Applied Thermal Engineering 75 (2015) 513–531

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

A review on the use of calcium chloride in applied thermal engineering

Kokouvi Edem N'Tsoukpoe [a,*], Holger Urs Rammelberg [b], Armand Fopah Lele [b], Kathrin Korhammer [b], Beatriz Amanda Watts [b], Thomas Schmidt [b], Wolfgang K.L. Ruck [b]

[a] LESEE, Laboratoire Energie Solaire et Economie d'Energie, Institut International d'Ingénierie de l'Eau et de l'Environnement (2iE), 01 BP 594 Ouagadougou 01, Burkina Faso

[b] Innovation Incubator “Competence Tandem Thermal Battery”, Leuphana University Lüneburg, Scharnhorststraße 1, 21335 Lüneburg, Germany

HIGHLIGHTS

- We review the use of $CaCl_2$ in PCM, sorption and thermochemical applications.
- For each application field, $CaCl_2$ exhibits various undesirable behaviours.
- Numerous specific additives have been identified to address these problems.
- The use of $CaCl_2$ as PCM for thermal storage has been widely demonstrated.
- More research is needed for the use of $CaCl_2$ in sorption and thermochemical units.

ARTICLE INFO

Article history:
Received 17 June 2014
Accepted 18 September 2014
Available online 30 September 2014

Keywords:
Calcium chloride
Adsorption cooling and heating
Absorption processes
Desiccation
Dehumidification
Thermochemical storage

ABSTRACT

The combination of its hygroscopy, heat of hydration, the low to medium melting points of its hydrates and its low material costs makes calcium chloride and the respective hydrates an attractive substance for various thermal processes. For refrigeration applications, the ammonia sorption is of high significance. The use of calcium chloride in pure or modified form is reviewed from the application point of view. A short analysis of the general physical and chemical properties highlights the advantageous properties. An overview is given about its use in the following applications: phase change material, desiccant, heat pumps and refrigeration and thermal energy storage. The advantages and challenges are discussed as well as approaches for technical improvement.

1. Introduction

Calcium chloride is a very common chemical in energy efficiency thermal engineering applications. Among other applications, this material has been used practically in various phase change material applications [1], closed sorption processes [2], desiccant cooling or dehumidification [3,4], refrigeration [5], drying [6,7], water recovery or extraction from atmospheric air [8–10], sorption [11] and thermochemical energy storage [12]. Calcium chloride is also applied in association (composites) with other materials in order to improve their suitability for the above-mentioned applications.

This paper reviews the use of calcium chloride in different forms, pure or in a composite material, in thermal applications. An emphasis is put on practical and experimental applications in order to point out interesting aspects of the material processing, properties, proven uses and challenges that remain.

The interest for calcium chloride lies in the following non-exhaustive features and advantages, depending on the application:

- Easy availability [13] because large quantities are produced as by-product of industrial processes [14,15].
- Subsequently, calcium chloride is one of the cheapest [13,16,9] (0.3–0.4 USD kg^{-1} [16–20], 2 USD kg^{-1} [15]), even the cheapest commercially available salt hydrate, depending on the application. This aspect makes it very attractive for many applications in particular those which need large quantities such as thermal storage applications.

* Corresponding author. Tel.: +226 64538850; fax: +226 50492801.
E-mail addresses: edem.ntsoukpoe@2ie-edu.org, n_christedem@yahoo.fr (K.E. N'Tsoukpoe).

http://dx.doi.org/10.1016/j.applthermaleng.2014.09.047

- A highly hygroscopic desiccating and sorption capacity [21,22], in solid or liquid state. This property is widely used in industry, laboratories, commercial and domestic buildings: it has been shown that anhydrous $CaCl_2$ could adsorb up to 90% of its own weight in moisture (water vapour) at ambient temperature and pressure [23]. The adsorption quantity is even higher than 100 wt% (weight percent) with ammonia [24] because 1 mol of calcium chloride can adsorb 8 mol of ammonia [25].
- A relatively higher thermal conductivity, whether in solid or liquid state, compared to other materials of the same kind [26,27].
- A better thermal [1,16] and chemical stability [15] than other salt hydrates
- A less corrosiveness than other salt hydrates [16,28]
- A high latent heat of fusion (hexahydrate) [15]
- A small volume change during phase transition [15]
- Non-toxicity [29]
- In sorption processes, it can be paired with different refrigerants (water, ammonia, methylamine, methanol, ethanol: see Fig. 1) [30], allowing various applications at various operation conditions
- Low or moderate temperature operating range [31]

However, this material exhibits some undesirable behaviour:

- Possible liquefaction of the material after absorbing a certain amount of water [24]
- Excessive swelling/expansion (2:1 [24]) and agglomeration in particular when used in absorption cycle with ammonia [32,22,24]: this degrades heat and mass transfer and results in the decrease of reaction rate after several cycles [33]
- Depending on the use, disintegration/decomposition/deterioration after several operating cycles [25,32,34] when no special measure is taken [13]
- Corrosive to certain metals in the presence of excess oxygen because of chloride-induced corrosion [35]. However, this corrosion problem is practically no real threat any more when the process is run under near vacuum conditions (limited air or oxygen in an adsorber [35]), which is usually the case.

