



Review

Review of the molten salt technology and assessment of its potential to achieve an energy efficient heat management in a decarbonized chemical industry

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ABSTRACT

Decarbonizing energy intensive industrial processes is a crucial starting point for accelerating the progress toward the net-zero emissions scenario. This review aims to investigate the potential of molten salts in facilitating the creation of energy efficient heat management in the chemical industry, mainly focusing on the imperative transition toward a carbon neutral industrial sector. To achieve this objective, the paper analyzes four types of molten salts—nitrates, chlorides, fluorides, and carbonates—by examining their properties and applications relevant to the chemical industry. The review then explores how molten salts can promote the integration of energy systems such as solar, nuclear, and fuel cells into chemical processes, as well as reduce CO₂ emissions to create energy efficient hybrid industrial plants. This study also delves into processes such as steam cracking of hydrocarbons and steam methane reforming, highlighting the implications of electrifying conventional furnaces and the role of molten salts in heat recovery and reuse. Finally, the paper identifies opportunities to advance and expand the molten salt field, including the exploration of new salt compositions, nano-enhanced mixtures, and similar fluids like ionic liquids and liquid metals.

1. Introduction

According to the 2015 Paris Agreement to combat climate change, it is necessary to reduce greenhouse gas (GHG) emissions from every sector of the global economy to limit the global average temperature rise to below 2 °C until 2050 [1]. The industry sector alone was responsible for 33 % of global anthropogenic GHG emissions in 2014 and consumed 37 % (157 EJ) of the total global energy use in 2018 [2,3]. A large part of industrial CO₂ emissions result from the combustion of fossil fuels, like coal, oil and natural gas for thermal energy production. Even though the industry sector is a great contributor to GHG emissions, it also has a vital role to play in fighting this same problem, since it also provides solutions like coatings for solar panels, lightweight plastics to reduce vehicles'

energy consumption and insulation materials for buildings [3,4].

The chemical industry, in particular, is the largest industrial consumer of energy in the form of gas and oil worldwide, with approximately 12 % (10 million barrels per day) for oil and 8 % (300 billion cubic meters) for gas worldwide [5,6]. Moreover, it is the third largest direct CO₂ emitter, with over 1 billion metric tons of global CO₂ per year in 2022. This results from the consumption of fossil fuels in two ways in the chemical sector: (1) as energy source to create direct heat, steam and electricity to drive the sector's processes, equipment and facilities; (2) and feedstock, as a source of carbon and hydrogen to constitute the chemical products [7,8].

Even though the chemical sector is responsible for the manufacturing of a large variety of chemicals, around 80 % (9 EJ per year) of energy

Abbreviations: BTX, Benzene Toluene and Xylene; CSP, Concentrated solar power; GHG, Greenhouse gases; HVC, High value chemical; HTF, Heat Transfer Fluid; IEA, International Energy Agency; MCFC, Molten Carbonate Fuel Cells; MSBR, Molten Salt Breeder Reactor; MSR, Molten Salt Reactor; MSRE, Molten Salt Reactor Experiment; NHES, Nuclear Hybrid Energy System; T, Temperature (°C); TES, Thermal Energy Storage; T_m, Melting temperature (°C); T_d, Decomposition temperature (°C); T_{max}, Maximum Temperature (°C); wt, Weight.

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demand and 75 % of greenhouse gas emissions (935 MtCO₂ per year) in the chemical industry sector are attributed to only seven compounds. These products are usually referred to as “primary chemicals”, which provide key building blocks of the chemical industry. These compounds have a few characteristics in common, such as being mainly produced from petrochemicals like oil, natural gas and coal and requiring very high-temperature processes that currently involve the combustion of large amounts of fossil fuels [8,9].

Therefore, a significant impact can be achieved by targeting the production processes of these primary chemicals. They are the high value chemicals (HVC), which are composed by light olefins, like ethylene and propylene, as well as benzene, toluene and xylenes, known as BTX aromatics; their production conventionally starts with a process called steam cracking of hydrocarbons like naphtha or ethane. The last two of the primary chemicals are methanol and ammonia; they have the same key process for their production, namely the steam reforming of natural gas [9].

A promising strategy to eliminate CO₂ emissions is to develop technologies that can replace fossil fuel combustion. An example is using electricity from renewable energy sources to generate high-temperature heat [10]. In the case of both methanol and ammonia, for example, water electrolysis powered by renewable electricity can replace the steam methane reformer [11]. However, on an industrial scale, the demand of renewable electricity necessary to produce 1 kg of H₂ through and electric steam methane reformer is less than one third of what is needed when using electrolyzers [12].

In general, chemical processes have adhered to consistent operational methods for decades, resulting in a high level of energy integration with existing technologies. Therefore, the introduction of electrification may necessitate a reassessment and likely a complete reintegration of the entire process. A significant challenge in managing heat within these processes is its transportation, mainly accomplished using steam, which accounts for 30 % of the heat produced from fossil fuels. However, steam, as an energy carrier, poses limitations related to pressure, temperature, corrosion, and capacity [13]. Hence, there is a need to explore alternative fluids beyond steam to achieve a breakthrough in the decarbonization of industrial processes. These fluids must exhibit thermal and chemical stability, along with good heat transfer properties at ambient pressure [14,15].

According to the International Energy Agency (IEA), enhancing energy efficiency across all sectors is key to reducing GHG emissions. The required improvement needs to be two to three times higher than historical rates, aiming for an annual increase of over 4 % between 2020 and 2030 to reach the Net Zero Scenario [16]. A strategic approach to attain this objective involves focusing on more efficient heat management, as industrial processes typically do not utilize all the energy present in the consumed heat. Instead, they often release waste heat into the atmosphere [14].

Fluids suitable for thermal energy storage (TES) offer advantages in managing intermittency in processes, providing flexibility. The versatility of TES materials is particularly pronounced when they are in the liquid phase, allowing them to serve as both TES material and heat transfer fluid (HTF) simultaneously. This dual functionality contributes to a simpler and more cost-effective system [17,18]. Consequently, this enhances the overall efficiency of the energy system, improving process performance and thermal reliability while reducing investment and operational costs as well as lowering CO₂ emissions. While only a few materials possess these characteristics, molten salt stands out as a highly promising option. Molten salt serves as a sensible thermal energy storage material and a heat transfer fluid, exhibiting a high heat capacity storage that allows for temperature adjustments without undergoing a phase change [19,20].

Molten salts have been utilized for years as a high-temperature heat transfer medium in the chemical industry, yet there is a scarcity of information in the literature regarding this specific application [21]. Nevertheless, the knowledge and experience gained from working with

molten salts in diverse fields like concentrated solar power and nuclear reactors can offer valuable insights into molten salt technology. This accumulated information can be harnessed to expedite the adoption of molten salts and contribute to the development of an efficient sustainable chemical industry [21–23].

Therefore, this review paper aims to investigate the potential of molten salts in facilitating enhanced heat integration in the chemical industry, particularly with a focus on the imperative transition toward a carbon-neutral industry. To achieve this objective, the paper will first analyze the four types of molten salts, providing examples of salt mixtures and their respective properties. We will also address these molten salts’ state-of-the-art leveraging information from their applications, point out their common limitations and highlight ongoing developments.

Next, we will explore how molten salts can promote synergy between energy systems and enable the successful and efficient utilization of energy sources, while reducing the GHG emissions of the process. Consequently, molten salts can become an effective solution for enhancing energy efficiency, minimizing waste heat and reducing energy demand in industry. Subsequently, the processes of steam cracking of hydrocarbons and steam methane reforming for the production of ammonia and methanol will be examined and used as basis to deduce a process principle for discussion. Drawing on these examples, the paper will explore the implications of electrifying conventional furnaces and how molten salts emerge as a viable option for heat recovery and reuse in the integration of this new decarbonized process.

The paper will finalize by presenting the opportunities for advancing molten salt research and exploring alternative materials to the molten salt presented in the paper, such as new salt compositions and nano-enhanced mixtures as well as similar fluids such as ionic liquids and liquid metals.

2. Introduction to molten salt technology for efficient industrial decarbonization

Molten salts are ionic liquids and constitute a large class of fluids that are named after their anion. The four types we will focus on within this paper are nitrate (NO₃⁻), chloride (Cl⁻), fluoride (F⁻), and carbonate (CO₃²⁻). These salts are typically mixtures of two or more salts designed in a way to achieve desirable thermophysical properties for their respective applications. Therefore, molten salts are often used in their eutectic composition. The eutectic point of a salt mixture provides transitions from a solid to a liquid phase at a unique temperature that is lower than the melting points of any of the individual components or any other combination of those components. Consequently, larger operational temperature ranges can be achieved, which make molten salts attractive fluids for high-temperature sensible heat storage and transfer. The effects that different salts have in a final mixture will be shown throughout this chapter [24–27].

In general, molten salts are not considered pollutant or flammable if they are within their thermal and chemical stability limits and are not mixed with other compounds. Besides offering an extended working temperature range, they also provide other advantages when it comes to their thermophysical properties [28].

