



Molten salt for advanced energy applications: A review

Robin Roper^{a,*}, Megan Harkema^b, Piyush Sabharwal^c, Catherine Riddle^c,
Brandon Chisholm^b, Brandon Day^a, Paul Marotta^d

^a University of Idaho – Idaho Falls, 1776 Science Center Dr, Idaho Falls, ID 83402, United States

^b Vanderbilt University, 2201 West End Ave, Nashville, TN 37235, United States

^c Idaho National Laboratory, 2525 Fremont Ave, Idaho Falls, ID 83402, United States

^d MicroNuclear LLC, 9005 Overlook Blvd #730, Brentwood, TN 37027, United States



ARTICLE INFO

Article history:

Received 24 June 2021

Received in revised form 4 November 2021

Accepted 15 December 2021

Available online 11 January 2022

Keywords:

Molten-salt

Energy

Power

Production

Chemistry

Challenges

ABSTRACT

The primary uses of molten salt in energy technologies are in power production and energy storage. Salts remain a single-phase liquid even at very high temperatures and atmospheric pressure, which makes molten salt well-suited to advanced energy technologies, such as molten salt reactors, or hybrid energy systems. The molten salt cooled reactor is an advanced nuclear reactor concept that utilizes molten salt as either a coolant for solid fuel or as a fuel salt. The liquid phase provides orders of magnitude higher heat capacity per cubic meter than the gas phase. This, coupled with the low-pressure environment required to maintain the liquid phase, provides significant advantages in terms of compact-sized systems constructed with relatively thin walls.

The heat from a heat-generating process is transferred to a heat transfer media and can be extracted later using a secondary power cycle. There are several types of facilities that use thermal energy storage with molten salts, such as concentrated solar power plants (CSP plants) or nuclear hybrid energy systems (NHES). A CSP plant is a power production facility that uses a broad array of reflectors or lenses to concentrate solar energy onto a small receiver. Since molten salt remains in the liquid phase, it has excellent heat retention properties, meaning heat from a solar-generation process can be stored for an extended period for later use. A Nuclear Hybrid Energy System (NHES) refers to several energy systems combined to generate energy more efficiently, such as nuclear reactors, renewable energy sources, process heat applications, and energy storage.

The selection of a salt type for a nuclear reactor or a thermal storage system requires careful consideration of the chemical and thermodynamic properties of the candidate salts. Different energy technologies will require different salt types, based on temperature and fluid property requirements. Fluoride salts are often the primary candidate salts for nuclear reactor systems. Chloride salts are another category of candidate salt that have been considered for power production because chloride salts often exhibit similar behavior to fluoride salts. Nitrate-nitrite salts contain NO₃ and NO₂ and are used in solar applications.

As with other nuclear reactors, molten salt systems involve radiological and chemistry challenges, including tritium production and corrosion. Tritium production can be problematic in a reactor system because it can be a hazard to human operators. Tritium is difficult to contain; therefore, the production of tritium must be minimized. Corrosion of structural materials is also an area requiring further study in molten salt systems. Corrosion in a molten salt system differs from standard nuclear reactor systems due to the lack of a passive oxide film on the surface of structural materials, making it necessary to mitigate corrosion by either purifying the salt, controlling its redox potential in a reducing state, or using redox buffers. Additionally, since molten salt reactors are constructed with much thinner structural members

Abbreviations: AHTR, Advanced High-Temperature Reactor; ANL, Argonne National Laboratory; ANP, Aircraft Nuclear Propulsion; ASME, American Society of Mechanical Engineers; CFR, Circulating Fuel Reactor; CSP, Concentrated Solar Power; DNP, Delayed Neutron Precursor; DOE, United States Department of Energy; FHR, Fluoride salt-cooled High-Temperature Reactor; FOM, Figures of Merit; GTCC, Gas Turbine Combined Cycle; HF, Hydrofluoric Acid; HTF, Heat Transfer Fluid; HTRE, Heat Transfer Reactor Experiment; INL, Idaho National Laboratory; LWR, Light Water Reactor; MARS, Minor Actinide Recycling in Molten Salt; MOSART, Molten Salt Actinide Recycler and Transmuter; MSBR, Molten Salt Breeder Reactor; MSFR, Molten Salt Fast Reactor; MSR, Molten Salt Reactor; MSRE, Molten Salt Reactor Experiment; NACC, Nuclear Air Brayton Combined Cycles; NARC, Nuclear Air Brayton Recuperated Cycle; NHES, Nuclear Hybrid Energy System; ORNL, Oak Ridge National Laboratory; PISA, Potential Inadequacies in Safety Analysis; RGRS, Reactive Gas Recovery System; SAMOFAR, Safety Assessment of the Molten Salt Fast Reactor; SCO₂, Supercritical CO₂; SCWR, Supercritical Water Reactor; TES, Thermal Energy Storage; TMSR, Thorium-breeding Molten Salt Reactor; TRL, Technology Readiness Level.

* Corresponding author.

E-mail address: rope1623@vandals.uidaho.edu (R. Roper).

due to low-pressure loads, reducing reactor operating lifetime and/or marginally increasing the structural thickness to provide additional corrosion allowance may be acceptable design approaches.

The behavior of volatile fission products in Fluoride and Chloride salts is also a consideration due to the volatility of insoluble fission products that precipitate and plate out on surfaces affecting thermal hydraulic parameters. Fission products such as cesium (Cs), iodine (I), strontium (Sr) and other salt seekers, have a complexing nature with fluoride (F) and iodine (I) and their behavior in molten salt reactors will have to be addressed. Molten salt reactors present a particular challenge for recycling fission products including solubility, volatility, and precipitation behavior, and how the fission products change the corrosivity of the salt melt. Current nuclear fuel recycling technology will not accommodate molten salt streams and will need to be redesigned. New molten salt recycling designs and chemistry will ultimately need to be applied to a variety of fluoride and chloride salts mixtures.

All thermal energy facilities either utilize the heat energy produced directly, such as space or process heating, or convert a portion of the heat energy to some other energy form such as electricity. The energy conversion cycles utilized in most (if not all) other types of base-load power plants (e.g., coal-fired power plants, gas-fired power plants, and nuclear power plants) are the Rankine and Brayton power conversion cycles. MSRs are also coupled with both Rankine and Brayton power-conversion cycles to transform heat into other energy forms. The feasibility for cycle coupling with MSRs depends on a variety of factors; two of the more important factors are technology readiness level (TRL) and efficiency. The application of existing steam cycle designs will likely require modifications to equipment. Steam generators and reheaters will present a particular problem in accommodating the molten salt. The adaptation of the plant to the molten salt reactor will require trade studies to obtain information necessary for further design.

© 2022 Elsevier Ltd. All rights reserved.

Contents

1.	Introduction	3
2.	Energy technologies	3
2.1.	Power production – nuclear energy	3
2.1.1.	The molten salt reactor experiment	3
2.1.2.	Pyrochemistry and fuel recycling	4
2.1.3.	Actinide burning	5
2.1.4.	Modern nuclear technologies	5
2.2.	Thermal energy storage	5
2.2.1.	Concentrated solar plants	6
2.2.2.	Solar Two	6
2.2.3.	Nuclear hybrid energy system	7
3.	Molten salt chemistry	8
3.1.	Selection of salts for energy technologies	9
3.2.	Chemistry challenges	9
3.2.1.	Tritium	9
3.2.2.	Corrosion and materials compatibility	9
3.2.3.	Irradiation and fission products	11
4.	Power production	11
4.1.	Unique MSR technologies	11
4.1.1.	Joining technologies	12
4.1.2.	Valve technologies	13
4.1.3.	Instrumentation technologies	13
4.2.	Power production technologies	13
4.2.1.	Rankine cycle	14
4.2.2.	Supercritical Rankine cycle	14
4.2.3.	Brayton cycle	14
4.2.4.	He Brayton cycle	15
4.2.5.	Supercritical CO ₂ Brayton cycle	15
4.2.6.	Air Brayton cycle	15
4.2.7.	Air Brayton combined cycles	15
4.2.8.	Air Brayton combined cycles energy storage	16
4.3.	Coupling and integration challenges	16
4.4.	Modeling challenges in reactor systems	17
5.	Conclusion	18
	Declaration of Competing Interest	18
	References	18

1. Introduction

Molten salts are becoming a prevalent part of today's ongoing energy technology developments. The original development of molten salt energy systems began in the 1950s with the Aircraft Reactor Experiment, and with the Molten Salt Reactor Experiment in the 1960s. Shortly after, research in that area declined in favor of light-water reactor (LWR) technology, due to the market demands to make step-change improvements to existing LWR technology. A renewed interest has taken hold in molten salt research, with many resultant developments. Nuclear reactor systems are being developed using fuel dissolved in molten salts, and thermal energy storage systems are being made more efficient using molten salt as a heat transfer fluid. This work contains a review of some molten salt energy technology systems and the use of molten salt in advanced nuclear power systems.

A 'salt' is an ionically bonded chemical, consisting of positively and negatively charged component ions. A typical example of a salt is sodium chloride (NaCl), commonly known as 'table salt.' Salts are typically named for their anion, or negatively charged component. Salts have typically high melting ranges, and molten salts are often used in energy technologies due to their reasonable thermodynamic properties at their melting temperatures. A more detailed discussion of molten salt chemistry and behavior can be found in section 2 of this work.

2. Energy technologies

The primary uses of molten salt in energy technologies are in power production and energy storage. The physical characteristics and heat transfer properties of molten salt are well-suited to advanced high-temperature energy technologies, such as molten salt reactors or hybrid energy systems. This section discusses the two primary energy applications for molten salts: nuclear power production and thermal energy storage.

2.1. Power production – nuclear energy

The molten salt cooled reactor is an advanced nuclear reactor concept that utilizes molten salt as either a coolant for solid fuel or as a fuel salt. The molten salt reactor concept originated in the 1940s and 1950s but has resurfaced as part of Generation IV advanced reactor initiative (Kelleher, 2015; Williams and Britt, 2017; Serp, 2014). The main advantage that the concept presents is high-temperature single phase liquid operation on the order of 600 °C at low, i.e., near atmospheric pressure. LWR technology produces steam temperatures on the order of 300 °C and requires that components withstand pressures that are 140 times atmospheric pressure. Thus, molten salt reactors have the inherent advantage of dramatically improved thermal performance due to high temperature, and at the same time reducing cost since LWR components are extremely thick and expensive to produce/construct (Kelleher, 2015).

A liquid-fueled molten salt reactor has many potential advantages to LWRs, including safety, economic, nonproliferation, and environmental advantages (Kelleher, 2015; Serp, 2014):

- MSRs are safer because they can operate at low pressure, without concern of melting fuel or clad leaking fission products (Dolan, 2017). Separation of fission products and noble gases can occur continuously, reducing the source term in the case of an accident. The liquid state stability of the fuel salt at high temperature eliminates energetic source term vectors such as rapid steam expansions/explosions typical of LWRs.

- Economically, the MSR concept is advantageous due to:
 - o Core design simplification and reduced manufacturing cost;
 - o Reduction of structural section thickness due to reduced operating pressure;
 - o The liquid nature of an MSR provides a higher heat capacity, which aids in the design of compact, less-expensive reactor designs;
 - o Compact reactors can be mass-produced and shipped to reactor sites, which reduces construction costs; and
 - o Used LWR fissile material could be used to start up a reactor, reducing waste materials.
- The MSR concept has the ability to breed thorium to produce fuel. Because thorium is much more abundant than uranium, (Dolan, 2017) this would expand the global fuel supply. MSRs could also recycle or burn actinides, reducing the global stockpile of nuclear waste. Plutonium can also be recycled and burned in an MSR core, reducing plutonium inventory for non-proliferation purposes.

2.1.1. The molten salt reactor experiment

The Molten Salt Reactor Experiment (MSRE) originated in the 1950s with the Aircraft Nuclear Propulsion (ANP) program. The ANP program was developed to satisfy the United States' need for long-range aircraft solutions. On-board nuclear reactors were considered for aircraft propulsion, however, to accomplish the power required for jet engines, nuclear reactors would need to produce high-temperature superheated gas. The Heat Transfer Reactor Experiments (HTREs) were operated to demonstrate this ability. Two of these reactors are now displayed at Idaho National Laboratory (see Fig. 1) (Kelleher, 2015).

The HTREs functioned well but had issues with the narrow fuel elements required for their compact design. At this point, it was proposed that the fissile material be dissolved into a liquid coolant, which would eliminate challenges with fuel-element structure (Kelleher, 2015).

The Molten Salt Reactor (MSR) program was eventually developed, and the Molten Salt Reactor Experiment (MSRE) began construction in 1960 (Kelleher, 2015). The MSRE consisted of a primary loop of LiF-BeF₂-ZrF₄-UF₄ (61.0:29.1:5.0:0.9 mol %), and a secondary loop of LiF-BeF₂ (66:34 mol %) (Kelleher, 2015). The reactor core was a multi-channel graphite structure, through which the salt flowed and became critical. Fig. 2 shows a schematic of the MSRE (Williams and Britt, 2017).

The MSRE successfully demonstrated the MSR concept, operating for 15,424 full power hours without significant incident. The experiment also demonstrated the ability of an MSR to operate on uranium-233, demonstrating the breeder concept. After this demonstration, design and development began on a Molten Salt Breeder Reactor (MSBR), but the project was eventually ended as funding was diverted to liquid metal breeder reactors (Kelleher, 2015). Although the development of a full molten salt reactor was halted, interest has reignited in the last decade. At the beginning of the century, the Generation IV International Forum highlighted six nuclear reactor designs as next-generation designs (Williams and Britt, 2017). The MSR concept is one of these Generation IV reactor concepts, and efforts around the globe have refocused on its development.

Although the MSRE ended, the facilities were not removed. In 1998, the decision was made to process fuel and flush fluoride salts from three MSRE drain tanks, to reduce risk from the salt to off-site and on-site locations (EPA Superfund Record of Decision, 1998). This decision was made to address the uranium in the fuel salt, which was a potential hazard. The salt in the drain tanks was



Fig. 1. Two of the Heat Transfer Reactor Experiments (HTRE). (Kelleher, 2015).

