Designation: D6302 – 98 (Reapproved 2017)

Standard Practice for
Evaluating the Kinetic Behavior of Ion Exchange Resins[1]

This standard is issued under the fixed designation D6302; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice is intended to evaluate changes in kinetic performance of ion exchange resins used in mixed beds to produce high purity water. Within strict limitations, it also may be used for comparing resin of different types. This standard does not seek to mimic actual operating conditions. Specific challenge solutions and conditions are specified. At the option of the user, other conditions may be tested.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D2187 Test Methods for Physical and Chemical Properties of Particulate Ion-Exchange Resins

D2687 Practices for Sampling Particulate Ion-Exchange Materials

D5391 Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

4. Summary of Practice

4.1 An apparatus is described in which a specified volume of regenerated resin sample is mixed with a corresponding new resin. The mixed bed then is operated at a controlled high flow rate on an influent of known composition, and the quality of the effluent is measured by conductivity, and if agreed upon, other appropriate analytical procedures.

5. Significance and Use

5.1 This practice is intended to evaluate changes in the performance of ion exchange resins used in mixed beds operating as polishing systems for solutions of low ionic strength, typically, <10 mg/L dissolved solids, that are intended to produce very high purity effluents. It is recommended that when new resins are installed in a plant it be used to provide a base line against which the future performance of that resin can be judged.

5.2 The conditions of this test must be limiting kinetically, such that kinetic leakage, and not equilibrium leakage, is tested. This leakage is influenced by a combination of influent flow velocity and concentration, as well as bed depth.

5.3 It is recommended that the practice be followed with the resin ratio, flow rate, and influent quality as indicated. The design of the apparatus permits other variations to be used that may be more appropriate to the chemicals used in a specific plant and the nature of its cooling water, but the cautions and limitations noted in the practice must be accommodated.

5.4 It is possible that the cation resin could experience kinetics problems. In many cases, however, the anion resins are more likely to experience the types of degradation or fouling that could lead to impaired kinetics. Testing of field anion and cation resins together is an option, especially when historic data on the mixed bed will be compiled. Recognize, however, that many variables can be introduced, making it difficult to interpret results or to compare to historical or new resin data on separate components.

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[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.08 on Membranes and Ion Exchange Materials.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

5.5 Provision is made for calculation of the mass transfer coefficient in the Appendix X1. When such calculation is to be made, a full wet sieve analysis, as described in Test Methods D2187, also is required. Electronic particle sizing may be substituted if it is referenced back to the wet sieve method.

5.6 This practice is intended to supplement, not displace, other indicators of resin performance, such as exchange capacity, percent regeneration, and service experience records.

