



A Review on Thermophysical Properties Data of High Temperature Phase Change Materials for Thermal Energy Storage

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Abstract

When compared with other energy storage methods, thermal storage offers a cheap solution for storing energy. A large amount of thermal energy can be stored at the phase transition temperature of phase change materials (PCMs). The thermophysical properties of PCMs are an important factor in designing latent heat thermal storage systems. Thermophysical properties provide information on the PCMs ability to store energy. The thermophysical properties of PCMs have been studied over the years, and data can be found in many handbooks and papers. However, this data does not cover all thermophysical properties of high temperature PCMs. This paper reviews the thermophysical properties (heat of fusion, melting/solidification temperature, specific heat capacity, thermal conductivity, viscosity and density) of high temperature PCMs found in the literature. This paper identifies the gaps existing in the data which is necessary for the design of efficient high temperature solar systems.

1. Introduction

Solar thermal power suffers from an inconsistent supply of solar flux and changeable weather throughout the day. This inconsistency can be overcome by using thermal energy storage to provide energy at a later time when a disparity between supply and demand occurs (Mehling & Cabeza 2008). In concentrated solar power plants thermal energy storage can be implemented with either sensible heat storage (achieved by the increase in temperature of materials and requiring a storage tank with large volume) or latent heat storage (increasing energy content without increasing the temperature, by utilizing phase change materials [PCMs]). The most significant advantage of PCMs is its capability of storing large quantities of energy within a narrow temperature range and therefore they have a high storage density (Wang et al. 2002).

Over the last 30 years, researchers have focused on thermal energy storage in general and PCMs specifically. The thermophysical properties of PCMs need to be defined in order to facilitate the analysis and design of latent heat thermal storage systems. Thermophysical properties provide information on the PCMs' ability to store energy. Research is needed to investigate several parameters to ensure longevity, reliability and feasibility. The appropriate selection of PCMs with desirable characteristics can reduce the cost of energy from concentrated solar power plants (Trahan et al. 2012). The thermophysical properties of PCMs have been studied over the years, and the resultant data is dispersed throughout many handbooks and papers. However, the available data does not cover all thermophysical properties of high temperature PCMs (Kenisarin 2010).

The objective of this paper is to review the available thermophysical properties data for high temperature PCMs (above 300°C).

2. Phase Change Materials

PCMs possess the ability to change state at a certain temperature. This enables energy to be stored and released from this material in a narrow temperature range known as the phase change stage. The phase change process is namely solid to liquid, as shown in Figure 1.

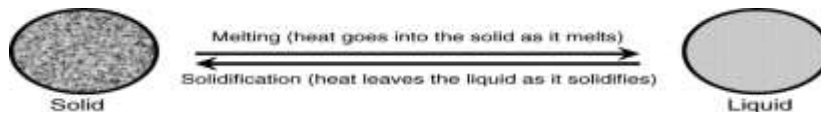


Figure 1 phase change process (Mondal 2008).

Latent heat storage materials that are used in latent thermal energy storage need to have accurately defined properties to ensure a correctly designed and effective system. According to Abhat (1980); Herrmann and Kearney (2002); Regin et al.(2008); Sharma et al. (2009) these criteria are shown in Table 1.

Table 1. Important properties of phase change heat storage materials.

Thermal	Physical	Kinetic	Chemical	Economic
Phase change temperature suitable for the application.	Low-density variation	Little or no supercooling of the liquid phase.	Chemical stability	Economical
High change of enthalpy.	High density	Sufficient crystallization rate	No phase separation	Abundant
High thermal conductivity in liquid, solid phases	Small volume change		Compatibility with container materials	Available

It is difficult to find all of the optimal properties that are shown in the above table in one PCM. Researchers in this field have attempted to select materials that meet most of these requirements.