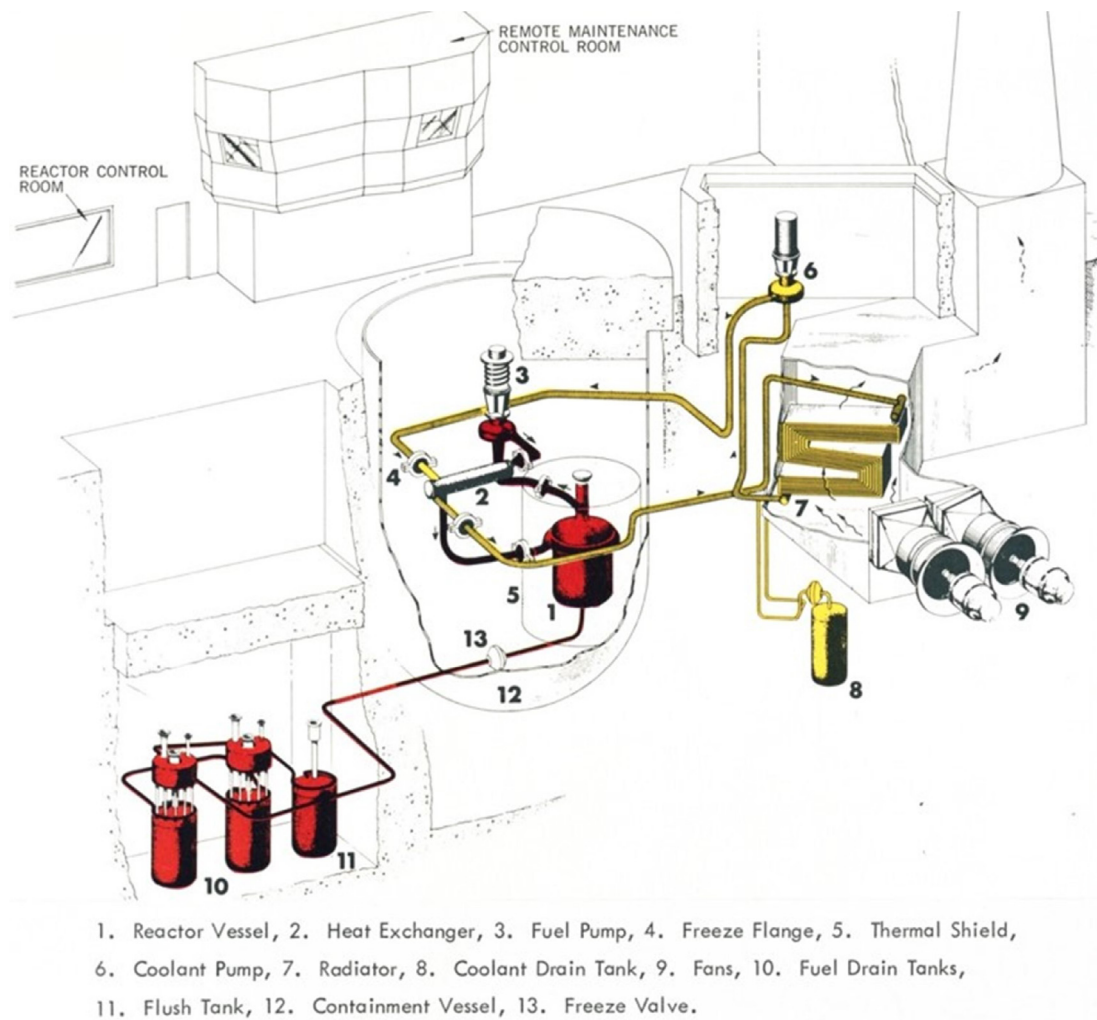


Fig. 2. Schematic of the MSRE. (Williams and Britt, 2017).

removed and processed to remove the uranium from the salt, and the remaining salt was placed in interim storage. In 2015 and 2016, Oak Ridge National Laboratory (ORNL) evaluated the MSRE facilities, identifying potential inadequacies in safety analysis (PISAs). These PISAs involved the potential corrosion in the reactive gas recovery system (RGRS) pump and piping, and the potential release of fluorine and hydrogen fluoride gases from the salt tanks and the spent sodium fluoride and alumina traps (STJ-02MSRE-D992). The

PISAs were used to evaluate the ability to maintain the facilities safely until they are decommissioned and demolished, which is scheduled for the year 2060 (STJ-02MSRE-D992).

2.1.2. Pyrochemistry and fuel recycling

With the creation of nuclear power plants, one of the most significant issues that arose was what to do with the waste once the fuel rods were decommissioned. Before 1984, when the fission

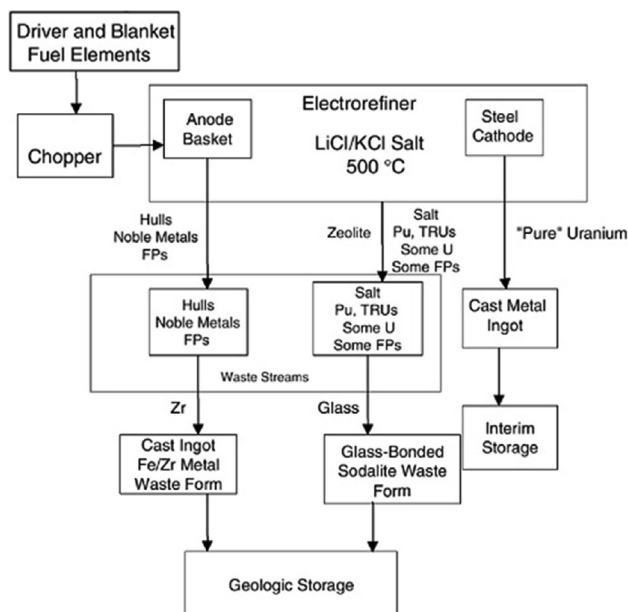


Fig. 3. Pyroprocessing schematic.

reaction had ceased in the fuel cells, the rods would be removed and stored in a water-containment vessel for an extended period before they were cool enough to store in an off-site facility. Additionally, not all the usable uranium was used during the fission process, but it was left unrecovered from the decommissioned rods. In 1984 Idaho National Laboratory (INL) and Argonne National Laboratory (ANL) pioneered a pyroprocessing method for recovering and recycling fissile material from used fuel (Simpson, 2012; Simpson and Law, 2010).

Pyroprocessing uses high-temperature molten salts as the electrolyte for an electrochemical process. Molten salts have several advantages over other electrolytes: excellent heat transfer characteristics, large heat capacities, and stability at high temperatures ranging from 120 to 1000 °C. Additionally, molten salts have large potential windows (LiCl-KCl eutectic −2.6 to 1.3 V Vs. Ag/AgCl) which allows for a wider variety of elements to be reduced. Fig. 3 shows a schematic of a pyroprocessing system (Utgikar, 2019).

Once fuel rods have been decommissioned from the reactor, those that still have enough recoverable material, known as used (instead of spent) fuel rods, are sent for processing. Before being placed in the molten salt bath, they are sent to be sectioned up into smaller pieces to fit in a basket that behaves as the anode (i.e., the electrode where oxidation reaction occurs) for the process. Once the electrorefining begins, depending on the ionic state of the element, some uranium will be attracted to a cathode while the rest remains in the solution. Other elements, such as rare-earth elements, can also be attracted to the cathode and recovered along with the uranium. Afterward, the uranium will be refined and cast to be reused in fuel rods. The remainder of the elements from the fission process can be left within the solution or deposited on the anode. These residual elements are processed through various means for storage. Noble metals are cast into ingots, while the salt and the elements contained within are turned into glass-bonded sodalites. Once this process is completed, they are placed in a facility for long-term storage.

2.1.3. Actinide burning

Nuclear power reactors typically operate commercially using a 'once-through' cycle. This means that spent nuclear fuel is

unloaded from the reactor and stored as nuclear waste. Much of this waste contains materials which can be reused in another reactor, or that can be transmuted, thus reducing the amount of waste. Actinides, such as neptunium, americium, and curium, can be 'burned' or transmuted under certain reactor conditions. Fast reactors have a large ratio of fission-capture cross-sections and are effective at burning actinides. (Yu et al., 2015).

2.1.4. Modern nuclear technologies

With the resurgence of molten salt nuclear technology research, there are many molten salt nuclear technologies being developed in the modern day (Ignatiev et al., 2015; Dolan, 2017; Europe – EVOL's Molten Salt Fast Reactor, 2021; Samofar; World Nuclear Association, 2021). Researchers and institutions, in both government and private industrial sectors, are developing molten salt reactors or molten salt processing technology. These include liquid-fueled reactors, or solid-fueled reactors with molten salt as a coolant. Some of these designs are projected to be operational in the coming decade. The Molten Salt Fast Reactor (MSFR) is one such reactor. It is a liquid-fueled design with a closed Thorium/Uranium fuel cycle (Europe – EVOL's Molten Salt Fast Reactor, 2021; World Nuclear Association, 2021). It is under development by EVOL, a Euratom project by six participating European countries. The Safety Assessment of the Molten Salt Fast Reactor (SAMOFAR) project is a molten salt development project in conjunction with the MSFR, with the goal of proving safety concepts of MSFR breeding and operation (Europe – EVOL's Molten Salt Fast Reactor, 2021; Samofar; World Nuclear Association, 2021).

The Advanced High-Temperature Reactor (AHTR), also known as the fluoride salt-cooled high-temperature reactor (FHR), is a solid-fueled design with a graphite and solid fuel core structure. It utilizes molten salt as a coolant, rather than as a fuel. A prototype is currently under construction. (World Nuclear Association, 2021). The Thorium-breeding molten-salt reactor (TMSR) is a thorium-based reactor design program under development in China, under the China Academy of Sciences, launched in 2011 (World Nuclear Association, 2021). The TMSR program includes the AHTR/FHR reactor, as well as a second track of development for a liquid fueled reactor. The US department of Energy is collaborating with the China Academy of Sciences on the program (World Nuclear Association, 2021).

Another reactor design to note is the Molten Salt Actinide Recycler and Transmuter (MOSART) project. This project is under the MARS (minor actinide recycling in molten salt) program, which involves research organizations such as Riar and Kurchatov. The MOSART is a fast reactor fueled by transuranic fluorides from uranium and light-water reactor spent fuel (Ignatiev et al., 2015; World Nuclear Association, 2021).

Many private companies are developing molten salt reactor technologies. These include companies such as Kairos Power, Moltex Energy, Flibe Energy, Terrestrial Energy, TerraPower, and Transatomic Power (World Nuclear Association, 2021). Many more organizations are in various stages of development, and are too numerous to list in this work. The contributions to the molten salt technology field from research organizations, both private and public, are quickly advancing the field of nuclear molten salt technology, and it is likely that the global energy sector will see functional molten salt reactors in the next decade.

2.2. Thermal energy storage

Thermal Energy Storage (TES) can be divided into three areas: sensible heat materials (solid and water), latent heat (phase change materials) and thermochemical (endothermic chemical reversible reactions) (Cabeza, 2014). Sensible heat is stored within a single-phase material with increasing or decreasing the temper-

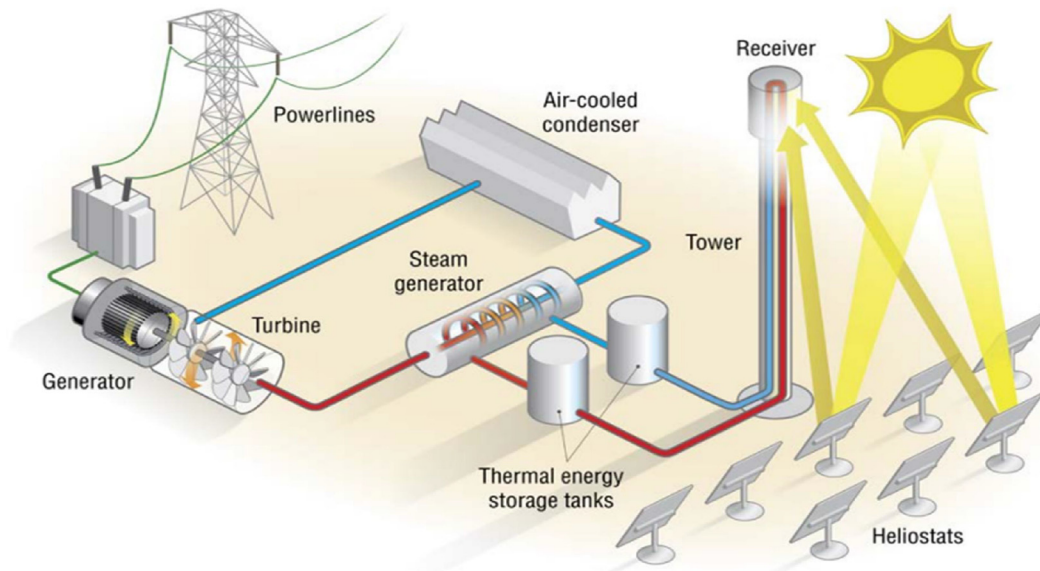


Fig. 4. CSP plant with thermal energy storage tanks. (U.S. Department of Energy, 2014).



Fig. 5. The Solar Two power plant. (Bradshaw et al., 2002).

ature, and latent heat is stored using material phase change properties such as solid–liquid phase change by melting and solidification using either heat or cold phase change materials (PCM). The heat from a heat-generating process is transferred to a heat-transfer medium and can be extracted later using a secondary power cycle.

There are several types of facilities that use thermal energy storage with molten salts. This work will focus on two types: the concentrated solar power plant (CSP) and the nuclear hybrid energy system (NHES).

2.2.1. Concentrated solar plants

A CSP plant is a power-production facility that uses a broad array of reflectors or lenses to concentrate solar energy onto a small receiver. Molten salt in the receiver is heated by solar energy and directed to thermal energy storage or a power cycle. Fig. 4 shows a schematic of a CSP plant containing thermal energy storage systems and a power cycle (U.S. Department of Energy, 2014). In this type of system, cold molten salt is pumped to the top of the power tower containing the receiver, where it is heated by the concentrated solar power. It then flows to a hot storage tank, which stores the hot salt until it is needed for power production. After the power cycle, cold molten salt is stored in a cold storage tank

until it is needed. Molten salt has excellent heat retention properties, meaning it can be stored for an extended period and retain the solar-generated heat for later use (U.S. Department of Energy, 2014).

