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SOLIDIFICATION OF OYSTER SHELLS USED AS CADMIUM ION REMOVAL MATERIAL WITH PORTLAND CEMENT

การทำก้อนเปลือกหอยนางรมที่ใช้เป็นวัสดุกำจัดไอออนแคดเมียมด้วยซีเมนต์ปอร์ตแลนด์

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Abstract

This research investigated the solidification of oyster shell (*Crassostre commercialis*) used as Cd^{2+} removal material with Portland cement by varying the oyster shell/Portland cement ratio and curing time. Leachability of Cd^{2+} was determined with Toxicity Characteristics Leaching Procedure (TCLP). The experimental result demonstrated that the optimum condition for oyster shell/Portland cement ratio was 4. After curing time for 7 d, densities of solidified oyster shell (OS-A) as well as burned oyster shell (OS-B) were 1.87 and 2.15 ton/m^3, respectively. Unconfined compressive strength of solidified OS-A and OS-B were 69.7 and 134.5 kg/cm^2, respectively. Cd^{2+} in leachates of solidified OS-A and OS-B were 0.45 and 0.73 mg/L, respectively, and less than 1.0 mg/L.

Keywords: Solidification, Oyster shell, Portland cement, TCLP

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการนำเปลือกหอยนางรมสายพันธุ์ *Crassostre commercialis* ที่ผ่านการใช้เป็นวัสดุดูดซับไอออนแคดเมียมมาทำเป็นก้อนแข็งด้วยซีเมนต์ปอร์ตแลนด์ โดยการเปลี่ยนแปลงอัตราส่วนของเปลือกหอยนางรมต่อซีเมนต์ปอร์ตแลนด์และระยะเวลาในการบ่ม แล้วนำมาทดสอบการชะละลายใช้วิธีมาตรฐาน Toxicity Characteristics Leaching Procedure (TCLP) จากผลการทดลองพบว่า อัตราส่วนของเปลือกหอยนางรมต่อซีเมนต์ปอร์ตแลนด์ที่เหมาะสมเท่ากับ 4 โดยน้ำหนัก โดยที่ระยะเวลาในการบ่ม 7 วัน ค่าความหนาแน่นของก้อนแข็งที่ทำจากเปลือกหอยที่ไม่ผ่านการเผา (OS-A) และเปลือกหอยที่ผ่านการเผา (OS-B) มีค่าเป็น 1.87 และ 2.15 ตัน/ลบ.ม. ตามลำดับ ค่ากำลังรับแรงอัดของก้อนแข็ง OS-A และ OS-B มีค่าเป็น 69.7 และ 134.5 กก./ซม.^{2} ตามลำดับ และความเข้มข้นของแคดเมียมในน้ำสกัดของก้อนแข็ง OS-A และ OS-B มีค่าเป็น 0.45 และ 0.73 มก./ล. ตามลำดับ ซึ่งไม่เกิน 1.0 มก./ล.

คำสำคัญ: การทำก้อน เปลือกหอยนางรม ซีเมนต์ปอร์ตแลนด์ TCLP

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Introduction

Many industrial sludges containing heavy metals are considered as hazardous waste. Conventionally, chemical precipitation has been the method often used to remove heavy metals from wastewater. The Stabilization/Solidification (S/S) process is currently being used to treat a wide variety of wastes containing contaminants such as metals, organics, soluble salts, and others. This technology is cheap and easy to apply, but its application should be analyzed case-by-case. Briefly, the process involves mixing hazardous wastes, either in the form of sludge, liquid or solid, into a cementitious binder system. The stabilized/solidified (S/S) waste product was used as a raw material to build concrete blocks, to be sold as pavement blocks or used in roadbeds and/or parking lots. The quality of the blocks containing a mixture of cement, lime and waste were evaluated by means of leaching and solubility tests according to the waste regulations(1).

This research investigated the solidification of oyster shell (*Crassostre commercialis*) used as Cd^{2+} removal material with Portland cement by varying the oyster shell/Portland cement ratio and curing time. The compressive strength and leachability of cadmium in concrete block were considered to optimum condition by Thailand regulation(2)(3).

