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date: June 25, 2025

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subject: GEOC 24-05 Milestone Report on Mineral Fragment Colloids Under TP 22-02

I. Source Note

This memo is a reformatting of the existing report titled "*GEOC 24-05 Milestone Report on Mineral Fragment Colloids Under TP 22-02*" dated September 24, 2024, with unique identifier ERMS 582426. The content of the report is unchanged from the original version and begins in Section II below. All revision and submittal information, including original Document Review and Comment (DRC) forms, are included with the records package for the original report (ERMS 582426). The purpose of this reformatting is to produce a clean version of the document suitable for public release alongside future regulatory documents in support of Waste Isolation Pilot Plant recertification.

II. Executive Summary

Dispersions of submicron MgO engineered particles in water were measured over short time scales (1-4 days) by dynamic light scattering. The signal intensity of scattered light was monitored versus time as a proxy for suspended particle concentration. The destabilization and sedimentation of colloidal particles from suspension via gravitational sedimentation was rapid, occurring over several days. The results of these experiments provide evidence that submicron MgO particle dispersions are unstable in H_2O. This observation supports the conclusion that pseudo-colloids forming from the hydration and carbonation products of MgO are sufficiently encompassed by existing conservatism and parameterization of actinides associated with mobile mineral fragment colloids in the Waste Isolation Plant Performance Assessment

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III. Introduction

Mineral fragment colloids (MFC) are naturally occurring crystalline particles which represent a vector for increased actinide mobility in the event of release from the repository following sorption of actinide to MFC surfaces and are consequently modelled in the Waste Isolation Pilot Plant (WIPP) Performance Assessment (PA). Experiments conducted in support of the original Compliance Certification Application (CCA) observed the behavior of numerous material types to assess the impact of MFC on repository performance [1]. Those experiments established a conservative maximum actinide concentration associated with mobile MFC, represented by the CONCMIN parameter in the WIPP PA. This parameter value has not been changed from the original CCA value of 2.60E−8 M (moles of colloidal actinide per liter of solution).

A large mass of MgO is emplaced as an engineered barrier to buffer the repository pH and reduce actinide solubilities. The U.S. EPA, in its technical support document associated with the 2009 Compliance Recertification Application (CRA), identified the possibility of the formation of MFC from MgO and its hydration or carbonation products as an uncertainty in the colloidal actinide source term model [2]. The experimental results summarized in this report address the EPA concern and support the conclusion that colloidal dispersions are unlikely to form in the WIPP. The current parameter value continues to conservatively encompass any uncertainty associated with MFC actinide concentrations.

IV. Goals and Hypotheses

The goal of this study is to determine the particle stability of MgO mineral fragment colloids in aqueous dispersions and examine potential implications for the WIPP PA. This work was conducted under Test Plan TP 22-02, Investigation of the Stability of Mineral Fragment Colloids Forming from Magnesium Oxide Revision 0 [3]. This report summarizes experimental results collected during fiscal year 2024 and examines implications in relation to the WIPP PA. Table 1 (replicated below) of the Test Plan frames the principal study question or hypothesis driving the experiments presented herein.

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Table 1. Principal study question, hypotheses, and recommended actions.

Principal Study Question: Will stable magnesium mineral fragment colloid suspensions be present in post-closure WIPP such that actinide mobility is augmented?	
Hypothesis	**Recommended Action**
Magnesium MFC suspensions likely stable in WIPP post-closure conditions	Strengthen CONCMIN parameter to encompass potential increased actinide mobility
Magnesium MFC suspensions not stable in WIPP post-closure conditions	Continue to use CONCMIN as currently defined

V. Magnesium Mineral Fragment Colloids

V.1. Experimental Description

The terms suspension and dispersion are used interchangeably in this report to refer to a mixture of undissolved mineral particles (<1000 nm in size dimension) in a liquid solute. Strictly speaking, a suspension is a dispersion of particles where gravitational sedimentation will remove particles from the liquid column.