The salt used in these types of CSP plants is called a heat transfer fluid (HTF). The salts selected for HTFs are typically chloride or nitrate salts. Chloride salts are promising due to their wide operating temperature ranges, but pose challenges with corrosion (Ding et al., 2019). Nitrate salts are more common, particularly a blend of sodium and potassium nitrate, known as ‘solar salt’ (Turchi et al., 2018). More discussion on the chemistry, corrosion, and challenges associated with these salts is found in Section 3 of this work.

2.2.2. Solar Two

An example of a CSP plant with thermal energy storage is the Solar Two power plant, operated by the U.S. Department of Energy. The Solar Two program was operated to validate sophisticated CSP technologies using molten salt and was built using existing facilities from the Solar One pilot plant.

The Solar One pilot plant was a power-tower technology plant that operated from 1982 to 1988. In the 1990s, it was retrofitted to produce Solar Two, which demonstrated more advanced power-tower technology (Bradshaw et al., 2002). The primary difference between Solar One and Solar Two was the HTF used for the receiver. Solar One used water, and Solar Two used molten nitrate salt. Switching the power-tower to salt allowed the plant to have a more sophisticated thermal storage system, which meant the electricity generation and solar energy collection could be separated, and the power generation could become dispatchable. (Bradshaw et al., 2002) Modifications to the Solar One plant required a new heat transfer system to accommodate the molten salt, as well as a new control system. (Bradshaw et al., 2002) However, the turbine and generator, tower, and heliostat field only required minor modifications. Fig. 5 shows a photo of the Solar Two plant during operation. (Bradshaw et al., 2002) Solar Two operated from June 1996 to April 1999. (Bradshaw et al., 2002)

Solar Two operated using a power tower system, which would collect solar energy from a field of heliostats. Fig. 6 shows a schematic of the Solar Two plant’s energy generation and thermal storage system. (Bradshaw et al., 2002) The heliostat field reflected sunlight to a receiver at the top of the tower, which would heat a feed of cold (290 °C) nitrate salt. The salt was then fed to a hot

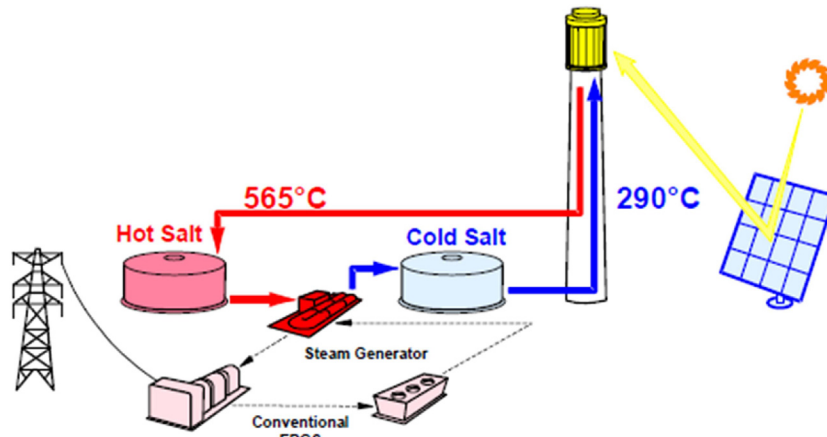


Fig. 6. Schematic of the Solar Two power generation system. (Bradshaw et al., 2002).



Fig. 7. Thermal energy storage tanks at the Solar Two plant. On the left is the cold tank, and on the right is the hot tank. (Bradshaw et al., 2002).

(565 °C) thermal storage tank, where it could be pumped as needed through a steam generator (Bradshaw et al., 2002).

The salt used for Solar Two consisted of approximately 3 million pounds (1300 tonnes) of 60 wt% NaNO_3 , and 40 wt% KNO_3 , which has a melting point of 205–220 °C (Bradshaw et al., 2002). This salt is typically only stable up to temperatures of 600 °C (Bradshaw et al., 2002). The nitrate salt mixture was chosen due to its heat transfer properties, which tolerated heat fluxes up to 1000 kW/m^2 , and had properties conducive to the double-tank thermal storage system. Equipment used for the hot salt, including pipes and valves, was constructed of stainless steel, which is more resistant to nitrate salt corrosion at elevated temperatures. Equipment used for the colder salt was constructed from carbon steel, which is more cost-effective.

The thermal energy storage system used at Solar Two used two tanks, a hot storage tank, and a cold storage tank. The cold storage tank was made from carbon steel, and the hot storage tank was made from stainless steel. Each tank was large enough to hold the entire plant's inventory of salt. Fig. 7 shows a picture of the Solar Two plant's thermal energy storage tanks (Bradshaw et al., 2002).

Table 1 shows the results of calculated and measured heat losses from the Solar Two plant (Bradshaw et al., 2002). As can be seen from the table, the heat loss from the thermal storage tanks was demonstrated to be very low. Because of these results at Solar Two, it was predicted that commercial power plants with similar thermal storage systems would have an annual thermal storage efficiency of about 99% (Bradshaw et al., 2002).

Table 1

Thermal losses at the Solar Two plant (Bradshaw et al., 2002).

Major Equipment	Calculated Thermal Loss, kW_t	Measured Thermal Loss, kW_t
Hot Salt Tank at 565 °C	98	102±21
Cold Salt Tank at 290 °C	45	44±6.6
Steam Generator System at 565 °C	14	29±3.5
Receiver Sump at 290 °C	13	9.5±1.0

2.2.3. Nuclear hybrid energy system

An NHES is a term referring to several energy systems combined to generate energy more efficiently. An NHES may include systems such as nuclear reactors, renewable energy sources, process heat applications, and energy storage.

An NHES design discussed by Green et al (Green et al., 2013) includes a high-temperature nuclear reactor, which allows a portion of thermal energy to be used for process heat applications. This reduces the carbon footprint of the system. Fig. 8 shows a

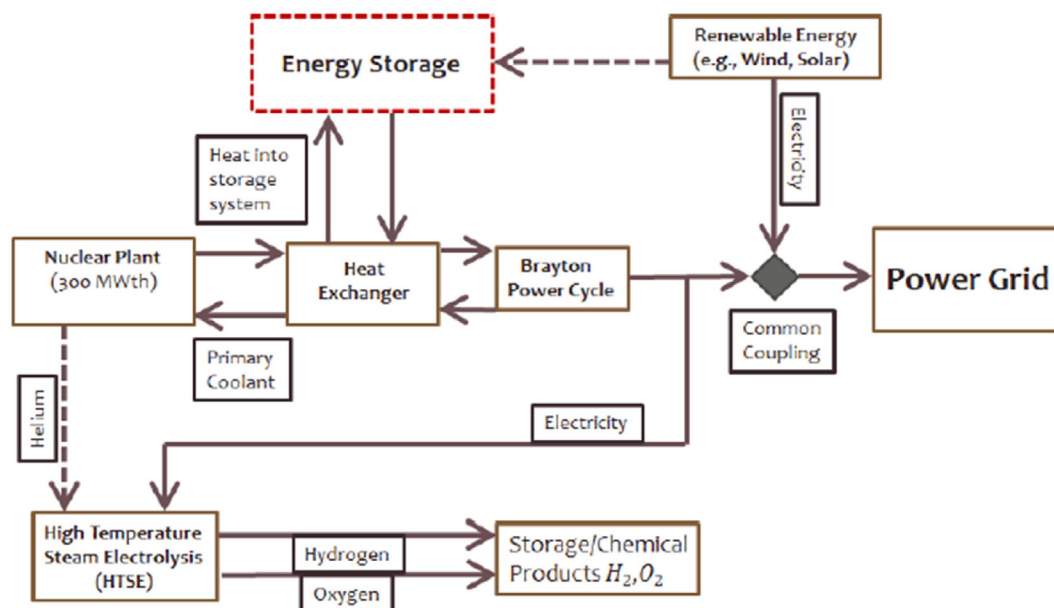


Fig. 8. The Nuclear Hybrid Energy System. (Green et al., 2013). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

schematic of the NHES. (Green et al., 2013) An energy storage system is required to allow the NHES to respond to fluctuating energy needs. A more detailed discussion of the efficiency and energy analysis of this type of system can be found in Section 5: Energy and Exergy Analysis.

This energy storage can be accomplished using molten salt thermal energy storage. Salt has a high temperature range and low viscosity, and there is existing experience in solar energy applications. Molten salt can be used in the NHES to store process heat from the nuclear plant, which can later be used when energy requirements increase. There are two different types of molten salt thermal storage options: a thermocline system, or a two-tank system. A two-tank system is like storage schemes used for CSP plants, in which a hot tank and a cold tank are used to store salt. A thermocline system uses only one tank, which contains both the cold and hot salt. The salt is separated by thermocline, which is a distinct layer of drastic temperature change. A thermocline prevents layers above and below it from mixing; therefore, the hot and cold salts do not mix in a thermocline storage tank. When the thermocline tank is charged, cold salt flows from the cold side of the tank, through a heat exchanger, and into the hot side, filling the tank with stored thermal power. When the tank is discharged, the hot salt flows out, through a heat exchanger, and returns to the cold side.

One challenge present in working with molten salt thermal energy storage is salt freezing. Molten salt has a high melting point. Freeze protection is required to prevent the salt from cooling too much. Otherwise, the salt freezes within the system, causing blockage. Freeze protection is often provided by heaters, but could also be provided using gas turbines by directing hot exhaust to the molten salt systems. (Green et al., 2013)

3. Molten salt chemistry

The chemical term “salt” refers to molecules that are ionically bonded. The components of salts consist of positively charged cations, and negatively charged anions, creating a bonded compound that has a neutral charge. A typical example of salt is sodium chloride (NaCl) or “table salt,” which is widely used. Molten salts melt at very high temperatures, often over 400 °C, because

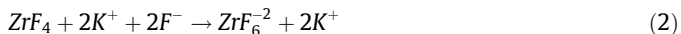
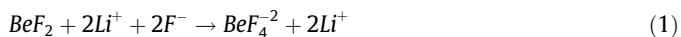
a lot of energy is required to break their ionic bond. Other salts, such as uranyl nitrate, which has a melting temperature of about 60 °C, do not require as much energy to break their bonds. These types of salts are referred to as “ionic liquids.” Energy production technologies, such as thermal energy storage or molten salt reactors, use molten salts because of their heat transfer and thermal properties at these high temperatures.

Salts are typically named for their anion, their negatively charged component. Salts typically used in energy applications include fluoride salts (LiF, NaF, KF, BeF₂), chloride salts (NaCl, MgCl₂, CaCl₂), and nitrate/nitrite salts (Ca(NO₃)₂, NaNO₃, KNO₃). Types of salts are mixed to produce salt eutectics with the properties desired for different applications. For example, ‘Flibe’ or LiF-BeF₂ (66:34 mol%) is a salt mixture often considered for molten salt reactor applications.

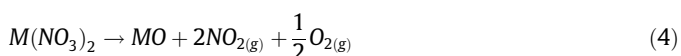
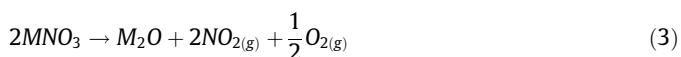
Chemicals interact with one another through either ionic or covalent interactions. In solid states, most chemicals are primarily ionic, with only a small amount of covalent character. Molten salts are unique because, in their molten state, they exhibit a mixture of ionic and covalent interactions. (Dolan, 2017) This fluctuates due to the changing nature of a molten salt system, such as the addition of components, fission-product generation, off-gassing, etc. This fundamental fluctuation of a molten salt system means that the chemical behavior and subsequent need for control can be complex.

Because molten salts are inherently ionic, they will disassociate into ions upon melting. Disassociation occurs when the thermal energy of each ion overcomes their bonding energy. Many salts disassociate at their melting point, or when dissolved into a solution. Lithium fluoride will disassociate at its melting point, forming the ions Li⁺ and F⁻. However, not all salts exhibit this disassociation behavior on their own. Beryllium fluoride will form a network of chained beryllium and fluoride atoms at its melting point, which can cause the salt to have a high viscosity. Zirconium fluoride also exhibits this non-disassociation behavior, causing a higher vapor pressure. ‘Flibe,’ a candidate MSR salt, was developed to combat the disassociation behavior of beryllium fluoride. Flibe is composed of lithium fluoride and beryllium fluoride. When beryllium fluoride melts, it can accept more fluorine atoms from an alkali fluoride,

forming a tetrafluoroberyllate coordination complex (see Equation (1)). Coordination complexes break the non-dissociative chaining behavior, allowing the salt mixture to have a lower viscosity. Zirconium fluoride also forms a similar coordination complex (see Equation (2)).



Molten nitrate-nitrite salt decomposition is more complicated than that of chloride and fluoride salts. The thermal decomposition of these salts depends on the composition, temperature, and experimental conditions. Nitrite may form from nitrate in the melt, releasing oxygen according to the following reactions, where M is a cation. (Bauer et al., 2013)



Alkali metal oxide can form in the melt, releasing nitrogen or nitrogen oxide gas. The nitrate salts may also vaporize. These thermal decomposition behaviors are influenced by intrinsic salt properties, such as the metal-nitrate bond. Polarization is induced by the cation, distorting the electron distribution in the nitrate, which lowers the decomposition temperature. (Bauer et al., 2013)

3.1. Selection of salts for energy technologies

The selection of a salt type for a reactor or a thermal storage system requires careful consideration of the chemical and thermodynamic properties of the candidate salts. Different energy technologies will require different salt types, based on temperature and fluid property requirements. Molten salt reactors require salts that are both chemically and radiolytically stable at high temperatures and have low melting and high boiling points. For optimum thermodynamic behavior, molten salt reactors also require a large specific heat and thermal conductivity and a vapor pressure lower than that of water (<1 mmHg at 900 °C). Low vapor pressure is required to allow for a molten salt reactor to operate at a high temperature without the working fluid volatilizing, which minimizes the vapor phase present in the system.

Fluoride salts are often the primary candidate salts for reactor systems. Lithium fluoride, beryllium fluoride, and sodium fluoride all have suitable melting ranges, and are often considered as candidate salt components. Beryllium fluoride is especially compatible with a reactor system because it has the lowest thermal neutron cross-section of the fluoride salts ($\sigma \sim 0.010\text{b}$). 'Flibe' or LiF-BeF₂ (66:34 mol%) was developed during the MSRE to combine the desired properties of beryllium and lithium fluoride, and was considered to have the most compatible properties for a reactor. (Roper et al., 2019) However, beryllium fluoride can be hazardous, and lithium fluoride can generate tritium in a neutron flux environment. Lithium material must be isotopically purified to 99.99% Li⁷ to avoid tritium generation, which can be costly (Roper et al., 2019).

