

Effect of Seawater Temperature on Uranium Recovery from Seawater Using Amidoxime Adsorbents

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Porous amidoxime hollow fibers, which were prepared by radiation-induced graft polymerization of acrylonitrile onto porous polyethylene hollow fibers and subsequent amidoximation, were used as packing materials of the adsorption bed for uranium recovery from seawater. Seawater was forced to flow through the bed charged with the amidoxime hollow fibers either by pumping or by ocean current. Uranium concentration decay through the bed could be well correlated with residence time based on the adsorption rate expressed in terms of the overall mass-transfer coefficient. The resultant activation energy of 20 kcal/mol for uranium adsorption was indicative of the chelate formation of the amidoxime group with uranyl species as a rate-determining step.

Introduction

Extensive research (Davies et al., 1964; Egawa et al., 1980a,b; Ogata, 1980; Kanno, 1981; Schenk et al., 1982; Katoh et al., 1982a,b; Astheimer et al., 1983; Kobuke et al., 1988; Kato et al., 1990) on the recovery of uranium from seawater has been conducted to replace uranium locally deposited as terrestrial ore with uranium uniformly dissolved in seawater. A predominant dissolved form of uranium in seawater is a stable uranyl tricarbonate complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Saito and Miyauchi, 1982). The adsorption method using solid adsorbents is promising for uranium recovery from seawater with regard to economic and environmental impact; the polymer adsorbent having the amidoxime (AO) group ($-\text{C}=\text{N}(\text{OH})-\text{NH}_2$) which chelates with the uranyl tricarbonate complex in seawater has been selected among various candidates (Egawa et al., 1980a).

The recovery system by the adsorption method is based on the following (Takeda et al., 1991): (1) shape of adsorbent (bead or fiber), (2) bed mode (fixed or fluidized), and (3) contact mode (pumping or ocean current). Nobukawa et al. (1989, 1990) proposed an efficient recovery system where a series of beds packed with fibrous AO adsorbents are suspended in the ocean current and uranium is collected during passage of seawater through the beds. From this, they estimated the uranium recovery cost as a function of the adsorption rate; the lowest cost was about 55 000 yen/kg of uranium.

We have developed AO hollow fibers with varying diameters using the radiation-induced grafting technique. Figure 1 shows the preparation scheme of our AO adsorbent: the trunk polymer is polyethylene which provides physical strength in a hollow-fiber form, and the graft polymer is polyacrylonitrile, in which a portion of its cyano groups is converted into the AO group. To date, we have proposed uranium recovery by introducing seawater

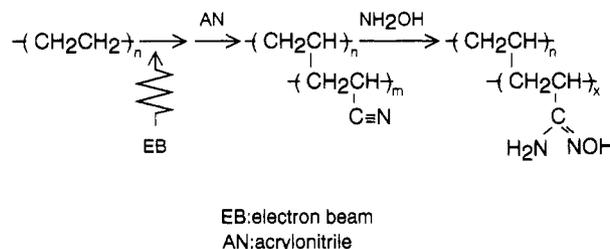


Figure 1. Preparation scheme of the amidoxime (AO) adsorbent.

into the AO-hollow-fiber-packed bed by pumping. First, preparation procedures of the AO hollow fiber, i.e., radiation-induced graft polymerization of acrylonitrile onto a porous polyethylene hollow fiber, subsequent amidoximation of the produced cyano group, and alkaline treatment, were optimized under the criterion of adsorption rate (Uezu et al., 1988; Saito et al., 1990). Alkaline treatment induced the formation of micropores favorable for diffusion of the uranyl tricarbonate complex into the AO adsorbent; this improved the uranium adsorption rate. Second, the uranium adsorption in an AO-hollow-fiber-packed bed was featured in the recovery system by pumping seawater along the coast of the Pacific Ocean (Takeda et al., 1991). A 30-day contact of a 90-cm-long adsorption bed with seawater at a superficial velocity of 4 cm/s and 303 K provided an average uranium content of 1 (g of U)/(kg on the bed), i.e., 0.1%, equivalent to that of terrestrial low-grade uranium ores. Third, deterioration of the AO hollow fiber due to fouling in seawater was quantified by stripping the deposits by oscillation with an ultrasonic generator (Konishi et al., 1991). Fouling was mainly due to the deposition of gelatinous iron oxides onto the fiber surface, and not to organic compounds.