Molten salts exhibit a high specific heat capacity associated with high density values, consequently, a large amount of energy can be stored and carried per unit of volume. Moreover, molten salts are considered efficient heat transfer fluids due to their suitably high thermal conductivity. Another significant advantage of these salts is their low vapor pressure, which allows operation at higher temperatures without pressure build-up, which offers advantages when compared to thermal oil and steam. This characteristic also enables the use of thin walls, reduces the wall temperature gradient, and temperature induced mechanical stress [28–30].

Furthermore, molten salts present low viscosity values which result in reduced pressure drops and associated pumping power, thereby

lowering the overall operational cost. Consequently, molten salts can contribute to simpler and more compact systems when compared to currently available alternatives, requiring fewer heat exchangers and simpler piping schemes, thereby reducing equipment costs as well [31].

However, one of the primary drawbacks of utilizing molten salts is associated with their high melting points, posing the risk of solidification within pipes. This necessitates the use of trace heating to prevent such solidification. After the salt is fully melted, it remains thermally stable until it reaches its maximum operational temperature, which is commonly limited by the salt's thermal decomposition, but can also be influenced by its vapor pressure at high temperatures. Lastly, corrosion in containers, pipes, valves, and pumps limits the application of molten salts in many areas and increases the capital cost. Therefore, the molten salt's temperature must be monitored and controlled at all times [27].

In the following subsections, each of the four salt types, nitrate, chloride, fluoride and carbonate salts, will be comprehensively examined. The structure of the following subchapters will start by addressing molten salt applications that are relevant to industrial chemical processes or can promote industrial decarbonization. Next, the composition of salt mixtures and their thermophysical properties will be shown. We will then present ongoing developments on the salt's applications, the main drawbacks associated with the respective molten salt type, and solutions developed to mitigate these limitations.

2.1. Nitrate salts

The use of molten nitrate salts began in the mid-1920s when the petroleum industry adopted them as a medium for process heat transfer. By the 1940s, the industrial applications of molten salts had expanded to provide heating and cooling for chemical reactors, for example, in phthalic and maleic anhydride catalytic converters, as well as for the efficient heat transport over significant distances in large-scale plants [19,27]. However, this industrial experience has not been well documented, so a study by the Sandia National Laboratories, including on-site inspections of the plants and discussions with plant operating personnel, was conducted to gather more information about this application. They visited seven different industrial plants and revealed that molten nitrate salt systems generally operated without concern, requiring minimal monitoring and maintenance. These systems, often operating below 450 °C, were noted for their trouble-free performance and excellent safety records. Typically, the reactor design consisted of a shell and tube heat exchanger, the reactant or product gas stream flowing in the tube side and the molten salt in the shell in countercurrent flow. Even today, a few processes and reactors still use molten salts as a heat transfer fluid, but limited information is available in the open literature [19,21,32].

Subsequently, nitrate molten salts found applications in the solar power field, particularly in Concentrated Solar Power (CSP) plants. The first molten salt power tower system was launched in 1984, featuring pioneering systems such as the THEMIS tower (2.5 MWe) in France and the Molten Salt Electric Experiment (1 MWe) in the United States of America. By 1996, a 10 MWe power system named Solar Two marked the first system using molten salt as both heat transfer and energy storage fluid. The introduction of molten salts has yielded numerous benefits for CSP plants. As molten salts can function as thermal energy storage material, heat can be stored in the salt and used during off-peak periods, such as nighttime or periods of low solar radiation. Consequently, this innovation has made it possible to increase energy generation and overcome intermittent behavior of solar energy [30,31]. This application has proven so successful that there are many commercial CSP plants operating with molten salts around the world.

Presently, Solar Salt stands out as the most popular nitrate salt, commonly applied in CSP plants. Even though most molten salt mixtures are designed to be eutectic, solar salt is a non-eutectic mixture of sodium and potassium nitrate salts. This composition was designed to reduce capital costs and increase heat capacity by increasing the quantity of

NaNO₃ compared to the equimolar eutectic composition. Consequently, Solar Salt has no single melting temperature, but a melting range starting at the solidus melting temperature of 223 °C and becoming fully liquid at 240 °C. The increased melting temperature is considered tolerable, given the improvements [27,33].

Meanwhile, in industrial applications, the widely used molten salt was Hitec, a mixture of nitrate and nitrite salts [17,27]. Ternary, quaternary and quinary mixtures are under investigation, incorporating other alkaline (e.g., lithium) or alkaline earth (e.g., calcium) cations or other anions (e.g., nitrite). Table 1 provides an overview of the nitrate-based molten salts' composition and their respective liquidus melting point and decomposition temperatures in air atmosphere [27,28,34,35].

From the mixtures depicted in Table 1, some of the following salts are included to provide their respective benefits:

- **Lithium nitrates (LiNO₃)** allow thermal stabilities up to approximately 550–600 °C, melting points below 120 °C, and a relatively high specific heat capacity of the eutectic mixture. The drawback lies in their high cost, although this can be mitigated through large-scale production by converting Li₂CO₃ with HNO₃ [28].
- **Calcium nitrates (Ca(NO₃)₂)** are added to salt mixtures to decrease their melting point and cost and increase their heat capacity. However, this additional salt makes the final mixture more hygroscopic. Furthermore, it has been observed that this addition can compromise the long-term stability of the final mixture, leading to increased viscosity. Consequently, accurately determining the crystallization point by calorimetric methods becomes challenging due to the presence of slow transitions with low enthalpies [36].
- **Nitrites (NaNO₂ and KNO₂)** are added to decrease the mixture's melting point, but their presence also limits the decomposition temperature to about 450 °C under air atmosphere due to decomposition and degradation reactions [28].

The most extensively investigated molten salts are binary or ternary, such as Solar Salt, Hitec, Hitec XL and NaKLiNO₃, but other high-order mixtures have been developed with no evidence of any commercial application to date [28]. One of these salts, named Sandia Mix, was created by the Sandia National Laboratory and constitutes a new eutectic quaternary molten salt mixture. Another, developed by Halotronics Inc., is known as Halotronics SS-500, is a quinary salt mixture that introduces the addition of cesium nitrate (CsNO₃) with the aim of further lowering the melting temperature of the salt, albeit at increased cost [37]. The thermophysical properties of these salts can be found in Table 2.

Currently, the Noor Ouarzazate Solar Complex in Morocco is the largest CSP plant in operation. It has a total capacity of 510 MW and uses 140 000 tons of solar salt for energy storage to allow electricity generation for up to 7–8 h after sunset [44]. Meanwhile, a larger CSP project with total capacity of 700 MW in Dubai is planned to be finalized in 2024 and will contain a total of 560 000 tons of molten salt with the goal of reaching new world record of levelized cost of electricity at USD 0.073/kWh; a cost level that competes with fossil fuel generated electricity [45].

Furthermore, the company MAN Energy Solutions provides an extensive range of molten salt operated reactors capable of achieving operating temperatures of up to 550 °C. These reactors are utilized to produce various compounds, including phthalic and maleic anhydride, methyl methacrylate, acrylic acid and acrolein. To ensure longevity and safety, the company employs high-grade materials such as carbon steel or vanadium-reinforced chrome steel, along with special cladding made from zirconium [46].

Nitrates are categorized as "Class I oxidizers", the least hazardous of the four classes. This classification defines them as "an oxidizing material whose primary hazard is that it may slightly increase the burning rate of combustible materials," but they "do not cause spontaneous ignition when they come into contact with them" [32]. Experiments

Table 1Composition, liquidus melting temperature (T_{melt}) and decomposition temperature (T_d) of different nitrate molten salts.

Name	Composition / wt %						T_m / °C	T_d / °C
	NaNO ₃	NaNO ₂	KNO ₃	KNO ₂	Ca(NO ₃) ₂	LiNO ₃	CsNO ₃	
Solar Salt	60		40					240
Hitec	7	40	53					140
Hitec XL	7		45		48			140
NaKLiNO ₃	18		52			30		120
CaLiNO ₃ NaKNO ₂		16.8		45	13.6	24.6		72
Sandia Mix	13		66		14	7		90
HalotechnicsSS-500	6		23		19	8	44	65
								500

Table 2

Thermophysical properties of nitrate molten salts.