3. Classification of PCMs

Classification of materials depends on the difference in their chemical and thermal behaviour. Abhat (1980) offers a useful classification of materials used for thermal energy storage, shown in Figure 2. Two essential requirements in materials, the melting temperature and the melting enthalpy, are shown in Figure 3. PCMs can be classified into three main families: organic, inorganic materials and metal alloys (Rousse et al. 2009). The figure covers commonly used organic materials and inorganic salts but does not include metal alloys.

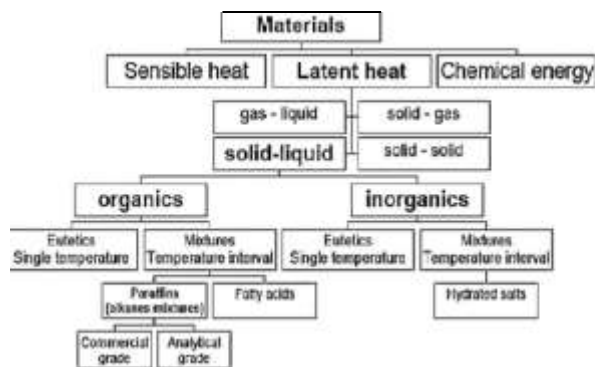


Figure 3 Families of energy storage substance (Cabeza et al. 2011).

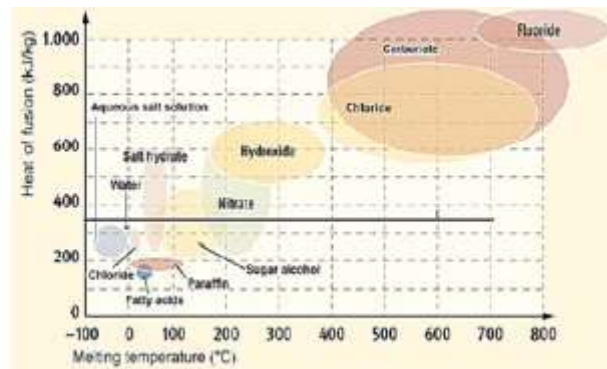


Figure 2. Typical melting temperatures and heat of fusion for different classes of PCMs (Mehling & Cabeza 2008).

According to Farid et al. (2004) and Liu et al. (2012), PCMs are distributed into three main groups.

1. PCMs used for low-temperature applications under 15°C, which are commonly used for storage of food and air conditioning.
2. PCMs used in mid temperature applications between 15 to 300°C, which are usually used in solar heating and absorption refrigeration.
3. PCMs that melt above 300 °C, offering the prospect of applications in thermal energy storage in concentrated solar power plants.

Other researchers such as Farid et al. (2004) and Pielichowska and Pielichowski (2014) suggested that the classification of PCMs depends on their applications and selection of materials based on their melting temperature.

3.1. Organic PCMs

Organic PCMs can be described as paraffin and non-paraffin substances. Organic materials are characterized as stable, recyclable; showing little or no supercooling, non-corrosive, and having no phase separation (Sharma et al. 2009). Their drawbacks are low thermal conductivity, flammability and their low fusion temperatures in comparison to inorganic materials (Bruno 2004).

3.2. *Inorganic salts*

Inorganic compounds include hydrate salts, binary salts and salt composites (Bruno 2004; Liu et al. 2012). These compounds are characterized by covering a wide temperature range (see Figure 2.5), compared to organic materials (Mehling & Cabeza 2008).

Salt hydrates have a high latent fusion temperature, higher thermal conductivity and are non-flammable. They are also low in cost compared with organic materials (Sandnes & Rekstad 2006). However, characteristic drawbacks of using salt hydrates are phase separation which adversely affects their cycling stability (Bruno 2004). Furthermore, some salt hydrates may be chemically unstable when used in applications above 150°C (Kenisarin & Mahkamov 2007).

Inorganic salts and salt eutectic compounds are currently used in applications above 300°C and can probably be employed as energy storage media for solar power plants (Liu et al. 2012). Moreover, mixtures of fluorides, carbonates, hydroxides, nitrates, and chlorides can be employed in latent heat thermal storage for the temperature range of 290-500°C (Trahan et al. 2012).

