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The Improvement of the Mechanical Stability and Leachability of Bituminized Waste Form of Radioactive Ash by Addition of Reused Polyethylene

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Abstract−This study was carried out in order to produce bituminized waste forms, which have dimensional and mechanical stability like cement-based waste forms. This paper reports the effects of adding polyethylene (PE) to the bituminized waste form. The additive used for the experiment was the spent PE generated from agricultural use. The bitumen used in the sample preparation is straight-run distillation bitumen of penetration 60/70 (paving asphalt). The waste used for the experiment was a bottom ash generated from an industrial (inactive) waste incinerator. Bituminized waste forms with PE contents of 5 wt% or more resulted in maintaining dimensional and mechanical stability. The compressive strength and softening point of bituminized waste forms increase in proportion to the amount of additional PE. The leaching test using ANS 16.1 shows that the principal leaching mechanism of elements (Cs, Sr, Co) from bituminized waste forms is diffusion. Furthermore, it is demonstrated that additive PE of 5-10 wt% does not change the leaching mechanism, and bituminized waste forms maintain a high leach resistance.

Key words: Bituminized Waste Forms, Polyethylene, Radioactive Waste, Bituminization

INTRODUCTION

The solidification of radioactive waste plays an important role in handling, transportation, interim storage, and disposal, etc. For preventing or delaying the release of hazardous material into the environment when it is contacted with water in the disposal site, waste forms should maintain stable chemical and physical properties. Portland cement has been so far the most common solidification agent, while use of bitumen has been gradually increased. Cement and bitumen have been used for radioactive waste from the beginning of the nuclear industry in the 1960's. Currently, their applications have been extended to mixed wastes [Swindlehurst et al., 1989; Mattus et al., 1994]. Mixed wastes contain both hazardous and radioactive constituents.

Bitumen is not reactive with the substances with which it contacts. Accordingly, quality control of bituminized waste forms can be done easily even in the case of changing the waste stream composition and pH. Also, bituminized waste forms exhibit very low leaching of contaminants because the matrix is impervious. Bituminization accompanied by both mixing and evaporation processes can lead to high volume reduction [IAEA, 1970, 1993].

The bitumen used for the solidification of radioactive wastes can be classified into a straight-run distillation bitumen and an oxidized bitumen. The former with relatively low viscosity is used in pot type and thin film evaporator systems. The latter with high viscosity is mainly used in extruder systems. Straight-run distillation bitumen has high leaching resistance and is economical in comparison with oxidized bitumen [Williamson, 1980; Rodier et al., 1968]. However, bituminized waste forms prepared by using especially straight-run distillation bitumen are mechanically and dimensionally unstable [IAEA, 1985]. This instability is closely related to the long-term mechanical stability of waste forms at the disposal site. The long-term integrity of the waste forms is linked to leaching stability. Moreover, a precise leach test cannot be performed because of the deformation of the bituminous specimen.

The objective of this study was to investigate the effect of polyethylene (PE) on the mechanical stability and leaching of bituminized waste forms. The ANS 16.1 leach test was carried out and the effect of PE addition was investigated. The diffusion model is applied in the analysis.

Polyethylene used in this experiment was spent agricultural polyethylene film for waste recycling. In Korea, agricultural polyethylene film generates about 90,000 tons of waste per year. If bituminized waste forms consist of 60 wt% ash and 15 wt% spent PE as binder, the spent PE used in this treatment is 100 kg for 1 ton of dry ash waste. This method has the benefit of saving 100 kg of bitumen and allows the spent PE to be reused.

MATERIALS AND METHODS

1. Equipment and Waste Form Preparation

1-1. Equipment Description

In this study the pot type equipment was employed in the bituminization, and the bituminization was carried out in batch operations. Fig. 1 shows the schematic diagram of experimental apparatus for the production of waste forms. As the reactor was heated, using a heating oil, local over heating could be avoided. An electrical heater adjusted the temperature of the heating oil; the temperature ranged between 25 °C and 240 °C. The temperature of the mixture in the pot was measured by temperature sensors and fed back to the heater controller for precise temperature control. A mixer with three mixing blades was operated by a DC motor with speeds from 70 to 550 rpm. A screw below the mixer was designed to help the

