GOCE DELCEV UNIVERSITY, STIP, NORTH MACEDONIA
FACULTY OF ELECTRICAL ENGINEERING

ETIMA 2023

SECOND INTERNATIONAL CONFERENCE

27-29 SEPTEMBER, 2023

TECHNICAL SCIENCES APPLIED IN ECONOMY, EDUCATION AND INDUSTRY

ЕЛЕКТРОТЕХНИЧКИ ФАКУЛТЕТ,
УНИВЕРЗИТЕТ „ГОЦЕ ДЕЛЧЕВ", ШТИП, СЕВЕРНА МАКЕДОНИЈА

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GOCE DELCEV UNIVERSITY, STIP, NORTH MACEDONIA

ВТОРА МЕЃУНАРОДНА КОНФЕРЕНЦИЈА
SECOND INTERNATIONAL CONFERENCE

ЕТИМА / ETIMA 2023

ЗБОРНИК НА ТРУДОВИ
CONFERENCE PROCEEDINGS

27-29 септември 2023 | 27-29 September 2023

ISBN: 978-608-277-040-6

DOI: **https://www.doi.org/10.46763/ETIMA2321**

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CIP - Каталогизација во публикација Национална и универзитетска библиотека "Св. Климент Охридски", Скопје

62-049.8(062)
004-049.8(062)

МЕЃУНАРОДНА конференција ЕТИМА (2 ; 2023)
Зборник на трудови [Електронски извор] / Втора меѓународна конференција ЕТИМА 2023, 27-29 септември 2023 = Conference proceedings / Second international conference, 27-29 September 2023 ; главен и одговорен уредник Сашо Гелев]. - Штип : Универзитет "Гоце Делчев", Електротехнички факултет ; Stip : "Goce Delcev" University, Faculty of Electrical engineering, 2024

Начин на пристапување (URL): https://www.doi.org/10.46763/ETIMA2321. - Текст во PDF формат, содржи 200 стр.илустр. - Наслов преземен од екранот. - Опис на изворот на ден 25.03.2024. - Трудови на мак. и англ. јазик. - Библиографија кон трудовите. - Содржи и: Appendix

ISBN 978-608-277-040-6

а) Електротехника -- Примена -- Собири б) Машинство -- Примена -- Собири в) Автоматика -- Примена -- Собири г) Инфоматика -- Примена – Собири

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PREFACE

The Faculty of Electrical Engineering at University Goce Delcev (UGD), has organized the Second International Conference ***Electrical Engineering, Informatics, Machinery and Automation - Technical Sciences applied in Economy, Education and Industry-ETIMA*.**
ETIMA has a goal to gather the scientists, professors, experts, and professionals from the field of technical sciences in one place as a forum for exchanging the ideas, strengthening the multidisciplinary research and cooperation, and promoting the achievements of technology and its impact on every aspect of living. We hope that this conference will continue to be a venue for presenting the latest research results and developments on the field of technology.
Conference ETIMA was held as online conference. More than sixty colleagues contributed to this event, from five different countries with more than thirty papers.
We would like to express our gratitude to all the colleagues, who contributed to the success of ETIMA'23 by presenting the results of their current research and by launching the new ideas through many fruitful discussions.
We invite you and your colleague to attend ETIMA Conference in the future as well. One should believe that next time we will have opportunity to meet each other and exchange ideas, scientific knowledge and useful information as well as to involve as much as possible the young researchers into this scientific event.

The Organizing Committee of the Conference

ПРЕДГОВОР

Меѓународната конференција ***Електротехника, Технологија, Информатика, Машинство и Автоматика-технички науки во служба на економија, образование и индустрија-ЕТИМА*** е организирана од страна на Електротехничкиот факултет при Универзитетот „Гоце Делчев“.
ЕТИМА има за цел да ги собере на едно место научниците, професорите, експертите и професионалците од полето на техничките науки и да претставува форум за размена на идеи, да го зајканува мултидисциплинарното истражување и соработка и да ги промовира технолошките достигнувања и нивното влијание врз секој аспект од живеењето. Се надеваме дека оваа конференција ќе продолжи да биде настан на кој ќе се презентираат најновите резултати од истражувањата и развојот на полето на технологијата.
Конференцијата ЕТИМА се одржа online и на неа дадоа свој придонес повеќе од шеесет автори од пет различни земји со повеќе од триесет труда.
Сакаме да ја искажеме нашата благодарност до сите колеги кои придонесоа за успехот на ЕТИМА'23 со презентирање на резултати од нивните тековни истражувања и со лансирање на нови идеи преку многу плодни дискусии.

