



AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
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THE PERFORMANCE OF POWDERED ION-EXCHANGE RESINS

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ABSTRACT

The coating properties and ion exchange performance of powdered ion-exchange resins were examined in a small test facility. Satisfactory resin coatings were obtained with cation:anion resin ratios in the range 1:1 to 3:1 but use of a 9:1 resin ratio resulted in a high pressure drop across the coating. The 'settled resin volume' proved to be a reliable guide to the coating performance of resin slurries. The ion-exchange capacity of the cation resin increased to a small extent with a decrease in sodium concentration in the influent water down to $500 \mu\text{g l}^{-1}$. Within the ranges examined, resin ratio, resin loading and flow rate had no significant effect on cation capacity. The effect of exhaustion on the pressure drop characteristics and flocculating properties of various resin ratios was investigated. The thermal stability of the powdered anion resin was markedly less than that quoted elsewhere for anion bead resin.

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ANIONS; COATINGS; FLOCCULATION; FLOW RATE; ION EXCHANGE MATERIALS;
MEDIUM TEMPERATURE; PERFORMANCE; POWDERS; PURIFICATION; RESINS;
TEMPERATURE DEPENDENCE; WATER

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1. INTRODUCTION

Ion-exchange plants are used in nuclear power stations to produce high quality water for the coolant and moderator circuits by removing dissolved and suspended impurities from the water. These impurities may consist of:

- (i) metal oxides (e.g. Fe, Ni, Cr) which arise primarily from corrosion of heat exchange surfaces;
- (ii) dissolved salts (e.g. Na, Ca, Mg, chlorides, sulphates and carbonates), silica and organic compounds from ingress of cooling water at the condenser (which can be a major problem in direct-cycle reactors); and
- (iii) fission products (e.g. Cs, Sr, I) from failed fuel elements in the core.

Failure to remove these impurities could cause conditions leading to corrosion, overheating of fuel element surfaces, restriction of flow, and other deleterious effects.

There are two main types of ion-exchange purification plant at present in use. The first consists of a deep bed of ion-exchange resin (mixed cation exchanger and anion exchanger) in the bead form, the beads being approximately 1 mm in diameter. When this resin becomes exhausted the cation and anion resins may be separated, regenerated and used again. The second type of plant uses powdered ion-exchange resins (60-400 mesh) coated as a thin (~ 5 mm) layer onto nylon filter candles or wire mesh. Mixed cation and anion resins are used and these flocculate on mixing to form a loosely packed coating on the candle which allows a free flow of water while acting as an efficient filter. These resins cannot be separated for regeneration and once a coating is exhausted it is discarded and a fresh coating is applied for the next cycle of operation.

Powdered resin is marketed, under the trade name 'Powdex', by the Graver Water Conditioning Company and the process was introduced in 1962 (Duff and Levendusky 1962). Patents on the use of the process were granted in 1966 (Levendusky 1966). [Levendusky and Olejar (1967) and Applebaum (1968) have reviewed the applications of powdered resins in power plant cycles and Ryan and Brown (1968) have similarly reviewed their applications in nuclear cycles.]

The vessels for large scale deep bed ion-exchange are approximately 2-2.5 m diameter by 2 m high (Sisson et al 1968 and Kennedy, Meyers and Crits 1968) and those for a similar capacity Powdex installation are 1 m diameter by 2 m high (Grant et al 1963). This use of narrower vessels and the fact that regeneration facilities are not required mean that less floor space and hence shielding is needed for powdered resin plants than for equivalent deep bed plants.

The advantages claimed for powdered resins by Duff and Levendusky (1962) and Martynova, Subbotina and Kopylov (1970) are as follows:

- (1) They allow greater utilisation of the total ion-exchange capacity because of the faster exchange kinetics associated with the small particle size.
- (2) They give greater filtration efficiencies for small crud particles.
- (3) Because they are not regenerated and reused a higher degradation rate is acceptable allowing them to be operated at higher temperatures. This increases the thermal efficiency of the plant (e.g. for reactor primary circuit purification) and in condensate polishing it allows the purification plant to be situated nearer the reactor, thereby removing impurities entrained from a greater proportion of the feed train (Grant et al 1963).
- (4) Since powdered resins are not regenerated, they produce only small volumes of radioactive waste instead of the large volumes produced from regeneration of the deep bed.

In practice, these advantages must be balanced against the following disadvantages of powdered resins:

- (1) The amount of powdered resin used is higher than that of bead resins because powdered resins are used only once and then discarded. The cost of operating a powdered resin plant may be much higher than that of a deep bed plant.
- (2) The total amount of resin in use at any time is small compared to a deep bed plant so the resin is exhausted more quickly following a condenser leakage than is the case with a bead resin plant.

To overcome these disadvantages of powdered resin for condensate polishing, while retaining its good crud removal properties, the possibility of combined deep bed/powdered resin plants has been examined by Ryan and Limon (1970). These authors showed that the high initial cost of a combined plant could only be justified under conditions of condenser leakage, fuel element failure and high waste treatment costs.

The formation of a floc by mixture of powdered anion and cation exchange resins is discussed by Martinola and Kühne (1969). The oppositely charged resin particles when mixed in water form neutral agglomerates that cannot easily be separated. These agglomerates settle to provide the loosely bound porous floc. Table 1 shows measurements of the zeta potential of the species made by Martinola and Kühne using an electrosmosis technique.

TABLE 1
MEASUREMENT OF ZETA POTENTIAL OF THE SPECIES
USING ELECTROSMOSIS (MARTINOLA AND KÜHNE 1969)

Resin Type	Zeta Potential
Sulphonic acid resin, H ⁺ - form	-48 to -52 mV
Trimethyl benzyl ammonium ion resin (Type 1), OH ⁻ - form	+32 to +35 mV
Agglomerate from both resins	No charge

Investigating the effect of various counter ions they found that the highest zeta potentials are obtained with H⁺ and OH⁻ ions. Thus replacement of the H⁺ and OH⁻ by other counter ions such as Na⁺ and Cl⁻, as might occur with sea-water ingress to a condensate polishing unit, will lower the zeta potentials of the anion and cation resins. This effect could weaken the electrostatic forces stabilising the floc structure sufficiently to cause collapse to a more dense, less porous form which in turn would result in increased resistance to water flow and higher pressure drop across the coatings. This tendency would be increased in the presence of high ionic strength and hence low dielectric constant water solutions, as again might occur during seawater ingress.

This report describes pilot plant studies of the likely effect of seawater ingress on these aspects of coating behaviour; also an attempt is made (a) to familiarise ourselves with the powdered resin ion-exchange system, (b) to examine the practical problems which arise in the operation of a powdered resin plant, and (c) to find the optimum conditions for operating such a system.

2. POWDERED RESIN TEST FACILITY

Figure 1 shows the arrangement of the plant. The nylon-wound filter element (candle) of 420 cm² surface area contained in a glass vessel to permit observation is shown in Figure 2.

