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Disodium Phosphate Dodecahydrate Salt Hydrate-Based Approach for Thermal Energy Storage Systems

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ABSTRACT

Salt hydrates, classified as inorganic phase change materials, are used in thermal energy storage (TES) systems. Due to their superior properties such as higher thermal conductivity and better thermal energy storage density, non-flammability and availability in wide temperature ranges at a reasonable cost than organic PCMs, salt hydrates are preferable PCMs. Disodium phosphate dodecahydrate (Na2HPO4·12H2O) have a favourable melting point and melting enthalpy for room temperature energy storage applications but supercooling, phase segregation, formation of lower hydrates, and corrosion to storage vessels are frequent limits to its employment, just as they are for other salt hydrates. These issues are addressed using various intensification techniques such as an aqueous saturated salt solution of Na2HPO4 (both non-gel and gel-based) instead of pure salt hydrate and using suitable nucleating, and gelling agents. Further, the intensification is done via the incorporation of solution in an open cell polyurethane (PU) foam. DSC analysis of PU-based PCM composite confirmed its melting temperature and melting enthalpy at about 35oC and 167.343 J/g recommends for its applications between 30oC- 40oC. Thermal performance observation, in a model system, shows the PU-Gel based PCM to be more efficient with a temperature difference of about 10oC- 14oC for repeated thermal cycles as compared to normal PU foam and PU-Salt based PCM.

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1. Introduction

Latent heat thermal energy storage (LHS) among the available TES techniques is widely in use. Here the energy storage medium is considered as the phase change material (PCM) as it undergoes a phase change (from solid to liquid or vice versa) within the applied temperature range and stores heat energy [1],[2]. There are several classifications in these PCMs but were mainly classified as organic, inorganic, and eutectic PCMs. Salt hydrates as an inorganic phase change material, consist of a typical crystalline solid with the general formula ($AB\cdot nH_2O$). Inorganic salts (AB) in the crystal structure strongly bonded to the water (H_2O) are known as hydrated salt. Salt hydrates provide relatively higher energy storage density, high thermal conductivity than organic PCM, and small volume change during the phase change. They are non-flammable and are available in wide temperature ranges with less cost [3],[4],[5],[6].

The use of salt hydrates for thermal energy storage devices has been linked to a number of issues in the literature. Supercooling, nucleation of unwanted lower hydrates due to its poor nucleation capabilities, phase segregation after repeated heat cycles, and corrosion to the PCM storage container are only a few of them [3],[4],[7]. Various researchers have proposed various methods for reducing these problems, like the use of nucleating agents, gelling agents, encapsulation method, incorporation in the porous medium etc [3],[4],[8],[9].

Present research work suggests an insulating media (between 40^{o}C to 10^{o}C) for TES application with the motivation to apply disodium phosphate dodecahydrate ($Na_2HPO_4\cdot 10H_2O$) solution as the PCM.$Na_2HPO_4\cdot 10H_2O$ has melting point around 35^{o}C-45^{o}C and has a melting enthalpy of about 280

J/g [4],[10],[11],[12]. The aqueous saturated salt solution based on Na_2HPO_4 has been proposed as an inorganic phase change material (PCM) instead of convectional used pure salt hydrates for thermal energy storage (TES) applications. The heat released/absorbed phenomenon with the aqueous saturated salt solution as PCM has been explained using its solubility diagram. A novel approach, open-cell polyurethane foam (PU foam) as heterogeneous support was introduced to mitigate the phase segregation problem during its repeated thermal cycles. Preparation of the PU-PCM composite PCM, having a combination of porous polyurethane foam sheet and the aqueous saturated inorganic salt solution has been discussed. The composite with having non-gel and gel-based PCM solutions within PU foam are named as PU-Salt PCM and PU-Gel PCM respectively. The thermal insulation capability of the PU-PCM composite sheets has been observed in a model experimental setup, for a temperature range between about 40°C to 10°C.

2. Experimental

2.1.Materials and equipment's used

Sodium phosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$) was purchased from THERMO FISHER Limited. Polyurethane (PU) foam of density 30-35 kg/m^3 and porosity of about 95-97% was used as a supporting matrix for the inclusion of aqueous saturated salt/gel-based salt solution.

