Summary of Key Performance and Testing Methods for Thermal Storage Materials

Liang Chang¹*, Gaoqun Zhang¹, Hui Tan¹, Zhanfeng Deng¹, Guizhi Xu¹, Xiaoyun Song¹, Linhai Cai¹

¹State Key Laboratory of Advanced Power Transmission Technology, Global Energy Interconnection Research Institute Co., Ltd., Beijing, 102211, China

*Corresponding author and e-mail:Liang Chang, frostfame@163.com.

Abstract. The development and application status of the key performance testing technology of heat storage materials in the application process are reviewed. According to the practical application requirements in terms of heat storage capacity, heat exchange capacity, material strength, service life, etc., the key performances of thermal storage materials that need to be focused on are sorted out, and the relevant testing techniques for each performance are sorted out and summarized. The specific test methods applicable to high-temperature heat storage materials are analyzed, and the related test technologies and evaluation methods for future heat storage materials are prospected.

1. Introduction
Heat storage technology can be used to resolve the contradiction between the supply and demand of thermal energy. It is an important technology to improve energy efficiency and protect the environment. It has a wide range of applications in the fields of solar energy utilization, waste heat and waste heat recovery, and building heating.

The key to heat storage technology is heat storage materials, which are divided into low temperature heat storage materials (<120 °C), medium temperature heat storage materials (120 °C to 400 °C), and high temperature heat storage materials (400 °C to 1000 °C) according to the application temperature. The current research focuses and difficulties are mainly on high temperature heat storage materials. The properties of heat storage materials include thermal properties, mechanical properties and chemical properties. Thermal storage materials should have requirements for large thermal energy storage, high stability, non-toxic, non-corrosive, non-flammable, high thermal conductivity, and small volume change during heat storage.¹,²

At present, in the field of heat storage, especially in the field of heat storage in China, the testing techniques for the performance of heat storage materials are uneven. Most of the test methods are based on the refractory and ceramic industries. There is no clear and standardized test and evaluation standards for reference. This article summarizes the current major performance and testing methods of high-temperature heat storage materials, analyzes the problems in related testing technologies in the field of heat storage materials, and looks forward to future development and improvement.

2. Thermal performance
The thermal properties of materials mainly include specific heat capacity, thermal conductivity, phase change enthalpy, etc. It will decide the heat storage capacity and thermal energy conversion efficiency of materials.
2.1. Specific heat capacity
At present, the test technology of comparative heat capacity in developed countries is relatively perfect. NIST of the National Institute of Standards and Technology and NMIJ of the National Metrology Institute of Japan have established standard configurations of various solid-state solid-liquid specific heat capacities. In China, the Institute of Metal Research of the Chinese Academy of Sciences has done systematic research on the thermal properties of metallic materials. The laser flashing method and the falling method have made some progress in the measurement of the specific heat capacity of materials. At present, the more mature specific heat capacity measurement methods are mainly known as differential scanning calorimetry, microcalorimetry, adiabatic calorimetry and drop method.\textsuperscript{[3]}

2.1.1. Differential Scanning Calorimetry. The principle of differential scanning calorimetry is to analyze the thermal properties of a calculated material by using the relationship between the thermal power difference and the time temperature between the measured sample and the reference sample. The method has the characteristics of wide temperature range, high resolution and small sample dosage, and is the most widely used specific heat capacity measurement method.

2.1.2. Microcalorimetry. The microcalorimetry method is simple and can be quantified when measuring the thermal change of a substance, and is widely used in the fields of biology and chemistry. However, the accuracy of this method still needs to be improved, and the measurement temperature range is small, and it is rarely used in the specific heat test of high temperature materials.

2.1.3. Adiabatic thermal method. The principle of the adiabatic thermal method is to measure the heating amount of the sample, measure its temperature rise, and then calculate the value of the specific heat capacity. The development of adiabatic thermal method is earlier, which is a more mature and accurate method for measuring the specific heat capacity of materials. It requires the experimental device to have very good thermal insulation performance, so the accuracy requirements of its measurement and control system are correspondingly higher. The medium-low temperature specific heat capacity test from room temperature to 500 °C will test the accuracy after 500 °C. The characteristics, advantages and disadvantages of the above several test methods are shown in Table 1.