The previous work presented in Foli (2023) [4] characterizing MgO colloidal particle size distributions found that dispersions of Martin Marietta MgO (MM-MgO) destabilize quickly in water and low-ionic-strength electrolyte solutions. Aggregation and sedimentation of MgO particles occurred at a rate rapid enough to preclude meaningful data collection as the signal-to-noise ratio grew very small over a short (~24–48 hour) timescale. These findings motivated an alteration to the experimental set-up to prioritize analytical confidence through maximizing instrument response.

Dynamic Light Scattering (DLS) relies on several assumptions to provide a particle size distribution. Two important assumptions of DLS are that: 1) particles are spherical; and 2) Brownian motion is responsible for maintaining dispersion (i.e., no gravitational sedimentation is occurring). Martin Marietta MgO is not engineered to be perfectly spherical, and previous work showed that typical MM-MgO does not produce a dispersion that can be demonstrated with any confidence from DLS measurement, implying that rapid agglomeration and gravitational sedimentation has occurred.

Consequently, the experimental set-up was altered for the experiments. The seed material was changed from MM-MgO to commercially acquired engineered submicron MgO particles with known size of 300 nm. While these submicron particles are also non-spherical, polydispersity and particle size became

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fixed variables. Secondly, the duration and frequency of analyses were shortened to maximize observations over the short time scales over which sedimentation would likely occur. Lastly, particle size (now fixed) is not the primary experimental metric to determine stability. Rather, as it is known, gravitational sedimentation will occur rapidly, destabilizing the dispersion. The loss of signal is now emphasized as a proxy for particle concentration. Signal strength decay observed as a function of time may demonstrate how MgO dispersions rapidly sediment in water.

Particle concentration is a critical facet of DLS measurements. To determine the initial reactor concentration, instrument sensitivity was conditioned using 300 nm engineered submicron MgO particles. A seed dispersion of 0.1% mass MgO: H_2O was found to yield the best signal-to-noise ratio. Experimental reactors were created using a mix of 300 nm MgO and DI H_2O. Details of the reactors created for these experiments are summarized below in Table 2.

After reactor creation, the dispersion was sonicated for 30 minutes prior to performing an inversion of the reactor bottle as a final mix and setting the bottle on a benchtop. At which point, a 1 mL aliquot was immediately sampled via pipette for DLS analysis. The DLS measurements were set up to measure 50 replicates. An additional 1 mL aliquot was sampled following the completion of the 50 replicate measurements. Each replicate measurement was completed in about a minute, with sampling of subsequent aliquots generally occurring after 1 hour. Sampling in this way was continued for 1-4 days of particle sedimentation until the signal-to-noise ratio became very low, meeting the lower limit of detection. Details of activities associated with the experiment described herein can be found in WIPP-Mineral-Colloids-1 pages 38-62. All associated electronic files for this milestone are archived at: /data/cvs/CVSLIB/WIPP_EXTERNAL/GEOC_24_05.

Table 2. MgO-300-X reactor details.

Reactor	Mass MgO (g)	Mass H_2O (g)	Concentration (Wt.% MgO)	Scientific Notebook Page
MgO-300-1	0.10320	99.98015	0.103	53
MgO-300-2	0.10052	99.87271	0.101	53
MgO-300-3	0.09918	100.02031	0.099	54
MgO-300-4	0.10061	100.01857	0.100	54-55
MgO-300-5	0.09923	100.01457	0.099	56-57
MgO-300-6	0.10386	100.12377	0.104	59-60

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Reactors MgO-300-1 and MgO-300-3 (highlighted in grey) will not be included in the presentation of results or discussion below due to experimental reasons. Measurements for MgO-300-1 were conducted on a single aliquot over several days, and consequently, MgO-300-1 displays a different sedimentation pattern than the rest of the reactors due to the smaller cross-sectional area and volume of the cuvette versus a plastic bottle. Analyses of reactor MgO-300-3 began after more than 24 hours of initial sedimentation and are too noisy to display any confident trends. The results of analyses for reactors MgO-300-2,4,5,6 are presented below in Section V.2

V.2. Results

In a monodisperse solution satisfying the assumptions of DLS, the count rate during analysis is proportional to particle concentration. The count rate is utilized here for this purpose, acknowledging a degree of error due to non-spherical particles, and the known occurrence of gravitational settling. Figure 1 below displays regressions of 1/count rate (CR) in millions of counts per second (Mcps) versus minute of sedimentation time during the first day of analysis.

