TRANSPORTATION CASK CONTAMINATION WEEPING: A PROGRAM LEADING TO PREVENTION*

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INTRODUCTION

This paper describes the problem of cask contamination weeping, and efforts to understand the phenomenon and to eliminate its occurrence during spent nuclear fuel transport. The paper summarizes analyses of field experience and scoping experiments, and concentrates on current modelling and experimental validation efforts.

The "weeping" phenomenon associated with spent fuel transportation casks (also known as "sweating") is believed to be due to the conversion of fixed contamination on the external surface of the cask to a removable form. Spent fuel transportation casks are loaded under water at nuclear power plants in a spent fuel storage pool, exposing the cask surfaces to contamination by radionuclides present in the pool water including ^{137}Cs, ^{134}Cs, and ^{60}Co. The external surfaces of loaded casks are routinely surveyed for removable contamination and decontaminated to 1/10 of the U.S. and IAEA regulatory limits prior to being released for shipment (49CFR 1983, IAEA 1989). However, 3% to 8% of U.S. spent fuel casks have arrived at final destinations with removable surface contamination in excess of that allowed by regulation, though many pre-shipment surveys have shown contaminant levels to be within allowable limits (Grella 1987). Attempts to reduce the incidence of weeping have met with limited success and resulted in time-consuming operational constraints and procedures that significantly increase cask processing times and occupational exposures at loading facilities. As the U.S. Department of Energy (DOE) moves toward a high volume spent fuel transportation campaign beginning in 1998, the elimination of weeping occurrence and minimization of operational constraints has received increased attention.

A DOE program is underway at Sandia National Laboratories (SNL) to determine the physical and chemical processes involved in radionuclide contamination and release on transportation cask surfaces. These activities are being conducted in order to provide a basis for: 1) the development of more effective decontamination procedures; and 2) the development of contaminant blocking methods to prevent initial cask surface contamination.

The program follows the approach illustrated in Figure 1. In-service data was collected and analyzed for weeping conditions during fuel and irradiated hardware transport campaigns, as well as during cask storage periods. Scoping experiments were also conducted to help clarify observations in this phase.

Based on these observations and analysis, an initial model of the weeping phenomenon was developed. We have proposed that ion-exchange characteristics of the stainless steel cask surface are responsible, at least in part, for weeping (Chambers et al. 1991). Radionuclide contaminants present in the spent fuel storage pool

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** A United States Department of Energy Facility in a dissolved, ionic state, are likely sources of cask surface contamination. Once fixed, these ionic contaminants are likely to remain chemically bound until some change in surface chemistry releases them.

SNL is now in the Experimentation and Validation phases, where various aspects of the model are being tested and refined. A computer code is being adapted to predict surface chemistry reactions to guide experiments, recommendations for methods of preventing weeping and field trials of such methods.

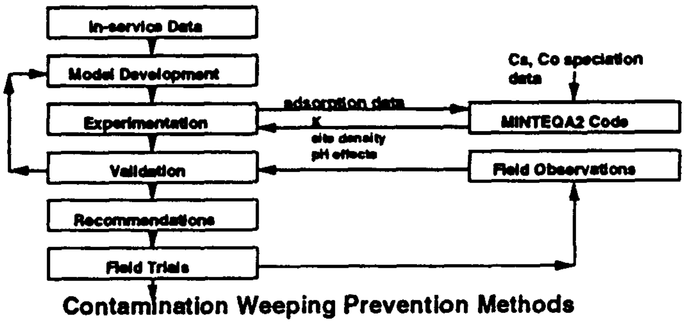

Figure 1. Contamination Weeping Project Flow

Initial recommendations will be made and field trials will begin within the next two years. Refinements to the weeping prevention methods will then be made with utility participation, and final recommendations on cask design and operational procedures will be made.

BACKGROUND

1. In-Service Data Analysis

In-service data analysis efforts focused on archival data and observation of on-going spent nuclear fuel and irradiated hardware transportation campaigns (176 cask movements), as well as cask storage conditions (Bennett et al. 1989). Weeping occurs as a transformation of apparently fixed surface contamination to a removable form. ^{137}Cs appears to be the primary contaminant in weeping, followed by ^{60}Co and ^{134}Cs. Weeping has been observed on a variety of cask surfaces and ages, both in transit and in storage, and on casks which were loaded and empty. A regression analysis conducted on transport data indicated a correlation of low ambient temperatures and high relative humidity with rises in removable contamination levels. This analysis also indicated more information is necessary to explain site-dependent factors. Reconstruction of previous shipments from archived data provided limited insights due to lack of detailed documentation. Cask pre-release surveys were of pass/fail nature, without mapped survey points or logged contamination values. Non-standardized instruments and swiping techniques were also used.