For the resin precoating operation, demineralised water was circulated from the resin precoating vessel, through the candle in the ion-exchange vessel and back to the precoating vessel. The resin floc was prepared separately (as described below) and poured into the precoating vessel. The resin was carried into the ion-exchange vessel and deposited on the candle as the water passed through it. Resin coatings between 3 mm and 12 mm thick were obtained. Resin precoating was complete when there was no turbidity in either

the precoating or ion-exchange vessels.

For demineralisation operation the inlet was switched from the precoat vessel to the test solution tank without interrupting the flow. Demineralisation was carried out either by recycle operation, in which the deionised water was returned to the test solution tank and the salt concentration kept constant by pumping in concentrated makeup solution, or by once-through operation with the outlet water sent to drain. At the completion of a run the resin was removed from the candle and sent to drain by backwashing the candle with demineralised water from the resin precoat vessel.

The loop has provision for controlling temperature and flow rate, and for measuring inlet and outlet pressures and electrical conductivities.

The resins used were Powdex ion-exchange resins manufactured by Graver Water Conditioning Company and distributed throughout Australia by William Boby and Company. The hydrogen-form cation resin and hydroxyl-form anion resin were used. By drying over anhydrous in a vacuum dessicator at 60°C for 24 hrs, the moisture content of these resins was determined to be 52 wt per cent for the cation resin and 57 wt per cent for the anion resin. The anion-exchange resin was packed in small airtight containers to minimise loss of capacity due to carbon dioxide absorption during storage.

All weights reported in this note are "as received" or moist weights.

3. EXPERIMENTAL

3.1 Physical Properties of the Resin Floc and Coating

3.1.1 Floc preparation and settled resin volume (SRV)

Weighed amounts of cation and anion resins were added to one litre of demineralised water in a 1-litre measuring cylinder while the water was being stirred by a laboratory stirrer. The resultant floc was stirred for five minutes and allowed to settle for a further five minutes. The volume occupied by the settled resin floc (the SRV) was noted and converted to a volume equivalent to 50 g total resin weight for comparison purposes. The SRV values observed were found to vary with the shape of the container (e.g. the observed SRV was approximately 30 per cent higher when a 2-litre beaker was used).

3.1.2 Coating

A satisfactory resin coating was one which coated uniformly over the candle, took less than 20 minutes to coat, and produced only a small pressure drop across the coating (less than 10^4 N m^{-2} (1.4 psi) at the operational flow-rate of $2.7 \text{ kg m}^{-2} \text{ sec}^{-1}$ (3.3 gal min^{-1} per square foot of candle surface area)). These conditions were always met with a resin floc whose SRV was in the range 350-600 ml. Coatings produced when the floc had an SRV less than 350 ml were

thin, tightly packed and had a high initial pressure drop. An SRV value in excess of 600 ml resulted in long coating times and a bulky, porous and uneven coating.

The evenness of the coating and time taken to coat the candle also depended to some extent upon the precoating flowrate. The optimum flowrate was found to be in the range $3.0\text{--}3.3 \text{ kg m}^{-2} \text{ sec}^{-1}$ ($3.7\text{--}4.0 \text{ gal min}^{-1} \text{ ft}^{-2}$ of candle surface area). However, the optimum flowrate is limited by turbulence in the vessel and may depend on the design of the plant.

3.1.3 Resin ratio

For a given resin ratio (i.e. weight ratio of cation to anion resin) the SRV was reproducible only to within $\pm 50 \text{ ml}$ even when the flocs were prepared from the same batch of resin. Flocs with high cation:anion ratios invariably had low SRV values. For resin ratios of 5:1 or greater it was not possible to obtain a floc with an SRV in the satisfactory range and hence poor resin coatings were obtained. Coatings of flocs with 3:1 resin ratio were usually just acceptable but some had very low SRV values (around 300 ml). Contrary to our observations the Graver Water Conditioning Company recommended adding more cation resin if the SRV were initially too low for a satisfactory coating.

For resin ratios of 1:1 and 2:1 the SRV usually fell in the higher end of the acceptable range. Graver Water Conditioning Company supplies a polyelectrolyte material (Solution A) which, when added to the resin floc, will reduce the SRV. This material was found to be useful when the resin floc had an SRV which was initially too high for coating, as occurred occasionally with 1:1 resin ratios. The polyelectrolyte had no detectable effect on the ion-exchange capacity of the resins. The amount to be added must be determined by trial but the amount recommended (5 ml for each 11 kg of resin) was found to be a good guide. Satisfactory coatings were always obtained with 1:1 and 2:1 resin ratios.

3.1.4 Ionic form of the resin and solution concentration

The effect of degree of conversion of the resin - hence its ionic form - and the interstitial solution on its flocculating properties was investigated. Resin slurries of various resin ratios were prepared as described and their SRVs were noted. Aliquots of 10% NaCl solution were added and after stirring and settling their SRVs were again noted. The SRV dropped rapidly in a linear fashion until sufficient NaCl had been added to fully convert the anion resin (Figure 3) to the chloride form; it then dropped more slowly until full conversion of the cation resin had taken place. Further additions of NaCl had little effect on SRV. The final SRVs were lower for the higher resin ratio slurries.

The compaction of the resin coating in a flowing system was examined. Resin slurries of various resin ratios were coated on the filter candle. The resins were converted from H^+ to Na^+ and OH^- to Cl^- form by passing through it a solution of $3 \text{ mg } l^{-1} \text{ NaCl}$ at $2.7 \text{ kg m}^{-2} \text{ sec}^{-1}$ and the flow was continued until well after the point of complete conversion. The pressure drop across the resin was used as a measure of its degree of compaction. The results are given in Figure 4. The time to full saturation in each case was in the range 1 to 6 hrs. The form of the resin had little effect on the pressure drop across resin coatings with 1:1 and 2:1 resin ratios. However, the pressure drop across the 3:1 resin coating rose rapidly until the resin was fully converted and increased slowly thereafter. The pressure drop across a 9:1 resin coating rose so quickly during saturation that the run had to be abandoned after 30 minutes (before the resin was fully saturated) due to excessive pressure drop.

After conversion the pressure drop across the 1:1, 2:1 and 3:1 resin coatings increased slowly with time, the rate of increase being about the same for all three ratios. The higher the resin ratio the greater was the pressure drop at all times after the beginning of the run.

3.2 Ion-Exchange Properties

Tests were performed to determine the effects of flowrate, coating weight, resin ratio, solution concentration and temperature on the ion-exchange capacity of the resins. The results are given in Figures 5-9.

A convenient and practical parameter for comparing resin capacities under different conditions is q_1 - the number of millimoles of the relevant ion presented to each gram of the appropriate resin, up to the point of 50 per cent breakthrough; q_1 may be read directly on the abscissae of Figures 5 and 6 at $C/C_0 = 0.5$.

