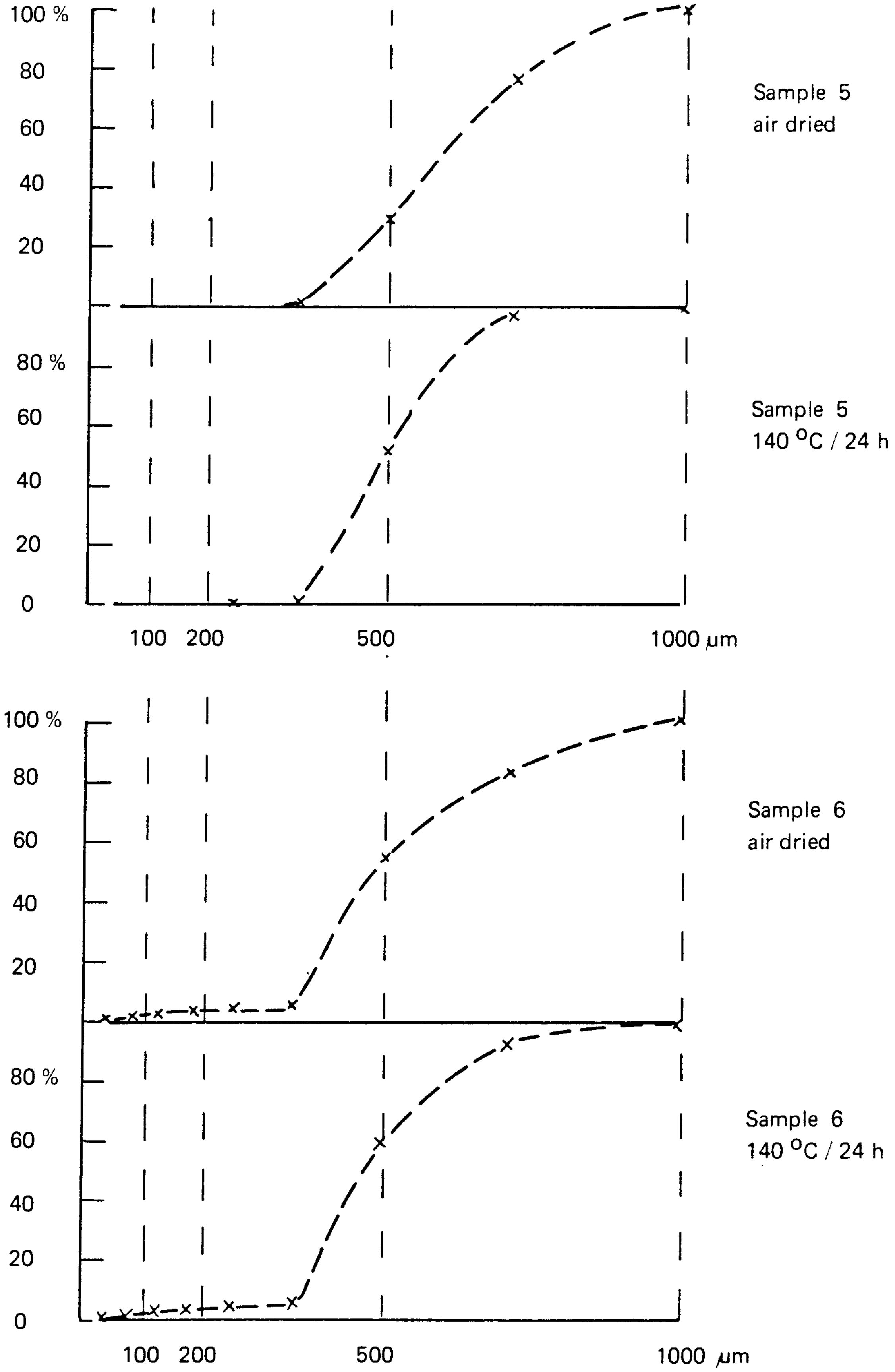


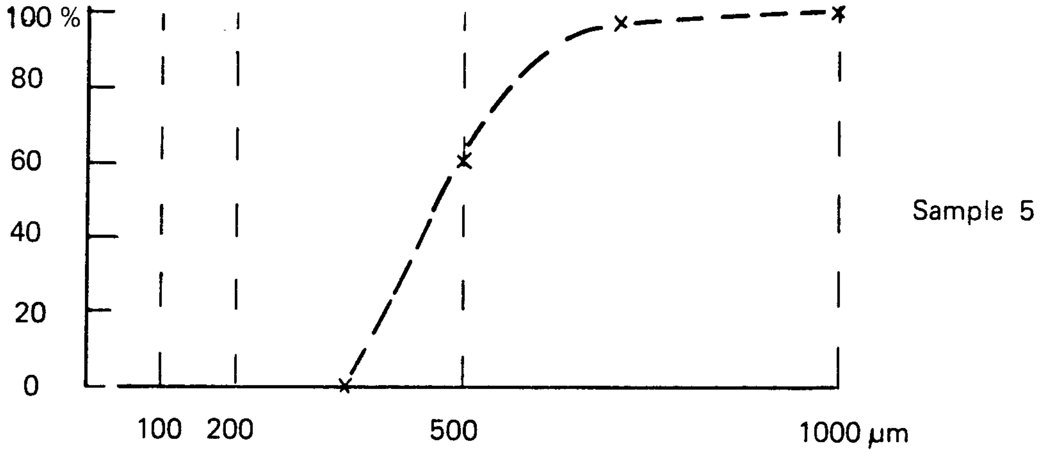
Diagram B.4

Sieving of expended granular resin, treated with Na_2SO_4. (Sample 8) 24 h air exposure after drying at 80, 105, 140 and 180°C.



<u>Diagram B.5</u>

Sieving of new anion resin (Samples 5 and 6). Drying temperatures 20 and 140°C.



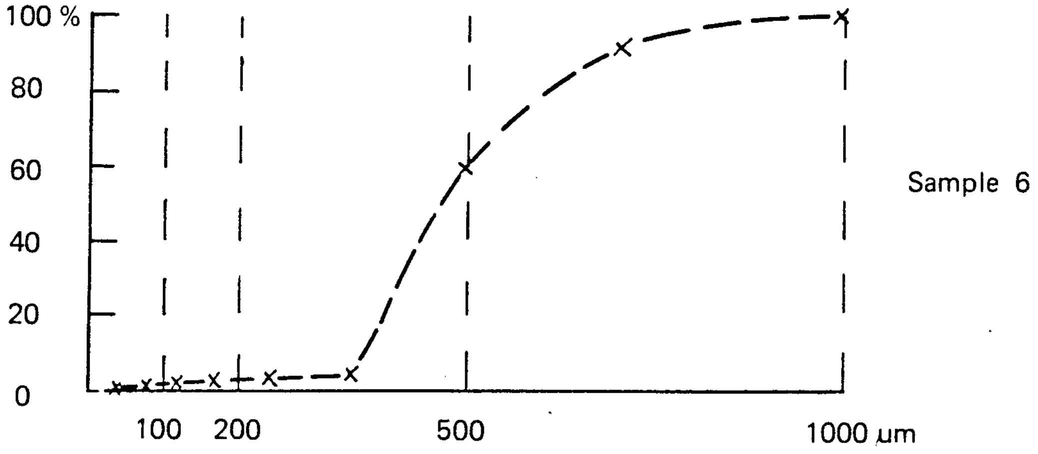


Diagram B.6

Sieving of new anion resin (Samples 5 and 6). 24 h air exposure after drying at 140°C

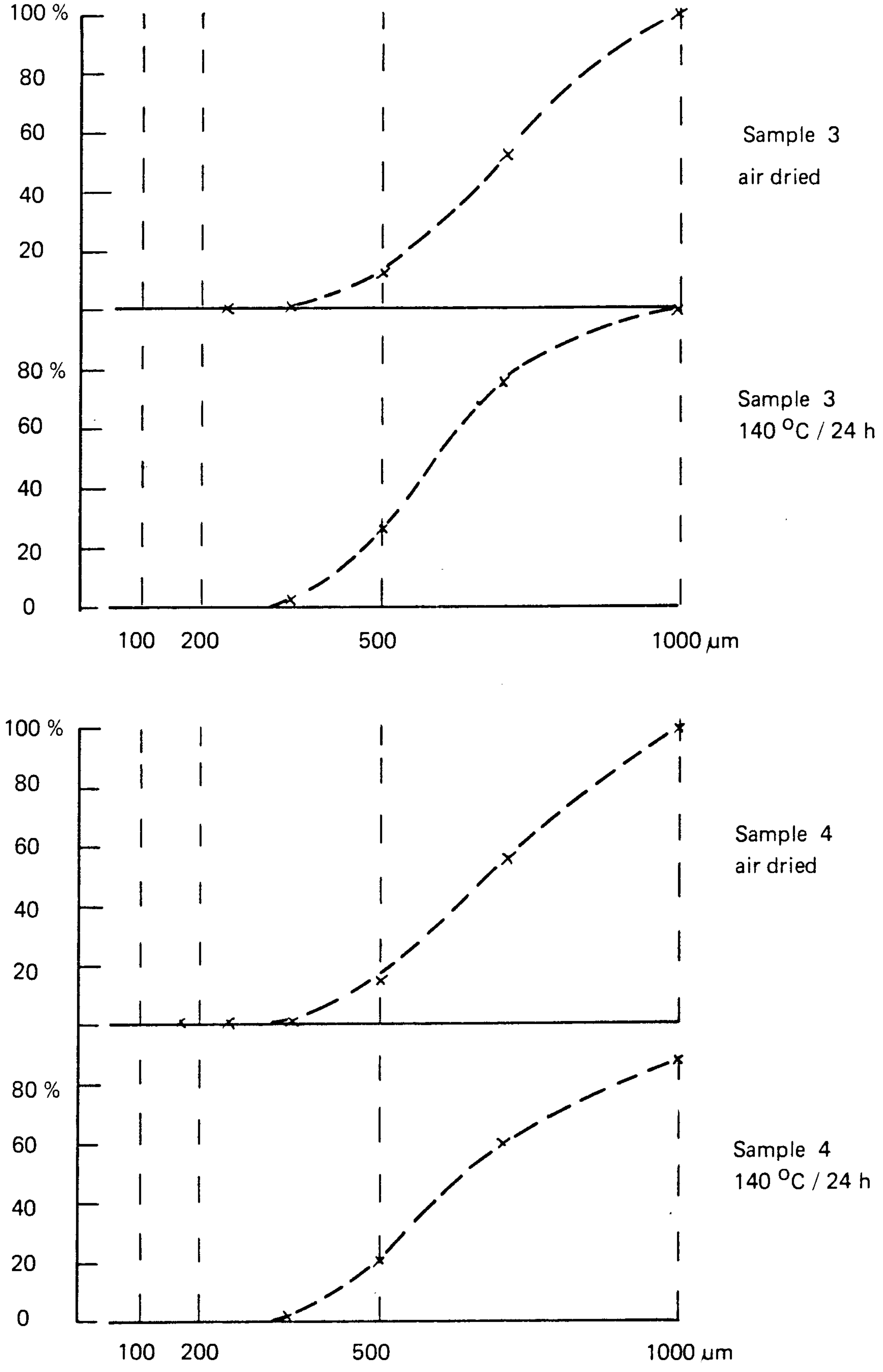
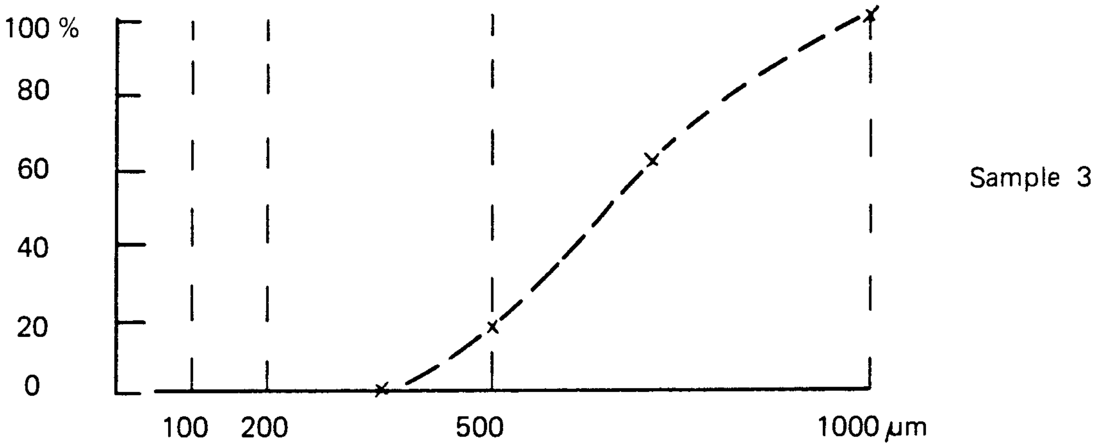


Diagram B.7

Sieving of new cation resin (Samples 3 and 4). Drying temperatures 20 and 140°C.



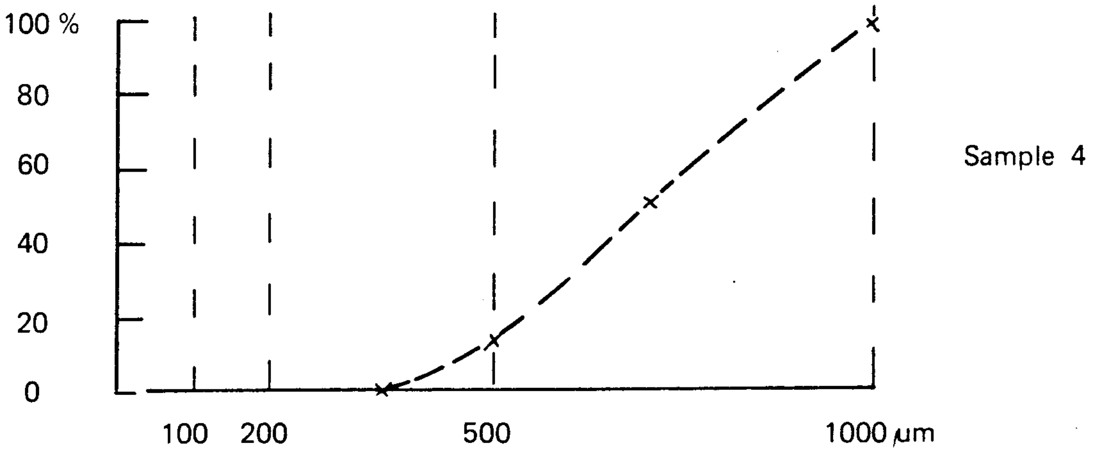


Diagram B.8

Sieving of new cation resin (Samples 3 and 4).
24 h air exposure after drying at 140°C.

