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CHLORIDE–SULPHATE EXCHANGE ON ANION-EXCHANGE RESINS

KINETIC INVESTIGATIONS. I

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SUMMARY

The exchange rates for the complete conversion of many anion-exchange resins from the chloride to the sulphate form when particle diffusion is the controlling mechanism have been measured. Infinite solution volume conditions were adopted, using the centrifugal stirrer–reactor technique. The exchange rates were found to be greatly dependent on the basicity of the functional groups of the resins, according to the "kinetic sequence" quaternary > tertiary > secondary > primary amino-type resins, which is the reverse of the "selectivity sequence" previously found for the same resins under equilibrium conditions. On this basis, it was found to be advantageous to use a weak anion-exchange resin of intermediate selectivity in the process for the desulphation of sea-water feed to evaporation plants.

INTRODUCTION

The formation of calcium sulphate scales on heat-transfer surfaces greatly reduces the performance of evaporation plants. Studies conducted at IRSA since 1969 to prevent this problem led to the development of a process for sea-water desulphation using anion-exchange resins regenerated by the brine discharged from such plants[1]. Investigations on the chloride–sulphate equilibrium on anion-exchange resins indicated that the selectivity of the resin toward sulphates is strongly dependent on the basicities of the amino-type fixed charges of the resins, according to the "selectivity sequence"[2]

$$\text{quaternary} < \text{tertiary} < \text{secondary} < \text{primary amino-type resins} \tag{1}$$

Investigations have also been conducted on the kinetics of the system using both commercial and experimental resins, all with amino-type functional groups. Experimental conditions (solution concentration, temperature, liquid–solid contact time, etc.) were widely varied throughout the study.

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This paper describes an investigation of kinetics at high solution concentration (1.8 N), where the experimental conditions allow ion interdiffusion within the particles to be assumed as the rate-controlling mechanism. As the regeneration step (in which 1.2–2.0 N brine is used) is the least efficient part of the desulphation process, a knowledge of resin performance under such conditions is of extreme importance in the evaluation of the process.

EXPERIMENTAL

The infinite batch technique was adopted, using a modified version of the Kressman–Kitchener stirrer–reactor[3], as shown in Fig. 1, which allows the beads to be uniformly flushed by the solution aspirated by centrifugal action. The stirring rate was 2000 rpm. The rotating reactor, filled with about 0.01 g of resin in the chloride form, was rapidly immersed in a jacketed vessel, pre-agitated by a supplementary stirrer, containing 800 ml of sodium sulphate–sulphuric acid solution with a total sulphate concentration of 1.8 N and a pH of 3.0, at $25 \pm 0.1°$.

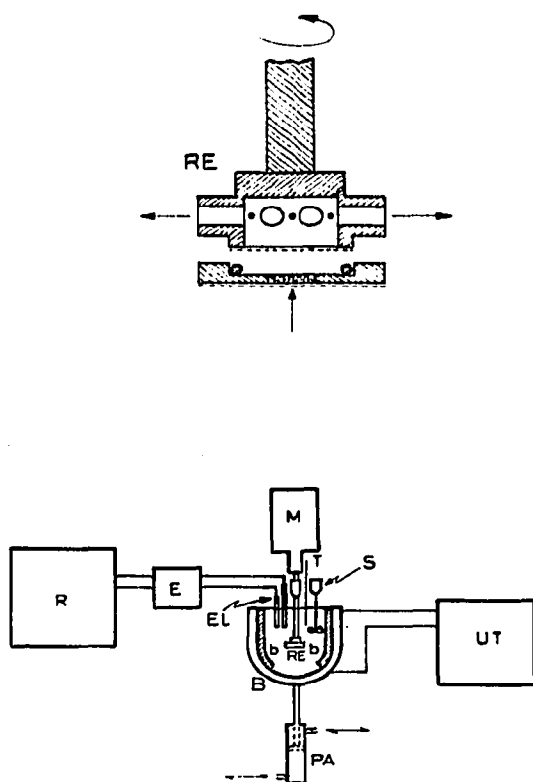The resin exchange capacities ranged from 2 to 7 mequiv./g, so that an

Fig. 1. Schematic diagram of the apparatus for kinetic measurements. R = potentiometric recorder; E = potentiometer; M = stirrer; T = thermometer; EL = electrodes; RE = centrifugal stirrer reactor; PA = pneumatic piston; UT = ultrathermostat; B = jacketed vessel; bb = baffles; S = supplementary stirrer.