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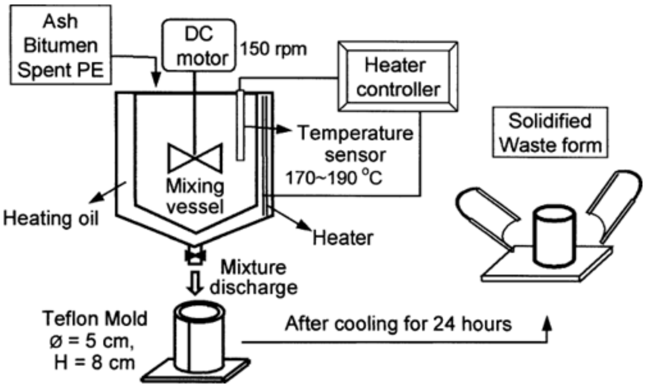

Fig. 1. Schematic diagram of experimental apparatus for the production of waste forms.

mixture to be discharged effectively. The pot cover was operated by oil pressure and was tightly sealed. A condenser was also installed to condense evaporated vapors.

1-2. Waste Form Preparation

Cylindrical waste form specimens (diameter of 5 cm and height of 8 cm) were cast into the teflon molds consisting of three pieces. The mixed bitumen flowed from the vessel directly into the teflon molds. After cooling for 24 hours at room temperature, the teflon mold was removed. The ash content of the waste form was defined as the weight of dry ash to the total weight of the waste form (waste+binder). The PE content of the waste form was defined as the weight of PE to the weight of the binder (bitumen+spent PE).

2. Materials

2-1. Bitumen

The bitumen used for the sample preparation was straight-run distillation bitumen, penetration 60/70 paving asphalt. Bitumen has a density of 1.03 g/cm^3 at 25 °C. Table 1 shows physical properties of the bitumen 60/70 used.

2-2. Bottom Ash

The ash used in this experiment was the bottom ash generated from an industrial (inactive) waste incinerator. Bottom ash was crushed to sizes smaller than 120 mesh (0.125 mm) and dried for 24 hours at 110 °C before bituminization. Bitumen as a solidification agent is used to deal with intermediate and low level radioactive waste. The typical radioactive contaminants in the low level radioactive waste are Co-60, Sr-90 and Cs137. Co, Sr and Cs were, therefore, selected as the typical elements in order to estimate the leaching mechanism from the bituminized waste form. For leach tests, bottom ash was spiked with a small amount of cobalt oxide (CoO : Co_3O_4), strontium chloride ($SrCl_2$) and cesium chloride (CsCl) as tracers. Two kinds of samples were prepared; Group L: bottom ash spiked with 4,000 mg of each element per kg of dry ash, and Group H: bottom ash spiked with 10,000 mg of each element per kg of dry ash. Table 2 shows detailed properties of the bottom ash used.

Table 1. Physical properties of bitumen 60/70

Property	Test condition	Value
Penetration	25 °C, 100 g, 5 sec (ASTM D5)	63 (1/10 mm)
Softening point	Ring and ball (ASTM D36)	48.8 °C
Flash point	Cleveland open cup (ASTM D92)	328 °C
Ductility	25 °C, 5 cm/min (ASTM D70)	150 cm
Solubility in trichloroethylene		99.8%

Table 2. Detailed properties of bottom ash

Property	Value (Test condition)		
Particle size	Less than 0.125 mm		
True density	1.781 g/cm^3 (dry base)		
Moisture content	28.9 wt% (wet base)		
pH	9.25 (10 g, 25 ml water)		
Chemical composition wt%			
SiO_2	49.71	CrO_3	0.22
Al_2O_3	6.99	PbO	0.16
TiO_2	8.17	CdO	0.003
Fe_2O_3	4.72	K_2O	0.79
ZnO	0.29	CaO	10.78
MgO	1.48	Na_2O	10.24
Cu_2O	0.33		
Spiking elements (Spiking form) mg/kg dry ash	Co (CoO)	Sr ($SrCl_2$)	Cs (CsCl)
Group L	4,000	4,000	4,000
Group H	10,000	10,000	10,000

2-3. Spent Agricultural Polyethylene Film (Spent PE)

Polyethylene is saturated aliphatic hydrocarbon polymer and thermoplastics, and is very stable chemically [Henkel, 1984]. In Korea, agricultural polyethylene film having 1-2 year life is made from mainly low-density polyethylene (LDPE) and generates about 90,000 tons of waste per year. Polyethylene used in this experiment was spent agricultural polyethylene film for waste recycling. Typically, LDPE has a density of 0.910-0.925 g/cm^3 and a softening point of about 105 °C [Henkel, 1984].