6. Interferences

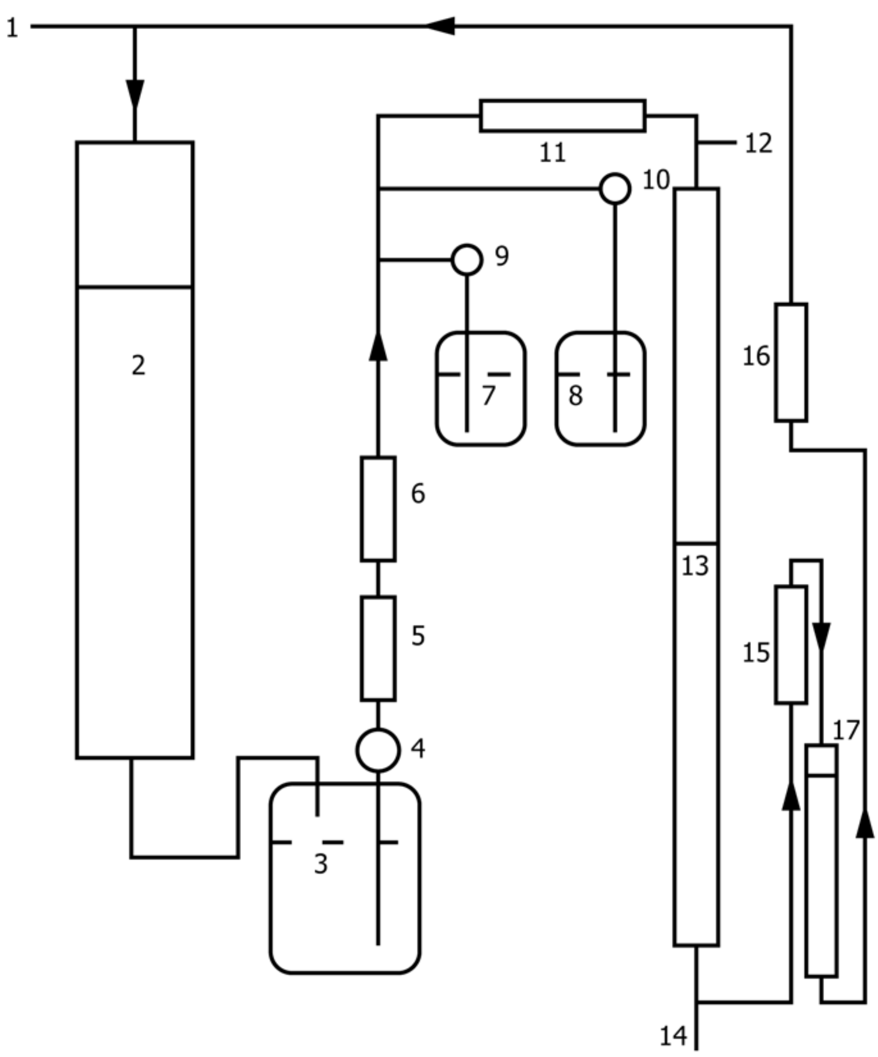
6.1 Interferences in the conventional sense are minimal, but variations in test conditions, such as flow rate, temperature, resin ratio, particle size, column configuration, regeneration efficiency, and influent concentrations can cause major differences in performance. This practice fixes or measures these variables so that true changes in resin kinetics can be demonstrated accurately. Other means will be needed to investigate other resin or equipment problems.

6.2 Contaminant ions in the resins themselves, if present when they are loaded into the test apparatus, may impact performance significantly and must be considered in the interpretation of the results. If the contaminant ions are different from those in the challenge solution, they may be determined by ion chromatography.

6.3 A constant velocity in the range of 50–60 gpm/ft^2 is used to insure that flow is turbulent and there is little or no resistance to mass transfer from the bulk solution to the resin surfaces. This constant velocity insures the desired testing of surface kinetics at the boundary layer.

7. Equipment

7.1 *Backwash/Separation and Regeneration Apparatus,* see Test Methods D2187. The column should be 50-mm ID × 600 or 900-mm length.



1. Water supply, ASTM Type I
2. Mixed bed polishing column
   (Required for recirc mode)
3. Polished water reservoir
   (Required for recirc mode)
4. Pump
   (Required for recirc mode)
5. Conductivity meter
   (Required for recirc mode)
6. Flow meter
7. and 8. Feed solution reservoir
9. and 10. Proportional metering pump
11. Mixing chamber or static mixer
12. Influent sample tap
13. Test column
14. Effluent sample tap
15. Conductivity meter
16. Conductivity meter
17. Cation column

NOTE 1—Recirculation of water is optional; final effluent also can be directed to drain.

FIG. 1 Test Apparatus for Kinetics

7.2 *Kinetics Test Apparatus (see Fig. 1):*

7.2.1 *Feed Pumps,* capable of controlled delivery of 0.5 to 3 mL/min. One is required, the second is optional for use where another reagent, such as ammonia, is to be added.

7.2.2 *Circulating Pump,* capable of delivery of 1 to 1.5 L/min.