Организационен одбор на конференцијата

СОДРЖИНА / TABLE OF CONTENTS:

UDC: 662.997-97:546.33'131-143]:620.92
https://www.doi.org/10.46763/ETIMA2321100st

MOLTEN SALT THERMAL ENERGY STORAGE FOR RENEWABLE ENERGY: SYSTEM DESIGN, MATERIALS, AND PERFORMANCE

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Abstract

This research paper thoroughly examines the fundamental principles and design concepts of molten salt thermal energy storage systems, focusing on the critical role of materials selection in choosing the appropriate material for the application. We also discuss the basic design components of these systems when integrated with renewable technology and classify practical systems by their applications.
Based on our analysis, we conclude that solar technologies with molten salt storage systems are particularly promising for practical implementation, and the two-reservoir type system utilizing the sensible heat storage method of molten salt is regarded as the most commercially viable and mature electrothermal storage system available. Solar salt is also considered the best choice for these systems due to its low cost and high energy density. The idea of retrofitting fossil fuel plants with molten salt storage systems is also mentioned. Overall, molten salt thermal energy storage systems have the potential to play a crucial role in future energy systems, and further research and development in this field is essential for maximizing the potential of these systems and achieving a sustainable energy future.

Keywords:

molten salt, thermal energy storage, two-tank sensible heat storage, design concept, material selection, performance evaluation

1. Introduction

As a promising solution for the integration of renewable energy sources into the power grid, molten salt thermal energy storage systems have been of interest to scientists and energy experts alike. In the energy industry, the intermittent nature of renewable energy sources, such as solar and wind power, is a major challenge. This challenge can be overcome by storing excess renewable energy generated during peak periods in molten salt thermal energy storage systems and use it when demand is high. This topic of research has become a crucial issue in recent years as societies worldwide seek to reduce their reliance on fossil fuels.

Molten salt storage systems are a type of thermal energy storage system that utilizes a mixture of salts as the storage medium to store thermal energy at high temperatures. These systems offer several benefits, including high energy density, cost-effective, and non-toxic behavior. They are also highly scalable, making them an excellent option for large-scale renewable energy projects. Additionally, due to their high temperature range and compatibility, molten salt storage systems are an excellent candidate for use with a wide range of solar energy technologies, including concentrated solar power, solar photovoltaics (PV), and hybrid solar thermal electric and PV plants with thermal storage [1] - [6], [8] – [10], [13] – [16], [21]. The use of molten salt thermal energy storage systems enables the electrothermal storage of large amounts of energy ranging from megawatts to gigawatts in the energy industry. At present, the two-reservoir type system utilizing the sensible heat storage method of molten salt is regarded as the most commercially viable and mature electrothermal storage system available. This concept of thermal energy storage systems that utilize solar energy, depending on the specific solar technology used, the working fluid – heat transfer fluid (HTF) can be molten salt, synthetic oil, water, or steam [4]. In some solar thermal power plants, such as those that use parabolic trough technology, synthetic oil or steam is used as HTF, while in solar tower technology, molten salt is used both as the storage medium and the working fluid (air and steam can also be used as working fluids). In others, such as those that use linear Fresnel technology, steam is used as the working fluid to generate electricity.