2. Scoping Experiments

To augment in-service observations and additional data regarding cask surface materials, finishes and environmental influences, scoping experiments were conducted at the University of Missouri. A surface area of 18.5 m^2 in the form of 122 stainless steel and titanium cylinders was contaminated in Union Electric's Callaway Plant spent fuel pool and subjected to environmental conditioning (Bennett et al. 1991). Contaminants involved in weeping on the test samples were identified as ^{137}Cs, ^{134}Cs, ^{60}Co and ^{54}Mn. The behavior of the main radioactive isotopes (Cs and Co) showed differences in the preferential rate at which they deposited onto the surfaces of the samples, and the rate at which they were removed by the swipes.

Rise in removable contamination occurred on the sample surfaces more often than not, and generally under a variety of conditions of changing temperatures. A source of potentially removable contamination approximately 100 times larger than what a health physicist can readily measure appears to be bound on the surface as "fixed" contamination. It has been demonstrated that a small portion (a few percent) of this initially fixed contamination will "weep" under certain conditions, becoming removable contamination. General indications of factors correlated to weeping were observed. Smoother cask surfaces, shorter pool exposures and protection from extreme temperature gradients correlate to lower rises in removable contamination.

The scoping experiment did not address the pool conditions or decontamination methods specifically. The parameters of a reactor spent fuel storage pool such as temperature, contaminant concentration and chemical form, and pH could conceivably affect reaction of contaminants with cask surfaces. The decontamination procedure could influence the percent of removable contamination is removed, and cause changes in the surface chemistry of the cask leading to increased rates of conversion to removable contamination.

3. Model Development: Adsorption of dissolved metals on oxide surfaces

Stainless steel is a chromium rich alloy that owes its corrosion resistance to a Cr-rich passive oxide layer (McCafferty and Brodd 1986). We have investigated the adsorption of dissolved metals on stainless steel surfaces using Cr_2O_3 powder as a model surface.

In order to recommend processes to prevent adsorption of Co^{2+} and Cs^+ on a cask surface (or remove it by controlled desorption) it is necessary to understand the interaction between the dissolved metals and the oxide surface. Specifically, it is necessary to:

1. Determine the time required to achieve equilibrium.

2. Determine the distribution coefficient of metals such as cobalt, cesium, and other relevant species that will adsorb on oxide surfaces.

3. Develop a model of the storage pool chemistry and adsorption thermodynamics and apply the model to predict chemical methods that might be used to avoid contamination or remove contamination from surfaces of nuclear waste shipping casks.

Determining the time required to achieve equilibrium is necessary in order to accurately determine the distribution coefficient of metal ion adsorption. The approach described below is generally applicable to any species adsorbed on a surface (Allison et al. 1991). Using the adsorption of Co2+ on Cr2O3 as a model, the distribution coefficient is related to the equilibrium constant for the reaction of dissolved cobalt on a chromium oxide surface:

$$Co^{2+}(aq) + Cr_2O_3 \overset{K_{eq}}{<========>} Co^{2+}(ads) -- Cr_2O_3$$

where:

$$K_{eq} = \frac{a(Co^{2+}(ads))}{a(Co^{2+})\, a(Cr_2O_3)}$$

In this expression, a(Co2+) is the activity of cobalt in solution and is described by:

$$a(Co^{2+}) = f(Co^{2+})\ [Co^{2+}]$$

where $[Co^{2+}]$ is the concentration of cobalt in solution as expressed in mol/L (M) and $f(Co^{2+})$ is the activity coefficient of cobalt in solution. Activity coefficients can be described by a variety of expressions. We have used the modified Debye-Huckel expression or the Davies equation for calculating activity coefficients.

There is no generally accepted method of computing activity coefficients for unreacted or reacted adsorption sites so we will define these coefficients as unity. Thus: a(Co^{2+}(ads)--Cr_2O_3) = a(Co^{2+}(ads)) = [Co^{2+}(ads)].