7.2.3 *Glass Column,* nominal 25-mm ID × 600 mm. The column shown in Fig. 1 of Test Methods D2187 may be modified for this purpose.

7.2.4 *Mixing Chamber.*

7.2.5 *Conductivity Meter With Recorder and Temperature Compensation*—See Test Method D5391.

7.2.6 *Flow Meter*—Capable of measuring flows in the range of about 1 L/min.

7.2.7 *Cation Column,* nominal 25-mm ID × 600-mm column, typically with a 15–45-cm depth of resin. This column should be prepared the day before testing to allow to rinse to >17.5 MΩ (see 8.3).

NOTE 1—Pressure relief should be provided for this system to allow no more pressure than the materials can tolerate, typically 50 psig or less.

8. Reagents

8.1 *Purity of Reagents*—Reagents meeting the specifications of the Committee on Analytical Reagents of the American Chemical Society may not be suitable for use in this practice. All reagents used should be of the highest grade commercially available and should be tested for both anionic and cationic impurities by ion chromatography after the feed solutions have been prepared.[3,4]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. It shall be checked by ion chromatography at the ppb level prior to use, if ion chromatography will be used for analysis.

8.3 *Standard Cation Resin*—New hydrogen-form, strong acid, cation resin is to be used; nuclear grade is preferred. Do not regenerate this resin. This resin should be stored in impermeable containers at temperatures that do not exceed 25°C. Backwash the resin with water at 100 % expansion for at least 15 min. The resin should be rinsed thoroughly with water to ≥17.5 MΩ resistivity before being used in a kinetics test. The same cation resin may be used in the test column, as well as the cation column. It is recommended that a specific type and brand of resin be used consistently where results are to be compared.

8.4 *Standard Anion Resin*—Use new, hydroxide-form, strong base anion resin; nuclear grade preferred. Follow other requirements as given in 8.3.

8.5 *Test Solutions*—Test solutions can be modified for specific systems, however, the following are recommended for routine testing. Although a target feed injection rate of 0.5 mL/min is used here, the feed concentrations and metering pump flows can be altered, so long as the test column influent concentrations and flow rate are nominal as specified.

8.5.1 *Ammonia Feed Solution (3.0 g/L as NH_3) Optional for Use with Ammoniated Systems*—Tare a beaker with about 50 mL of water on an analytical balance with 0.01-g sensitivity. Add 20.9 g of concentrated ammonium hydroxide (sp. gr. 0.90) from a dropping bottle. Transfer to a 2-L volumetric flask, and dilute to volume. Mix well. When delivered at the rate of 0.5 mL/min into 1 L/min flow, the concentration in the influent should be 1.5 mg NH_3/L.

NOTE 2—Ammonium hydroxide generates irritating ammonia vapors.

8.5.2 *Sodium Sulfate Feed Solution (0.9 g Na_2SO_4/L)*—Dry the Na_2SO_4 for 1 h at 100–105°C, then store in a desiccator. Weigh 0.900 g of the anhydrous sodium sulfate, and dissolve it in 1 L of water. Mix well. When delivered at the rate of 0.5 mL/min into 1 L/min flow, the concentration of the influent should be 0.145 mg/L Na and 0.300 mg/L SO_4.

8.6 *Regenerant, Sodium Hydroxide Solution (87 g/L)*—Add 345 g NaOH to 3.5 L of water with stirring. Cool and dilute to 4.0 L. This solution is caustic and liberates heat during dissolution. This is equivalent to 8 % NaOH by weight.

NOTE 3—This solution is intentionally stronger than typical field processes so that maximum percent regeneration is achieved.

Reagent grade 50 % NaOH (763 g NaOH/L) also can be used and would require 456 mL to make 4.0 L.

8.7 *Regenerant, Hydrochloric Acid Solution (1 + 9)*—Carefully pour 200 mL of hydrochloric acid (HCl, sp. gr. 1.19) into 1800 mL of water, stirring constantly. Cool to 25 ± 5°C.

