

Leaching studies of the lead-iron phosphate radioactive waste glasses under different chemical environments

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Abstract

Lead-iron phosphate (LIP) glasses are a promising new waste form for the safe immobilization of both high level defence and high level commercial radioactive waste for long term disposal. LIP glasses have several advantage such as lower aqueous corrosion rate, lower processing temperature etc. From all the measurements of the leaching studies of different LIP glasses in different chemical environments, it is shown that the resistance of lead iron phosphate glasses to aqueous attack varies considerably with pH of the leachate soln. The best chemical resistance is exhibited at neutral pH of around 7 and the corrosion of the LIP glasses increases very rapidly with decreasing the pH (at very low pH) of the leaching medium.

This can be understood by considering the size of the migrating species at the water/glass interface. In the most acidic solutions where both modifying cations are drawn into solution, cross links in the $(PO_4)_n$ chains will be broken which will inevitably lead to a loss of phosphorus and the congruent leaching of cations and anions.

Keywords: Nuclear waste glass, leach resistance, congruent leaching, chemical environments and glass interface.

Introduction

Radioactive wastes are generated from the various sources such as nuclear power plants, medical isotope applications, defence, communication systems and atomic industries. The utilization of nuclear energy resulted in the accumulation of large amounts of liquid high-level radioactive waste (HLW) which contains environmentally hazardous elements like plutonium and other actinides in addition to fission and corrosion products. The fission products with the usual fuel materials viz. U, Pu and Th contain about 35 elements with 200 different isotopes¹⁻⁷. Safe disposal of HLW is of key concern in the application of nuclear energy.

The dominant technology for the solidification of HLW is vitrification. The immobilization of wastes that represent a risk to the environment or to public health avoids their dispersion in soil, in the atmosphere and in water bodies and reduces the waste volume. Glasses are an excellent option for such immobilization because in general, they exhibit high chemical durability, slow dissolution rates in water, high mechanical resistance and high thermal stability. The main reason for the focus on glasses is that they are able to

homogeneously accommodate a wide range of substances in their disordered structures and exhibit good tolerance in terms of changes in composition inherent to the nature of wastes.⁸ Some of the desirable properties are good chemical durability i.e. low leachability so that activity released if any, into the environment is minimum. Heat generated due to radioactive decay does not increase glass temperature beyond maximum crystallization temperature. Other properties are: ability to contain high proportion of waste and to have high volume reduction, resistance to alpha, beta and gamma radiations, acceptable processing temperature, high mechanical strength and shock resistance, readily available raw materials at reasonable cost.⁸⁻¹¹

Vitrification is a mature technology and has been used for high level nuclear waste (HLW) immobilization for more than 40 years in France, Germany, Belgium, Russia, Japan and the USA.⁸⁻¹³ The first glasses investigated were borosilicate ones. They were extensively investigated for the immobilization of radioactive waste and are still used by countries such as France, the USA and England; the most favourable composition is based in SiO_2 and borax ($Na_2O \cdot 2B_2O_3$).^{14,15} Despite the fact that borosilicate glasses are chemically and thermally stable materials for long periods, they require relatively high encapsulating and processing temperatures (1200–1500°C). This requirement is, perhaps, the main disadvantage in using borosilicate glasses because some isotopes (e.g. ⁹⁹Tc and ¹³⁷Cs) may volatilize at such high temperatures.

Furthermore, several other elements specifically, sulfur, chlorine, phosphorous, chromium and aluminium may interfere with the vitrification process of borosilicate glasses¹⁶ leading to phase separation. At present, no single type of glass that will be totally satisfactory and cost effective in the immobilization of all the different types of waste in the world exists.