The purpose of this paper is to examine the topic of molten salt thermal energy storage for renewable energy, focusing on system design, materials, and performance. We will begin by reviewing the current state of the field and highlighting some of the key challenges and opportunities of these systems. Then, we will discuss molten salt systems in detail, describing their design principles, materials properties, and performance characteristics. In addition, we will explore the factors that influence heat transfer, thermal stability and corrosion resistance. Lastly, the paper will discuss potential future developments in molten salt thermal energy storage systems and their implications for renewable energy.

2. Fundamental Principles

Molten Salt Thermal Energy Storage (MSTES) has emerged as a prominent technology for storing thermal energy derived from renewable energy sources, particularly wind and solar power. The essence of MSTES lies in harnessing the superior heat storage and transfer properties of molten salts, which exhibit an exceptionally high specific heat capacity, enabling them to absorb and dissipate significant quantities of heat while undergoing only minimal temperature fluctuations.

MSTES systems are composed of several key components, including a storage tank, heat exchangers, and a fluid circulation system [3]. During the charging phase, MSTES systems utilizes renewable energy to heat the molten salt in the storage tank. Subsequently, the heated molten salt is transported through heat exchangers, where it transfers heat to a HTF such as water or steam (or other HTF as described previously). This HTF can then be utilized to produce electricity or stored for future use. The discharging phase involves the reverse process, where the HTF is utilized to heat the molten salt, which is then conveyed back to the storage tank [5].

The effectiveness of MSTES systems is influenced by several factors, including the selection of the molten salt, the design of the storage tank and heat exchangers, and the efficiency of the HTF. Among these factors, the thermal characteristics of the molten salt play a crucial role in determining the operating temperature range and the amount of heat that can be stored. The selection of an appropriate molten salt is a critical factor in achieving high efficiency and long-term durability. Factors that must be considered during the selection process include the molten salt's melting point, specific heat capacity, thermal conductivity and corrosiveness [6]. These properties play a crucial role in determining the overall performance of the MSTES system. Furthermore, to achieve optimal performance, it is imperative to design the storage tank and heat exchangers with careful consideration of the heat transfer efficiency and heat loss minimization. A well-designed system can enhance the transfer of heat between the molten salt and the heat exchangers, leading to improved overall efficiency. It is worth noting that the choice of the HTF fluid is an equally critical aspect that cannot be overlooked in the design of MSTES systems. The fluid should exhibit high heat transfer coefficient and low viscosity to facilitate efficient heat transfer between the molten salt and the heat exchangers. By doing so, it is possible to achieve optimal heat transfer performance and maximize the efficiency of the MSTES system.

The selection of appropriate materials is a factor of vital importance that plays a significant role in the design of MSTES systems. It is essential to choose materials that can withstand the high temperatures and corrosive nature of molten salts to ensure the long-term durability and reliability of the system. When selecting materials for the construction of the storage tank and heat exchangers, several factors must be considered, such as thermal stability, corrosion resistance and mechanical strength. Carbon steel, stainless steel, and nickel alloys are some of the materials that have been used in MSTES systems due to their ability to withstand high temperatures and resist corrosion [7]. In addition to material selection, it is also crucial to consider the design of the storage tank and heat exchangers. Proper design can further enhance the durability of the materials by minimizing exposure to corrosive molten salts and optimizing heat transfer efficiency. Overall, material selection is a critical aspect of designing MSTES systems, and careful consideration must be given to ensure the long-term performance and reliability of the system.

While there have been significant advancements in the development of MSTES systems, ongoing research is necessary to address the challenges associated with these systems and identify opportunities for further improvements, ultimately supporting the transition to a more sustainable energy future.

3. The Design Concept of Molten Salt Thermal Energy Storage Systems with Optimal Performance and Durability: The Critical Role of Materials Selection in Choosing the Appropriate Material for the Application

In addition to the concept of storage [8] (Fig. 1), the classification of high-temperature MSTES systems is an important consideration in the design of energy storage systems. These systems can be classified as either active or passive, depending on their mode of operation. Active systems involve the use of external energy inputs to maintain the desired storage temperature, while passive systems rely on the inherent thermal properties of the storage material to maintain the desired temperature. High-temperature MSTES systems can also be classified as direct or indirect, depending on the nature of the heat transfer process. In direct systems, the storage material is in direct contact with the HTF, while in indirect systems, the HTF is separated from the storage material by a heat exchanger. High-temperature thermal storage systems (direct and indirect systems), including molten salt storage systems and concentrated solar power (CSP) technologies are illustrated in Fig. 3 (a) and (b).