Solar Salt [30,38,33]			
Specific heat capacity	J (kg K) ⁻¹	1443 + 0.172 T	
Density	Kg m ⁻³	2090 - 0.636 T	
Thermal conductivity	W (m K) ⁻¹	0.443 + 1.9010 ⁻⁴ T	
Viscosity	Pa s	2.2710 ⁻² - 1.2010 ⁻⁴ T + 2.2810 ⁻⁷ T ² - 1.4710 ⁻¹⁰ T ³	
Hitec [38–40]			
Specific heat capacity	J (kg K) ⁻¹	1560	
Density	Kg m ⁻³	2084 - 0.74 T	
Thermal conductivity	W (m K) ⁻¹	0.411 + 4.3610 ⁻⁴ T - 1.5410 ⁻⁶ T ²	
Viscosity	Pa s	10 ^{2.737} T ^{-2.104}	
Hitec XL [28,30,38]			
Specific heat capacity	J (kg K) ⁻¹	1440	
Density	Kg m ⁻³	2240 - 0.827 T	
Thermal conductivity	W (m K) ⁻¹	0.52	
Viscosity	Pa s	10 ^{6.137} T ^{-3.364}	
NaKLiNO ₃ [41,42]			
Specific heat capacity	J (kg K) ⁻¹	1600	
Density	Kg m ⁻³	2077 - 0.735 T	
Thermal conductivity	W (m K) ⁻¹	-3.3010 ⁻⁴ T + 0.449	
Viscosity	Pa s	1.33 10 ³ T ^{-2.24}	
CaLiNO ₃ NaKNO ₂ [41]			
Specific heat capacity	J (kg K) ⁻¹	1650	
Density	Kg m ⁻³	2084 - 0.732 T	
Thermal conductivity	W (m K) ⁻¹	0.50	
Viscosity	Pa s	5.69 10 ⁵ T ^{-3.32}	
Sandia Mix [30,31]			
Specific heat capacity	J (kg K) ⁻¹	1440 (at 300 °C)	
Density	Kg m ⁻³	2015 (at 150 °C)	
Thermal conductivity	W (m K) ⁻¹	0.65 (at 250 °C)	
Viscosity	Pa s	0.006 (at 300 °C)	
Halotechnics SS-500 [30,42,43]			
Specific heat capacity	J (kg K) ⁻¹	1220	
Density	Kg m ⁻³	2788 - 0.872(T+273)	
Thermal conductivity	W (m K) ⁻¹	0.35	
Viscosity	Pa s	0.004 (at 300 °C)	

have shown that liquid and gaseous oxidizable materials do not react or react only minimally when in contact with nitrate molten salts. It has been observed that there is a high risk of deflagration only when the salt reacts with finely divided solids. Recognizing the salt as an oxidizing agent and treating the molten salt with the same precautions as any oxidizing hot liquid can help avoid potential hazards [32,47,48].

Another challenge associated with nitrate salts is corrosion to

ferroalloys at high temperatures, requiring careful selection of materials that come into contact with the salt. Stainless steels, such as 304, 316L, 321H and 347H, are commonly used for nitrate molten salts and exhibit good corrosion resistance. For high-temperature stability, elements like chromium (Cr) are preferred in high percentages due to the formation of a stable protective Cr oxide on the alloy, enhancing corrosion resistance. Nickel (Ni) is another crucial element that stabilizes the mechanical properties and corrosion resistance of metal alloys at elevated temperatures. Additionally, titanium (Ti) and niobium (Nb) are relevant elements, working to decrease the corrosive effect of carbon by forming a stable carbide. Molybdenum (Mo) is also noteworthy for its ability to improve the corrosion resistance of the metal alloy to chloride ions [49–51].

In general, nitrate salts exhibit low corrosivity for stainless steel below approximately 500 °C, and within the CSP field, no critical issues have been reported [52]. However, at higher temperatures, corrosion can significantly increase due to two main reasons: (1) metal alloys like Cr may begin to dissolve in the salt, and the protective oxide films are no longer formed; (2) nitrates can start to decompose into nitrites, generating gaseous oxygen and enhancing corrosion propensity. Additional factors that may exacerbate or trigger corrosion with nitrate salts include the presence of impurities such as metal ions (Mg, Ca), metal oxides, halides (Cl⁻, Br⁻, I⁻) and moisture, as these salts are hygroscopic. These impurities are known to interact with elements of the salts and metal alloys, altering the kinetics of corrosion, interfering in the formation of the protective oxide layer, and creating insoluble compounds that may cause cracking along grain boundaries. Therefore, salts should be pretreated to remove possible impurities, and the salt containers should be kept closed and under an inert or trace N₂ or NO_x gas blanket to prevent contact with air [49–51,53]. Moreover, the thermal stability and longevity of nitrate salts are significantly influenced by the surrounding gas atmosphere, for example, a study by DLR demonstrated that by controlling the partial pressure of oxygen in a sealed tank, it was possible to extend the upper temperature limit of Solar Salt by 40 °C. This led to an increase in storage capacity by more than 16 % and a reduction of the concentration of unstable nitrite ion and corrosive oxide ion by 16 % and 75 %, respectively, compared to a salt system with an open atmosphere [54].

2.2. Chloride salts

Chloride molten salts do not have a well established commercial application, but they have been explored to be used in the nuclear field, more specifically, in Molten Salt Reactors (MSRs) in two primary ways. First, as fuel salts, which involves the dissolution of actinides such as uranium, thorium and plutonium in a molten salt. This fuel salt is then utilized to generate heat through nuclear fission within a reactor core. The second approach involves using a non-nuclear molten salt as a coolant HTF, indirectly extracting heat from the fuel, which can subsequently be safely utilized for electricity generation, process heat, or thermal storage [55].

Chloride salts consist primarily of a mixture of sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), lithium chloride (LiCl), or zinc chloride (ZnCl₂) in

various compositions. In the case of chloride salts, vapor pressure presents a more significant limitation to their high-temperature stability than thermal decomposition (without considering corrosion). This characteristic is important since one of the key advantages of molten salts is their ability to operate at ambient pressure [56,57]. Therefore, Table 3 provides examples of chloride salts along with their melting and approximate maximum temperature restricted by vapor pressure, while their thermophysical properties are listed in Table 4 [56–59].

Different salts can be mixed to achieve the desirable thermal energy storage and heat transfer fluid properties while maintaining cost-effectiveness. Some known characteristics of individual salts [56,60,61]:

- **Alkali metal chlorides (NaCl and KCl)** are added to enhance heat capacity, increase the decomposition temperature, decrease the vapor pressure, reduce hygroscopicity, and lower the overall cost of the salt.
- **Alkaline earth metal chlorides (CaCl₂ and MgCl₂)** can be added to lower the melting point and vapor pressures while increasing the heat capacity of the mixture. However, it is worth noting that both salts are highly hygroscopic.
- **Other chloride salts like LiCl and ZnCl₂** are often included in a salt mixture to reduce its melting point. However, a significant drawback is that they may increase the overall cost of the salt mixture. In particular, ZnCl₂ tends to elevate the vapor pressure, decrease heat capacity, and it is highly hygroscopic.

Chloride molten salts hold particular significance in the nuclear field. They can accommodate a higher content and offer better solubility of actinides in a reactor, when compared to the state-of-the-art salt investigated in nuclear field, fluoride salts, which will be discussed in chapter 2.3, along with functioning at high temperatures and low pressures. This characteristic allows neutrons to move at very high speeds, enhancing the efficiency of the fission reaction and enabling fast neutron spectrum operations. Consequently, the reactor can more efficiently breed fissile materials from fertile materials, contributing to high fuel utilization and increased energy production. Additionally, fast neutron spectrum operation helps minimize the impact of fission contamination byproducts, thereby reducing the production of long-lived radioactive waste [64–66].

The combination of these advantages, coupled with the demand for new and flexible carbon-free energy sources, has led to the reconsideration of molten salts as a promising breakthrough technology for the new generation of nuclear reactors. However, there is very limited practical information available about chloride salts applied in nuclear reactors. Consequently, numerous companies, international research organizations, and universities are rapidly developing MSR designs. [66,67] For example, the Delft University of Technology in the Netherlands is researching a promising fuel salt for a fast neutron spectrum Molten Salt Reactor: NaCl-ThCl₄-PuCl₃ [65]. Additionally, two noteworthy projects are the Molten Salt Research Temperature-Controlled Irradiation experiment from the Idaho National Laboratory and the Molten Chloride Fast Reactor by the company TerraPower [68–70].

Moreover, the interest in chloride molten salts extends beyond the nuclear field, as they have recently garnered attention in the

Table 3

Composition, liquidus melting temperature (T_{melt}) and maximum temperature restricted by vapor pressure (T_{max}) of different chloride molten salts.

Name	Composition / wt %					T _m / °C	T _{max} / °C
	NaCl	KCl	MgCl ₂	LiCl	ZnCl ₂		
KMgCl		62.5	37.5			430	700
KLiCl		40.5		59.5		355	700
NaKZnCl	7.5	23.9			68.6	204	800
NaKMgCl	22.2	21.3	56.5			385	800

Table 4

Thermophysical properties of chloride molten salts.