'Flinak' or LiF-NaF-KF (46.5:11.5:42 mol%) has been developed as a surrogate for Flibe. (Roper et al., 2019) Flinak has properties similar to Flibe but is not as toxic. NaF-ZrF₄ and KF-ZrF₄ are salt candidates that do not have the issue of tritium generation by lithium fluoride. However, these salts may have other undesirable fluid properties, such as the high melting point of NaF-ZrF₄ and the high vapor pressure of KF-ZrF₄.

Chloride salts are another category of candidate salt that have been considered for power production. Chloride salts often exhibit

similar energy and behavior to fluoride salts and have similar corrosive effects. (Roper et al., 2019) Candidates mixtures such as KCl-MgCl₂ (67:33 mol%) could be used as primary coolants if measures are taken to prevent the generation of Cl-36 by nuclear transmutation. (Manohar, 2010) If a candidate chloride salts contain lithium, similar problems arise as those seen in fluoride salts, where the lithium must be isotopically purified to avoid the generation of tritium in a neutron flux.

Nitrate-nitrite salts contain NO₃ and NO₂ and are used in solar applications. A typical mixture is NaNO₃ – NaNO₂ – KNO₃, industrially known as Hitec. The stability of nitrate-nitrite salts in radioactive environments is mostly unknown. The salts may be stable, but this has not been tested because nitrate-nitrite salts lose stability at high temperatures (~550 to 600 °C). At higher temperatures, the salt will decompose to nitrites and oxides. This occurs at around 600 °C in air, but under inert gas, the salt will decompose at even lower temperatures, depending on the temperature and impurities. Above 800 °C, the reaction is fast, forming so much gas that the salt appears to boil. (Manohar, 2010) The products of the decomposition can be problematic because oxide impurities can contribute to corrosion. Nitrate-nitrite salts can also react with fuel, precipitating actinide oxides, and react with a graphite moderator. (Rosenthal et al., 1972)

3.2. Chemistry challenges

3.2.1. Tritium

Many salt candidates for molten salt reactors use lithium fluoride salt (LiF). Naturally occurring lithium consists of mostly the isotope ⁷Li (92.58%) (Dolan, 2017), with the remainder being ⁶Li. Tritium can be produced from lithium if a neutron is absorbed, by the following reactions: (Dolan, 2017)



Tritium can be problematic in a reactor system because it can be a hazard to human operators. Tritium can permeate through metals to secondary systems, exposing workers to radiation. (Wang et al., 2020) If tritium permutates into water, humans can absorb tritiated water with severe consequences. Tritium is difficult to contain at high temperatures (Kelleher, 2015), and therefore the production of tritium needs to be prevented.

Because only fast neutrons can cause ⁷Li to absorb a neutron and produce tritium, the main concern for tritium production is with the less-common isotope ⁶Li. Even though there is only a small amount present in naturally occurring lithium, the salt would need to be isotopically purified to ⁷Li to avoid tritium production. Isotopically purifying lithium can be an expensive process, which means that lithium enrichment could be a prohibitive cost to molten salt reactor development.

3.2.2. Corrosion and materials compatibility

Corrosion of structural materials is a significant concern in molten salt systems. Salt systems can be extremely corrosive, especially at the high temperatures present in reactor or thermal storage systems. Redox potential is an electrochemical property of materials that can be used to evaluate the corrosivity of a salt. Redox potential describes the tendency of a material to reduce or oxidize. A reducing material will have a more negative redox potential, and an oxidizing system will have a more positive redox potential. When a salt is reducing, it craves electrons and will gain them from a donor species through a reduction-oxidation (redox) reaction. When a salt is oxidizing, it will seek to donate electrons to an accepting species. When a species undergoes a redox reaction,

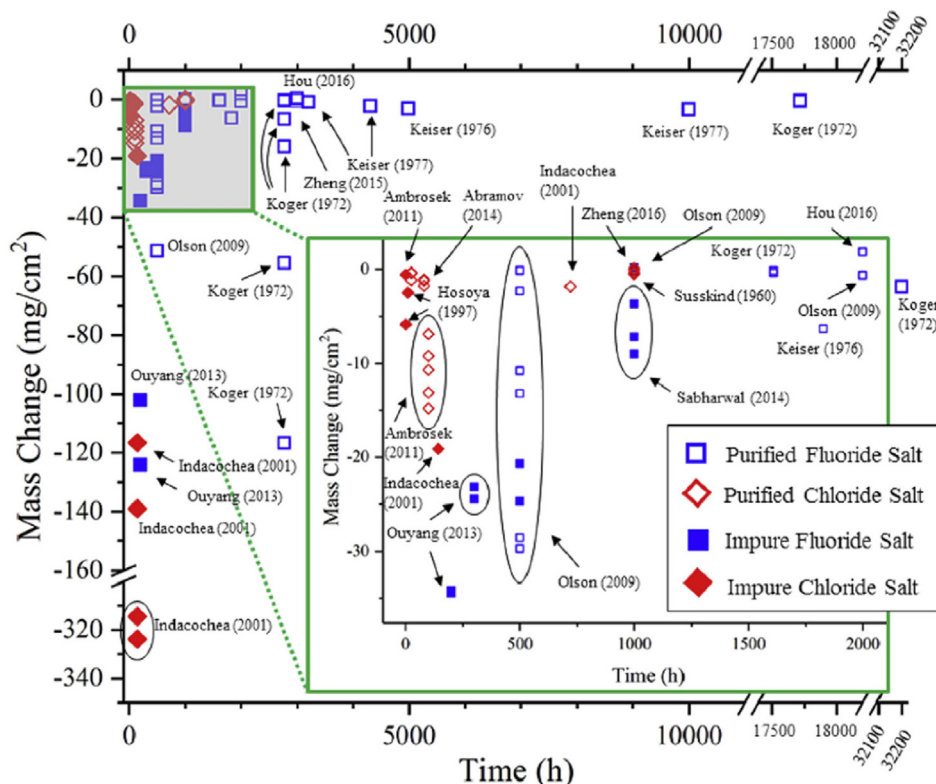


Fig. 9. Aggregation of mass change data for impure and pure molten salts. (Raiman and Lee, 2018).

its oxidation state will change. A typical example of a redox reaction is the reaction between hydrogen and fluoride:



In this reaction, hydrogen is oxidized from a state of 0 to +1, by losing two electrons. Fluoride is reduced to an oxidation state of -1 from 0 by gaining 2 electrons. The chemical composition of a material determines its redox potential. A more reducing salt will be less likely to corrode (oxidize) structural material.

Corrosion in a molten salt system differs from standard reactors systems due to the lack of a passive oxide film on the surface of structural materials. Typical alloys have an oxide film on their surface, which protects the alloy from corrosion from fluids. Reactions with air or moisture form these films. Gaseous fluorine can also form a protective fluoride layer. However, oxides and fluorides are soluble in fluoride salts, which will dissolve any protective layers that were present.

In their pure state, fluoride and chloride salts are naturally reducing, and are not likely to corrode surrounding material. The introduction of impurities in the salt increases the redox potential, forming a more oxidizing mixture. Fig. 9 shows an aggregation of corrosion studies on fluoride and chloride salts. (Raiman and Lee, 2018) Impure salts show considerably more mass change than pure salts.

These data show that it is essential to remove impurities from molten salts to prevent the system from becoming too oxidizing and corroding structures. However, a salt should also not be kept in an overly reducing state, which can form metal suspensions that react with carbon to form metal carbides. (Kelleher, 2015) Therefore, the salt must be kept in a balanced, reduced state.

The metals most prone to attack in a molten salt system can be determined by Gibbs free energy of formation. Gibbs free energy indicates the energy available in a system to carry out chemical reactions and can be calculated using the activity of a species. A

more negative free energy indicates that a metal is more prone to attack, and a more positive free energy indicates a metal is less prone. From this information, it has been determined that structural alloy components are increasingly prone to attack in the following order: W, Mo, Ni, Co, Fe, Nb, Cr, Mn, Ti, Zr, and Al. (Kelleher, 2015) In corrosion-resistant alloys, the most prone element present is typically chromium, which is then attacked at grain boundaries. Because there is no passive film to protect the structural alloy, it is necessary to mitigate corrosion by either purifying the salt or by controlling the redox potential of the salt in a reducing state. Redox potential can be controlled through the use of reducing and oxidizing agents. These agents are chemicals that either reduce or oxidize the salt on addition, which can bring the salt to a more reducing or oxidizing state, thereby controlling the corrosion.

Redox buffers are another method of controlling molten salt corrosion. Buffers are chemicals which exist in two different oxidation states, such as U(IV/III), V(III, IV), Tm(III, II), Sm(III, II), Yb(III, II), Ce(IV, III), and Eu(III, II). (Kelleher, 2015) They can be mixed with or suspended in a salt mixture, and will be preferentially oxidized or reduced in place of the salt. The above-listed elements are all viable options for redox buffers; however, the selection of a buffer is dependent on the system. A primary fuel salt can use uranium as a buffer, but if a salt is not a fuel salt, other options must be used. Some options are not viable due to high neutron cross-sections. If no buffer material is viable for use in a salt system, then other redox potential control methods must be used.

Chloride salts behave very similarly to fluoride salts. Similar to fluorides, pure molten chlorides are reducing; they therefore do not corrode alloying metals in contact with the salt. The impurities, such as metal oxides or water, therefore drive corrosion in molten chlorides in the salt. The presence of moisture in molten chlorides can lead to the formation of HCl, which will enhance corrosion rates dramatically. Like fluoride, chloride salts will dissolve passive

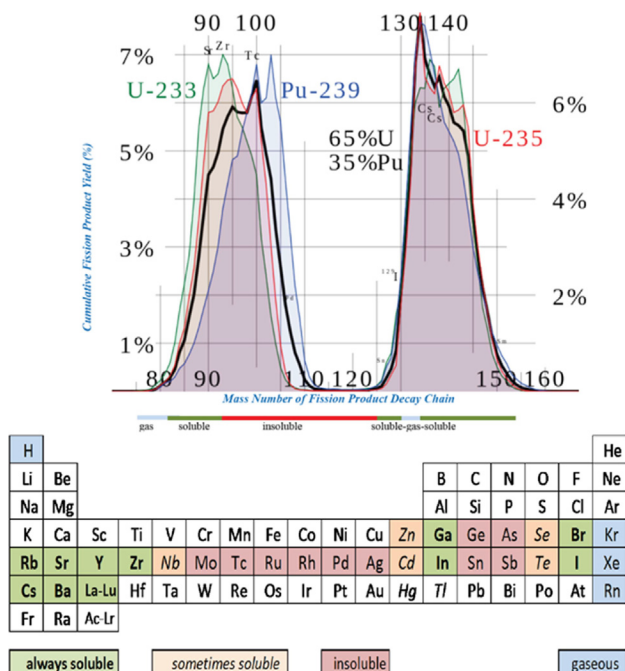


Fig. 10. Fission product classes identified during MSR operation highlighted as groups in the periodic chart and the fission-yield curve (Report for the US Department of Energy Office of Nuclear Energy Workshop and Chemistry, 2017).

protective films on structural alloys, but not as severely as fluoride salts. (Sridharan and Allen, 2013) Corrosion behavior in corrosion-resistant alloys is similar to that of fluoride; the salt selectively attacks chromium along grain boundaries.

Nitrate-nitrite salts behave much differently from fluoride and chloride salts. Unlike fluorides and chlorides, nitrate-nitrites have an oxidizing redox potential. These salts will form a protective oxide layer on metals, which becomes thicker as oxidation progresses. (Manohar, 2010)

3.2.3. Irradiation and fission products

It is important to understand where fission products end up in MSR's and how they behave in order to determine what is dissolved, plated or insoluble in the MS and which fission products will need to be removed. The detailed chemical behavior of many fission products remained uncertain at the conclusion of the MSBR program in 1976, and there have been few studies since then. Loss of criticality is as much an issue in molten salt reactors as it is in LWRs. Fuel recycling for molten salt, also known as fuel salt cleanup, has renewed interest since the removal of fission products such as neodymium (Nd) and Cesium (Cs) contribute almost 50% to the loss of criticality making it vital that they are separated during molten salt recycling schemes. In addition to the separation of Cs and Nd, it is advantageous to remove zirconium (Zr) and samarium (Sm) from the salt since they supply nearly 80% of the fission products that could also contribute to loss of criticality. (Merk et al., 2018)

Four classes of fission products have been identified based on previous MSR work. (Report for the US Department of Energy Office of Nuclear Energy Workshop and Chemistry, 2017) The four species, shown in Fig. 10, are: gaseous (noble gases); soluble (alkali, rare earths, active refractories and halogens); insoluble (transition metals between Nb and Te); and sometimes soluble (Nb, Te and Zn periodic columns). (Report for the US Department of Energy Office of Nuclear Energy Workshop and Chemistry, 2017) The 'sometimes soluble' group tends to change with the redox state

of the MS. The chemistry of the interaction and transition of the insoluble and sometimes soluble phases is not completely understood. The majority of the fission product remain as salt soluble species; however, the decay behavior of the fission product chain is complex and can result in longer lived isotopes partitioning after the short-lived isotopes. This scenario occurs in some of the noble metal fission products as well as key isotopes such as Cs-137, Mo-99, and I-131.

Molten salt reactor fuel will require comprehensive investigation into its immunity to radiolysis damage due to the irradiation of the salt fission products. The current understanding of radiolytic effects in chloride salts is based on experience within the reprocessing industry which uses molten salt media to dissolve solid used nuclear fuels in preparation for separation. Experiments are yet to be conducted to confirm the stability of molten chlorides under the more intense conditions of irradiation as a fuel salt and studies conducted on solid fluoride and chloride salts using alpha, beta, gamma, and xray irradiation; however, data collected from interim storage solid salts showed radiolytic damage and chemical changes associated with dissolved fission and activation products. (Report for the US Department of Energy Office of Nuclear Energy Workshop and Chemistry, 2017). The impact from fission and activation product distribution due to the nature of the molten salt as well as the impact of irradiation will also need further analysis since areas of the molten salt could receive more or less radiolysis effects depending on the eb-and-tide of the salt flow. There are many areas of focus requiring study related to fission products and irradiation and ultimately both areas are tied together with one effecting the other in the molten salt.