3. Methods

3-1. Compressive Strength

The unconfined compressive strength of bitumen and bitumen-based waste form is measured by the ASTM D 1074-83 "Test Method for Compressive Strength of Bituminous Mixtures". The rate of vertical deformation for these tests is set at 0.05 cm/min/cm of the specimen height. The U.S. Nuclear Regulatory Commission (NRC) has recommended that the unconfined compressive strength should be evaluated at the point where 10% deformation in specimen height occurs. For radioactive wastes, the NRC suggests that waste forms have a minimum unconfined compressive strength of 414 kPa (60 psi) [NRC, 1983].

3-2. Softening Point

Softening point testing was performed in accordance with the ASTM D 36-70 "Test Method for Softening Point of Asphalts and Tar Pitches (Ring and Ball)".

3-3. Form Stability

The form stability was simply examined by checking the appearance change of the specimen during storage in air or water for 90 days at room temperature.

3-4. Leach Test

The leachability of the waste forms was tested by using the American Nuclear Society's leaching test procedure (ANS 16.1) [American Nuclear Society, 1986]. The leachant was demineralized water and has a pH range in the range 6.8-7.2. The ratio of the surface area of the specimen to the leachant volume was 10 in the leach test. The samplings and replacements of the leachate were made at the cumulative leach times of 2, 7 and 24 hours and every 24 hours thereafter for the next four days. Three leach intervals of 14, 28 and 43 days were added and the test was completed up to 90 days.

3-5. Analytical Methods

The waste materials and the leachate after contacting the waste forms have been analyzed with an atomic absorption spectrophotometer for cesium and strontium, and an induced-coupled plasma emission spectrometer for cobalt. When the concentrations of elements were too low to measure, the leachate was concentrated by evaporation at 80 °C for 2 days. The pH of the leachates was adjusted to a pH of about 2 by adding a few droplets of nitric acid (HNO_3) to avoid precipitation of the elements.

RESULTS AND DISCUSSION

1. Effect of Spent PE on the Mechanical Stability

Experiments were performed with a mixing condition of 150 rpm and 170-190 °C. Fig. 2 shows the scanning electron micrograph of fracture surface of the matrix with bitumen and 10 wt% spent PE. In Fig. 2, the threadlike white lines represent PE. PE is distributed physically in bitumen due to a stable material. It was found that the spent PE existed as net structures in bitumen. Fig. 3 shows the effect of spent PE contents on the softening point of the bituminized waste forms. Adding spent PE of 5 wt% or more to bitumen leads to an increase of the softening point above 118 °C. However, above a certain loading of PE it has no effect on the softening point. This is due to the effect of softening point of spent PE (about 105 °C). For radioactive waste, the U.S. NRC has recommended that waste forms exhibit a minimum softening point of 70 °C. When the softening point of the mixture is above 170 °C, it has an effect on the operation condition, including discharge to reactor and the formation of waste forms in the drum after discharging. If the bituminized waste forms contained 40, 50, and 60 wt% of ash, the waste forms with spent PE above 25, 20, and 15 wt%, respectively, could not be made because the pot type mixer could not discharge the mixtures due to high viscosity.

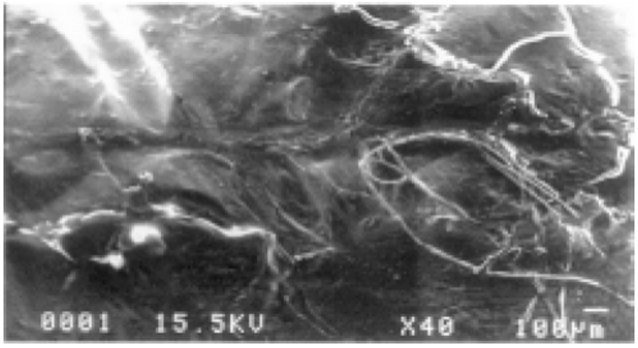

Fig. 2. The scanning electron micrograph of fracture surface of the matrix (bitumen+spent PE 10 wt%).