Lead iron phosphate (LIP) glasses are processed at temperatures from 100°C to 250°C lower than the temperatures necessary to process borosilicate glasses. Furthermore, dissolution rates (in water) are three orders of magnitude lower for LIP glasses compared to those for borosilicate glasses at 90 °C in solutions with pH levels ranging from 5 to 9.16. LIP glasses can also be employed to immobilize waste with high Na and S contents.¹⁶

Iron phosphate glasses without Pb have also been investigated in the immobilization of spent nuclear fuels and nuclear wastes containing 15% P_2O_5 by mass.¹⁷⁻¹⁸ Generally, leaching characteristics of radioactive/nuclear waste

matrices are highly dependent on the chemical compositions of the waste matrices and leaching experimental conditions.¹⁹⁻²¹ A huge research report was directed at studying the leaching characteristics of glass-based waste matrices using static and dynamic leaching experiments i.e. PCT (product consistence test), MCC (Material Characterization Center) and single pass flow through tests, by investigating waste matrices and leachant compositions at varying pH and temperature values and leachant-to-waste volumes.²²⁻²⁴ These studies identified hydrolysis, ion exchange, diffusion, dissolution and re-precipitation as the main corrosion processes for glass structural elements that led to glass degradation.²⁵⁻²⁷

It is well known that the water durability of phosphate glasses is improved by introduction of one or more of divalent metal oxides (MO) ($M = \text{Cu, Zn, Cd, Pb}$)²⁸⁻³¹ or trivalent metal oxides ($M^*_2\text{O}_3$) ($M^* = \text{Al, Bi, Fe}$)³²⁻³⁴ to P_2O_5 network, which results in the formation of M-O-P or $M^*\text{-O-P}$ bonds leading to increase the degree of condensation of the phosphate network. The adding of alkali oxides (A_2O) or alkaline earth oxides (MO) to P_2O_5 glasses results in conversion of the three-dimensional network to linear metaphosphate chains when the molar ratio of alkali or alkaline earth oxide to P_2O_5 [$R = \text{A}_2\text{O}/\text{P}_2\text{O}_5 = \text{MO}/\text{P}_2\text{O}_5$] increases from 0 to 1.³⁵⁻³⁷

The A_2O and MO act only as the network modifiers. Among various modifier oxides that play the role of glass modifiers in P_2O_5 glass network, the lead-oxide (PbO) is considered as unique since PbO is known to play a dual structural role as well as a network modifier and a network former.

Recently, extensive studies have been made on $\text{PbO-P}_2\text{O}_5$ glasses using Raman, FTIR, NMR, X-ray diffraction techniques.³⁸⁻⁴⁰ These studies revealed that lead oxide takes the role of both glass former and glass modifier.

As a glass former, PbO enters the network with PbO_4 structural units by sharing the corners of phosphate network which in turn form P-O-Pb linkages. When PbO acts as a network modifier, Pb becomes of octahedral coordination like any other conventional alkali oxide modifier.

Glasses in the system of lead-iron phosphate (LIP) loaded with simulated nuclear waste were melted. Leaching study of these glasses up to a time period of 300 hrs. was conducted under Soxhlet distillation condition with steam distilled water. Weight losses and residual activities by 'Radiotracer technique' were followed with respect to time period of leaching. SEM of some of the selected glasses has been reported. The variation of different properties was taken into account in terms of the changes in the ionic charges and ionic radii and hence ionic potentials of the different modifier ions, the source of which being the respective modifier oxides viz., $\text{PbO, Pb}_3\text{O}_3, \text{BaO, Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{Y}_2\text{O}_3, \text{CaCO}_3, \text{CeO}_2, \text{SrO}_2$ and $\text{UO}_2 (\text{CH}_3\text{COO})_2$ as for the different glass system are discussed.

Material and Methods

Preparation of glass batches and melting operation:

Different glass compositions based on that supplied by Nuclear Recycle Group, BARC, Trombay, Mumbai have been discussed elsewhere^{5,6} and are shown in table 1. The glass batches were prepared from the AR grade ingredients after reviewing earlier works in reference to the corresponding ternary diagrams as shown in table 2. All the glass batches were synthesized from the respective oxides/carbonates/acetates in acetone medium and mixed repeatedly after taking them in an agate mortar and pestle.

They were next dried and taken in high alumina crucibles and fired in a programmed Muffle furnace in the range $750^\circ\text{C} - 1000^\circ\text{C}$ for soaking periods of 60 min under ambient condition. For some of the LIP glasses (LIP 8 – LIP 10), the batches were composed by taking uranyl acetate directly into itself. The logic behind using uranyl acetate is that U is α / β active and by measuring the net counts per sec (c.p.s.), the leaching characteristics can be traced by such 'radiotracer technique' with the help of a Geiger-Muller counter.