Distilled water to make the salt solutions. Cellophane zipper pouch to provide outer cover to PU-PCM composite. LAPONITE® powder, supplied from BYK Additives and Instruments, Pune, India, was used as a gelling agent. The equipments used are hot plate, stirrer, vacuum filtration unit, double jacketed glass vessel, chiller/thermostat, temperature data logger, and differential scanning calorimetry (DSC).

2.2. Formation methodology of Na2HPO4·12H2O from its aqueous saturated salt solution

In TES systems, instead of using molten salt hydrates directly, an aqueous saturated salt solution of Na_2HPO_4 as PCM is proposed [13]. This TES system with this PCM will have the extra saturated solution (other than water of hydration as with pure salt hydrate crystals), it is expected that during repeated hydration/dehydration processes in TES systems the problem related to lower hydrates formation will be reduced. The heat absorbed/released during the formation of aqueous saturated salt solution has been explained, with the help of its solubility diagram.

A phase diagram for the Na_2HPO4 and H_2O system is shown fig. 1 [14]. The region for the formation of all types of hydrated salts of Na_2HPO_4 from its salt solution was shown. This data helped in the interpretation of the required concentration needed to be considered for the aqueous saturated salt solution of Na_2HPO_4. The proposed PCM should have the phase change around the temperature range around 25°C-35°C.

According to the phase diagram (fig. 1), for the required phase change at 30°C, the required concentration of the solution should be 27 wt% of Na_2HPO_4. when about 27 wt% of Na_2HPO_4 aqueous solution will be cooled below the saturation temperature at liquidous line (about 30°C, corresponds to 27 wt% Na_2HPO_4 solutions), the phase change phenomenon/ nucleation of hydrates ($Na_2HPO_4{\cdot}12H_2O$) will occur within the solution.

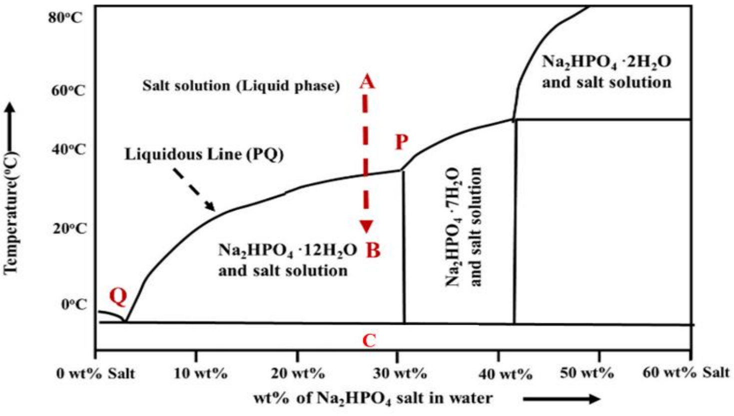

Fig. 1.*A phase diagram for the Na_2HPO4 and H_2O system [14]*

Consider A to be the point in region 1 (above PQ) having a concentration (27 wt% of Na_2HPO_4 aqueous solution) and the temperature (more than 30ºC) of the initial aqueous saturated salt solution used in the TES system. At this higher temperature, the 27 wt% of Na_2HPO_4 solute will be fully dissolved within the solution. The temperature of the solution decreases below section PQ during cooling (from point A to B) (liquidous curve). The solute concentration will be higher than equilibriumat a temperature below the segment PQ, and the solution will eject the surplus solutes as salt hydrate crystal $Na_2HPO_4\cdot12H_2O$ to achieve equilibrium. Heat will be released from the solution to the surroundings due to the production of crystals (exothermic process). More crystals develop as the temperature of the solution drops more, and the heat release process continues until all of the solutions are frozen (at point C).The operating temperature range for PCM as TES system, is represented by the temperatures at points A and B. The binary phase combination for salt hydrate and saturated salt solution will be found in Region 2 (fig. 1).The solid phases present in the PCM will transform from solid to liquid during heating (from point B to A), and heat will be absorbed (endothermic process) from the surroundings. The heat transition event during the hydration and dehydration of $Na_2HPO_4\cdot12H_2O$ in an aqueous saturated solution is depicted in equations (1) and (2).