Since the activity of a pure solid is unity, a(Cr_2O_3) = 1, therefore:

$$K_{eq}=\frac{[Co^{2+}(ads)]}{f(Co^{2+})\,[Co^{2+}(aq)]}$$

The equilibrium constant (K_{eq}) thus described is defined as the Activity Distribution Coefficient (Activity K_d) for adsorption of an ionic species onto an oxide surface. Variations of this model yield Activity Langmuir and Activity Freundlich expressions (Allison 1991). The distribution coefficient is directly related to the cask contamination model in that it describes how effectively a dissolved species is bound to a solid adsorbent. The larger the distribution coefficient, the more strongly the Co is adsorbed. The distribution coefficient for adsorption of other metal ions can also be measured to determine the potential for blocking the adsorption of Co^{2+} and other ionic radionuclides with more strongly bound metals. The addition of other chemicals, such as chelating agents, which bind Co^{2+} in the aqueous phase reduce the activity of Co^{2+} and therefore reduce the available concentration of Co^{2+} that can contaminate the oxide surface. These chemicals can be evaluated for use as decontamination agents.

EXPERIMENTAL METHODS

Modelling

We are applying an Environmental Protection Agency (USEPA) computer code, MINTEQA2, to the problem of adsorption of Co^{2+} and Cs^{+} on metal oxide surfaces. MINTEQA2 is a geochemical equilibrium speciation model capable of computing equilibria among the dissolved, adsorbed, solid and gas phases in an environmental setting. MINTEQA2 includes an extensive database of reliable thermodynamic data for these calculations.

Because the system that we are working with is not a common environmental situation, data needed to describe this system is not readily available in the data base. We are both generating thermodynamic data to allow the use of MINTEQA2 and exploring the seven different models that are available to describe adsorption phenomena to see which one(s) best model our system.

Adsorption studies:

The experimental methodology used in the studies described in this paper has previously been published (Chambers et al. 1991). In that earlier work, we described the reversible binding of Co^{2+} to Cr_2O_3. We noted that Cs^{+} binding had not been observed.

An experiment was designed to determine the kinetics for the adsorption reaction. A 20 wt% slurry of Cr_2O_3 in a solution containing 1.67 mM Co^{2+} was prepared. The concentration of Co^{2+} in this slurry was estimated to represent approximately 20% of the available adsorption sites on the Cr_2O_3 (assuming a surface binding site density of 2.5 sites/nm^2 as calculated previously (Chambers et al. 1991)). Less than 50% of the available sites were targeted for adsorption to avoid saturation effects in calculating the equilibrium distribution. The unadjusted, natural pH of the slurry was approximately 6.5, and remained relatively stable (i.e. slowly increased to 7.0) over the duration of the experiment. The slurry was sampled at various time intervals for up to 6 days, filtered, and the solution analyzed for cobalt concentration. This experiment was repeated in triplicate and the individual experiments are identified in the following discussion as: #SMI-26, #PWI-26, and #PWI-28.

Experiments were also performed to determine the distribution coefficient for Co adsorption on Cr_2O_3 as a function of pH. A slurry composed of 10 wt% Cr_2O_3 in 0.2 mM Co^{2+} was prepared and titrated from pH=7.52 to pH=3.09 (#PWI-36). In this case, the concentration of Co was estimated to represent 100% of the available adsorption sites. Samples were collected at intervals, filtered, and analyzed for Co concentration. The experiment was repeated with the addition of 0.1M tetramethylammonium chloride to the solution (#WSA-6). The tetramethylammonium ion provides for a constant ionic strength solution but does not compete for adsorption sites or sequester the Co^{2+}.