Two uranium recovery systems using the AO hollow fibers have a high feasibility for practical use: (1) seawater is forced to flow upward by pumping through the AO-hollow-fiber-packed bed. The bed was charged with a bundle of the AO hollow fibers, and the seawater flowed in the direction parallel to the bundle and (2) the bed charged with the AO hollow fibers is submerged in the

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ocean current, and the inclined bed permits the inflow of seawater driven by the pressure difference across the sides of the bed. Here, the inflow velocity is determined mainly by the magnitude of the ocean current and the structure of the bed. A low aspect ratio of the adsorption bed, e.g., height of 0.3 m and diameter of 4 m, is desirable to secure the inflow of seawater (Nobukawa et al., 1992).

Seawater temperature on the coast and in the ocean depends on the particular year, season, time, and location. However, the effect of seawater temperature on the uranium adsorption rate has not yet been studied because data on the adsorption rate are restricted to temperatures employed in screening adsorbent.

The objective of our study was to elucidate the effect of seawater temperature on the uranium adsorption rate in pumping and ocean-current systems using the amidoxime hollow fibers.

Experimental Section

Properties of Amidoxime Hollow Fibers. Two variations of amidoxime(AO)-group-containing hollow fibers were applied to systems for the recovery of uranium from seawater. The details of preparation of the AO hollow fibers by the radiation-induced grafting technique have been described in our previous publication (Saito et al., 1987). The inner diameters of two AO hollow fibers were 0.35 and 0.75 mm with corresponding thicknesses of 0.065 and 0.32 mm. The AO hollow fibers will be referred to as the AO-H and AO-C fibers, where H and C denote hollow and capillary, respectively. The amount of acrylonitrile grafted onto 1 kg of the original hollow fiber was set to 24 and 19 mol for preparation of the AO-H and AO-C fibers, respectively. Subsequently, the corresponding conversion of the produced cyano group into the AO group was 41% and 30% on a molar base; the AO group densities of the AO-H and AO-C fibers were 9.8 and 5.6 mol/kg of the original hollow fiber, respectively. The AO-H and AO-C fibers have been adopted in pumping and ocean-current systems, respectively, and the uranium adsorption rate has been determined at different temperatures and bed heights.

Uranium Adsorption in the Ocean-Current System.

In the summer of 1990, about 45 000 pieces of 1-cm-long AO-C fibers were placed into a plastic net in a disk form whose height and diameter were 4 and 30 cm, respectively. Figure 2 shows the photograph of the net charged with the AO-C fibers. The net with a mesh size (1.2 mm) smaller than the outer diameter (1.39 mm) of the AO-C fiber prevented the adsorbents from leaking out. The volume ratio of the adsorbent excluding its lumen to the net was 0.17. Figure 3 shows the schematic illustrations of an adsorption unit and a boat for towing the adsorption unit. An adsorption cage loaded with the AO-C fiber-charged net was attached to the adsorption bed. The adsorption unit consisted of five adsorption beds which were arranged below the sea surface by suspending ropes hung from a buoy with a hole in the center. Then, the boat towed the adsorption unit located at the Imari Gulf, Saga Prefecture, Japan at a speed of 1 m/s, which corresponds to an ocean current of about 2 knots. The adsorption unit was in contact with seawater for 10 h at a speed of 1 m/s generated by the boat and for 14 h as carried by the waves and tides, per day. The adsorption experiment was performed for 3 days. During each day of seawater contact, about 300 pieces of the AO-C fibers were removed from the net, and the uranium adsorbed on the fibers was eluted with two 50-mL aliquots of 1 M HCl. After 3 days, the adsorption