$$Na_2HPO_4 + nH_2OQ(\uparrow) \rightarrow\ Na_2HPO_4\cdot 12H_2O + (n{-}12)H_2O \tag{1}$$

$$Na_2HPO_4\cdot 12H_2O + (n-12)H_2OQ(\downarrow) \rightarrow\ Na_2HPO_4 + nH_2O \tag{2}$$

2.3. Preparation of Na2HPO4 (gel and non-gel) based PCM composite

This 27 wt% aqueous saturated salt solution of Na_2HPO_4 (27 wt% Na_2HPO_4 + 73 wt% water (50 gm $Na_2HPO_4\cdot2H_2O$ in 100 mL water)) taken as the non-gel based composite PCM. When employing this salt solution as a PCM, during cooling cycles in solution phase segregation of salt hydrates was still a problem due to its viscosity. To reduce crystal phase segregation, adding an adequate amount of gelling agent to this salt solution (PCM) is one possible method.It was anticipated that the gel created would prevent crystals from freely settling throughout the cooling thermal cycle. In the present research, a saturated salt solution was mixed with water-based inorganic gelling agent termed "LAPONITE®" to avoid salt hydrate phase separation. The composition of prepared gel-based composite PCM was 25.6 wt% Na_2HPO_4 + 3.85 wt% LAPONITE® + 70.55 wt% water (50 gm $Na_2HPO_4\cdot2H_2O$, 6 gm LAPONITE® in 100 mL water). The DSC analysis of these gel and non-gel-based composites was performed to understand their phase change properties and the results were discussed.

2.4. PU-Salt PCM and PU-Gel PCM composite preparation

By inserting the samples (gel and non-gel based PCM) into the PU foam, polyurethane-based PU-Salt PCM and PU-Gel PCM composites were made.A two-step technique was used to create these composites. The first stage was to make sample solutions (as described in section II C), and the second stage was to add fully dry and squeezed PU foam to the PCM solution (gel and non-gel based PCM).Due to capillary action during polyurethane foam expansion, PCM samples are supplied to the interior voids of polyurethane foam pores. To avoid the contact from external environment cellophane bag was applied to enclose the PU foam incorporated with PCMs. The DSC analysis of these PU-Salt PCM and PU-Gel PCM composites were performed to understand their phase change properties and the results were discussed.

2.5. Thermal performance analysis of the PU-PCM composite

Thermal performance of a prototype model of PU-Gel PCM composite layer compared thermal performance of prototype model of to PU-Salt PCM and PU foam after DSC analysis confirmed phase transition inside PU foam. To test the thermal performance, a cylindrical glass vessel (double jacketed) was built and these PU-based PCM composite layers were used as an insulation layer. Fig. 2 shows a cross-sectional schematic design of a double jacketed vessel the model with dimensions.

In fig, 2 thick black line represents the glass wall of thickness 2 mm. In the experiment setup double jacketed glass vessel (cylindrical) was connected to the chiller through which coolant fluid is flowing and it maintains the temperature of the outer/ jacket (TJ) between 10ºC to 40ºC. The inside of the double-jacketed glass vessel is divided into three sections. A dry foam was placed at the bottom of the inner space of the glass vessel to provide sufficient insulation and to restrict heat loss from the bottom of the vessel. The PU-PCM composite was installed in the vessel's sidewall towards the topmost inner region. Further to provide mechanical strength, placed a glass layer over the PU-PCM composite insulation layer. Each cylindrical insulation layer of PU-PCM foam (PU foam, PU-Gel PCM, and PU-Salt PCM) was separated into 3 vertical layers of PU foam. Each dry PU foam weighed around 2 gm and measured 7 cm x 7 cm x 1.2 cm (length X width X thickness) in size. Each vertical section of the PU-Gel PCM and PU-Salt PCM layer has a PCM holding capacity of about 63 ± 3 gm and 68 ± 2 gm respectively. Fig. 3 shows an image of the experimental setup. The inner temperature of the jacketed vessel (T1) was measured with a temperature sensor (attached to the temperature data logger) was inserted in the middle empty space of the prototype vessel (as illustrated in fig. 2).