RESULTS AND DISCUSSION

Adsorption experiments:

The results of the three adsorption rate experiments described above for Co^{2+} on Cr_2O_3 are shown in Figure 2. These results show that equilibrium between $Co^{2+}(aq)$ and Co(ads) on Cr_2O_3 is achieved slowly, although most (>90%) of the available cobalt was adsorbed within 60 minutes. The distribution coefficient at 98 hours was calculated to be:

$$K_d = [Co^{2+}(ads)] / [Co^{2+}(aq)] = 438$$

Graphs that show the dependence of K_d on pH as determined from the titration experiments are shown in Figures 3 and 4. Figure 3 is in agreement with data obtained from the equilibrium adsorption experiments (Fig. 2) as the extrapolated K_d at pH = 7 is very close to 438, the average value from the adsorption experiments. Figures 3 and 4 display the dependence of K_d for the first titration step (acidification). Previous experiments described in Chambers (1991) note hysteresis on cycling between acid and basic pH, which would affect K_d values. Note that agreement of Figure 3 and Figure 4 is poor. We presently ascribe the difference to the ionic strength effects of the tetramethylammonium ion. We plan to investigate these effects with the aid of the MINTEQA2 model and, if necessary, experimental studies.

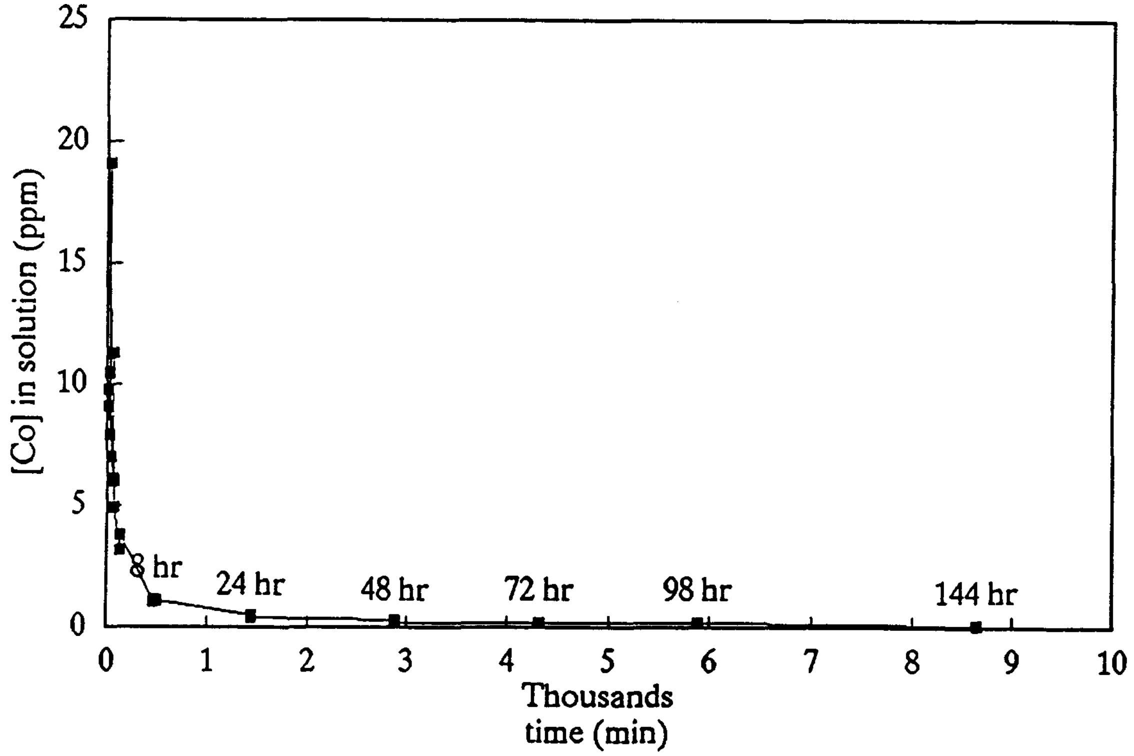

Figure 2. Equilibrium adsorption rate; Co^{2+} on Cr_2O_3

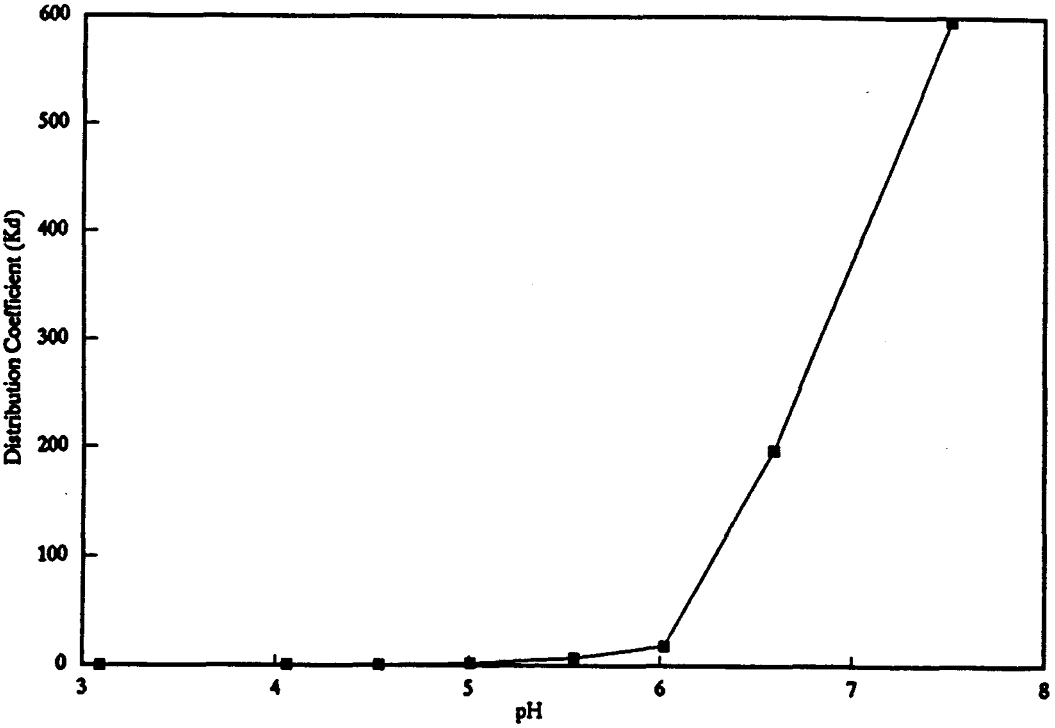

Figure 3. Distriubtion coefficient (K_d) vs. pH

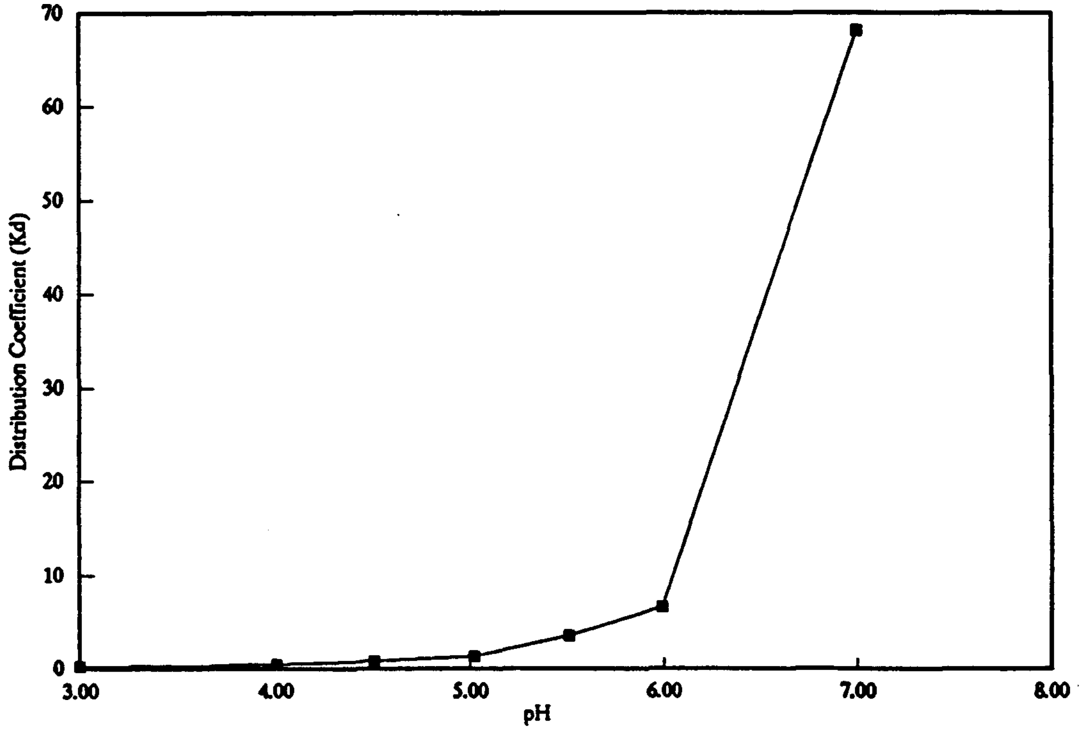

Figure 4. Distribution coefficient (K_d) vs. pH with ionic buffer

Adsorption modeling

We find that two of the adsorption models in the MINTEQA2 code yield promising results. These results are especially encouraging since several of the thermodynamic constants that are needed for accurate modeling are not currently available. The calculational runs described below are simulations substituting cadmium for cobalt as the solution species.

