

STUDY OF HOT CORROSION BEHAVIOR OF INCONEL 625 WITH MOLTEN SALTS IN AN AGGRESSIVE ENVIRONMENT

Submitted in partial fulfilment of the requirements
for the award of
Bachelor of Engineering degree in Mechanical Engineering

by

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SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

Accredited with Grade "A" by NAAC I
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **N. ARUNKUMAR (37150021), P. VENKTESAN (37150209)** who carried out the project entitled **"STUDY OF HOT CORROSION BEHAVIOR OF INCONEL 625 WITH MOLTEN SALTS IN AN AGGRESSIVE ENVIRONMENT"** under our supervision from November 2020 to March 2021.

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We **N. ARUNKUMAR (37150021), P. VENKATESAN (37150209)** hereby declare that the Project Report entitled “**STUDY OF HOT CORROSION BEHAVIOR OF INCONEL 625 WITH MOLTEN SALTS IN AN AGGRESSIVE ENVIRONMENT**” done by me under the guidance of Dr. M. SANGEETHA M.E., Ph.D., is submitted in partial fulfillment of the requirements for the award of Bachelor of Engineering degree In Mechanical Engineering

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ABSTRACT

Inconel 625 is the nickel based super alloys with outstanding resistance to high temperatures and oxidation., Inconel 625 is having the material properties as pitting and crevice corrosion resistance, high corrosion- fatigue strength, high tensile strength, and resistance to chloride-ion stress- corrosion cracking. A eutectic mixture of 7:3, Sodium and potassium chloride having the melting & boiling point as 7700C and 14200 C is used with Inconel 625 in this study. These salts have been used in Concentrated Solar Power (CSP) technology as thermal energy storage applications. In this work Inconel 625 stored with sodium & K chloride molten salts are heated with an aggressive temperature environment approximately 9000C. The experimental work was performed for 25 hours of time period and the hot corrosion behaviour of Inconel 625 heated to very high temperature environment was studied. The mechanical tests such as tensile and hardness tests were performed for the super alloy specimens and the results were compared. Metallurgical Characterization of the base substrates have been investigated with Porosity images, X - ray Diffraction results and Scanning Electron Microscope images.

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CHAPTER 1

INTRODUCTION

Solar energy at a high the sensible heat of molten salt is used for storing temperature. It is termed as molten-salt technology or molten-salt energy storage (MSES) This is a commercially used technology to store the heat collected by concentrated solar power (e.g., from a solar tower or solar trough). The heat can later be converted into superheated steam to power conventional steam turbines and generate electricity in bad weather or at night. Molten salts have high boiling points, low viscosity, low vapour pressure, and high volumetric heat capacities.

1.1 COMMERCIALLY AVAILABLE MOLTEN SALTS USED IN SOLAR PLANTS

- Chlorides of Sodium, Zinc, Pottasium & Beryllium
- Nitrates of Sodium & Pottasium,
- Fluorides of Lithium & Pottasium
- Sulphates of Sodium & Pottasium

1.2 THERMAL ENERGY STORAGE

The latent heat thermal energy storage has been investigated by numerous researchers as an energy-dense and lower cost alternative to the two-tank molten salt sensible heat thermal energy storage for concentrated solar power plants. However, in order to achieve a high storage efficiency without decreasing the efficiency of the receiver and power block, many design restrictions should be applied in the design, including the total storage capacity, charging/discharging rate, charging /discharging period and the temperature difference of heat transfer fluid between the inlet and outlet of the storage system for both the charging and discharging process. There is no methodology or guideline currently available in the literature to design such a storage system

Therefore, a new methodology has been proposed, and it was successfully demonstrated in a case study. To achieve the final design, three major steps are involved: preliminary design, coarse optimization and fine optimization. Though intensive simulation is needed, the proposed methodology is appropriate to design the cascade latent heat thermal energy storage system.

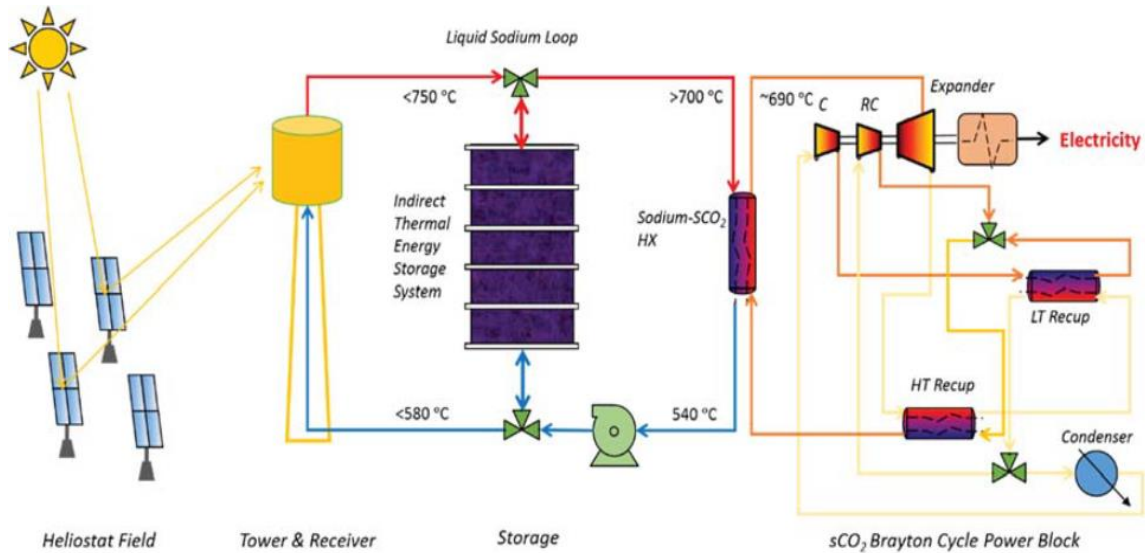


Fig :1 Thermal energy storage

1.3 TYPES OF THERMAL ENERGY STORAGE

Thermal energy storage (TES) systems can store heat or cold to be used later, under varying conditions such as temperature, place or power. TES systems are divided in three types:

- sensible heat,
- latent heat,
- Thermochemical.

Sensible heat storage systems utilize the heat capacity and the change in temperature of the material during the process of charging or discharging - temperature of the storage material rise when energy is absorbed and drops when energy is withdrawn.

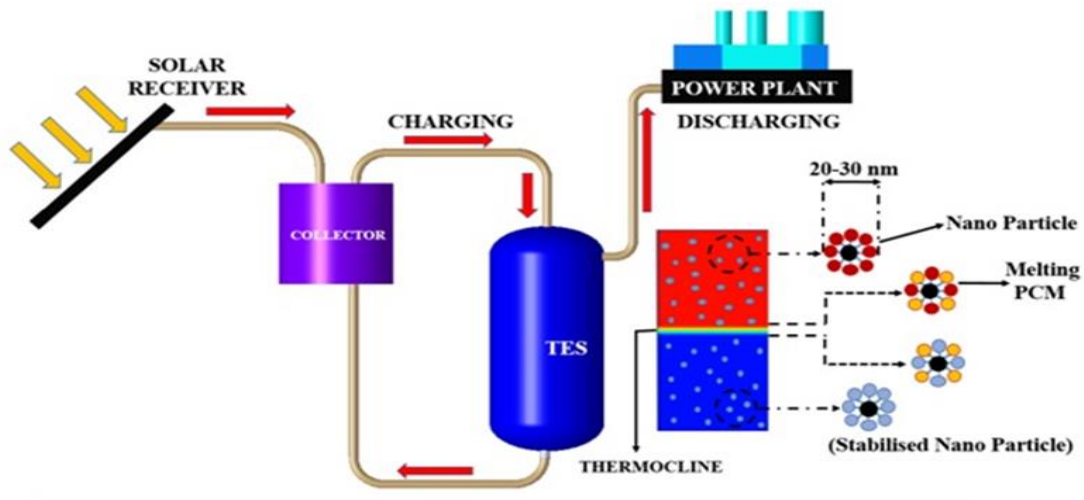


Fig: 2 Sensible heat thermal energy storage

Latent heat storage uses the phase transition of a material. Usually solid–liquid phase change is used, by melting and solidification of a material. Upon melting heat is transferred to the material, storing large amounts of heat at constant temperature; the heat is released when the material solidifies.

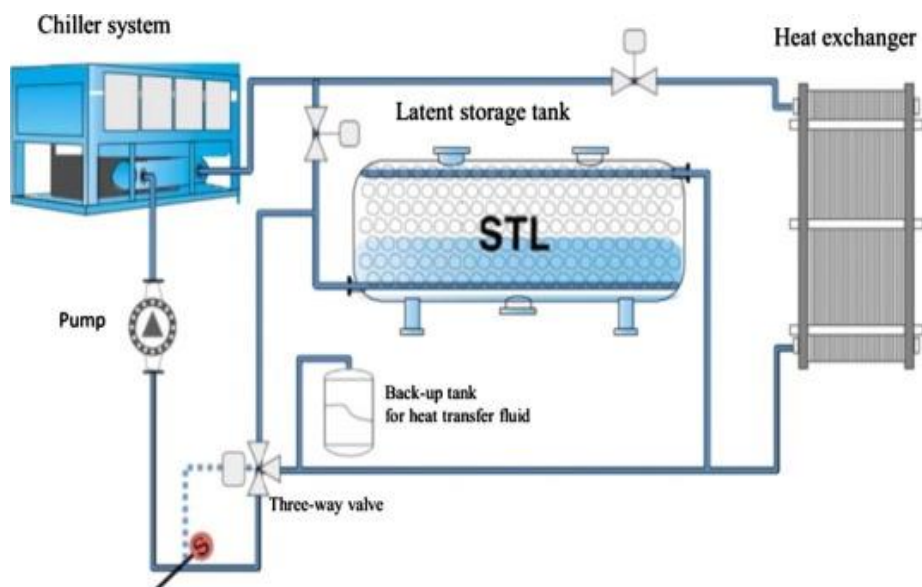


Fig:3 Latent heat thermal energy storage

Thermal energy from the sun can be stored as chemical energy in a process called solar thermochemical energy storage (TCES).

