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State of the art on phase change material slurries

Ziad Youssef[a,*], Anthony Delahaye[a], Li Huang[b], François Trinquet[a], Laurence Fournaison[a], Clemens Pollerberg[c], Christian Doetsch[c]

[a] Laboratoire de Génie des Procédés pour l'Environnement, l'Energie et la Santé (LGP2ES – EA21), Irstea GPAN, 1 rue Pierre-Gilles de Gennes, CS 10030, 92761 Antony Cedex, France
[b] Ningbo University, Faculty of Architecture, Civil Engineering College, Fenghua Street 818, 315211 Ningbo, China
[c] Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Osterfelder Strasse 3, 46047 Oberhausen, Germany

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ABSTRACT

The interest in using phase change slurry (PCS) media as thermal storage and heat transfer fluids is increasing and thus leading to an enhancement in the number of articles on the subject. In air-conditioning and refrigeration applications, PCS systems represent a pure benefit resulting in the increase of thermal energy storage capacity, high heat transfer characteristics and positive phase change temperatures which can occur under low pressures. Hence, they allow the increase of energy efficiency and reduce the quantity of thermal fluids. This review describes the formation, thermo-physical, rheological, heat transfer properties and applications of four PCS systems: Clathrate hydrate slurry (CHS), Microencapsulated Phase Change Materials Slurry (MPCMS), shape-stabilized PCM slurries (SPCMSs) and Phase Change Material Emulsions (PCMEs). It regroups a bibliographic summary of important information that can be very helpful when such systems are used. It also gives interesting and valuable insights on the choice of the most suitable PCS media for laboratory and industrial applications.

1. Introduction

Lately, it has become necessary to reduce power consumption and the propagation of the refrigerants in the atmosphere. One of the solutions to that issue is to improve the performance of the refrigerating machine. In this context, the use of thermal energy storage techniques is an interesting solution. Thermal energy can be stored as a change in internal energy of a material as either sensible heat, latent heat or thermal-chemical or combination of the aforementioned. Latent heat storage is based on heat adsorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice versa. Latent heat storage materials are also known as phase change materials (PCMs). In recent years, PCMs have been developed in the form of slurries to increase the heat transfer rate by raising the surface to volume ratio. A binary system consisting of a carrier fluid, mostly water, as the continuous phase and a PCM as the dispersed phase, are called phase change slurries (PCSs). PCSs use the latent heat capacity of the PCM as well as the sensible heat capacity of the carrier fluid and that of the PCM in order to store or transfer thermal energy.

In the literature, many articles discuss ice slurries but few ones present a review on some PCS systems that can be used at positive temperatures [1,2]. For instance, the first authors treated only microencapsulated phase change slurry (MPCS) and clathrate hydrate slurry (CHS) and the second ones dealt with Phase Change Material Emulsions (PCMEs) and microencapsulated phase change slurry (MPCS). Therefore, it is necessary and important to present a general updated review on the main type of PCS, including CHS, MPCS, PCME and in addition shape-stabilized PCM (SPCM).

Different types of PCSs have been studied for secondary refrigeration and air conditioning in a range of melting temperature from 0 to 20 °C as follows:

- Clathrate hydrate slurry CHS consisting of water and fine solid clathrate particles of 5–50 μm in diameter.
- Microencapsulated PCM slurries MPCMS, where a PCM is encapsulated within a thin film to form microcapsules and suspended in a water.
- Shape-stabilized PCM slurries SPCMS, where a PCM is enclosed in a support material with a cross-linked structure to form the shape-stabilized PCM and then suspended in water.
- PCM emulsions PCME, where a PCM is directly dispersed in water. The use of a surfactant allows the stabilization of the solution.

At the moment, apart from ice slurries below 0 °C, only hydrate slurries have been used in industrial applications, the other slurries are still at the development phase in laboratories. The PCMs used for preparing MPSMS, SPCMS and PCME are commonly paraffins. Table 1 lists PCMs in the form of slurries with a melting temperature in the range of 0–20 °C. Previous works [3] indicated that sta-

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* Corresponding author. Tel.: +33 (0)1 40 96 65 94; fax: +33 (0)1 40 96 60 75.
E-mail address: ziad.youssef@irstea.fr (Z. Youssef).