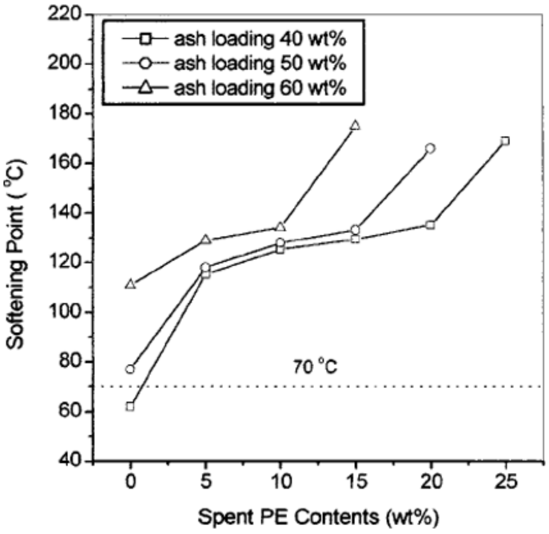

Fig. 3. The effect of spent PE contents on the softening point of the waste forms.

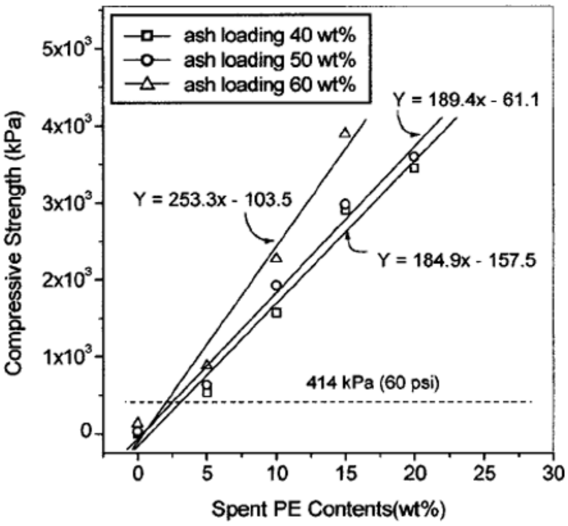

Fig. 4. The effect of spent PE contents on the compressive strength of the waste forms.

Fig. 4 illustrates the effect of the additional spent PE on the compressive strength of the bituminized waste forms. When the ash content is 60 wt% without the spent PE, the compressive strength of waste forms is only 138 kPa (20 psi). When more than 5 wt% of the spent PE is added to waste forms, its compressive strength increases above 414 kPa (60 psi). In Fig. 4, the compressive strength becomes higher as the amount of the spent PE is increased, but the amount of ash content does not show a large difference in the range of 40 and 50 wt%. It seems that a physical change in the structure of the bituminized waste forms occurs when the ash content exceeds 50 wt%.

Fig. 5 illustrates the appearance of waste forms after being exposed at room temperature to air (A, B) or water (C) for 90 days. As shown in Fig. 5(A), the waste forms without PE and containing 40 and 50 wt% ash collapsed entirely after exposure of 20 days, and the shape of the waste forms with ash contents of 60 wt% deformed after 90 days. The waste forms containing the spent PE are shown in Fig. 5(B, C). As shown in Fig. 5(C), even after being exposed to water for 90 days, the waste forms kept their original

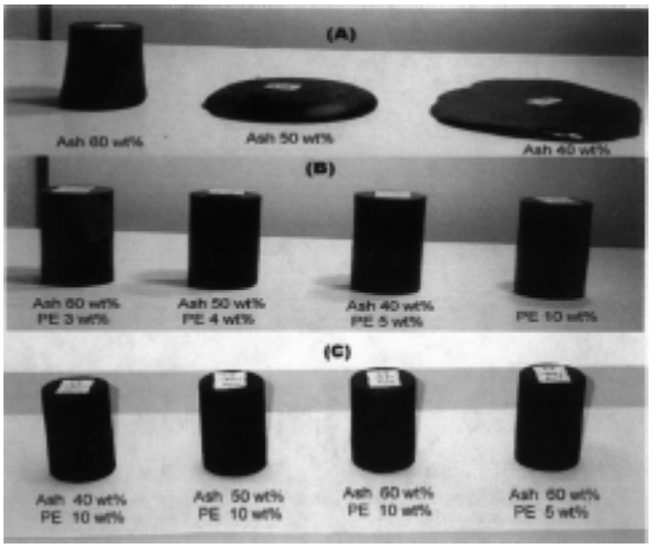

Fig. 5. The appearance of waste forms after being exposed into air (A, B) or water (C) for 90 days.