Materials and Methods

Preparation of oyster shells

Oyster shells *(Crassostre commercialis)* were collected from Chonburi Province, Thailand. Oyster shells were prepared by 2 different methods. For the first method, oyster shell was washed with distilled water, dried in the oven at 105°C, then, crushed and sieved to particle size of 75-106 µm in diameter. This was called OS-A. For the second method, oyster shell was crushed and burnt in furnace at 850°C for 2 hr, then, sieved to particle size of 75-106 µm in diameter. This was called OS-B.

OS-A and OS-B were used as cd^{2+} adsorbent in wastewater treatment process. The Cd^{2+} removal of OS-A and OS-B were 80 and 99 % at initial concentration 50 mg/L, respectively. After wastewater treatment process finished, total cadmium concentrations of OS-A and OS-B were analyzed, according to U.S. EPA : Method 3050B(4).

Stabilization/solidification treatment

Cement pastes with a water/Portland cement (W/PC) ratios of 1 and oyster shell/ Portland cement (OS/PC) ratio of 2, 3 and 4 were mixed and poured in 50 x 50 x 50 mm molds. The molds were kept in sealed bags to retain moisture. The cement pastes were cured for 7 and 28 d. After the cement pastes were cured for 7 and 28 d, some cement pastes were kept in dry air for 21 and 14 d, respectively. The curing time of cement pastes was given in Table 1. The density and compressive strength of concrete blocks were determined, following ASTM C188-95[5] and ASTM C109/C109M-95[6], respectively.

Table 1. Curing time of cement pastes (days)

Curing time	Kept at saturated humidity	Kept in dry air
7+0	7	0
7+21	7	21
28+0	28	0
28+14	28	14

Leaching test

The TCLP test was conducted by using U.S. EPA : Method 1311 in order to determine the mobility of cadmium ions in solution[7]. The samples were crushed and sieved to particle sizes which are smaller than 9.5 mm. Ten grams of each sample were added with 200 ml of dilute acetic acid (pH 2.88$\pm$0.05) in a closed polyethylene containers and agitated at 29 rpm for 18 hr. The leachate was filtered with Whatmam GF/C glass fiber filter paper. The pH of the filtrate was measured and the leachate was acidified by a small amount of concentrated nitric acid to pH < 2 before being analyzed by flame atomic absorption spectrophotometer.

Result and Discussion

Characterization of the OS-A and OS-B

The OS-A has a high percentage of calcium carbonate ($CaCO_3$) about 80%. The latter, which is OS-A, has silica oxide (SiO_2) and alumina oxide (Al_2O_3). The OS-B has a high percentage of calcium oxide (CaO) about 69%. The latter, which is OS-B, has 18% of silica oxide (SiO_2) and 2.4% of magnesium oxide (MgO) (Table 2).

Table 2. Chemical composition of OS-B

Chemical composition	Wt. %
SiO_2	17.67
Al_2O_3	1.10
CaO	68.99
MgO	2.43
Fe_2O_3	0.29
TiO_2	0.01
MnO_2	0.01
K_2O	0.04
Na_2O	0.53
Loss of ignition	8.93

The OS-B has a high percentage of CaO because $CaCO_3$ was converted to CaO at 850 °C in pretreatment process. The calcination reactions were shown in Equation (1).

$$CACO_3(s) \xrightarrow[\Delta]{} CAO(s) + CO_2(g) \qquad (1)$$

Cd^{2+} were adsorbed with OS-A and OS-B in wastewater treatment process. After OS-A and

OS-B were used as adsorbent, total cadmium concentrations of OS-A and OS-B were analyzed, according to U.S. EPA : Method 3050B[4]. Table 3 showed that cadmium concentration of OS-A and OS-B were 2,499 and 2,625 mg/kg, respectively. According to the Thailand regulations, levels of cadmium in waste were limited to 100 mg/kg so they were stabilized and solidified to reduce the environmental impact[2]. Hazardous waste could be solidified and stabilized in a matrix of Portland cement. Heavy metal compounds bound themselves strongly with ettringite during its formation and were permanently immobilized, therefore, the stabilized matrixes exhibited at very high retention of heavy metals and very low leaching concentrations owing to ettringite formation.