KMgCl [62,63]			
Specific heat capacity	J (kg K) ⁻¹	1000	
Density	Kg m ⁻³	1903	$-0.552 T$
Thermal conductivity	W (m K) ⁻¹	0.505	$-10^{-4} T$
Viscosity	Pa s	14.965	$-0.0291 T + 1.78410 \cdot 10^{-5} T^2$
KLiCl [58]			
Specific heat capacity	J (kg K) ⁻¹	1200	(700 °C)
Density	Kg m ⁻³	1520	(700 °C)
Thermal conductivity	W (m K) ⁻¹	0.42	(700 °C)
Viscosity	Pa s	1.15	10^{-3} (700 °C)
NaKZnCl [28,59]			
Specific heat capacity	J (kg K) ⁻¹	920	
Density	Kg m ⁻³	2625	$-0.926 T$
Thermal conductivity	W (m K) ⁻¹	0.514	$-2.33 \cdot 10^{-4} (T+273)$
Viscosity	Pa s	0.121	$\exp\left(\frac{-(T+273)}{204.7}\right) + 4976 \exp\left(\frac{-(T+273)}{29.9}\right) + 3.4010 \cdot 10^{-3}$
NaKMgCl [57]			
Specific heat capacity	J (kg K) ⁻¹	1040	
Density	Kg m ⁻³	1940	$-0.42 T$
Thermal conductivity	W (m K) ⁻¹	0.53	$-1.32 \cdot 10^{-4} T$
Viscosity	Pa s	0.0277	$\exp(-3.64 \cdot 10^{-3} T)$

concentrated solar power sector. The U.S. Department of Energy (DOE) initiated the Concentrating Solar Power Generation 3 program to promote the development of advanced CSP systems capable of generating electricity at a levelized cost of energy less than USD 60/MWh [71]. As a comparison, the current CSP system, operated with nitrate salts, as mentioned in chapter 2.1, had a levelized cost of energy of USD 118/MWh in 2022, according to IRENA's global renewable power generation costs study [72]. Within this program, three potential pathways are being explored based on the form of the thermal carrier: liquid (molten salt), solid particle, or gaseous [61,73–75].

The liquid pathway aims to raise the hot salt system temperature from 565 °C to approximately 720 °C by substituting nitrate salts with chloride salts. This temperature increase facilitates a rise in overall power cycle efficiency from 41.2 % to 55 % through the utilization of a supercritical CO₂ Brayton power cycle for electricity generation. However, this shift introduces significant challenges, particularly in terms of material interaction with molten chloride salts. Consequently, the Liquid Pathway project has benefited from several complementary projects with research groups worldwide, often in collaboration with the nuclear field. The most promising chloride salts investigated by the project are mixtures of NaCl-KCl-MgCl₂, with the nominal salt composition being 46 % MgCl₂, 39 % KCl, and 15 % NaCl by weight [57,61,73–75].

The main challenge when dealing with chloride salts is related to their corrosiveness. However, in theory, commonly used metals found in commercial alloys, including Fe, Cr and Ni are not susceptible to corrosion solely by chloride salts. This is attributed to their higher thermodynamic stability compared to compounds like FeCl₂, CrCl₂ and NiCl₂. Also, the chloride salts, CaCl₂, MgCl₂ and ZnCl₂, exhibit highly hygroscopic properties, meaning they tend to absorb water from their surroundings. Consequently, corrosion is typically triggered from the presence of water, impurities and O₂, which originate from exposure to the environment [76].

Extensive research has been conducted on the corrosion mechanisms of salts containing MgCl₂, as they are considered the most promising

candidates for high-temperature applications. This mechanism primarily involves the interaction of MgCl_2 with moisture in the air, leading to the formation of MgOHCl . Subsequently, the dissolution of MgOHCl results in the generation of MgOH^+ [57]. This particular ion is believed to be primarily responsible for the corrosive behavior observed in metallic alloys, as it reacts with alloying elements such as Cr, Fe, Mn, Si and Ni, initiating the formation of oxide layers. However, at high temperatures, these protective oxide layers do not fully develop and instead dissolve into the molten salt, causing depletion of the metal alloy. Furthermore, over time and as the temperature increases, corrosion gradually diminishes due to the decomposition of MgOH^+ into MgO precipitate and HCl [77–80].

Despite the challenges posed by corrosion, various strategies have been developed to address the potential of chloride molten salts for high-temperature applications.

- **Material selection:** Superalloys with a high content of nickel, such as, Inconel (IN617 and IN740H), Haynes (H230) and Hastelloy (C276), provide better corrosion resistance when compared to regular stainless steel. The main drawback is that these materials may not be feasible for commercial scale applications due to their high prices [57,73,79].
- **Corrosion prevention:** In order to eliminate moisture, chloride salts — which exhibit highly hygroscopic properties — need to undergo thermal purification before melting. This purification process must be carried out in a dry and inert environment. Alternatively, a method to purify salts containing magnesium chloride involves adding Mg to the salt and mixing it slightly above the melting point. As a result, the metal reacts with the remaining impurities, leading to the formation of a precipitate that can be subsequently filtered out [61]. Chloride salts tanks must be kept in a sealed environment filled with an inert gas like Argon. Additional methods to prevent corrosion include the use of sacrificial metals that serve as oxygen scavengers, surface passivation through the formation of a protective Al_2O_3 layer on the alloys, thermal spray coatings, cladding and on-line salt purification via electrolysis [56,81,82].
- **Corrosion monitoring:** Despite making significant efforts to eliminate possible causes of corrosion, it remains crucial to maintain constant monitoring of the concentration of corrosion product concentrations (e.g., Cr^{2+} , Fe^{2+}), salt impurity concentrations (O^{2-} , MgOHCl), the redox potential of the molten salt, and the corrosion rate of the alloys [57].

Recently, the Oak Ridge National Lab has developed the Facility to Alleviate Salt Technology Risks (FASTR) with the primary objective to facilitate and de-risk the use of chloride salts in high-temperature applications [83]. FASTR was constructed primarily of alloy C-276, since it is a salt-compatible and high-strength material, except for the main heater, which was constructed of alloy 600. The salt being tested in this facility is a molten ternary mixture of NaCl-KCl-MgCl_2 , it melts at 400°C and will be used up to 725°C . These tests will help the development of the fundamental understanding of salt composition selection, salt preparation methodology, chemistry control scheme, corrosion monitoring and control as well as material compatibility. Additionally, the project incorporates additional efforts focused on demonstrations of major components such as flanges, heat trace, heat exchangers, pumps, and innovative electrochemical sensors to monitor the salt and the structural materials [83–85].

The FASTR became operational in 2022 and a range of tests have been completed to support the commissioning of the system, starting with the shakedown phase, which had the purpose of ensuring that the subcomponents meet performance expectations before salt introduction. Now, with the successful start of forced-circulation salt operations, the facility has transitioned into the startup phase and to date, several activities that were predefined for this phase have been completed. The successful test performed paves the path towards the actual test

campaign, which strives to obtain quality scientific data, such as corrosion control demonstration, REDOX control system and oxygen/impurity sensors demonstration [84,85].

2.3. Fluoride salts

In the mid-1940's the nuclear industry began using fluoride salts as fuel salt and coolants as explained in section 2.2. It started with the Aircraft Nuclear Propulsion program, a U.S. Air Force's effort to develop a molten salt nuclear-powered long-range bomber aircraft through the Aircraft Reactor Experiment. The Aircraft used the fuel salt $\text{NaF-ZrF}_4\text{-UF}_4$ and NaF as coolant, and Inconel was used for the reactor structural material. However, in 1961, the project was terminated [86,87]. Simultaneously, in 1958, officials from the Oak Ridge National Laboratory and the Atomic Energy Commission funded a study of molten-salt powered reactors, marking the beginning of the Molten Salt Reactor Experiment (MSRE). Molten salt reactors were primarily envisioned as a pathway to utilize thorium, which is three to four times more naturally abundant than fissile uranium (U-235), as a fuel for nuclear power plants [88–91]. The design of the MSRE began in 1960, reaching full capacity in early 1969 and the fuel salt of choice was the $\text{LiF-BeF}_2\text{-ZrF}_4\text{-UF}_4$ while LiF-BeF_2 salt was used as coolant, the reactor material was Hastelloy-N. However, the experiment was shut down due to several problems such as failures of the blowers responsible for removing the reactor heat and material problems arising from difficulties in maintaining integrity in highly radioactive and corrosive environments at elevated temperatures [90–93].

Despite the perceived challenges, plans to construct the Molten Salt Breeder Reactor (MSBR) continued to progress [94,95]. The goal of this last project was to use fertile thorium (Th-232) and uranium (U-238), which are abundant materials, in the form of ThF_4 and UF_4 to breed fissile uranium through the thorium-uranium fuel cycle. The MSBR used the fuel salt $\text{LiF-BeF}_2\text{-ThF}_4\text{-UF}_4$ and employed the $\text{NaBF}_4\text{-NaF}$ salt as coolant, the reactor material used was Hastelloy-N. However, despite these efforts, the persistent issues led to the termination of the entire molten salt reactor program by 1976 [91,94–97].

The composition of the fluoride salt mixtures used for nuclear application is carefully designed to meet the criteria outlined by Grimes for their use as either coolants or as fuel salts, when the fuel is dissolved in the salt [97,98]. The main candidates for these mixtures include alkali fluoride salts, ZrF_4 and BeF_2 . Table 5 provides examples of non-fuel fluoride salt mixtures, along with their respective compositions, melting and decomposition temperatures [99].

Furthermore, Table 6 provides an overview of the thermophysical properties of these salts.