MSTES systems are designed to operate in different modes depending on the energy requirements and availability of the system. These systems consist of primary and secondary charge and discharge cycle subsystems, which work in tandem to provide the energy storage capacity of the system. An example is given for the concentrated solar technology. During charging, energy is transferred from the solar receiver (or other solar, and wind technology) to the hot storage tank, while during discharge, energy is extracted from the hot storage tank and transferred to the power block for conversion to electricity. The system is designed to maintain a constant temperature in the hot storage tank, which is achieved by recirculating the molten salt through a heat exchanger. The system also includes a cold storage tank, which stores the cooled molten salt until it is needed for the next charging cycle. The entire process is illustrated in Fig. 2 and is further described below.

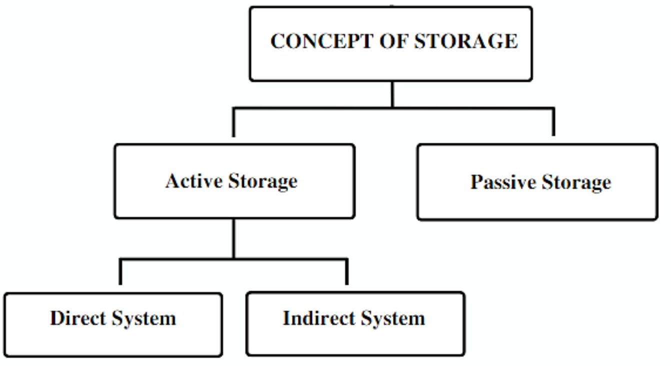

Fig. 1. Classification of storage concept for MSTES systems

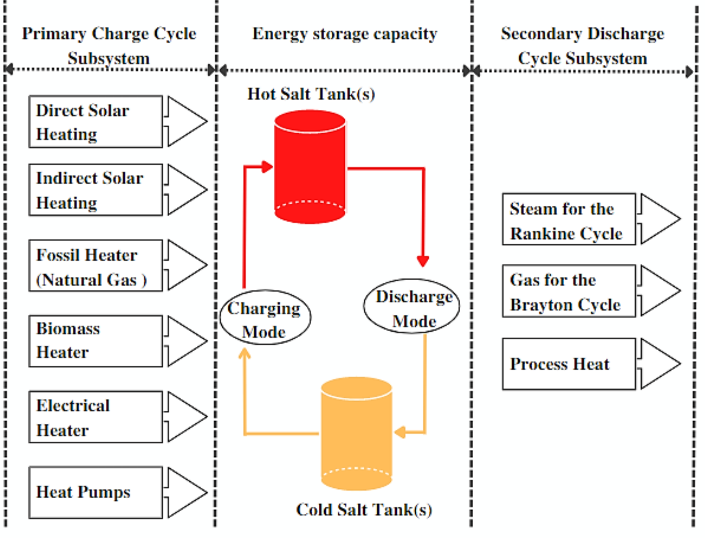

Fig. 2. Construction of subsystems for energy storage and operational mode utilizing MSTES systems

As shown in Fig. 2, MSTES systems are characterized by three modes of operation: charge, storage (standby) and discharge. Carnot batteries [11], [14] is a term commonly used to describe the three operating modes of molten salt energy storage systems.

1. **Charge mode**: during the charge mode, heat is transferred to the molten salt, usually through direct solar heating or indirect heating through thermal oil or steam (or through the other forms listed in the Fig. 3), raising the temperature of the salt and storing heat energy.
2. **Storage mode**: after the molten salt is heated, it is stored in a thermal capacity, a hot tank where it can be kept at a high temperature until it is needed for later use (generation of electricity).
3. **Discharge mode**: When the stored thermal energy is needed, the salt is pumped from the hot reservoir to a cold reservoir and passes through a heat exchanger, transferring the thermal energy to a secondary fluid, such as water, which generates steam and drives the turbine for electricity production.