NOTE 4—For field cation samples, sulfuric acid typically would be substituted for HCl, since H_2SO_4 is the usual regenerant in the field.

9. Sampling

9.1 Collect the sample in accordance with Practices D2687. It is extremely important that the resin sample properly represent the entire bed being evaluated. Core sampling is required. A sample containing at least 300 mL of anion, or cation resin, or both, must be provided. The sample may be taken before or after separation of a mixed bed, so long as it is representative. Use a plastic or glass container with a water-tight cap and label in accordance with Practices D2687.

9.2 Subsamples taken in the laboratory also must be taken by careful coring to preserve the representativeness of the sample.

10. Backwash and Separation Procedure

10.1 Place about 800 mL of mixed bed resin sample or about 500 mL of individual resin sample in the backwash/separation apparatus. Backwash with water at a flow sufficient to give about 50 % bed expansion. This should allow crud to rinse away while separating any cation from the anion in the sample.

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[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[4] McNulty, J. T., Bevan, C. A., et al., "Anion Exchange Resin Kinetic Testing: An Indispensable Tool for Condensate Polisher Troubleshooting," *Proceedings of the 47th International Water Conference*, Engineers' Society of Western Pennsylvania, October 1986.

10.2 Using a siphon or aspiration assembly, remove and collect the resin of interest, anion resin (above the interface) or cation resin. Try to minimize cross-contamination by leaving behind or wasting resin as needed. This, however, must be minimized in order to avoid sample bias. Inspection of the interface with a hand lens may show a bead size variation at the interface. If less than 300 mL of the resin of interest is recovered, repeat 10.1 with another portion of sample.

10.3 Remove a small amount of the separated resin to a plastic petri dish and examine under low power (12–15×) magnification to estimate the percentage of whole beads. If the resin is less than about 90 % whole beads, this practice should not be continued.

NOTE 5—Ion exchange kinetics are affected by particle size and shape.

10.4 After decanting excess water, measure, by coring, 300 mL of the separated resin in a graduated cylinder under water. Tap gently to settle before measuring resin. Disconnect the regeneration column, and transfer the resin as a slurry to the column. Keep a small amount of water above the resin and try to minimize air bubbles. Leave the bottom effluent line shut off while filling the column. Open it and immediately begin the flow of regenerant. Regenerate the resin as follows. For anion, use NaOH regenerant solution at a flow rate of 25 mL/min for 60 min, maintaining a temperature of 50°C either by jacketing the column or warming the regenerant. For cation resin, use the HCl regenerant with the same conditions, except that ambient temperatures are used.

10.5 Make sure that the water level is no more than about 5 mm above the top of the resin before beginning the rinse step. Rinse the regenerated resin with water at 25 mL/min for 15 min, then increase flow to about 100 mL/min, and rinse until the effluent conductivity is 20 µS/cm or less. Rinsing should take no more than a total of 1 h.

10.6 Transfer the regenerated resin from the column to a beaker. Transfer, by coring, a 75-mL portion to a graduated cylinder, containing 10–15 mL of water. Cover to protect from CO_2 until resin is to be used. If mass transfer coefficient is to be calculated according to Appendix X1, use the rest of the regenerated resin sample, at least 200 mL, to measure the particle size distribution as directed in Test Methods D2187, Test Method D. No other pretreatment is required prior to sieving. Measurement of particle size distribution is recommended for all samples to verify the representativeness of samples and comparability of results; however, be cautious in using this measurement to compare to specifications for size since some resin may be lost in this procedure.

11. Preparation of Column and Rinse Down

11.1 Transfer, by coring, 150 mL of the hydrogen-form cation resin either new or regenerated sample in a graduated cylinder under water. Tap the graduated cylinder gently when measuring the resin volume to get an accurate reading. Transfer the cation and the 75 mL of new or regenerated sample anion resin to a 400-mL beaker, and decant excess water, then mix well with a glass rod.