MSRs offer an alternative to the majority of nuclear reactors worldwide, which use pressurized water as a cooling fluid and to slow down nuclear reactions. Conventional reactors operate at around 300°C and require a pressure of about 150 atm [91]. These conditions not only make conventional reactors less efficient due to the low temperature of the coolant but also raise safety concerns. Therefore, in 2001, during the Generation IV forum, the MSR was recognized as a promising nuclear reactor concept [100,101]. However, it was not until the early 2010 s that new MSR activities commenced worldwide, and two concepts garnered the attention of researchers and companies: Liquid Fluoride Thorium Reactors, which are a continuation of the efforts from the

Table 5

Composition, liquidus melting temperature (T_{melt}) and decomposition temperature (T_d) of different fluoride molten salts.

Name	Composition / wt %					T_m / $^\circ\text{C}$	T_d / $^\circ\text{C}$
	NaF	KF	LiF	ZrF_4	BeF_2		
Flibe			53		47	459	1430
Nafzirf	36			64		500	1357
Flinak	12	59	29			454	1570

Table 6
Thermophysical properties of fluoride molten salts.

Flibe [99]		
Specific heat capacity	J (kg K) ⁻¹	2386
Density	Kg m ⁻³	2330 – 0.42 (T + 273)
Thermal conductivity	W (m K) ⁻¹	1.00
Viscosity	Pa s	$1.1810^{-4} \exp\left(\frac{3760}{(T + 273)}\right)$
Nafzirf [99]		
Specific heat capacity	J (kg K) ⁻¹	1172
Density	Kg m ⁻³	3827 – 0.889 (T + 273)
Thermal conductivity	W (m K) ⁻¹	0.49
Viscosity	Pa s	$7.6710^{-5} \exp\left(\frac{3977}{(T + 273)}\right)$
Flinak [99]		
Specific heat capacity	J (kg K) ⁻¹	1884
Density	Kg m ⁻³	2579 – 0.624 (T + 273)
Thermal conductivity	W (m K) ⁻¹	$0.36 + 5.6 \cdot 10^{-4} (T + 273)$
Viscosity	Pa s	$410^{-5} \exp\left(\frac{4170}{(T + 273)}\right)$

MSBR, and the Fluoride Salt-Cooled High-Temperature Reactors, which use solid fuel and fluoride salts just as coolants. [102–106].

In the field of space exploration, nuclear thermal propulsion has been on NASA's radar for more than 60 years, and space molten salt reactors are considered an interesting option in terms of economics, safety, operational robustness and power density. Several studies are being performed in this area to enable this technology for future crewed missions to Mars in the 2030 s. [107–109].

A main drawback of fluoride salts is their susceptibility to corrosion which causes material degradation and thermal stress from high operational temperatures. Similarly to chloride salts, fluoride salts are natural reducing agents and do not corrode metal alloys on their own. The presence of water, oxygen, or other impurities in the salts combined with the high temperatures is what triggers the oxidizing process and solubility of protective oxide layers, leading to corrosion of the containment materials. These issues become even more challenging when it comes to irradiated fuel salts due to the lack of practical information. Therefore, few research groups are dedicated to studying the behavior of these fluoride salts with and without fuels when it comes to maintaining the integrity of the metal alloys used as containment. Some of the corrosion mitigation strategies discussed in section 2.2 for chloride salts, can also be extended to the use of non-fuel fluoride salts [24,50]. Furthermore, fluoride salts are considered hazardous to humans and should be handled with caution, with adequate protective equipment and ventilation to prevent breathing air containing it. This is especially important when BeF salt is used, as beryllium is a toxic element itself. Additionally, lithium fluoride, in nuclear applications, can generate tritium, which is harmful to humans if not isotopically purified [24,97,110].

2.4. Carbonate salts

Carbonates are not commonly used or studied directly as heat transfer fluids or thermal energy storage, but they have properties that offer the potential to do so and will be explored in this section. Therefore, this chapter will discuss some applications of carbonate salts that are relevant for industrial chemical processes or can enable industrial decarbonization: Molten carbonate fuel cells (MCFC), CO₂ capture and utilization, gas separation and cleaning, as well as pyrolysis and gasification processes. To this day, only MCFCs have reached commercial scale.

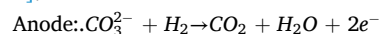
Carbonate salts can be used for power generation through molten carbonate fuel cells. Their origin traces back to the 1930 s in Switzerland, where experiments with high-temperature solid oxide cells encountered issues with electrical conductivity and unwanted chemical reactions involving gases like carbon monoxide. Two decades later, scientists in the Netherlands, recognizing the limitations of solid oxides,

turned to molten carbonate salts. Thus, in 1960, they announced the successful operation of a MCFC using a mixture of lithium, sodium, and potassium carbonate impregnated in a porous magnesium oxide disc, which ran continuously for six months [111,112]. This concept evolved over the decades and is becoming an important technology, currently reaching megawatt-scale commercial power plants [113–116].

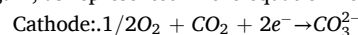
The current configuration of a typical MCFC is based on a nickel alloy anode and a nickel oxide cathode in contact through an electrolyte, which can be binary or ternary mixtures of Na₂CO₃, Li₂CO₃, K₂CO₃ retained in a porous LiAlO₂ matrix. Since the system operates at temperatures around 600 to 700 °C, the carbonate salt mixture is liquid and has a high conductivity, which allows the transport of carbonate ions from cathode to anode. Moreover, the use of high-strength stainless steels, SS310 and SS347, is common in MCFC technologies thanks to their compatibility with alkali carbonate salts at temperatures of around 650 °C [117–120].

MCFC can be fed directly with various types of hydrocarbons, such as natural gas, which, inside the cell, undergoes a chemical reaction called steam reforming catalyzed by the nickel contained in the cell. The reform is the reaction of steam with natural gas; it produces hydrogen, CO₂ and CO. Additionally, the carbon monoxide molecules react with water vapor in a water–gas shift reaction, producing more hydrogen and carbon dioxide [121,122].

In addition to the reactions with natural gas within the cell, the typical oxidation–reduction reactions also occur and produce water in the form of steam, carbon dioxide, heat, and electricity. At the anode, the reaction occurs between hydrogen and carbonate ions, forming water, carbon dioxide, and two electrons as shown in the equation below [121].

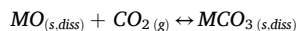


At the cathode, oxygen from the air and CO₂ react with electrons from the anode, which are routed through an external circuit generating electricity and heat as a by-product. This reaction produces the carbonate ion, CO₃²⁻, which will pass through the electrolyte to the anode again, as represented in the equation below [120–122].



MCFC technology's greatest disadvantage is its low durability due to operating temperatures and corrosive electrolytes, which accelerate the breakdown of cell components. Research focuses on new materials to improve durability, addressing issues like corrosion, electrolyte loss, and cathode dissolution [117].

The field of carbon capture, utilization and storage benefits from the absorbent capacity of carbonate salts. In this application, carbon dioxide or flue gases from industrial processes can be used to form stable carbonate salts, reducing greenhouse gas emissions. Carbon capture in molten salts uses the reversible carbonation reaction controlled by a thermal swing, either in a continuous flow reactor or a batch reactor. The reaction is represented below [123,124].



Alkaline earth metal (M) = Be, Mg, Ca, Sr, Ba

At lower temperatures, the reaction between CO₂ and an alkaline earth metal oxide sorbent such as CaO or MgO is favored in order to form a carbonate salt. The carbonate is then transferred to a second reactor chamber and decomposed at high temperatures in a decarbonation reaction to regenerate the oxide sorbent and pure CO₂ gas. The transfer of the decarbonated solid (CaO) back to the absorption chamber completes the loop. For naturally occurring minerals, CaO-based sorbent reactivity is severely reduced after around 3 cycles representing a big challenge identified with the technology [124–127].

Carbonate salts have also been investigated as a way to clean industrial process gases by removing impurities such as sulfur compounds like H₂S and SO₂, halogens like HCl and HF and tar. These harmful compounds can be toxic or corrode the equipment, besides decreasing

the energy conversion efficiency of the process gas of interest and, therefore, must be removed to meet acceptable concentration levels. To solve this problem, carbonate salts (Na_2CO_3 , Li_2CO_3 , K_2CO_3 , BaCO_3 , CaCO_3 or mixtures) can act as absorbents at high temperatures for desulfurization and dehalogenation and as a catalyst for tar cracking. The mechanism consists of the contaminated gas reacting with the melted carbonate salt isolating the impurity and producing H_2O and CO_2 [128,129].