4. Power production

4.1. Unique MSR technologies

The high radiation/high-temperature environment necessary for MSR operation, as well as the potential for rapid corrosion, poses unique challenges for the components and structures constituting MSRs. Recent government, industry, and international interests have propelled the reconsideration of MSRs for power generation; however, the large gap since the last operation of an MSR (1969) indicates that many of the technologies developed for use in MSRs may require modernization, if not complete redesign. The MSRE was one of two fully-realized MSRs; it operated at ORNL from 1965 to 1969 and was used as a test reactor to study molten salt chemistry and heat transfer, materials feasibility and degradation, and neutronics within the fluid-fueled MSRE. The MSRE also served as a proving-grounds for novel MSR technologies, including freeze flanges, freeze valves, and instrumentation technologies.

The following sections present a discussion of unique MSR technologies and assign a technology readiness level (TRL) or TRL range to the technologies. The TRL range suggested in DOE G 413.3-4A (U.S. Department of Energy, 2011) was used to assign TRLs to the MSR technologies presented here.^a The suggested TRL range is from 1 (basic principles observed) to 9 (total system used successfully in project operations). (U.S. Department of Energy, 2011) Technologies for which modern research is limited (i.e., low TRL) include more information about historical examples (i.e., the equivalent technology featured in the MSRE^b). Technologies with higher TRLs include a greater focus on recent research efforts.

^a Unless recent works have already characterized the TRL of the technology. In these instances, the TRL given in these works is reported here.

^b The technologies developed for the MSRE incorporate lessons learned from the first MSR ever operated, the Aircraft Reactor Experiment (ARE) and thus present more advanced technologies to draw knowledge from today.

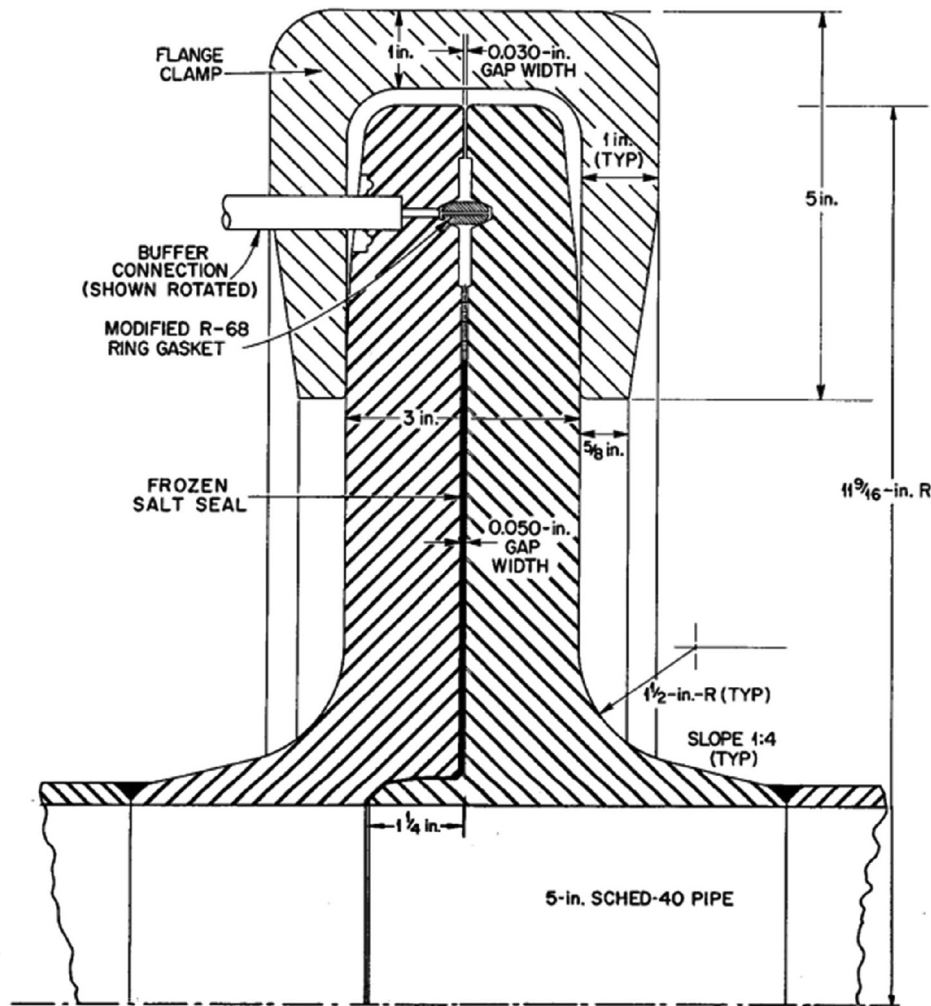


Fig. 11. Design of the freeze flanges used in the MSRE (Robertson, 1965).

4.1.1. Joining technologies

The high temperatures expected within MSRs and the characteristics of molten salts complicate the use of traditional maintenance-accommodating mechanical pipe and vessel joining technologies (i.e., bolted flanges). Molten salts exhibit exceptional wetting capabilities (Rodriguez, 2017), which, in conjunction with bolt and gasket relaxation at high operating temperatures (Black, 2016), can increase the possibility of salt leakage at pipe connections.

A unique component within the MSRE was the freeze flange (Fig. 11) (Robertson, 1965), which was used on five fuel and coolant salt lines to permit remote maintenance or replacement of the reactor vessel, the fuel salt pump, and the primary heat exchanger. The Hastelloy-N freeze flanges were developed to make joints that are salt-leakproof and can be remotely mated and separated for repair or replacement of major components within the MSRE. Some of the essential design criteria for the MSRE freeze flanges include material compatibility with the molten fuel and coolant salt, an ability to withstand repeated thermal cycling, and leak-tightness under a variety of conditions.

The motivation for the use of the freeze flange stemmed from its reliability in completely preventing salt leakage under all thermal cycling conditions expected within the MSRE. The freeze flanges did not require additional cooling because the cell atmosphere provided sufficient cooling outside of the flanges. The male

and female flange faces were mated together with two semi-circular spring steel flange clamps, which provided for the use of specially-designed equipment for remote assembly and disassembly of the flanges and also provided a constant gasket loading. Between the two flange faces was a frozen salt seal that prevented salt leakage. A ring gasket (above the frozen salt seal) served as a redundant seal.

Twenty freeze flanges (Macpherson, 1959) were tested at the Remote Maintenance Demonstration Facility. Experience within this facility proved to designers that the freeze flanges could support remote assembly and disassembly; however, the experience made evident the need for minimizing the “salt cake” formed in the freeze flanges and confining the salt cake when separating the flange faces so that it does not fall on the floor. A salt screen was added to the final freeze flange design to perform this function. Although the Remote Maintenance Demonstration Facility did prove that the freeze flanges would support remote maintenance for the MSRE, the freeze flanges were eliminated from the MSRE drain lines because they were “cumbersome, make the layout difficult, and may never be required.” (Briggs, 1960)

The freeze-flange design used within the MSRE was developed and refined over a several-year period before MSRE operation began. A cast-metal seal flange joint and indented seal flange joint was considered for use within the MSRE; however, both designs exhibited weaknesses, such as the need for reworking of the flange

faces after separation and poor performance of the sealing materials, that ultimately led to their dismissal as feasible joining technologies for the MSRE. (Macpherson, 1958)

The MSRE staff reported that the MSRE freeze flanges performed acceptably. Throughout the operation of the MSRE, the freeze flanges were never identified to be leaking fuel salt or radioactive gas. (Guymon, 1973) The flanges did, however, leak buffer gas (used for leak detection), particularly when the system was cold. The MSRE never required replacement of the major components connected via freeze flange-fitted lines. Therefore, one primary function of the freeze flanges, the ability to remotely manipulate the flanges to facilitate the replacement of major components, was never tested in the MSRE. Post-MSRE reports (Guymon, 1973) suggest that remote welding or brazing techniques should be used where maintenance is expected to be infrequent because maintenance with the freeze flanges was considered time-consuming and costly.

After the operation of the MSRE, Section III of the ASME code and ASME Code Case 1331-5 were revised to require more rigorous analysis and higher safety factors for systems operating in the creep range. The freeze-flange design did not include the required finite-element analysis and high safety factors in the updated code and code case. (Gabbard, 1972) Based on this information, the MSRE staff determined that, if the relevant sections of the revised ASME code and code cases were in effect during the design process for the freeze flanges, the design would probably be deemed unacceptable for the intended operation. (Gabbard, 1972)

Research re-evaluating molten salt joining technologies appears to be in preliminary stages. In 2015 (Li et al., 2015), a slightly-modified freeze-flange design was suggested, which included the addition of multiple gasket grooves, and was compared to bolted flange joints with double gaskets used in traditional liquid salt systems. The authors of the 2015 study indicated that additional mechanics analysis and experimentation were needed for design development. A 2018 ORNL report (Holcomb et al., 2018) suggested the use of alternate gasketed flanges, with the caveat that these flanges will be subject to high-temperature sealing issues requiring prolonged demonstration before being at a TRL acceptable for coupling with fuel salt. Additionally, due to significant advances in pipe cutting/welding automation, MSR designs could potentially eliminate all mechanical flanged joints and rely solely on welded joints. (Agapakis et al., 1986) The limited analytical experimentation and different design concepts suggested for MSR-compatible joining technologies indicates that the technology falls within a TRL range of 2–3.

4.1.2. Valve technologies

Mechanical valves for use in the high-temperature, highly corrosive environment within MSRs have yet to be proven reliable enough for inclusion in MSRs. Research on methods for isolating fuel salt without the use of mechanical valves dates back to before the operation of the MSRE and is still ongoing. The MSRE accomplished the function of isolating flowing salt through the use of “freeze valves” (often referred to as “freeze plugs”).

Chisholm et al. (Chisolm et al., 2020) describe the MSRE freeze-valve design in detail, including the three different freeze-valve designs initially considered for the MSRE. The final MSRE design comprised a flattened pipe section that was externally cooled to maintain a frozen salt plug that inhibited salt flow. The MSRE freeze valves also performed the safety function of allowing the salt to flow into the drain tanks to achieve safe shutdown (i.e., sub-criticality) of the reactor. Although this melting would ideally be passive, the MSRE freeze valves required active heating in the form of radiant heaters to melt quickly.

Recent work (Chisolm et al., 2020) also describes some of the difficulties encountered with the MSRE freeze valves. First, the

requirement of active heating and cooling reduces the passive safety characteristics of the concept. Second, freeze-valve cooling failure resulted in at least three unscheduled drains of the MSRE, presenting a safety issue and reducing the operability of the reactor. Third, in 1969, one of the freeze valves in the MSRE exhibited mechanical failure that led to the leakage of fuel salt into the reactor cell. Fourth, consistently holding the salt at a temperature just below melting was challenging with the technology available in the 1960s.

The SAMOFAR project, which performs experimental and analytical work supporting the development of a 300 MW_{th} thorium-fueled MSR, has worked on the development of a freeze plug design for use in the European Molten Salt Fast Reactor (MSFR). (Giraud et al., 2019; Makkinje, 2017; Shafer, 2018; Swaroop, 2016; Tiberge et al., 2019; Van Tuyll, 2016) Chisholm et al. (Chisolm et al., 2020) also summarize the SAMOFAR contributions to freeze-plug development to date. The ongoing research by SAMOFAR and Chisholm et al. (Chisolm et al., 2020) suggests that the freeze-valve/freeze-plug technology for MSRs is within a TRL range of 4–5.

4.1.3. Instrumentation technologies

The sensitivity of many commercial instrumentation and control (I&C) technologies (e.g., flowmeters, neutron counters, etc.) to high temperatures, radiation damage, and corrosion requires the development of new I&C technologies capable of withstanding the challenging environment within an MSR. A 2015 report (Gougar et al., 2015) identified the TRL of I&C technologies as a whole for fluoride high-temperature reactors (FHRs) and liquid-fueled molten salt reactors (LF-MSRs) at 4 and 6, respectively. More recently, a 2018 report (Holcomb et al., 2018) assigned TRLs to a number of instrumentation technologies as they would be applied in MSRs, which are summarized in Table 2. Holcomb et al. (Holcomb et al., 2018) also evaluated the feasibility of other MSR instrumentation technologies (e.g., neutron instrumentation) but did not assign TRLs to such technologies; thus, they are not included in Table 2.

4.2. Power production technologies

Like most (if not all) other types of base-load power plants (e.g., coal or gas-fired power plants), MSRs are coupled with traditional energy conversion cycles that transform heat into usable energy. The primary steps of the power cycles discussed within this report include heat addition, power generation (expansion), heat rejection, and compression. (Sabharwall et al., 2011) Molten salts considered for use within MSRs exhibit chemical stability at elevated temperatures, low vapor pressures at operating temperatures, and high heat capacities. (Sabharwall et al., 2011) The thermophysical properties of molten salts lend to their consideration as superior heat transport and transfer fluids that can allow for high energy conversion efficiencies for various cycles. (Sabharwall et al., 2010; Latzko, 1970)

Both Rankine and Brayton power conversion cycles have been previously considered for coupling with MSRs. The feasibility for cycle coupling with MSRs depends on a variety of factors; two of the more important of these are TRL and efficiency. Regardless of cycle, optimal thermodynamic efficiency for heat engines is measured as the ratio of electrical work produced by the system to heat added to the system. The TRLs of the cycles considered here span a broad range, indicating that those with lower TRLs, though they may exhibit excellent efficiencies, may not be deployable in time for the first generation of commercial MSRs.

The presence of lithium (particularly ⁶Li) in many of the molten salt compositions considered candidates for use within MSRs results in the production of tritium (Forsberg et al., 2017), which

Table 2

TRLs for instrumentation technologies as applied to MSRs.