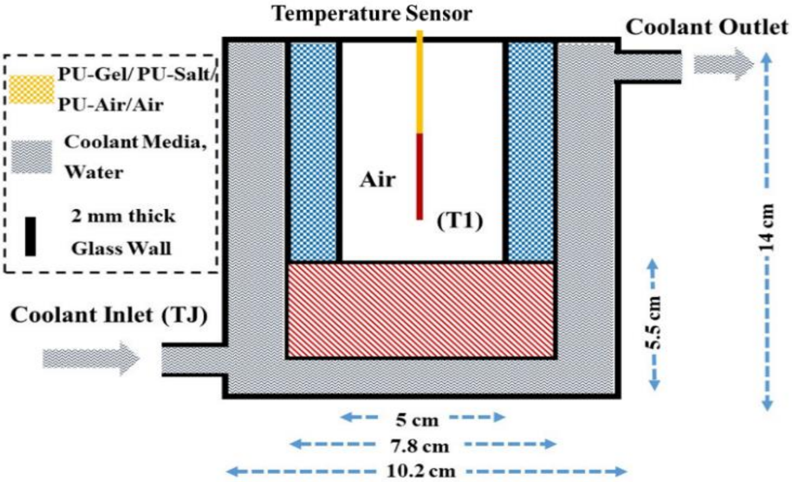

Fig. 2. *Schematic diagram for cross-sectional view for thermal performance test of PU-Salt PCM/PU-Gel PCM composite in a double-jacketed glass vessel*

These composite layers are supported as a layer of insulation in a cylindrical double jacketed glass vessel. These glass vessels were coupled to a chiller, through which coolant circulates in the outer jacket of the glass vessel, keeping the temperature of the outer/jacket (TJ) between 10 and 40 degrees Celsius. Outer/jacket temperature (TJ) was lowered from 40°C to 10°C in 150 minutes to complete a thermal cooling cycle. Again after 150 minutes, to perform thermal heating cycle again this temperature (TJ) was increased to 40ºC and maintained at this temperature for the next 120 minutes. We get one thermal cycle by combining thermal cooling and heating cycles (in 270 minutes). Temperatures TJ and T1 were recorded with respect to time using a temperature data logger for this thermal cycle (at five-second intervals). This was repeated for ten thermal cycles and the results are discussed.

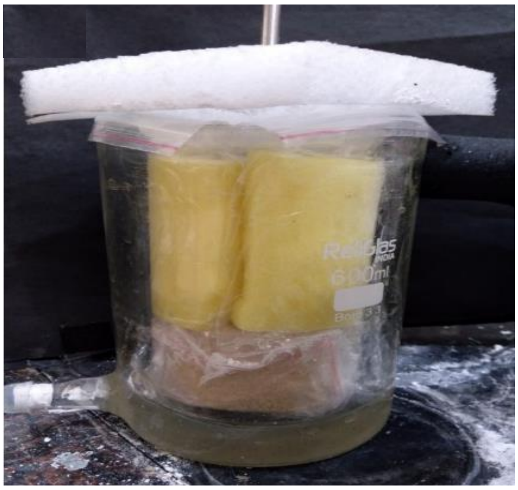

Fig. 3. *Image of the jacketed vessel with PU-Salt PCM/PU-Gel PCM as an insulation layer*

2.6. DSC analysis of PU-PCM composite

DSC analysis of PU-salt PCM was done for understanding the melting point and melting enthalpy of the composite. The samples were heated from -15 °C to 75 °C with a heating rate of 5°C per minute.

3. Results and Discussion

3.1. Differential scanning calorimetry (DSC) analysis of PU-PCM composite

Differential scanning calorimetric (DSC) analysis was used to determine the melting temperature and melting enthalpy of the PU-salt PCM composite. The melting curve result of the sample is shown in fig. 4.

According to the melting curves, three peaks were identified during the heating of the PU-PCM composite sample from -15^{o}C to 75°C. The first melting peak was observed at a temperature of -1.34°C with a melting enthalpy of 28.95 J/g, the second peak observed at a temperature of 35.66°C with a melting enthalpy of 167.343 J/g and the third peak observed at a temperature of 52.49°C with a melting enthalpy of 294.67 J/g.