The third segment of the secondary discharge cycle subsystem in a molten salt energy storage system typically includes a combined thermodynamic cycle that utilizes both the Rankine and Brayton cycles.These two thermodynamic cycles are used to produce electricity supported by heat to energy reconversion processes.

When renewable energy is available, it can be used to power electric heaters, which transfer the salt's energy into heat by a process known as energy-to-heat conversion. When energy is needed, the heat stored in the salt can be used to generate electricity through the Rankine cycle. It allows the thermal energy stored in the salt to be converted back into electrical energy by reconversion during discharge operation mode.

On the other hand, the reconversion of heat into energy during discharge operation mode is also performed by the Brayton cycle with a closed loop that uses gas under pressure (air as the working fluid). This reconversion process follows the energy to heat conversion process with the use of high temperature heat pumps for efficient conversion of renewable energy to heat in the molten salt in charge mode operation.

Molten salt is a desirable option for sensible heat storage material in high-temperature (>100°C) thermal applications [12]. Its advantages make it a potential candidate for integration into thermal systems together with technologies that are commercial, mature (e.g., CSP, PV) and used to serve services at the power grid level. For a more comprehensive discussion of the thermophysical properties of molten salts as a heat storage media and HTF, further details can be found in [13].

Different types of molten salts that are used are: nitrates, chlorides, carbonates, fluorides, etc. These different types of salts have special properties that make them suitable for specific system designs. Table 1 summarizes some of the important features with an overview of the specific properties and cost of several selected molten salt mixtures. More properties can be found in the literature [14] – [17].

Table 1 Molten salts for high-temperature applications of thermal storage systems

Acronym	Molten Salt Composition [wt%]	T_m [°C]	T_{max} [°C]	C_p [$Jg^{-1} K^{-1}$]	ρ [g cm^{-3}]	T_{stab} [°C]	Cost ($ kg^{-1})
Solar Salt	KNO3 – NaNO3 (40-60)	220-240	530-565	1.55 [400°C]	~1.84 [400°C]	600	0.5
Hitec	KNO3 – NaNO2 – NaNO3 (53-40-7)	142	450-540	1.54 [400°C]	1.79 [400°C]	535	0.73
HitecXL	Ca (NaNO3)2 – KNO3 – NaNO3 (42-43-15)	130-140	460-500	1.43 [400°C]	1.91 [400°C]	/	1.19
LiNaK carbonates	Li2CO3 – Na2CO3 – K2CO3 (32-33-35)	397	>650	1.85 [700°C]	1.98 [700°C]	800-850	2.5
LiNaK fluorides	KF– LiF– NaF (59-29-12)	454	>700	1.89 [700°C]	2.02 [700°C]	>700	>2
ZnNaK chlorides	ZnCl2 – NaCl – KCl (68.6-7.5-23.9)	204	>700	0.8 [300-600°C]	2.02 [600°C]	850	0.8
MgNaK chlorides	MgCl2 – NaCl – KCl (68.2-14.0-17.8)	380	800	~1.84 [500-800°C]	~1.84 [600°C]	>800	<0.35

Source: Data are based on literature [14] – [17]