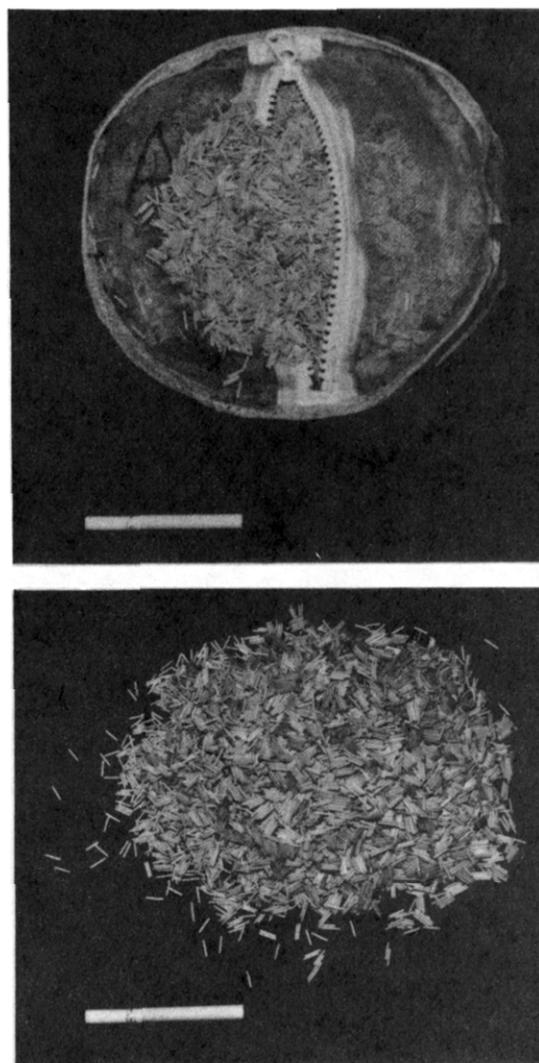


Figure 2. Photographs of (a, top) the net charged with the 1-cm-long AO-C fibers and (b, bottom) the AO-C fibers.

bed was taken out from the seawater, and the remaining AO-C fibers were immersed in 1 M HCl to elute the uranium.

In the summer of 1991, a larger adsorption bed with a height of 15 cm and a diameter of 90 cm was towed at a speed of 1 m/s by the boat. One part (about 1% of total area) of the net was charged with 1-cm-long AO-C fibers, and the remaining part was filled with a dummy fiber ball with almost the same flow resistance as that of the AO-C fiber. The 39-day contact included towing and mooring: the first 3 10-hour periods of towing were followed by a 19-day mooring; another 10-hour towing was followed by an 18-day mooring; and then the last 10-hour towing was performed. Seawater temperature was measured continually throughout the experiments. The samples of the AO-C fiber were taken out of the net before and after every 10-hour towing period. The uranium adsorbed onto the AO-C fiber was eluted with 1 M HCl and determined by spectrophotometry (Motojima et al., 1969).

Analysis

The mass balance equation of uranium can be described for axial flowing of seawater through the hollow-fiber-packed bed as follows.

$$u \frac{\partial C}{\partial z} + \rho_a(1 - \epsilon_p) \frac{\partial q}{\partial t} = 0 \quad (1)$$