Table 3. Cadmium concentration adsorbed in OS-A and OS-B

Materials Type	Cadmium concentration (mg/kg)
OS-A	2,499
OS-B	2,625

Effect of oyster shells/portland cement (OS/PC) ratio

In Figure 1, when the OS/PC ratio increased from 2 to 4, density of both OS-A and OS-B concrete blocks at 7^{th} day of humidity curing increased from 1.83 to 1.87 ton/m^3 and 1.98 to 2.16 ton/m^3, respectively. The density of both OS-A and OS-B concrete blocks at all OS/PC ratio were higher than 1.15 ton/m^3, according to Thailand regulation[3].

In Figure 2, when the OS/PC ratio increased from 2 to 4, compressive strength of both OS-A and OS-B concrete blocks at 7^{th} day of humidity curing decreased from 107.0 to 69.7 kg/m^2 and 177.0 to 134.5 kg/m^2, respectively, because cement hydration products decreased when Portland cement content in concrete block increased. This has effectively reduced the amount of cement available for binding the fine and coarse aggregates required to provide adequate strength[8]. However, the compressive strength of both OS-A and OS-B concrete blocks for all OS/PC ratio were higher than 3.5 kg/m^2, according to Thailand regulation[3]

In Figure 3, when the OS/PC ratio increased from 2 to 4, Cd^{2+} in leachant of both OS-A and OS-B concrete blocks at 7^{th} day of humidity curing increased from 0.06 to 0.45 mg/L and 0.09 to 0.73 mg/L, respectively. The results also showed that the leaching of Cd^{2+} was a function of initial concentration in concrete block and increased when initial concentration increased. The retained percentage of cadmium in blended concrete block of OS-A and OS-B were observed in the range of 99.55-99.93% and 99.31-99.90% when OS/PC ratio increased from 2 to 4, respectively. In the s/s treatment, the fixation mechanism for heavy metals was through the chemical precipitation. In suspensions with large Cd content, Cadmium was fixed into the cement matrix in forming of cadmium hydroxide $Cd(OH)_2$; in suspensions with low Cd contents, Cd was sorbed on calcium silicate hydrate (C-S-H)[9]. When Portland content in concrete blocks decreased, Cd^{2+} were decreasingly precipitated and adsorbed[10]. However Cd^{2+} in leachant of both OS-A and OS-B blended concrete blocks for all OS/PC ratio were lower than the Thailand regulatory limits (1mg/L)[2].

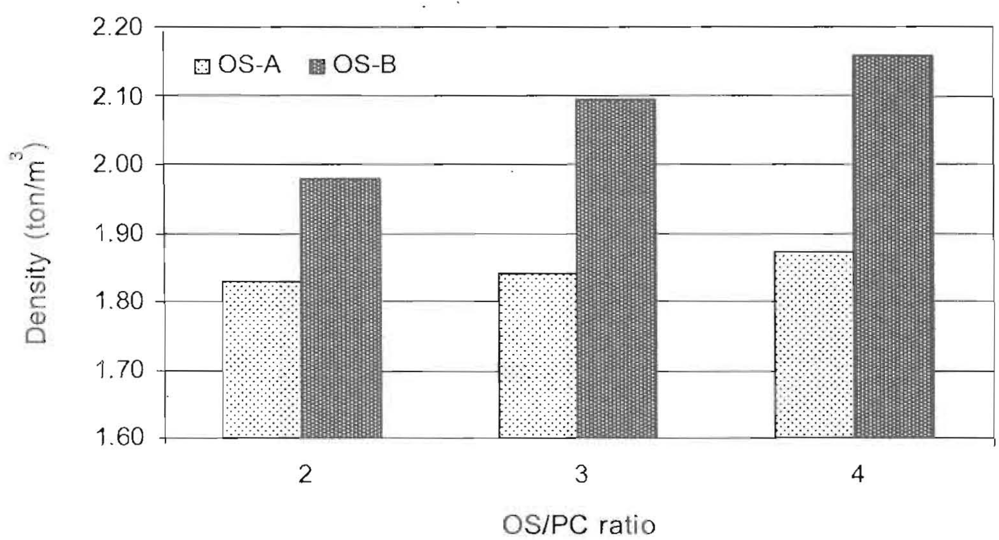

Figure 1. Relation of density of OS-A and OS-B concrete blocks against OS/PC ratio