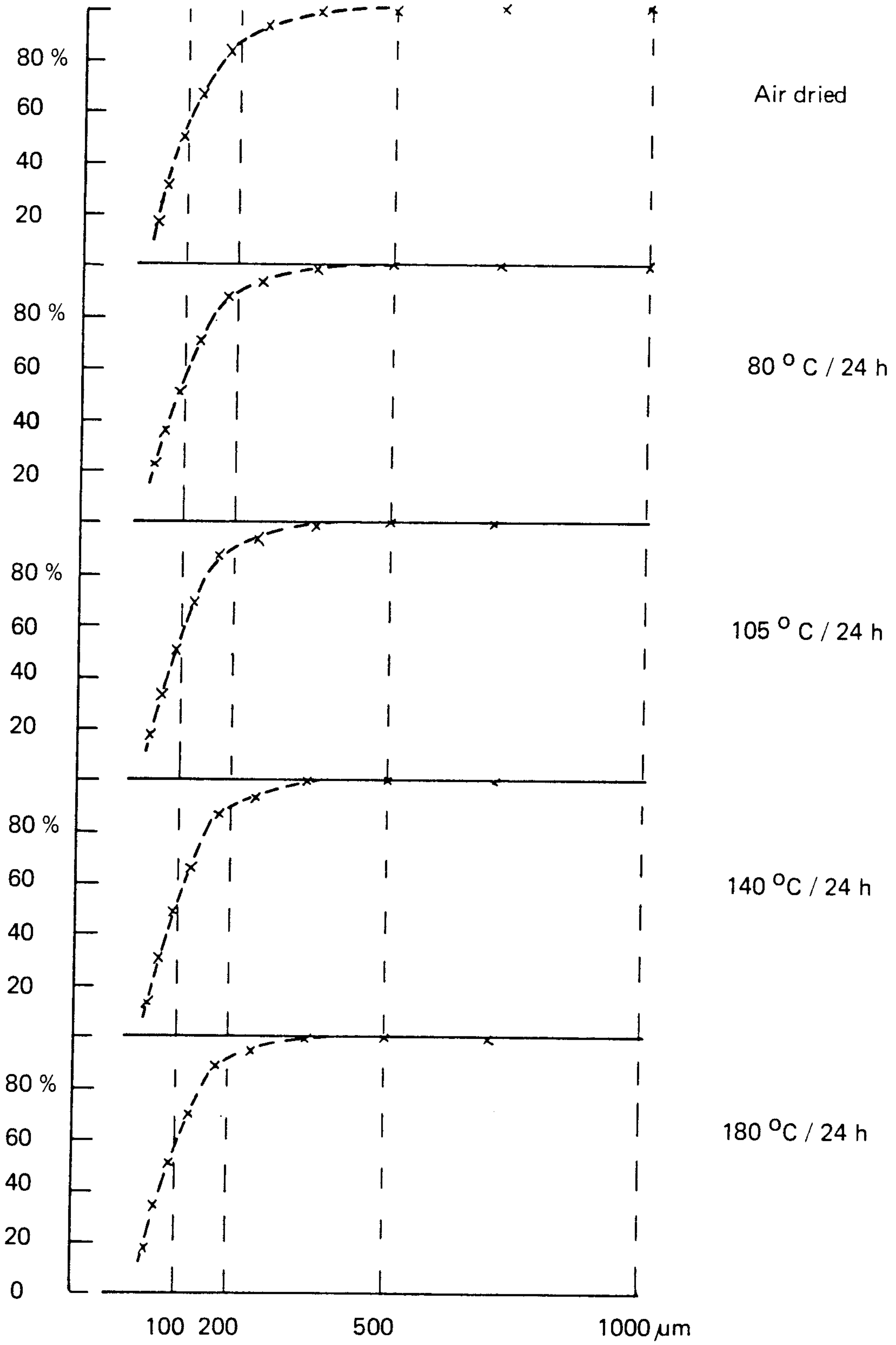


Diagram B.9

Sieving of used powdered resing (Sample 1).
Drying temperatures 20, 80, 105, 140 and 180°C.

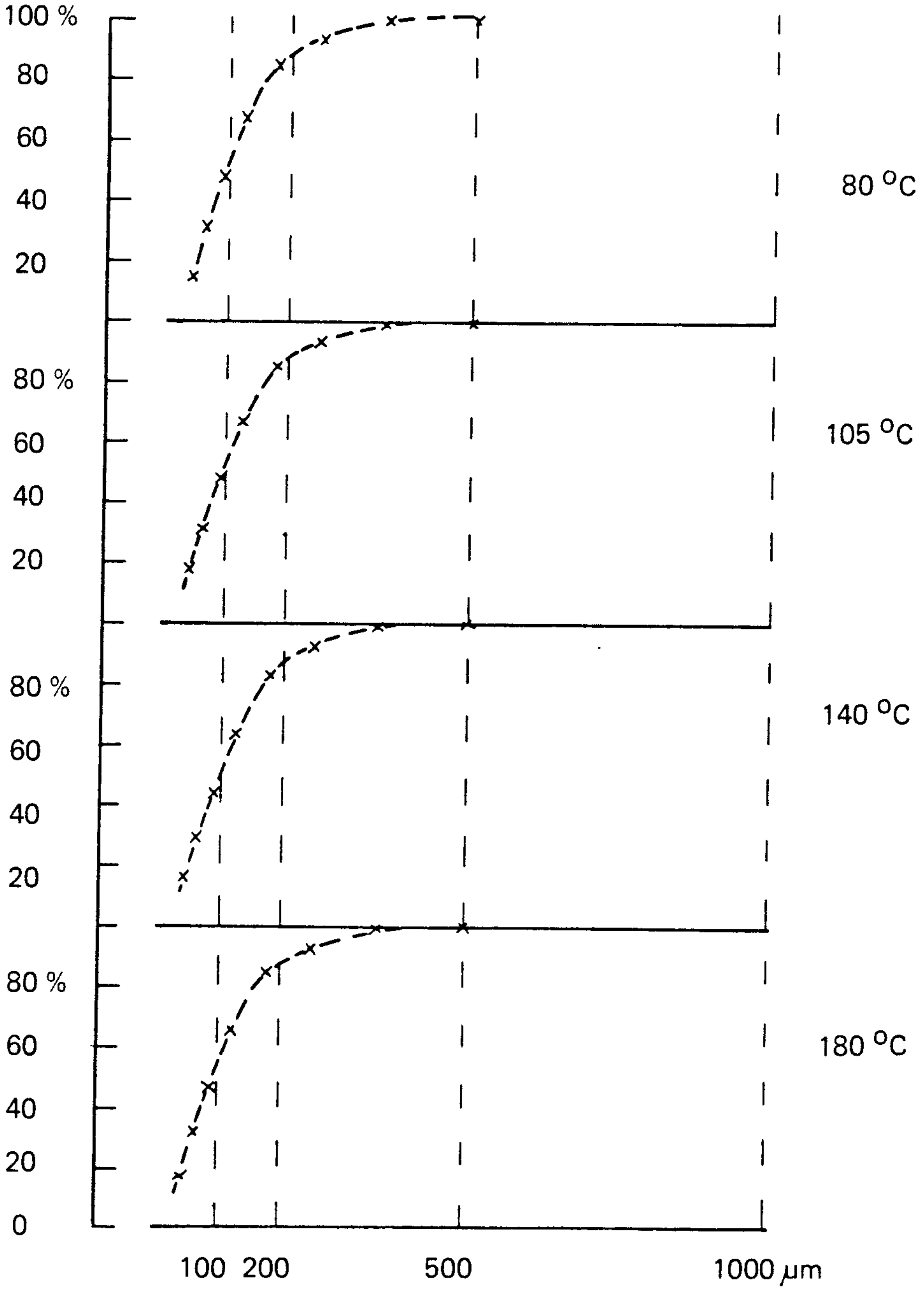


Diagram B.10

Sieving of expended powdered resin (Sample 1). 24 h air exposure after drying at 80, 105, 140 and 180°C.

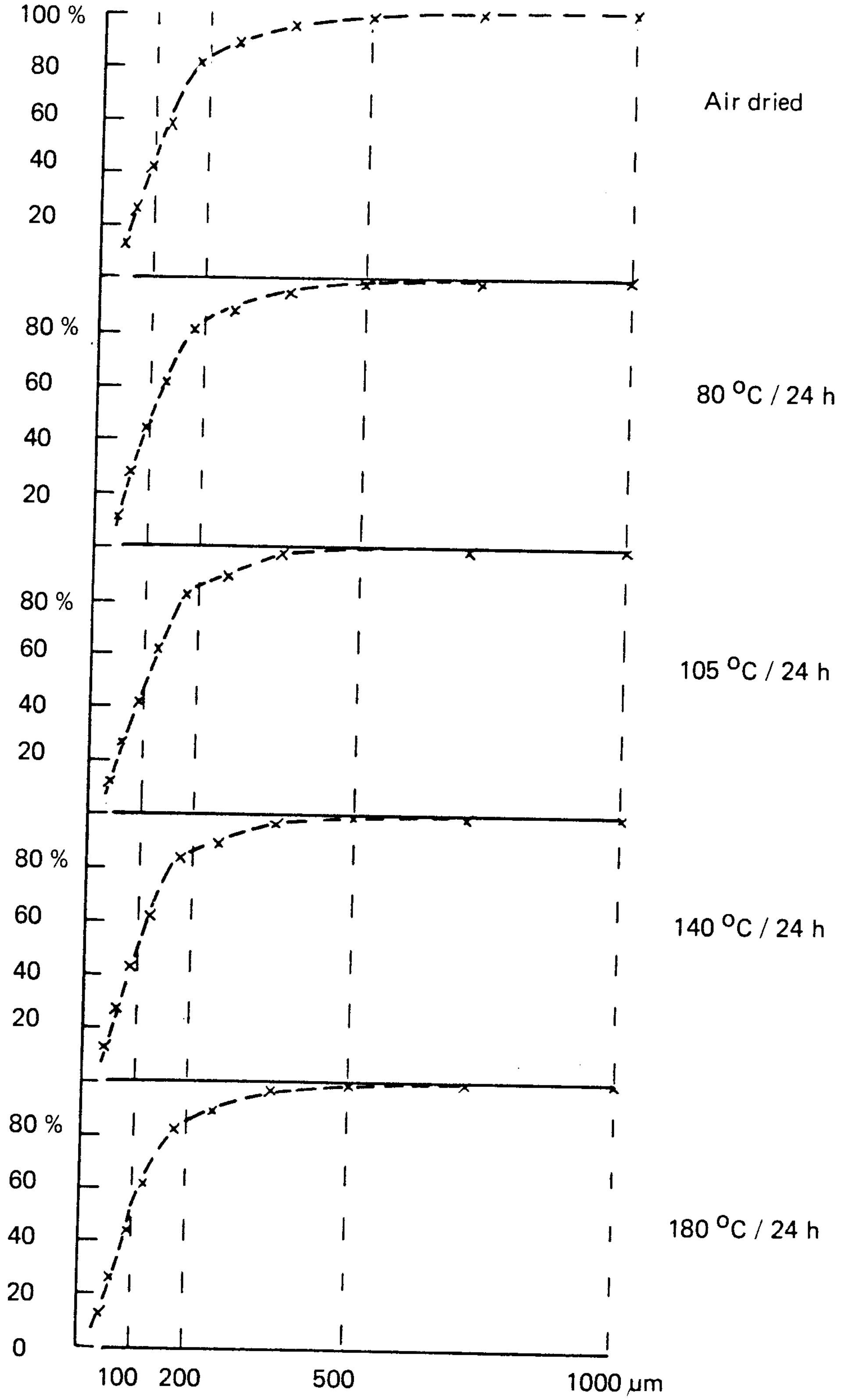


Diagram B.11

Sieving of expended powdered resin, treated with Na_2SO_4 (Sample 2). Drying temperatures 20, 80, 105, 140 and 180°C.