The thermal energy is used to drive a reversible endothermic chemical reaction, storing the energy as chemical potential. ... It also reduces the cost of solar energy through higher utilization

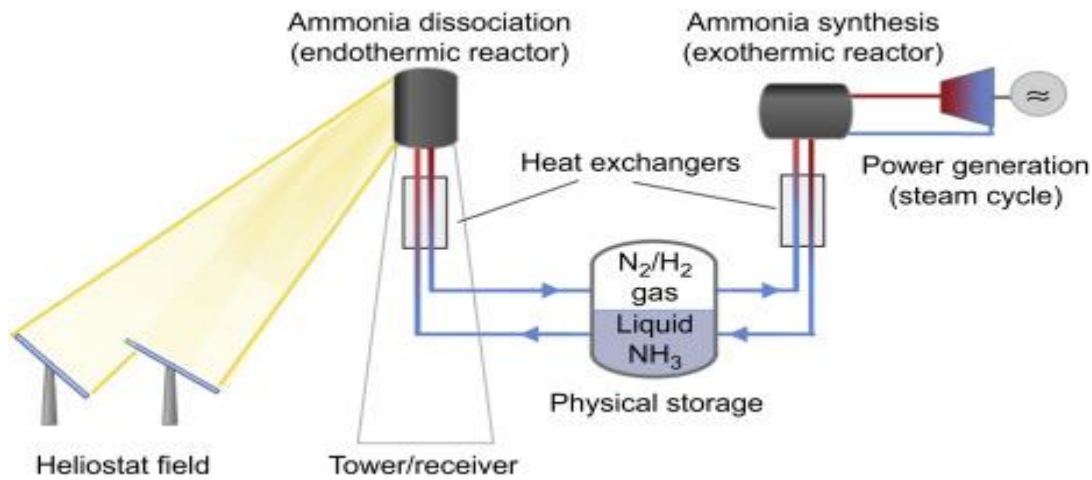


Fig:4 Thermochemical heat energy storage

1.4 CONCENTRATED SOLAR POWER

Concentrated solar power (CSP) technologies have been encouraged by many countries as solar energy is clean and renewable. However, one of its drawbacks is the intermittence of the solar resource. A thermal energy storage (TES) system solves the time mismatch between the solar energy supply and the electricity peak demand. The state-of-the-art TES technology for the current CSP plant is the two-tank molten salt sensible TES and its maximum applicable temperature is 565 °C. The supercritical carbon dioxide (sCO₂) Brayton cycle, having a higher thermal-to electricity efficiency (~50 %) when operating at elevated temperatures of around 700 °C, has been identified as an alternative to the steam Rankine power cycle for the power block. Latent heat storage using phase change materials (PCMs) is very promising for the next generation Brayton cycle CSP plants¹ since this cycle requires a narrower operating temperature range (for example 170 °C).

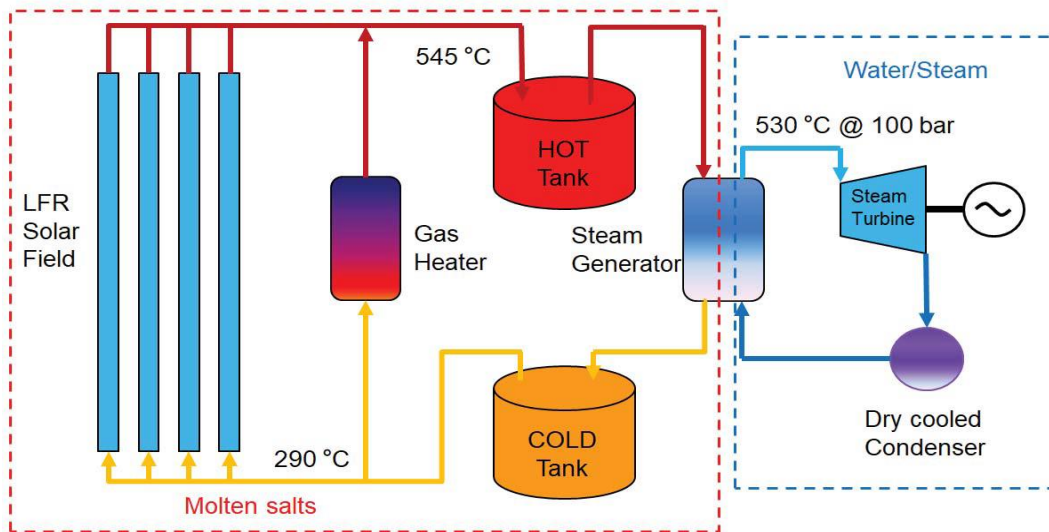


Fig:5 Concentrated Solar power Plants

A ternary molten chloride has been suggested as a high temperature (550-720 °C) sensible heat storage medium for a two-tank system. An effective thermal insulation is proposed to provide an opportunity for the fabrication of both the hot and cold storage tanks from lower cost metals, e.g. A240-347H, by maintaining the tank wall below 500 °C. To achieve this, the hot storage tank mainly comprises of inner shell (11.4 cm of a refractory brick as liner (KX-99□), 30 cm of insulation brick) and outer metal shell, where 5 cm of frozen layer of PCM800 (NaCl), and 5 cm of ceramic wool fill the annular space between the shells. Another layer of ceramic wool was introduced at the outer side of the metal shell to keep the temperature lower than 60 °C. ANSYS Fluent was used for the numerical study of the cool down behaviour of the system during idle period when tank is quarter-filled. The heat transfer modes were considered as radiation and natural convection heat transfer from the hot molten salt at 720 °C, conduction through the solid layers and convection heat transfer from the outer shell to the environment at 15 °C.

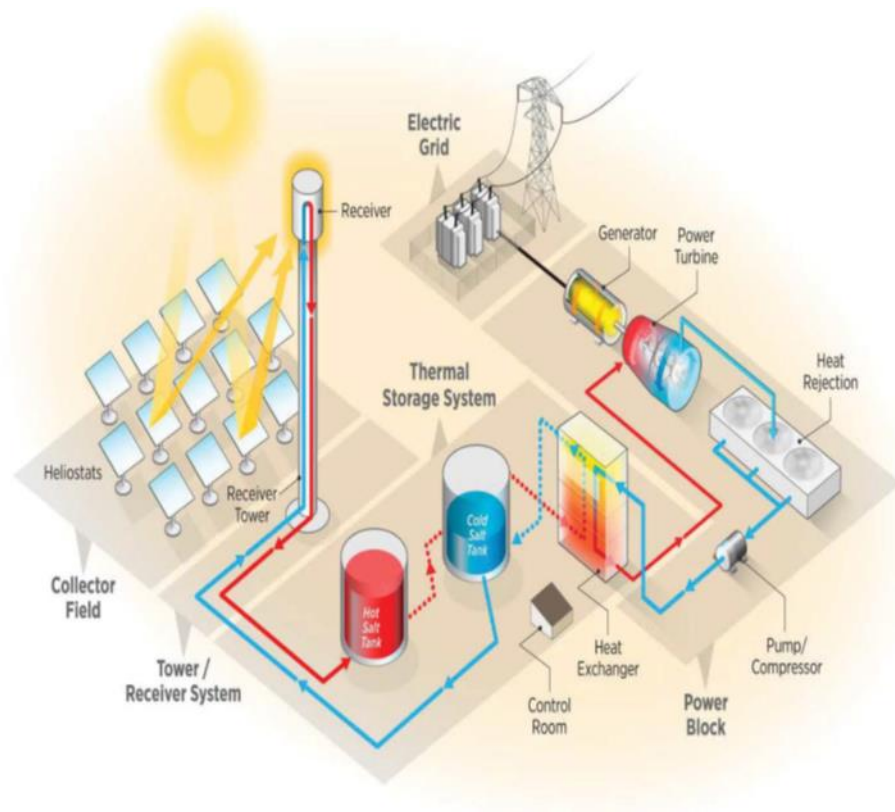


Fig: 6 Concentrating tower solar plants

1.5 MOLTEN SALT



Fig: 7 Sodium Nitrate

Molten Salts are nowadays the preferred choice to store thermal energy in CSP plants, either using MS Power Towers and “direct” storage or using parabolic troughs with MS “indirect” storage, employing thermal oil as Heat Transfer Fluid in the solar field.

The use of Molten Salts as Heat Transfer Fluid with “direct” storage in linear parabolic troughs has been proposed and studied since 2000. Starting in 2001, ENEA fully developed such concept in its “Solar Thermodynamic” project. Such effort led to the construction of full size 100 m. test plant in 2003 at the ENEA Test Field, and to a 5 MW demonstrative unit by the Italian Utility ENEL commissioned in 2010.

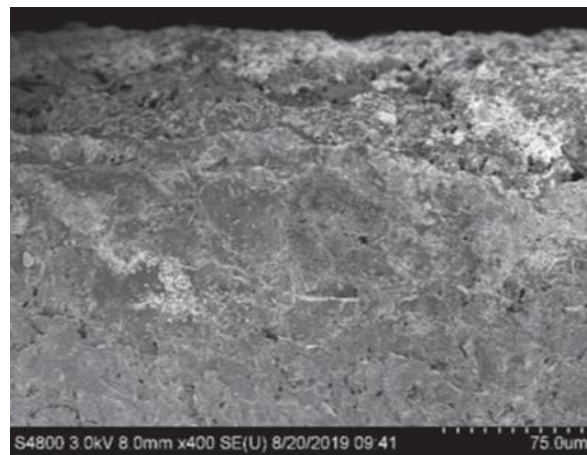


Fig:8 Molten Salt SEM images

As the Linear Fresnel technology became more mature, also such type of solar collector began to be studied to adopt molten salts as HTF. The Italian company specialized in renewable energy plants, recently decided to adopt the Fresnel technology with Molten Salts both as Heat Transfer Fluid and storage Medium for the development of a new power plant in Sicily, that comprises a 5.6 MWe Photovoltaic section and a 4.26 MWe CSP section. Since no plants of this type are actually in operation, such plant will be therefore a First of a Kind of such concept. The paper describes the design and operative main data, presently in the construction phase and expected to be commissioned not later than spring.

1.6 TYPES OF MOLTEN SALT

Molten salt is salt which is solid at standard temperature and pressure but enters the liquid phase due to elevated temperature. A salt that is normally liquid even at standard temperature and pressure is usually called a room temperature ionic liquid, although technically molten salts are a class of ionic liquids.

- Sodium nitrate,
- Lithium nitrate,
- Potassium nitrate,
- Sodium chloride,
- A mixture of 60% sodium nitrate and 40% potassium nitrate (by weight), commonly called solar salt.

Molten salts have a variety of uses. Molten chloride salt mixtures are commonly used as baths for various alloy heat treatments, such as annealing and martempering of steel. Cyanide and chloride salt mixtures are used for surface modification of alloys such as carburizing and nitrocarburizing of steel. Cryolite (a fluoride salt) is used as a solvent for aluminium oxide in the production of aluminium in the Hall process. Fluoride, chloride, and hydroxide salts can be used as solvents in nuclear fuel. Molten salts (fluoride, chloride, and nitrate) can also be used as heat transfer fluids as well as for thermal storage. This thermal storage is commonly used in molten salt power plants. A commonly used thermal salt is the eutectic mixture of 60% sodium nitrate and 40% potassium nitrate, which can be used as liquid between 260-550 °C. It has a heat of fusion of 161 J/g, and a heat capacity of 1.53 J/ (g K). Ambient temperature molten salts (also known as ionic liquids) are present in the liquid phase at standard conditions for temperature and pressure. Examples of such salts include N-ethyl pyridinium bromide and aluminium chloride mix, discovered in 1951[7] and ethyl ammonium nitrate discovered by Paul Walden.