The first goal was to identify which of the seven adsorption models supported by MINTEQA2 most accurately describes our experiments. To date, three of the models have been used: the Activity K_d Adsorption model, the Activity Langmuir Adsorption model, and the Activity Freundlich model. The evaluation consists of using the K_d or K_L, total concentrations of species, and the total amount of adsorbate as input parameters for the code. The output (final concentration of metal adsorbed and dissolved) is calculated and compared to the actual measured concentrations. Table 1 gives the results using either the average Kd value of 438 or the average K_L of 33,710 obtained from the three Co^{2+} on Cr_2O_3 adsorption experiments (#PWI-26, #PWI-28 and #SMI-26).

Table 1

Comparison of Calculated and Measured Cobalt Adsorption on Cr_2O_3
(all concentrations expressed in mol/L)

	Measured	Calculated		
		Activity K_d	Activity Langmuir	Activity Freundlich
#PWI-26				
[Co]aq	3.74E-6	3.84E-6	2.21E-4	3.80E-6
[Co]ads	1.56E-3	1.66E-3	1.44E-3	1.66E-3
#PWI-28				
[Co]aq	3.57E-6	3.84E-6	2.21E-4	3.80E-6
[Co]ads	1.56E-3	1.55E-3	1.44E-3	1.66E-3
#SMI-26				
[Co]aq	3.40E-6	3.84E-6	2.21E-4	3.80E-6
[Co]ads	1.56E-3	1.66E-3	1.44E-3	1.66E-3

These data clearly show that the Activity K_d and the Activity Freundlich models are superior to the Activity Langmuir model and are in good agreement with the experimental data. Since the Activity Freundlich model is a special case of the Activity K_d model and since the results are comparable, we will continue evaluations at this stage using the Activity K_d model.

CONCLUSION AND FUTURE WORK

Several conclusions can be drawn from the results described in this report:

1. Adsorption of Co^{2+} onto Cr_2O_3 is close to equilibrium after several hours but takes a few days to achieve complete equilibrium.