In pyrolysis and gasification processes, carbonate salts can be used simultaneously as heat carriers, catalysts, and solvents. This occurs when carbonaceous feedstocks are thermally decomposed in a molten salt bath in the presence of a gasifying agent, which can be CO_2 or water. This technology came to the forefront by an experiment where gasification of active carbon and coal was performed with CO_2 in a mixture of potassium and sodium carbonate (K_2CO_3 - Na_2CO_3) at 900°C . As a result, the carbonate salt mixture was found to enhance the gasification rate by 3.3 and 1.5 times for coal and active carbon, respectively, when compared to the absence of molten salt [130–132]. Similarly, another study on the pyrolysis of cellulose in a eutectic mixture of lithium, potassium and sodium carbonates (K_2CO_3 - Na_2CO_3 - Li_2CO_3) at temperatures ranging from $851 - 962^\circ\text{C}$, showed that the pyrolysis rate was increased by 74 % in the presence of molten salt. Despite the potential for high thermal efficiency, using carbonate salts for gasification purposes has not been commercialized due to high construction and running costs. [133].

The thermal stability of carbonate salts is significantly influenced by atmospheric conditions. For example, exposure to air and argon results in relatively low thermal stability, leading to decomposition temperatures of only 600°C and 700°C , respectively. However, when exposed to a CO_2 gas atmosphere, the stability increases significantly, with decomposition temperatures reaching up to 1000°C [134]. Table 7 provides information on LiNaKCO_3 , including its composition, melting temperature and decomposition temperature considering a CO_2 gas atmosphere. The thermophysical properties of this salt can be found in Table 8. [135].

A more recent application for carbonate salts is as potential heat transfer fluid in the generation 3 of CSP plants to produce electricity at a lower levelized cost of energy, like mentioned in Section 2.2 for the chloride salts. Carbonate molten salts are also being considered as an alternative fluid because they are inherently less corrosive than chloride salts and do not require controlled purification and pre-melting procedures. Besides the high values for heat capacity and density, carbonate salts also have a good compatibility with CO_2 , and previous experience in other fields make this type of salt a promising option for CSP applications. The salt being studied is an eutectic mixture (LiNaKCO_3) of Na_2CO_3 , Li_2CO_3 , K_2CO_3 and has been shown to be compatible with alloy 347 up to 650°C and Haynes 230 up to 720°C [61].

The main disadvantages of dealing with carbonate molten salts are its corrosiveness and high cost of lithium carbonate. These issues have been a common barrier for the large scale commercialization of carbonate salt applications due to associated high costs and short lifetime of equipment. In terms of corrosion of metal alloys, carbonates generally exhibit a higher propensity to corrosion compared to nitrate salts, but their corrosive nature is lower than that of chloride and fluoride salts. Additionally, carbonates do not typically require controlled purification or pre-melting processes [53]. Some corrosion mitigation strategies for carbonate salts include:

Table 7

Composition, liquidus melting temperature (T_{melt}) and decomposition temperature (T_d) of different carbonate molten salts.

Name	Composition / wt %			T_m	T_d
	Na_2CO_3	K_2CO_3	Li_2CO_3	/ $^\circ\text{C}$	/ $^\circ\text{C}$
LiNaKCO_3	33.4	34.5	32.1	397	1000

Table 8

Thermophysical properties of carbonate molten salts.

LiNaKCO_3 [53,136,137]		
Specific heat capacity	J (kg K) ⁻¹	1610
Density	kg m ⁻³	$2270 - 0.434 T$
Thermal conductivity	W (m K) ⁻¹	$0.336 + 2.58 \cdot 10^{-4} T$
Viscosity	Pa s	$6.5010^{-5} \exp\left(\frac{4431}{(T + 273)}\right)$

- **Aluminide coatings** of the form MCrAlX, where “M” can refer to Ni and/or Co, and “X” can be Y, Hf, Si, and/or Ta [53].
- **Spray-graphitization**, a method that prevents the dissolution of chromium into the molten carbonate salt by creating carbonate and carbide layers on the surface of the metal alloy [138].

These strategies help mitigate corrosion issues and protect the metal alloys when interacting with carbonate salts. Moreover, efforts have been made in different areas to optimize carbonate salt composition to minimize or replace lithium content while maintaining acceptable thermophysical properties. [135].

3. Molten salts potential to enable interconnected networks of energy systems

In this chapter, we will explore how molten salts can promote synergy between energy systems and enable the successful and efficient utilization of renewable energy sources. Considering that the chemical industry is highly energy-intensive, opportunities for optimization should be considered to increase energy efficiency and reduce energy demand and waste heat.

Since molten salts are in the liquid phase, they can be used as both thermal energy storage material and heat transfer fluid simultaneously, potentially making the system simpler and more cost-effective. Consequently, molten salts can be used to promote synergy with other application fields mentioned in this paper, such as CSP and nuclear [17,139].

TES materials are recognized as a key technology that enables the successful and efficient utilization of renewable energy sources. This is achieved by storing excess energy into a TES material, allowing for its utilization during periods of low availability, contributing to more sustainable energy systems. Therefore, these TES materials can address the intermittent behavior of renewable energy sources such as wind and solar by minimizing the mismatch between energy supply and demand. For example, this concept is already applied in solar thermal; molten salts are essential to ensure continuous operation of CSP plants by storing heat to be used during the night and during periods of low solar radiation [139,140].

Some key advantages of TES materials for the industry consist in peak shaving and thermal buffering, which can reduce costs and congestion in electricity grids as well as improve the thermal energy efficiency of processes. Firstly, peak shaving consists of storing cheap off-peak electricity as thermal energy by charging a TES material that can later be discharged during high demand periods or when heat demand exceeds availability. TES materials are also thermal buffers that work by storing excess process waste heat that can be used later when needed, reducing the demand for auxiliary heating sources [139–141].

Figure 1 represents the concept of how the solar and nuclear fields, vastly explored in this paper, can be used to establish interconnected networks of energy systems. This integration can be done by storing the molten salts’ thermal energy obtained from nuclear reactors or solar towers in tanks for usage in industrial processes and later return to their respective original systems to be recharged; or by converting the hot salt to steam to produce electricity by a power cycle, generating off-grid electricity [142].

One approach to achieve this level of interconnection is establishing full-scale nuclear or CSP plants near industrial sites. Molten salts, with

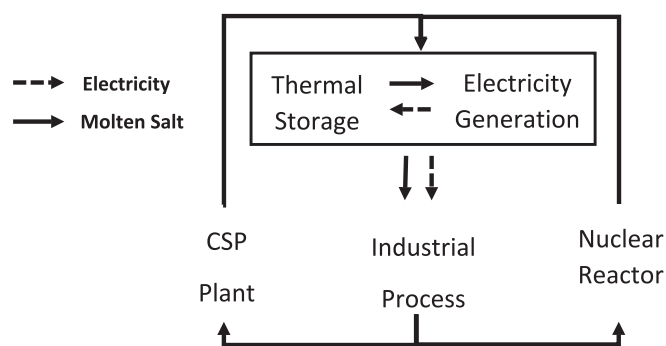


Fig. 1. Interconnected networks of energy systems using molten salts.

their high heat storage capacity, are able to transport this thermal energy between a facility or across nearby facilities and could reach at least similar distances as steam supply lines. Alternatively, modular systems, such as solar collectors and advanced small modular nuclear reactors, can be implemented by individual industrial plants in locations not suitable for larger power plants. These systems have relatively small physical footprints and can reduce capital investment by providing incremental power additions as well as off-grid low-carbon power for industry [142,143].

Currently, companies like Kyoto Group are actively developing modular and scalable systems, such as the “Heatcube thermal battery”. This technology uses molten salts as thermal storage medium combined with solar collector installations. The use of these heat batteries allows for temporary storage of heat from peak solar production during the daytime and its release to meet the demand when it is needed without the need for conversion [144,145].

Furthermore, the development of Generation IV nuclear reactors has prompted researchers and institutions in both government and private industrial sectors to embark on the development of Nuclear Hybrid Energy System (NHES). This concept has emerged as a more efficient technology for energy generation, capable of overcoming energy fluctuations by integrating multiple energy systems. An NHES may include nuclear reactors that use fluoride salts as coolants to store and transport heat for reuse, for example, in hydrogen production plants [88,146].

Considering the large-scale commercial use of molten salt in CSP plants, recent developments in this field are targeting the potential molten salts to decarbonize energy-intensive industrial processes in a hybrid-plant configuration [147,148]. A study assessed the economic sustainability of using a nitrate salt as a heat source from a CSP plant to decarbonize the dehydrogenation of ethylbenzene to styrene, an energy-intensive endothermic process. Considering the presence of the plant in Priolo Gargallo in Italy, 70 CSP collectors would be needed to operate the process. Furthermore, the model predicted a 50 % reduction in CO₂ emissions, with a return on investment of 9.1 % and 410 k€/year savings from reduced methane usage and emissions. The results demonstrated that CSP can economically decarbonize chemical processes without compromising profitability [149].

Furthermore, the European project “CoMETHy” has developed and validated experimentally an innovative low-temperature steam reformer for hydrogen production. This process is tailored for integration with CSP plants, using a molten nitrate salt mixture as the heat transfer fluid. The reactor is a compact membrane reformer designed to operate at temperatures below 550 °C, which allows it to simultaneously carry out methane steam reforming, water–gas-shift reaction and hydrogen separation. A pilot reactor producing 2 Nm³/h of pure hydrogen was successfully tested for 700 h, achieving twice the conversion efficiency of conventional reformers. The system provided 99.8 % pure hydrogen and was continuously operated for 150 h with no significant performance loss, even during cloudy periods. Moreover, the addition of a heat storage system for the molten salt mitigated the variability of solar radiation, ensuring stable operation and minimizing

thermal stresses to the catalyst and the membranes, as well as reducing start-up periods [150,151].