MSR Instrumentation Technology	TRL (as assigned in Holcomb et al., 2018, unless otherwise noted)
Temperature Measurement	
Type N Thermocouples	9
Distributed Fiber-Optic Bragg Thermometry	"high"
Blackbody Radiation Temperature Measurement	4
Johnson Noise Thermometry	3–4
Ultrasonic Guided Wave Temperature Measurement	5–7
Noninvasive Free Liquid Ultrasonic Temperature Measurement	3
Flow Measurement	
Time-of-Flight Ultrasonic Flowmeter	8–9
Differential Pressure Flowmeter	9
Rotameters	8–9
Pressure Measurement	
Impulse Lines	7–9
Bubblers	8
Direct Measurement Sensors	3–4
Clamp-on Ultrasonic Flowmeter	3–4
Level Measurement	
Guided-Wave Microwave	8
Bubbler	8
Heated Lance	9
Pump Monitoring	
Vibration and Acoustic Pump Monitoring	9
Power Signature Analysis	7
Chemistry Monitoring	
Online Salt Sampling	2–4 (Sabharwall et al., 2011; McFarlane et al., 2019)
Online Corrosion Monitoring	3–6
Online Redox Condition Measurement	"low"

is capable of migrating through metallic heat exchangers and contaminating the components of the power cycle (Sabharwall et al., 2011). MSR designs can include intermediate salt loops (also referred to as coolant salt loops) to inhibit tritium migration from the primary fuel salt loop into the power cycle components; however, the addition of an intermediate loop incurs heat losses.

4.2.1. Rankine cycle

The fundamental power conversion cycle, the Rankine steam cycle, is used in LWR nuclear power plants and many coal-fired power plants today for producing electricity. High-pressure water, the working fluid in a Rankine cycle, receives heat from a heat source via a heat exchanger, converting it to steam. The steam is then expanded through a turbine/generator to produce alternating current (AC) electricity that is distributed to the grid. The saturated steam at the outlet of the turbine is sent through a condenser and turned back into low-pressure liquid water. A pump is then used to pressurize this water, which then returns to the heat exchanger to continue the cycle. (Van Wylen and Sonntag, 2015) The efficiency of the steam Rankine cycle can be improved by adding more stages (i.e., adding feedwater heaters and more turbines). Optimizing Rankine steam cycle efficiency for MSRs requires adding several stages (~7–8, depending on the design).

The high temperatures within MSRs result in higher thermal efficiencies that achievable from LWR Rankine steam cycles. The thermal efficiency of a Rankine cycle coupled to an MSR is dependent upon reactor characteristics and power cycle component choices. A 2011 study of the Advanced High Temperature Reactor (AHTR) indicated a thermal efficiency of 41.9–42% for the reactor design and power production cycle chosen. (Sabharwall et al.,

2011) One downside of the Rankine steam cycle is the large volume of water required for cooling purposes (Dolan, 2017), which limits possible deployment locations for MSRs.

Rankine steam cycles are commercially available and thus at a TRL of 9. Molten salt steam generators (the point of interface between Rankine cycle components and the molten salt) have been developed for solar power tower (SPT) applications; however, the molten salt steam generators for the Solar Two project (Bradshaw et al., 2002) and the Molten Salt Electric Experiment (Allman et al., 1988) feature different design approaches. One 2017 study (Gonzalez-Gomez et al., 2017) did report using genetic algorithms to optimize steam generators for use in a 110 MW_e SPT plant; however, because the chemical makeup of the molten salts of interest for SPT applications differs from those considered for use within MSRs, it has yet to be seen whether similar steam generator designs could be viable for MSRs.

4.2.2. Supercritical Rankine cycle

The supercritical Rankine cycle is similar to the Rankine steam cycle; however, the steam generator produces superheated steam that is expanded through a turbine. The higher temperature of the superheated steam compared to the saturated steam used in the Rankine steam cycle results in increased efficiency.

Supercritical Rankine cycles have been commercially demonstrated in coal-fired power plants to achieve efficiencies greater than 40%, thus placing them at a TRL of 9. Advanced reactor applications of supercritical Rankine cycles are primarily being investigated for use in supercritical water reactors (SCWRs); however, high temperature and pressure operation suggests that more research is needed into supercritical Rankine cycles for advanced reactor applications. (Gougar et al., 2015) An investigation into supercritical Rankine cycles for MSR power production is limited. One investigation into secondary heat exchangers for the AHTR (Sabharwall et al., 2011) did consider coupling with a supercritical Rankine cycle with an efficiency of 44%; however, the high turbine inlet pressure associated with this cycle may inhibit its usefulness for MSRs.

4.2.3. Brayton cycle

Many advanced reactor concepts have considered using the open Brayton cycle. The high-power density associated with the open Brayton cycle can result in lower capital costs associated with gas-turbine power conversions systems than with steam-turbine systems. (Peterson, 2003) Particular applications of the open Brayton cycle appear to be leading candidates for coupling with MSRs, in part because the absence of a steam cycle removes a primary tritium-leakage pathway. (Dolan, 2017) The open Brayton cycle was developed for power cycle applications with gaseous working fluids (Wright et al., 2006). A heat exchanger is first used to heat the working fluid. The resulting hot working fluid is expanded through a gas turbine/generator to produce electricity. A pre-cooler is then used to cool the fluid before it passes through a compressor. The compressed fluid then returns to the heat exchanger to continue the cycle. The use of a working fluid other than water reduces water-cooling requirements for the cycle, potentially increasing the number of geographic locations for MSR deployment.

There are two general methods to increase the efficiency of a Brayton cycle. (Guo et al., 2019) The first, similar to the Rankine cycle, is to change the layout of the plant by adding recuperation, recompression, reheat, cogeneration, or a combination of these options. The second method is to change the working fluid; this could either be a bulk fluid change (e.g., change from He to supercritical CO₂), or changing to a binary mixture of the primary fluid and an additive to alter the molecular weight of the fluid, such as the addition of Xe to a He Brayton cycle.

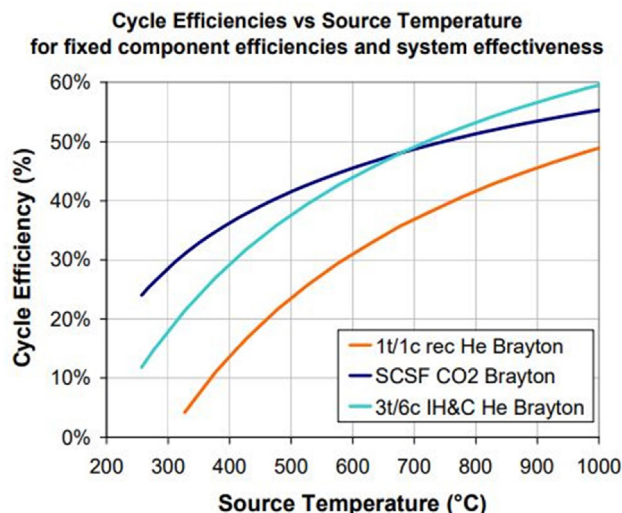


Fig. 12. Cycle efficiencies for SCO₂ Brayton, single-stage recuperated He Brayton, and the three turbine/six compressor interstage heating and cooling (IH&C) He Brayton (Wright et al., 2006).

4.2.4. He Brayton cycle

Pure He is regarded as a superior coolant at elevated temperatures because of its high thermal conductivity and low dynamic viscosity. (Malik et al., 2019) The He Brayton cycle takes advantage of these properties by utilizing He as the working fluid. However, impurities commonly found in He can attack metals, causing damage to cycle structural materials. (Dolan, 2017) Also, He exhibits poor compressibility, (Malik et al., 2019) which can result in increased aerodynamic losses. The compressibility, as well as heat transfer coefficient (El-Genk and Tournier, 2008), of He has been shown to improve with the addition of a secondary noble gas, particularly Xe, which may increase the feasibility of He Brayton cycle coupling with advanced reactors.

As with all thermodynamic power production cycles, the He Brayton cycle exhibits increases in efficiency with increased source temperatures. Fig. 12 shows that the He Brayton cycle exhibits a lower cycle efficiency than the Supercritical CO₂ (SCO₂) cycle for most of the operational temperature range considered for MSRs (i.e., 500–700 °C). As such, He Brayton cycles have primarily been investigated for advanced reactor concepts that operate at very high temperature ranges (e.g., the very high temperature reactor [VHTR] or gas-cooled fast reactor [GFR]). (Gad-Briggs et al., 2016; Wright et al., 2006)

He Brayton cycles typically include multiple expansion steps (i.e., multiple gas turbines are required) to improve efficiency, but can still be reasonably compact and efficient. (Dolan, 2017) For the IH&C Brayton cycle in Fig. 12, the physical size of the cycle is comparable to a current Rankine cycle, because they have similar pressure in the low pressures leg of the loop. (Wright et al., 2006)

In considering the coupling of a He Brayton cycle with a very high temperature reactor, a 2015 report (Gougar et al., 2015), suggested that the low TRL of He gas-turbine components (e.g., He compressor, high-speed turbine⁴) will likely result in the first very high temperature reactors being coupled with a Rankine cycle. Additionally, a He Brayton cycle was considered for the AHTR, reaching thermal efficiencies of 40.3–40.4%; still, lack of commercial availability precluded its use. (Sabharwall et al., 2011) Given that He Brayton cycles have been considered much more thoroughly for VHTRs than for MSRs and are characterized as low TRL for VHTR applications, it is reasonable to conclude that He Brayton cycle coupling with MSRs are also at a low, if not very low, TRL.

4.2.5. Supercritical CO₂ Brayton cycle

As suggested by the name, supercritical CO₂ is used as the working fluid in the SCO₂ Brayton cycle. SCO₂ is non-toxic, non-corrosive, non-flammable, and non-explosive. (Liu et al., 2019) Similar to the He Brayton cycle, the addition of inert gases (including N, O₂, He, Ar, Xe, Kr, H₂S, etc.) to improve cycle efficiency has been investigated extensively in recent years. (Guo et al., 2019)

As seen in Fig. 12, SCO₂ cycles are capable of achieving high cycle efficiencies for temperatures in the range of 450–700 °C (Liu et al., 2019) than the He Brayton cycle. The SCO₂ Brayton cycle offers the added benefit of featuring a more compact turbine than those used for the He Brayton cycle. (Dolan, 2017) Mechanical methods of increasing SCO₂ Brayton efficiency include: (1) recovering heat from a recuperator or adding reheat; (2) reducing the inlet temperature of the compressor and adding intercooling; or (3) adding an appropriate bottoming cycle. (Liu et al., 2019)

The SCO₂ Brayton cycle is still experimental, indicating a TRL range of 4–5. Test loops in the United States, at facilities such as Sandia National Laboratory, (Wright et al., 2010) the Southwest Research Institute, (Turchi, 2014) and in South Korea, including at the Korea Advanced Institute of Science and Technology (Baik et al., 2016) and the Korea Institute of Energy Research (Shin et al., 2017), have been created for evaluating the performance of SCO₂ Brayton cycle components. Obtaining accurate measurements of the efficiencies of radial and axial gas turbines, centrifugal and pump-type compressors, and printed circuit heat exchangers (PCHes) is an essential area of research for the SCO₂ Brayton cycle because the efficiencies of this turbomachinery can significantly impact the SCO₂ Brayton cycle efficiency. (Liu et al., 2019)

Interest in SCO₂ Brayton cycles for MSR coupling is limited at best. In recent years, molten salt applications of SCO₂ have focused on improving power production efficiencies of concentrating solar power (CSP). (Guo et al., 2019; Liu et al., 2019; Wang and He, 2017) Furthermore, Liang et al (Liang et al., 2015) suggests that SCO₂ Brayton cycles are most appropriate for coupling with other advanced reactor concepts, including the gas-cooled fast reactor, sodium fast reactor, and lead-cooled fast reactor.

4.2.6. Air Brayton cycle

The concept of coupling an air Brayton cycle to a nuclear reactor was first considered during the Aircraft Nuclear Propulsion (ANP) project in the 1950s, before the invention of intercontinental missiles eliminated military interest in the project. (Andreades et al., 2014) Advances in gas turbine technology, such as those used in natural gas power production (Dolan, 2017), have restored interest in coupling the air Brayton cycle to a nuclear heat source. However, gas turbines have not yet been coupled to an MSR, resulting in a TRL 6 overall for MSR power production. (Gougar et al., 2015)

4.2.7. Air Brayton combined cycles

Air Brayton combined cycles coupled to nuclear reactors (also known as Nuclear Air Brayton combined cycles or NACCs) are capable of accepting heat from a nuclear and non-nuclear source(s) to facilitate operation in two modes: base-load and peak electricity. (Dolan, 2017) Both liquid-fueled MSRs and fluoride high-temperature reactors (FHRs) have been considered for NACC systems. Such cycles have the potential of achieving higher efficiencies than standalone natural gas plants. (Forsberg and Peterson, 2016) The concept of a NACC is similar to a commercial gas turbine combined cycle (GTCC), in which natural gas provides baseload energy, and a Rankine bottoming cycle is driven by a heat recovery steam generator. In a NACC, the gas turbine combustion chamber is replaced by a nuclear-driven heat exchanger. (Fathi et al., 2018)

Nuclear heat is used to provide base-load power. During peak electricity times, a topping cycle, such as natural gas or hydrogen firing, can be used to input additional heat, because the tempera-

tures within an MSR do not approach maximum allowable gas turbine temperatures. As seen in Fig. 13, traditional NACC efficiencies are well below SCO_2 Brayton cycle efficiencies at the lower end of MSR operating temperatures; however, the addition of a recuperator and intercooler (RIC) results in efficiencies near those of an SCO_2 Brayton cycle. (Fathi et al., 2018) Another option is the use of a nuclear air Brayton regenerated cycle (NARC) with a RIC, which can achieve efficiencies greater than that of an SCO_2 Brayton cycle over the range of MSR operating temperatures.

4.2.8. Air Brayton combined cycles energy storage

NACC or NARC systems coupled to MSRs have also been postulated for energy storage, particularly when considered along with renewable energy (e.g., solar or wind) systems. When renewable energy systems are unable to provide power, NACC or NARC systems can operate normally, delivering stable base-load power to the grid. When renewable power is supplying sufficient energy to the grid or when energy prices are low or negative, nuclear heat can be transformed into stored energy. (Fathi et al., 2018) The converse is also suggested. The unpredictability of wind and solar can lead to rapid excess energy generation, which, in a NACC system could be stored. (Forsberg and Peterson, 2016) In either scenario, the stored energy can be released to the grid during peak power.

Different methods for NACC energy storage have been suggested, the most popular being through the use of high-temperature firebricks, seen in Fig. 14. When excess electricity is available, it can be used to heat the high-temperature firebrick. In times of peak power, compressed air can be driven over the firebrick, causing it to heat up. (Forsberg et al., 2017; Forsberg and Peterson, 2016) The hot air can then be sent through a turbine for electricity production. Another option illustrated in Fig. 15, is to use excess nuclear heat for hydrogen production via high-temperature electrolysis (Fathi et al., 2018). The hydrogen can then be co-fired to produce electricity at peak power times or used as an independent fuel source for hydrogen fuel cells or internal combustion engines.