2. K_d for adsorption of Co^{2+} onto Cr_2O_3 is dependant on pH and has a value of approximately 438 at pH = 7.

3. K_d for pH titration experiments agree with pH-static experiments as long as pH swings are not too extreme.

4. Distribution coefficients are dependant on ionic strength.

5. Activity K_d model describes our experimental results with sufficient accuracy.

From these experiments we have determined that adsorption of Co^{2+} on Cr_2O3 is kinetically favored in the pH range of a boric acid modified fuel storage pool. The value for K_d is higher at pH=7, the approximate pH of de-ionized H_2O. This suggests that a de-ionized water wash would have little effect in decontaminating these surfaces, whereas an acidic wash would be more effective.

We plan to continue our experiments and modelling efforts in order to define the chemical issues as completely as possible. While the data presented here supports the ion-exchange model for Co^{2+} adsorption on Cr_2O_3, scoping experiments have been performed that allow calculation of adsorption equilibria for other systems and which indicate that pure Cr_2O_3 is not the best model for adsorption on stainless steel. Experiments investigating the adsorption of Co^{2+} and Cs^+ on Fe_2O_3 and stainless steel powders are in progress.

We will continue to develop the MINTEQA2-based adsorption model with emphasis on incorporating appropriate thermodynamic constants. Furthermore, we will use the model to explore solution chemistry of storage pools and decontaminating solutions in order to gain insight into factors that will reduce initial surface contamination as well as remove contamination with more effective decontamination procedures. Recommendations based on the insights will be made, followed by field testing to evaluate the recommendations. Finally, the developed procedures will be available to prevent contamination weeping.

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