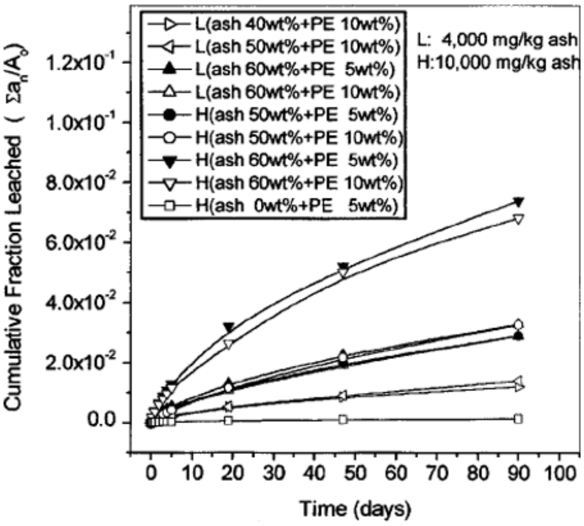

Fig. 6. The leaching behavior of Cs under ANS 16.1 test condition.

shapes.

2. Effect of Spent PE on the Leaching

Fig. 6 shows the cumulative fraction of Cs leached from the specimen as a function of time. For the waste forms with the same ash content, there is no difference between the two curves containing 5 wt% and 10 wt% of the spent PE. That is, the cumulative fractions leached from the specimens with the same ash content are independent of the added spent PE amount. Thus, added PE has no effect on the leaching process. Similar results are obtained for Co and Sr. After discarding the atypical initial data (2 hours) due to surface effects and wash-off [Colombo, 1985], the cumulative fractions of Cs, Co and Sr leached from the specimen are plotted as functions of the square root of time.

From the mathematical theory of transport by diffusion from solids based on Fick's law, the analytical solution has been applied to the leaching of radionuclides from waste forms [Machiels, 1982; Thomas, 1987]. The cumulative fraction leached is derived as:

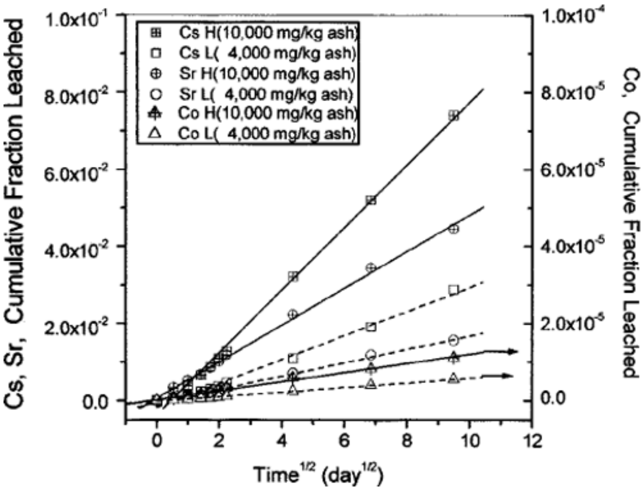

Fig. 7. The cumulative fraction of elements leached from the specimen (60 wt% ash and 10 wt% PE) are plotted as a function of the time$^{1/2}$.

$$CFL=\Sigma a_n/A_o=2(S/V)(D_e\cdot t/\pi)^{1/2} \quad (1)$$

where, Σa_n=the total amount of substance released in all leaching periods up to time, t,

A_o=the initial amount of substance of interest originally present,

V=the volume of waste form,

S=the surface area of waste form.

In Fig. 7 the cumulative fraction of Cs, Co and Sr leached from the specimen (60 wt% ash and 10 wt% PE) are plotted as functions of the square root of time. The linear correlation is found in the figure; thus, we conclude the leaching process was controlled by diffusion.