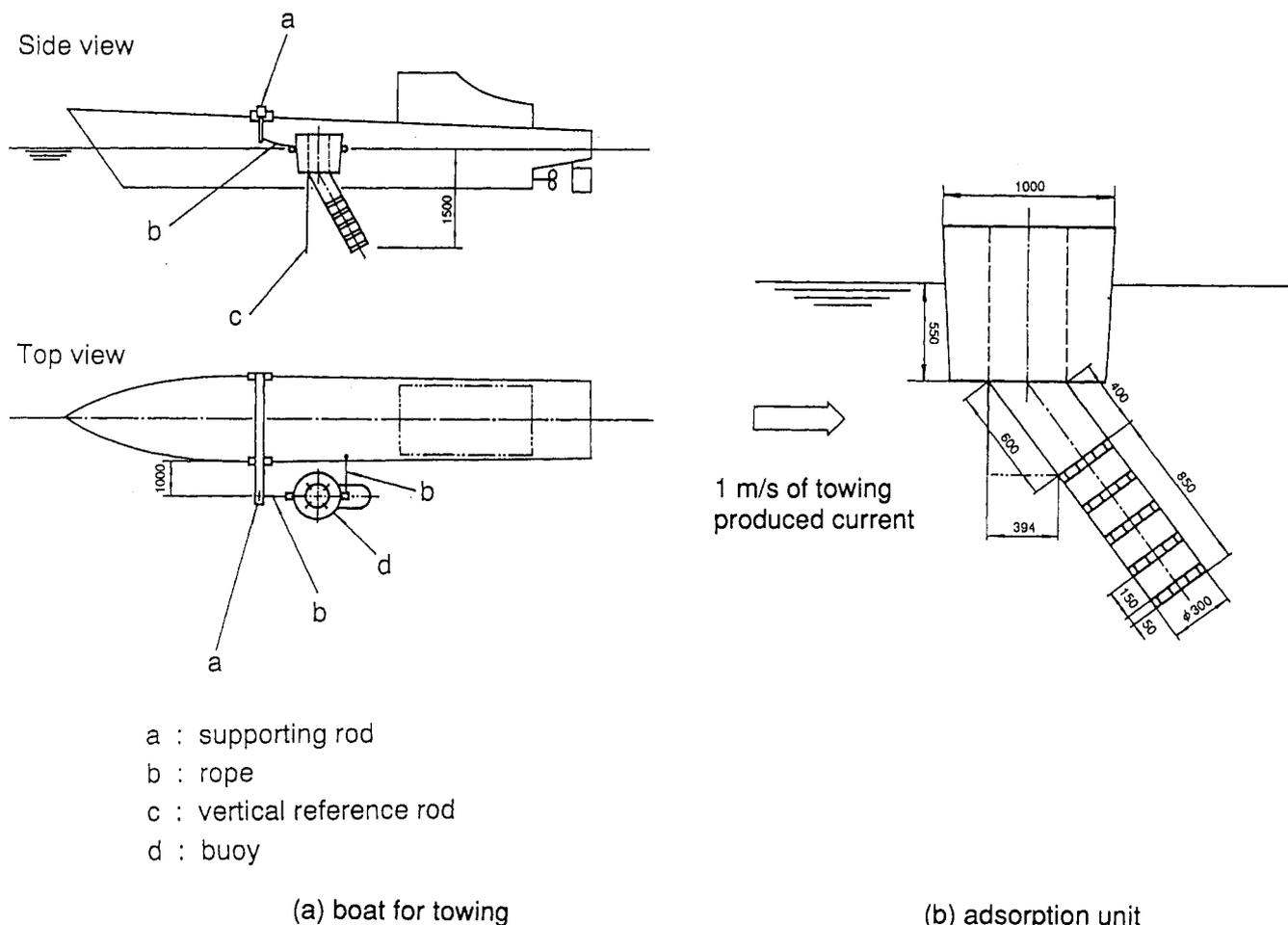


Figure 3. Schematic illustrations of (a) a boat for towing and (b) an adsorption bed.

where C and q are the uranium concentration in the bulk seawater and the amount of uranium adsorbed on the AO hollow fiber, respectively, and u , ϵ_b , and ρ_a are the superficial velocity, the void fraction of the bed, and the apparent density of the hollow fiber, respectively. The apparent density of the fiber was defined as the dry weight divided by its wet volume.

Here, the adsorption rate can be expressed in terms of the overall mass-transfer coefficient, K , and specific surface area, a .

$$\rho_a \partial q / \partial t = Ka(C - C_s) \quad (2)$$

where C_s is the uranium concentration in equilibrium with q and is approximated to be zero at the initial stage because the AO adsorbents have a sufficiently high capacity for uranium in seawater (Saito et al., 1988). Then, the mass-balance and rate equations (1-2) can be integrated under a boundary condition of $C = C_{in}$ at $z = 0$ for the bed entrance:

$$\ln(C_{out}/C_{in}) = -Ka(1 - \epsilon_b)L/u \quad (3)$$

$$= -Ka(1 - \epsilon_b)t_r \quad (4)$$

where C_{out} is the uranium concentration at $z = L$ for the bed exit, and t_r is defined as the mean residence time, L/u .

We can determine the uranium concentration at the bed exit against different t_r values by varying the superficial velocity. Also, this equation is indicative of a steady concentration profile along the bed at the initial stage.