1.7 MOLTEN SALT HISTORY

Excess energy from solar, nuclear or coal power stations can be stored in molten salts (MS) in the 565 °C range. At elevated temperature, large containers can be used to store energy for up to a week and generate eight hours or more, depending on the container size, of electricity to be used at night or during peak demand hours. A stable diurnal energy supply is made available by energy storage and the fluctuation experienced at thermal solar power stations caused by weather conditions is reduced. Supported by Office of Naval Research (ONR), this paper presents a survey of molten salt properties used in solar power storage, as well as the history of molten salt usage for energy storage and production. The history of molten salt usage includes past, current, and future developments involving molten salt usage for nuclear and solar energy storage and production. Density, melting temperature, viscosity, electric conductivity, surface tension, and heat capacity of various molten salts are discussed. Since costs are important factor in selecting a molten salt compound, salts costs are presented. Recommendations are made regarding the efficient use of various types of molten salt

Molten solar salts are effective at storing excess energy because they have considerable capacities for heat storage. Large insulated tanks provide a closed system for these molten salts to be properly contained. This paper examines the various molten salts available for MS storage, including their physical and thermodynamic properties, and corrosion properties. In addition, the history of molten salts and the usage in nuclear and solar energy is discussed. The material presented in this paper has been collected by the researchers in the University of Nevada, Las Vegas (UNLV) Molten Salt Project and information provided by Craig Tyner in a report to the project.

The first use of molten salts dates back to 1950, which is when Oak Ridge National Laboratory (ORNL) started to develop and test a nuclear power aircraft engine using molten salts. In 1954, ORNL shifted their molten salt focus to nuclear reactors. The thermal stability of molten salts was of great interest in the development of these nuclear reactors since they would not decompose when exposed to the high temperatures associated with nuclear reactors. The U.S. Atomic Energy Commission (AEC) was interested in studying various breeding reactor concepts. A relatively successful molten salt test breeding reactor was developed in the 1960s at ORNL. However, during this time, the Molten Salt Reactor Experiment (MSRE) was directly competing with another nuclear reactor project, which was the Liquid Metal Fast Breeding Reactor (LMFBR) project. During the 1960s, the LMFBR project pursued an aggressive funding campaign to develop its reactor. After the MSRE was successfully completed in 1969, ORNL wanted to pursue additional funding from the AEC. When the MSRE was ready to pursue \$350 million of total funding in the 1970s, the AEC was committing \$400 million per year through 1975 on the LMFBR project, and the AEC did not want a competing project. This ultimately led to the end of molten salt nuclear reactor research in the United States, as ORNL published its last report on the MSRE to the AEC in 1976.

The final reactor from the MSRE was a demonstration breeding reactor that addressed both the tellurium induced cracking in the reactor as well as the interactions involving tritium and the reactor coolant. Finally, once the MSRE had been terminated at ORNL, societal changes doomed the molten salt nuclear reactor, particularly the avoidance of a uranium shortage that meant that molten salt reactors were not in high demand, as well as fears of uranium proliferation and reactor accidents. However, in 1980, ORNL did publish one last report on a conceptual design for new type of breeding molten salt reactor using denatured uranium, but the design never came to fruition. The first molten salt reactor built by ORNL was completed in 1954 and operated for several days, operating a maximum temperature of 1,620 °F. The early molten salt reactor concepts were non-breeding reactors using various molten fluorides, including uranium fluoride (UF₄) and thorium fluoride (ThF₄). However, by 1959, all interest in molten salt reactors from the AEC was solely with breeding reactor concepts.

As such, the MSRE was proposed to the AEC in order to develop and test a molten salt breeding reactor (A breeding reactor is a reactor that produces more fissionable material than it consumes).

The breeder reactor, which was designed to produce 10 MW of electricity, started construction in 1962 and was made operational in 1965. The MSRE, along with the LMFBR project, were both included in the 1962 "Report to the President" for President John F. Kennedy, a report that promoted the benefits of breeding reactor research. It was after this report that the LMFBR pursued its aggressive funding campaign. While the MSRE project was considered a success, there were some concerns that needed to be addressed, including three major concerns. The first concern was that the Hastelloy-N being used in the reactors was subject to radiation hardening in which helium was accumulating at grain boundaries due to carbide precipitates in the alloys. The second concern was when the tritium, which is radioactive hydrogen, was produced by neutron reaction with lithium. This is a concern because the tritium can penetrate various metals. The final concern was the development of small cracks in Hastelloy-N piping due to tellurium. Ultimately, the solutions to these issues were addressed.

To prevent the radiation hardening, it was recommended that fast neutron radiation be limited around vessel walls. For the excess tritium production, it was discovered that a salt coolant could absorb the tritium, and that the coolant could further be removed, which would allow for the purging of tritium. As for the tellurium cracks, research showed that cracking could be limited if the fuel was kept on the reducing side of the reactor. Despite finding the solutions to these issues, which lead the research team at ORNL to believe the project was ready for the next step once the original MSRE was completed, it found itself competing with the LMFBR project for funding, which was further along and heavily invested in than the MSRE. In addition, the AEC wanted industrial support for the MSRE research. absorb the reflected sunlight and use the energy as heat, which would then heat the molten salt and therefore store the energy in the salts as heat.

Industrial support was available for the molten salt reactors, but the AEC ignored this support and eventually ordered the research be ceased. This was also despite the fact that it was expected that the capital cost of the molten salt reactors was less than the LMFBR. This was because of the fact that the fuel handling is simpler, molten salts have a higher heat capacity than sodium, molten salt reactors do not have to worry about a “core disruptive accident” happening, molten salts have a smaller thermal conductivity to limit thermal shock, and the coolant is more compatible with water [5]. For energy storage uses, this shows that molten salts are useful because of their thermal capacity and conductivity, as well as being relatively safe, even in a nuclear reactor environment. The first solar power plant that used molten salts for energy storage was developed in 1993. Solar Two, located in the Mojave Desert in California, was designed a test facility for molten salt energy storage (MSES). This facility was designed to store 10 MW of electricity for one hour. As a concentrating solar power (CSP) facility, various reflective panels, or heliostats, were used to reflect sunlight into centralized tower. These towers would

While Solar Two provided valuable insight into use of both MSES and CSP, the maintenance had become exhaustive and the facility was not being maintained properly, which was undercutting the performance of the system. Ultimately, Solar Two was decommissioned in 1999. Afterwards, the NREL published a short report in 2000 on their findings, while Sandia National Laboratory published its detailed report in 2002, documenting the full research provided by this project [11, 12]. This information has proven valuable to the commercial development of MSES worldwide as widespread efforts are made to introduce MSES to the world.

3. Molten Salt Usage

The biggest feature of molten salts is their ability to conduct heat. This is the defining characteristic for molten salt technology in both molten salt reactors (MSR) and molten salt energy storage systems (MS-ESS). They can also be used to conduct electricity, which is useful in decomposing molten salts.

As stated earlier, molten salts were first used to develop nuclear reactors. These reactors use molten salt fuels, usually fluoride mixed with any of the following: thorium, uranium, lithium and beryllium. This contrasts with the solid fuel used in traditional nuclear reactors. MSR's are known for their unrivalled safety when compared to various other types of reactors. Compared to other nuclear reactors, molten salt nuclear reactors cannot melt down because the fuel is already molten to start with. A safety feature of molten salt nuclear reactors is that if the resulting fission produces overheating in the reactor, which would be over 700 °C, the fuel will spill out of the reactor, usually by melting a spill plug, into a circulation loop filled with water. This in turn decreases the fission in the tank, and as a result, the tank cools down. In addition, in the event of a tank breach, the fuel will simply freeze at atmospheric temperatures. Also, since the fuel is not pressurized like traditional reactors, radiation will not disperse into the atmosphere during a breach. Molten salt nuclear reactors also produce less nuclear waste than traditional reactors.

1.8 MOLTEN SALT REACTORS

In traditional reactors, the fission produced by the uranium rods creates xenon, which can crack the ceramic rods. Once the rod is cracked, it must be disposed of even if there still is usable fuel. With molten salt reactors, the fuel is in liquid form and therefore does not use ceramic rods. As for the gas that is produced in molten salt reactors during fission, it simply rises to the top of the tank where it can be captured and removed. Because of its inherent safety, molten salt nuclear reactors are cheaper than traditional reactors because molten salt reactors require fewer safety measures and less redundancy than traditional reactors. Lastly, molten salt reactors can limit nuclear weapons proliferation because most of the actual fuel, which are the actinides, is consumed by the actual reactor, reducing the amount of waste available for proliferation. Also, the reactor can use the nuclear waste from traditional reactors as fuel, which can reduce the waste that is available for proliferation. One of the biggest benefits of molten salt nuclear reactors, as well as molten salt energy storage systems, is that they do not emit carbon like coal and natural gas power plants.

Some molten salt nuclear reactor concepts, such as the liquid fluoride thorium reactor (LFTR), can consume 99% of its fuel. Whatever waste products that are produced only have to be buried for only 300 years compared to the minimum of 10,000 years for most traditional reactors.

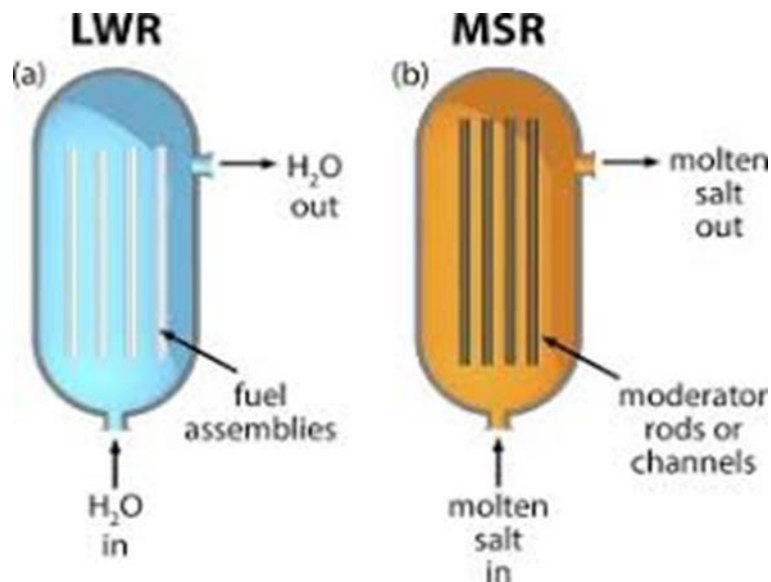


Fig :9 Molten Salt Reactor

LFTRs can be made to be smaller than traditional reactors, allowing for a wider range of applications. Also, since LFTRs operate at higher temperatures than traditional reactors, LFTRs can take advantage of more efficient conversion cycles in converting heat into electricity. The most unique feature of molten salts compared to other reactors is that they serve as both the fuel and coolant for the reactor. In addition, molten salts are chemically inert, meaning that neither air nor water will cause them to combust. The operating temperature of the molten salt reactor (973 K) is significantly less than the melting point of the molten salts, which is at least 1,670 K. The only concern for molten salt nuclear reactors is that there has not been any recent accident analysis performed on these reactor concepts to provide insights into what a molten salt reactor accident would resemble. This can pose challenges to regulators in trying to assess the full risk of molten salt reactors.

The sensible heat of molten salt is also used for storing solar energy at a high temperature. It is termed molten-salt technology or molten-salt energy storage (MSES). Molten salts can be employed as a thermal energy storage method to retain thermal energy. Presently, this is a commercially used technology to store the heat collected by concentrated solar power (e.g., from a solar tower or solar trough). The heat can later be converted into superheated steam to power conventional steam turbines and generate electricity in bad weather or at night. It was demonstrated in the Solar Two project from 1995–1999. Estimates in 2006 predicted an annual efficiency of 99%, a reference to the energy retained by storing heat before turning it into electricity, versus converting heat directly into electricity. Various eutectic mixtures of different salts are used (e.g., sodium nitrate, potassium nitrate and calcium nitrate). Experience with such systems exists in non-solar applications in the chemical and metals industries as a heat.