Some of the uses of molten carbonate salts, as mentioned in Chapter 2.4, can significantly contribute to the decarbonization of industry by providing cleaner energy alternatives and reducing greenhouse gas emissions [152]. MCFCs offer an efficient mean of generating electricity, with up to 60 % efficiency, using flue gas or CO₂-rich waste streams as fuel. This efficiency can be further optimized, reaching up to 85 % by reusing the heat generated in combined cycles or hybrid systems, such as coupling MCFCs with the Organic Rankine Cycle and gas turbines [153–156]. Additionally, integrating CO₂ capture technologies at the MCFC outlet, where the stream is rich in carbon dioxide, can achieve carbon capture ratios of up to 91 %, further enhancing the decarbonization potential of the system [157–160]. These advancements represent a promising pathway for sustainable synergy of industrial advanced energy solutions.

4. Molten salts applied as heat transfer fluids in the chemical industry for heat management

Several factors can influence the selection of molten salts for heat integration in the chemical industrial processes. As discussed in Chapter 3, this choice can be impacted by the type of energy system integrated with the process. For instance, hybrid plants combining concentrated solar power and chemical industries may favor nitrate salts [147–151]. In this chapter, we examine the implications of electrifying traditional furnaces and consider how molten salts can serve as an effective option for heat recovery and reuse. We will outline the essential considerations based on the specific characteristics of the process that can affect the choice of molten salts to be used. Detailed calculations of heat integration concepts for specific chemical processes are beyond the scope of this review. Future research will delve into these calculations, providing comprehensive analyses and practical implementations.

The production processes of primary chemicals, more specifically, steam cracking of hydrocarbons and steam methane reforming, are responsible for a significant share of the energy demand and GHG production within the chemical industry [161–163]. Both processes can be divided into three main sections, as illustrated in a simplified way in Figure 2 and described below [162–167].

- **Radiant Section:** This section is necessary for the high-temperature endothermic reactions. It consists of two elements. The first element

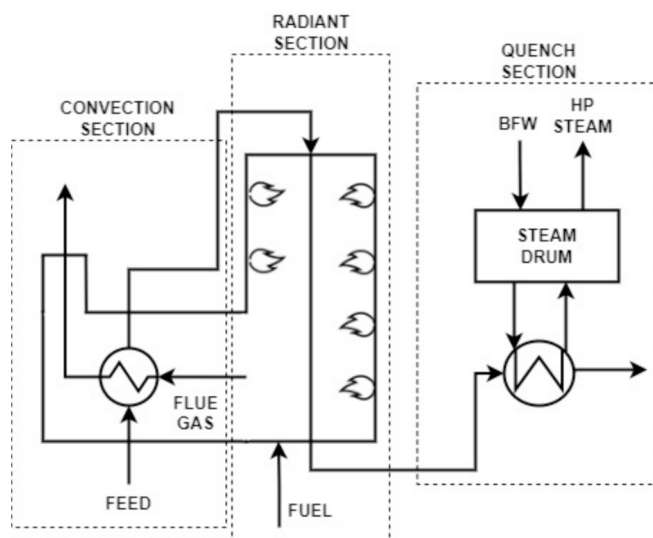


Fig. 2. The three main sections of the primary chemicals' production processes: convection, radiant and quench.

is the furnace, where burners located in the walls, roof and/or floor combust fuel gases to generate temperatures exceeding 1000 °C. The second element is the reactor tubes, which are suspended along the center line of the furnace to facilitate efficient radiative heat transfer. Endothermic reactions occur within these tubes, with temperatures typically ranging from 600 °C to 900 °C.

- **Convection Section:** This section is responsible for heating various streams, including the feed, dilution steam, process air, boiling feed water and high-pressure steam for use in compressors. It is directly connected to the furnace and serves to recover and reuse heat from the flue gases. Typically, the flue gases enter this section at approximately 1000 °C and exit at around 100 °C.
- **Quench Section:** The primary purpose of this section is to cool down the products and stop the endothermic reactions. Indirect quenching is employed by vaporizing boiler feed water to rapidly cool down the hot reacted gases. In the case of steam cracking of hydrocarbons for high value chemicals, the gases leave the radiant section at temperatures ranging from 750–850 °C and need to be quickly cooled to around 300–400 °C. In the case of steam reforming to produce ammonia and methanol, the process gases exit the primary reformer at approximately 800 °C. Subsequently, the gas products pass through a secondary reformer, which further heats up the gases to temperatures between 1000–1200 °C before entering the quench section.

Electrification of these industrial processes eliminates the flue gases from the radiant section. As a result, the convection section described above would no longer exist, and alternative methods are required to preheat the incoming gases. One possibility is utilizing steam for this purpose. However, there are limitations associated with this approach. The high pressure of the steam poses challenges in terms of complex design, while the low temperature (around 300 °C) of the steam leads to the destruction of exergy [166]. Considering these limitations, molten salts emerge as a viable option for heat recovery and reuse in the integration of this new decarbonized process. The selection of an appropriate molten salt is crucial and should be based on the specific thermal requirements of the process streams, allowing for efficient heat transfer and integration within the system.

Figure 3 illustrates the operational temperature ranges of the convection and quench sections (for the case in which the product gases come from the primary and secondary reformers) where the potential heat recovery and reuse is targeted. Also, in Figure 3 is represented the operational temperature range of the molten salts, which will be considered to start at the liquidus melting temperature and end at the decomposition temperature, except the chloride salts, which are limited

by vapor pressure, with the addition of a relevant safety margin of 30 °C [27]. Effects of corrosion, interaction with equipment material, or other limiting parameters are not being considered for this range.

At first, identifying suitable molten salts based on their temperature range is preferred to avoid risks of solidification, thermal decomposition, or pressure build-up during the heat exchange. This choice is preferred since the heat transfer resistance from the process side (usually a gas) is dominant when compared to the molten salt side (a liquid) making the wall temperature closer to that of the bulk of the process stream.

Once the potential molten salt or combinations of salts has been selected, a pinch analysis is performed to identify the minimum temperature difference between hot and cold streams. By analyzing these streams, we are able to determine the minimum energy requirements for heating and cooling to design a more energy-efficient system. The ultimate goal is to maximize heat recovery and reuse within the chemical process, reduce utility consumption, and minimize costs, leading to more sustainable and cost-effective operations.

The next step is the design of the heat exchange network, which is based on the specific boundary conditions and the limitations of the chemical process/molten salt system, for example:

- **Residence time:** The streams coming out of the furnace in the steam cracking of hydrocarbons need to be quenched quickly from 0.02 to 0.1 s to stop any undesirable endothermic reactions [166].
- **Pressure drop:** Another indicator of process selectivity is the pressure drop of the effluent, which can not be too high in order to preserve the selectivity towards the desired products [165,166].
- **Safety concerns:** Safety aspects need to be verified, and potential risks need to be mitigated. For instance, the corrosion of the equipment at high temperatures may result in salt leakages to the effluent side. Additionally, nitrate salts offer the risk of deflagration if they get in contact with hydrocarbons or coke through possible leakages at high temperatures [32]. Lastly, the impact of fluoride salts should be considered, given their hazardous nature if inhaled accidentally [110].
- **Wall temperature:** The near-wall temperature of the molten salt side needs to be constantly checked to determine whether the salt is at risk of solidifying, decomposing, or evaporating. Even if the bulk temperature of the molten salt is within acceptable limits, the temperature gradient towards the wall may be enough to exceed the threshold.

If any of these constraints are not met after optimizing the heat exchanger geometry, it is necessary to reconsider the pinch analysis

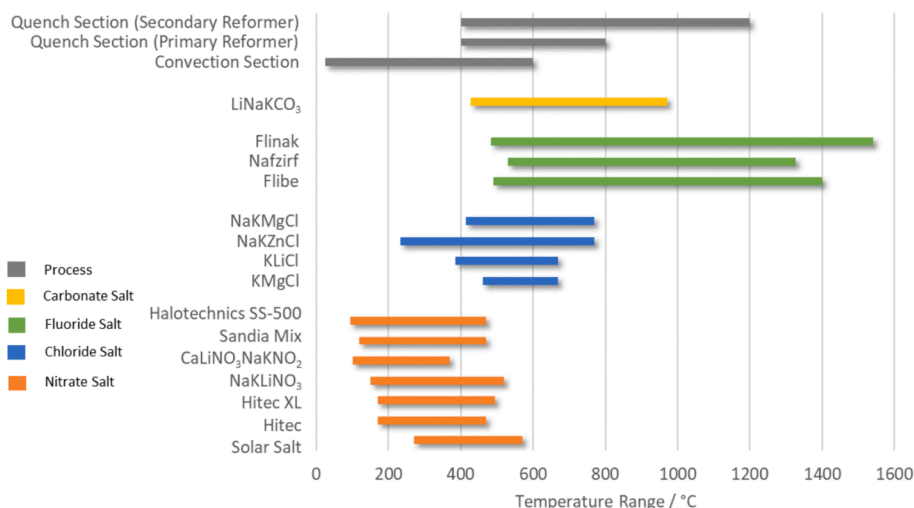


Fig. 3. Temperature range of the quench and convection sections of the primary chemicals' production processes and the molten salts.

and/or identify a different salt or combination of salts in an iterative process. Otherwise, a molten salt with a temperature range that does not overlap with the one of the processes can be chosen. However, the flowrate of the salt will need to be carefully controlled reducing degrees of freedom during the calculation of the heat exchanger based on the process side specifications.