Leaching Study: For leaching studies, the glass samples were crushed to 300 – 425 mesh taken in nylon net. Then 0.5 gm of each sample glass was vapour distilled in Soxhlet apparatus with a round bottom flask (500 ml. capacity) fitted with a condenser.^{3,6}

Table 1
Compositional details of simulated low and intermediate level radioactive liquid waste

Properties	Low level radioactive liquid waste	Intermediate level radioactive liquid waste
pH	8-9	9-13
CsNO_3 (milimoles/L)	6.56×10^{-6}	8.39×10^{-4}
$\text{Sr}(\text{NO}_3)_2$ (milimoles/L)	2×10^{-6}	2.4×10^{-5}
RuCl_3 (milimoles/L)	2×10^{-9}	2.93×10^{-7}
NaNO_3 (moles/L)	1×10^{-2}	2
Na_2CO_3 (moles/L)	--	5×10^{-2}
CaCl_2 (moles/L)	2×10^{-3}	--
NaOH (moles/L)	Traces for adjustment of pH	5×10^{-3}

Table 2
Composition of different glasses (wt%)

Glass ID	Pb ₃ O ₄	PbO	Fe ₂ O ₃	P ₂ O ₅	CeO ₂	SrO ₂	BaO	Uranyl acetate
LIP3	49	-	8	33	10	-	-	-
LIP4	-	52.4	7.9	33.2	6.5	-	-	-
LIP5	49	-	8	33	-	10	-	-
LIP6	49	-	8	33	5	5	-	-
LIP7	49	-	8	33	-	-	10	-
LIP8	-	52.4	7.9	33.2	-	-	-	6.5
LIP9	-	51.4	7.9	33.2	-	-	-	7.5
LIP10	-	45.8	7.0	30.2	10	-	-	7.0
LIP11	-	44.05	6.76	28.45	-	-	-	20.47

The distillation was carried out for varying period of time up to a maximum of 300 hr. The heating was done in a heating mantle. The weight loss after each run of leaching was measured by a four-decimal electronic balance (Satorius) and was converted into % wt. loss.

In order to find the leach rates, BET surface area of the U-containing LIP glasses was determined under liquid nitrogen temperature.^{3,4,6} For LIP glasses, the leaching study was augmented by noting the cps after each interval of time from its residual activity of α and/or β with the help of a G-M counter (Nucleonix, Hyderabad, India).

The leach rates (LR) for LIP8, LIP9 and LIP10 glasses after leaching are determined from BET surface area analysis. The leach rates (LR) were measured by weight loss according to the relationship:

$$LR = \frac{W_i - W_f}{SA \times t} \quad (1)$$

where W_i and W_f are the initial and final sample weights respectively, SA is the BET surface area of the sample and t is the time exposed to the leachant.

Results and Discussion

Leaching Study of the LIP Glasses in Distilled Water under Soxhlet Condition: Leaching Study of the LIP glasses not containing U (LIP3 to LIP7) was performed under Soxhlet condition up to 24 hours and the cumulative weight loss with respect to time (hrs.) observed that the total wt. loss (or % wt. loss) with respect to cumulative time varies as:

$$LIP\ 6 > LIP\ 4 > LIP\ 5 > LIP\ 3 \approx LIP\ 7$$

where the LIP3, LIP4 and LIP6 contain CeO₂ and LIP7 contain BaO and LIP5 contain SrO as modifier. For the three glasses (LIP3, LIP4 and LIP6), the CeO₂ content varies as: LIP3 (10%) > LIP4 (6.5%) > LIP6 (5%) and the observed wt. loss with respect to cumulative time varies as: LIP 6 > LIP 4 > LIP3 leading to a trend that with increasing CeO₂

content, the % wt. loss decreases. Hence CeO₂ (Ce⁴⁺) can function as good binder-modifier.⁴¹⁻⁵⁰

Leaching Study of the Uranium containing LIP Glasses in Distilled Water under Soxhlet Condition (Using Radio Tracer Technique): The residual activity of the leachant was measured with the help of the Geiger-Muller counter and Gamma-ray Spectrometer using NaI(Tl) scintillator detector coupled with Multichannel Analyser. For U-containing glasses, the wt. loss data was further accompanied from the results of "radiotracer technique" (net cps vs. cumulative time). Figure 1 shows the corresponding plots. It is observed that with increasing cumulative time, the net cps ($\alpha/\beta/\gamma$) is decreasing in an exponential way signifying that with increasing leaching time, the release of uranium along with other constituents becomes slower and slower until getting stopped.