11.2 Disconnect the test column (see Fig. 1), decant excess water from the resin, and transfer the mixed resin as a slurry to the rinsed, drained test column. Keep only a very small amount of water above the resin, so the resins do not stratify, and try to minimize air pockets. Leave the bottom effluent line shut off while filling the column, except that a small amount of liquid can be drained off while liquid is being added. A small amount of demineralized water can be used to rinse resin off the sides of the column, but keep only about 5 mm of free liquid above the resin to keep resins from separating out. If mass transfer coefficient will be calculated, measure the inside diameter of the test column with a micrometre, divide this by two, and convert to metres.

11.3 An alternative is to drain the test column as above, but transfer the mixed resin in 25-mL portions, about one tablespoon, to a long-stemmed plastic funnel inserted in the top of the test column. Again, a minimum amount of rinse water can be used to facilitate the transfer.

NOTE 6—If the resin is poorly mixed or contains air pockets, test results will be erroneous. If resin stratification or air bubbles can be seen in the column, remove the resin to the beaker, and repeat the mixing and transfer steps.

11.4 Fill the cation column to a depth of at least 15 cm with the new hydrogen-form cation resin (8.4), then reconnect it in the test apparatus. This column is not used if the sample tested is cation resin.

11.5 Before connecting to the test apparatus, turn on the water supply system and allow it to recirculate or flush to drain until the conductivity indicator reads 0.06 µS/cm or less. Adjust the valves to allow flow to the test column, and connect the influent and effluent lines to the column.

12. Column Test Procedure

NOTE 7—Normally this test is conducted at laboratory temperatures, but other temperatures can be used if they can be maintained uniformly during the test. In either case, record the temperature at which the test is conducted, and for comparative purposes, data must be generated at temperatures within a 10°C range.

12.1 Turn on the water source and adjust the flow rate through the column with the resin in place until it measures 1 L/min on the discharge side.

12.2 Turn on the recorder and continue the water flow until a stable reading is obtained. This should require a minimum of 15 min but usually less than 1 hour. It may be useful to record the rinse down time for comparison purposes. Although a reading of less than 0.06 µS/cm is expected, an occasional test sample will not attain this. Repeat the entire procedure carefully, but if the conductivity is still too high, try to determine the cause of the poor rinse down before proceeding. It may be helpful to check for the presence of other ions. If mass transfer coefficient is to be calculated, measure the test column resin bed depth.

12.3 If analysis other than conductance is to be made, open the effluent sample tap and take a sample of the water, as a background blank, with care to minimize its contamination. Sample containers should be suitable for high purity water. Close the effluent sample tap.

12.4 If the optional ammonia solution is to be used, turn on the feed pump calibrated to feed the ammonia feed solution reagent at the chosen flow rate. Continue to feed this reagent until the reading on the conductivity recorder restabilizes. A ½-h run time is recommended. A sample(s) may be taken at the influent sample tap if desired to verify the ammonia concentration.

12.5 Turn on the sodium sulfate feed pump for the sodium sulfate solution and continue running as in 12.4, taking samples at the influent and effluent sample taps for analysis if required. Again, the conductivity should stabilize within a ½-h.

12.6 Verify that the test column effluent and cation conductivities are being recorded, or record manually.

12.7 Shutdown of the feed pumps in reverse order until the sample is again running on water alone. Record the conductance. Shut down the system.

13. Reporting

13.1 Tabulate the data from the test, including run time, test temperature, flow velocity, influent concentrations, conductivities, and analysis of specific ions if performed. It is recommended that bed depth and particle size data also be noted.

13.2 Where data is available, graph the present data in comparison with the data obtained from new resins or previous samples tested in the same protocol.