The salt melts at 131 °C (268 °F). It is kept liquid at 288 °C (550 °F) in an insulated "cold" storage tank. The liquid salt is pumped transport fluid through panels in a solar collector where the focused sun heats it to 566 °C (1,051 °F). It is then sent to a hot storage tank. With proper insulation of the tank the thermal energy can be usefully stored for up to a week. When electricity is needed, the hot molten salt is pumped to a conventional steam-generator to produce superheated steam for driving a conventional turbine/generator set as used in any coal or oil or nuclear power plant. A 100-megawatt turbine would need a tank of about 9.1 metres (30 ft) tall and 24 metres (79 ft) in diameter to drive it for four hours by this design. Single tank with divider plate to hold both cold and hot molten salt, is under development. It is more economical by achieving 100% more heat storage per unit volume over the dual tanks system as the molten-salt storage tank is costly due to its complicated construction. Phase Change Material (PCMs) are also used in molten-salt energy storage, while research on obtaining shape-stabilized PCMs using high porosity matrices is ongoing.

Several parabolic trough power plants in Spain and solar power tower developer Solar Reserve use this thermal energy storage concept.

The salt is a combination of sodium and potassium nitrate, with a melting temperature of 460°F. In the liquid state, molten salt has the viscosity and the appearance similar to water. “In solar applications, molten salt is used for a number of practical reasons,” says Terry Murphy, Chief Executive Officer for Solar Reserve, who along with others helped develop the molten salt technology at Rocketdyne. “Molten salt is a heat storage medium that retains thermal energy very effectively over time and operates at temperatures greater than 1000°F, which matches well with the most efficient steam turbines. Second, it remains in a liquid state throughout the plant’s operating regime, which will improve long-term reliability and reduce O&M costs. And third, it’s totally ‘green,’ molten salt is a non-toxic, readily available material, similar to commercial fertilizers.

Table 1.1 Effective thermal conductivity of dry and wetted refractory at different temperature

This table shows the Effective Thermal Conductivity of dry and wetted refractory at different temperature

Hot Face Brick			Insulating Firebrick		
T°C	Dry	Wetted	T°C	Dry	Wetted
149	1.20	1.26	260	0.13	0.49
316	1.28	1.34	540	0.17	0.62
704	1.37	1.43	815	0.20	0.70
871	1.51	1.58	1100	0.24	0.83

A primary advantage of molten salt central receiver technology is that the molten salt can be heated to 1050°F, which allows high energy steam to be generated at utility-standard temperatures (1650 psi minimum, 1025°F), achieving high thermodynamic cycle efficiencies of approximately 40 percent in modern steam turbine systems. This high cycle efficiency is maintained while allowing the use of dry cooling towers, which is important in arid states with the best solar potential. The molten salt heat transfer loop through the receiver is isolated from main steam temperatures and pressures, resulting in cost savings through the use of low-pressure salt piping. Finally, the system is designed to minimize the length of the molten salt loop to less than 2,500 feet, which is heat traced to prevent 'freezing.'

Thermal storage systems using molten salt have been identified for use with other solar technologies, such as parabolic trough systems, which have been the dominant solar thermal technology installed to date. Trough plants will require an additional heat exchanger to transfer the energy from the working fluid to storage and to transfer the energy in storage back to the steam system. It is estimated that the additional heat exchanger required for a trough plant causes a loss in cycle efficiency loss of up to 7 percent. In addition, a trough facility that can only achieve a hot working fluid temperature of 700°F will require approximately 3 times the thermal storage volume to generate a given amount of electricity as an integrated thermal storage system which stores energy at 1050°F.

At present, two-tank molten salt storage systems are the established commercially available concept for solar thermal power plants. Due to their low vapor pressure and comparatively high thermal stability, molten salts are preferred as the heat transfer fluid and storage medium. However, due to pricing pressure, the development of alternative, more cost-effective concepts is an important step in making thermal energy storage more competitive for industrial processes and solar thermal applications. A closer look at the capital cost distribution of two-tank storage systems, reveals that indirect systems with a maximum operating temperature of 400 °C have differing heat transfer fluids (HTF) and storage media.

For those systems, the molten salt storage media (about 35 % of the direct capital costs) and the storage tanks (about 24 % of the direct capital costs) are the main bearers of cost. For direct systems with operating temperatures up to 560 °C, using molten salt as the HTF and the storage media, the capital cost ratios are 34 % for the storage media and 31 % for the storage tank, respectively

Thermal storage stores energy in the form of heat that is either "sensible" or "latent". Sensible heat corresponds to thermal storage in a single phase where the temperature of the material varies with the amount of stored energy. [2-4] The equation for heat flow from hot to cold is: $Q = m C \Delta T$ where Q is the (sensible) heat, m is the mass, C is the specific heat, and ΔT is the temperature difference. Both liquid (water, oil, molten salt) and solid (rock, metal) media can be used. This requires insulation to maintain a temperature gradient to store the heat. For low temperature (25 - 90°C), water is ideal; it has a relatively high specific heat is cheap, and over a 60°C temperature difference can store 250 kJ/kg. Operating at low temperatures avoids complications associated with the high vapor pressure and containment.

Latent heat is stored using phase-change materials that take advantage of the (specific) latent heat L associated with a phase transition: $Q = m C \Delta T + m L$ though this is not as efficient at high temperatures. [3] Phase-change materials are appealing because of their high energy storage density; water, for example, has a latent heat of fusion 335 kJ/kg which is approximately 80 times the amount of heat that is required to raise the temperature of 1 kg of water by 1°C. [4] While latent heat may be suitable for a house with solar panels, additional complications associated with cost and repeated use currently make sensible heat a better option for large-scale storage. Molten salts have high boiling points, low viscosity, low vapor pressure, and high volumetric heat capabilities. A higher heat capacity corresponds to a smaller storage tank volume. In choosing the chemical mixture, it is advantageous to have the lowest possible melting point (and highest boiling point) to maximize the available temperature range for the molten salt.

If the melting point is too high, additional heating may be required to prevent freezing. Salts used for storage (such as sodium nitrate NaNO_3 and potassium nitrate KNO_3) have melting points between 300-500°C and volumetric heat capacities between 1670 - 3770 kJ/m³°C. Sodium hydroxide NaOH has a melting point of 320°C and can be used up to 800°C, but is highly corrosive. Commercially available "HITEC" salt used in solar plants consists of potassium nitrate (53% by weight), sodium nitrite NaNO_2 (40% by weight), and sodium nitrate (7% by weight) with a liquid temperature range of 149 - 538°C. There are two different configurations for the molten salt energy storage system: two-tank direct and thermocline. The two-tank direct system, using molten salt as both the heat transfer fluid (absorbing heat from the reactor or heat exchanger) and the heat storage fluid, consists of a hot and cold storage tank.

The salts are heated and stored in an insulating container during off-peak hours. When energy is needed, the salt is pumped into a steam generator that boils water, spins a turbine, and generates electricity. The conversion of thermal energy to electricity can proceed by different cycles such as the Rankine, Brayton, and Air-Brayton cycles. [2] The Brayton gas cycle, for example, involves (1) adiabatic expansion of the high-pressure and high-temperature gas across a turbine to do work, (2) isobaric cooling, (3) adiabatic compression to high pressure, and (4) isobaric heating whereupon the cycle is repeated. Other applications include using the stored heat directly for high temperature processes (such as H_2 production and coal-to-liquid conversion), which avoids the thermodynamic cost incurred from converting to electricity.

The two-tank direct system, using molten salt as both the heat transfer fluid (absorbing heat from the reactor or heat exchanger) and the heat storage fluid, consists of a hot and cold storage tank. The thermocline system uses a single tank such that hot and cold salt are separated by a vertical temperature gradient (due to buoyancy force) to prevent mixing. There are two cycles in the thermocline system charging and discharging. To charge, salt flows out of the cold side, is heated by the heat exchanger (reactor), and flows into the tank's hot side.

Thermal energy storage (TES) is achieved with widely different technologies. Depending on the specific technology, it allows excess thermal energy to be stored and used hours, days, months later, at scales ranging from the individual process, building, multiuser-building, district, town, or region.

The sensible heat of molten salt is also used for storing solar energy at a high temperature. It is termed molten-salt technology or molten-salt energy storage (MSES). Molten salts can be employed as a thermal energy storage method to retain thermal energy. Presently, this is a commercially used technology to store the heat collected by concentrated solar power (e.g., from a solar tower or solar trough).

1.9 PARABOLIC TROUGH POWER PLANTS

Thermal storage for parabolic-trough power plants offers the potential to dispatch electricity without fossil fuel backup. The value of the electricity is often higher during peak periods. A plant that can meet the peak demand independent of the solar resource has the potential to generate more revenue. The Solar Electric Generating Station (SEGS) I plant had a two-tank thermal storage system that used heat transfer fluid. This fluid was pumped through the collector field. The storage tanks were conventional atmospheric tanks. It is a liquid at atmospheric pressures when its temperature is below about 315°C. The SEGS I thermal storage system operated at temperatures between about 175°C and 295°C. The hot oil was pumped through a steam generator to make saturated steam. Fossil fuel was used to superheat the steam to generate electricity. The Solar One central receiver pilot plant also used, but in a thermocline tank. A thermocline tank is one that uses a single tank to store thermal energy. A thermal gradient separates the hot from the cold fluid. A low-cost filler material is used to displace the higher-cost liquid.

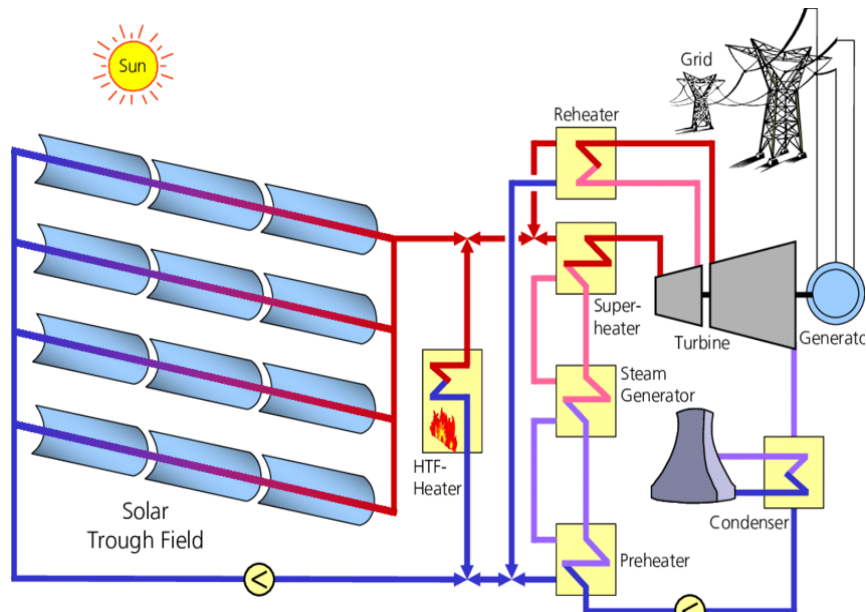


Fig: 10 Parabolic trough power plants

The filler material as well as buoyant forces help to maintain the thermal gradient. When the system is charged, cold fluid is drawn from the bottom, heated as it passes through a heat exchanger (heated with the receiver heat transfer fluid) and returns to the top of the tank. When the tank is discharged, hot fluid is drawn from the top, cooled as it passes through a heat exchanger (to transfer heat for steam generation), and returns to the bottom of the tank. In the Solar One thermocline storage system, steam from the receiver passed through a heat exchanger, which heated the oil drawn from the bottom of the tank. Because of the favourable experience of the two-tank molten-salt thermal storage system used at the Solar Two demonstration plant (Pacheco, Gilbert, 1999), its low risk and cost-effectiveness, selected this design as a baseline. In this design to charge the storage system, hot oil coming from the collector field would transfer heat through an oil-to-salt heat exchanger, and then it would return to the collector field to be heated again. Salt pumped from the “cold” tank would be heated as it passed through the oil-to-salt heat exchanger and would flow into the “hot” tank. To discharge the storage system, hot salt would be pumped from the hot tank and would transfer its heat through the same oil-to-salt heat exchanger and return to the cold tank.