The first melting peak represented the melting of free water present in the PU-salt PCM solution. The second melting peak is the actual energy stored by the PCM in the desired temperature range. The third peak, even though have a very high amount of enthalpy of melting, is well above the desired temperature range. Thus, this energy is unused for storage. Hence DSC results convey that partial melting of salt hydrate has happened in the desired temperature range.

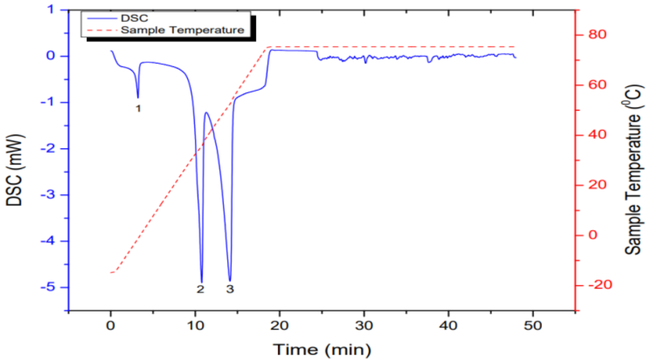

Fig. 4. *DSC melting curve for the PU-PCM composite sample*

3.2. Results for thermal performance test of Na2HPO4 based PU-PCM composite

Fig. 5 shows the average (for the first three cooling and heating cycles) of the temperature difference profile for three different insulation layers (PU-Air, PU-Gel PCM, and PU-Salt PCM), as mentioned in section II E produced from the thermal performance test. The time of cooling and heating (in minutes) was represented on the horizontal axis. While double jacketed vessel outer jacket temperature (TJ) were represented on the primary vertical axis and the absolute temperature differential (|TJ-T1|) between inside space temperature of the jacketed vessel (T1) and the outer jacket temperature (TJ) were represented in the secondary vertical axis. The temperature variation graph (TJ vs time) shows the system cooled from 40°C to 10°C for the first 150 minutes, then heated from 10°C to 40°C until the 270th minute.

PU-Air (triangle) as an insulating medium indicated a maximum average temperature difference profile (|TJ-T1|) of roughly 6 to 7^{o}C throughout the initial three cycles of the cooling and heating process. During the first 150 minutes of the cooling cycle, the insulating layer with PU-Salt PCM (circle) and PU-Gel PCM (square) produced a maximum average absolute temperature difference (|TJ-T1|) of about 10 and 13^{o}C, respectively. PU-Salt PCM and PU-Gel PCM insulating layers reached maximum temperatures of around 10 and 14^{o}C throughout the next 120 minutes of the cycle (heating).

To compare the stability of the insulation performance of the PU-Gel PCM layer with the PU-Salt PCM insulation layer, a 270-minute cooling/heating thermal cycle was repeated ten times. The absolute temperature difference |TJ-T1| profile with time after the first, fifth and tenth thermal cycle for PU-Salt PCM and PU-Gel PCM are shown in fig. 6 and 7 respectively. The absolute temperature difference |TJ-T1| profile was observed to be a maximum of about 10-11^{o}C (PU-Salt PCM) and 12-14^{o}C (PU-Gel PCM) till the tenth thermal cycle. Hence, no leakage of liquid PCM was detected outside these composites until the tenth thermal cycle and the temperature difference profiles are not decreased. But with increasing the number of thermal cycles, the profile of PU-Salt PCM may decrease as compared to PU-Gel PCM.

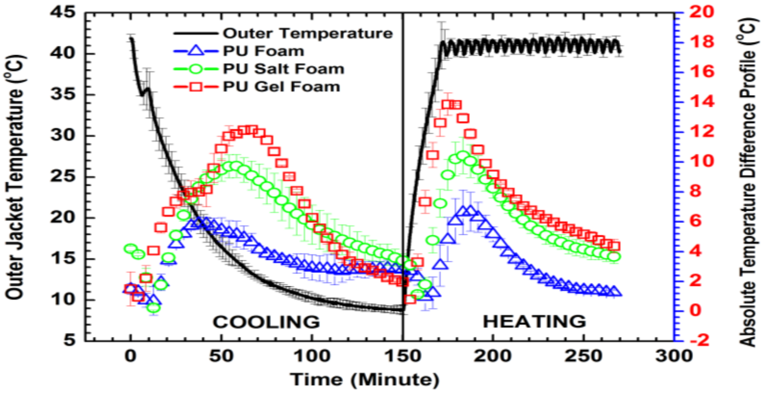

Fig 5. *Average absolute temperature difference (|TJ-T1|) and outer jacket temperature (TJ) profiles for PU-Air, PU-Salt PCM and PU-Gel PCM composites (with Na_2HPO_4) as an insulation layer*