3.2.1 Flowrate

The ion-exchange capacity was independent of the flowrate within the range $2.2\text{-}3.3 \text{ kg m}^{-2} \text{ sec}^{-1}$ (Figure 5). (The recommended flowrate for this system is $2.7 \text{ kg m}^{-2} \text{ sec}^{-1}$ [$3.3 \text{ gal min}^{-1} \text{ ft}^{-2}$] (William Boby and Co, undated)).

3.2.2 Feed concentration

The cation-exchange capacity of the resin increased slightly as the feed concentration decreased (Figures 5 and 6). This result is consistent with the formula derived by Glueckauf (1955) for bead resin ion-exchange with particle diffusion as the rate controlling step in the exchange reaction.

3.2.3 Resin loading and resin ratio

Coating weight (i.e. total weight of resin in the coating) had a negligible effect on anion-exchange capacity. There was, however, a small effect with different resin ratios. As shown in Figure 7, the resin mixture with the

lower proportion of anion resin appeared to have a slightly greater anion-exchange capacity per gram of resin.

3.2.4 Temperature

The use of ion-exchange at elevated temperatures is limited by the loss of capacity by the anion-exchange resin. This capacity loss is due to a Hofmann degradation reaction in Type 1 strong base anion resins (Baumann 1960). The anion resins used in the Powdex process are of this type. The degradation proceeds as a first order reaction and the rate of degradation of some conventional resins has been examined by Marinsky and Potter (1953). The experiments of both Marinsky and Potter and Baumann were carried out in sealed tubes and, in the case of the former, with the absence of cation resin.

To examine the temperature effects on the anion capacity of Powdex resin, a run was carried out at 80°C immediately after resin coating (Figure 8). This gave a capacity close to that obtained at room temperature. Subsequently three capacity tests were carried out by circulating hot demineralised water through a resin coating for a period of four days before doing the breakthrough measurements. These results at 25°C, 65°C, 80°C and 90°C are given in Figure 8. The higher the temperature the greater was the capacity loss. These results were then used to calculate a first order rate constant, k , for the degradation reaction. In Figure 9 $\log k$ is plotted against $\frac{1}{T}$ where T is the temperature in degrees Kelvin. Results for a conventional resin are also given for comparison. These plots are linear following the Arrhenius relationship $k = A \exp(-\frac{E}{RT})$. From these data the activation energy, E , for the degradation reaction was calculated and is compared with that for IRA-400 in Table 2.

TABLE 2
COMPARISON OF DATA FOR POWDEX AND IRA-400 RESINS

	Powdex 65°C	IRA-400* 65°C
$10^7 k \text{ min}^{-1}$	190	5.15
Half-life (days)	25.3	930
Activation Energy $E \text{ (kcal mole}^{-1}\text{)}$	22	30

* Data from Marinsky and Potter (1951)

4. DISCUSSION

The parameters evaluated here show that it is possible to obtain high

quality treated water from the powdered resin system under a wide range of conditions. In practice, the limiting factor was the quality of the resin coating. This was affected by the settled resin volume, the precoating flow-rate and the condition of the nylon filter candle.

The effect of SRV has already been noted.

An incorrect precoating flowrate caused turbulence in the containing vessel which resulted in areas of thin coating. The higher the flowrate and the greater the SRV the more likely was this to occur. It is probable that careful vessel design could reduce this effect, although in a full scale plant there are not one but many candles in each vessel. This means that any turbulence in full scale plant could lead to even greater variation in coating thickness, both along candles and from one candle to another.

The filter candles may become blocked with fine resin particles. This leads to higher pressure drops and less flow through the blocked portion and again causes thin patches and irregular candle coating. However, the candles can be returned to their original condition by reverse air scouring.

Where filtration is the prime requirement of the purification plant, it is commonly recommended that high cation:anion resin ratio mixtures be used; ratios as high as 9:1 are recommended (William Boby and Co., undated). High ratios are used because the anion-exchange resin is the more expensive and so for a given weight of mixed resin a mixture with a high resin ratio is cheaper. A high ratio also ensures maximum utilisation of the ion-exchange capacity of the more expensive anion resin because it will be the first to be exhausted. Also, the increased negative charge associated with the higher proportion of cation resin may be expected to increase filtration efficiencies for the positively charged crud particles. However, from Figure 4, the pressure drop across the 9:1 resin ratio coating would cause termination of the run before either the ion-exchange or the filtration capacities had been exhausted. (The manufacturer recommends termination of the run when the pressure drop exceeds $\sim 2 \times 10^5 \text{ N m}^{-2}$ [25 psi] (William Boby and Co., undated)). Resin ratios up to 3:1 appear to be satisfactory for filtration and ion-exchange applications.

In general, the lower the SRV of the floc used to prepare a resin coating, the higher will be the pressure drop across the coating at any stage of operation. Replacing H^+ and OH^- ions with Na^+ and Cl^- resulted in a lower SRV (Figure 3). This is in agreement with observations of Martinola and Kühne (1969) on the decrease of zeta potential when H^+ and OH^- ions are exchanged for other ions. Compaction of the resin by this mechanism resulted in a rise in pressure drop across the resin coating at saturation point (Figure 4).

The effect was most noticeable in the higher resin ratio coatings but only with the 9:1 ratio did it result in an excessive pressure drop. Variation in ionic strength of the interstitial solution up to 0.17 M NaCl had very little if any measurable effect on the stability of the floc formed by the fully converted resins, as shown by SRV (Figure 3). This was borne out by the measured pressure drop changes. Since the SRV of saturated resin mixtures is independent of the ionic concentration of the solution, then it should still be possible to use resin coatings (up to 3:1 resin ratio) as particulate filters even after their ion-exchange capacity has been exhausted. For this reason, condenser leakage conditions are not expected to affect the pressure drop characteristics of such a coating. This is shown in Figure 4 where with resin ratios up to 3:1 only slight rises in pressure drop occurred even after several days' operation with fully saturated resins. The efficiency of filtration under these conditions was not investigated.

At temperatures of 70°C and greater, anion resin degradation causes a significant loss of exchange capacity which can be estimated from the results given in Figure 9. The thermal stability of powdered anion resin used in these experiments was considerably less than has been quoted for bead resins of the same type. It has not been established whether this difference in thermal stability is due to the powdering process or to differences in the formulation and manufacture of the resin. In addition the use of a flowing system and the presence of cation resin, both of which would be expected to remove decomposition products and hence aid decomposition, could exaggerate the differences.