Thus, the glass becomes resistant to leaching and is a better choice for the disposal of nuclear waste compared.^{4,41,48} In case of all U-containing LIP glasses, a similar type of plot is obtained. The exponential decay must not be confused with the decay of ²³⁸U, the present radio isotope present in the system, since its half life period is too high (~10⁹ years) to be reflected in such decay. The rate decreasing the residual activity of the leachant (net c.p.s.) with respect to cumulative time is as follows:

$$(LIP\ 11) > (LIP\ 8) > (LIP\ 9) > (LIP\ 10)$$

It is further indicated that the LIP10 glass which contains CeO₂ is more leach resistant than that of the others U-containing glasses which does not contain CeO₂. Hence from the radiotracer leaching studies, the role of Ce⁴⁺ as good binder-modifier is again established.^{41,51}

The leach rates (LR) for LIP8, LIP9 and LIP10 glasses after leaching are determined from BET surface area analysis (liq. N₂ temp.). The BET surface area and leach rates are as follows:

$$(SA)LIP8 = 0.076\ m^2/g$$

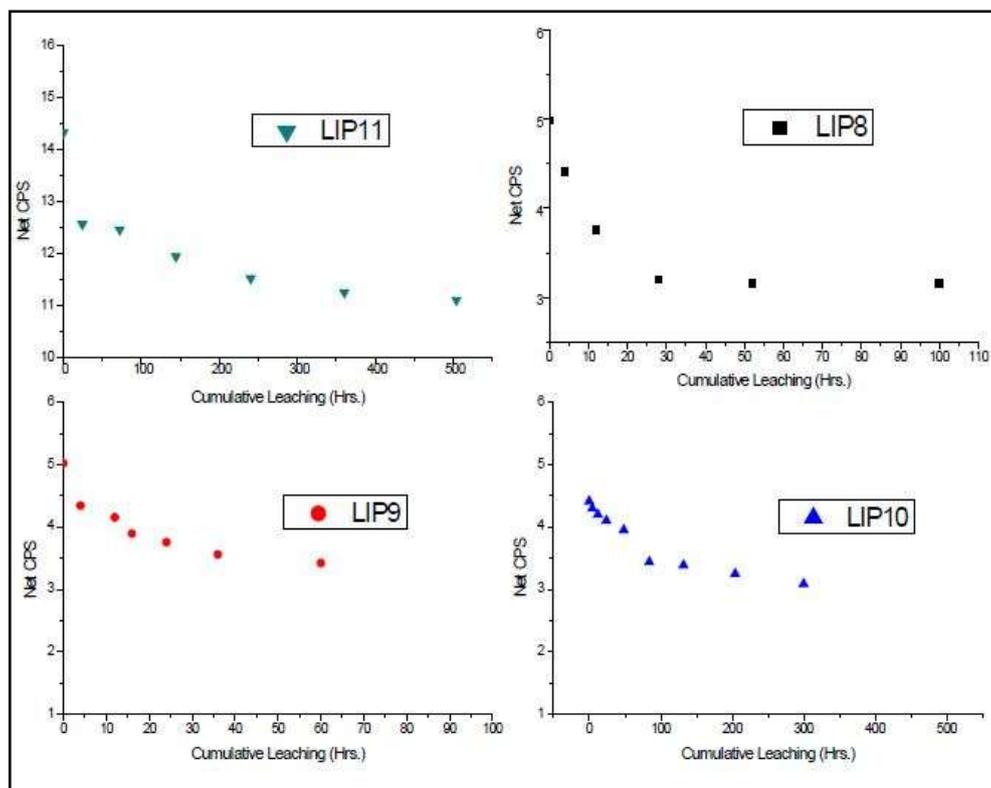


Figure 1: Plots of Net c.p.s. vs. Cumulative Leaching Time (hr.) for LIP8 to LIP11

(SA)LIP9= 0.512 m²/g

(SA)LIP10= 0.480 m²/g

[(LR)LIP8] = 4.3 × 10⁻³ g.m⁻².hr⁻¹

[(LR)LIP9] = 8.2 × 10⁻⁴ g.m⁻².hr⁻¹

[(LR)LIP10] = 1.8 × 10⁻⁴ g.m⁻².hr⁻¹

The Leach Rate decrease in the order:

(LR)LIP8 > (LR)LIP9 > (LR)LIP10

These rates as compared to other borosilicate systems are 1000 times lower^{3,4,6,48} and thus LIP glasses have much improved chemical durability. This is due to Fe₂O₃ content and structural role of Fe^{2+/3+}, which strengthens the cross bonding between the polyphosphate chains. Mechanically, iron ions can enter the network structure of phosphate, Fe³⁺ and replace P⁵⁺ because of its stronger electro-positivity, thus forming a Fe - O - P bond which has better water resistance.

Furthermore, the smaller radius of the iron ion (Fe³⁺, Fe²⁺) can hinder the larger water molecule from passing through the solidification form, therefore, significantly improving the chemical stability of immobilization matrix.⁴⁹⁻⁵¹ Percent weight loss studies show a distinct decrease in the % wt. loss value with extended period of time of leaching signifying that the extent of leaching die down with time. It is observed that the % wt. loss decreases in the order:

(LIP11) > (LIP 8) > (LIP 9) > (LIP 10)

In case of the glass LIP10, CeO₂ is present which is not present in LIP8, LIP9 and LIP11 other. Thus the role of Ce⁴⁺ as binder modifier is evident.

The leaching rates of the LIP glasses (both with and without U) containing ceria are lower than without cerium. This is due to having higher coordination number linked with oxygen in the phosphate network. Hence the durability of the LIP glasses may be increased with the addition of CeO₂.^{52,53} From some other point of view, our observations on the U-containing LIP glasses the leach rates were found to increase with increase in the amount of U within the glass composition. This may be due to the high mass no. of the ²³⁸U atom being released during leaching or may be due to maximum internal dose of radiation.

Leaching Characteristics at different medium: From the figure 2 and figure 3, measurements of the leaching studies of different LIP glasses in different chemical environments show that the resistance of lead iron phosphate glasses to aqueous attack varies considerably with pH of the leachete soln. The best chemical resistance is exhibited at neutral pH of around 7 and the corrosion of the LIP glasses increases slowly with increasing the pH (at very high pH) of the leaching medium.^{53,54}

On the other hand, the corrosion of the LIP glasses increases very rapidly with decreasing the pH (at very low pH) of the leaching medium. However, the leaching of anions and cations is not always congruent.⁵³⁻⁵⁶ This can be understood by considering the size of the migrating species at the water/glass interface. In the simplest model, the modifying cations will exchange with H₃O⁺ and the phosphate groups with OH⁻. As Pb and hydronium are of similar size with radii of around 1 Å, they should exchange readily.

