Enhancement of the Characteristics of Cement Matrix by the Accelerated Carbonation Reaction of Portlandite with Supercritical Carbon Dioxide

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This research investigated the feasibility of the accelerated carbonation of cement waste forms with carbon dioxide in a supercritical state. Hydraulic cement has been used as a main solidification matrix for the immobilization of radioactive and/or hazardous wastes. As a result of the hydration reaction for major compounds of portland cement, portlandite $(Ca(OH)_2)$ is present in the hydrated cement waste form. The chemical durability of a cement form is expected to increase by converting portlandite to the less soluble calcite $(CaCO_3)$. For a faster reaction of portlandite with carbon dioxide, SCCD (supercritical carbon dioxide) rather than gaseous CO_2 in ambient pressure is used. The cement forms fabricated with an addition of slaked lime or Na-bentonite were cured under ambient conditions for 28days and then treated with SCCD in an autoclave maintained at 34℃ and 80atm. After SCCD treatment, the physicochemical properties of cement matrices were analyzed to evaluate the effectiveness of accelerated carbonation reaction. Conversion of parts of portlandite to calcite by the carbonation reaction with SCCD was verified by XRD (X-ray diffraction) analysis and the composition of portlandite and calcite was estimated using thermogravimetric (TG) data. After SCCD treatment, the cement density slightly increased by about 1.5% regardless of the SCCD treatment time. The leaching behavior of cement, tested in accordance with an ISO leach test method at 70℃ for over 300 days, showed a proportional relationship to the square root of the leaching time, so the major leaching mechanism of cement matrix was diffusion controlled. The cumulative fraction leached (CFL) of calcium decreased by more than 50% after SCCD treatment. It might be concluded that the enhancement of the characteristics of a cement matrix by an accelerated carbonation reaction with SCCD is possible to some extent.
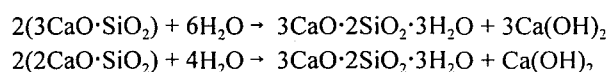Keywords: cement, solidification, carbonation, portlandite, supercritical carbon dioxide.

Introduction

Solidification is one of the most widely used techniques for the treatment and ultimate disposal of both radioactive and chemically hazardous wastes. Of the many potential immobilization matrices, ordinary portland cement has been accepted as an attractive matrix because of its many advantages such as low cost, good mechanical and thermal properties, and easy processing and handling (1). Portland cement consists mainly of lime, silica, alumina, and iron oxide. Clinkering a mixture of these major oxides of a portland cement composition results in the formation of C_3S (3CaO·SiO2), C_2S (2CaO·SiO2), C_3A (3CaO·Al$_2$O$_3$), and C_4AF (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$). The combined content of the four major compounds is approximately 90% of the cement weight (2).

The setting and curing processes that occur in cement are complex as they involve several primary compounds and many reaction products. The solidification process can be described as proceeding through three stages (3). The initial stage occurs as the cement powder is mixed with water and the hydration reaction forms a coating of a silicate gel around the powder particles. These hydration reactions are exothermic and cause heating of the cement after it is mixed with water. As the reaction continues, calcium hydroxide (portlandite) precipitates and fibrils and sheets of tobermorite begin to form an interlocking network that gives strength to the cement. The third stage,

curing, consists of continued slow fibril growth and drying. In actuality the three stages continue indefinitely at very slow rates as moisture enters the cement causing additional hydration. In the curing of cement paste, hydration reactions occur which bring to the formation of the four major compounds. As a consequence of the hydration reactions, a considerable amount of calcium hydroxide (portlandite) is present in the hydrated cement according to the following reactions.

$$2(3CaO·SiO_2) + 6H_2O \rightarrow 3CaO·2SiO_2·3H_2O + 3Ca(OH)_2$$
$$2(2CaO·SiO_2) + 4H_2O \rightarrow 3CaO·2SiO_2·3H_2O + Ca(OH)_2$$

Over time, the cement abstracts carbon dioxide from the air, converting portlandite to anhydrous calcium carbonate (calcite). The solubility of portlandite in water is about 100 times higher than that of calcite. Thus it can be expected that the carbonation reaction to convert portlandite in a cement matrix into calcite can improve the chemical durability and other properties of the cement matrix. However, the natural carbonation reaction under ambient conditions results in the closure and/or blockage of pores, impeding the ingress of reactants (CO_2 in the air) and the egress of reaction product (H_2O), drastically slowing the carbonation reaction rate with time.