Because of its multiple uses, the properties of calcium chloride have been extensively studied; they are provided in Table 1 for the calcium chloride hydrates. As for the aqueous solution of calcium chloride and other working pairs involving calcium chloride, Table 2 and Table 3 summarise some references that give their properties. Solubility data in water, methanol and ethanol [36] are given in Fig. 2.

Various tetrahydrates are reported, among which the α and β tetrahydrates are deemed to be stable [37–39].

The pH of melted $CaCl_2 \cdot 6H_2O$ has been reported to be 6 [28]. Corrosion data of the calcium chloride aqueous solution for some materials can be found in Table 4. Corrosion is increased with the mass fraction and the temperature. For example, the stainless steel 304 is resistant to calcium chloride aqueous solution when the mass fraction is at about 10 wt% and when the mass fraction is about 28 wt%, the corrosion is about 0.003 mm year^{-1} at 79 °C [40]. Further corrosion data on $CaCl_2 \cdot 6H_2O$ have been reported by Cabeza et al. [28]. The study indicates that $CaCl_2 \cdot 6H_2O$ can be used in a metal container of brass and copper for long term service. Steel and aluminium are less resistant to $CaCl_2 \cdot 6H_2O$ and are recommended only for short term applications, but with caution. As for stainless steel, no corrosion was observed by the authors but they suspected that pitting could appear.

2. Use of $CaCl_2$ as phase change material (PCM)

2.1. The interest in $CaCl_2$ for PCM applications

The term “phase change material” (PCM) is commonly used to describe a substance that undergoes melting or solidification at nearly constant temperature, while absorbing or releasing a significant amount of energy. Heat is absorbed while the PCM changes from solid to liquid phase; conversely, heat is released while the PCM changes from liquid to solid phase. The heat transferred at nearly constant temperature is called latent heat. Salt hydrates belong to the most studied PCMs.

Calcium chloride is one of the most encountered salt hydrates in phase change material applications, mainly in latent heat storages.

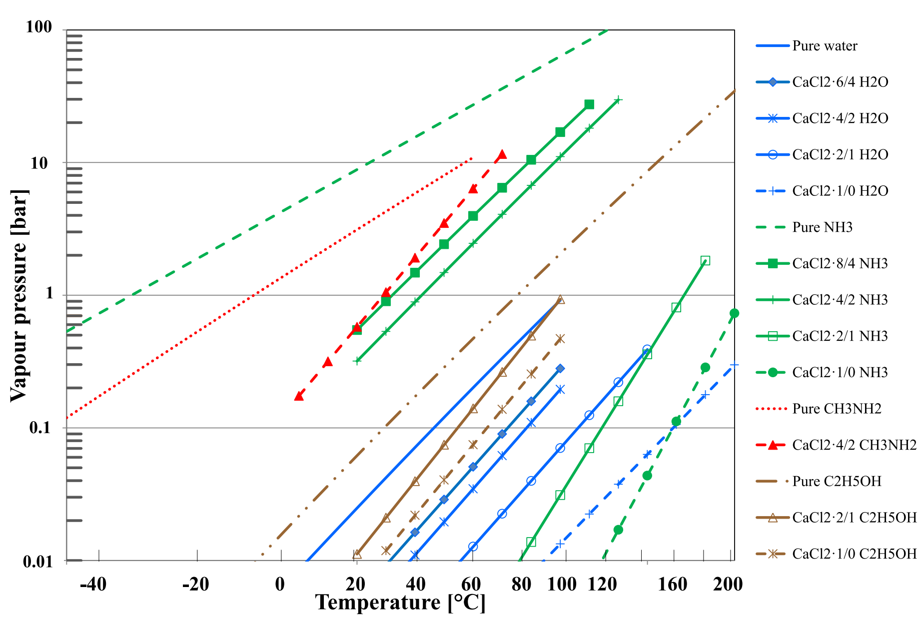

Fig. 1. Equilibrium relationship between temperature and pressure for various $CaCl_2$ based solid–gas reactions. Data are gathered from various sources: $CaCl_2$–H_2O [33,41], $CaCl_2$–NH_3 [42–44], $CaCl_2$–CH_3NH_2 [42,45], $CaCl_2$–C_2H_5OH [46,47].