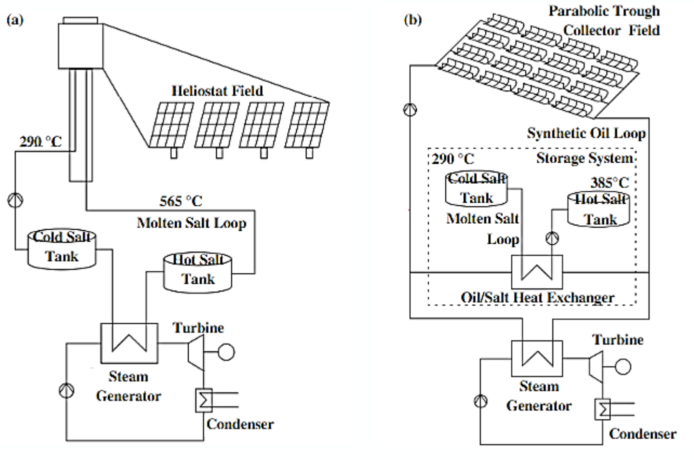

Fig. 3. This schematic illustration displays examples of direct and indirect storage in solar thermal systems that incorporate CSP technology. The direct system depicted in (a) uses molten salt as both the transfer and storage medium, with a solar field comprising heliostats focused on a solar tower. In contrast, the indirect system illustrated in (b) utilizes synthetic thermal oil as the HTF and molten salt as the storage medium. The solar field in this system is composed of parabolic collectors.
Image data has been modified accordingly [9], [10]

The temperature range of the various molten salt compositions (Table 1) shows different temperatures that define the limits of their use. These limits are defined as the melting temperature T_m and the maximum operating temperature T_{max}. The melting temperature for selected molten salts varies from 130-454 °C, depending significantly on the type of anion and cation composition [3]. The T_{max} value is the maximum temperature at which the molten salt composition can withstand certain conditions such as thermal decomposition, high vapor pressure or high corrosion rate [15]. The table also shows values of heat capacity C_p and density ρ, and their product is equal to the volumetric heat capacity which determines the size of the sensible heat storage system. The volumetric heat capacity $C_p \cdot \rho$ varies with values from 2.9 to 3.8 J cm^{-3} K^{-1}, which are important as a characteristic for the transfer heat fluid. The last value in the table is the material price, which is expressed in dollars kg^{-1}, which together with the heat capacity and the temperature difference between charging and discharging $\triangle T$, constitute the specific material investment cost (dollars kWh^{-1}).

A molten salt mixture consisting of 60% by weight of sodium nitrate ($NaNO_3$) and 40% by weight of potassium nitrate (KNO_3), also known as solar salt or nitrate salt [2] – [6], [9], [10], [12], [14] – [17] has emerged as a practical and proven choice especially for solar thermal energy storage systems. Solar salt boasts a low cost and excellent thermal performance, making it an attractive option for thermal applications that use both direct and indirect storage systems, with particular attention to CSP and PV technologies. This molten salt mixture has a melting point in the range of 220-240 °C, depending on the measurement conditions with a temperature stability of ~560 °C.

3.1 Basic Design Components of Molten Salt Thermal Energy Storage Systems Integrated with Renewable Technology

Example Table 2 outlines the main components and description for a MSTES.

Table 2 Main and basic components of a molten salt thermal energy storage system

Component	Description
Storage Tank	Central component of the storage system. Material: Stainless steel (or are lined with insulating materials to minimize heat loss). It is important to follow typical design standards such as API. For cold storage tanks, carbon steel (ASTM A-516 Gr.70) is commonly used, while stainless steel (ASTM A-347H or ASTM A-321H) is used for hot tanks that need to withstand higher operating temperatures [14].
Heat Exchangers	Transfers heat between the molten salt and other components of the thermal energy system. Materials such as nickel alloys or ceramics are often used for this purpose [18].
Pumps	Responsible for circulating the molten salt through the system to transfer heat and store energy. There are typically two types of pumps used in a molten salt storage system. - Charge pumps: These pumps are used to fill the storage tank with molten salt at the beginning of a storage cycle [14]. They are typically centrifugal pumps [19] and are designed to handle the high temperatures and corrosive nature of molten salt. - Circulation pumps [20]: Circulation pumps are utilized to move the molten salt through the system during charging and discharging cycles when the storage tank is filled. These pumps are typically positive displacement pumps and are designed to manage high temperatures and flow rates. Materials such as stainless steel or nickel alloys are typically used for the pumps, and they must be designed to prevent leakage and minimize the risk of corrosion.
Insolation System	Reduces heat loss from the thermal energy storage tank and prevents the molten salt from solidifying. The isolation system typically consists of insulation materials, valves, and expansion joints. Insulation materials such as ceramic fiber or mineral wool are commonly used in molten salt storage systems [21].
Freeze Protection System	The freezing protection system in a molten salt storage tank is crucial to maintain the temperature of the salt above its melting point, which is typically around 220°C to 260°C, depending on the composition of the salt mixture. Below this temperature, the salt can freeze and cause blockages in the system, which can damage the equipment and affect the performance of the molten salt system [14].
Generator Unit	The generator unit is a critical component of a molten salt storage system because it allows the stored thermal energy to be converted into a usable form of energy that can be dispatched to the grid as needed. The generator unit typically consists of a heat exchanger, a turbine, and a generator. The heat exchanger is used to transfer the heat from the molten salt to a working fluid, such as water or steam. The working fluid is then used to drive a turbine, which in turn drives a generator to produce electricity.