For any pure chemical species, there exists a critical temperature and pressure immediately below which an equilibrium exists between the liquid and vapor phases. Above these critical points a two-phase system coalesces

into a single phase referred to as a supercritical fluid. Supercritical fluids offer a convenient means to achieve solvating properties which have gas-like and liquid-like characteristics without actually changing chemical structure. By proper control of pressure and temperature one can access a significant range of physicochemical properties (density, diffusivity, dielectric constants, etc.) without ever passing through a phase boundary, e.g., changing from gas to liquid form. That is, a supercritical fluid can be considered a continuously adjustable solvent (4, 5). Its gas-like properties of low viscosity ($10^{-3} \sim 10^{-4}$ g/cm·s compared to 10^{-2} for liquid) and high diffusivity ($10^{-3} \sim 10^{-4}$ cm²/s compared to 10^{-5} for liquid) provide for effective mass transport into granular and micro-porous matrices and the liquid-like property of high density ($0.1 \sim 1$ g/cm³ compared to 10^{-3} for gas) provides for a relatively good solvating power. Hence the carbonation reaction of portlandite can be accelerated by using supercritical carbon dioxide (SCCD) rather than using gaseous CO_2 in ambient pressure. The critical point of carbon dioxide is 32°C and 73atm (6, 7).

In this presentation, leaching characteristics such as cumulative fraction leached (CFL) and leach rate of major cement elements will be given. Also investigated are the change of density, thermogravimetric behavior, and XRD pattern of the cement matrix to assess the effect of SCCD treatment.

Experiment

The cement forms cured under ambient conditions for 28 days reacted with SCCD in an autoclave maintained at 34℃ and 80atm. To investigate the effect of SCCD reaction time on the properties of the cement matrix, the sample holding time in the autoclave was changed from 30 minutes to 4 hours. The physicochemical properties of the cement matrices before and after SCCD treatment were analyzed and compared to evaluate the effectiveness of the accelerated carbonation reaction with SCCD.

Fabrication of cement forms

Two series of cement forms were fabricated with Portland type I cement and additives: one with slaked lime (CL series) as an additive, the other with slaked lime and Na-bentonite (CB series). For both series of samples the content of slaked lime was changed from 0 to 10wt% by 2.5wt%. For example, in this study, the cement sample denoted CL-01 or CB-06 contains 0wt% of slaked lime and CL-04 or CB-09 contains 7.5wt%. The content of Na-bentonite was fixed at 5wt% in the CB series cement forms.

The water to cement ratio was kept constant at 0.3. For slaked lime and Na-bentonite, extra water equivalent to 50wt% and 100wt% of each material, respectively, was added. After mixing the feed materials in the standard mixer, the cement pastes were put into a cylindrical PVC mold, compacted to remove air bubbles inside cement pastes, and allowed to cure under ambient conditions for 28days. The cement forms produced measure 5 cm in diameter and 10 cm in height.

Carbonation of cement forms with SCCD

The carbonation reaction of portlandite in the cement matrix with SCCD was done in an autoclave (Parr Model 4851) maintained at 34°C and 80atm. The carbonation reaction proceeds as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
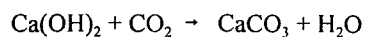
In this study, the effect of SCCD reaction time only on the physical and chemical properties of cement matrices was investigated. The supercritical condition of CO_2 is maintained constant at 34°C and 80atm. The reaction time was changed for 30 minutes, 1 hour, or 4 hours.

Characterization of cement forms

To analyze the change of portlandite content in the cement matrix by virtue of the SCCD treatment, a thermo-gravimetric analysis (Seiko Instrument, TG/DTA 6300) was done from 25℃ to 1000℃ at a heating rate of 10℃/min, under a nitrogen atmosphere (flow rate = 100 ml/min). The formation of various crystalline materials and the conversion of portlandite to calcite were checked by XRD analysis (Japan Rigaku). The ISO-6961 leaching tests were performed to compare the chemical durability of cement forms before and after SCCD treatment (8). The leaching test was conducted at 70°C for 308 days with deionized distilled water as leachant. The SA/V ratio was 10m^{-1} (surface area of cement specimen 108~119cm² and leachant volume 1,080~ 1,190mL). The concentrations of cement components and heavy metals in the leachate were analyzed by using AA (Perkin Elmer, 5100PC) and ICP-MS (Varian, Ultramass 700).