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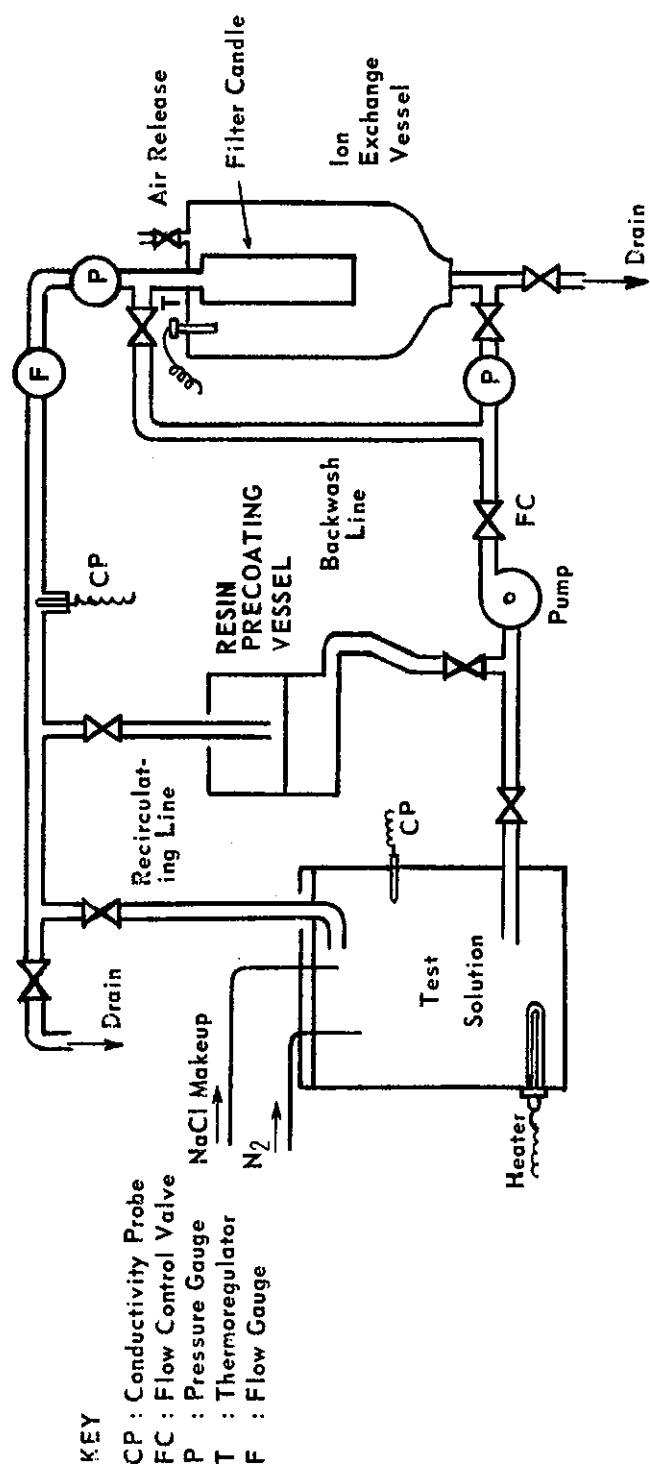