"equivalent ratio" less than 10^{-7} equiv. of resin per equiv. of solution was used consistently. The infinite solution volume condition was assumed under these conditions. The chloride release was followed potentiometrically by means of ion-selective electrodes, the potential variations recorded and, by suitable reference curves, the Cl⁻ concentration *versus* time curves obtained. In order to account for electrode response delays, the reference curves were determined "dynamically" before each set of experiments, adding to the vessel an appropriate amount of standard sodium chloride solution with an automatic constant-speed burette.

After preliminary acid–base cycles, the resins were converted into the chloride form with sodium chloride–hydrochloric acid solution having the same pH and ionic strength as the reacting sodium sulphate–sulphuric acid solution, in order to prevent hydrolysis during the exchange. Fractions of 16–18, 20–30, 30–35 and 60–70 (U.S.) mesh were collected for each resin, using the same sodium chloride–hydrochloric acid solution as screening carrier, the mesh size being assumed to be the average radius of each fraction of the wet resin, r_0.

The resins were then washed with methanol and heated to constant weight in a vacuum oven at 60°. The broken beads were removed by rolling on an inclined plane, and the imperfect particles were discarded after final microscopic observation. Before each kinetic experiment, a weighed amount of dry resin was allowed to re-swell completely for 12 h in a saturated humidity box. For each mesh fraction, about 1 g of dry resin was thoroughly regenerated with an excess of warm 2 N sodium hydroxide solution, in order to obtain its chloride exchange capacity. This was used to calculate $[Cl^-]_\infty$, the chloride solution concentration after an infinite time, assuming complete conversion from the chloride to the sulphate form of the resin. The variation of Cl⁻ concentration with time was expressed as the fractional attainment of equilibrium: $U = [Cl^-]_t/[Cl^-]_\infty$.

Interruption tests performed on each resin confirmed that particle diffusion was the rate-controlling mechanism in all experiments.

RESULTS

As an illustration of the reproducibility of the system, Fig. 2 shows the kinetics obtained with one resin, under the same experimental conditions, over a period of several months. Fig. 2 also shows the kinetics obtained with the resin previously immersed for 4 h in distilled water (as it is a strong resin, hydrolysis was virtually undetectable). In Table I are reported the main physico-chemical characteristics of the resins investigated, and Table II gives the half-exchange times and the corresponding values of the interdiffusion coefficients, $\bar{D}_{0.5}$. The latter were calculated according to the well known solution to Fick's diffusional model for spherical particles, with a constant boundary condition (infinite solution volume), and a constant interdiffusion coefficient, as given by Barrer and Cranck (see ref. 4):

$$U = 1 - (6/\pi^2) \sum_{n=1}^{\infty} (1/n^2) \exp(-\bar{D}t \, \pi^2 \, n^2/r_0^2) \tag{2}$$

which, for $U = 0.5$, gives
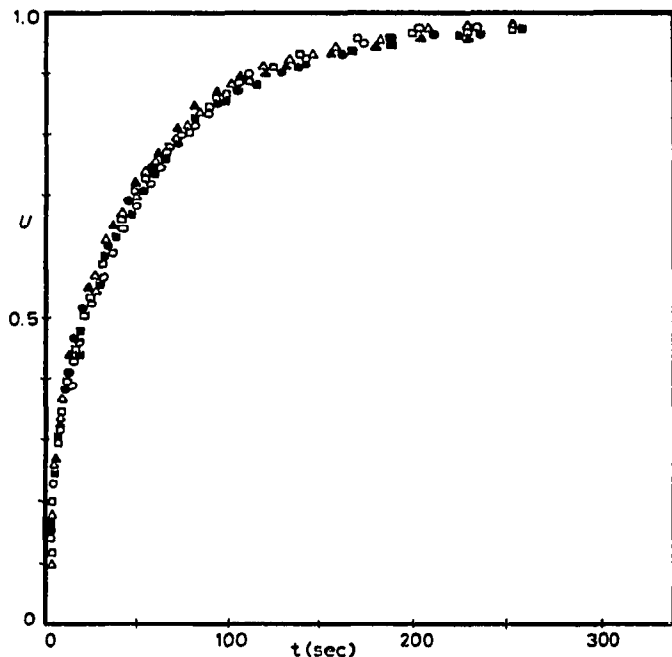
$$\bar{D}_{0.5} = 0.03 \, r_0^2/t_{0.5} \tag{3}$$