The regressions of reciprocal count rate versus time indicate that a substantial decay in signal is exhibited in the first 500 minutes of settling. Observations of the derived count rate over several days are consistent with the regression slopes. Over the course of several days, the count rate dwindled from billions of counts per second to hundreds of thousands of counts per second. After four days of sedimentation, the average count rate for an aliquot of sample is indistinguishable from background scattering in the dispersant (DI H_2O) without the addition of sample.

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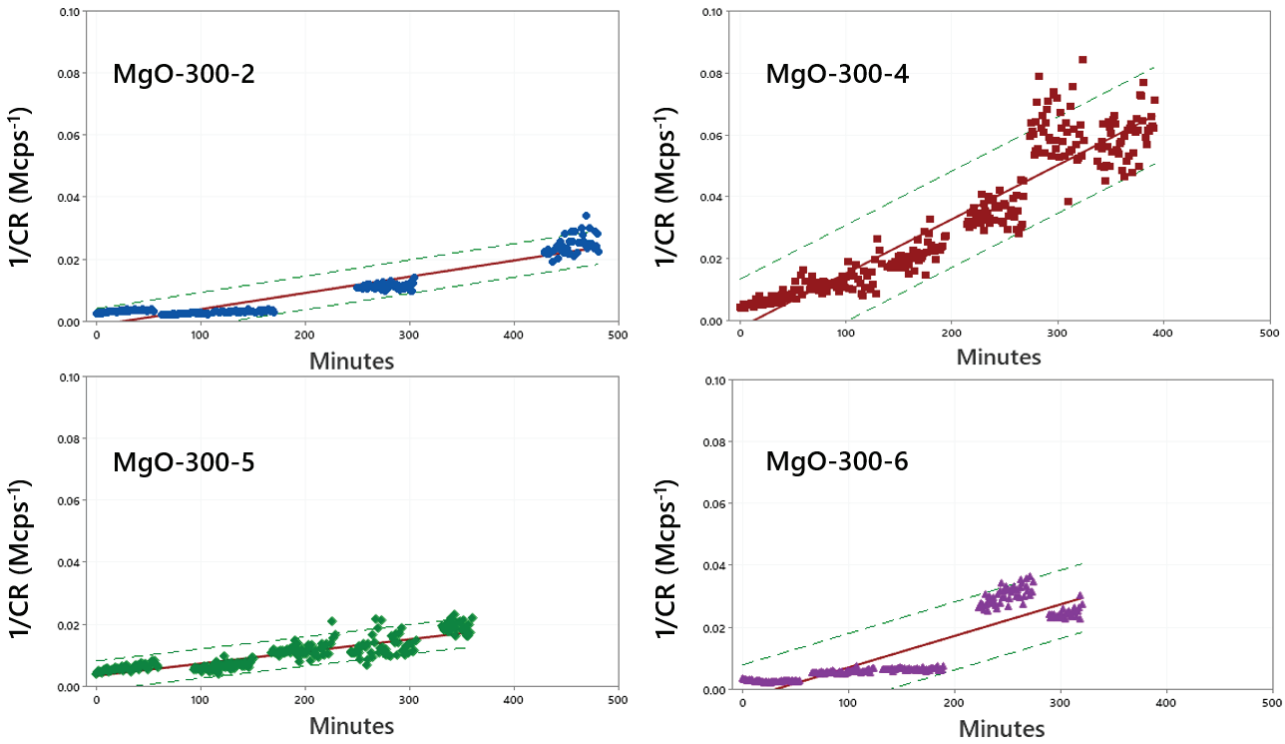


Figure 1. Linear regression (red bold line) of 1/Count rate (Mcps^{-1}) for MgO-300-2,4,5,6. The 95% prediction interval (PI) of the regression is bounded by dashed green lines.