Salts however have some disadvantages including a low thermal conductivity, supercooling and corrosion. Some salts also have a high cost. Phase separation, phase segregation and lack of thermal stability are also major disadvantages (Kenisarin. 2010; Zalba et al. 2003).

3.3. *Metals and metal alloys*

Whilst salts have several disadvantages limiting their application, metals can reduce these problems and are quite competitive despite the lower thermal storage density (Liu et al. 2012). Khare et al. (2012) have examined materials employed for high-temperature thermal energy storage, and shown that metals and alloys have beneficial properties when compared with molten salt. Some of the characteristics of these metallic materials, include low heat of fusion per unit weight, high heat of fusion per unit volume, high thermal conductivity, low specific heat and relatively low vapour pressure (Sharma et al. 2009). The comparison of the advantages and disadvantages of organic, inorganic materials and metals alloys are summarised in Table 2.

Table 2-Comparison of organic, inorganic materials and metals alloys for heat storage

	Organic	Inorganic	Metals alloys
Advantages	Stable	Greater phase change enthalpy	High heat of fusion per unit volume
	Recyclable		High thermal conductivity
	Little or no supercooling		
	Non-corrosive		
	No phase separation		
Disadvantages	Low thermal conductivity	Low thermal conductivity	Lower thermal storage density
	Flammability	Supercooling	Low specific heat
	Low heat of fusion	Corrosion	
	High cost	Some salts a high cost	
		Phase separation	
		Phase segregation	
	Lack of thermal stability		

4. **Thermophysical properties**

Familiarity with the data from thermophysical properties of PCMs is essential, including fusion heat, melting/solidification temperature, specific heat capacity, thermal conductivity, viscosity and density of PCM at a temperature range covering both solid and liquid states. The thermal energy storage system is designed to store energy when production exceeds demand and to make it available upon user request. The key properties of such systems are described below (IRENA 2013; Kenisarin & Mahkamov 2007; Kenisarin. 2010).



1. Thermal capacity: the capacity defines the total energy that can be stored in the system, which depends on the properties of the medium, the size of the system and operating conditions.
2. Power: the power defines how fast the energy can be stored into the system and the rate at which it can be extracted from the system when the energy is needed.
3. Charge and discharge time: it defines how much time is needed to charge the system for storage and how long it takes the energy to be extracted from system in the discharge process. It is closely related to the thermal properties of the storage medium and heat transfer fluid, as well as the operating conditions of the TES system.
4. Cost: the cost usually refers to the cost per unit of storage capacity in \$/kWh, which includes the capital cost, operation and maintenance costs over its lifetime.
5. Efficiency: the efficiency is the ratio of the energy provided to the user to the total energy needed to charge the storage system. It accounts for the efficiency of the transmission between the different forms of the energy as well as the energy loss during the storage period and charging/discharging period.

The latent heat during fusion is expressed as the change of enthalpy of the PCM at the melting/freezing point. The phase transition temperature is significant when selecting a PCM suitable for a particular application (Lane 1983). Moreover, a high density indicates that a material can store more heat for any given volume (Lane 1983). Also, a high thermal conductivity indicates the material's ability to store and release energy in a short time (Mehling & Cabeza 2008). Likewise, the heat capacity shows the amount of sensible heat storage associated with change of temperature. A high specific heat is a useful feature for materials used in energy storage to reduce the storages system size (Sharma & Sagara 2005).

Data on thermophysical properties are found in many handbooks and papers. However, this data does not cover all the thermophysical properties of high-temperature PCMs (Kenisarin. 2010). One of the reasons for the paucity of complete data is that the thermophysical properties are calculated instead of being experimentally measured (Kenisarin. 2010; Trahan et al. 2012). Reliance on calculated values creates a problem when evaluating storage system cost and design, as both are contingent upon actual material property values, which can be significantly different from theoretical values (Trahan et al. 2012).