Results and Discussion

Uranium Adsorption Rate in the Ocean-Current System. Figure 4 shows a uranium uptake curve after a

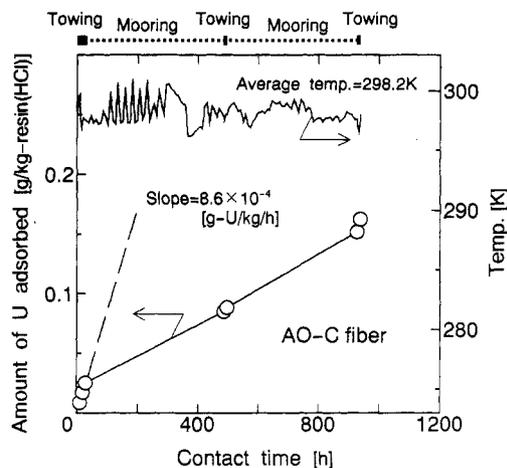


Figure 4. Uranium uptake curve in the system simulating ocean-current uranium recovery.

39-day contact with seawater in the summer of 1991. The upper bar of this figure indicates the operating conditions of the adsorption unit: towing and mooring. The seawater temperature ranged from 296 to 301 K. The adsorption rate on the AO-C fiber during towing by the boat, 8.6×10^{-4} (g of U)/(kg h), was 6-fold higher than that during mooring by the waves and tides, 1.4×10^{-4} (g of U)/(kg h). If this adsorption unit were continuously towed in the ocean current with a speed of 1 m/s, a contact of about 48 days would provide a uranium content of 1 (g of U)/kg of the AO adsorbent, i.e., 0.1% uranium ore.

Figure 5 compares a time course of the amount of U adsorbed on the AO-C fiber during a 30-hour towing in

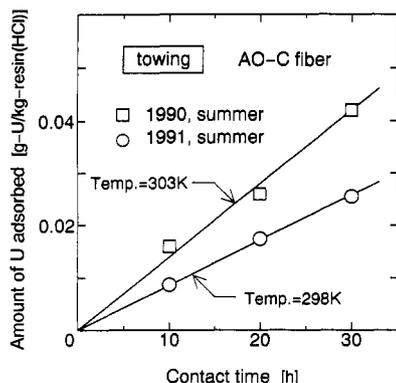


Figure 5. Uranium adsorption during towing at a speed of 1 m/s for 30 h.

Table 1. Experimental Conditions of Pumping Modes Using the AO-H Fiber

researcher	bed height, cm	void fraction	superficial velocity, cm/s	temp, K
Saito et al. (1988)	30	0.66	0.25-1.0	298
Takeda et al. (1991)	90	0.75	4	303
Konishi et al. (1991)	15	0.75	1-10	288

seawater in the summers of 1990 and 1991. Seawater temperature during towing in 1990 and 1991 ranged from 300 to 305 K and from 297 to 300 K, respectively. Nobukawa et al. (1992) determined the velocity of seawater flowing through the part charged with the AO-C fibers for 1 m/s towing to be 1.1 cm/s from the measurement of the pressure distribution around the adsorption bed of 15-cm height and 90-cm diameter. Thus, the recovery ratio in the summer of 1991 was evaluated to be less than 7% by the following equation.

$$\text{recovery ratio} = \rho_a(1 - \epsilon_b)L(av \text{ ads rate})/(uC_{in}) \quad (5)$$

The difference in adsorption rate in Figure 5 is due to the seawater temperature because there is no substantial decrease in uranium concentration throughout the bed. The analytical equation for the kinetic data of downward flow, driven by towing force, through the packed bed of the AO-C fibers is approximated as follows:

$$Ka = \rho_a q / C_{in} t \\ = \rho_a (\text{slope of the straight line in Figure 5}) / C_{in} \quad (6)$$

The product of K and a , i.e., the overall capacity coefficient, was calculated as 4.7×10^{-2} and $2.9 \times 10^{-2} \text{ s}^{-1}$ for the adsorption rates obtained in the summers of 1990 and 1991, respectively.