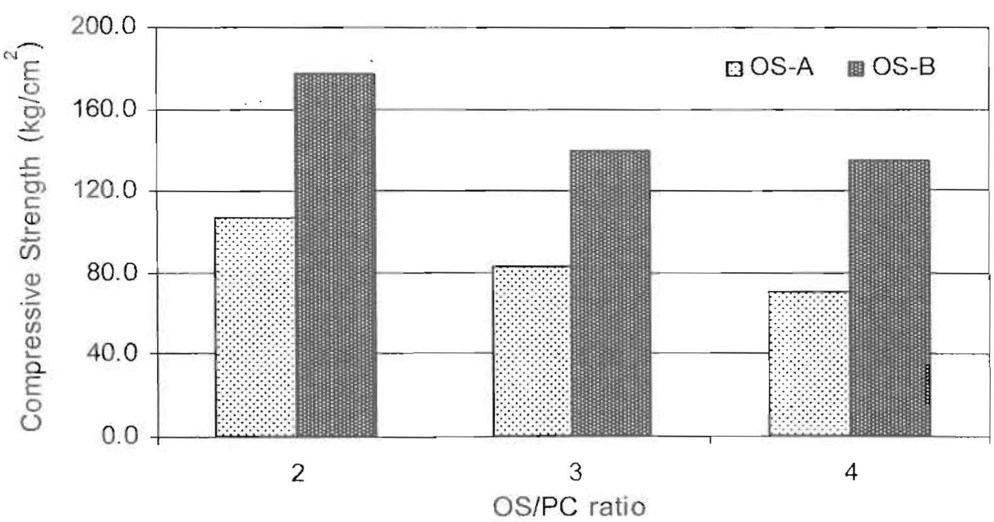

Figure 2. Relation of compressive strengths of OS-A and OS-B concrete blocks against OS/PC ratio

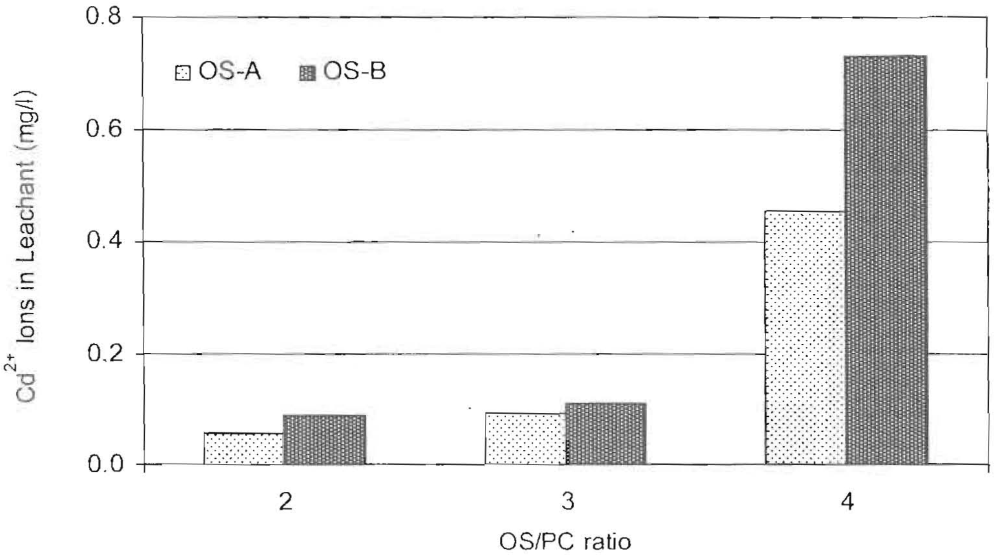

Figure 3. Relation of Cd^{2+} in leachant of OS-A and OS-B concrete blocks against OS/PC ratio

Effect of curing time

In Figure 4, when the humidity curing time increased from 7 to 28 d, density of both OS-A and OS-B concrete blocks (its OS/PC ratio was 4) increased from 1.87 to 1.91 ton/m^3 and 2.15 to 2.17 ton/m^3, respectively. After 7th day of humidity curing, some OS-A and OS-B cement pastes were cured in dry air for 21 d and density of both OS-A and OS-B concrete blocks were 1.90 and 2.16 ton/m^3, respectively. However the density of both OS-A and OS-B concrete blocks for all curing time condition were higher than 1.15 ton/m^3, according to Thailand regulation[3].