1.10 TWO TANK MOLTEN SALT SYSTEM

The oil would be heated by the heat exchanger, then pass through a steam generator to make steam. A schematic of the two-tank molten-salt system integrated into a trough plant. It estimated the capital cost of a 688 m w h t two-tank molten-salt system used with the current state-of-technology troughs to be about \$31/kW h t including the nitrate salt inventory, the installed tanks, and the oil-to-salt heat exchangers. To come up with a feasible molten salt thermocline system, we broke the development activity into three major areas:

Modelling - where we simulated the performance and estimated the economics of a thermocline system,

Filler Evaluation: Isothermal Testing - where we screened potential candidate filler materials in isothermal baths of molten salt - and Thermal Cycling Testing - where we took the most promising fillers and subjected them to repeated thermal cycling, and

Thermocline Test - where we built a small (2.3 MWh) thermocline system to validate performance and evaluate practical operational issues of a thermocline system. Also as part of this effort we evaluated potential low melting-point salts and evaluated salt-safety issues re...

Molten-salt thermal storage systems are already being commercially implemented since they provide reliability to concentrating solar power plants. Based on the operational experience of the first concentrating solar power (CSP) plants that in the 1980s used molten salt as heat transfer fluid or as thermal energy CSP plants that have been constructed use molten salt for thermal energy storage.

Industry has largely progressed and many of the problems related to the use of molten salt, such as the materials corrosion, the plug formation or the problems in valves, have been solved leading to higher thermal capacities (M W h t). A depicts the MOSA facility, which we have already reported. It is a reproduction of a commercial two-tank molten salt thermal energy storage in smaller scale. The cold salt tank is placed in a concrete pit placed below ground level and all the piping has at least a 1 degree inclination to allow the complete drainage into this tank, by gravity, of the whole facility. In this facility, all pipes and equipment in contact with molten salt are provided with an electrical heat tracing system (EHT) in order to heat pipes...and components before the operation with molten salt. The facility is linked to an experimental parabolic trough facility with CO₂ as heat transfer fluid by means of a molten salt/ CO₂ heat exchanger. It is also linked to a thermal oil loop using a molten salt/ thermal oil heat exchanger.

1.11 USES OF MOLTEN SALTS

Heat Storage Fluid is nowadays the most common choice in CSP plants for electricity production (see the Solar PACES database. Molten salt, State-of-the-art designs are based on two main concepts: “Direct Storage”, with Central Receiver Heliostat Field (Power Tower); MS is either the Heat Transfer Fluid (The use of Molten Salts HTF) of the Central Receiver and Storage Fluid in a Two Tanks based Thermal Energy Storage (TES). Such concept was prototyped in Solar Two ([2]) and recently adopted in commercial units, see in Masen Noor III plant “Indirect Storage”, with Parabolic Trough (PT) Solar Field using oil as HTF and MS Two Tank TES.

Molten salts are crucial materials in energy applications, such as batteries, thermal energy storage systems or concentrated solar power plants. Still, the determination and interpretation of basic physio-chemical properties like ionic conductivity, mobilities and transference numbers cause debate. Here, we explore a method for determination of ionic electrical mobilities based on non-equilibrium computer simulations.

Partial conductivities are then determined as a function of system composition and temperature from simulations of molten $\text{Li F}\alpha\text{Cl}\beta\text{I}\gamma$ (with $\alpha + \beta + \gamma = 1$). High conductivity does not necessarily coincide with high Li^+ mobility for molten $\text{Li F}\alpha\text{Cl}\beta\text{I}\gamma$ systems at a given temperature.

In salt mixtures, the lighter anions on average drift along with Li^+ towards the negative electrode when applying an electric field and only the heavier anions move towards the positive electrode. In conclusion, the microscopic origin of conductivity in molten salts is here based on accurate ionic electrical mobilities and an analysis of the local structure and kinetics of the mate. Molten salt is used in solar power tower systems because it is liquid at atmosphere pressure, it provides an efficient, low-cost medium in which to store thermal energy, its operating temperatures are compatible with today high-pressure and high-temperature steam turbines, and it is non-flammable and nontoxic.

Molten salt is a heat storage medium that retains thermal energy very effectively over time and operates at temperatures greater than 1000°F , which matches well with the most efficient steam turbine. Thermally activated (“thermal”) batteries are primary batteries that use molten salts as electrolytes and employ an internal pyrotechnic (heat) source to bring the battery stack to operating temperatures. They are primarily used for military applications, such as missiles and ordnance, and in nuclear weapons. The salts are heated and stored in an insulating container during off-peak hours. When energy is needed, the salt is pumped into a steam generator that boils water, spins a turbine, and generates electricity.

The hot molten salt is then routed to an insulated hot thermal storage tank where the energy can be stored with minimal energy losses (Step 3). When electricity is to be generated, the hot molten salt is routed to a heat exchanger (or steam generator) and used to produce steam at high temperature and pressure. Molten salt can function as a large-scale thermal storage method that would allow other energy sources, such as nuclear and solar, to become more feasible by smoothing out the fluctuations in demand and weather.

1.12 MOLTEN SALT FOR HEAT TRANSFER FLUID & THERMAL ENERGY STORAGE

Concentrating solar power (CSP) technologies employ mirrored reflectors hours of TES to direct and focus the sun's energy on a receiver containing a working fluid. The energy from this heat transfer fluid (HTF) is used to drive a conventional steam-electric turbine-generator. Relative to solar photovoltaic (PV) systems, CSP plants have a key advantage, in that solar radiation. Modern CSP plant designs commonly include multiple capacity to better match output with load and increase the time value of solar energy production. Direct-storage plant designs use one material as both HTF, collecting solar energy within the receiver, and storage medium, providing load-matching capability. Indirect-storage designs use one material as the HTF and a second for thermal storage.

Molten salt is commercially employed in central receiver direct-storage plants and parabolic trough indirect-storage plants. Demonstrations are under way for parabolic trough and linear Fresnel reflector systems served by direct molten salt storage. A binary mixture of sodium nitrate and potassium nitrate, commonly referred to as "solar salt," has proven effective as a thermal storage medium in diverse CSP applications which span more than 20 trough plants deployed since 2008. For plants that incorporate TES, solar heat collected at the receiver may be provided directly to a steam generator for energy production, may be directed to storage tanks for later use, or may be split between the two options depending on operating conditions and market dynamics. It provides a simplified view of CSP plant operations.

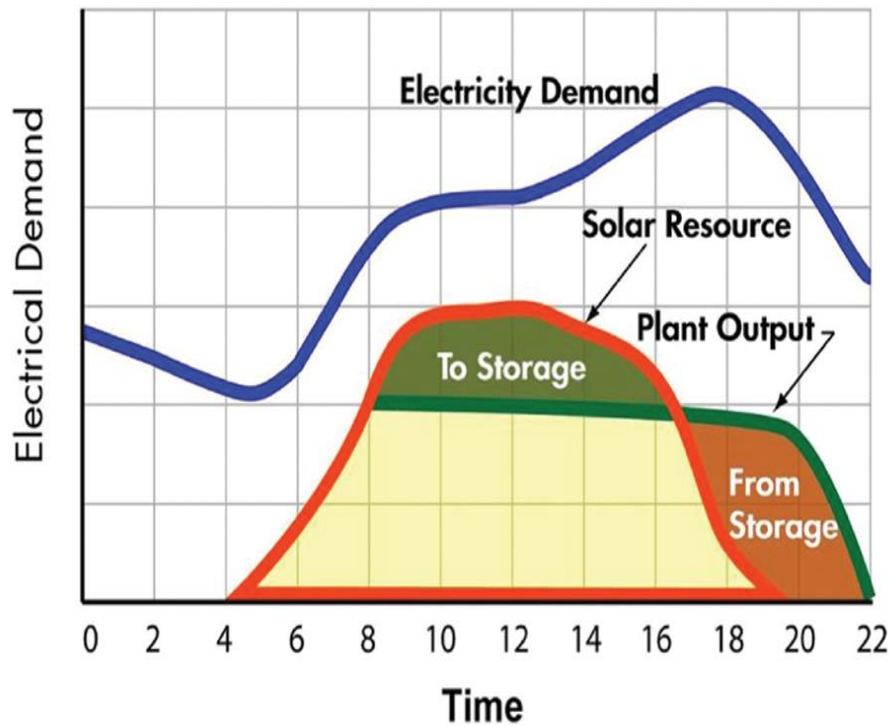


Fig:11 Simplified operational schedule for CSP plants with TES.

The utility load profile, solar resource availability, and plant dispatch are shown for an example day. Rather than generating at full power when the sun is available, the plant can store some energy during the day for dispatch during peak hours. During real-world operations, the optimal dispatch strategy may vary based on seasonal differences in daily solar insolation and consumer load profile, as well as other factors. Total global CSP capacity exceeds 3000 MW with more than 2000 MW under construction or in advanced stages of development, and even more in the pipeline. Roughly 50% of total operational capacity integrates an on-site TES system. Most new plants include storage because its value outweighs the additional capital investment and the continuing operations and maintenance costs.

Several TES media have been employed over time, but storage systems based on molten salt account for the majority of recent installations. Many existing CSP plants, served by molten salt storage,

accounting for more than 1200 MW of capacity, consist almost entirely of parabolic trough plants with indirect TES – typically having 50 MW of generating capacity and at least 7,5 hours of storage capacity at full power. By far the most common TES technology for current CSP plants is a two-tank molten salt configuration, based on a sodium nitrate-potassium nitrate ($\text{NaNO}_3\text{-KNO}_3$) mixture commonly referred to as binary or solar salt. The molten salt is pumped from a “cold” tank and cycled through the solar receiver in direct designs and through a heat exchanger in indirect plants. Flow rates vary considerably depending on design and operating conditions.