Effect of Seawater Temperature on Uranium Adsorption Rate. We have so far accumulated the kinetic data of upward flow, driven by pumping force, through the packed bed of the AO-H fibers. Experimental conditions of the pumping mode are summarized in Table 1. The seawater temperature was maintained at a prescribed temperature within a fluctuation of 1° . Figure 6 shows an example of the uranium concentration decay correlated with the residence time of seawater through the adsorption bed. The overall capacity coefficient (Ka) can be obtained from the slope of the straight line using eq 4.

Figure 7 summarizes the values of Ka versus the reciprocal of the seawater temperature for variations of the uranium recovery system using the AO hollow fibers. Different from the pumping system, since seawater temperature cannot be controlled in the adsorption

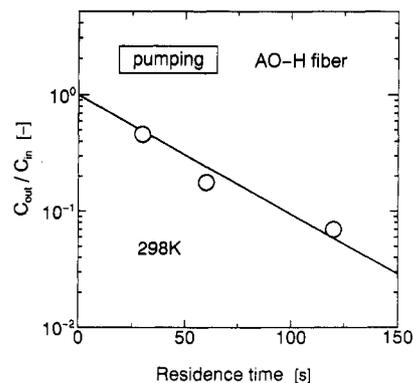


Figure 6. Example of uranium concentration decay correlated with residence time of seawater through the adsorption bed.

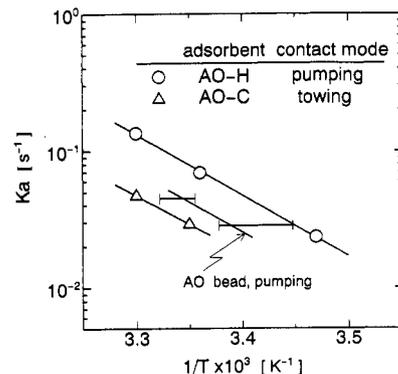


Figure 7. Effect of seawater temperature on uranium adsorption rate.

experiment in the ocean-current, the variation of seawater temperature measured is shown with an error bar in Figure 7. In spite of various adsorbent dimensions and contact modes, the slopes of each straight line agreed well. Egawa et al. (1991) determined the adsorption rate of uranium onto the AO beads in a fluidized bed at two different temperatures due to the climate of season. The value of Ka derived from their results exhibited a similar dependence on seawater temperature, as plotted in Figure 7. The magnitude of the resultant activation energy was about 20 kcal/mol for uranium adsorption onto the AO adsorbents. The diffusion process of the uranyl tricarbonate complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ with an activation energy of 5.3 kcal/mol (Saito and Miyauchi, 1981) simply cannot explain the overall adsorption process. The amidoximation of the cyano group and subsequent alkaline treatment produced various kinds of the moieties such as amidoxime, imidedioxime, and carboxyl groups, depending on the reaction time and solvent. Amidoxime (Hirotsu et al., 1986) and imidedioxime (Kobuke et al., 1990) groups are reported to bind to the stable uranyl tricarbonate complex in seawater as follows:



where HL and H_2L denote the amidoxime and imidedioxime groups, respectively. Our result indicates that these chelate-forming reactions as well as the diffusion process are responsible for the high activation energy of 20 kcal/mol as a rate-determining step. Practically, a 10° increase in seawater temperature, e.g., an increase from 293 to 303 K, leads to a 3-fold higher adsorption rate of uranium onto the AO adsorbents. Therefore, seawater temperature

is a decisive factor in the selection of the location of a uranium recovery plant in ocean.

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Nomenclature

- a = specific surface area, m^2/kg
 C = concentration of uranium in seawater, $(g \text{ of U})/m^3$
 C_{in} = concentration at bed entrance, $(g \text{ of U})/m^3$
 C_{out} = concentration at bed exit, $(g \text{ of U})/m^3$
 C_s = concentration of uranium in equilibrium with q , $(g \text{ of U})/m^3$
 K = overall mass-transfer coefficient, m/s
 L = bed height, m
 q = amount of uranium adsorbed on the AO adsorbent, $(g \text{ of U})/kg$
 t = time, s
 t_r = mean residence time, s
 u = superficial velocity of seawater through the bed, m/s
 z = axial distance, m

Greek Symbols

- ϵ_b = void fraction of the adsorption bed
 ρ_a = apparent density of the AO adsorbent, kg/m^3

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