Since 1963, the national bureau of standards in the United States Department of Commerce started publishing and developing plans to meet high-priority needs for reliable reference data. The target of establishing the national standard reference data system (NSRDS) is to provide the technical community of the United States with the reliable data of physical science (Janz 1968). The NSRDS has published a series of molten salts properties as shown in table 3. These are of data for density and viscosity of single and salt mixtures. They also provide empirical equations and tables for density and viscosity, as shown in these examples: For single salts (Janz et al. 1972):

The Viscosity of KNO_3 :

$$\eta = 19.16312 - 2.75146 \cdot 10^{-2}T - 1.512603 \cdot 10^{-5}T^2 + 2.721704 \cdot 10^{-8}T^3$$

The density of NaNO_3 :

$$\rho = 2.3339 - 7.665 \cdot 10^{-4}T$$

Table 3 NSRDS molten salts data series.

(For single salts and their binary mixtures relative to the data for electrical conductance (κ), viscosity (η), density (ρ) and surface tension (γ))		
Molten salts	NSRDS recommendations	Ref.
Vol. 1 (1968)	Single salts (κ , η , ρ)	(Janz, GJ 1968)
Vol. 2 (1969)	Single salts (γ)	
Vol.3 (1972)	Binary and mixtures: Nitrates, Nitrites	Janz, GJ et al. (1972)
Vol.4, Pt. 1 (1974)	Binary and mixtures of Fluorides	Janz, G et al. (1974)
Vol.4, Pt. 2 (1975)	Binary and mixtures of Chlorides	Janz, GJ et al. (1975)
Vol.4, Pt. 3 (1977)	Binary and mixtures: Bromides, Iodides	Janz, G et al. (1977)
Vol.4, Pt. 4 (1979)	Binary and mixtures: Mixed Halides	Janz, G, Tomkins and Allen (1979)
Vol.5, Pt. 1 (1980)	Binary and mixtures: Mixed Anions, other than Nitrates, Nitrites and Halides	Janz, GJ and Tomkins (1980)
Vol.5, Pt. 2 (1983)	Additional single and multi-component salt systems.	Janz, G and Tomkins (1983)

Pelton and Chartrand (2001) have evaluated all available phase diagrams and thermodynamic data by using binary and ternary subsystems to predict thermodynamic properties for multicomponent systems. Gomez et al. (2011) have illustrated the melting temperature and composition that is calculated by Factstage® thermochemistry software for the same eutectic. The latent heat is calculated rather than experimentally measured and is often assigned different values which becomes problematic when evaluating storage cost and design, since both are contingent upon actual materials property values, which can differ significantly from theoretical values (Trahan et al. 2012).

Some thermophysical properties of different inorganic salts and salt eutectic mixtures have been summarised by Cornwell (1971); Kenisarin. (2010); Liu et al. (2012); Zalba et al. (2003). (See Appendix 1). Some PCMs have different thermophysical property values.

5. Conclusions

The existing literature on thermophysical properties of PCM at high temperature (above 300°C) has been summarised in this paper. These properties are usually determined using a mathematical method. Using mathematical methods in evaluating thermophysical properties of PCM can be less reliable in comparison with experimental results. Current experimental methods has the severe limitation of not being able to measure the entire extent of thermophysical properties. In order to accurately evaluate storage system cost and design, experimental results from thermophysical properties is desirable. Experimental examination of these properties is essential prior to developing any comprehensive database for them. Existing data for them is scattered throughout various handbooks and journals.



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Acknowledgments

The first author would like to thank the Iraqi Government especially the Ministry of Higher Education and Scientific Research (MOHESR) for the scholarship support to pursue my PhD studying at the University of South Australia. This research are funded as part of the Australian Solar Thermal Research Initiative (ASTRI), a project supported by the Australian Government, through the Australian Renewable Energy Agency (ARENA).