In Figure 5, when the humidity curing increased from 7 to 28 d, compressive strength of both OS-A and OS-B concrete blocks (its OS/PC ratio was 4) increased from 69.7 to 110.5 kg/m^2 (58.5% increasing) and 134.5 to 185.6 kg/m^2 (38.0% increasing), respectively. The curing of cement pastes in dry air for 21 d after the 7th day of humidity curing affected the increasing of strength of concrete block and compressive strength of both OS-A and OS-B concrete blocks were 90.0 and 144.8 kg/m^2, respectively. Moreover, Figure 5 showed that, at the initial stage of hydration reaction, the hydration products rapidly occurred and the initial higher strength was developed by cement. After the initial stage, the hydration production rate was slowly declined. However, the compressive strength of both OS-A and OS-B concrete blocks at all curing time were higher than 3.5 kg/m^2, according to Thailand regulation[3].

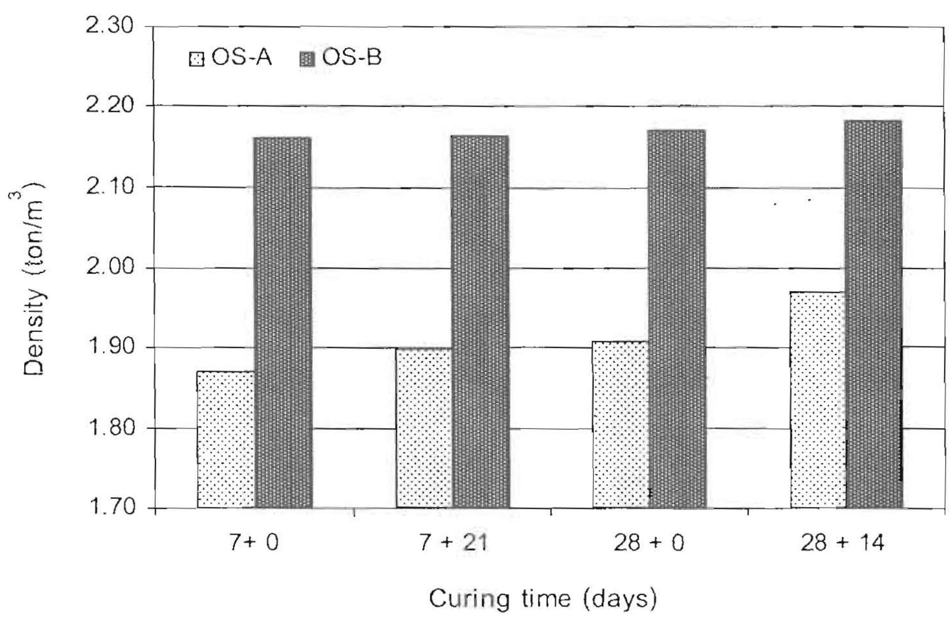

Figure 4. Relation of density of OS-A and OS-B concrete blocks against curing time