4.3. Coupling and integration challenges

The adaptation of a typical fossil power plant steam cycle to a molten salt reactor includes many challenges. The application of existing steam-cycle designs will likely require modifications to equipment. Steam generators and reheaters will present a particular problem in accommodating the molten salt. The adaptation of the plant to an MSR will require trade studies to obtain information necessary for further design. A feasibility study by Sabharwall et al (Sabharwall et al., 2011) discusses two generic Rankine steam cycles for a 3400 MW_{th} reactor. It identifies trade studies needed for the design and development of a steam plant coupled with an MSR.

Fig. 16 shows a schematic of a Rankine cycle coupled to an MSR, using a supercritical steam cycle with steam-to-steam reheat. (Sabharwall et al., 2011)

The main challenge for the incorporation of an MSR into a steam-cycle plant is the high freezing temperature of the salt. A candidate salt, KF-ZrF_4 , has a freezing point of 390 °C, which is similar to the freezing point of other candidate salts. The freezing temperatures of these salts are higher than the critical temperature of water. A supercritical or superheated steam cycle is required to reach these high temperatures. Because of structural limits, the steam temperature limit for the steam cycle is around 620–640 °C. (Sabharwal et al., 2011) To prevent freezing of the salt, feedwater temperatures will need to be higher than typical steam cycles. Salt may freeze, causing extreme temperature changes, which will consume large amounts of fatigue life. Salt may also freeze on the feedwater heater, causing thermal resistance. Colder

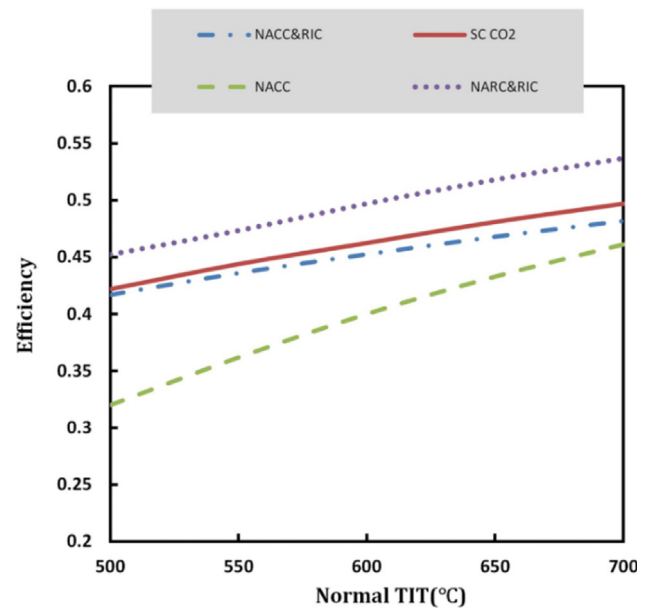


Fig. 13. Cycle efficiencies for SC CO₂ Brayton, NACC, NACC&RIC, and NARC&RIC (Fathi et al., 2018).

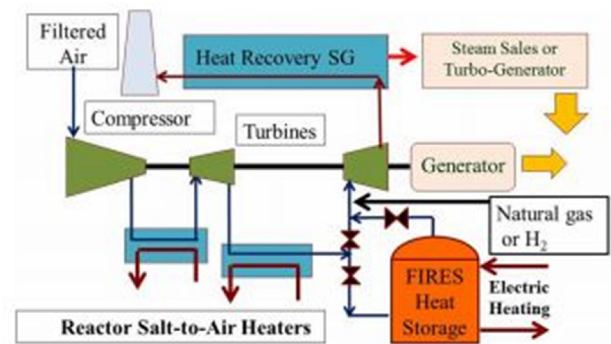


Fig. 14. NACC layout with FIRES firebrick energy storage (Forsberg and Peterson, 2016).

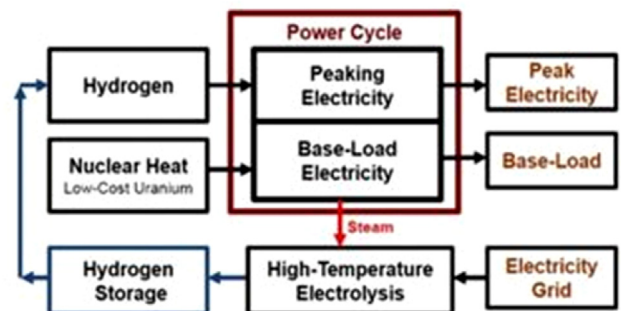


Fig. 15. NACC layout with FIRES firebrick energy storage (Fathi et al., 2018).

water resulting from additional thermal resistance will cause additional salt freezing. This propagation of cold water and freezing salt will impact fatigue usage. (Sabharwall et al., 2011) Trade studies are required to evaluate the effects of freezing on the need for heaters, and to determine material and thermodynamic specifications for the heaters, steam generator, and piping.

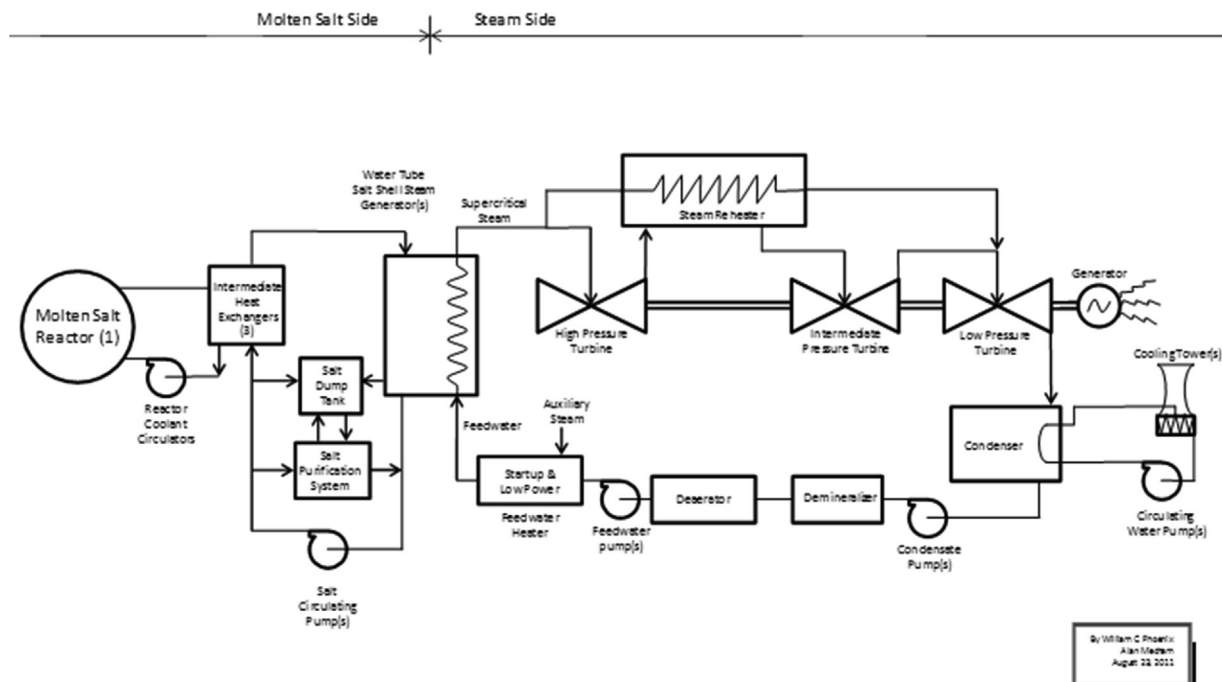


Fig. 16. MSR coupled with a Rankine supercritical steam cycle (Sabharwall et al., 2011).

Steam generators must be designed to suit the thermophysical and thermodynamic properties of the coolants, and the plant must be designed to incorporate a modified steam generator. The design of the steam generator may be open to different arrangements than for those used in other nuclear reactor plant designs. This is possible due to the large pressure difference between salt and steam, and the high freezing temperature of the salt. (Sabharwall et al., 2011) Trade studies are needed to evaluate the steam generator design, including the size, number, and internal configuration. (Sabharwall et al., 2011) Trade studies are also needed to determine chemistry requirements, structural materials, instrumentation, and controls. (Sabharwall et al., 2011) The need for a dump tank to remove salt quickly should be evaluated, and other thermodynamic cycles, such as a Brayton cycle, should be considered.

The properties of liquid salt will significantly influence the design of the steam generators and feedwater heaters. Limited information is available for the properties of molten salts, including heat transfer and heat capacity, and the changes in salt properties as a function of water impurities. (Sabharwall et al., 2011) It is particularly important to determine the impact of water content on salt, due to the possibility of water entering the salt in the system. This is especially important for fluoride salts; exposure of fluoride salts to water can form hydrofluoric acid (HF), an extremely corrosive substance. Trade studies are required to determine salt chemistry requirements for the plant equipment, instrumentation, and to identify the events that would require removing the salt to a dump tank to minimize corrosion damage. (Sabharwall et al., 2011) Trade studies are also required for the design of the intermediate salt loop, including circulating pumps, isolation valves, piping material, and also for cost estimation. (Sabharwall et al., 2011)

The supercritical steam cycle will require pure water to limit corrosion and impurity deposits. (Sabharwall et al., 2011) A demineralizer is usually incorporated into typical supercritical steam cycles. Additionally, materials resistant to corrosion can be used to minimize damage. Galvanic corrosion should also be accounted for between piping and equipment. A protective oxide layer on the material can be maintained by control of the water oxygen content through the use of deaerators. Trade studies are needed to identify

chemistry requirements for the plant, to determine the need for demineralizers and deaerators. (Sabharwall et al., 2011)

4.4. Modeling challenges in reactor systems

Modeling a molten salt system comes with unique challenges. MSR systems are considered a type of circulating fuel reactor (CFR). The CFR type also includes aqueous homogeneous reactors and liquid-metal fueled reactors. Despite sophisticated modeling technology and tools, modeling a CFR system such as an MSR is challenging. This is due to major differences between CFRs and typical power reactors: liquid fuel, fission product migration, and online reprocessing and refueling processes. The key difference is the liquid fuel, which adds a fluid mechanics aspect to typical reactor scenarios. A modeling system for MSRs needs to be dynamic, to include all of the various properties of the circulating fuel. This would include neutron transport, thermal hydraulics, isotopic transmutation and thermochemical properties of the fuel and fuel salt, and corrosion effects. (Williams and Britt, 2017)

Kinetics modeling, or predicting reactor-response behavior, is especially challenging when considering systems with liquid fuel flow. Typically, delayed neutron precursors (DNPs) remain in the same place in a solid-fueled reactor, and are therefore easier to predict, and can be treated as a simple delayed source of neutrons. (Wooten and Powers, 2018) However, in a liquid-fueled reactor, these DNPs migrate with the liquid fuel, moving from their original position and subsequently decaying in various places in the reactor system.

The neutronics properties of the reactor not only depends on the movement of DNPs but the neutronic properties of the fuel salt. Changes in fuel composition and temperature will affect the viscosity and density of the fuel salt, and therefore the fluid flow. Surface-salt interactions, liquidus temperature, and speciation will also change with fuel composition. (Williams and Britt, 2017) These chemical challenges will need to be combined with the fluid and thermodynamic complexities, and the presence of DNPs. A simulator or modeling platform which combines all of the chemi-

cal, neutronic and thermodynamic complexities of a CFR has not yet been fully developed. (Williams and Britt, 2017)

5. Conclusion

Molten salt is quickly becoming an essential component of advanced energy technologies. Molten salt is used for both thermal energy storage and power production. Thermal energy storage technologies include CSP plants, which use an array of reflectors to heat salt, which is subsequently stored for later use in a power cycle. MSRs also use molten salt for power production, operating using molten salt as a circulating fuel. These energy technologies have many advantages, such as higher efficiencies, safer operation, and economic success. Combinations of these technologies can also be advantageous; the NHES is a concept combining several energy technologies to produce power more efficiently. An NHES was reviewed in this work which includes thermal energy storage and a high-temperature nuclear reactor.