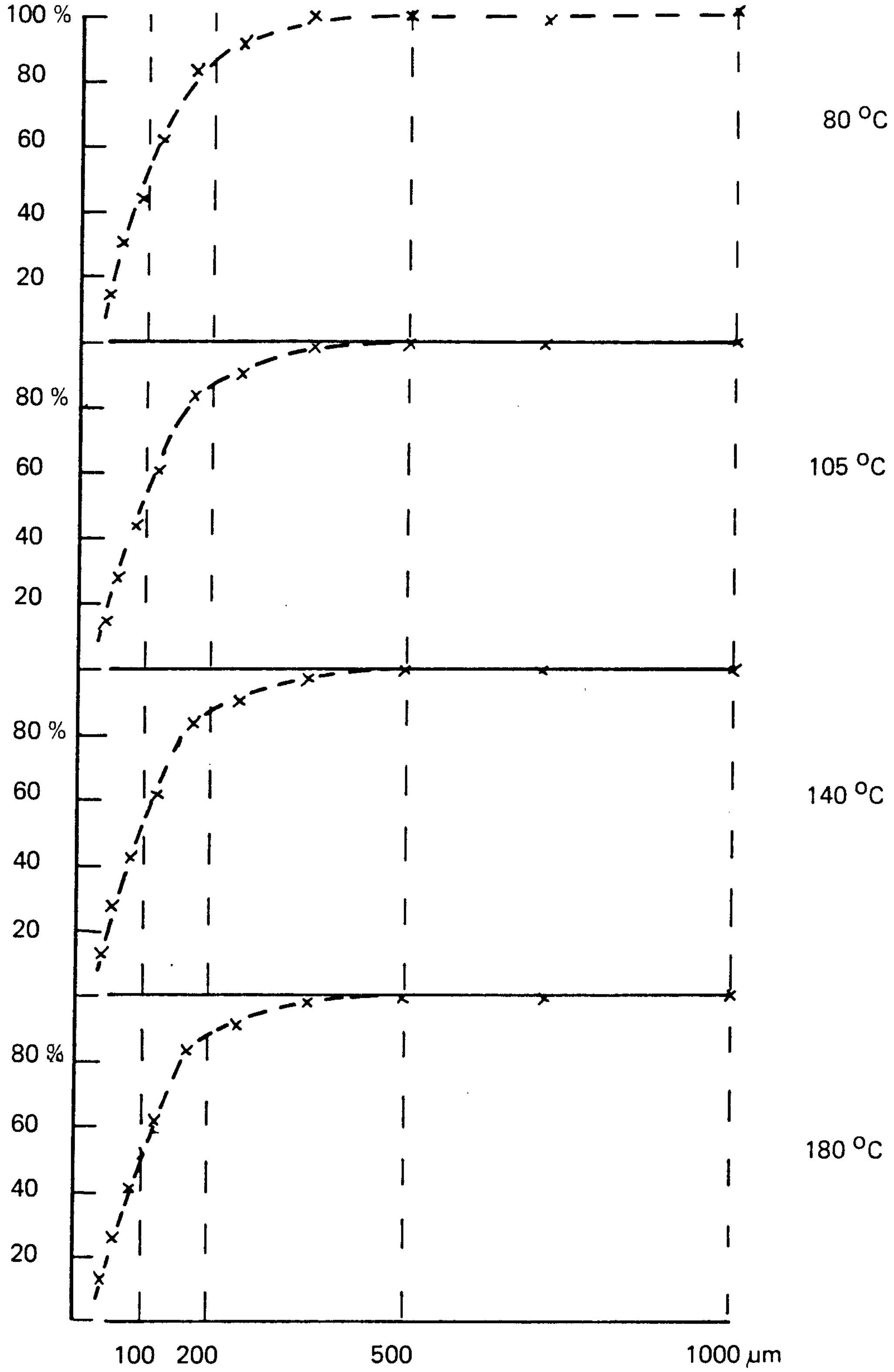


Diagram B.12

Sieving of expended powdered resin, treated with Na_2SO_4 (Sample 2). 24 h air exposure after drying at 80, 105, 140 and 180°C.

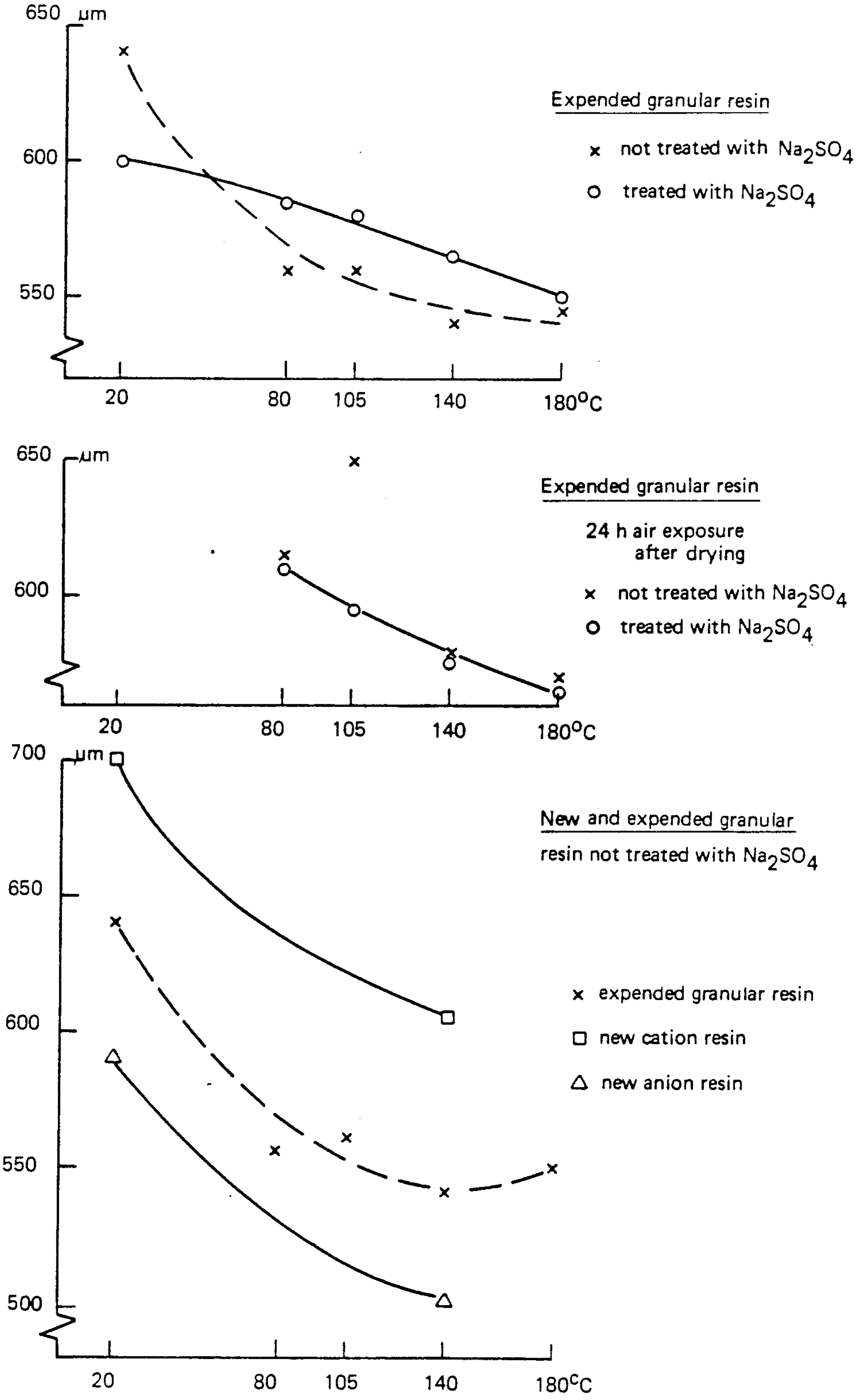


Diagram B.13

"Mean" particle size taken from the sieving curves. The values are the "50 %" level values.

THE SWELLING OF DIFFERENT ION-EXCHANGE MATERIALS IN WATER

TABLE OF CONTENTS

1. INTRODUCTION

Swelling experiments were carried out on expended granular mixed-bed and powdered ion-exchange resins. The effect of Na_2SO as an additive was studied. Some tests with new resins were performed as well. The parameter of interest was the volume change of the resins in water (swelling) as a function of drying temperature and time.

2. EXPERIMENTAL

2.1 Materials

Ion-exchange resins used in this work were:

A	Expended powdered resins (Microinex) from the cold run tests at Forsmark power plant
B	New, granular cation resins (Duolite ARC-351)
C	New, granular anion resins (Duolite ARA-366)
D	Expended granular resins(60 % Duolite ARA-366 and 40 % Duolite ARC-351) from the cold run test at Forsmark power plant

Part of the ion exchange resins has been pretreated with Na_2SO_4. 1 kg anhydrous Na_2SO_4 was addes to 12.5 kg ion-exchange resin/water mixture ("even level"). The sodium sulphate addition is representative to the pretreatment of ion-exchange resins at Barsebäck power plant before solidification in bitumen.

The following samples were used in the experiments

Sample	1	A*
"	2	A + Na_2SO_4
"	3	B
"	4	B + Na_2SO_4
"	5	C
"	6	C + Na_2SO_4
"	7	D
"	8	D + Na_2SO_4

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* Capital letters refer to ion-exchanger used.

2.2 Swelling experiments

2.2.1 Sample preparation

The swelling experments were performed with air dried resins and with heat treated resins. The temperatures used for the heat treatments were 80, 105, 140 and 180°C, and the heating times 0.5 h, 1 h, 24 h and 1 week.

The heat treatment was carried out on an iron tray in a heating chamber.

In Table C.1 a complete list of the test matrix is given.

2.2.2 Experimental procedure

100 g of air dried or heat-treated ion-exchange resin was poured into a 250 ml graduated cylinder which was dropped from a height of ~ 3 cm 100 times in ~ 2 min. The volume was noted (dry volume after shaking) and the density was calculated.

The ion-exchange resin (100 g) was then poured into a 500 ml graduated cylinder containing water. The water level was adjusted to ~ 500 ml, the cylinder opening was covered, and the cylinder was turned upside down a few times until there was a homogeneous mixture of water and ion-exchange resin.

The volume of the ion-exchange resin in the cylinder was noted after 1 h, 24 h and 1 week. A few hours after the start and after the 24 h reading the water-ion-exchange resin mixture was stirred very carefully in order to remove any gas bubbles which had been formed. On the basis of recorded values the swelling percent was calculated.

The swelling is expressed as per cent (S %)

$$S\,\% = \frac{\text{(volume in water)} - \text{(dry volume after shaking)}}{\text{dry volume after shaking}} \times 100\,\%$$

A swelling of 100 % represents a volume increase in water of a factor 2, in comparison with the dried material.

3. RESULTS

The results of the swelling experiements have been collected in the diagrams at the end of this appendix. In Diagrams C.1 - C.6 the swelling in water is shown, for the different ion-exchange resin samples, as a function of drying temperature and time. In Diagram C.7 - C.12 weight, volume and density data are given for the heat treated resins before the swelling experiment was started.

NOTE: It must be noted that swelling in all diagrams is presented in the manner defined in 2.2, using the volume of "oven dried" material as the reference for each drying temperature.

In Tables C.2 and C.3 the volume after swelling is compared instead with the volume of air dried resins. The first method is relevant for determining the potential for the swelling of resins in waste products, whilst the latter method gives the true value of the final volume of a certain amount of ion-exchange resin. In the following the results are commented for each sample type.

3.1 Expended granular resins (mixed bed)

From Diagram C.1 the following results can be seen:

- Resins dried in air at room temperature swelled in water ~ 80 %

- Treatment at 80°C will double the swelling compared to the swelling of air dried resins for all treatment times. The same result is obtained for heat treatment at 105°C for less than 1 day or at 140°C less than 1 hour

- Treatment at 140°C for more than 1 hour or treatment at 180°C gives a markedly reduced swelling capacity (40 %). The volume after heat treatment and swelling is less than the original volume of air dried resins (Table C.2).

3.2 New granular resins

To find out if the swelling in mixed-bed resins is due to anionic or cationic resins, experiments were performed using new resin materials: "Duolite ARC-361" and "Duolite ARA-366" for cationic and anionic resin respectively. Two different drying temperatures, 105°C and 140°C, were used. The results are shown in Diagrams C.3 and C.4.

3.2.3 Comparison between new anion and cation and expended mixed-bed resins

When comparing the swelling of expended granular mixed-bed resins (anion: cation ~ 60:40) with the individual swelling properties of anion and cation resins it can be seen that:

- Anionic resins constitute 65 - 75 % and cationic resins 25 - 35 % of the swelling in water for drying times shorter than one day and drying temperatures below 140°C.
- The cationic resins are responsible for the swelling in water after treatment for longer times and higher drying temperatures

In Table C.4 a calculation of the swelling behaviour of a hypothetical mixed-bed resin is compared to the measured behaviour of the expended mixed-bed resins. The hypothetical resin is a mixture of 60 % new anion and 40 % new cation resins. The results are very similar. The small deviations depend mainly up on experimental conditions, and the variations of resin moisture after air drying. This indicates that the swelling in mixed-bed resins before and after drying is proportional to the behaviour of individual resin fractions.

3.3 Expended powdered resins

The results obtained in experiments with powdered resins (Diagram C.5) are similar to those with granular resins. However, two large differences can be seen:

- The absolute level of swelling registered is about 50 - 90 % higher for powdered resins than for granular resins. This is due to the fact that some "extra water" can be absorbed in between the smaller particles of the powdered resins.
- However, it appears that a longer heating time is needed to reach the same result as for granular resins at each temperature.

3.4 The effect of Na_2SO_4 as an additive

In order to study the possibility reducing the swelling of ion-exchange resins (mixed-bed, anion and cation resins) in water after the thermal treatment, Na_2SO_4 was added to resins and tests corresponding to those for untreated resins were made.

3.4.1 Expended granular resins (mixed-bed) (Diagram C.2)

Results obtained in experiments were:

- The swelling of Na_2SO_4 treated resins after air drying at room temperature is ~ 110 %, compared to ~ 80 % for untreated resins.
- Na_2SO_4 treatment of resins only have a small effect on the swelling properties of heat treated resins

3.4.2 New granular resins

Anion exchange resins (Diagram C.3)

- The swelling of Na_2SO_4 treated resins after air drying at room temperatures is ~ 100 % compared to ~ 70 % for untreated resins.
- The addition of Na_2SO_4 inhibits the increased swelling found for untreated anionic resins after short treatment times.
- For longer drying times (> 1 day) the Na_2SO_4 treatment has no effect

Cation exchange resins (Diagram C.4)

- The addition of Na_2SO_4 will reduce the swelling of heat treated resins to 80 %, as compared to 110 % for untreated resins at the temperatures used.

3.4.3 Comparison between new anion and cation and expended mixed-bed resins

The effect of Na_2SO_4 additions on the swelling properties after heat treatment is stronger on the new anion and cation resins than on the expended mixed-bed resins. A comparison is given in Tables C.2 and C.4.

3.4.4 Powdered resins

The addition of Na_2SO_4 had a drastic effects on the swelling properties of the powdered resins, both for air dried and heat treated resins. After the addition of Na_2SO_4 the swelling was practically the same for all treatment temperatures and times: about 80 %. This is probably due to the electrolytic nature of Na_2SO_4; the salt solution reacts with the ion-rechange resin and thus causes the decrease in swelling properties. It can also be seen that the "extra" water up take found for powdered resins not treated with Na_2SO_4 does not occur for Na_2SO treated powdered resins, Diagram C.6.

4. CONCLUSIONS

In this study the swelling/shrinking properties of different ion-exchange materials have been studied in air and water as a function of the drying time and -temperature. The effect of sodium sulphate as a possible swelling inhibiting additive was studied.

The swelling in water was considerable for all the ion-exchange materials studied after different thermal treatments. The maximum swelling in general was obtained after drying these materials for short times at low treatment temperatures. By successively increasing the treatment time and temperature the swelling could be reduced.