FIGURE 1. SCHEMATIC OF THE POWDERED RESIN FACILITY

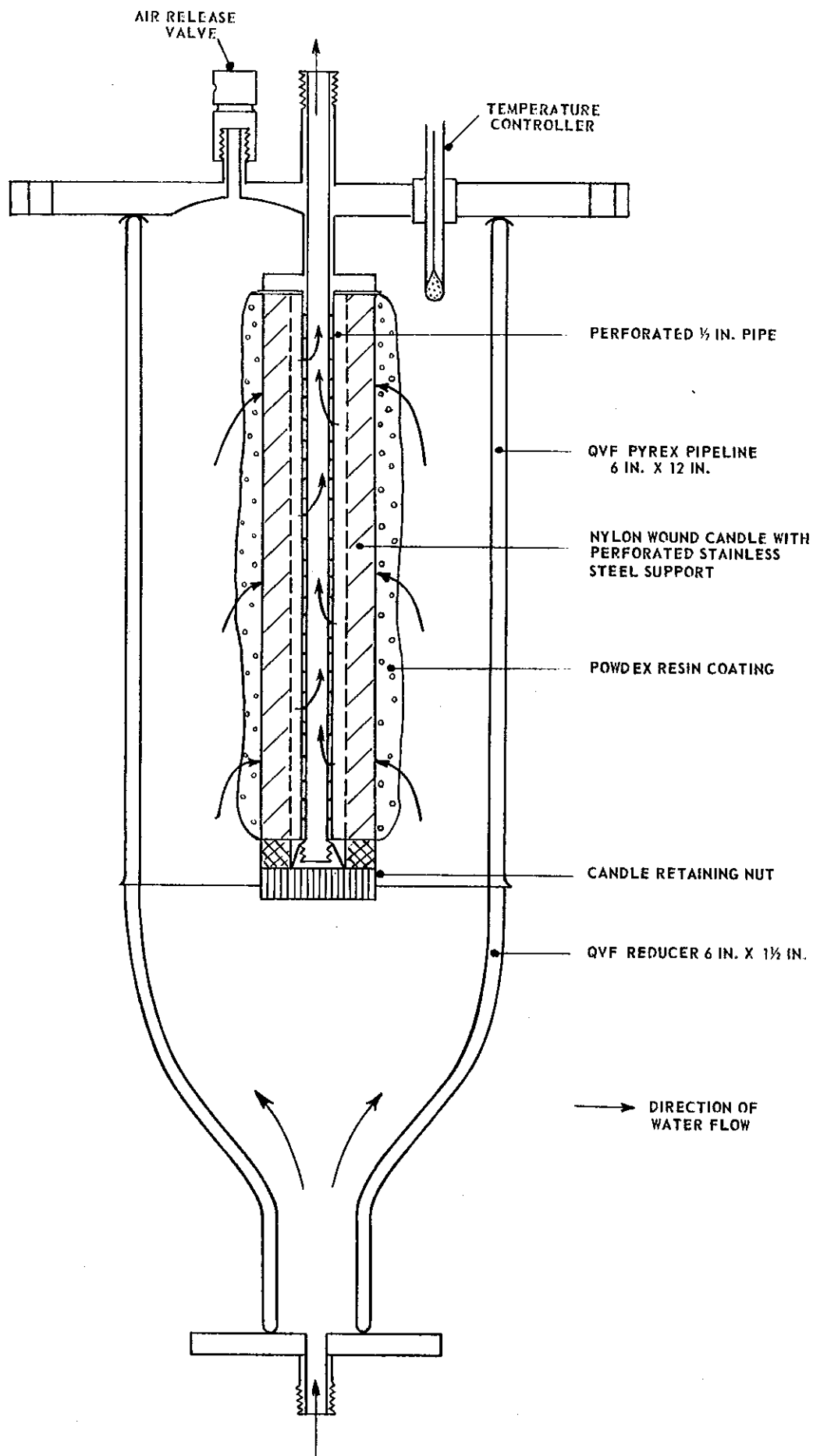


FIGURE 2. CANDLE AND CONTAINING VESSEL

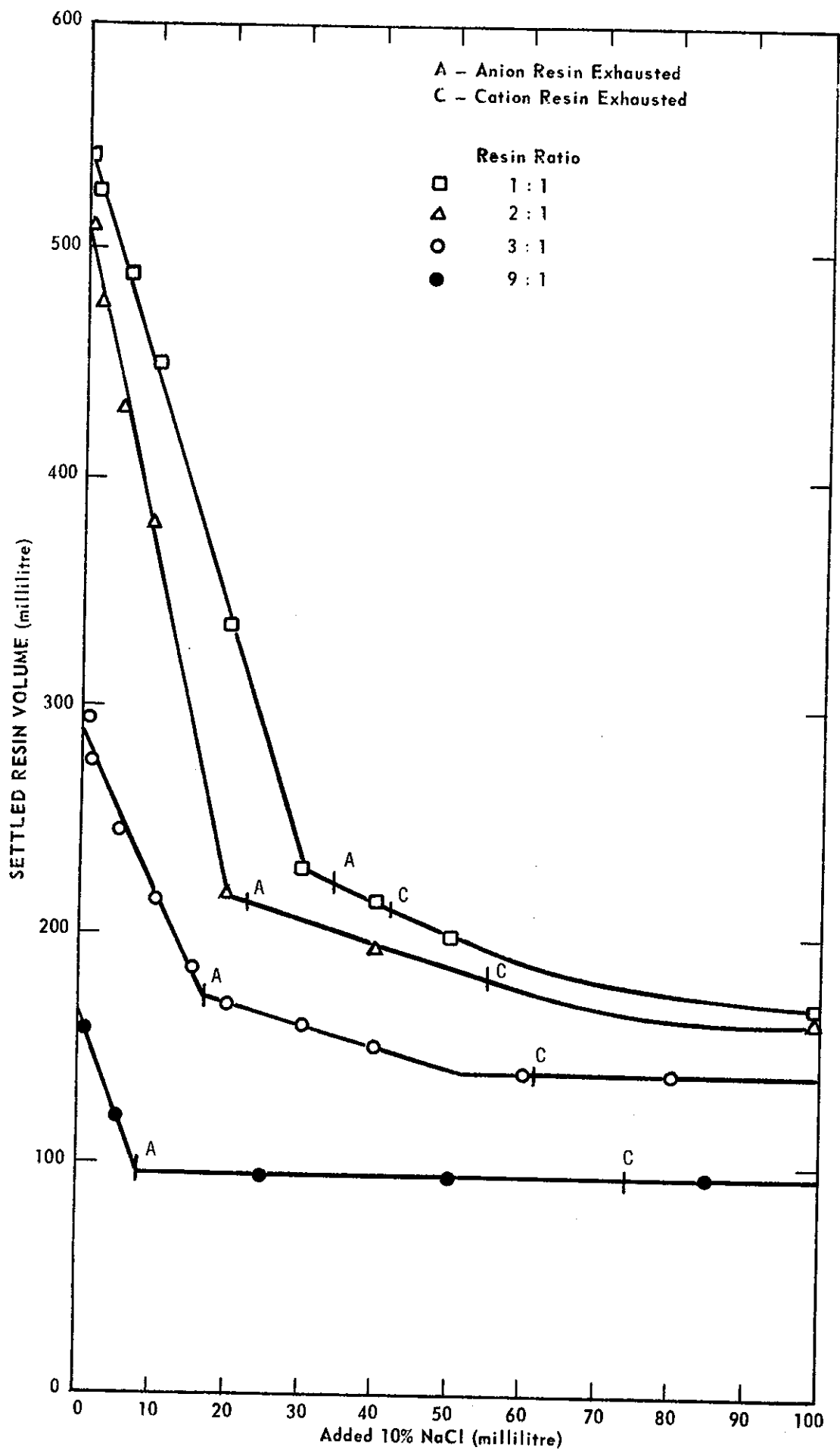


FIGURE 3. SETTLED RESIN VOLUME VERSUS DEGREE OF CONVERSION