According to Eq. (1), the effective diffusion coefficient (D_e) can be determined from the slope of Fig. 7. The value of V/S is 0.95 cm in this experiment. The unit of $\Sigma a_n/A_o$ is dimensionless.

Fig. 8 shows the effective diffusion coefficient versus ash contents. The D_e for ash content of less than 50 wt% is almost the same,

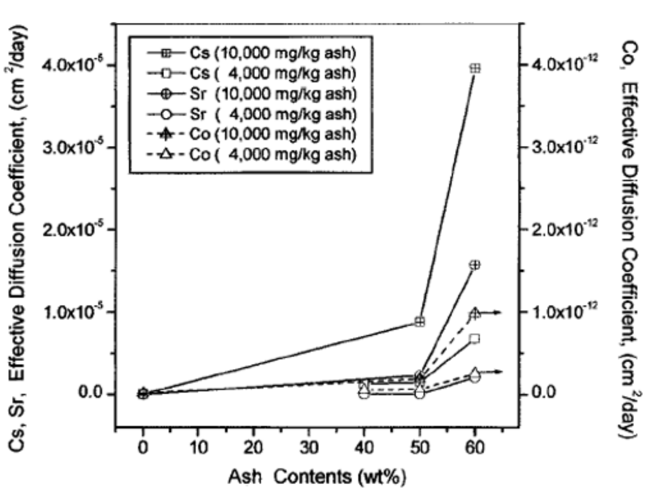

Fig. 8. The effective diffusion coefficient plotted versus ash contents from the bituminized waste forms.

Table 3. Leachability Index (LX) of elements

Ash/(PE) loading (wt%)	Leachability Index (LX)					
	Group L (Low concentration)			Group H (High concentration)		
	Cs	Sr	Co	Cs	Sr	Co
50/(10)	10.75	12.35	18.12	10.00	10.57	17.66
60/(10)	10.12	10.62	17.54	9.34	9.74	16.94

but the D_e for 60 wt% of ash contents increases rapidly. Also, in Fig. 4, the compressive strength does not show a large difference in the range of 40 and 50 wt% of ash content, but shows a large difference in the 60 wt% of ash content. Considering the trends of D_e value and compressive strength, it is speculated that the physical change in the structure of the bituminized waste forms exists above a 50 wt% of ash content. However, in the case of waste forms containing 60 wt% ash, the D_e of cesium, which is the highest value among the elements, is 3.95×10^{-5} cm^2/day (4.57×10^{-10} cm^2/sec). The Leachability Index (LI) is defined as

$$LX=-\log D_e$$

where D_e is the effective diffusion coefficient of waste forms. For waste forms, the U.S. NRC requires that the LX should be a value 6 [NRC, 1983].

In the case of waste forms containing 60 wt% ash, the Leachability Index (LX) is 9.34. Accordingly, the D_e of cesium is a relatively very low value. Table 3 shows the Leachability Index (LX) of elements.

The D_e value of Co is much smaller than those of Sr and Cs. The relatively high De values of Cs and Sr are due to the solubility of the spiking reagents-- strontium chloride ($SrCl_2$) and cesium chloride (CsCl)–while the reagent used for Co was insoluble cobalt oxide (CoO). It is therefore speculated that the solubility of elements is the principal factor of leachability.

CONCLUSION

1. The addition of more than 5 wt% spent PE maintains dimensional and mechanical stability of waste forms, and increases the softening point and the compressive strength of waste forms. The maximum allowable amount of additional spent PE is 25, 20, 15 wt% in the case of ash contents of 40, 50, 60 wt% respectively. When the PE content exceeds these amounts, a pot type mixer is unable to discharge mixtures due to high viscosity.
2. The leaching mechanism of bituminized waste forms with ash is controlled by diffusion. Additive PE of 5-10 wt% does not change the leaching process, and bituminized waste forms maintain a high leach resistance.
3. The effective diffusivities of Cs, Sr and Co increase rapidly in the above 50 wt% of ash content. However, in the case of waste forms containing 60 wt% ash, the effective diffusion coefficient (D_e) is still very low.
4. With the addition of spent PE in bituminization of ash waste, two advantages are observed: (1) to make very stable bituminized waste form, (2) to reuse the spent PE.

ACKNOWLEDGEMENT

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