The use of sodium sulphate (Na_2SO_4) as an additive had only a minor effect on the swelling behaviour of expended granular mixed-bed resins. For new anionic granular resin the Na_2SO_4 treatment inhibits the increased swelling found for untreated anionic resins after short treatment times. No effect was observed after the Na_2SO_4 of new cationic resins.

The addition of sodium sulphate to powdered resins had, contrary to the case for granular resins, a drastic effect. The influence on the swelling properties of the heat treatment is totally inhibited. The swelling is almost the same after heat treatment at all the different temperatures and times, Table C.3.

In this study the swelling of both Na_2SO_4-treated and untreated mixed-bed resins could be calculated very accurately on the basis of the individual volume changes of anion and cation resins in water, Table C.4. This indicates that the swelling in this material is proportional to the behaviour of individual resin fractions.

Table C.1

Samples used in the swelling experiments.

Sample	Heating time	Temperature °C			
		80	105	140	180
1	0.5 h	x	x	x	x
"	1 h	x	x	x	x
"	24 h	x	x	x	x
"	1 week	x	x	x	x
2	0.5 h	x	x	x	x
"	1 h	x	x	x	x
"	24 h	x	x	x	x
"	1 week	x	x	x	x
3	1 h		x	x	
"	24 h		x	x	
"	1 week		x	x	
4	1 h		x	x	
"	24 h		x	x	
"	1 week		x	x	
5	1 h		x	x	
"	24 h		x	x	
"	1 week		x	x	
6	1 h		x	x	
"	24 h		x	x	
"	1 week		x	x	
7	0.5 h	x	x	x	x
"	1 h	x	x	x	x
"	24 h	x	x	x	x
"	1 week	x	x	x	x
8	0.5 h	x	x	x	x
"	1 h	x	x	x	x
"	24 h	x	x	x	x
"	1 week	x	x	x	x

Table C.2 Granular resins

The swelling of mixed bed, anion and cation resins in water in comparison to the air dried resins

The volume of air dried resins $V_{1-3} = 1$

t=(h) / T °C	MIXED BED - RESINS 0.5	1	24	168	CATION RESIN 0.5	1	24	168	ANION RESIN 0.5	1	24	168	REMARKS
20				1.84				1.56				1.71	V_1/m_1 = 133 ml/100g
80	3.01	2.52	2.31	2.16									V_2/m_2 = 129 ml/100g
105	2.94	2.67	1.97	1.32		1.56	1.59	1.65		2.99	2.35	1.25	V_3/m_3 = 152 ml/100g
140	2.54	2.07	1.01	0.97		1.55	1.50	1.55		2.36	0.70	0.65	
180	1.50	1.11	0.98	0.95									
	V_1				V_2				V_3				

The swelling of Na_2SO_4-treated resins

The volume of air dried resins $V_{4-6} = 1$

t=(h) / T °C	0.5	1	24	168	0.5	1	24	168	0.5	1	24	168	REMARKS
20				2.12				1.50				1.97	V_4/m_4 = 132 ml/100g
80	2.49	2.70	2.68	2.37									V_5/m_5 = 121 ml/100g
105	2.64	2.80	1.64	1.33		1.46	1.49	1.53		1.99	1.78	1.23	V_6/m_6 = 143 ml/100g
140	2.48	1.78	1.17	1.19		1.50	1.43	1.47		1.84	0.86	0.73	
180	1.61	1.14	1.09	1.14									
	V_4				V_5				V_6				

Table C.3 Powdered resins

The swelling of powdered resin in water in comparison to the air dried resins

The volume of air dried resins V_1* = 1 (164 ml)

T °C \ t = (h)	1/2	1	24	168
20				2.70
80	2.78	2.75	2.84	2.80
105	2.72	2.76	2.63	2.01
140	2.66	2.61	2.24	1.34
180	2.45	1.66	1.36	1.23

Na_2SO_4 - treated resins V_2* = 1

T °C t = (h)	1/2	1	24	168
20				1.83
80	1.71	1.79	1.82	1.79
105	1.72	1.72	1.78	1.72
140	1.66	1.79	1.79	1.87
180	1.74	1.74	1.74	1.66

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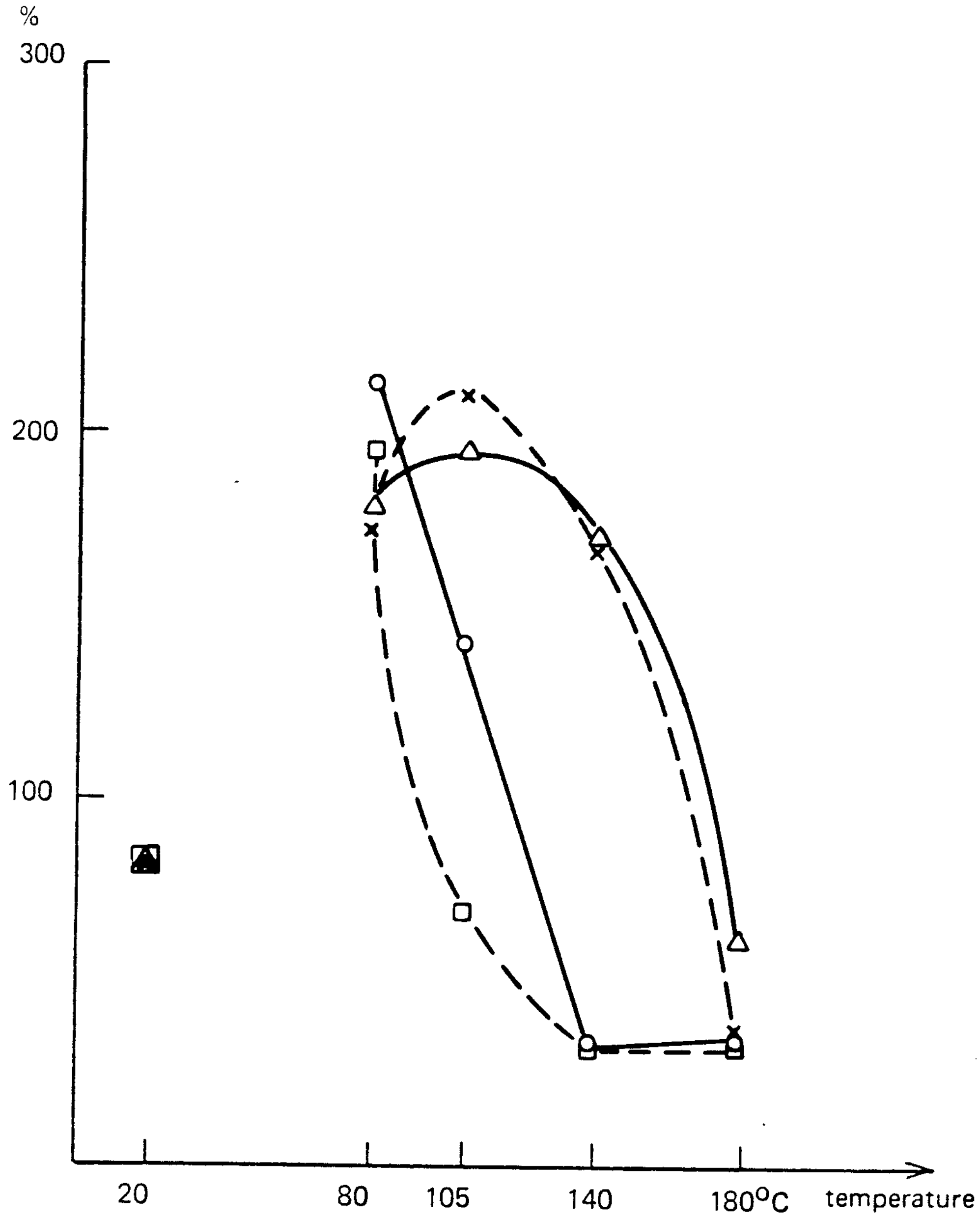
* V_1 = 164 ml

* V_2 = 143 ml

Table C.4 Calculated swelling in the mixed bed resins on the basis of individual swelling of anionic and cationic components (mixed resin, an:cat = 60:40)

A comparison with the observed swelling in used mixed-bed resins.

	GRANULAR NEW RESINS				MIXED-BED RESINS	
	Anionic component		Cationic component		Volumes in water (ml)	
	swelling factor	volume (ml)	swelling factor	volume (ml)	calculated	observed average
20°C	V_A = 80 ml		V_C = 53 ml			
168 h	1.71	137	1.56	83	220	245
105°C						
1 h	2.99	239	1.56	83	322	355
24 h	2.53	202	1.59	84	286	262
168 h	1.25	100	1.65	87	187	175
140 °C						
1 h	2.36	189	1.55	82	271	275
24 h	0.70	56	1.50	80	136	134
168 h	0.65	52	1.55	82	134	129
			Na_2SO_4 - treated resins			
20 °C	V_A = 79 ml		V_C = 53 ml			
168 h	1.97	156	1.50	80	235	275
105 °C						
1 h	1.99	157	1.46	77	235	370
24 h	1.78	141	1.49	79	220	216
168 h	1.23	97	1.53	81	178	176
140 °C						
1 h	1.84	145	1.50	80	225	235
24 h	0.86	68	1.43	76	144	154
168 h	0.73	56	1.47	78	136	157



$$^{*}\text{Swelling (\%)} = \frac{\text{volume in water} - \text{volume after shaking}}{\text{volume after shaking}} \times 100\%$$

Diagram C.1 EXPENDED GRANULAR MIXED BED RESIN
Swelling* as a function of drying
temperatures and times.

△ = 1/2 h ○ = 1 d
× = 1 h ☐ = 1 week

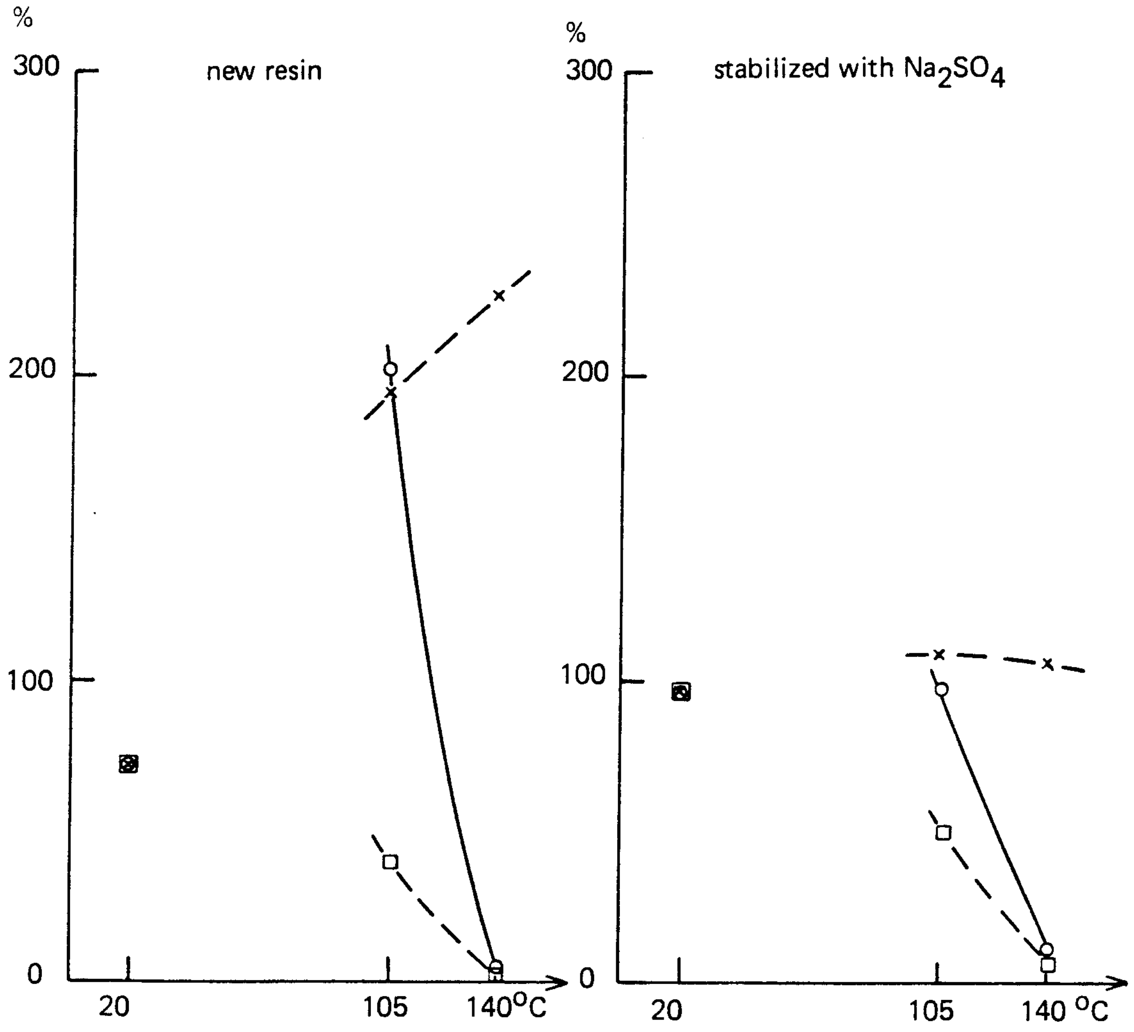


Diagram C.3 GRANULAR ANION - EXCHANGE RESIN
Swelling after different drying times
at different temperatures