14. Precision and Bias

14.1 Precision and bias are not given since this is a practice, and data will be compared over time on actual systems.

15. Keywords

15.1 anion resin; cation resin; condensate polishing; ion exchange; kinetics; leakage; mixed bed

APPENDIX

(Nonmandatory Information)

X1. CALCULATION OF MASS TRANSFER COEFFICIENT FOR SULFATE

X1.1 Calculation of the mass transfer coefficient for sodium or sulfate requires a full wet sieve analysis (see Test Methods D2187) in addition to the above procedure. Further, it requires that sodium or sulfate be measured by ion chromatography, or other suitable means, in the effluent from the kinetics test itself. Even with unused resins, calculation of the ion concentration from conductivity alone is not recommended since other ions that interfere frequently are present.

X1.2 The full equation typically used to calculate the mass transfer coefficient in experiments of this kind is that proposed by Harries.[5]

$$k = \frac{1}{6(1-\varepsilon)R} \times \frac{F}{A \times L} \times d \times (1nC_o/C),$$

k = mass transfer coefficient for sulfate or sodium, m/s,
ε = bed porosity, m^3/m^3 bed,
R = volume fraction of sample resin:

$$\frac{\text{Anion, m}^3}{\text{Cation, m}^3 + \text{Anion, m}^3}$$

or

$$\frac{\text{Cation, m}^3}{\text{Cation, m}^3 + \text{Anion, m}^3}$$

F = flow rate, m^3/s,
A = bed cross sectional area,
m^2 = πr^2, where r is radius in metres (as measured in 11.2),
L = bed depth, m (as measured in 12.2),
d = sample resin harmonic mean size, m,
C = sulfate or sodium effluent concentration, µg/L,
C_o = sulfate or sodium feed concentration, µg/L,
m = metres, and
s = seconds.

X1.2.1 As an example, assuming the 26-mm column diameter and 14-min flow rate, the term is as follows:

$$\frac{F}{A \times L} = \frac{1.667 \times 10^{-5}}{5.06 \times 10^{-4}\ L} = \frac{3.29 \times 10^{-2}}{L} \qquad \text{(X1.1)}$$

X1.2.1.1 The initial term is as follows:

$$\frac{1}{6(1-\varepsilon)R} = \frac{1}{6(1-0.35)R} = \frac{0.256}{R} \qquad \text{(X1.2)}$$

X1.2.1.2 The bed porosity or void volume equals 0.35. Combing these, the calculation is as follows:

$$k = \frac{8.43 \times 10^{-3}}{R} \times \frac{d}{L} \times (1nC_o/C) \qquad \text{(X1.3)}$$

where:

F = decimal fraction of anion or cation volume in the mixture,
C_o = influent concentration of sulfate or sodium in ppb,
C = effluent concentration of sulfate or sodium ppb,
L = bed depth, in m, and
d = harmonic mean size of sample resin in m, which equals $\frac{0.10}{\sum(\chi/dp)}$.

X1.2.1.3 This is calculated by filling the values from the wet screen analysis of the sample resin and adding up the values χ/dp. The value of dp is equal in each case to the square root

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[5] Harries, R. R., "Anion Exchange Kinetics in Condensate Purification Mixed Beds," *Proceedings of the 5th EPRI Condensate Polishing Workshop*, Richmond, VA, October 1985.

of the product of the two size openings of $\sqrt{d_1 \times d_2}$. This already has been calculated below.

Screen Cut	Size Open, mm	% Retained, X	Factor, 1/dp	X (or X Times Factor) dp
Through 16 on 20	1.19 to 0.84	____________	1.000	_______________
Through 20 on 30	0.84 to 0.59	____________	1.420	_______________
Through 30 on 40	0.59 to 0.42	____________	2.009	_______________
Through 40 on 50	0.42 to 0.30	____________	2.817	_______________
Through 50 on 60	0.30 to 0.25	____________	3.651	_______________
Through 60 on 100	0.25 to 0.15	____________	5.164	_______________

X1.3 Typical reproducibility error has been found to be on the order of ±2 to 8 % of the mass transfer coefficient value.

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