Results and Discussion

When portlandite is reacted with carbon dioxide to produce calcite, the density of the cement matrix changes due to the difference in density between the portlandite and calcite. Because the specific gravity of portlandite is 2.24 and that of calcite is 2.71, the density of the cement matrix is expected to decrease as carbonation reaction proceeds. Fig.1 shows the effects of additives (slaked lime and Na-bentonite) and SCCD reaction time on the density of a cement matrix.

The density of the cement matrix with slaked lime only added (CL series) ranged from 2.03 to 2.12 g/cm³ and was higher than that of the cement matrix containing slaked lime and Na-bentonite (CB series). It decreased with an increase of the amount of slaked lime added. After SCCD treatment, the cement density slightly increased by 1.5%. The effect of SCCD reaction time on the density change seemed negligible after 1 hour of SCCD treatment for all the cement samples. This means that only parts of portlandite are converted into calcite. And free water in the cement pores and water produced from the

carbonation reaction are thought to transport out of the cement matrix after being dissolved in SCCD.
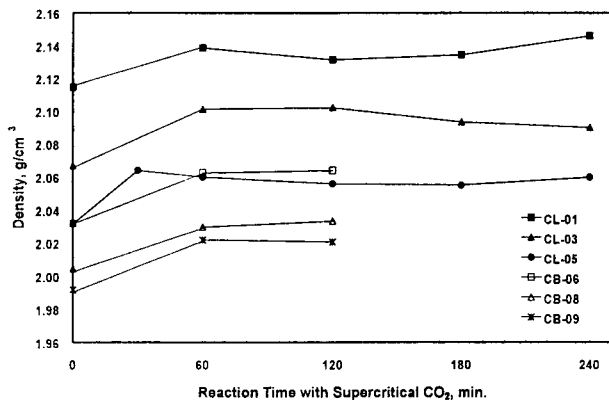

Fig.1. Density of cement matrices before and after SCCD treatment

The result of thermogravity and differential thermal analysis (TG/DTA) for the CL-01 cement samples before and after SCCD treatment is shown in Fig.2. The weight loss of the cement sample near $465°C$ (region A) decreased after SCCD treatment.
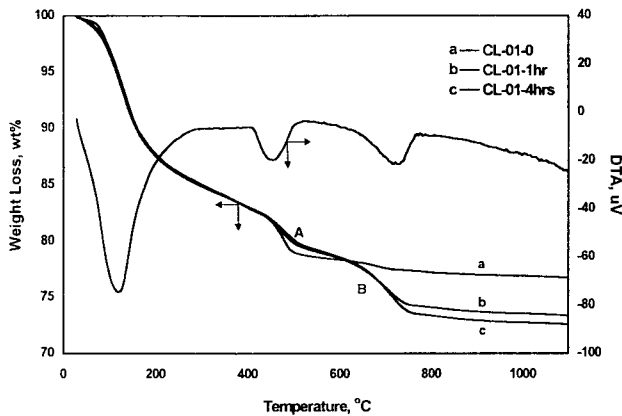

Fig.2. Comparison of TG/DTA result for CL-01 cement matrix before and after SCCD treatment.

In high temperature conditions, chemical compounds decompose which results in the evaporation of volatile components, typically the chemically combined water and carbon dioxide. This often leads to energy absorption and mass loss, which corresponds to the endothermic peak in DTA and weight decrease in TG curves. Portlandite is known to decompose to calcium oxide and H_2O near $465°C$, known as the peak temperature (9). Thus the weight loss of the cement matrix near $465°C$ could be used to quantify the amount of portlandite in the cement matrix. However, it should be noted that the thermal peak usually spans a temperature range of about $100°C$. The weight loss near $720°C$ (region B) is due to the decomposition of calcite because the weight loss in this region is negligible for a cement matrix before carbonation reaction. And the TG analysis for pure $CaCO_3$ confirmed this. Consequently the decrease of

weight loss in region A and the subsequent increase of weight loss in region B verified that parts of portlandite underwent the carbonation reaction to form calcite.