Table 1. Comparison of several specific heat capacity test methods

| Test method                  | Advantage                      | Disadvantage                                                  |
|------------------------------|--------------------------------|---------------------------------------------------------------|
| Differential scanning calorimetry | High accuracy, wide temperature range, simple data processing | Insufficient operation and high equipment cost               |
| Microcalorimetry             | Simple operation and wide application | The accuracy needs to be improved, and the measurement temperature range is small |
| Adiabatic calorimetry        | Simple principle, mature development | Generally suitable for specific heat capacity test from room temperature to about 500 °C, the measurement takes a long time |

2.2. Thermal conductivity.
The thermal conductivity test method is divided into two types: steady state method and transient method; the steady state method includes flat plate method, guard plate method, heat flow meter method, hot box method, etc.; transient method includes hot wire method, probe method, heat Disc method, tropical method, laser method, etc. At present, the flat plate method, the laser transient method and the hot wire method are three common thermal conductivity measurement methods, among which the flat plate method is the most common, the principle is simple, the equipment is simple, and the experimental platform can be built by itself, but it is not suitable for materials with
high thermal conductivity. The principle and calculation of the laser method and the hot line method are relatively complicated, but the reaction speed is fast, the measurement accuracy is high, and the thermal conductivity suitable for measurement is wide. The advantages and disadvantages of the above several test methods are shown in Table 2.

Table2. Comparison of several thermal conductivity test methods

| Test method               | Advantage                                           | Disadvantage                                      |
|--------------------------|-----------------------------------------------------|---------------------------------------------------|
| Plate thermal method     | Simple model, easy results, wide temperature range  | Solid with long test time, high sample requirements, and low thermal conductivity |
| Protected heat flow method | Wider temperature range and thermal conductivity range | Long test time, high sample requirements, only solids |
| Protected Hot Plate Method | No need to calibrate the measurement unit          | Suitable for materials with thermal conductivity less than 2W / (m • K) |
| Hotline method           | Simple equipment, simple operation and more accurate | Suitable for isotropic and homogeneous materials  |
| Laser scattering         | The sample requires small size, the widest measurement range, and high international recognition | Not suitable for materials with low thermal conductivity such as thermal insulation materials |

3. Mechanical properties

The mechanical properties of materials refer to the mechanical properties exhibited by materials under various external loads. Specific to the heat storage material, its mechanical properties mainly investigate the material in the working environment to show viscosity, thermal expansion coefficient, load softening temperature and so on.

3.1. Viscosity

Viscosity is generally used to indicate the flow characteristics of a liquid substance. The liquid heat storage material not only functions to store heat but also transport and convert heat.

There are many ways to measure the viscosity. The traditional methods mainly include capillary method, rotation method and vibration method. In recent years, some new test methods have been developed.

3.1.1. Capillary method. It is a method for testing viscosity by measuring the liquid flow rate and the pressure difference generated by the flow of liquid through the capillary. The method is low in cost, easy to control in temperature, and convenient to operate, but has high purity requirements and is not suitable for use at high temperatures.\(^4\)

3.1.2. Rotation method. The viscosity of the fluid is determined by measuring the viscous moment of the fluid acting on the object or the rotational speed of the object. The advantage is that the test is easy to obtain, but the accuracy is low.

3.1.3. Vibration method. By supplementing the energy lost by the viscoelasticity of the vibrating object, the vibrating object maintains a constant vibration frequency and amplitude, and the viscosity value is calculated from the relationship between the replenished energy and the viscosity of the liquid. The vibration method has many measurement methods, and the commonly used ones are torsional vibration type measurement, including attenuated vibration type and strong vibration type.