Fig. 2. Typical high-salinity kinetics. Resin: Kastel A-500, 30–35 mesh. Temperature, 25°; stirring speed 2000 rpm; concentration, 1.8 N. ●, Test 160; ○, 161; ■, 289; □, 290; △, 313; ▲, 314. Tests 160 and 161 dated November, 1973; tests 289, 290, 313 and 314, January, 1974. Tests 313 and 314: resin previously immersed in distilled water for 4 h.

TABLE I

MAIN PHYSICO-CHEMICAL PROPERTIES OF THE RESINS INVESTIGATED

Concentration = 1.8 N; temperature = 25°.

Resin	Predominant functional group	Matrix	Porosity	Exchange capacity (equiv./kg)		
				16–18 mesh	20–30 mesh	30–35 mesh
Kastel A-500	Quaternary (type I)	Styrenic	Gel	3.05	3.22	3.48
Lewatit M-500	Quaternary (type I)	Styrenic	Gel		4.05	
Amberlite IRA-400	Quaternary (type I)	Styrenic	Gel	3.94	3.89	3.72
Relite 3A	Quaternary (type I)	Styrenic	Gel		3.75	
Kastel A-300	Quaternary (type II)	Styrenic	Gel		3.28	
Lewatit M-600	Quaternary (type II)	Styrenic	Gel		3.35	
Relite 2A	Quaternary (type II)	Styrenic	Gel		3.63	
Kastel A-101	Tertiary	Styrenic	Gel		3.90	
Amberlite IRA-93	Tertiary	Styrenic	Macroreticular	3.97	3.88	3.81
Relite 4-MS	Tertiary	Styrenic	Gel		3.89	
Lewatit MP-60	Tertiary	Styrenic	Macroporous		4.23	
Relite MS-170	Tertiary	Styrenic	Gel		4.65	
Amberlite IRA-68	Tertiary	Acrylic	Gel		4.70	
Kastel A-105	Tertiary	Acrylic	Gel	5.28	5.80	5.32
Lewatit Ca-9222	Tertiary	Acrylic	Gel		4.70	
Wofatit AK-40	Secondary	Styrenic	Porous	5.38	5.35	5.33
Kastel A-102	Secondary	Acrylic	Gel	6.20	6.20	6.20
Relite MG-1	Secondary	Acrylic	Gel		6.49	
Duolite A-366	Secondary	Acrylic	Gel		6.75	
Kastel A-103/1	Primary	Styrenic	Gel	3.13	2.88	2.33
Duolite S-2002	Primary	Styrenic	Porous		3.45	

TABLE II

KINETIC DATA FOR THE Cl⁻–SO₄²⁻ EXCHANGE IN THE PARTICLE DIFFUSION REGION

Concentration $= 1.8\ N$; temperature $= 25°$; stirring rate 2000 rpm.

Resin	16–18 mesh		20–30 mesh		30–35 mesh		$\bar{D}_{0.5,av.} \cdot 10^7$ (cm²/sec)
	$t_{0.5}$ (sec)	$\bar{D}_{0.5} \cdot 10^7$ (cm²/sec)	$t_{0.5}$ (sec)	$\bar{D}_{0.5} \cdot 10^7$ (cm²/sec)	$t_{0.5}$ (sec)	$\bar{D}_{0.5} \cdot 10^7$ (cm²/sec)	
Kastel A-500	45	20	28	13.7	23	10	15.7
Lewatit M-500			55	7.1			
Amberlite IRA-400			34	11.3			
Relite 3A			35	11			
Kastel A-300			55	7.0			
Lewatit M-600			94	4.1			
Relite 2A			45	8.5			
Kastel A-101			51	7.5			
Amberlite IRA-93	107	8.4	39	9.8	24	9.3	8.8
Relite 4-MS			50	7.7			
Lewatit MP-60			73	5.3			
Relite MS-170			42	9.1			
Amberlite IRA-68			41	9.4			
Kastel A-105	114	7.9	58	6.6	29	7.4	7.5
Lewatit Ca-9222			40	9.6			
Wofatit AK-40	105	8.6	38.5	10.1	25	8.9	8.9
Kastel A-102	124	7.2	59	6.5	38	6.0	6.8
Relite MG-1			38	10.1			
Duolite A-366			62	6.2			
Kastel A-103/1	174	5.2	118	3.2	75	3.0	4.5
Duolite S-2002			108	3.6			