The coefficient of determination for the regressions indicates a moderate to strong association between count rate decay and time. Across the reactors, the lowest correlation occurred in reactor MgO-300-5, where 75% of the change in count rate is explained by a change in time. Reactor MgO-300-2 displayed the strongest linear relationship between count rate and time, where 90% of the change in signal is explained by a change in time.

The positive linear relationships exhibited by all reactors indicate that there is a lack of stability in the dispersion. The decrease in count rate with time indicates that particle concentration is decreasing. The moderate-to-strong relationship with time indicates the active mechanism for particle removal is gravitational sedimentation.

Some observations, all occurring after 200 minutes of settling, fall outside the 95% prediction interval of the regression. This variability is expected when dealing with polydispersity introduced by agglomeration. Large particles scatter more light compared to smaller particles. Aliquots with large agglomerations, the scattering profile of which was sampled by the detector, will report an anomalously high count rate. Similarly, a relatively sparse aliquot with a lower particle concentration or only small

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particles (relative to previous agglomeration-bearing samples) will return a low count rate. Because of this expected behavior, it is difficult to classify data points outside the prediction interval as true outliers. More likely, they reflect a measurement artifact of the underlying physical process at work.

Table 3. Second-order slopes for the aggregation kinetics of MgO-300-X reactors.

Reactor	Slope ($Mcps^{-1}\ min^{-1}$)·10^4	Coefficient of determination (R^2)
MgO-300-2	0.52 ± 0.01	0.90
MgO-300-4	1.76 ± 0.04	0.85
MgO-300-5	0.39 ± 0.01	0.75
MgO-300-6	1.02 ± 0.04	0.76

The variation in the slope for the linear regression of the reactors is evident in Figure 2. Experimental variability in sampling is the most likely cause of the divergence of each reactor from a very similar slope. This sampling variability is expected due to the agglomeration of particles during random sampling. The divergence of reactor MgO-300-4 is likely due to sampling of contrasting agglomerations and particles, as evidenced by the particle size at early time (<500 minutes), as displayed in Figure 3.

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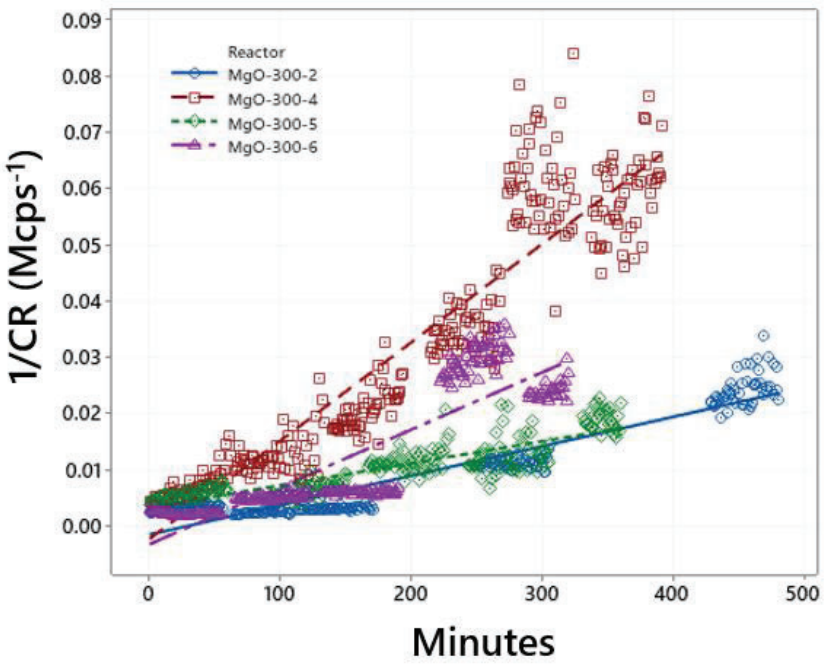


Figure 2. Regression of 1/CR overlaid for reactors MgO-300-2,4,5,6.