3.1.4. New viscosity test method. In recent years, there have been methods for measuring the cantilever resonance frequency of an atomic stress microscope with the principle that it is immersed in different viscous medium, and there is also a method for measuring the viscosity value of the sealed
liquid by using ultrasonic technology. In order to prevent chemical or physical reaction between the sample to be tested and the contact surface of the container at high temperature, in 2009, Peng Qiang and other tests on the high-temperature viscosity of the ternary nitrate molten salt were studied, and the viscosity of the three pure substances was fitted and reused. The Arrhenius mixing rule was calculated for its high temperature viscosity. These new methods are highly accurate, require less measurement of the sample size, and have a better development prospect.\[^{[5]}\]

3.2. Thermal expansion coefficient.
The measurement principle of thermal expansion coefficient is basically the same. At present, it is mainly applied in the fields of metal materials, building materials and refractory materials. The standard GB/T 7320-2008 "Test method for thermal expansion of refractories" uses the ejector method and the differential method to test thermal expansion. The method of the coefficient. Most of the domestic refractory industry tests are carried out by the ejector method. The principle is to heat the sample to the specified test temperature at the specified heating rate, measure the change of the length of the sample with the increase of temperature, and calculate the line of the sample as the temperature rises. The expansion ratio and the average linear expansion coefficient of the specified temperature range. In foreign countries, NETZSCH, LINSEIS and other companies have developed a mature thermal expansion device, which has the advantages of simple operation and high precision.

3.3. Load softening temperature.
At present, there are two main methods for testing the softening temperature of refractory load in China: direct heating method and differential-temperature method (referred to as differential method). In recent years, the international refractory product standard has increasingly adopted the differential method, because the same product has the same load and deformation, the differential method results are lower than the direct temperature method.

In China's refractory load-softening temperature related standards, there are two test methods YB370-1995 "loading softening temperature test method" and GB 5989-2008 "dense shaped refractory product load softening temperature test method (differential-heating method)". As a reference for the high temperature heat storage material load softening temperature test.

4. Chemical properties
The chemical properties of the material can reflect its stability and safety to a certain extent, and it is reflected in the macroscopic adaptation and compatibility with the surrounding environment. The evaluation of the chemical properties of the thermal storage material mainly focuses on thermal stability, weather resistance, etc. On the indicator.

4.1. Thermal stability
It refers to the heat resistance of materials, which is reflected in the ability of materials to resist temperature fluctuations and their own chemical reactions in high temperature applications.

At present, the performance of the heat storage material before and after the cycle is generally examined through multiple cycles of thermal cycling, including phase transition temperature, latent heat of phase change, and degree of subcooling. The thermal stability properties of the samples can also be evaluated by the stability analysis method before and after the specific high temperature thermal cycle before and after the thermal properties, appearance, mass loss, composition and so on.\[^{[7-8]}\]

From the point of view of the practical application of high temperature heat storage materials, thermal stability analysis can be evaluated in the following ways:

1) DSC analysis of trace phase change heat storage materials; 2) mass loss rate curve analysis; 3) thermal cycle storage and release heat analysis; 4) composition changes before and after continuous high temperature and thermal cycling.
4.2. Weather resistance
Weather resistance refers to the ability of materials to resist external environmental conditions and maintain the original properties of materials when used in outdoor environments. Moisture, weathering and light exposure are the main causes of material aging.

At present, there is no specific test standard for the evaluation of weather resistance of heat storage materials, mainly in the fields of exterior wall coatings, tires, textiles and the like.

Regarding the test methods for aging resistance or weather resistance of textiles, some standards have been developed at home and abroad, such as ISO 1419-1995, AATCC 186-2009, FZ/T 01008-2008, etc. The overall can be divided into two categories: 1) direct aging test in the natural environment; 2) artificial accelerated aging by heating, humidification, lighting, etc., mainly in the future.

The function and practical application of high-temperature heat storage materials are different from those of textiles and coatings. When evaluating the weather resistance, the characteristics of the materials themselves and the application environment should be considered first, but the test methods are basically the same as textiles and coatings.

5. Conclusion
With the increasing application temperature of thermal storage materials, the classical methods for testing and evaluating the performance of thermal storage materials are facing challenges. It is necessary to systematically comb and study the test methods and test procedures for various properties of materials under high temperature conditions.

Through the specification of the material performance evaluation technology, not only can each evaluation data be rationally made, and the research and test system for heat storage materials is more perfect, but it is also conducive to the long-term development of heat storage materials and has significance for the development of heat storage technology major.

Acknowledgement
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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