The third condition for the application of eqn. 2 (*i.e.*, constancy of $\bar{D}$), in fact, did not prove to be valid in this experiment. Further examination of the experimental results, based on the application of the Nernst–Planck model, is currently being carried out[5]. $\bar{D}_{0.5}$ is therefore merely one value of $\bar{D}$ during that experiment, and not even the most representative value for the resin under the conditions used. Fig. 3 shows the general dependence of the exchange rates on the predominant fixed charge of the resins (closed circles indicate the potential resins for use in the sea-water desulphation process).

The same dependence in Fig. 4 is restricted to strong anion-exchange resins with a type I or type II quaternary ammonium group. In Fig. 5 the exchange rates of resins of intermediate basicity with tertiary amino groups are compared, according to the nature of the matrix. Fig. 6 shows the half-exchange times of different mesh fractions of some resins.

DISCUSSION

The difficulty of making valid comparisons among different resins must be recognized. When comparing, for instance, resins with the same kind of matrix, porosity, degree of cross-linking, charge density, etc., which differ only in the predominant functional groups, in principle it cannot be excluded that other, less appar-
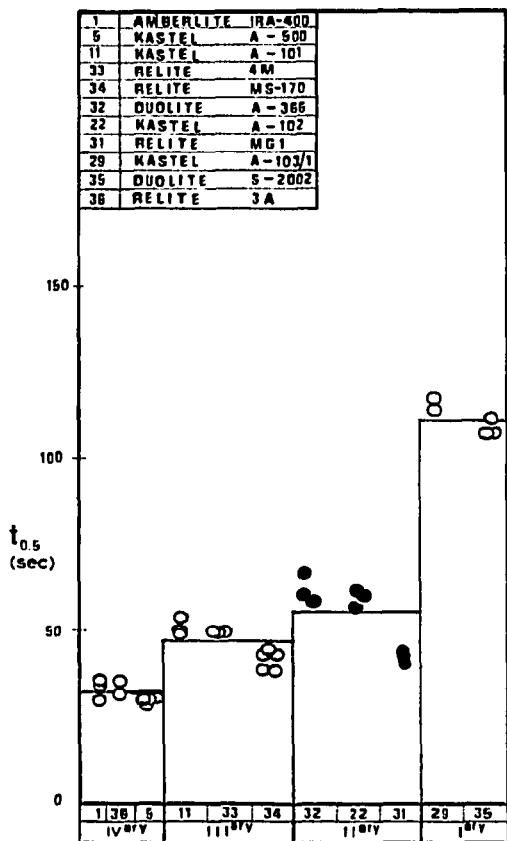
Fig. 3. Half-exchange times of polystyrenic gel resins with different amino-type functional groups (20–30 mesh).
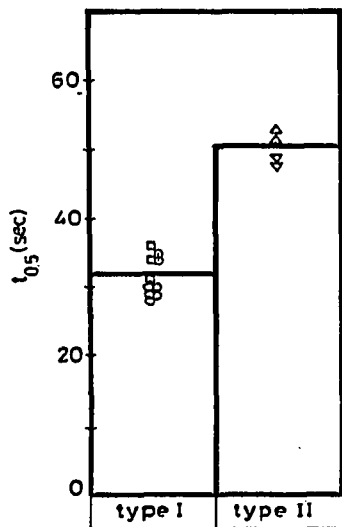