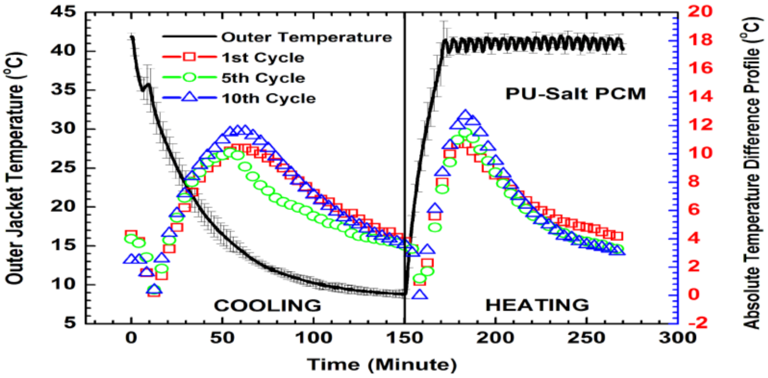

Fig. 6 *Absolute temperature difference (|TJ-T1|) and outer jacket temperature (TJ) profiles for PU-Salt PCM composite (with Na_2HPO_4) as an insulation layer (after the first, fifth and tenth thermal cooling/heating cycle)*

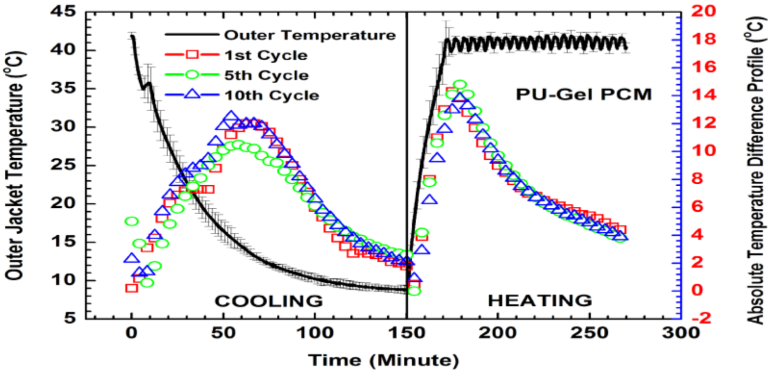

Fig. 7. *Absolute temperature difference (|TJ-T1|) and outer jacket temperature (TJ) profiles for PU-Gel PCM composite (with Na_2HPO_4) as an insulation layer (after the first, fifth and tenth thermal cooling/heating cycle)*

4. Conclusions

In this paper disodium phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) which is one of the probable PCM is incorporated with polyurethane (PU) foam is used for thermal energy storage. PU-Salt PCM and PU-Gel PCM which are non-gel and gel-based PCM solutions within PU are performed in the experimental setup. DSC analysis of PU-Salt PCM composite confirm its use in room temperature applications (30ºC-40ºC). The findings of the thermal performance test revealed that PU-Gel PCM was more suitable than the other combinations examined. It can be concluded from thermal performance test results that the conventional problems like incongruent melting, phase segregation, and supercooling can be reduced by using PU-Gel PCM composite for thermal energy storage. Since PU-Gel PCM contains less salt hydrate than pure salt hydrate, the quantity of energy released or absorbed during a phase change is decreased during initial cycles. The performance of the PU-Gel PCM composite is greatly influenced by variations in characteristics such as melting enthalpy, freezing enthalpy and thermal conductivity in the presence of borax, Laponite®, and PU foam. Further detailed study will be performed in future to understand the melting and freezing behaviour of PU-Gel PCM which helps in promoting $Na_2HPO_4\cdot 12H_2O$ aqueous solution as PCM.

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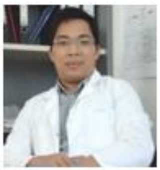

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