Review on Thermophysical Properties and Corrosion Performance of Molten Salt in High Temperature Thermal Energy Storage

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Abstract. Molten salt is a type of material for high temperature thermal energy storage. The thermophysical property, thermostability, and corrosion performance of molten salt are the main points of interest in thermal energy storage field. How to further broaden the usage temperature range of molten salt, develop more molten salts with low melting points, and optimize the thermal conductivity and viscosity of materials has been widely concerned by researchers. Recently, thermal storage technology of molten salt has been applied to the field of concentrating solar power. The thermophysical property, and corrosive performance of molten salt are very important for the large-scale preparation and application of molten salt materials. Based on the classification of molten salt materials, this paper reviews the thermophysical properties of some common molten salts (carbonate, chloride, nitrate, polybasic salt, etc.), and summarizes the current research progress of improving its thermophysical properties. Moreover, the corrosive performance of several types of commonly used molten salts in thermal energy storage applications is analyzed. Besides, some corrosion protection technologies are proposed according to the current application of molten salt and the corrosion mechanism. Finally, the development trend of the application of molten salt in the field of heat storage is prospected.

1. Introduction

Molten inorganic compounds are usually called molten salts, which are molten liquids formed by salts at high temperatures. Like an aqueous solution, molten salt is a solvent, but it is a high temperature solvent that does not contain water. A main feature of molten salts is that it can be dissociated into positive and negative ions after melting at high temperature. And these two ions interact by Coulomb force. So the molten salts can be used as a medium at high temperature. Molten salt has become a very promising high-temperature liquid thermal energy storage material, because it has shown significant advantages in concentrating solar power, waste heat recovery and industrial heat utilization. [1, 2] At present, it has been widely used in many fields such as solar thermal utilization, electric power “peak shifting and valley filling”, recovery of waste heat or waste heat, and energy saving of industrial and civil buildings. [3-5] Common molten salts include nitrates, chlorides, fluorides, carbonates, and mixed molten salts. With the development of concentrating solar power technology, molten salts have been used as a heat transfer and storage medium. It is considered to be the most realistic material for large-scale high temperature thermal energy storage at present.
The molten salt mainly includes the following advantages. [6-8] (1) Good conductivity. Molten salts usually consist of cations and anions, so they often have good electrical conductivity. Their electrical conductivity can be an order of magnitude or higher electrolyte solutions. (2) Wide liquid temperature range. Generally, molten salt shows relative thermal stability use temperature is between 200-1000 °C. For example, the binary mixed nitrate has a liquid temperature range of 240-565 °C. (3) low saturated vapor pressure. Molten salt has a lower saturated vapor pressure, especially for mixed molten salts. The saturated vapor pressure is lower and close to normal pressure, which can ensure the safety of molten salt equipment at high temperatures. (4) High density. Liquid molten salts are generally twice as dense as water. (5) Low viscosity. The viscosity of the molten salt changes significantly with temperature. The viscosity of the molten salt in the high temperature is even lower than that of water at room temperature, so the molten salt usually has a good fluidity. (6) Good chemical stability. The molten salt exhibits very stable chemical properties in the used temperature range. (7) Low price. For example, the price of high-temperature heat-conducting oil is 4200 to 7000 dollar/ton, and the price of commonly used mixed molten salts is generally less than 1400 dollar/ton, which is significantly lower than that of thermal conductivity oil. Moreover, most molten salt is non-toxic and non-flammable. Based on these above advantages, molten salt can therefore meet the high-temperature and high-pressure operating conditions in the field of thermal energy storage. Therefore, it has become a research focus of thermal energy storage materials.

Common molten salts mainly include chlorides, nitrates, carbonates, fluorides, and other salts. Different types of salts have different properties. The main properties of these three common salts are shown in Table 1. [9-14]

| Materials | Phase transition temperature (°C) | Advantages | Disadvantages |
|-----------|----------------------------------|------------|--------------|
| Chlorides | 600~900                          | Low price, wide variety, can be made into mixed salts with different melting points, the service temperature range of mixed salts is wide. | Highly corrosive. |
| Fluorides | 700~1300                         | High melting point and latent heat, low viscosity, good compatibility with metal materials. | Large solid-liquid phase change volume shrinkage, low thermal conductivity, prone to "thermal ratcheting" and "thermal spots". |
| Nitrates  | 300~400                          | Low corrosiveness, cannot decompose at 500 °C. | Low thermal conductivity, easy to produce local overheating during use. |
| Carbonates| 600~900                          | Low corrosiveness, high density and solubility, high melting point. | Some salts are easy to decompose and have high viscosity. |