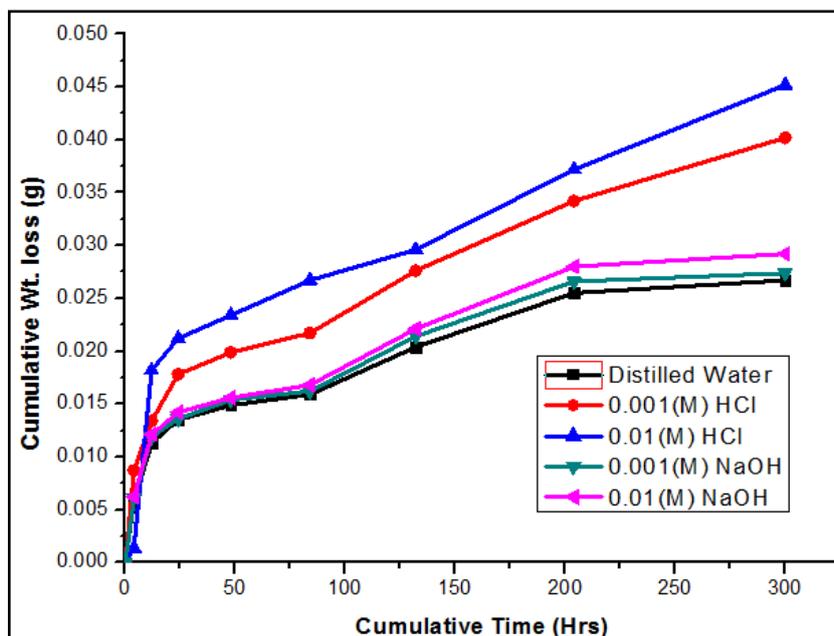


Figure 2: Leaching study of LIP10 glass in different media

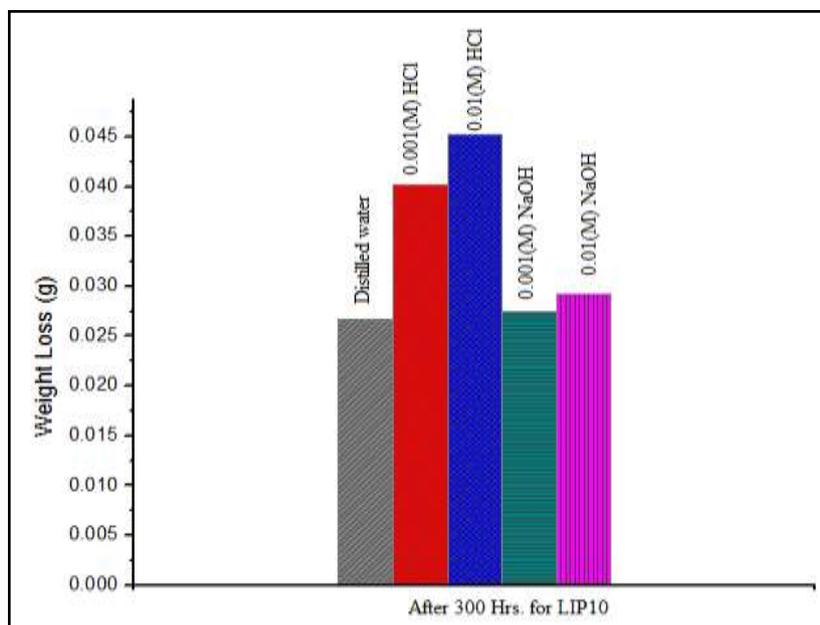


Figure 3: Bar Diagram of Wt. loss in different medium after 300 hours for LIP10 glass.

Ferric ions on the other hand with a radius of 0.7 \AA are less well-matched and dissolve less readily.^{54,61} In the most acidic solutions where both modifying cations are drawn into solution, cross links in the $(\text{PO}_4)_n$ chains will be broken which will inevitably lead to a loss of phosphorus and the congruent leaching of cations and anions. At high pH, however, the scarcity of H_3O^+ will diminish cation exchange leaving anion exchange comparatively enhanced. If phosphorus is lost from chain ends, as is likely, modifying metals will not be casualties and the incongruent leaching behavior will occur.⁵³⁻⁵⁵

Conclusion

Chemical and physical properties of LIP glasses depend on the glass composition. The P_2O_5 is assumed to be the glass

former and PbO is added to reduce the viscosity and consequently the melting point. By adding Fe_2O_3 it was possible to improve the chemical resistance and to decrease the crystallization rate. Thus improvement chemical durability is due to Fe_2O_3 content and structural role of $\text{Fe}^{2+/3+}$, which strengthens the cross bonding between the polyphosphate chains. Thus it may be concluded that a structural rearrangement occurs in the role of Fe in the glass structure from modifier to former. The structure of LIP glasses consists of Fe-O-P-O chains with Pb atoms intercalating the structure, bounded to non-bridging oxygen atoms. The cumulative wt. loss i.e. leaching or leaching rate of the simple LIP and uranium containing LIP glasses depends on the addition of modifier oxides into their compositions.

It is shown that the addition of CeO₂ into LIP glass compositions decreases the leaching rate and increases the durability in aqueous solution. With increasing the amount of CeO₂ into the composition, the leaching of the LIP glasses decreases. The addition of CaO, SrO and BaO into the composition of LIP glasses increases the leaching of the glass. In general, addition of alkaline earth oxides increases the corrosion of the LIP glasses whereas addition of intermediated oxides decreases the corrosion of the LIP.

The best chemical resistance is exhibited at neutral pH of around 7 and the corrosion of the LIP glasses increases slowly with increasing the pH (at very high pH) of the leaching medium as well as the corrosion of the LIP glasses increases very rapidly with decreasing the pH (at very low pH) of the leaching medium.

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