The content of portlandite was estimated through an investigation of TG curve and the result is shown in Fig.3 for some cement samples. It shows the change of portlandite content with the initial amount of slaked lime and SCCD treatment time.
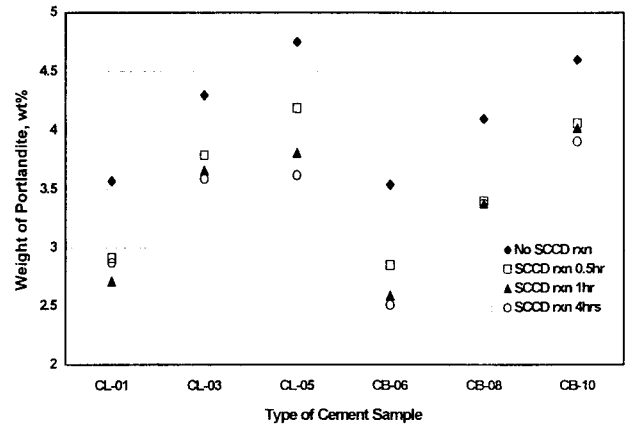

Fig.3. Contents of portlandite in cement matrices estimated by the weight change in the TGA curve.

The amounts of portlandite were increased from 3.5% to 4.7% with increasing initial slaked lime content regardless of the addition of Na-bentonite. The difference in the amount of portlandite in the cement matrix before and after SCCD treatment was not high with a change of SCCD reaction time. The amounts of portlandite were decreased by about 0.75wt% after the carbonation reaction with SCCD, which indicated portlandite was converted to calcite. The formation of calcite was confirmed through an investigation of the XRD peak pattern of the cement sample before and after the SCCD treatment. The intensity of the calcite peak for sample CL-05 became stronger after the SCCD reaction, as shown in Fig. 4. Other cement matrices showed nearly the same XRD patterns.
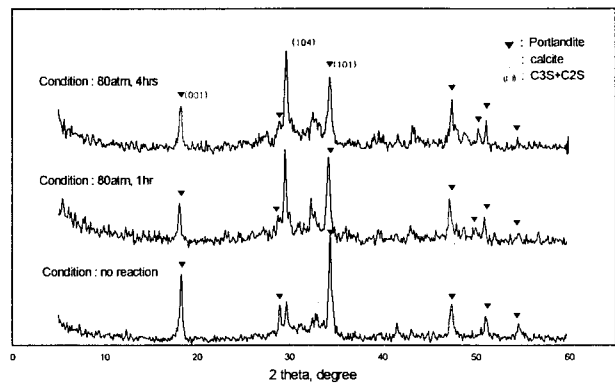

Fig.4. Change of XRD peak pattern for CL-05 cement matrix with SCCD treatment time.

Analysis of ISO leaching data performed for 308 days for cement matrices not treated by SCCD showed that the order of CFL for cement elements was K > Na > Ca > Al > Fe > Si > Mg > Ti. It seemed that the elemental CFL is affected by its solubility in water. As a result of the cement hydration reaction, many of the cement elements exist in the hydroxide form. When the cement form is brought to contact water, the hydroxide chemicals react with water to leach out of the cement form. The solubility of potassium or sodium hydroxide is greater than 40 g/mL, while that of calcium hydroxide is about 1.7 g/mL and that of the hydroxide form of Al, Fe, Si, Mg or Ti is less than 10^{-4} g/mL. This may explain the order of elemental CFL in the ISO leach test. The CFL of potassium and sodium ranged from 2.85×10^{-2} to 3.26×10^{-1} in the ISO leach test for 308 days. It is noted that the major elements affecting leaching characteristics of the cement matrix are not potassium or sodium whose composition is below 2wt% in cement but are calcium and silicon which are over 70 and 11wt% in cement, respectively. The CFL of calcium and silicon was below 2×10^{-2} and 4×10^{-3}, respectively. The initial leach ratio of sodium or potassium was higher than that of calcium. The total amount of calcium leached out in 120 days was 90% of that in 308 days while it took only 60 days for sodium or potassium to reach the same level.