Appendix 1- PCMs above 300°C which have been investigated by difrent researchers

Data source:

A- "1" in the table means (Liu et al. 2012)

B- "2" in the table means (Zalba et al. 2013)

C- "3" in the table means (Kenisarin 2010)

D- "4" in the table means (Cornwell 1971)

Inorganic substances with potential use as PCM									
Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)		Density (kg/m ³)		Specific heat (kJ/kg-K)		Source
			Solid	Liquid	Solid	Liquid	Solid	Liquid	
NaNO ₃	306	172	0.5		2261		1.10		1
	306	175					1.5	1.7	1
	306	178		0.514	2260	1908		1.655	1
	306	175			1900				1
	307	172	0.566		2260				2,4
	308	200	0.5		2257				1
	310	174							1
	310	172			2260	1.82	0.5		1
RbNO ₃	311		0.377						4
CsNO ₃	314		0.285						4
NaOH	318	165			2100	2.08	0.92		1
	319		0.92						4
ZnCl ₂	320		0.305						4
KNO ₃	330	266			2110	1.22	0.5		1
	333	266			2110		0.5		1,2
	334		0.431						4
	335	95	0.5	0.425	2109		0.953		1
	336	116	0.5		2.110				2
KOH	360	134	0.5		2040		1.34		1,2
	380	150	0.5		2044	1.47	0.5		1,2
Mg(NO ₃) ₂	426								1
AgBr	460		0.277						4
Ca(NO ₃) ₂	560	145							1
MgCl ₂	714	452			2140				1,2
KCl	771	353							1
NaCl	800	481							1
	800	482							1
	801		0.88						4
	802	420			2160		0.5		1
	802	466.7	5		2160				2
Inorganic eutectics with potential use as PCM (Salts Compositions)									
Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)		Density (kg/m ³)		Specific heat (kJ/kg-K)		Source
			Solid	Liquid	Solid	Liquid	Solid	Liquid	
LiCl - LiOH (37:63)	262	485	1.1		1550		2.4		3
NaCl - Na ₂ CO ₃ - NaOH (7.8:6.4:85.5)	282	316			2130		2.51		3
AgCl - AgI (47:53)	300		0.182 near melting point						4
LiOH-KOH (40:60)	314	341							1
KNO ₃ - KCl (95.5:4.5)	320	74	0.5		2100		1.21		1
KNO ₃ - KCl (96:4)	320	150							1
KNO ₃ - NaNO ₃ (71:29)	330		0.36 near melting point						4
KNO ₃ - NaNO ₃ (40:60)			0.38 near melting point						4
KNO ₃ - KBr - KCl (80:10:10)	342	140							1
NaCl-KCl-LiCl (33:24:43)	346	281							1
LiCl-KCl (59:41)	353		0.69 near melting point						4
NaOH-NaCl (80:20)	370	370							1
MgCl ₂ -KCl-NaCl (60:20.4:19.6)	380	400			1800		0.96		1
MgCl ₂ -NaCl-KCl (63.7:22.3:14)	385	461	0.95		2250		0.96		3
Li ₂ CO ₃ -K ₂ CO ₃ -Na ₂ CO ₃ (32.1:34.5:33.4)	397	276	2.04		2310		1.69		1,3
MgCl ₂ -KCl (39:61)	435	351		0.81	2110		0.8	0.96	1
MgCl ₂ -NaCl (52:48)	450	430		0.95	2230		0.92	1	1,3
MgCl ₂ -KCl (64:36)	470	388		0.83	2190		0.84	0.96	1
MgCl ₂ -KCl-CaCl ₂ (48:25:27)	487	342		0.88	2530		0.8	0.92	1