A notable feature of the data evident in Figure 3 is the en-echelon striations evident in the dispersion of the peak 1 size measurements. This trend is present in all reactors for the duration of sampling. Sample polydispersity from a population of mixed particles and agglomerations in addition to signal fluctuations due to movement by gravitational sedimentation both contribute to this trend in the size measurements. The short (~1 minute) measurement interval of each replicate measurement generates a distribution of sizes within a single hour of settling. Notably in reactor MgO-300-6, the last series of measurements beginning at 4300 minutes of settling are disperse compared to the previous measurements conducted on that day. This distribution of measurements is coincident with a 40% loss of signal relative to the previous measurements and exemplifies the state of low particle concentration brushing up against the low detection limit of the employed methodology.

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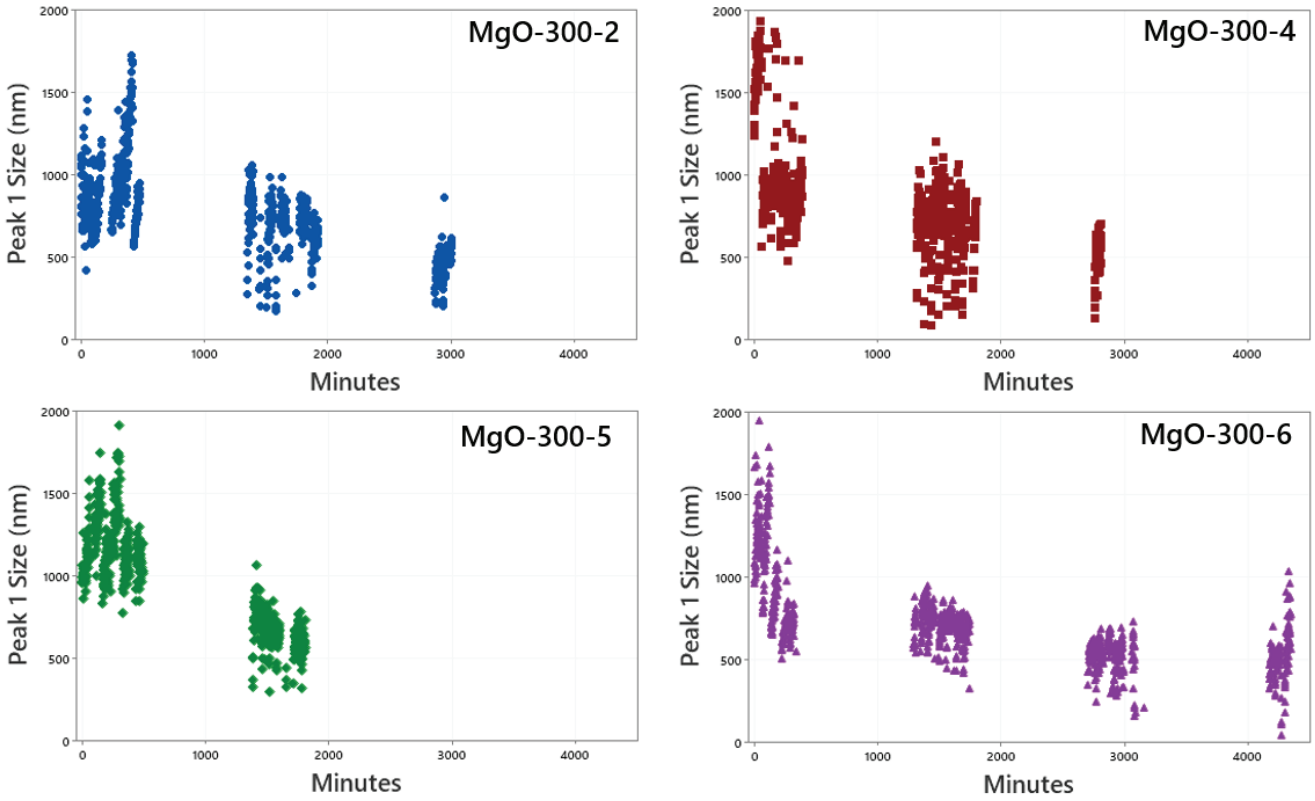


Figure 3. Intensity weighted particle size (peak 1) versus minutes of settling.