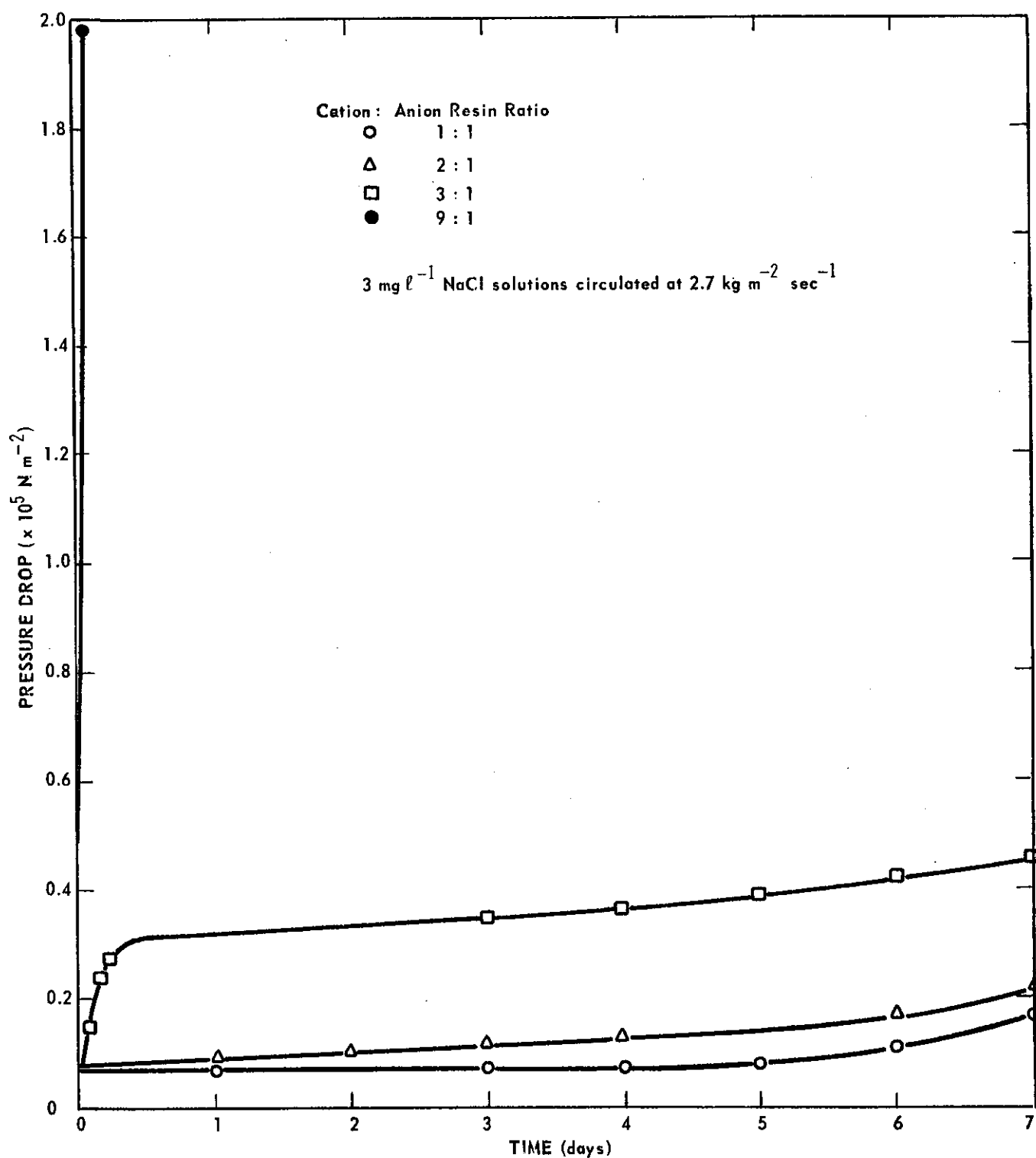


FIGURE 4. PRESSURE DROP ACROSS POWDERED RESIN COATINGS
FOR DIFFERENT RESIN MIXTURES

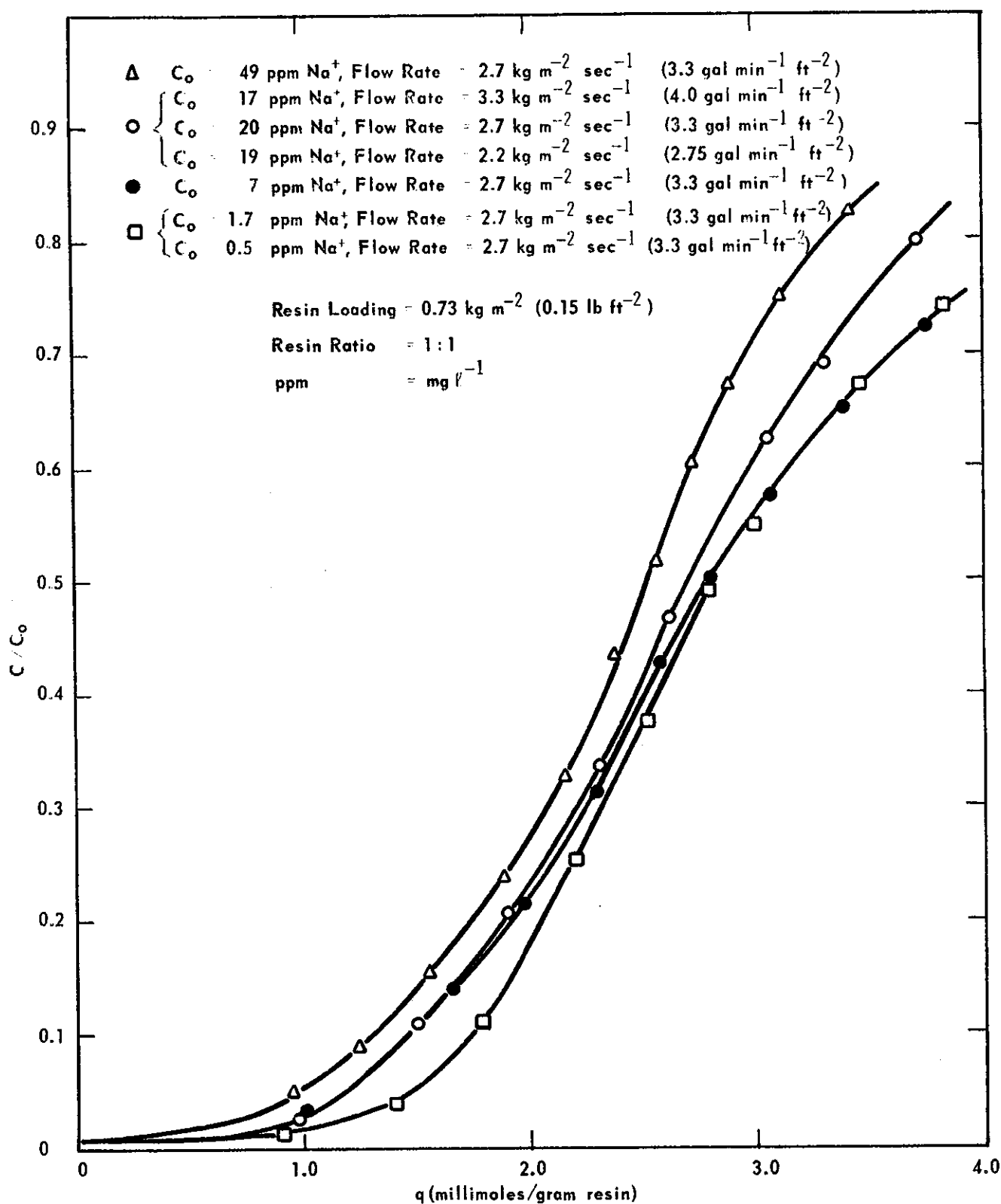


FIGURE 5. CATION-EXCHANGE BREAKTHROUGH CURVES (25°C)