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NaCO ₃ -Li ₂ CO ₃ (56:44)	496	368	2.11		2330		1.85		3
CaCl ₂ -NaCl (67:33)	500	281		1.02	2160		0.84	1	1
NaF-KF-LiF (11.5:42:46.2)	500			0.6 near melting point					4
NaCl-KCl-CaCl ₂ (29:5:66)	504	279		1	2150		1.17	1	1
BaCl ₂ -KCl-NaCl (53:28:19)	542	221		0.86	3020		0.63	0.8	1
BaCl ₂ -KCl-CaCl ₂ (47:24:29)	551	219		0.95	2930		0.67	0.84	1
LiF-MgF ₂ -KF (64:30:6)	710	782							1
NaF - KF - LiF - MgF ₂ (11.8: 54:3 : 26:6 : 7:3)	449					2160			2
LiF - NaF - CaF ₂ (35.1: 38:4: 26:5)	615				2820	2225			2
LiF - NaF - MgF ₂ (32.5: 50:5: 17:0)	632				2810	2105			5
LiF-NaF ₂ -MgF ₂ (46:44:10)	632	858	1.2		2240		1.4		3
NaF-CaF ₂ -MgF ₂ (51.8: 34:0: 14:2)	645				2970	2370			2
LiF-NaF ₂ -MgF ₂ (33.4:49.9:17.1)	650	860	1.15		2820		1.42		3
LiF + NaF (48.1: 51:9)	652				2720	1930			2
KF - NaF - MgF ₂ (63.8: 27.9: 8.3)	685					2090			2
NaF-CaF ₂ -MgF ₂ (65: 23 : 12)	745	574			1580		1.17		3
LiF - MgF ₂ (45.8:54.2)	746				2880	2305			2,3
NaF - MgF ₂ + KF (53.6: 28.6: 17:8)	809				2850	2110			2

Metals and metal alloys with potential use as PCM.

Material	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)		Density (kg/m ³)		Specific heat (kJ/kg ¹ K)		Source
			Solid	Liquid	Solid	Liquid	Solid	Liquid	
Pb	328	23							1,3
Al	660	397							1,3
Cu	1083	193.4	350		8930- 8800				1,3
Mg - Zn (46.3:53.7)					4600				1,3
Mg - Zn (48:52)	340	185							1,3
Zn - Al (96:4)	340	180			6630				1,3
Al - Mg - Zn (59:33:6)	381	138			2380		1.63	1.46	1,3
Al - Mg - Zn (60:34:6)	443	310							1,3
Mg-Cu-Zn (60:25:15)	450.3	329.1			2800				1,3
Mg-Cu-Ca (52:25:23)	452	254			2000				1,3
Mg-Al (34.65:65.35)	453	184			2155				1,3
Al-Cu-Mg (60.8:33.2:6)	497	285			3050				1,3
Al-Si-Cu-Mg (64.6:5.2:28:2.2)	506	365			4400				1,3
Al-Cu-Mg-Zn (54:22:18:6)	507	374			3140		1.51	1.13	1,3
Al-Si-Cu (68.5:5:26.5)	520	305			2938				1,3
Al-Cu-Sb (64.3:34:1.7)	525	364			4000				1,3
Al-Cu (66.92:33.08)	545	331			3600				1,3
Al-Si-Mg (83.14:11.7:5.16)	548	372			2500				1,3
Al-Si (87.76:12.24)	555	485			2540				1,3
Al-Si-Cu (46.3:4.6:49.1)	557	498			5560				1,3
Al-Si-Cu (65:5:30)	571	406			2730		1.3	1.2	1,3
Al-Si-Sb (86.4:9.6:4.2)	571	422			2700				1,3
Al-Si (12:86)	575	471	160		2700		1.038	1.741	1,3
Al-Si (20:80)	576	560							1,3
Zn-Cu-Mg (49:45:6)	585	460			8670		0.42		1,3
Cu-P (91:9)	703	176			5600				1,3
Cu-Zn-P (69:17:14)	715	134			7000				1,3
Cu-Zn-Si (74:19:7)	720	368			7170				1,3
Cu-Si-Mg (56:27:17)	765	125			4150		0.75		1,3
Mg-Ca (84:16)	770	420			1380				1,3
Mg-Si-Zn (47:38:15)	790	272							1,3
Cu-Si (80:20)	800	314			6600		0.5		1,3
Cu-P-Si (83:10:7)	803	197			6880				1,3
Si-Mg-Ca (49:30:21)	840	92			2250				1,3
Si-Mg (56:44)	865	305			1900		0.79		1,3