2. Thermal properties of molten salt materials in thermal energy storage

From the current research literature, molten salts generally include carbonates, chlorides, halide salts and nitrates. Because eutectic materials in different temperature ranges can be obtained by mixing the same acid ion, the binary or ternary mixtures of molten salts have become widely used energy storage materials. Murat M. Kenisarin et al. [15] and Belen Zalba et al. [16] have summarized the thermal properties of some inorganic salt heat storage materials. Table 2 lists the thermophysical properties of some single and complex salts used for high-temperature heat storage.[17-20] The biggest advantage of mixed salts is that the melting temperature can be adjusted. So different salts can be formulated into energy storage materials with a phase transition temperature changed from several hundred degrees Celsius to thousands of degrees Celsius according to needs. Recently, some researchers have mixed salts of different acid ions to obtain composite molten salts with better thermal properties. For examples, the Na₂CO₃–NaCl molten salt was investigated as a new high-temperature phase change material for solar thermal energy storage in the work of Yifeng Jiang et.al. The melting point of the eutectic salt is 637.0 °C and its heat of fusion is 283.3 J/g. [21] And the results show that this eutectic Na₂CO₃–NaCl salt is a
promising high temperature phase change material when used in a CO2 environment or encapsulation. Yushi Liu et al. [22] design and prepared a novel Na2CO3·10H2O-Na3HPO4·12H2O eutectic hydrate salt phase change material. Results show that Na2CO3·10H2O and Na2CO3·10H2O in the eutectic hydrate salt interact with each other, causing alteration on crystal growth. The research results also indicate that the 40 wt% Na2CO3·10H2O-60 wt% Na3HPO4·12H2O eutectic hydrate salt is suitable phase change material for comfort applications in buildings in terms of phase change temperature of 27.3 °C, supercooling degree of 3.6 °C and latent heat of 220.2 J/g. As we all know that a low thermal conductivity of phase change materials leads to low heat transfer rate. Thus, numerous studies have been carried out to composite the molten salt with other materials (e.g. expanded graphite, metal matrix, ceramic) to improve thermal conductivity and storage density of molten salt.[24-26] Zhijun Duan et. al [27] prepared a CaCl2·6H2O/expanded graphite composite as a novel form-stable composite phase change material through vacuum impregnation method. The results display that conductivity of this composite have been significantly improved due to the highly thermal conductive expanded graphite. The thermal conductivity of this composite including 50 mass% CaCl2·6H2O (8.796 W m⁻¹ K⁻¹) is 14 times as that of pure CaCl2·6H2O (0.596 W m⁻¹ K⁻¹). Baorang Li et. al [23] prepared a Na2CO3-K2CO3 eutectic salt/ceramic composite, which had good thermal reliability and chemical stability. R. Sudheer et. al [28] have analyzed the effect of addition of micro sized (50 nm) and nano sized (400 nm) graphite particles on thermal energy storage parameters of potassium nitrate in his work. The result showed that the addition of graphite micro and nanoparticles reduced the solidification time of the PCM significantly enhancing the heat removal rates.

Table 2 The thermal physical performances of several single and complex energy storage materials

| Salt composition       | Melting temperature | Heat of fusion (J/g) | Density (g/cm³) | Thermal conductivity [W/(m·K)] |
|------------------------|--------------------|----------------------|-----------------|-------------------------------|
| NaCl                   | 800                | 492                  | 1.9             | 5.0                           |
| CaCl2                  | 782                | 253                  | 2.15            | 2.2                           |
| Na2CO3                 | 854                | 276                  | 2.53            | 2                             |
| KNO3                   | 337                | 266                  | 2.13            | 0.5                           |
| 36KCl–64MgCl2          | 470                | 388                  | 2.19            | 0.83                          |
| 56Na2CO3–44Li2CO3      | 496                | 368                  | 2.33            | 0.96                          |
| 50NaCl–50MgCl2         | 450                | 429                  | 2.24            | 0.95                          |
| 75NaF–25MgF2           | 832                | 650                  | 2.68            | 4.66                          |
| 67LiF–33MgF2           | 746                | 947                  | 2.63            | 1.15                          |
| 33.4LiF–49.9NagF2–17.1MgF2 | 650          | 860                  | 2.82            | 2.11                          |
| 7.8NaCl–6.4Na2CO3–85.5NaOH | 282         | 316                  | 2.13            |                               |

3. Corrosion property of high temperature molten salts in heat storage applications and its corrosion protection

High temperature molten salts have a wide operating temperature range and large latent heat of fusion. It is mainly used in heat engines, solar power stations, magnetic fluid power generation, and artificial satellites. However, due to its corrosive nature, the large-scale use of molten salts has been limited. [29, 30] Generally speaking, the corrosiveness of molten salts will affect molten salts tanks, molten salt pumps, electric molten salt heaters, test elements in the tank, molten salt pipelines, valves, molten salt heat sinks, connecting hoses, flanges, etc. Thereby, a certain amount of chemical corrosion or stress corrosion occurs, and the stress corrosion caused by the great temperature difference during the use of molten salts can cause a weld seam of the molten salts tank to crack.