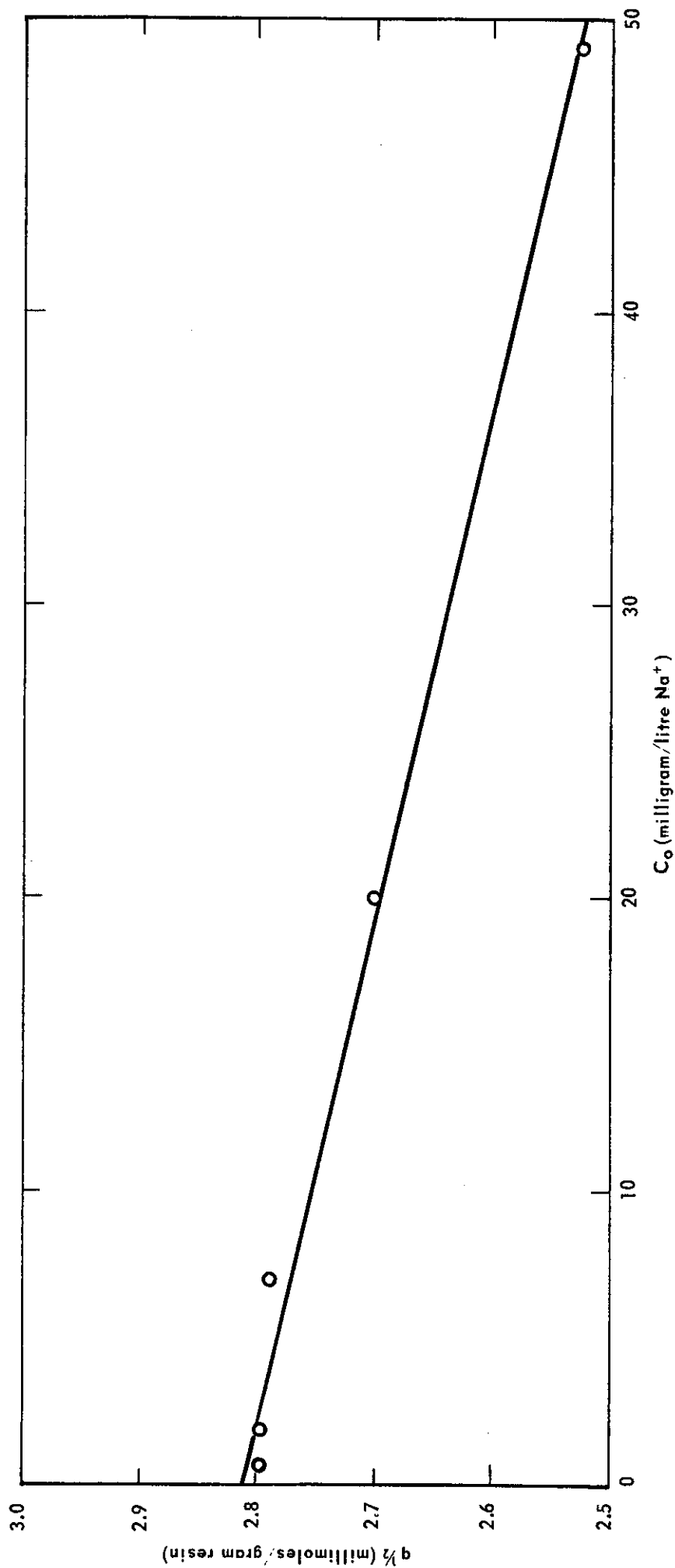


FIGURE 6. CATION-EXCHANGE CAPACITY ($q_{1/2}$) AS A FUNCTION OF INLET CONCENTRATION

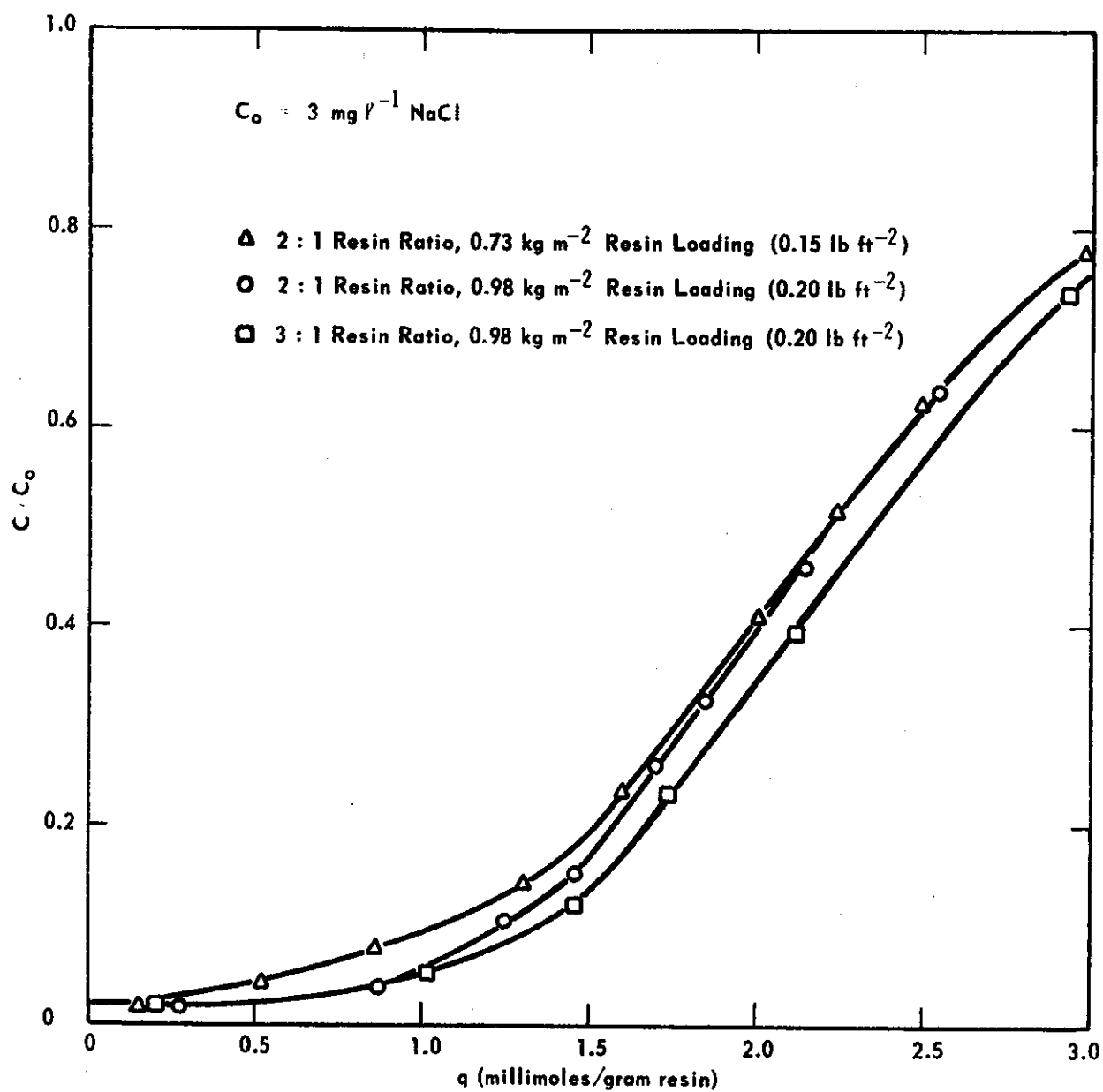


FIGURE 7. ANION-EXCHANGE BREAKTHROUGH CURVES (25°C)