x = 1 h ☐ = 1 week

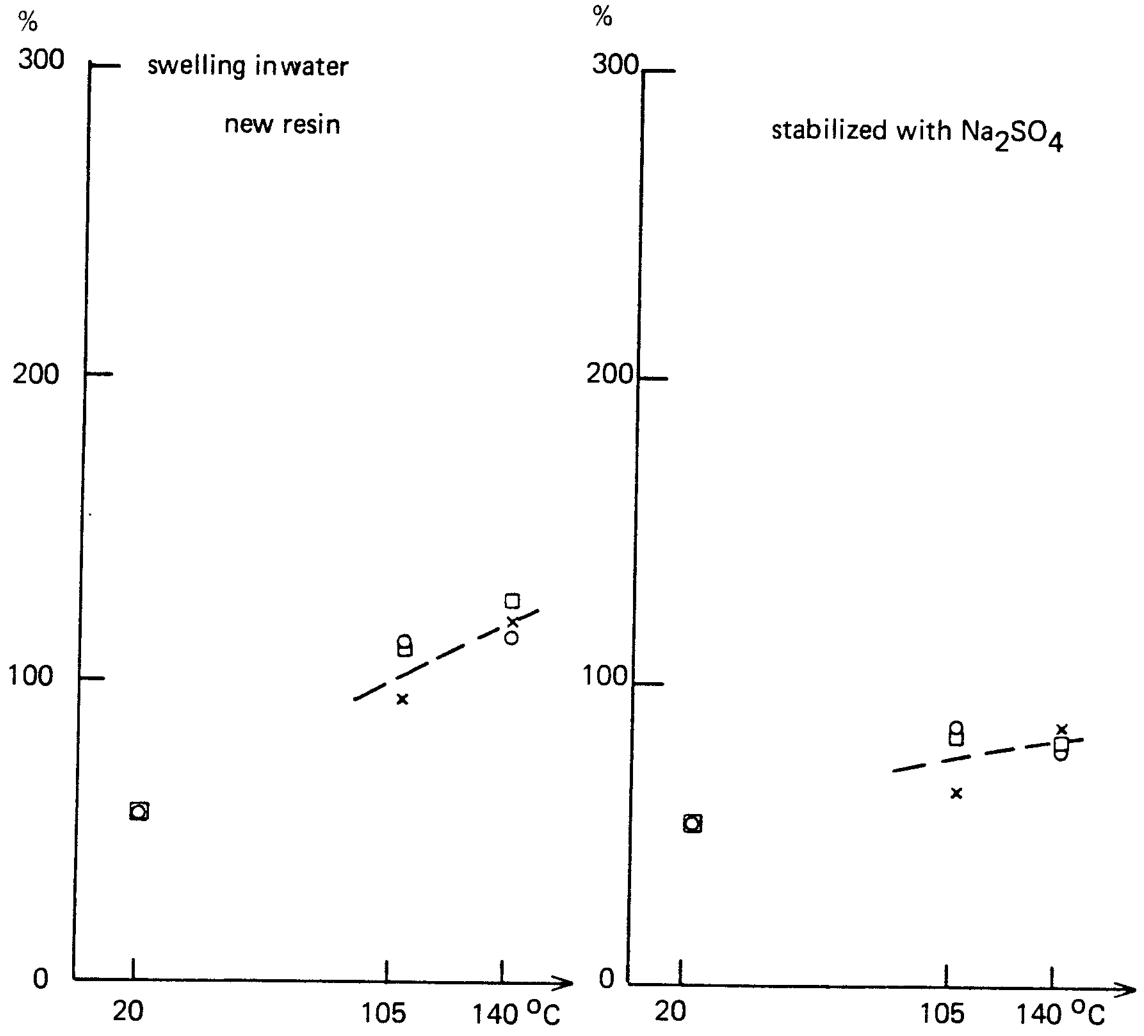
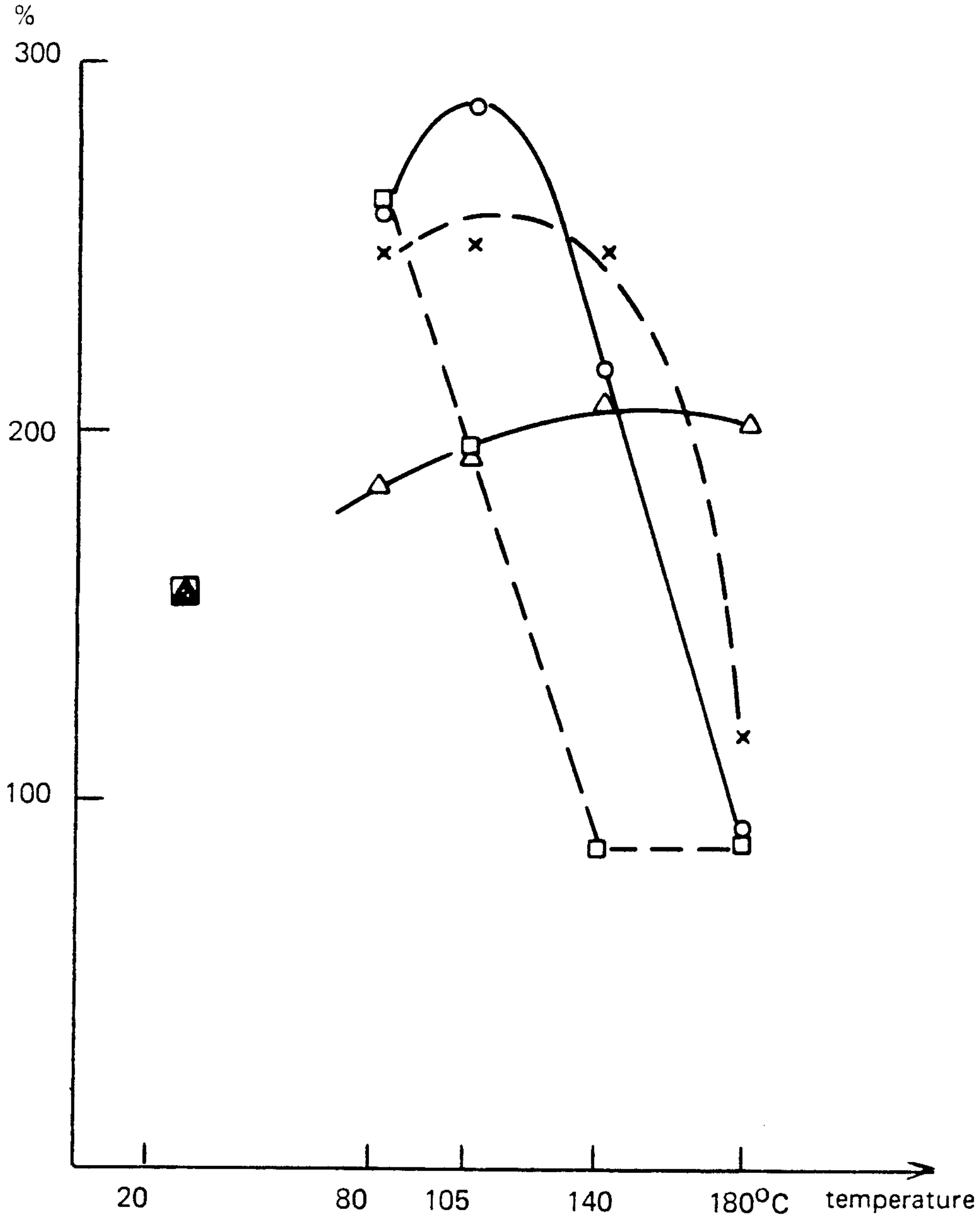


Diagram C.4 GRANULAR CATION - EXCHANGE RESIN
Swelling after different drying times
at different temperatures

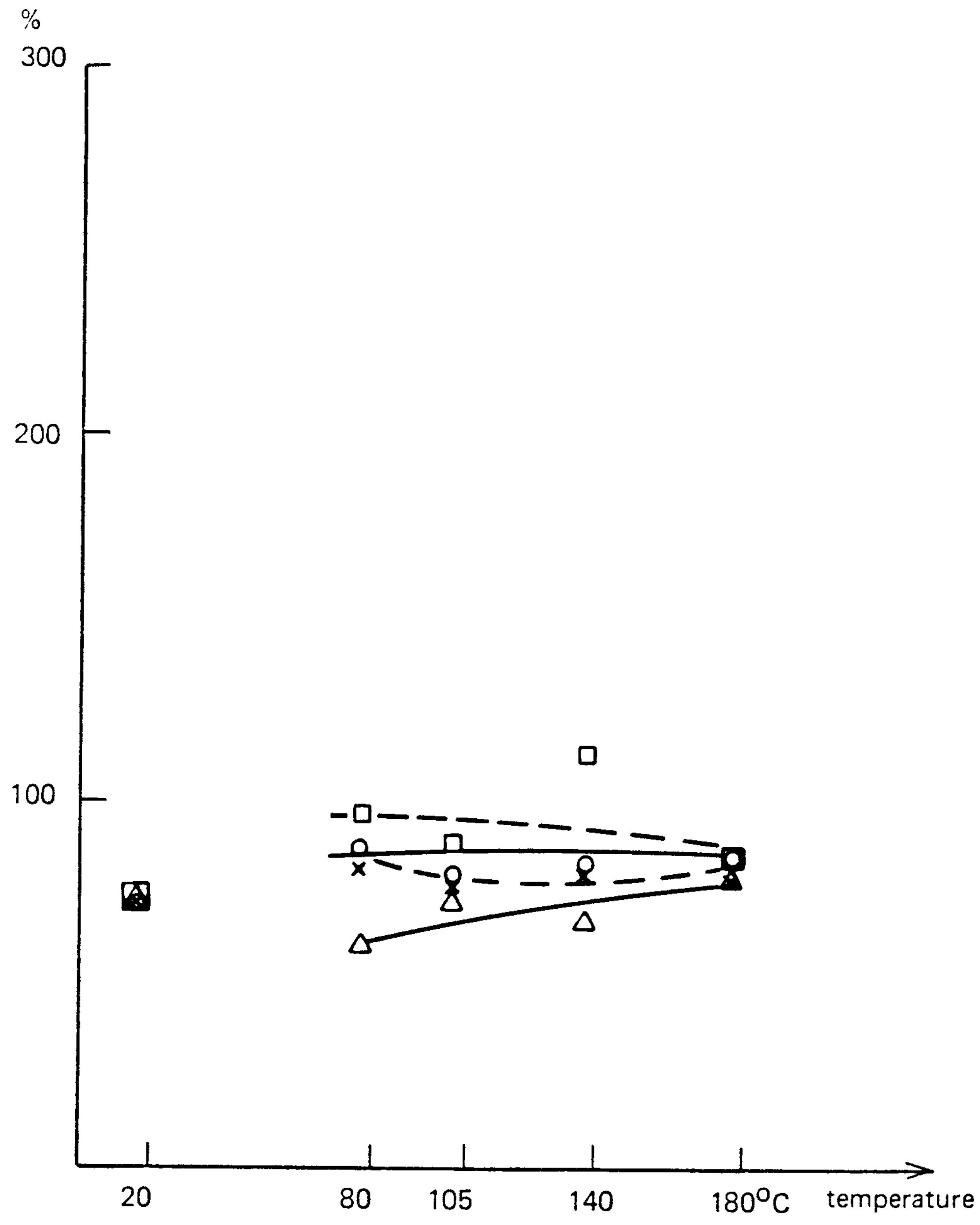
× = 1 h ○ = 1 d □ = 1 week



$$^{*}\text{Swelling (\%)} = \frac{\text{volume in water} - \text{volume after shaking}}{\text{volume after shaking}} \times 100\%$$

Diagram C.5 EXPENDED POWDERED RESIN
Swelling* as a function of drying temperatures and times

△ = 1/2 h × = 1 h □ = 1 week



$$^*\text{Swelling (\%)} = \frac{\text{volume in water} - \text{volume after shaking}}{\text{volume after shaking}} \times 100\%$$

Diagram C.6 EXPENDED RESIN, Na_2SO_4 stabilized
Swelling* as a function of drying temperatures and times

△ = 1/2 h
x = 1 h
○ = 1 d
□ = 1 week

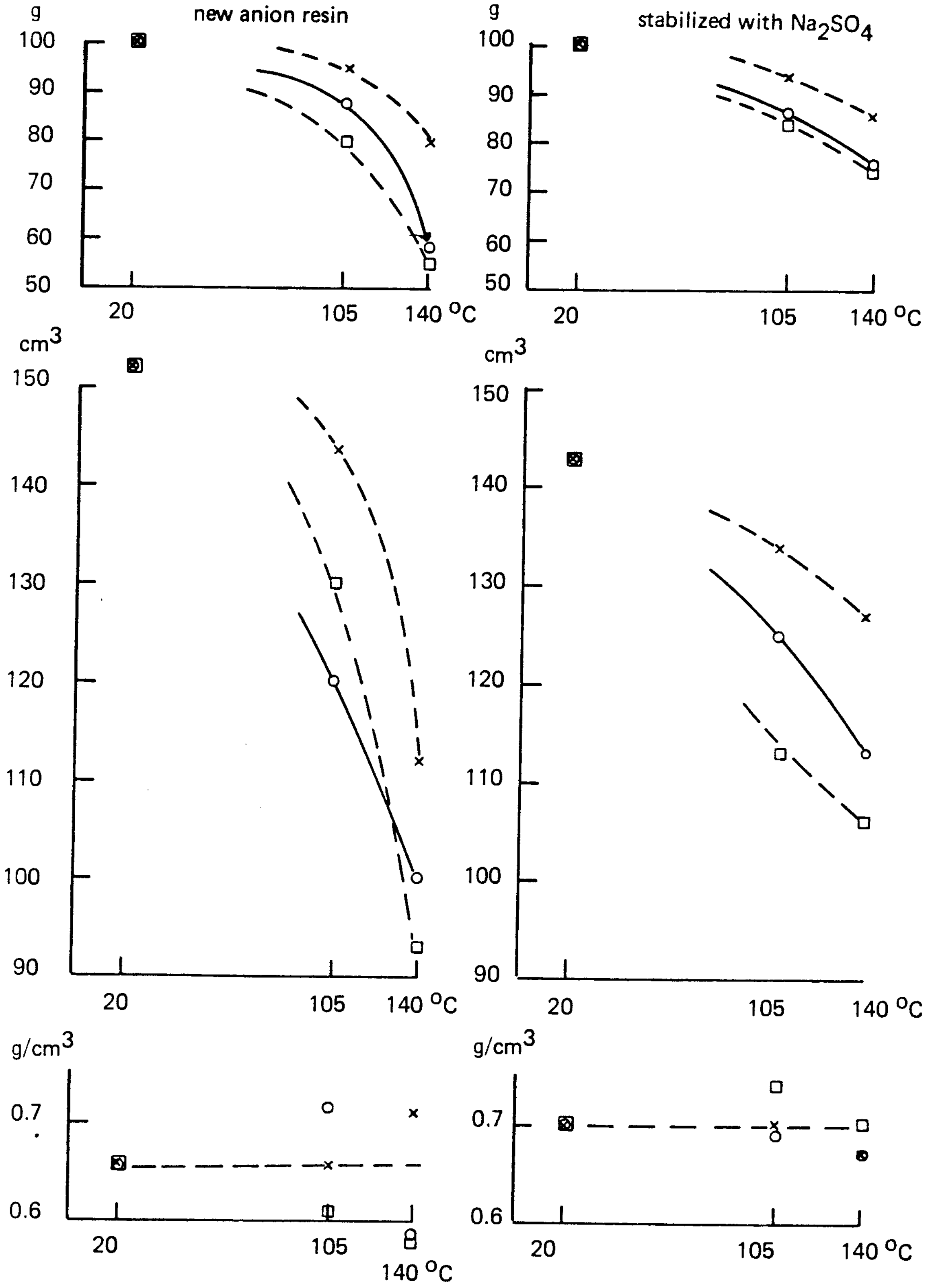


Diagram C.7 GRANULAR ANION - EXCHANGER RESIN
Weight, volume and "density after shaking" after drying.