After heating, the molten salt is returned to a “hot” tank, where it is stored for later use to generate electricity when needed. This approach always uses the molten salt mixture in liquid rather than solid state. Avoiding salt freezing is an essential element in CSP design and operation, as this can reduce conversion efficiency, while freeze-thaw cycling within pressure-retaining systems can lead to maintenance problems. Trough collectors heat a synthetic oil HTF to about 390°C. When the sun is shining, the hot HTF may be diverted to a heat exchanger for charging the molten salt TES system, and it may be used immediately to produce steam by flowing through a series of heat exchangers in the power block. In storage mode, solar salt in the cold tank, held at a temperature of about 290°C, flows through an oil-to-salt heat exchanger. The heated salt is stored in the hot tank at about 390°C until it is needed for power generation. Upon being directed back through the heat exchanger, the molten salt gives up its heat to oil passing from the receiver on its way to the power block. The cooled molten salt is returned to the cold tank, where it is maintained about 50°C above 238°C, the point at which solar salt begins to solidify (freeze).

The upper temperature limit of indirect trough TES systems is about 400°C, the maximum operating temperature of the synthetic oil. For new parabolic trough plant designs, molten salt is being considered as an HTF alternative. The anticipated benefits include higher-temperature operation (~550°C) and avoided losses in the oil-to-salt heat exchanger. Further, the size of the storage system required to deliver a given amount of capacity is directly proportional to the hot-cold temperature difference, meaning that a TES system operating at 550°C can be much smaller than one operating at 390°C if both share a nominal cold return temperature of 290°C. However, thermal losses from molten salt flowing through receiver tubes distributed throughout the trough array present significant challenges. First, the large receiver area imposes a larger energy penalty at higher operating temperature, reducing field efficiency. Second, excess cooling could result in freezing. Heat tracing – cable containing electric resistance heating elements – is applied at all molten salt CSP plants for freeze protection, as solidification and thawing cycles can lead to damage within enclosed piping and other components.

During periods with high energy input, molten salt is pumped through the receiver faster to maintain a constant outlet temperature to the hot tank. When less sunlight is available, the flow rate slows considerably, giving the molten salt additional residence time to achieve the required temperature gain. To drive the power block, molten salt from the hot tank is used to produce superheated steam for a conventional Rankine-cycle turbine-generator system. During normal operations, the solar salt is removed from the cold tank at about 290°C and pumped through the receiver at the top of the tower, where it is heated by solar energy reflected by the heliostat field. The salt is heated to about 565°C and returned to the hot tank. The flow rate through the receiver varies throughout the day depending on the available solar flux.

From the steam generator, the salt is returned to the cold tank for storage and eventual reheating in the receiver. Overnight, molten salt in the receiver and associated piping is drained to the cold tank to avoid freezing.

The capacity of trough, central receiver, and linear Fresnel plants typically is reported based on the generating capacity of the steam turbine in MW of electricity, rather than the solar field in MW of thermal energy. The size of the solar field relative to the steam turbine is defined as the solar multiple (SM). For example, a field that produces 10% more thermal energy (at its design point) than the rated steam turbine capacity has an SM of 1.1. An SM >1 means that the CSP plant can operate at its nameplate capacity for more hours of the year, including when solar conditions are not optimal. This increases the plant's capacity factor, but at times excess thermal energy must either be dumped or stored. CSP plants with TES employ higher SMs – and larger fields – to deliver higher capacity factors.

Fig:12 Parabolic trough CSP plant with indirect molten salt TES.

Indirect trough two-tank molten salt storage systems are about 93% efficient, while direct central receiver two-tank molten salt storage systems are up to 98% efficient. TES systems offer an additional efficiency advantage, in that their annual average power block efficiency tends to be higher than for CSP plants without storage since their turbine-generator system operates at full load more frequently.

1.13 THE VALUE OF ENERGY STORAGE

The addition of TES to a CSP plant's design can lower its cost of electricity (LCOE) production, as well as deliver value to the power grid in helping to accommodate increasing amounts of variable-output wind and PV capacity. Today's plant designs commonly incorporate TES because the incremental cost of storage is offset by LCOE reductions attributable to a higher capacity factor for the turbine-generator system, greater operating flexibility, and increased availability of solar power during peak demand periods. Determining the optimum storage size to meet power dispatch requirements is an important part of the CSP plant design process.

The energy contained in the storage system can be dispatched in any number of ways, but operational strategies typically adjust the CSP plant's output profile to take advantage of higher electricity prices during periods characterised by high demand or high time-of-use rates. In some regions, the on-peak period can extend well into the evening hours when solar facilities without storage are no longer capable of delivering energy.

Two main options exist for altering energy output from the collector field to better match typical demand peaks occurring in late afternoon and evening. The first strategy involves diverting a portion of the output over the course of daily operation to charge the storage system. Stored energy is dispatched once the sun has set to extend the period over which power is supplied to the grid. Alternatively, all of the output from the collector field can be used to charge the storage system at the beginning of daily operation, delaying power generation until the system has been fully charged.

The plant will then have sufficient energy in storage to continue operating through the peak and into the evening use period.

This strategy simply shifts the delivery period to increase CSP plant revenues by increasing the time value of electricity supplied to the grid. For individual CSP plants, the optimal operational profile is likely to vary based on seasonal differences in daily solar insolation and in load profile, as well as on other technical and market factors. For example, alternate dispatch strategies for stored energy can optimise plant value during periods with cloudy forecasts or reduced winter-time insolation, or to better match early morning peaks, the winter customer demand profile, or energy needs during weekend operations. Alternatively, during night hours, a smaller amount of capacity may be dispatched to maintain the steam turbine at operational temperature and thereby reduce thermal cycling and heat loss at morning start-up.

CSP plants with storage also deliver value to the grid. Relative to PV, CSP systems have sufficient thermal inertia to avoid major ramps in power generation during cloud passage; TES can further buffer output fluctuations and dampen effects on voltage and other grid parameters. CSP plants with TES are also much more dependable, in terms of supplying power during the highest-price periods of the year.

As well as producing power on peak, these plants can mitigate the impacts created by PV and wind projects and allow higher penetration of these variable-output resources by being dispatched to afford voltage regulation and frequency control, provide ramping and spinning reserves, and reduce renewable curtailment. Under certain PV deployment and policy scenarios, CSP with TES is estimated to have an additional value of \$0,05 to \$0,06/kWh by being available to serve load and provide grid support services during peak pricing periods. The emergence of ancillary service markets allowing CSP plant owners to monetise these benefits is expected to further reduce LCOE.

1.14 OPERATIONS AND MAINTENANCE CONSIDERATIONS

To support initial start-up after construction, CSP plants require substantial salt handling and storage infrastructure. Generally, solid salt mixtures, are delivered in large “super sacks” containing up to 1 MT of solid crystalline feed material; salt also may be shipped and delivered as bulk, unbagged feed. Salts are hygroscopic, absorbing moisture and consolidating even when not exposed to the weather. Warehouse storage or other cover can help mitigate this issue. A hammer mill or other crushing device is needed to process solid salt to sizes appropriate for melting.

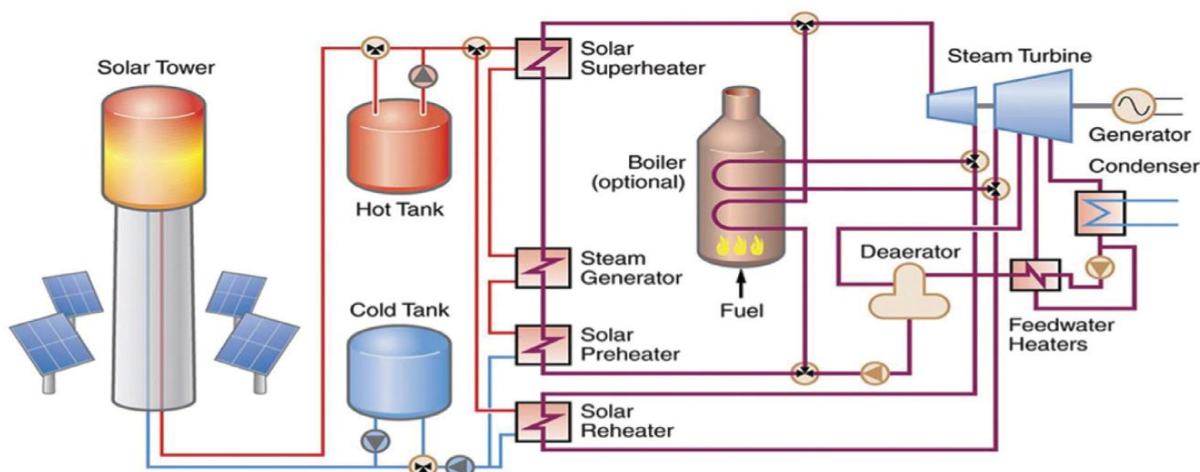


Fig:13 Central receiver CSP plant with direct molten salt.

CSP plants use propane-fired, gas-fired, or electric heaters to melt the salt in a settling tank. During melting a reaction involving magnesium impurities results in NO_x emissions that may be reduced as required using environmental control systems. Heavy contaminants, such as sand, fall to the bottom of the settling tank. Molten salt is then loaded into the hot storage tank, which is preheated to avoid refreezing.

Tank design specifications define appropriate temperature ramps and/or practices for tank preheating as the molten salt is introduced. As with any closed circuit operated at elevated temperatures, molten salt CSP systems need to be pressure-tested prior to operation. Hydro-testing should be conducted consistent with standards specifying the chloride content of the water loading, as a maximum. Much lower concentrations, as low as 2 ppm chloride, are often specified to preclude the possibility of stress corrosion cracking (SCC) of 300-series SS materials. This mode of metal failure is particular to the intermittent introduction of water in the system, either during pressure testing or for the flushing of residual salt from the conveyance system during repairs. It is distinct from the molten salt environment, which does not promote SCC.

Typically, hydro-testing is conducted at ambient temperature on a section-by-section basis during commissioning. This may be followed by testing of the entire system, then preheating with heat trace before charging with molten salt. At initial start-up and after outages, close visual inspection is essential for detection of small leaks. During normal operations, conventional direct programmable logic controllers are used to monitor and manage salt temperature, flow, pressure, and other factors.

Anomalous readings may provide indications of significant leaks. Leaks are normal, most commonly occurring at pipe flanges and valve stem packings. Precipitation of crystalline salt into valves over time also represents a problem by accelerating shaft wear due to scoring by hard salt particles. For nonwelded piping connections, retorquing of flanges may be required during commissioning and after outages to address any loosening attributable to thermal cycling. Maintaining correct temperature at the valve packing gland area is essential for preventing molten salt leakage and the potential for locking.

While visual inspection during normal maintenance rounds is the most common leak detection method, at least one company has started deploying a device that monitors stem packing friction changes over time as an indicator of leakage.

Targeted maintenance is effective for leak control by ensuring the correct adjustment of all valves while avoiding over-tightening of the packing. Checking valve packing for bolting tightness and leakage every six months is recommended. Packing typically must be replaced annually due to harsh operating conditions.

Valve surface defects caused by corrosion can be machined up to a certain depth. Beyond that point, field modifications can be applied (special gland followers and bottom rings) to allow continued use and delay valve replacement. Heat exchanger design, in conjunction with operating procedures that limit the rates of temperature cycling to allowable values specified by the component supplier, is the most important element in managing degradation processes and avoiding leaks. Because steam pressures are normally higher than salt pressures, even in the reheater at low turbine loads, contamination of the molten salt system with steam represents the most likely outcome of a leak. In such a case, steam will carry over into the ullage space of the cold storage tank. When the tank next fills with salt, steam-enriched ullage gas will vent to the atmosphere. If the steam generator leak continues, the cycle of steam entering and then leaving the tank will repeat.