Molten chlorides are highly corrosive. Conversely, carbonates and nitrates are relatively less corrosive. The chloride and sulfate ions of potassium nitrate and sodium nitrate in the molten salts for
heat storage need special attention. It is similar to cholesterol in human blood vessels, which at least can cause obstruction, and worst of all, endanger safety. In particular, chlorine ions can dramatically corrode equipment in high temperature conditions, which seriously affects production safety and operating life. It is reported that under the condition of the same material, every 10 PPM increase of chloride ion in high temperature will increase the corrosion by 8-12%, and exceeding the limit value will greatly reduce the design life. [31, 32] To reduce the corrosion problem of molten salts on heat storage equipment, it is necessary to use molten salt products with low chlorine and low sulfur.

As a heat storage material, molten salts have the advantage that other materials cannot replace. Therefore, the corrosion problem of high temperature molten salts must be solved before large-scale application. Different molten salts heat storage media have different corrosion mechanisms, so their corrosion resistance methods are also different. The process of metal or alloy being corroded is actually a process in which the passivation film on the surface of the substrate is destroyed and the substrate material reacts with the corrosive medium. To sum up, there are several ways to mitigate the corrosion of high temperature molten salts. [33-35]

(1) The first is to improve the quality of molten salt products, especially to reduce chloride ions, sulfate ions, etc. that are liable to cause corrosion, and to reduce impurity ions that are easy to deposit and scale. Compared with other salts, chloride salts corrode metal parts of heat storage systems much faster, but the working temperature of chloride salts is as high as 900 °C, which is more economical as a heat transfer and heat storage medium. If the use of chloride salts is completely abandoned, the application potential of molten salts as heat storage materials will be greatly reduced.

(2) The second is to use appropriate materials with strong corrosion resistance to make equipment, and perform anti-corrosion treatment on the equipment before the equipment is manufactured and used. Research shows that the corrosion resistance of several common stainless steel metals to chloride salts is: 2520>321>304>316L. The use of corrosion-resistant materials to make equipment is the simplest and effective way. In addition, the preparation of high temperature corrosion-resistant coatings and additives on the surface of structural materials can also effectively slow down the corrosion effect of molten salts on metals. Current reports on high temperature coatings include Ni coatings, Al coatings, and perovskite-type coatings, but these metal or oxide coatings must have low solubility in molten salts.

(3) Reducing some oxidative impurities in molten salts or adding additives to molten salts in order to reduce the oxidation-reduction potential of molten salts is another way of inhibiting the corrosion of structural materials by molten salts.

(4) During the operation, temperature monitoring should be done to avoid local overheating which will cause the molten salts to deteriorate and exacerbate corrosion of equipment.

(5) For some molten salt products, protection with an inert gas is also required.

4. Conclusions and outlook
In conclusion, molten salts have lots of advantages such as higher operating temperature, thermal stability, specific heat capacity, convective heat transfer coefficient, as well as low viscosity, saturated vapor pressure, and low price. Therefore, molten salt is an excellent medium for heat transfer and energy storage. Also, the molten salts have application prospects in building heating, valley heating, and wind power dissipation.

In order to realize large-scale preparation and application of molten salt materials, researches should focus on the development of a multi-component molten salt formula with a low melting point, a wide operating temperature range, low cost, stability and thermal conductivity are key technologies.

(1) Development of low-melting molten salts. At present, commercial molten salt materials have a high solidification temperature which is 140~240 °C. In order to prevent the molten salt from solidifying at low temperatures, storage tanks and pipes need to be insulated and preheated at startup. These methods will increase the system's preheating and accompanying.

(2) The temperature range of molten salt should be further expanded. At present, even in solar-thermal power station with a more mature nitrate heat storage system, the maximum operating temperature does not exceed 600 °C. This always leads to a low efficiency of solar thermal power
generation, and the efficiency is even less than 1/2 of the thermal power generation.

(3) The thermal stability of molten salt at a high temperature should be further improved. When the temperature is too high, molten salt will undergo ion decomposition and structural change. All these changes will cause a change of the thermophysical properties of molten salts, which will greatly affect the power generation efficiency and safety of molten salt.

(4) The search for a simple and safe preparation method is also an important research content of high temperature molten salt materials.

(5) The corrosion characteristics of high-temperature molten salt and its corrosion mechanism also should be further researched. High-temperature molten salt has corrosion hazard to metal materials, which may cause pitting corrosion, crevice corrosion, and stress corrosion. The current heat storage, heat exchanger and other equipment are usually made of stainless steel or high temperature alloy. Study about corrosion behavior and mechanism of structural materials in molten salt heat storage applications, is of great significance to studying the corrosion resistance methods. Therefore, investigation and development of corrosion resistant materials have been one of the important topics in the field of molten salts.

Acknowledgments
The work was supported by the technology projects of state grid corporation of China. (The key technologies for improving thermophysical properties of high temperature phase change heat storage materials, No. SGGR0000DLJS1800085).

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