× = 1 h ○ = 1 d □ = 1 week

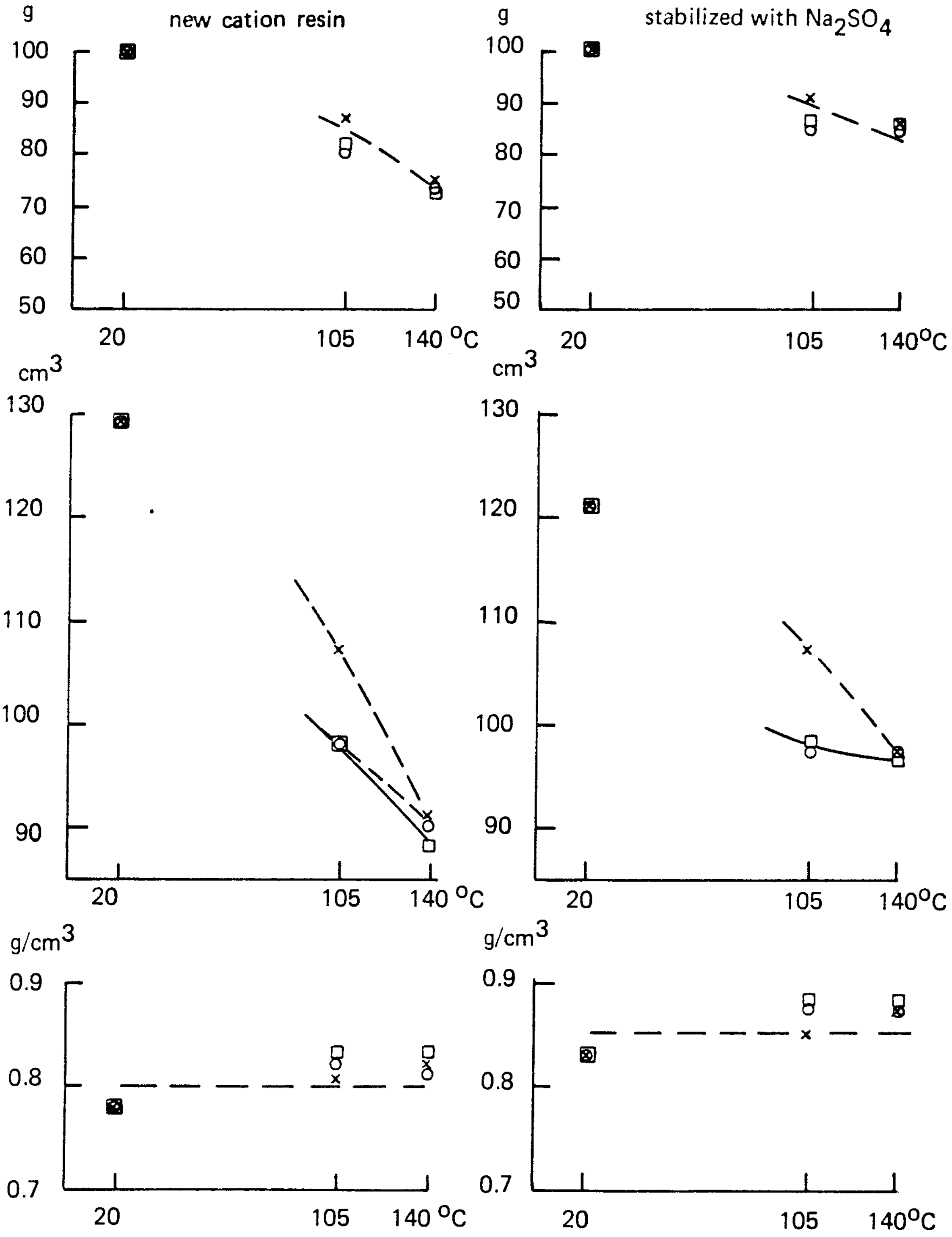


Diagram C.8 GRANULAR CATION - EXCHANGE RESIN
Weight, volume and "density after shaking" after drying

x = 1 h   O = 1 d   ☐ = 1 week

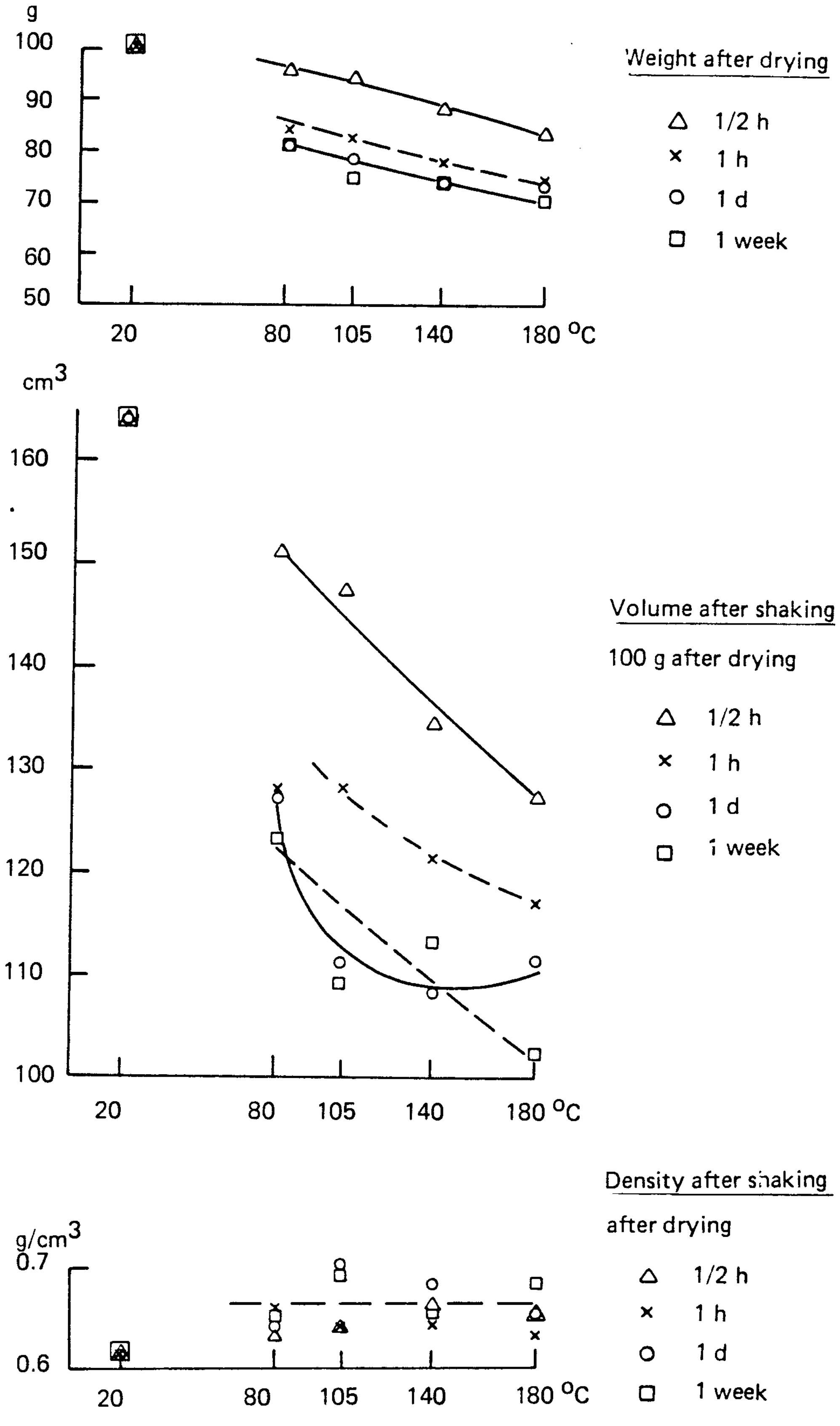


Diagram C.9 EXPENDED POWDERED RESIN
Weight "volume and density after shaking" after drying

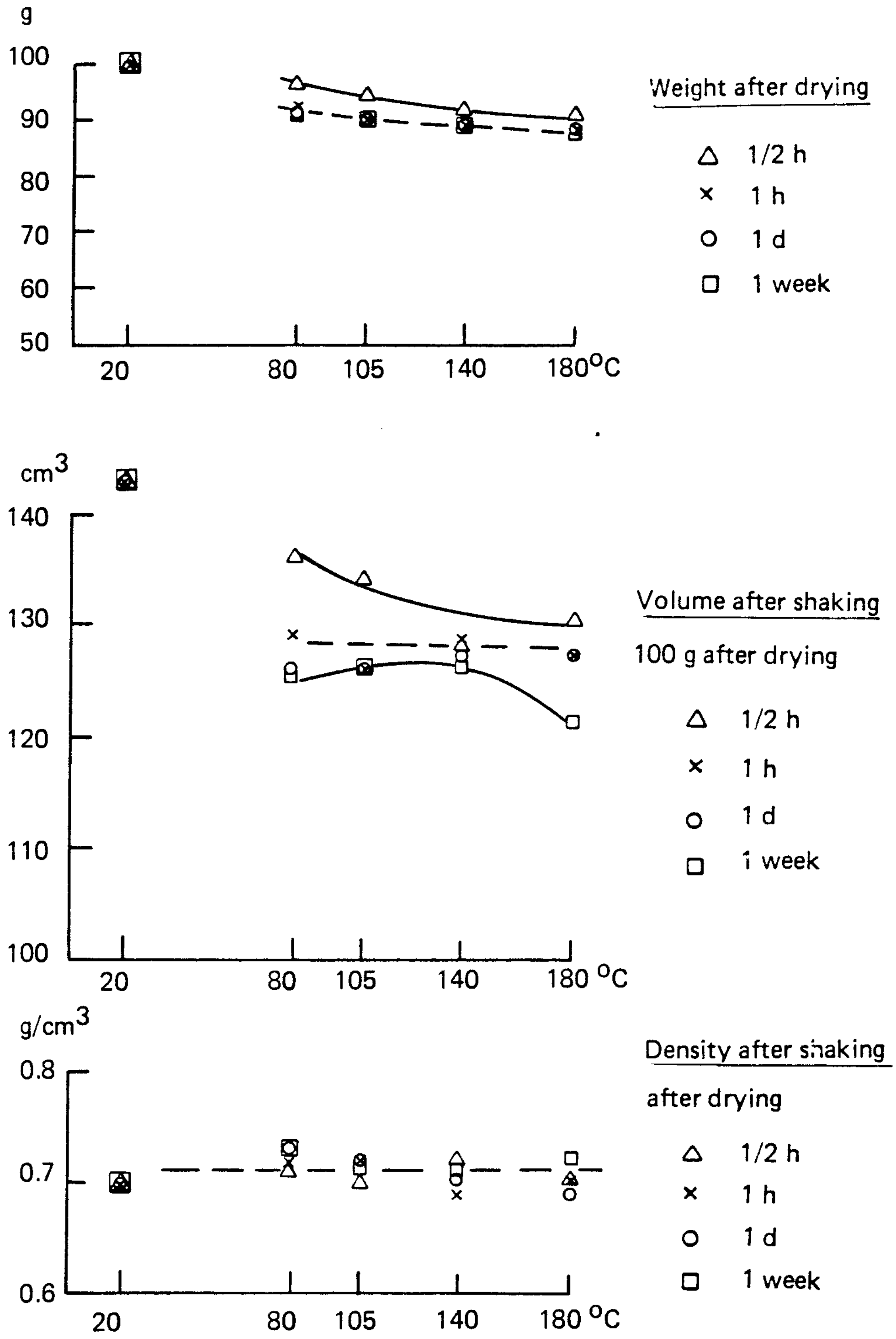


Diagram C.10 EXPENDED POWDERED RESIN
Stabilized with Na_2SO_4
Weight "volume and density after shaking" after drying