Molten salt technologies retain many challenges. Chemically speaking, issues such as corrosion and tritium generation require chemical control systems. The chemical issue of control and capture of fission products will also be necessary since it is intimately tied to irradiation and the issues concerning an MSR it will create. Coupling a molten salt system to a steam cycle requires many modifications to equipment, especially in the steam generators and reheaters. A feasibility study by Sabharwall et. al (Sabharwall et al., 2011) discussed in this work identified trade studies required to develop a functional power cycle coupled to an MSR. Although considerable research is required, many technologies have already been developed for molten salt usage. The MSRE resulted in technologies uniquely adapted to molten salts, including freeze flanges, freeze valves, and many molten salt instrumentation technologies. The technology and experience developed in the past will be a valuable foundation for the future development of molten salt energy technologies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Agapakis, J.E., Masubuchi, K., Von Alt, C., 1986. Fundamentals and advances in the development of remote welding fabrication systems. *Weld. J.* 65, 21–32.
- Allman, W.A., Smith, D.C., Kakarala, C.R., 1988. The design and testing of a molten salt steam generator for solar application. *J Sol Energy Eng* 110, 38–44.
- Andreades, C., Scarlat, R.O., Dempsey, L., Peterson, P., 2014. Reheat-air brayton combined cycle power conversion design and performance under nominal ambient conditions. *J. Eng. Gas Turbines Power* 136, (6) 062001.
- Baik, S., Heo, J.Y., Kwon, J., Lee, J.I., 2016. Preliminary study of friction disk type turbine for S-CO₂ cycle application. *Transactions of the Korean nuclear society autumn meeting*.
- Bauer, T., Pfeleger, N., Laing, D., Steinmann, W.-D., Eck, M., Kaesche, S., 2013. High-temperature molten salts for solar power application. In: *Molten Salts Chemistry*. Elsevier, pp. 415–438. <https://doi.org/10.1016/B978-0-12-398538-5.00020-2>.
- Black; Veatch. Molten Salt: Concept Definition & Capital Cost Estimate; B&V File No. 40.1200; 2016.
- Bradshaw, R. W.; Dawson, D. B.; De La Rosa, W.; Gilbert, R.; Goods, S. H.; Hale, M. J.; Jacobs, P.; Jones, S. A.; Kolb, G. J.; Pacheco, J. E.; Prairie, M. R.; Reilly, H. E.; Showalter, S. K.; Vant-Hull, L. L. Final Test and Evaluation Results from the Solar Two Project; SAND2002-0120, 793226; 2002; pp SAND2002-0120, 793226. 10.2172/793226.
- Briggs, R.B. Molten-Salt Reactor Program Progress Report for Period from August 1, 1960 to February 28, 1961; ORNL-3122; Oak Ridge National Laboratory, 1961.
- Cabeza, L.F., 2014. *Advances in Thermal Energy Storage Systems: Methods and Applications*. Elsevier.
- Chisolm, B. M.; Krahn, S. L.; Sowder, A. A Unique Molten Salt Reactor Feature – The Freeze Valve System: Design, Operating Experience, and Reliability.; 2020.
- Ding, W., Shi, H., Jianu, A., Xiu, Y., Bonk, A., Weisenburger, A., Bauer, T., 2019. Molten chloride salts for next generation concentrated solar power plants: mitigation strategies against corrosion of structural materials. *Sol. Energy Mater. Sol. Cells* 193, 298–313. <https://doi.org/10.1016/j.solmat.2018.12.020>.
- Dolan, T.J., 2017. Molten Salt Reactors and Thorium Energy. 841.
- El-Genk, M.S., Tournier, J.-M., 2008. On the use of noble gases and binary mixtures as reactor coolants and CBC working fluids. *Energy Convers. Manag.* 49 (7), 1882–1891.
- Europe – EVOL's Molten Salt Fast Reactor <https://www.daretothink.org/europe-evols-molten-salt-fast-reactor/> (accessed 2021 -11 -02).
- Fathi, N., McDaniel, P., Forsberg, C., de Oliveira, C., 2018. Power cycle assessment of nuclear systems, providing energy storage for low carbon grids. *J. Nucl. Eng. Radiat. Sci.* 4, (2) 020911.
- Forsberg, C.W., Lam, S., Carpenter, D.M., Whyte, D.G., Scarlat, R., Contescu, C., Wei, L., Stempien, J., Blandford, E., 2017. Tritium control and capture in salt-cooled fission and fusion reactors: status, challenges, and path forward. *Nucl. Technol.* 197 (2), 119–139.
- Forsberg, C., Peterson, P.F., 2016. Basis for fluoride salt-cooled high-temperature reactors with nuclear air-brayton combined cycles and firebrick resistance - heated energy storage. *J. Nucl. Eng. Radiat. Sci.* 196 (1), 13–33.
- Gabbard, C.H., 1972. Thermal Stress Analysis and Life Prediction of MSRE Freeze Flanges; ORNL-TM-4121. Oak Ridge National Laboratory.
- Gad-Briggs, A., Pilidis, P., Nikolaidis, T., 2016. Analyses of a high pressure ratio intercooled direct brayton helium gas turbine cycle for generation IV reactor power plants. *ASME J. Nucl. Rad Sci* 3, (1) 011021.
- Giraud, J., Ghetta, V., Rubiolo, P., Retamales, M.T., 2019. Development of a cold plug valve with fluoride salt. *EPJ Nucl. Sci. Technol.* 5.
- Gonzalez-Gomez, P.A., Gomez-Hernandez, J., Briogones, J.V., Santana, D., 2017. Thermo-economic optimization of molten salt steam generators. *Energy Convers. Manag.* 146, 228–243.
- Gougar, H. D.; Bari, R. A.; Kim, T. K.; Sowinski, T. E.; Worrall, A. Assessment of the Technical Maturity of Generation IV Concepts for Test of Demonstration Reactor Applications; INL/EXT/3647 Rev. 2; Idaho National Laboratory, 2015.
- Green, M., Sabharwall, P., Mckellar, G., Yoon, S.-J., Abel, C., Petrovic, B., Curtis, D., 2013. Nuclear Hybrid Energy System: Molten Salt Energy Storage; INL/EXT-13-31786. Idaho National Laboratory, p. 51.
- Guo, J.-Q., Li, M.-J., Xu, J.-L., Yan, J.-J., Wang, K., 2019. Thermodynamic performance analysis of different supercritical Brayton cycles using CO₂-based binary mixtures in the molten salt solar power tower systems. *Energy* 173, 785–798.
- Guymon, R.H., 1973. MSRE Systems and Components Performance; ORNL-TM-3039. Oak Ridge National Laboratory.
- Holcomb, D. E.; C.L. Britton Jr.; V.K. Varma; Worrall, L. G. Remote Operations and Maintenance Framework for Molten Salt Reactors; ORNL/TM-2018/1107; Oak Ridge National Laboratory, 2018.
- Holcomb, D.E., Kisner, R.A., Cetiner, S.M., 2018. Instrumentation Framework for Molten Salt Reactors; ORNL/TM-218/868. Oak Ridge National Laboratory.
- Ignatiev, V., Feynberg, O., Gnidoi, I., Konakov, S., Kormilistyn, M., Merzliakov, A., Surenkov, A., Uglov, V., Zagnitko, A., 2015. MARS: Story on Molten Salt Actinide Recycler and Transmuter Development by Rosatom in Co-Operation with Euratom; NEA/NSC/R(2015) 2. NRC Kurchatov Institute, Russian Federation.
- Kelleher, B.C., 2015. Purification and Chemical Control of Molten Li₂BeF₄ for a Fluoride Salt Cooled Reactor. University of Wisconsin-Madison. Dissertation.
- Latzko, D. G. H. Sodium-Cooled Fast Reactor Engineering. In *Proceeding of a Symposium on Progress in Sodium-Cooled Fast Reactor Engineering*; IAEA: Monaco, 1970; Vol. IAEA-SM-130/20.
- Li, Q., Tian, J., Zhou, C., Wang, N., 2015. A new method to evaluate the sealing reliability of the flanged connections for molten salt reactors. *Nucl. Eng. Des.* 287, 90–94.
- Liang, D., Zhang, Y., Guo, Q., Shen, D., Huang, J., 2015. Modeling and analysis of nuclear reactor system using supercritical CO₂ Brayton cycle. *J. Xiamen Univ. Nat. Sci.* 54 (5), 608–613.
- Liu, Y., Wang, Y., Huang, D., 2019. Supercritical CO₂ brayton cycle: a state-of-the-art review. *Energy* 189 (115900).
- Macpherson, H.G. Molten-Salt Reactor Program Quarterly Progress Report for Period Ending January 31, 1958; ORNL-2474; Oak Ridge National Laboratory, 1958.
- Macpherson, H. G. Molten-Salt Reactor Program Quarterly Progress Report for Period Ending April 30, 1959; ORNL-2723; Oak Ridge National Laboratory, 1959.
- Makkinje, A., 2017. Design of a Freeze Plug Grate. Delft University of Technology, Department of Applied Physics.
- Malik, A., Zheng, Q., Lin, A., 2019. The design and performance analysis of highly loaded compressor of closed Brayton Cycle HTGR power plant with helium xenon gas mixture as working fluid. *Prog. Nucl. Energy* 117, 103084.
- Manohar S. Sohail; Matthias A. Ebner; Piyush Sabharwall; Phil Sharpe. Engineering Database of Liquid Salt Thermophysical and Thermochemical Properties; INL/EXT-10-18297, 980801; 2010; p INL/EXT-10-18297, 980801. 10.2172/980801.
- McFarlane, J.; Taylor, P.; Holcomb, D.; Poore, W. P. Review of Hazards Associated with Molten Salt Reactor Fuel Processing Operations; ORNL/TM-2019/1195; Oak Ridge National Laboratory, 2019.
- Merk, B., Litskevich, D., Gregg, R., Mount, A.R., 2018. Demand driven salt clean-up in a molten salt fast reactor – defining a priority list. *PLoS ONE*.
- Peterson, P.F., 2003. Multiple-reheat brayton cycles for nuclear power conversion with molten coolants. *Nucl. Technol.* 144, 279–288.
- Raiman, S.S., Lee, S., 2018. Aggregation and data analysis of corrosion studies in molten chloride and fluoride salts. *J. Nucl. Mater.* 511, 523–535. <https://doi.org/10.1016/j.jnucmat.2018.07.036>.

- Report for the US Department of Energy Office of Nuclear Energy Workshop, Molten Salt Chemistry Workshop: Technology and Applied R&D Needs for Molten Salt Chemistry; 2017.
- Robertson, R.C., 1965. MSRE Design and Operations Report, Part I: Description of Reactor Design; ORNL-TM-0728. Oak Ridge National Laboratory.
- Rodriguez, S. Advancing Molten Salts and Fuels at Sandia National Laboratories - White Paper; SAND2017-10478R; 2017.
- Roper, R., Sabharwall, P., Christensen, R., 2019. Chemical Overview of Molten Salts. American Nuclear Society Annual Meeting, Minneapolis, Minnesota.
- Rosenthal, M., Haubenreich, P., Briggs, R., 1972. The Development Status of Molten Salt Breeder Reactors; ORNL 4812. Oak Ridge National Laboratory.
- Sabharwall, P., Patterson, M., Utgikar, V., Gunnerson, F., 2010. Phase change heat transfer device for process heat applications. Nucl. Eng. Des. In Press.
- Sabharwall, P., Kim, E.S., Siahpush, A., Anderson, N., Glazoff, M., Phoenix, B., Mizia, R., Clark, D., McKellar, M., Patterson, M.W., 2011. Feasibility study of secondary heat exchanger concepts for the advanced high temperature reactor; INL/EXT-11-23076. Idaho National Laboratory.
- Samofar <http://samofar.eu/> (accessed 2021-11-02).
- Serp, 2014. The molten salt reactor (MSR) in generation IV: overview and perspectives. Prog. Nucl. Energy 77, 308–319. <https://doi.org/10.1016/j.pnucene.2014.02.014>.
- Shafer, T.D., 2018. Design and Melting Behavior of the MSFR Freeze Plug. Delft University of Technology.
- Shin, H., Cho, J., Baik, Y.J., Cho, J., Roh, C., Ra, H.S., Huh, J., 2017. Partial admission axial impulse type turbine design and partial admission radial turbine test for SCO₂ cycle. Proceedings of ASME turbo expo.
- Simpson, M.F., 2012. Developments of Spent Nuclear Fuel Pyroprocessing Technology at Idaho National Laboratory; INL/EXT-12-25124. Idaho National Laboratory.
- Simpson, M.F., Law, J.D., 2010. Nuclear Fuel Reprocessing; INL/EXT-10-17753. Idaho National Laboratory.
- Sridharan, K., Allen, T.R., 2013. Corrosion in molten salts. In: Molten Salts Chemistry. Elsevier, pp. 241–267. <https://doi.org/10.1016/B978-0-12-398538-5.00012-3>.
- STJ-02MSRE-D992 / Molten Salt Reactor Experiment Engineering Evaluation and Extended Life Study, URS | CH2M Oak Ridge LLC, Oak Ridge, Tennessee. 157.
- EPA Superfund Record of Decision; DOE/OR/02-1671&D2; Oak Ridge National Laboratory: Oak Ridge Reservation (USDOE), Molten Salt Reactor Experiment, 1998.
- Swaroop, P., 2016. Design of a Freeze Plug for the Molten Salt Fast Reactor (MSFR). Delft University of Technology, Department of Sustainable Energy Technology.
- Tiberga, M., Shafer, D., Lathouwers, D., Rohde, M., Kloosterman, J.L., 2019. Preliminary investigation on the melting behavior of a freeze-valve for the molten salt fast reactor. Ann. Nucl. Energy 132, 544–554.
- Turchi, C.S., Vidal, J., Bauer, M., 2018. Molten salt power towers operating at 600–650 °C: salt selection and cost benefits. Sol. Energy 164, 38–46. <https://doi.org/10.1016/j.solener.2018.01.063>.
- Turchi, C. 10 MW Supercritical CO₂ Turbine Test; Office of Scientific & Technical Information Technical Reports, 2014.
- U.S. Department of Energy. Technology Readiness Assessment Guide; DOE G 413.3-4A; 2011.
- U.S. Department of Energy. 2014: The Year of Concentrating Solar Power; DOE/EE-1101; 2014.
- Utgikar, V. Pyroprocessing Schematic, 2019.
- Van Tuyl, F., 2016. A New Design for the Safety Plug in a Molten Salt Fast Reactor. Delft University of Technology, Department of Applied Physics.
- Van Wylen, G.; Sonntag, R., 2015. Chapter 9: Some Power and Refrigeration Cycles. In Fundamentals of Classical Thermodynamics; John Wiley and Sons, Inc: New York.
- Wang, K., He, Y.-L., 2017. Thermodynamic analysis and optimization of a molten salt power tower integrated with a recompression supercritical CO₂ Brayton cycle based on integrated modeling. Energy Convers. Manag. 135, 336–350.
- Wang, C., Qin, H., Tian, W., Qiu, S., Su, G.H., 2020. Transient analysis of tritium transport characteristics of thorium molten salt reactor with solid fuel. Ann. Nucl. Energy 141, <https://doi.org/10.1016/j.anucene.2020.107337> 107337.
- Williams, D.F., Britt, P.F., 2017. Technology and Applied R&D Needs for Molten Salt Chemistry. Oak Ridge National Laboratory.
- Wooten, D., Powers, J.J., 2018. A review of molten salt reactor kinetics models. Nucl. Sci. Eng. 191 (3), 203–230. <https://doi.org/10.1080/00295639.2018.1480182>.
- World Nuclear Association. Molten Salt Reactors <https://world-nuclear.org/information-library/current-and-future-generation/molten-salt-reactors.aspx> (accessed 2021 -10 -29).
- Wright, S.A., Vernon, M.E., Pickard, P.S., 2006. Concept Design for a High Temperature Helium Brayton Cycle with Interstage Heating and Cooling; SAND2006-4147. Sandia National Laboratory.
- Wright, S.A., Radcliff, R.F., Vernon, M.E., Rochau, G.E., Pickard, P.S., 2010. Operation and Analysis of a Supercritical CO₂ Brayton Cycle; SAND2010-0171. Sandia National Laboratory.
- Yu, C., Li, X., Cai, X., Zou, C., Ma, Y., Han, J., Chen, J., 2015. Analysis of minor actinides transmutation for a molten salt fast reactor. Ann. Nucl. Energy 85, 597–604. <https://doi.org/10.1016/j.anucene.2015.06.014>.