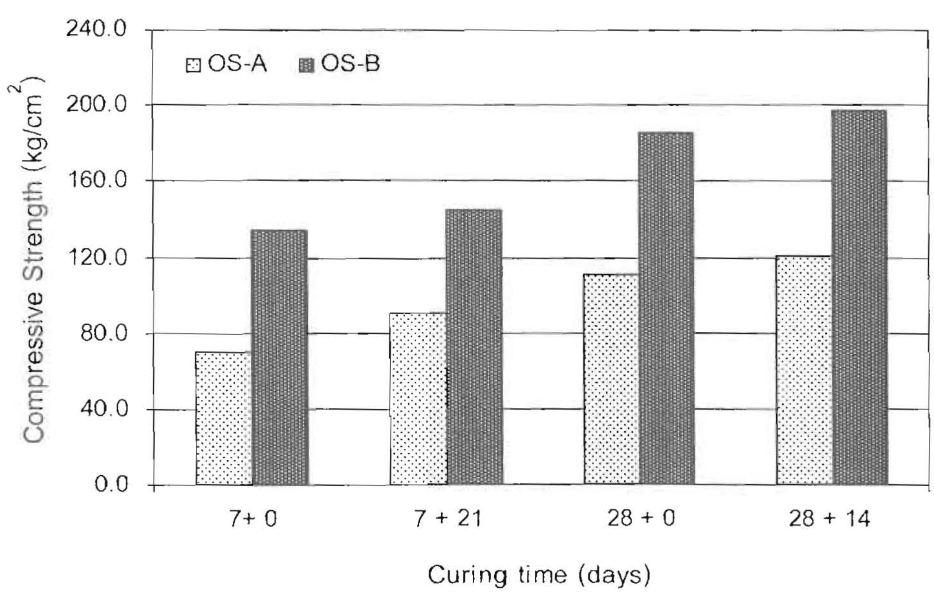

Figure 5. Relation of compressive strengths of OS-A and OS-B concrete blocks against curing time

In Figure 6, the humidity curing increased from 7 to 28 d, Cd^{2+} in leachant of both OS-A and OS-B concrete blocks (its OS/PC ratio was 4) decreased from 0.45 to 0.03 mg/L and 0.73 to 0.04 mg/L, respectively. The curing of cement pastes in dry air for 21 d after 7th day of humidity curing affected the leachability of cadmium in OS-A and OS-B concrete blocks decreased. At curing time 28+14 d, Cd^{2+} in leachant could not be detected. However Cd^{2+} in leachant of both OS-A and OS-B blended concrete block for all OS/PC ratio were lower than the Thailand regulatory limits (1 mg/L)[2].

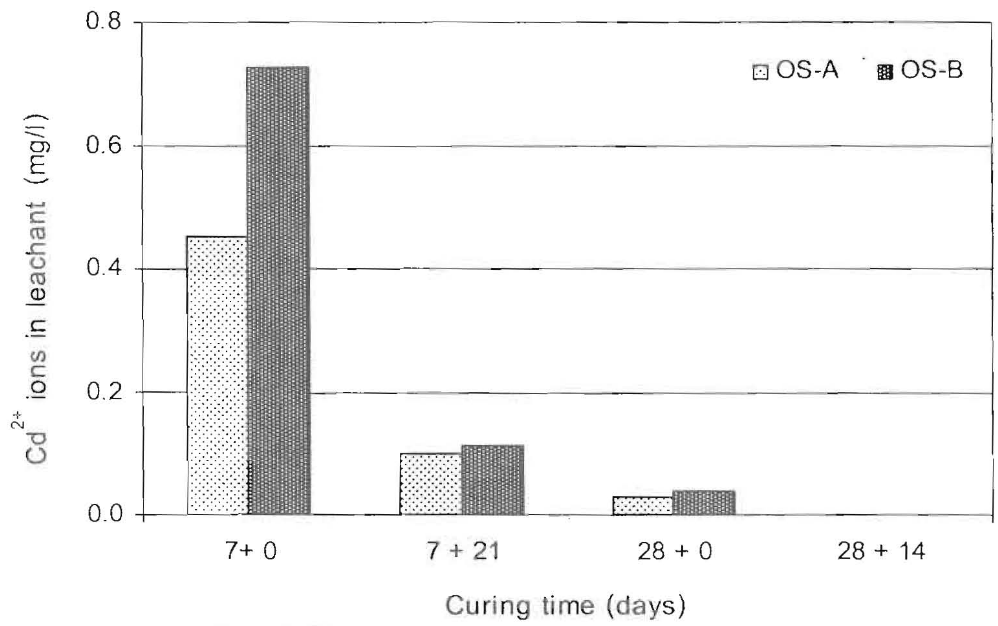

Figure 6. Relation of Cd^{2+} Ions in leachant of OS-A and OS-B concrete blocks against curing time

Conclusion

This study showed that the OS-A and OS-B from wastewater treatment process can be safely solidified/stabilized in a cement-based S/S system. The leachability of cadmium presence in OS-A and OS-B concrete blocks were lower than the Thailand regulatory limits[2]. The compressive strength of OS-A and OS-B concrete block for all conditions were much higher than 3.5 kg/m^2, according to Thailand regulation. The compressive strength of OS-B concrete block (its OS/PC ratio was 4 and 28+14 d curing time) was 197.4 kg/m^2.

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