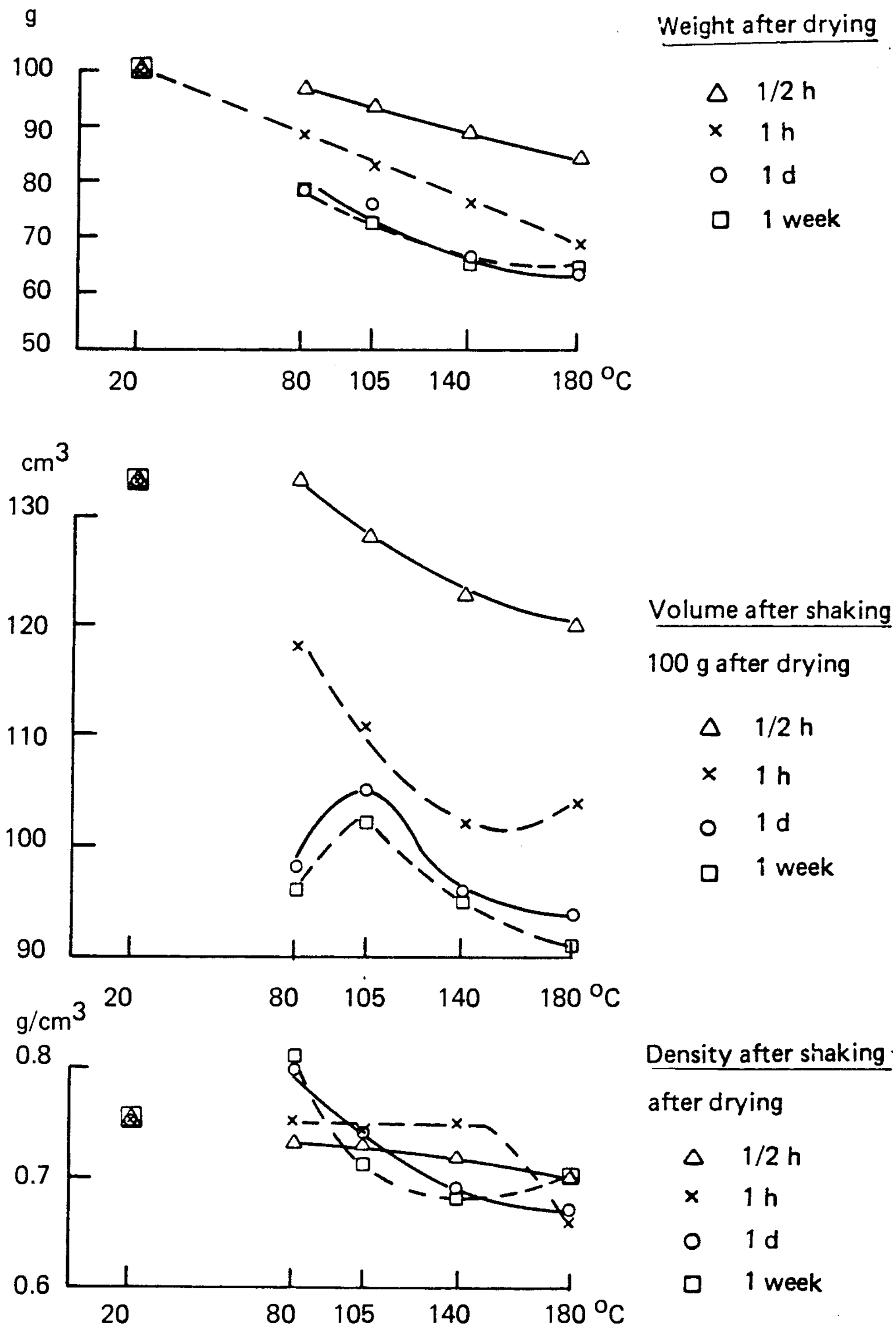


Diagram C.11 EXPENDED GRANULAR MIXED BED RESIN Weight, "volume and density after shaking" after drying

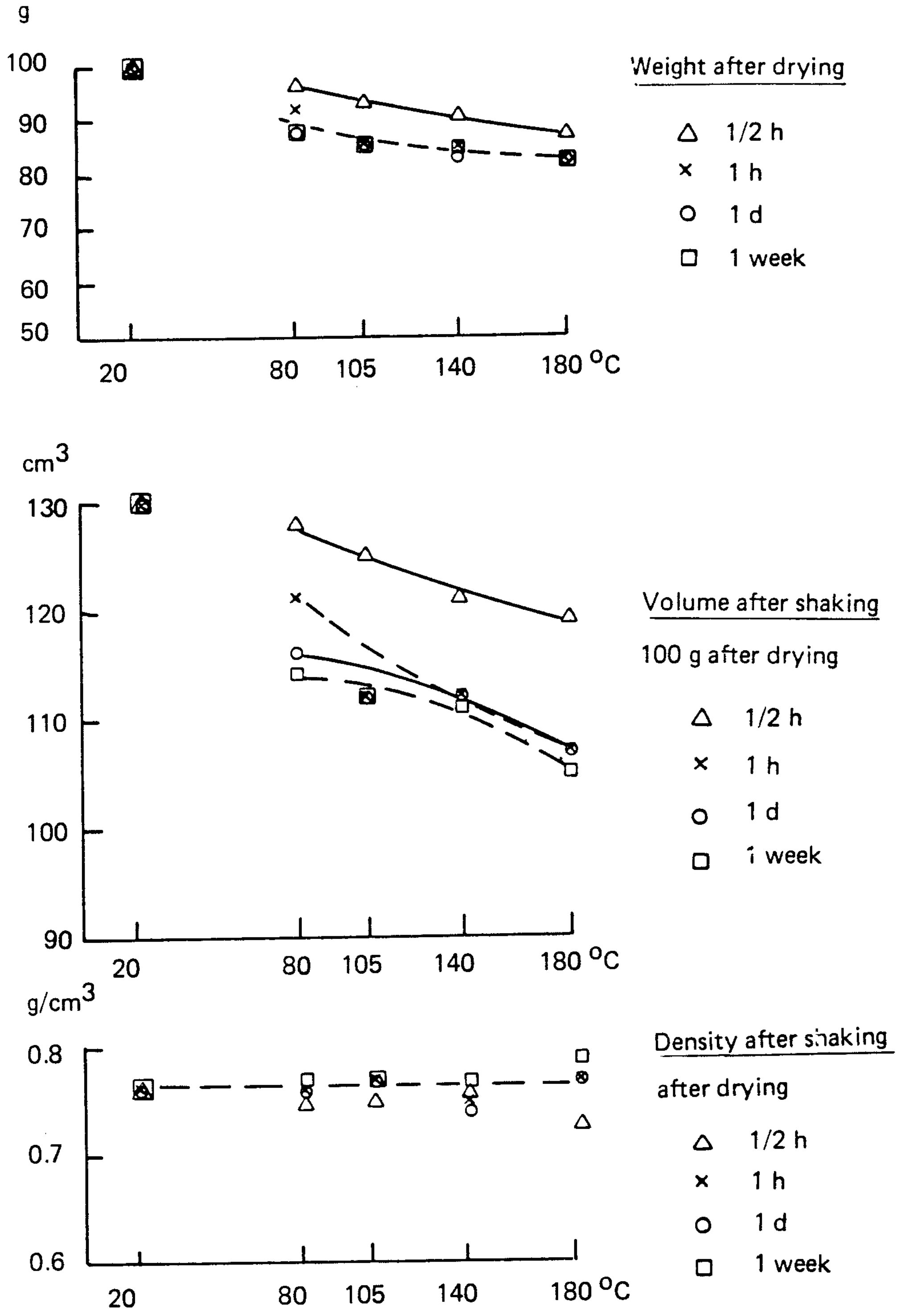


Diagram C.12 EXPENDED GRANULAR MIXED BED RESIN
Stabilized with Na_2SO_4
Weight, "volume and density after shaking" after drying

80-06-12   K1/4-80/47

THERMAL STABILITY OF ION-EXCHANGE RESINS

Sven Hedlund
J-P Aittola

Claes Thegerström

5626001

1. INTRODUCTION

Information on the thermal stability of ion-exchange resins is of vital importance in evaluating the risks for fire and explosion during the drying period, and for the optimization of the solidification process.

This literature survey on the thermal properties of ion-exchange resins has been carried out by STUDSVIK as part of a project, in which the swelling/shrinking of different ion-exchange materials was followed as a function of drying temperature and time in air and water.

2. DISCUSSION AND CONCLUSIONS

On the basis of this study it can be concluded that some real differences exist between different ion-exchange materials. The swelling of KU-2 (cationic) resin, for example, decreases when the capacity decreases, that of Dowex increases /11/. Amberlite behaves like KU-2, this should however, be, verified better.

As well as swelling the capacity also decreases after the thermal treatment of resins. The quantity of hydrophilic groups / 1, 2, 11, 18, 19, 20, 21/ decreases as well. It is notable that a certain type of ion exchange resin does not swell after the thermal treatment /18/. The risk for cracking and pulverization is obvious /17/. A method - an osmometer - has been described to measure the swelling pressure /23/.

The information on the properties of anion, cation and mixed-bed ion-exchange resins is not very extensive. Definitions of terms such as relative swelling and water amount at "even level" are rare. The swelling properties should be followed as a function of drying temperature and time in both air and water in a special study.

3. BIBLIOGRAPHY

1 Russian Journal of Physical Chemistry, 52(5), 1978.

Prediction from Kinetic Data of the Functioning of Ion Exchangers at High Temperatures.

P E Tulupov.

Sets of equations, kinetic parameters and graphs for calculating the life-time of various exchangers at a fixed temperature and the residual exchange capacity, the maximum temperature of use with a specific duration of heating, and the residual exchange capacity when the temperature and duration of heating are known. Decrease of exchange capacity when used at $160^{\circ}C$ in H_2O (AV-17(Cl^-)). Increased capacity (KF-1(H^+)) when heated in H_2O and different dihydroxyphosphinyl groups at 15-25, 43-63, 110-120 and $134-145^{\circ}C$.

2 Russian Journal of Physical Chemistry, 53(3), 1979.

Kinetics of the Substitution of the Functional Groups of Ion-exchange Resins on Heating with Simultaneous Ion-Exchange Processes. Kinetics of the Desulphonation in Water of Mixed Hydrogen-salt-forms of Cation-exchange Resins under Stationary Conditions.

P E Tulopov and A I Gantman.

Describes the variation of the total capacity and the content of sulpho-groups in the H-form with time on heating the KU-2x8 cation-exchange resin in the hydrogen and the mixed forms in water. The exchange capacity decreases when swollen resin is heated.

3 Journal of Thermal Analysis, vol. 7 (1975) 95-110.

Studies on the Self-Ignition of High-Molecular Substances at Low Temperatures. Part 1.

Thermooxidative Degradations of a Polystyrene Sorbent and of a Methacrylic Acid Polymer.

V Marinov and D Mitov, Energoproekt, Department for Scientific Research, Sofia, Bulgaria.

Degradation of the resins was investigated both in air and in nitrogen by means of simultaneous TG and DTA. A regime of slow oxidation and a regime of burning process were realized. Some stages of the thermal and oxidative degration could be identified based on the examination of the composition and the IR spectra of the residues obtained by heating the resin up to different temperature levels. Self-ignition occurs in air at about 300° parallel to the process of depolymerization.

4 VGB Kraftwerkstechnik 57
Heft 3 März 1977

Ioneaustrauscher - ihre Beständigkeit gegen chemische und physikalische Einwirkungen.

Von G Kühne und F Martinola.

Der Einfluss des Temperaturschocks ist untersucht.

Rasches Aufheizen und Wiederabkühlen kann zu Spannungen führen und damit zu Kornzerfall. Ein Versuch wurde im Labor so ausgeführ, dass je ein gelförmiger und ein makroporöser Kationenaustrauscher in einer Beladungskolonne 60 Minuten lang mit heissern Rohwasser (90°C) durchströmt wurde. Darauf folgte kalte 10-prozentiger Kochsalzlösung. Dieser Zyklus wurde 60 mal wiederholt. Die Gechwindigheit der Temperaturänderung war bei diesem Versuch sehr gross, da die verschieden temperieren Lösungen unmittelbar aufeinander folgten.

Kationenharze auf Basis von Polystyrolsulfonsäure zeigen ab etwa 150°C in der (H^+)form einen verlust am Totalkapazität und eine Verringerung des Quellwasser gehaltes.

5 STUDSVIK K1/4-80/26

Jonbytarmassor: Differential termisk analys (DTA)

Jan Chyssler

In this study some DTA analyses have been made in different atmospheres by using grounded ion-exchange resins.

6 Journal of Chromatography, 148 (1978)

The dependence of the swelling of ion-exchange resins on their crosslinking

J. Naveh, Israel Atomic Energy Commission, Nuclear Research Center, Negev, Israel

Y. Marcus, Department of Inorganic & Analytical Chemistry, The Hebrew University, Jerusalem, Israel

The swelling of ion-exchange resins is a factor of prime importance in determining their selectivity and their behavior in a chromatographic column. It depends on many factors, including the nature of the solvent, the presence or absence of an electrolyte in the solution, and its nature and concentration, the nature of the fixed and counter ions, the nature of the resin skeleton and the degree of crosslinking.

For a given type of resin (given skeleton and fixed ion) and solvent (water) and in the absence of electrolyte, the swelling depends on the nature of the counter ion and on the degree of crosslinking.

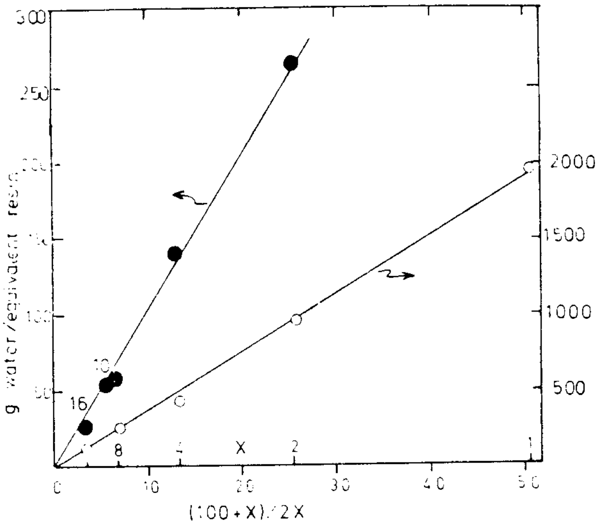


Fig. 1. The swelling, in grams of water per equivalent of dry resin, of a polystyrene sulphonate cation exchanger (H⁺) ( ) and a polystyrene methylene trimethylammonium anion exchanger (Cl⁻) (●) as a function of the crosslinking X.

7 Journal of Physical Chemistry Vol 57 (1953)

Studies on Ion Exchange Resins. VII. Water Vapor Sorption by Cross-Linked Polystyrenesulfonic Acid Resins

By Benson R. Sundheim, Monroe H. Waxman and Harry P. Gregor

The sorption of water vapor by cross-linked polystyrene sulfonic acid has been studied in systems differing in ionic states and in degrees of cross-linking. The net free energies, heats and entropies of the sorption process are calculated and discussed. The sorption is interpreted in terms of the three important factors: polymer-polymer interaction, restraining cross-links and electrolytic effects.

This paper presents a systematic study of the water sorption properties at two temperatures of a family of resins of variable degrees of cross-linking and in various ionic states. The free energies, heats and entropies of the sorption reaction are calculated and discussed.