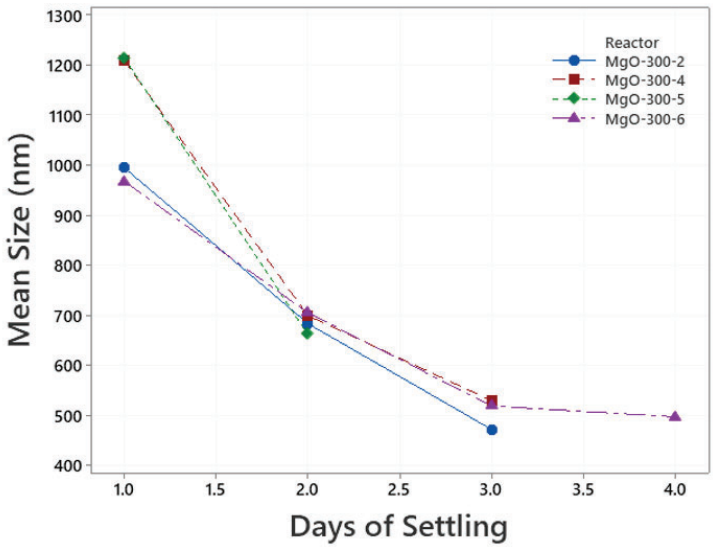


Figure 4. Mean size (peak 1) versus days of settling, compilation of reactors MgO-300-2,4,5,6.

Figure 4 displays the daily mean particle size for each reactor. Over the course of several days the mean daily particle size decreases rapidly from ~1500-1000 nm to ~480-500 nm. Given the known particle size of the MgO is 300 nm, the trend displayed in Figure 4 is indicative of rapid formation and

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subsequent sedimentation of large particle agglomerations destabilized from the dispersion by gravitational sedimentation. The rate of agglomeration and sedimentation becomes less rapid over time as the suspended particle concentration decreases proportionally until the mean size begins to plateau after 3-4 days of settling and sedimentation.

VI. Discussion

The results indicate instability in the dispersion of submicron MgO particles in water. The variance in size data and rapid rate of signal decay is indicative of gravitational sedimentation rapidly removing particles from suspension. After three to four days of settling measurement signal to noise ratio becomes very low and approaches the background dispersant scattering signal. Collectively these observations indicate that MgO mineral fragment colloids will be removed from solution rapidly enough to be considered as almost instantaneously in the performance assessment.

Additionally, these measurements were conducted in conditions which are most theoretically favorable to formation of a stable dispersion. Colloids exhibit stability with prevailing low aggregation rates. These conditions occur when the attractive Van der Waals forces are opposed by strong repulsive forces of the particle electrostatic double layers. Collectively these interactions are described by DLVO theory [5, 6] At higher ionic strengths, in more concentrated electrolyte solutions, the electric double-layer responsible for sustaining dispersion of particles is suppressed; agglomeration is highly promoted in conditions of a suppressed double layer as the repulsive force keeping the particles from forming agglomerations is no longer present [7, 8]. In WIPP brines (greater than 5 M ionic strength) vectors of agglomeration would be much higher than in the conditions for the reactors presented above, leading to quicker and more complete removal of particles from suspension.

VII. Conclusion

Dispersions of submicron MgO particles in water were observed to be instable, with gravitational sedimentation acting as the primary kinetic mechanism for removing particles from suspension. The low detection limit of the employed analytical methodology was met within four days of reactor lifetime. The observation of kinetic instability through sedimentation of particle aggregations dispersed in water supports the theoretical assertion of MgO particle instability at higher ionic strengths.

MgO mineral fragment colloids are expected to sediment rapidly in the high ionic strength brines modeled in the WIPP PA or in the surrounding groundwater. Experimental observation of particle sedimentation extended to and below the low detection limit analytical methods, and consequently, it is impossible to conclude that terminated reactor suspensions contained *zero* MgO mineral fragment

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colloids. However, the observations and theory predict that it is highly unlikely that MgO particles will form mobile mineral fragment colloids in water to eclipse the conservatism already present in the concentration of actinide associated with mobile mineral fragment colloids as currently parameterized in the WIPP PA.

VIII. References

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