The presence of steam in the cold tank will not increase corrosion rates of carbon steel, which are influenced mainly by chloride concentration in the salt. Further, steam and salt are chemically inert, to a large degree. Steam will ever-so-slightly dissociate into hydrogen and hydroxide ions. The latter can react with nitrate ions to form H₂O and NO₂, resulting in some NO_x production but in quantity insufficient to have a measurable effect on total plant emissions. Though unlikely, a heat exchanger tube failure could have severe consequences.

Contact between salt and water/steam could cause an over-pressure transient, deforming and ruining the shell if a pressure relief valve does not actuate fast enough to divert molten salt away from the heat exchanger and into a containment enclosure. It is highly unlikely that salt would ever leak into the steam or condensate systems due to the pressure differential.

If salt were to leak into the reheater, it would deposit in the low-pressure turbine at that point in the expansion path where the steam temperature has fallen to 220°C.

With sufficient TES capacity, these plants can operate continuously, acting as baseload sources of carbon-free power. Almost all recent or planned CSP projects include two-tank TES systems because their economic value outweighs the additional costs, and molten salt represents the storage medium of choice. At operational parabolic trough plants totalling more than 1200 MW in capacity, solar energy captured by synthetic oil HTF is available for indirect molten salt storage. Deployment of direct-storage systems – where molten salt serves as both the HTF and the TES medium – is limited to the 20 MW Gama solar central receiver and 5 MW trough installations. However, the worldwide development pipeline includes more than 1000 MW of central receiver capacity with direct storage, and demonstrations of trough and linear Fresnel CSP systems with direct TES are planned.

Solar salt, a binary 60-40 mixture (by weight) of sodium nitrate and potassium nitrate, has proven effective in CSP applications. It offers relatively low cost and a manageable freezing point, along with exceptional heat transfer, chemical stability, and energy storage characteristics at normal operating temperatures up to 565°C.

Novel molten salt formulations and storage system designs are being explored in ongoing research by EPRI and others. Lower-cost storage media with wider temperature ranges could make the value proposition for CSP with TES even stronger. Based on the current state of knowledge and real-world experience, the use of sound design, materials selection, freeze protection, construction, salt procurement, commissioning, operations, maintenance, occupational health and safety, and environmental management practices is expected to result in CSP plants with molten salt storage systems capable of meeting cost, performance, reliability, and sustainability objectives.

CHAPTER 2

LITERATURE SURVEY

S.Bell ,T.Steinberg (2019), in this paper, Corrosion, and corrosion mechanisms in molten salts is complex and dependent upon many variables. The salt anion and cation species, temperature, temperature gradient and thermal cycling rate, impurity concentration, atmosphere gas and pressure, alloying elements, composition and microstructure all greatly influence corrosion mechanism and rates.(8)

Angel G, Fernandez (2019), in this paper Molten salts act as the electrolyte in a corrosive system that attacks the metal containers. High operating temperature is necessary to improve efficiency in the CSP system and molten salts are the most promising TES materials at high temperatures. In702 showed the best corrosion resistance in carbonates molten salts tested due to the protective layers formed, composed mainly by Al_2O_3 and NiCr_2O_4 and establish a start point for chloride molten salts assessment.(5)

Hao chi chen, Bowen (2018), in this paper The molten chlorine salt was found to have the strongest corrosive ability in four eutectic salts and the weight loss of the sample with the thermal cycling times as 120 can reach 1347.91667 g/m^2 . The corrosion strength of the four eutectic salts should be in the order of chloride eutectic salt > mixture composed of carbonate eutectic salt and magnesium oxide > carbonate eutectic salt > nitrate eutectic salt for Fe-Al-Cr alloys. (13)

Hao shi , Alexander (2018) , in this paper The degradation of Fe-Cr-Ni based alloys in molten chloride salts could be considered as impurity-driven corrosion.In molten chlorides with Mg addition, Mg preferentially reacts with the impurities in the salts until either Mg or the impurities are consumed. The formed MgO layer on the alloy surface might act as a barrier to inhibit direct contact between salts and metals.(6)

CHAPTER 3

SCOPE AND OBJECTIVE

SCOPE

Improving the high temperature corrosion resistance of Inconel 625 used in Molten salts technology in thermal energy storage applications.

OBJECTIVES

To study the high temperature corrosion behaviour of Nickel based super alloys in the presence of molten salts environment at various elevated temperature. To increase the corrosion resistance property of super alloys in molten salt technology by using “Thermal Barrier Coatings”. Optimizing the coating thickness to resist the high temperature corrosion attack on super alloys. To study the mechanical properties of the base substrate of uncoated & coated samples used in various molten salts environments. To study the topographical information of the various substrate of uncoated & coated samples used in various molten salts environments.

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS FOR THE BASE SUBSTRATE

Inconel 625 is a high oxidation corrosion resistance material well suited for service in extreme environments subjected to pressure and heat. The addition of molybdenum niobium strengthens Inconel 625 which permits the metal to uphold great strength and toughness at temperature fluctuating from cryogenic (-150 °C) to 1093 °C. This alloy has high amount of nickel content to immune the stress-corrosion caused by chloride-ions, and cracking and pitting corrosion. The chemical composition of the Hastelloy X and the Inconel 625 materials has been found using Master pro ,Oxford, Germany' equipment.

Inconel 625 sheets with the size of 500 X 500 X 1.6 mm in thickness are initially procured. The specimens for the mechanical testing and characterization study have been p

CHEMICAL COMPOSITION OF INCONEL 625

Elements	Inconel 625
C	0.04
MnO ₂	0.10(Mn)
P	0.0050
S	0.0060
Si	0.14
Cr	20.34
Ni	70.829

Co	0.07
Cu	0.15
W	0.06
Nb	3.59
V	0.05

4.2 Mechanical Testing & Characterization study - Specimens in ASTM standards:

The specimens for tensile testing for the measurement of tensile strength, breakage strength, rough elongation and area reduction are prepared in the following dimensions as per ASTM standards. All the dimension shown in the figures are in milli meters.

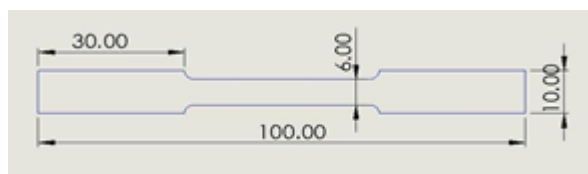


Fig :14 Tensile specimen- Top View

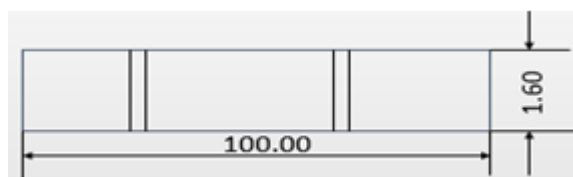


Fig: 15 Front View of the Tensile Specimen

The specimen for porosity test is in the dimension of 50 X 50 mm and for the SEM & XRD characterization specimen in the dimension of 10 X10 mm respectively.

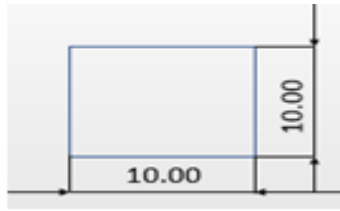


Fig:16 Top view of SEM & XRD specimen

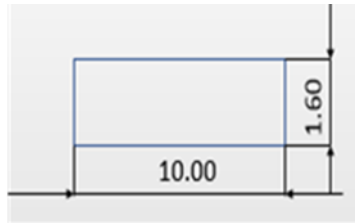


Fig:17 Front View of SEM & XRD specimen

The various test specimens like, tensile test, porosity, scanning electron microscope images, X-Ray diffraction were prepared as per the ASTM standards.

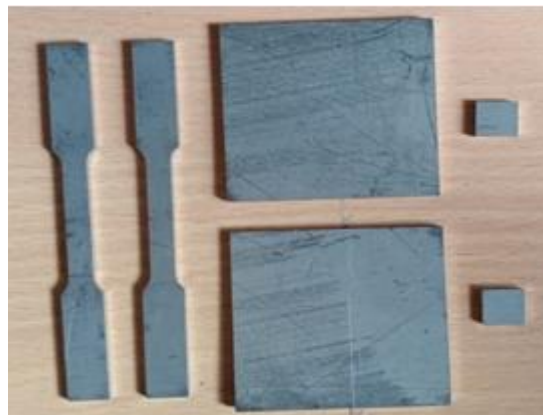


Fig:18 Various Specimens machined in LBM process

4.3 Characterization study:

To study about the topographical information of the specimens, scanning electron microscope images were taken for all heated specimens. For this study “Hi-Resolution Scanning Electron Microscope (HRSEM)” machine with make/model of “Thermo scientific Apreo S” has been used.



Fig:19 High Resolution SEM



Fig:20 AERIS- High Resolution Bench Top XRD

To examine the structure of crystalline material and its crystalline phase XRD analysis were examined. For this study “X-Ray Diffractometer (XRD)” machine with make/model of “AERIS- High Resolution Bench Top XRD” has been used. Thereby XRD analysis reveals the information chemical composition of the specimens being investigated.

4.4 EXPERIMENTAL WORK

The specimens were cleaned and washed with kerosene and acetone to remove the scaling and deposits before starting the heating process in the muffle furnace. The specimens were placed in an alumina crucible and immersed in a salt bath for the heating process. Alumina crucibles were preferred because of its high temperature withstand ability and non-reactive to the molten salts. Hastelloy X specimen were put in sodium sulphate salt bath whereas Inconel 625 specimen were placed in sodium and potassium chloride salt with a eutectic mixture of 7:3. The amount of salt in each crucible were 100 grams. The temperature in the muffle furnace was set to a range of around 900 °C. The heating process was carried out for a period of 25 hrs.

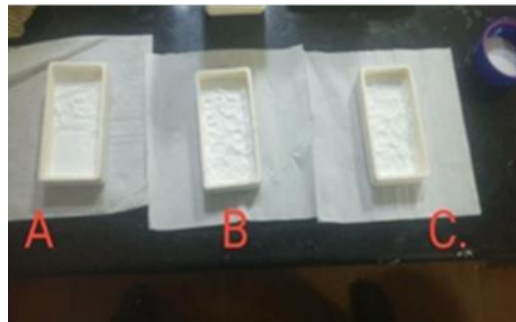


Fig:21 Specimens with molten salts in alumina crucibles



Fig:22 Alumina Crucibles in Muffle furnace and Heating process

After the heating process for 25 hours the samples were allowed to cool down to room temperature inside the furnace. After cooling period, the samples were removed from the crucible salt bath.

The excess salt deposit was on the specimens were removed by polishing the surface gently using abrasive paper. The samples after polishing were tested for various mechanical properties like tensile and hardness values.



Fig:23 Inconel 625 Specimens after 25 hours of Heating



Fig:24 Porosity and SEM & XRD and Inconel 625 specimen

Figure 21,22,23,24 are the various test specimens taken from the muffle furnace after completion of 25hours of heating at 9000C. The scaling formed over the specimens was removed with gentle scrubbing with the abrasive paper. The specimens were polished with the soft sheets for getting better results.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Mechanical Testing- Tensile test

After doing the experiments, i.e., heating the various specimens for 25 hours the specimens were used for mechanical testing like tensile test and Hardness measurements.