8 The Journal of Physical Chemistry, Vol 81, No 12, 1977

Solvent Sorption Isotherms, Swelling Pressures, and Free Energies of Swelling of Polystyrenesulfonic Acid Type Cation Exchangers in Water and Methanol

Deoki Nandan and A. R. Gupta

Swelling pressures (π) in H^+, Li^+, Na^+ and K^+ forms of Dowex 50W resins of 2, 4, 8 and 12 % DVB content in methanol and water have been determined from their solvent sorption isotherms, treating 1 % DVB resins as reference "uncross-linked" exchangers. These swelling pressures have been discussed in terms of ionic solvation and ion pair formation in the resins. The linear relationships between π and the measured equivalent volumes of the various ionic forms have been discussed in terms of properties of solvents particularly dielectric constant and ion-solvent interactions. The total electrostriction of the solvent at zero swelling pressure ($\Delta\bar{V}_{es}(b)$) and at maximum swelling ($\Delta\bar{V}_{es}$) was found to be the same within experimental precision. The electrostriction per mole of solvent is much higher in MeOH than in water indicating stronger binding of methanol to cations in the resin phase. The integral free energies of swelling (ΔG_{sw}) of these resins are negative. The $-\Delta G_{sw}$ values follow the sequence $H^+ > Li^+ > Na^+ > K^+$ and 1 % > 2 % > 4 % > 8 % > 12 % DVB. The contribution of the resin cross linking (swelling pressure) to the free energy of swelling of cross-linked resins has been computed with reference to 1 % DVB resins. This contribution was found to be small and positive. It has been concluded that generation of swelling pressures is at the expence of secondary solvation of ions and osmotic effects.

9 Russian Journal of Physical Chemistry. Vol 39 no 11.Nov 1965.

The Form of binding of Moisture in Ion-Exchange Resins According to Thermographic Data.

Yu M Marchevskaya and O D Kurilenko.

The report states that there are endothermic effects at two levels, 100-110° and 150-180°. When dried over phosphorus pentoxic, the cation exchangers give rise to a single broad endothermic effect at 130-150°C.

10 Russian Journal of Physical Chemistry, 42 (5) 1968.

Effect of Desulphonation on the Properties of Sulphonated Styrene Ion-Exchange Resins.

V S Soldatov, A I Pokrovskaya and L I Tsukurova.

Desulphonated specimens of KU-2x2†, KU-2x 8, and Dowex-50-V x 16 ion-exchanges resins have been obtained by treatment with superheated steam. Thermograms of the desulphonated specimens of Ku-2x2 resins and of specimens obtained with insufficient sulphonation have been recorded.

The swelling of KU-2 resin decreases as the capacity falls, while Dowex-50-Vx16 shows the opposite variation. The variation for desulphonated KU-2 resins is more pronounced than for the insufficiently sulphonated specimens. It is suggested that in the temperature range 200-300°C the elimination of sulphonic acid groups can be accompanied by two side processes: the formation of additional cross-links (possibly sulphonyl) and the initial stage of depolymerisation.

The method involving the desulphonation of resins by superheated steam can lead to the preparation of specimens with various properties, depending on the process conditions.

11 Russian Journal of Physical Chemistry vol 39 no 11 nov 1965.

Dynamics of Ion Exchange on Strongly Swelling Ion Exchangers.

M S Safonov and V I Gorshkov.

A description of the dynamics of ion exchanges on strongly swelling resins, stating it is essential to make allowance for the change in the swelling properties of the resin and in the amount of electrolyte absorbed without exchange during the transition from one ionic form to the other.

12 Oak Ridge National Laboratory, Chemistry Division, Oak Ridge, Tennessee.

Temperature Dependence of Some Cation Exchange Equilibria in the Range 0 to 200° .

By Kurt A Kraus and Richard J Raridon.

The temperature dependence of a number of cation-exchange equilibria (tracers of Na+, K+, Rb+, Cs+, Be++, Ba++, Co++, Zn++, La+3. Eu+3 vs.H+; tracers of K+, Rb+, Cs+ and Ba++ vs. Na+) was studied in dilute aqueous electrolyte solutions. The temperature range was 0 to 150° for exchanges with the H^{+}-form of the resin and 0 to 200° for those with the Na^{+}-form. The upper temperature limits were imposed by the stability of the resin (H^{+}-form) and the "safe" operating range of the equipment(Na^{+}-form).

Tables showing the selectivity coefficients as a function of the temperature

13 Journal of Chemical Physics 67(12) 1977

Selective uptake of counterions of different size by ion-exchange gels: Effect of swelling pressure and Coulombic interactions

Harry P. Gregor and Richard J. Greff. Department of Chemical Engineering and Applied Chemistry, Columbia University, New York.

The selective uptake of potassium ions versus tetramethyl-ethyl-, ethyl and propylammonium ions by fully neutralized, crosslinked polymethacrylate gels was measured in aqueous, and nonaqueous solvents. Swelling pressures in water were calculated from isopiestic data, so the Coulombic contribution to the total free energy of the exchange process could be calculated and compared with theory. A good fit between experiment and theory was possible only by assigning values for the dielectric constant of water in these gels of about 30 in the K-TMA state and 15 in the K-TEA state.

14 United States Patent Office. Dec 21, 1971.

Method of Dissolving Radioactive Contaminated Organic Ion Exchange Resins.

Malcolm W Wilding.

The patent describes a method, which results in the complete destruction and dissolution of organic ion exchange resins without leaving any residue.

The process of this invention involves employing a solution containing $KMnO_4$ and HNO_3 to dissolve the ion exchange resin. A mixture of the solvent solution and the resin is heated at 70 to 90°C. until the resin is completely dissolved.

15 Journal of Thermal Analysis, Vol 13 (1978)

Thermoanalytical Investigation of Ion Exchange Resins. The Swelling of Anion Exchange Resins

J. Inczédy. Department of Analytical Chemistry, University of Chemical Engineering, Veszprém, Hungary

The water uptakes of completely swollen and air dried anion exchange resins were investigated by traditional and also by thermoanalytical measurements. In investigations on the air dried resin samples of HSO_4, H_2PO_4, HPO_4 forms, two types of water (strongly and loosely bound) were found. The sequence of water uptake on the resins investigated was compared to the opposite order of the adsorption strengths of the anions and to the entreopies of the hydrated anions.

A conclusion was made regarding the role of the hydration of the anions in the selectivity sewuence of anion exchange.

The operation rate and selectivity of ion exchange resins are strongly correlated with their swelling properties.

16 AE-KTA-208. Sönderfall av jonbytarmassa Dowex 21 K och 50 W vid upphettning i vatten. Orienterande försök.

Mac Arnell.

To study if the ion exchange resins used at R - 3 have a tendency to degradate at elevated temperatures in water a number of tests in an autoclave had been performed.

The results show that a certain amount of these resins will pulverize and split at actual operation temperatures at R - 3.

17 Cation-exchange Resins formed by the Acid Condensation of Phenolsulphonic Acid with Formaldehyde.

A O Jakubovic.

Part Result: Heat drying. Drying below 100°C was unsatisfactory as constant weight was not reached for many days. Heating at 115-120° gave good results in several hours. The resins could generally not be re-swollen, however. To ascertain whether this was due to further reactions which could affect the water content, an alternative drying technique was investigated.

TABLE 1. *Molar composition of the reactants, reaction conditions and characteristics of resins.*

Resin no.	CH_2O	H_2O	Hours of heating		H_2O content (%) at eq. swelling of H^+ form	Molar ratio, water to phenol, at eq. swelling	Exchange capacity (meq./g.)	
			At 85°	Addl. at 100°			Swollen resin	Dry resin
1	1·3	8	2·0		65·0	12	0·963	2·75
1S			0·5	1·5	63·7			
1H			16·0		65·1		0·963	2·76
2	1·3	15	4·0		75·7	25	0·681	2·81
2S			0·5	3·0	73·7			
2H			34·0		73·7		0·709	2·70
3	1·3	30	10·0		88·5	63	0·328	2·84
3S			0·5	9·5	84·5			
3H			61·0		84·4		0·422	2·70
4	1·7	9	2·0		63·3	13	0·849	2·31
4S			0·5	1·5	60·2			
4H			16·0		60·7		0·767	1·95
5	1·7	16	4·0		74·7	23	0·603	2·38
5S			0·5	3·5	71·6			
5H			34·0		71·2		0·584	2·03
6	1·7	31	10·0		86·2	47	0·319	2·32
6S			0·5	9·5	82·4			
6H			61·0		81·6		0·379	2·05
7	3·5	11	2·0		71·3	17	0·441	1·54
7S			0·5	1·5	66·9			
7H			32·0		63·9		0·263	0·73
8	3·5	20	4·0		87·8	51	0·229	1·89
8S			0·5	3·5	86·4			
8H			55·0		84·2		0·263	1·02
9	3·5	37	15·0		89·4	57	0·190	1·80
9S			0·5	14·5	84·5			
9H			75·0		83·9		0·195	1·21
10	1·58	24	5·0		81·9		0·476	2·64
11	3·38	31	8·0		86·7		0·234	1·76
12	3·38	31	30·0		82·3		0·274	1·55
13	4·23	26	10·0		82·8		0·259	1·50
14	2·06	25	6·0		81·2		0·422	2·22
15	2·05	38	145·0		86·7		0·177	1·33
16	2·06	25	60·0		82·9		0·246	1·42

TABLE 2. *Swelling of the resins in the alkali-metal forms.*

Resin no.	Counter-ionic form	Equil. swelling (% water)	Alkali-metal content (%)
10	H	81·9	
	Li	81·7	0·327
	Na	80·7	1·10
	K	79·7	1·894
	Cs	75·8	6·278
11	H	86·7	
	Li	86·6	0·161
	Na	86·1	0·538
	K	85·6	0·925
13	H	82·8	
	Li	82·6	0·180
	Na	82·3	0·593
	K	81·8	1·012
	Rb	80·6	2·210
14	H	81·2	
	Li	81·1	0·290
	Na	80·3	0·965
	K	79·4	1·660
	Rb	77·7	3·582
	Cs	75·8	5·548
16	H	82·9	
	Li	82·8	0·170
	Na	82·4	0·562
	K	82·0	0·959
	Rb	81·2	2·090
	Cs	79·9	3·217

The fact that resins could not generally be re-swollen after drying indicates the occurrence of some irreversible process. One explanation could be that some hydroxymethyl groups formed in the resin condense to methylene or ether bridges. Alternatively, sulphonic acid groups could be split off during the heating, the consequent decrease in the content of hydrophilic groups reducing the capacity for re-swelling. Such losses have been observed by other workers; for instance, heating Dowex 30, which is of the PSA-formaldehyde type, for 16 hr. at 135° halved its exchange capacity, and a loss of about 23% in capacity was sustained at 120°C.

18 Russian Journal of Physical Chemistry. vol 39 no 11 nov 1965.

Thermal Stability of Sulphonated Cation-Exchange resins in a medium of Tertiary Pentenes.

P E Tulupov.

The report states that thermal treatment of the cation-exchange resins produces a contraction of the space lattice structure; in the condensation resins this can be detected at 125° and 150°, whilst in KU-2 a temperature of 200° is needed.

The relative swelling (a function of the concentration of sulpho-groups) and the density of the dried KU-2 resin are linearly decreasing functions of the loss of exchange capacity.

19 Oak Ridge National Laboratory, Oak Ridge, Tennessee (Ursprungskälla okänd).

Ionic Equilibria and Self-Diffusion Rates in Desulfonated Cation Exchangers.

G E Boyd, B A Soldano and O D Bonner.

Sulfonated polystyrene-divinylbenzene type cation-exchangers of variable capacity were prepared by acid hydrolysis at 180-220°. Evidence for some rupture of divinylbenzene cross-links was found in an increased moisture absorption. Ionic selectivity coefficients measured for the sodium-hydrogen exchange decreased with decreasing capacity. Complete selectivity reversal at all exchanger compositions (i e, hydrogen preferred over sodium ion in the exchanger) was found for a 50% desulfonated nominal 16% DVB exchanger.

In contrast, the uptake of silver ion in the silver-sodium exchange was increased by decreasing capacity. Self-diffusion coefficients for sodium, silver, zinc, yttrium and lanthanum ions showed initial increases with lowered exchange capacity reflecting the breakig of cross-links. At still lower capacities, however, the self-diffusion coefficients decreased and the activation energies increased to large values.

Part Result: Part of the observed decrease in selectivity for sodium over hydrogen ion, however, may be attributed to the breaking of cross-links in the desulfonation. Thus, from swelling measurements it may be estimated that the nominal 16% DVB cross-linked exchanger decreased to approximately 12% DVB when its capacity was reduced to roughly one-half.

20 Russian Chemical Reviews, 40(12), 1971.

Thermal stability of Cation-exchange Resins.

N G Polyanskii and P E Tulupov.

Experimental work on the thermal stability of cation-exchange resins in air, water, certain aqueous solutions, and also organic media is summarised for the first time. Conclusions are reached about the effect of various factors on the thermal stability and about the nature of the processes responsible for the decrease in exchange capacity. Special attention is paid to the existence of an inherent relation between the thermal stability and the catalytic activity of ion-exchange materials.

21 Jpn. Kokai Tokkyo Koho 79.

Solidification of wastes containing ion exchange resins.

The wastes are solidified with plastic or asphalt in the presence of $PO_4 3-$ to prevent the emission of toxic gases (e g, amines) during solidification and to obtain a solidified substance having a high ignition point. Thus, a simulated slurry contg. 80% H_2O and 50 g of 1:1 strongly acidic cationic resin: strongly basic anionic resin was premixed with 3 g Na_2HPO_4 then with 50 g asphalt at 180 x for 1 h. No odorous gas was evolved and the ignition point of the solidified substance was 290^o vs. 180^o without Na_2HPO_4.

22 87 (1968) Recueil

A New Swelling Pressure Osmometer
By E. J. van de Kraats, Laboratory of Physical Chemistry,
Technische Hogeschool Delft, The Netherlands

A svelling pressure osmometer has been constructed in which gels can swell isotropically in interchangeable swelling chambers having accurately fixed dimensions. The gels are in contact with the pure diluent via a porous steel disc. The swelling pressures is balanced and measured directly by a mercury column which is servocontrolled by a displacement transducer attached to a thin platinum foil forming one side of the swelling chamber. The mercury column exerts a counter-pressure on the platinum foil. If the mercury column is replaced by another counter-pressure device, swelling pressures as high as one hundred atmospheres or as low as one hundredth of an atmosphere can be measured with an accuracy of about 1 ^{o}/oo.

This method of pressure detection is in principle also applicable to the determination of pressure changes at constant volume, such as occur, for example, in the study of the kinetics of phase transitions and equilibria.

23 Leverantörers uppgifter på kommersiella jonbytarmassor.

Specifications for commercial ion exchange resins.

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