Fig. 4. Half-exchange times of polystyrenic gel strong anion-exchange resins with type I or type II ammonium groups (20–30 mesh). O, Kastel A-500, type I; □, Amberlite IRA-400, type I; ⊙, Relite 3A, type I; △, Kastel A-300, type II; ▽, Relite 2A, type II.
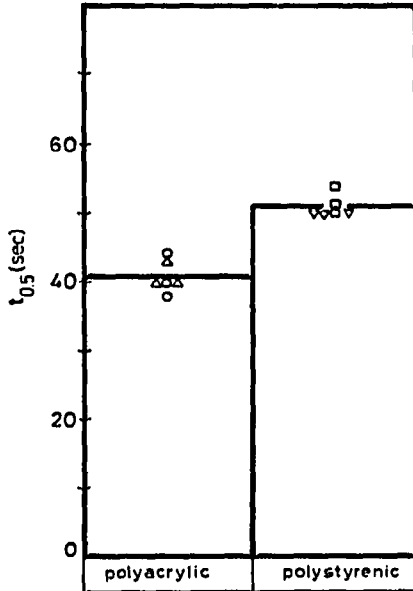
Fig. 5. Half-exchange times of tertiary gel resins with different matrices (20–30 mesh). ◯, Lewait Ca-9222; △, Amberlite IRA-68; ☐, Kastel A-101; ▽, Relite 4-MS.
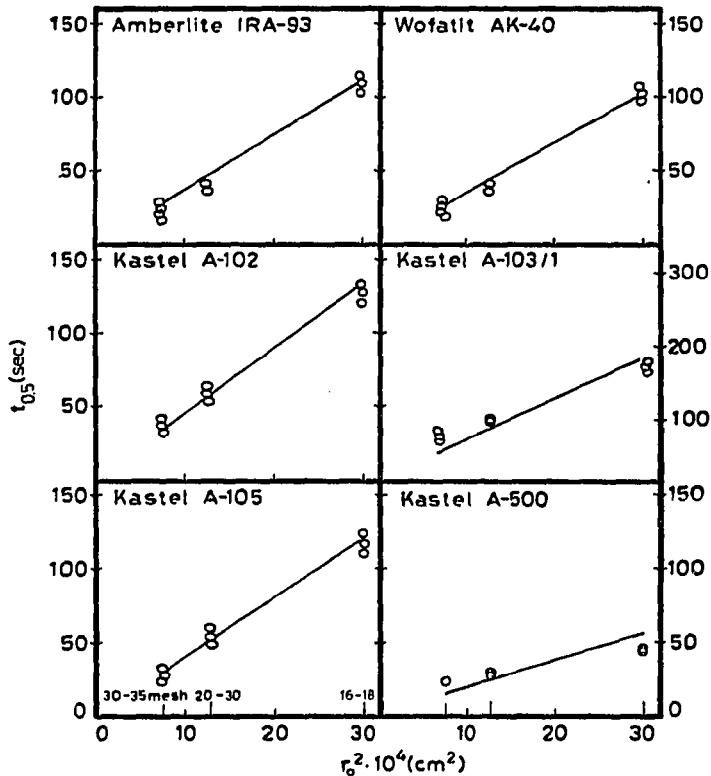

Fig. 6. Half-exchange times of different mesh fractions as a function of the average particle radius of the resins.

ent, physical differences in the resin morphology may have been introduced by the type of fixed charge itself. However, the hypothesis of physical homogeneity in groups of resins seems to be valid if one observes the reproducibility obtained over each group of similar resins.

The main result of this study was the finding of a close dependence of the $Cl^--SO_4^{2-}$ exchange rate on the nature of the amino-type functional group in the anion-exchange resins. According to the results in Fig. 3, the following "kinetic sequence" occurs:

$$\text{quaternary} > \text{tertiary} > \text{secondary} > \text{primary amino-type resins} \qquad (4)$$
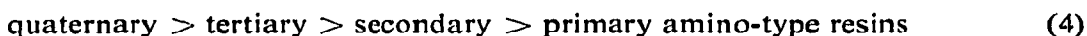
which is the reverse of the selectivity sequence in eqn. 1.

It must be noted that strongly basic anion-exchange resins, (*i.e.*, with quaternary ammonium groups) have often been reported to show higher exchange rates than weakly basic ones in deionization and similar processes. In such cases, however, the parallel neutralization reaction of OH^- ions influences the overall exchange rate of the weaker resins. This is not the case in this work, where strict pH control prevents exchange reactions other than $Cl^--SO_4^{2-}$ from occurring.