Fig. 5 shows the CFL of calcium with leaching time before and after SCCD treatment. The effect of the Na-bentonite addition on the CFL of calcium was negligible. With an increase of initial slaked lime content, the CFL of calcium increased. This is consistent with the result of TG analysis in which the content of more soluble portlandite showed the same trend. After the SCCD treatment for 1 hour, the CFL decreased by 50~60% compared to those for untreated cement matrices. And the CFL differences among cement matrices were small regardless of the type or content of additives. This, in combination with the density change with SCCD treatment time as in Fig.1, would explain the reason that the carbonation reaction, in this study, is claimed to occur only in the near-surface zone.
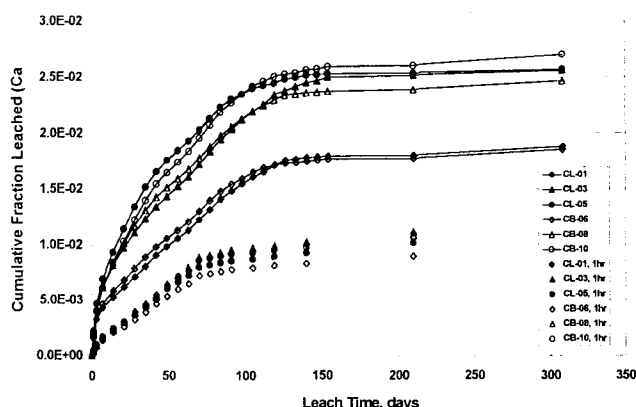

Fig.5. Cumulative fraction leached of calcium before and after SCCD treatment (ISO leach test, 70 ℃).

The influence of SCCD treatment time on the leaching

behavior of the cement matrix is shown in Fig.6. The leach rates of calcium were 2.40 ~ 3.53 g/m²·day before SCCD treatment. After carbonation reaction with SCCD, the calcium leach rates decreased to about 1/3 of those of untreated cement matrices; 1.38 ~ 1.54 g/m²·day for 30 minutes of reaction, 1.02 ~ 1.33 g/m²·day for 1 hour, 0.96 ~ 1.21 g/m²·day for 4 hours. As can be seen in Fig. 6, the effect of SCCD reaction time on the leach rate of calcium became smaller after 1 hour of SCCD treatment for all the cement matrices. This, combined with the result of density change (Fig.1), means that SCCD reaction time of about 1 hour is enough for the carbonation of portlandite in the cement waste form. This, however, does not mean all the portlandite is converted to calcite by the SCCD treatment.
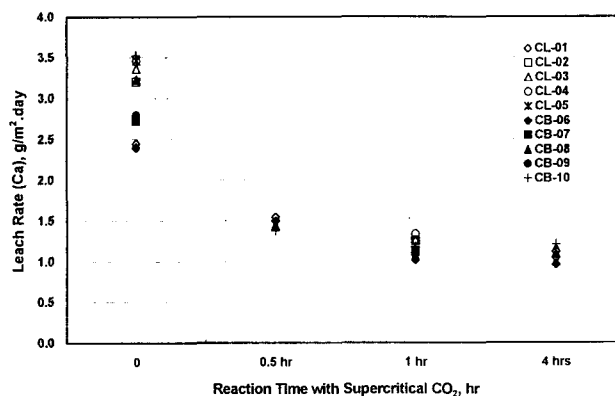

Fig.6. Leach rate of calcium with SCCD reaction time (ISO leach test, 70 ℃).

The leaching mechanism of the chemical elements from waste forms under various conditions or at different times during a leaching process can be classified into wash-off, diffusion and dissolution at the interface. The following time-dependent terms for cumulative fraction leached describing important rate-limiting leaching mechanisms were used to analyze the leaching behavior of materials as a function of leaching time and to determine the controlling leaching mechanism (10).

- $K_1(1-\exp(-K_2 t))$: Wash-off (chemical reaction between the cement surface and the aqueous solution).
- $K_3 t^{1/2}$: Transport by diffusion in a porous matrix.
- $K_4 t$: Leaching as a result of matrix dissolution.

These terms were combined into one general expression to describe the overall leaching behavior.

$$F(t) = K_1(1-\exp(-K_2 t)) + K_3 t^{1/2} + K_4 t \tag{1}$$

By comparing the order of magnitude of K_i values, which could be obtained by the least-square fitting of the experimental leaching data to Eq.(1), one can estimate which mechanism controls the leaching behavior.