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Nomenclature

A	peak surface (cm^2)
c_i	volume fraction of component *i*
C_p	specific heat capacity ($kJ\ mol^{-1}\ K^{-1}$)
d	diameter (μm)
h	enthalpy ($kJ\ kg^{-1}$)
k	consistence index (Pa s)
L_s	latent heat of crystallization ($kJ\ kg^{-1}$)
n	hydration number
N	molar number of crystallized water droplets
Nu	Nusselt number
Q	volume flow rate ($m^3\ s^{-1}$)
R	gas constant ($J\ K^{-1}\ mol^{-1}$)
Re	Reynolds number
u	fluid velocity ($m\ s^{-1}$)
V	volume (m^3)
X_i	mass fraction of component i
Z	compressibility factor

Abbreviations

CHS	clathrate hydrate slurry
DSC	differential scanning calorimetry
DTA	differential thermal analysis
HDPE	high density polyethylene
HS	hydrate slurry
MPCM	microencapsulated PCM
MPCMS	microencapsulated PCM slurry
PCM	phase change material
PCME	PCM emulsion
PCS	phase change slurry
PE	polyethylene
PEMA	polyethyl methacrylate
PIT	phase inversion temperature
PMMA	polymethyl methacrylate
SBS	styrene-butadiene-styrene
SEM	scanning electron microscopy
SPCM	shape-stabilized PCM
SPCMS	shape-stabilized PCM slurry
TBAB	tetrabutyl ammonium bromide
TBAC	tetrabutyl ammonium chloride
TME	trimethylolethane
TBAF	tetrabutyl ammonium fluoride

Subscripts

cont	continuous phase
G	guest molecules
shell	shell material

Greek letters

α	calorimetric constant ($kJ\ kg^{-1}\ cm^{-2}$)
γ	interfacial tension ($N\ m^{-1}$)
H	heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
κ	thermal conductivity ($W\ m^{-1}\ K^{-1}$)
$\dot{\gamma}$	shear rate (s^{-1})
μ_0	plastic dynamic viscosity (Pa s)
ρ	density ($kg\ m^{-3}$)
τ	shear stress (Pa)
τ_0	yield shear stress (Pa)
ϕ_i	volumetric fraction of *i*

bility and subcooling are two major problems in the development of a PCS. This paper presents a literature review of the researches accomplished on CHS, MPCMS, SPCMS and PCME in a range of melting temperature from 0 to 20 °C.

2. PCS formation

2.1. Clathrate hydrate slurry, CHS

Clathrate hydrates are ice-like crystalline inclusion compounds formed from a network of hydrogen-bonded water molecules organised in host cavities in which guest molecules are physically trapped [4]. These compounds are commonly called gas hydrates when the enclosed molecules are gases. Water molecules form a lattice structure and the gas molecules occupy the interstitial vacancies of the lattice. The phenomena of inclusion of the guest molecule and the Van der Waals attraction between water and gases stabilize the hydrate molecule.

Depending on the nature and the size of the guest molecules, various arrangements of the water molecules are encountered, corresponding to three main hydrate structures: cubic structures I and II and hexagonal structure H. The exothermic crystallisation of hydrates can be expressed by:

$$G + nH_2O \rightleftarrows G \cdot nH_2O \ \text{(Hydrate)} \qquad (1)$$

where G is the guest molecule and n the hydration number, i.e. the average number of water moles per mole of guest molecules. The hydration number depends on the guest molecule, temperature and pressure.

Discovered by Sir Humphry Davy in 1810, interest in clathrate hydrates were purely academic until it was pointed out that these compounds were responsible for plugging natural gas pipelines [5]. Since, clathrate hydrates have steadily emerged in many areas, including flow assurance of oil and gas lines, potential sources of natural gas from permafrost and deep-sea hydrate deposits and use as a medium for energy storage and transportation as well as gas (hydrogen, carbon dioxide…) capture, storage, separation, and transportation [6–8].

The first studies on hydrates for refrigeration applications aimed at developing cold storage systems. Thus, in the Eighties, various authors studied refrigerant gas hydrates in direct-contact crystallisers using water and various refrigerant gases among which CFC-11 [9], CFC-12 [10,11], HFC-134a [12]. Later, Matsuo et al. [13] studied the possibility of replacing CFC-type and HFC-type refrigerants by refrigerants with “zero” ozone-depleting potential (ODP) and minimal global warming potential (GWP) and concluded that propane and CO_2 hydrates were thermodynamically viable for cold storage system. More recently, the review of Guo et al. [14] highlighted the first Chinese work on the development of hydrate-based cold-storage systems. Since, various studies based on HCFC-141b use were undertaken in glass tubes [15] or in storage tank [16].

The use of gas hydrate slurries for cold transport applications was also studied by various authors. Fournaison et al. [17] proposed studying CO_2 hydrate for this purpose because of its high dissociation enthalpy ($500\ kJ\ kg^{-1}_{water}$: higher than that of ice of $333\ kJ\ kg^{-1}_{water}$). Hydrate slurry production has the advantage of being formed using a non-mechanical process. That is not the case with the generation of the classical two-phase refrigerants or ice slurries, in which power is limited by mechanical parts. In order to reduce equilibrium pressures of CO_2-containing hydrate slurries, various thermodynamic studies were carried out on CO_2-THF-water, CO_2-TBAB-water, and CO_2-TBPB-water mixtures and were