TABLE 5.1: AVERAGE TENSILE RESULTS FOR INCONEL 625

This table shows the Average Tensile Results for various parameters

Test Parameters	Observed Value	Observed Value	Observed Value	Average Value
Sample ID	T1	T2	T3	
Yield Strength (MPa)	400	415	387	400.67
Ultimate Tensile Strength (MPa)	682	722	683	689
% of Elongation in 25mm GL	36	34	33.5	34.5



Fig:25 Specimens after Tensile testing

5.2 Mechanical Testing: Hardness Measurement

The hardness test was carried out to measure the average hardness of all the 25 hours heated specimens. Vickers hardness tester was used to carry out the hardness test of the heated specimens.

TABLE 5.2: AVERAGE HARDNESS RESULTS FOR INCONEL 625

This table shows the Average Hardness Results

Sample ID	Hardness in HV 10kg	Average Value in HV 10kg
1	163,161,164	162.67
2	179,180,177	178.67
3	173,174,170	172.33
Average Value of Hardness		513.67 HV

Based on the experimental validation the tensile strength of the Hastelloy X specimen was increased to 4.25 % since the tensile strength of unheated specimen from 773 MPa changed to 807.34 MPa for heated specimen. The changes of the tensile strength are occurred due to the high temperature aggressive environment. Similarly, the hardness value was decreased to 10.68%, since the average hardness from 260 HV is reduced to 232.22 HV.

In the view of Inconel 625, the tensile strength of was increased to 8.56% since the tensile strength increases from 630 MPa of untreated specimen to 689 MPa for heated specimen. The hardness value of Inconel 625 heated specimens reduced by 5.83%, since the average hardness from 545.55 HV is reduced to 513.67 HV for heated specimen.

Variations in the Tensile Strength

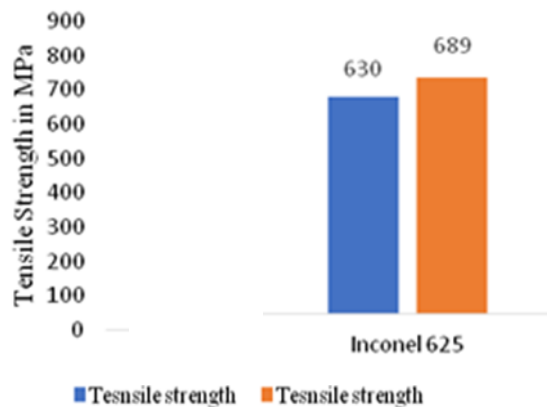


Fig:26 Changes in the Tensile Strength

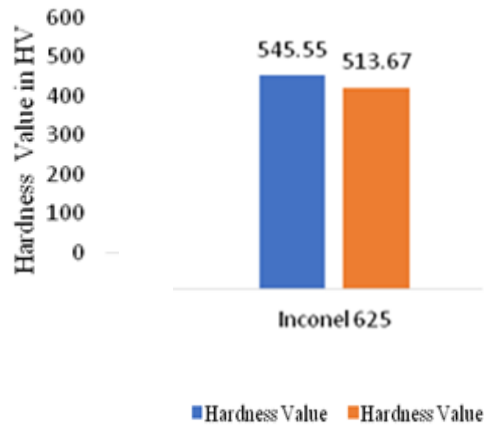
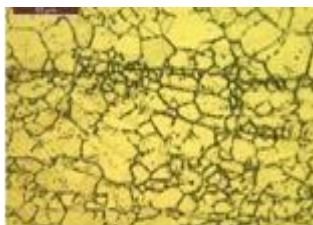


Fig:27 Changes in the Hardness value

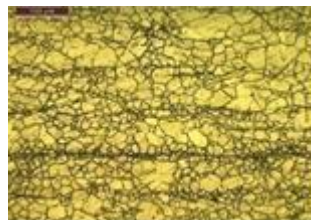
5.3 Microstructural Analysis: Porosity Results:

The porosity images of Inconel 625 specimens were taken to know about the micro structure and elemental void formation in the materials.

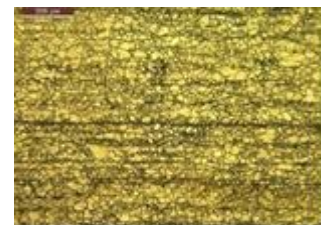
Inconel 625



500 X magnification



200 X magnification



100 X magnification

Fig:28 Porosity Images with 100x, 200X & 500 X magnification

The microstructure of Inconel 625 samples is shown in Fig.28. From the above porosity images, it has been inferred that more amount of void formation is seen in the 25 hours heated specimen when compared with the raw material. Uniform presence of carbides is seen on the grain boundaries and on the grains. The grain growth in the heat-treated specimens established the occurrence of the crystallization process.

5.4 Microstructural Analysis: SEM Analysis

The Scanning electron microscope images were taken to know about the topographical information of both specimens after the heat treatment process.

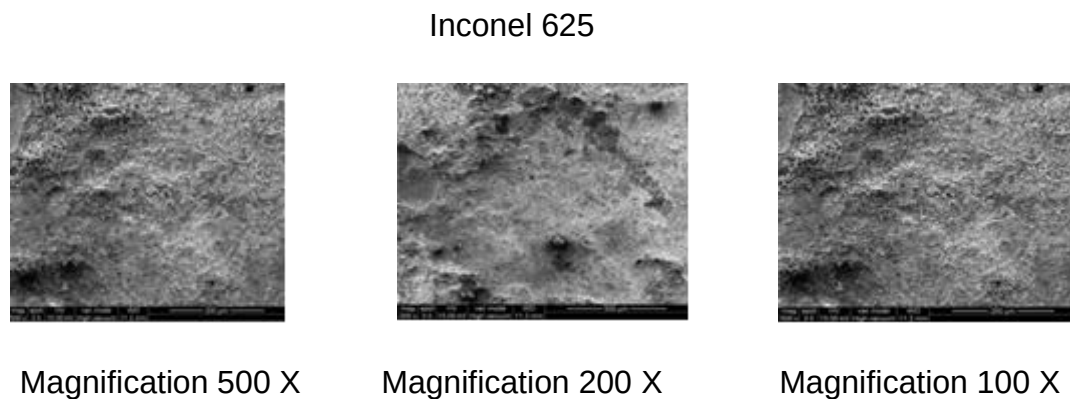
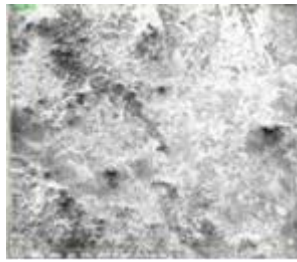


Fig:29 SEM Images of Inconel 625 specimens

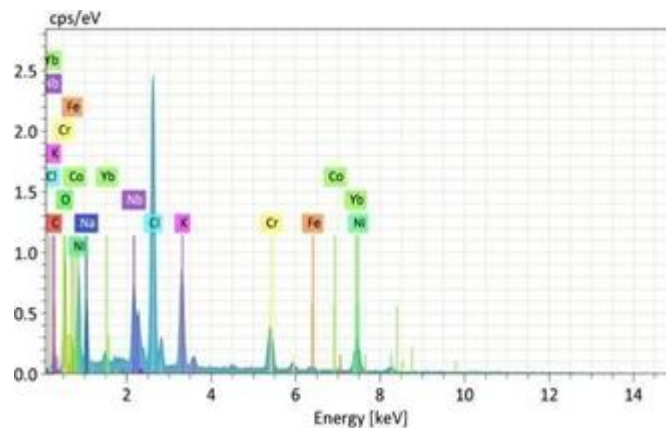
The 25-hour heated specimen's topographical images were taken with a scanning electron microscope (SEM). The figures show topographical structure of the Inconel 625 specimens under 500X, 200X and 100X magnifications respectively. The topographical information of the heated specimens can be clearly assessed by the SEM images [28-29]. Influence of heating, leads the specimen with surface deposits of corrosion. This indicates that corrosion and scaling of salt deposits on the surfaces were caused by heating.

5.5 Elemental Analysis: EDS analysis:

Inconel 625



EDS Image in 2000 X magnification



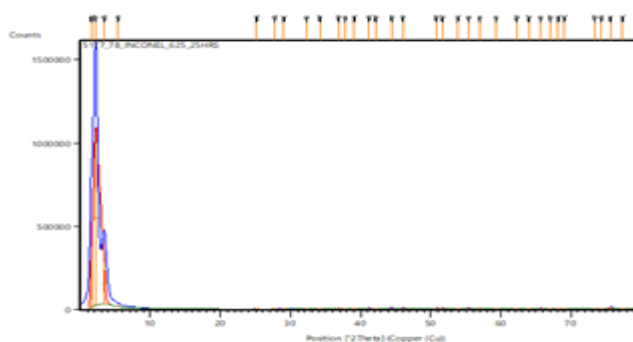
Energy Spectrum of Inconel 625

Fig:30 EDS Analysis results of Inconel 625 specimens

From the above EDS images, the degradation of substrate material due to the continuous corrosion attack can be clearly seen. The voids and scaling formation on the substrate material are available throughout the material surfaces. The EDS images of the super alloys expose that Inconel 625 material is much corroded on compare with other alloys.

From the EDS energy spectrum, the sodium from the molten salt is formed highly on the surface can be seen in the alloy. In a similar manner the chloride scaling was formed over the Inconel 625 surface and the presence of potassium and sodium from the salt can be seen on the Inconel 625 surface.

5.6 Elemental Analysis: XRD Analysis



XRD DATA: Inconel 625

Fig:31 XRD Results & Inconel 625 specimens

X-Ray diffraction analysis is used to examine the materials subjected to dislocations, twinning, micro stresses, grain boundaries... etc. [20-22]. From the XRD results, the presence of sodium and potassium chemical content in Inconel 625 is again sustained comparing with EDS results. Similar to that there is considerable amount of deposition of the sulphur content on the Hastelloy X specimen is also verified.

CHAPTER 6

CONCLUSION

It is apparent that super alloys based on nickel chromium are ideal for service with high temperatures. Na₂SO₄ (sodium sulphate) and eutectic mixture of sodium and potassium chloride molten salts atmosphere were heated to a temperature range of 850 °C – 900 °C for a period of 25 hours with Inconel 625 specimens respectively. After the heat treatment process, corrosion was found on the surface of both specimens. The heated specimens were tested and interpreted for mechanical measurements such as tensile and hardness and other morphological and topographical measures such as porosity, SEM, XRD and EDS Analysis.

- The heating process of the specimens leads to decrease in hardness value 5.83 % in Inconel 625 specimens.
- Since, the hardness decreases, the micro structural changes on the material likewise leads to substantial increase in tensile strength up to 8.26% in Inconel 625 specimens.
- The Scaling and void formation on the Inconel 625 specimens were visualized with Porosity, SEM and EDS images.
- Sodium and potassium chemical deposits on the Inconel 625 specimens were clearly supported with SEM-EDS & XRD analysis.

Inconel 625 with molten salts in aggressive thermal environment is continuously subjected to corrosion which degrades the material property to a considerable amount. Hence it is suggested that for thermal energy storage applications, the above said materials can be used with thermal barrier coatings, which may improve the stability of the material in high temperature applications.

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