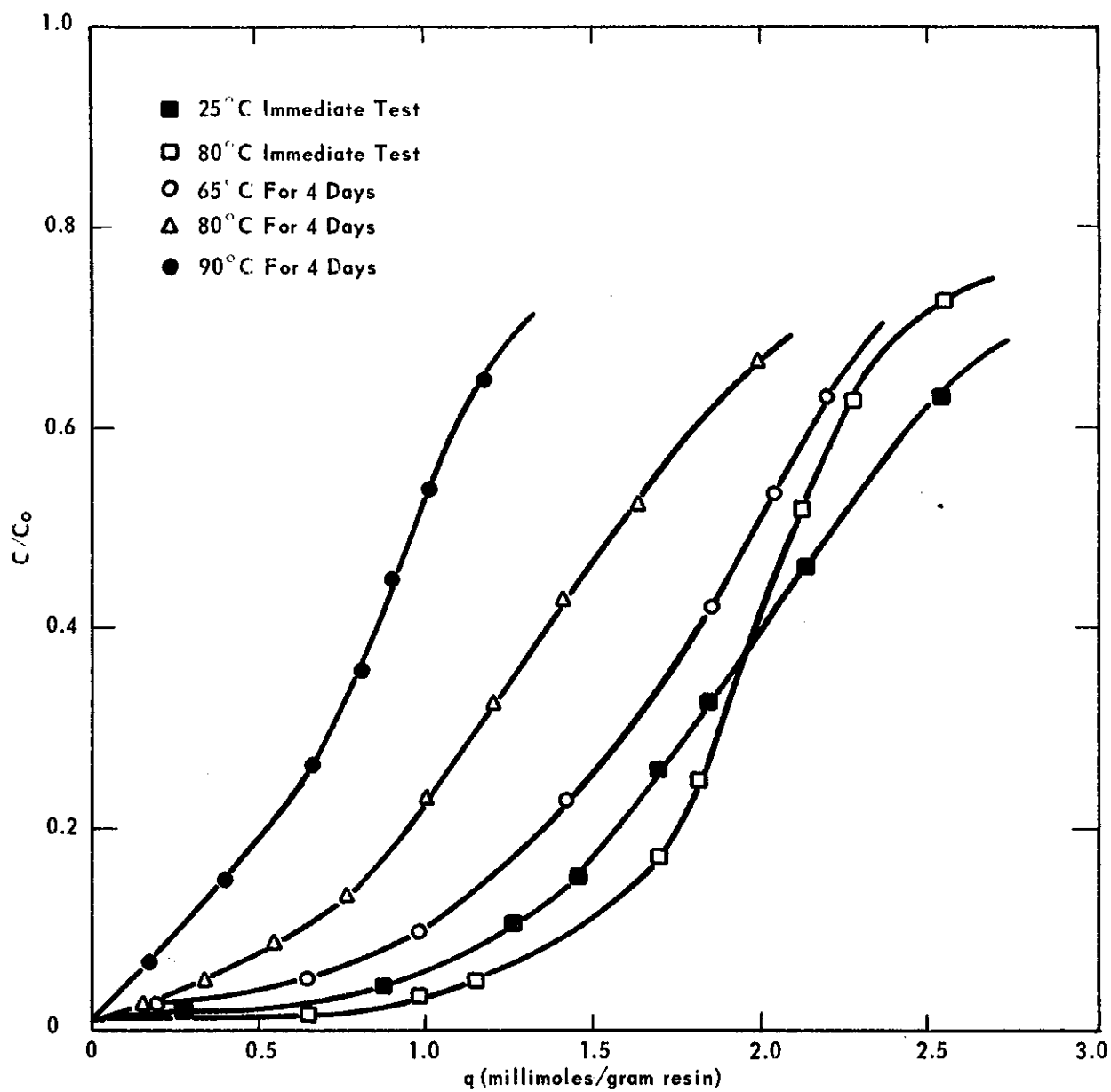


FIGURE 8. EFFECT OF TEMPERATURE ON ANION CAPACITY

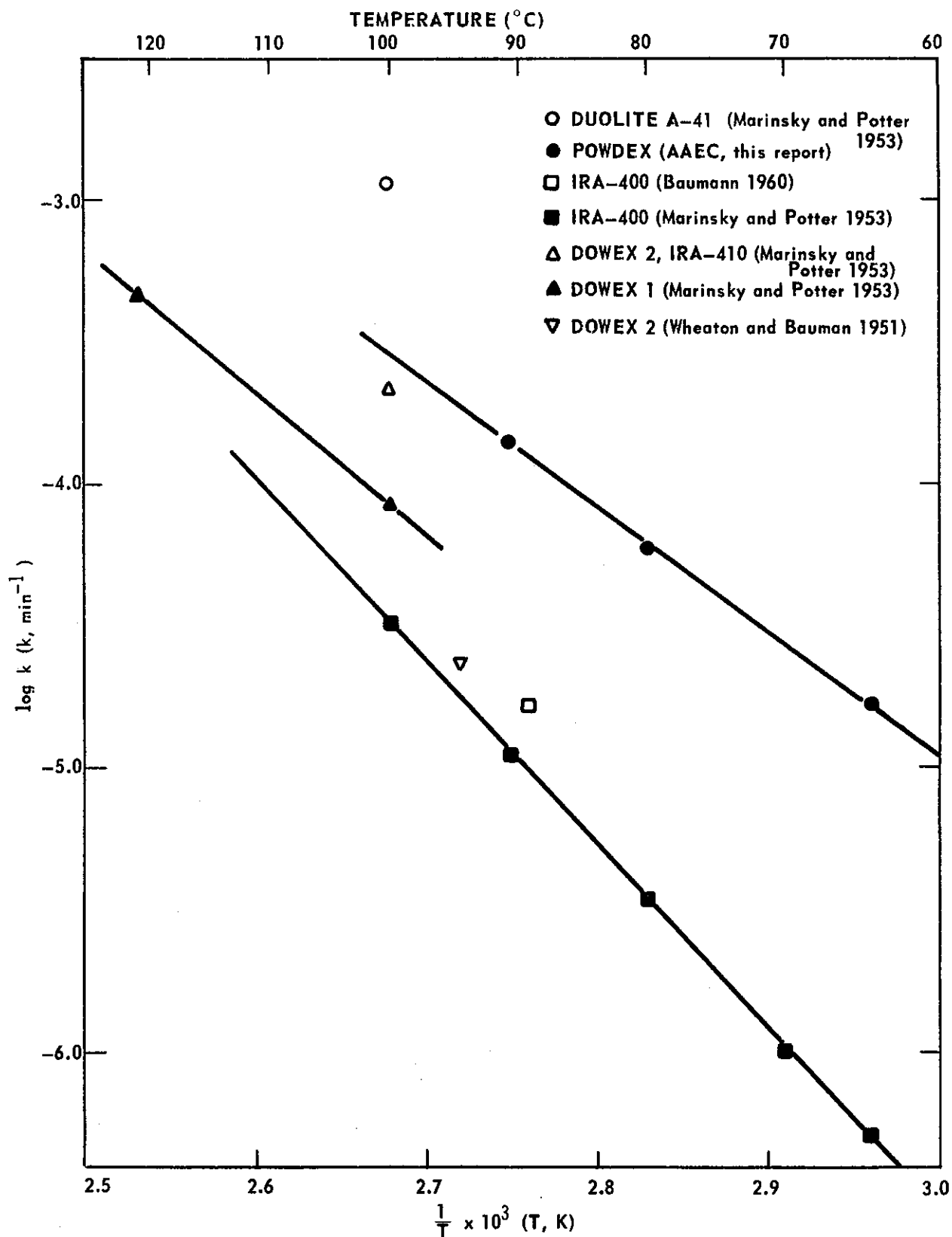


FIGURE 9. TEMPERATURE VARIATION OF THE RATE OF THERMAL DECOMPOSITION OF ANION-EXCHANGE RESINS