The K_i values for calcium obtained from experimental leaching data for different cement matrices are shown in Table 1. For calcium, a major cement element, the leaching mechanism could be considered as diffusion because the degree of contribution of $K_3 t^{1/2}$ term

Table 1. Leaching mechanism constants for Ca according to Eq.(1) before and after SCCD treatment

	Before SCCD treatment					After SCCD treatment for 1 hour				
	CL-01	CL-02	CL-03	CL-04	CL-05	CL-01	CL-02	CL-03	CL-04	CL-05
K_1	-7.9E+2	-1.2E+3	-9.5E+2	-1.2E+3	-1.2E+3	-3.6E+2	-5.1E+2	-3.3E+2	-4.1E+2	-4.1E+2
K_2	5.2E-08	8.1E-08	6.4E-08	7.7E-08	8.2E-08	2.4E-08	3.4E-08	2.2E-08	2.7E-08	2.7E-08
K_3	1.8E-03	3.1E-03	2.7E-03	3.1E-03	3.3E-03	9.8E-04	1.1E-03	9.8E-04	1.1E-03	9.4E-04
K_4	2.8E-16	1.9E-16	9.0E-16	1.9E-16	2.0E-16	8.0E-16	1.3E-15	7.2E-16	9.5E-16	9.1E-16
	CB-06	CB-07	CB-08	CB-09	CB-10	CB-06	CB-07	CB-08	CB-09	CB-10
K_1	-8.6E+2	-1.1E+3	-1.1E+3	-1.2E+3	-1.1E+3	-3.9E+2	-4.5E+2	-3.7E+2	-3.0E+2	-3.5E+2
K_2	5.8E-08	7.2E-08	7.1E-08	8.1E-08	7.3E-08	2.6E-08	3.0E-08	2.5E-08	2.0E-08	2.3E-08
K_3	2.0E-03	2.6E-03	2.8E-03	2.9E-03	3.0E-03	8.4E-04	9.4E-04	9.4E-04	8.6E-04	9.5E-04
K_4	5.5E-16	1.4E-16	1.2E-15	1.5E-16	1.3E-15	8.1E-16	1.0E-15	8.0E-16	6.0E-16	7.6E-16

to Eq. (1) was much larger than those of other terms. Other major cement elements such as silicon, aluminum, iron, and sodium also were thought to leach out by the diffusion mechanism. So, the leaching mechanism of a cement matrix is diffusion controlled. The leaching mechanism remained unchanged even after SCCD treatment of the cement matrix, as shown in Table 1.

Conclusion

The carbonation of portlandite in the cement matrix to calcite was successfully accelerated by the use of supercritical carbon dioxide to result in the enhancement of cement properties. The addition of slaked lime into the cement feed decreased the density of cement matrix. After SCCD treatment, the cement density slightly increased by 1.5%. The formation of calcite was checked by XRD analysis. It was found that the amounts of portlandite were increased from 3.5wt% to 4.7wt% with increasing initial slaked lime content, regardless of the addition of Na-bentonite. After SCCD treatment they were decreased by about 0.75wt%. The leaching mechanism of cement was diffusion controlled because leaching behaviors of nearly all the cement elements showed a linear relationship with $time^{1/2}$. In the ISO leaching test, the effect of Na-bentonite addition on the CFL of calcium was negligible while it increased with an increase of initial slaked lime content. After SCCD treatment for 1 hour, the CFL of calcium decreased by 50~60% compared to those for untreated cement matrices. And the CFL differences among the cement matrices were small regardless of the type or content of additives. From the changes in cement density and calcium leach rate with SCCD reaction time, there might exist an optimal reaction time, which is 30 minutes to 1 hour in this experiment, for the carbonation of portlandite in the porous cement matrix.

Nomenclature

F : Cumulative fraction leached [-]
K_i : Leaching mechanism constants
[K_1: -, K_2: day^{-1}, K_3: $day^{-1/2}$, K_4: day^{-1}]
L : Leach rate [$g/m^2 day$]
SA: Surface area of specimen [m^2]
t : Leach (contact) time [day]
V : Leachant volume [L]

Acknowledgment

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