The co-existence of the selectivity and kinetic sequences 1 and 4 may be considered to be reasonable if one simply examines the particular pattern of ion transfer inside the resin. In order to allow for further sulphate ions to be adsorbed by the particle, the exchanged sulphate ions migrate towards the inner parts of the bead, jumping from one fixed charge to another, with an iterative attach–detach mechanism. As the exchange process proceeds, each fixed charge repeatedly exchanges its sulphate ion with new sulphate ions. According to the established collision theory, this can be described by the following reaction:

$$X^- + RY \rightleftharpoons [X\text{--------}R\text{--------}Y]^- \rightleftharpoons RX + Y^- \qquad (5)$$
$$\text{(activated complex)}$$
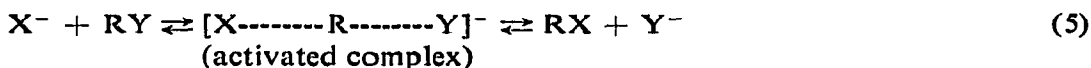
where $X^- = \frac{1}{2} SO_4^{2-}$, $Y^- = \frac{1}{2} SO_4^{2-}$ (except in the first exchange, where $Y^- = Cl^-$) and R = amino-type fixed charge. Assuming that approximately the same energy content applies to the activated complex, irrespective of the type of amino group, the activation energy required for such a reaction to proceed is inversely proportional to the energy content of the sulphate form of the amino groups themselves.

It follows that the reaction rate is lower with the more selective resins, characterized by lower values of the energy content of the sulphate form and, therefore, by higher values of the activation energy involved in reaction 5. This helps to explain the large rate differences found between type I and type II quaternary ammonium resins. Type II strong anion-exchange resins (with a dimethylethanolammonium group) are often preferred to the stronger type I resins (with a trimethylammonium group) in industrial applications, because of their hydrophilic nature, which would enable faster rates to be obtained. Our findings, which contrast with this general statement, may be explained on the basis of a selectivity–kinetic correlation, the selectivity towards sulphate ions of the type II ammonium resins (like their basicity) lying between the first and second positions in sequence 1.

Our results agree with the data of Eliasek and Talasek[6], who studied several

anion-exchange kinetics in the particle diffusion region and found a strong superiority of type I over type II anion-exchange resins in exchange reactions such as OH^--Cl^- and $OH^--SO_4^{2-}$.

In full agreement with the expectations are the higher kinetics showed by polyacrylic over polystyrenic matrix resins, according to the hydrophobic nature of the latter. This result, among other considerations, confirms the possibility of using a polyacrylic product for the desulphation process.

Finally, as shown in Fig. 6 for some of the resins investigated, the half-exchange times lie on a straight line when plotted against the square of the particle radius. While definitely confirming the particle diffusion control, this allowed for the $\bar{D}_{0.5,av.}$ values in Table II to be calculated for these resins by the least-squares method applied to eqn. 3. As confirmed by further investigations, however, although useful for comparison purposes, $\bar{D}_{0.5,av.}$ is not yet suitable for quantitative measurements of the Cl^- and SO_4^{2-} diffusivities within the resins.

CONCLUSIONS

The basicity of functional groups has been seen to influence greatly both the equilibrium and the kinetic features of the $Cl^--SO_4^{2-}$ exchange on anion-exchange resins. For the sea-water desulphation process, thermodynamic considerations and laboratory runs[7] suggested the selection of intermediate weak anion-exchange resins, with predominantly secondary amino functional groups and a polyacrylic matrix, for substantially removing sulphates from sea-water, being capable of regeneration by the limited amount of brine available in the evaporation plants. This choice is now supported by kinetic considerations, which indicate that weaker resins (such as primary amino-type anionic resins), being extremely selective towards sulphates, would exhibit too low exchange rates. Due also to the hydrophilic nature of the polyacrylic matrix, with the selected resins half-exchange times less than 1 min can be expected, while 90% exchange can be reached in less than 5 min. These figures ensure high over-all kinetics coupled with high selectivity in the desulphation process.

In general, according to the diffusive nature of the ion-exchange mechanism, it can be concluded that selectivity may adversely influence the over-all kinetics of ion-exchange processes. This must be accounted for each time one is dealing with selective applications of ion exchange.

ACKNOWLEDGEMENT

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