In the design and implementation of a molten salt storage system integrated with renewable technology, it is crucial to ensure that the system components and specifications are tailored to the specific needs and requirements of the project. While the main components outlined in the table provide a general guideline, the unique conditions and constraints of each project may require modifications or alternative solutions. To ensure the success of the project, it is recommended to consult with a professional engineer or contractor with expertise in molten salt thermal energy storage systems. This will help to ensure that the system is designed and installed correctly, and that any potential issues or challenges are identified and addressed early in the process.

4. Applications of Molten Salt Thermal Energy Storage Systems for Various Power System Applications and Classification of Practical Systems

The key characteristics highlighted in Table 3 provide a detailed framework for assessing the capabilities and limitations of molten salt storage systems, considering factors such as power output, cycle life and response time. These metrics are essential for understanding the performance of these systems in various contexts, and for optimizing their design and operation to meet specific application requirements.

Table 3 Key characteristics of molten salt thermal systems for power system applications

Application	Power [MW]	Discharge Time	Cycles [daily]	Response Time
Energy Management	>100	hours to days	0.14 - 0.7	minutes
Support of Renewable Energy Sources	<100 and above	hours	0.5 - 2	minutes
Investment Deferral	~10 - 500	2 – 5 hours	0.75 - 1.25	hours
Black Start	0.1 - 400	hours	< 1 per year	< 1 hour
Load Following	1 – 2,000	15 minutes to 1 day	1 - 29	< 15 minutes
Spinning Reserve/Non-Spinning Reserve	10 – 2,000	15 minutes to 2 hours	0.5 - 2	< 15 minutes
Waste Heat Utilization	1 – 10	12 hours to 1 day	1 - 20	< 10 minutes
Combined Heat and Power	1 - 5	minutes to hours	1 - 10	< 15 minutes

Thermal energy storage systems using molten salt can be classified into several types according to their practical applications [1] – [6], [8] – [10], [13] – [16], [21]. MSTES systems are classified as follows:

- Molten salt thermal energy storage systems with thermal electric parabolic trough collectors.

- Molten salt thermal energy storage systems with thermal electric solar receivers.
- Molten salt thermal energy storage systems with hybrid solar thermal electric and PV plants.
- Systems for pumped-thermal energy storage in molten salt.
- Molten salt thermal energy storage systems for conversion of fossil fuel power plants.

5. Conclusion

In conclusion, molten salt thermal energy storage systems are emerging as a promising solution for renewable energy integration and electrification. With the critical role of materials selection and system design, these systems can achieve optimal performance and durability in various power system applications. The fundamental principles of these systems are based on the unique properties of molten salt, which enable low cost, high energy density, thermal stability, and efficient heat transfer. The design concept of these systems must carefully consider the materials selection, system integration with renewable technology, and practical implementation of different types of systems. Solar technologies with molten salt storage systems are particularly promising for practical implementation, while retrofitting fossil fuel plants can further accelerate the transition to a sustainable energy future. Based on current research and industry trends, the two-reservoir type system with sensible heat storage method using solar salt is currently the most commercially available and mature electrothermal storage system, and it is expected to play a key role in future energy systems.

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