Let us apply the first part of this methodology, for example, to the steam cracking and steam methane reforming process. These processes span a wide range of temperatures, as low as ambient conditions and as high as 1200 °C, as indicated in Figure 3.

By analyzing only the convection section of these process (stream temperature between ambient and 600 °C), we can identify nitrate salts as an appropriate heat transfer fluid. On the other hand, the quenching of the effluent of the primary reformer, both carbonate and chloride salts are well suited. Even though nitrate salt could be used as a potential coolant for this effluent, the temperature in the near-wall region of the nitrate salt may be above the thermal decomposition temperature of this salt resulting in several safety concerns (i.e., material corrosion and potential of salt leakage to the effluent resulting in a potential deflagration risk).

Finally, for quenching the effluent from the second reformer, where stream temperature ranges from 1200 °C to 400 °C, fluorides salts seem to be the only salt capable of withstanding such higher temperatures without any risk of thermal degradation. If the toxicity hazard of fluoride salts cannot be mitigated, or the heat exchanger material cannot withstand it, carbonates and chlorides salt can potentially be an option, but as mentioned already, the temperature of the near-wall region of the salt needs to be carefully checked.

Furthermore, process heat integration can be improved by extracting and reusing heat from exothermic reactions with molten salt to increase the overall energy efficiency. Within the production process of ammonia and methanol, exothermic reactions play a crucial role. These reactions are thermodynamically favored at lower temperatures but kinetically favored at higher temperatures. To address this challenge and enhance the conversion and efficiency of the reaction, heat needs to be continuously removed from the reactor to create a quasi-isothermal process. The heat can then be reused later in the process [164,168], allowing for the maximization of the potential of molten salts in process heat integration. This approach not only improves temperature control in the synthesis reactors but also increases conversions and reduces recycle ratios, leading to enhanced overall process performance.

5. Expanding the molten salt research Field: Alternative materials for TES and HTF

In this review paper, we have delved into some of the state-of-the-art molten salts as documented in the open literature. Nevertheless, there remains ample room for further exploration within the realm of molten salts, investigating their capabilities in optimizing material and energy exchange. This research can significantly contribute to advancing the journey toward achieving net-zero CO₂ emissions.

First, an area showing promising developments in molten salts is the evolution of their next generation through the use of nano-enhanced mixtures. This concept involves the addition of nanoparticles to enhance thermophysical properties and broaden the temperature application range of the salts [169]. These nano-enhanced molten salts have primarily been developed to increase heat capacity, thermal conductivity, and operational temperature range by introducing nanoparticles such as SiO₂, MgO, Al₂O₃, CuO, TiO₂, and multi-walled carbon nanotubes. For example, adding 10 wt% of MgO nanoparticles increases the heat capacity of a nitrate salt by over 168 %. Furthermore, incorporating 1.0 wt% of multi-walled carbon nanotubes into a carbonate salt increases thermal conductivity by around 149 % and heat capacity by 78 % [92]. Regarding corrosion, it has been observed that incorporating 1 wt% TiO₂ nanoparticle into eutectic binary nitrate salt can reduce the corrosion rate of carbon steel by more than 2 times [170]. Nevertheless,

more research needs to be done to investigate these nano-enhanced molten salt mixtures' long-term chemical and thermal stability.

Considerable efforts have been directed towards developing new nitrate salt mixtures, as mentioned in chapter 2.1, mainly due to their significance in CSP applications [28,37]. Nevertheless, there is also potential for expanding the use of other salt types such as carbonates and chlorides, which are emerging candidates in CSP, and nuclear fields as mentioned in chapters 2.2 and 2.4 [43]. Furthermore, besides the four molten salt types with common examples found in the open literature, there are also less commonly used salts, such as:

- **Bromide salts:** Lithium bromide (LiBr) melts at 550 °C and decomposes at 1265 °C [170]
- **Sulfate salts:** Sodium sulfate (Na₂SO₄) melts at 884 °C and decomposes at 1100 °C and Potassium pyrosulfate (K₂S₂O₇) melts at 325 °C and decomposes around 600 °C [171,172,178]
- **Hydride salts:** lithium hydride (LiH) melts at 680 °C and decomposes at 950 °C [173]

Additionally, mixtures of different salt types are possible, as evidenced by examples like LiF-Na₂CO₃-K₂CO₃, NaCl-Na₂SO₄ and NaCl-Na₂CO₃ [136,174].

Another class of molten salts, known as molten organic salts or ionic liquids, should be explored, especially for low-temperature processes. These salts are commonly used in fields of electrochemistry, analytical chemistry and extraction processes, being considered the “green solvents of the future”. Ionic liquids present low vapor pressure, non-inflammability, wide electrochemical windows, high thermal stability and good electrical conductivity. Ionic liquids are known for their ability to remain in a liquid state at low temperatures even below 0 °C and their thermophysical properties can be tuned by the variation in constituting ions [175,176]. Even though they are not commonly used as HTF, they have the capacity to be — especially in the field of ionic liquid nano-fluids — also called “IoNanofluids” which are combinations of ionic liquids and nanoparticles to enhance thermophysical properties [177–180].

In a study, the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) were analyzed in relation to their thermophysical properties and compared to typical thermal oils like Therminol® VP-1. The conclusion was that the ionic liquids were comparable or superior to most of the commercial heat transfer oils analyzed in regard to temperature range and low vapor pressure, besides being able to store substantial heat. Nevertheless, the cost of ionic liquids remains a drawback and further research needs to be performed in this area [180,181].

Meanwhile, a few recent studies are being conducted to show the potential of ionic liquid nanofluids as advanced heat transfer fluids, mainly for future use in the solar field. Notably, the use of [C₄mim]NTf₂ with 0.9 vol% Al₂O₃ in flat-plate solar collectors increased thermal efficiency by up to 54.08 % when compared to water-based nanofluids [182]. Another study determined the effect of multi-wall carbon nanotubes on the thermophysical properties of ionic liquid-based nanofluids such as 1-ethyl-3-methylimidazolium diethylphosphate [EMIM][DEP], or its aqueous solution [EMIM][DEP](1) + H₂O(2). Results showed that the thermal conductivity of nanofluids increases within the range of 1.3 %–9.7 % compared to their base liquids [183].

Phase change materials can also be a solution for waste heat recovery and reuse, since they allow for the capture, storage, and release of thermal energy at a nearly constant temperature. In theory, the salts already mentioned in this paper can also be used as phase change materials. For example, a mixture of 50 % NaNO₃ and 50 % NaNO₂ presents an enthalpy of 185.6 J/g with a phase change starting and ending at 228.4 °C and 238.6 °C, respectively. [184].

Apart from salts, other liquids should also be taken into consideration, such as molten metals, also referred to as liquid metals. These

fluids offer efficient heat transfer, primarily due to their low viscosities and high thermal conductivities, typically at least one order of magnitude higher than conventional fluids. Similarly to some of the molten salts discussed in this paper, liquid metals have found applications in advanced nuclear reactors, as heat transport media in CSP plants and in methane pyrolysis [185–188]. Some of the well-known drawbacks associated with these molten metals are safety concerns such as flammability and strong corrosion towards structural materials. Nevertheless, research programs, like the one developed at Karlsruhe Institute of Technology (KIT) in Germany [189,190], have been working for more than 50 years to overcome these limitations. Liquid metals are usually classified into three types:

- **Alkali metals** (Li, Na, K, and their alloys). For example: sodium can be applied between 98 °C and 883 °C.
- **Heavy metals** (Pb, Bi, and their alloys). For example: lead–bismuth eutectic alloy, which can be used from 125 °C to 1533 °C.
- **Fusible alloys** (Ga, Cd, In, Sn, Ti, and their alloys). For example: molten tin, which can be applied from 232 °C to 2687 °C.

6. Conclusion

This review paper provided insights into how molten salts can be an essential technology for achieving a net-zero emissions scenario in the process of decarbonizing the energy-intensive chemical industry sector. In this study, we explored four types of molten salts—nitrates, chlorides, fluorides, and carbonates—by examining the literature regarding their mixtures, properties, applications, limitations, and ongoing developments. With the knowledge gathered, we identified how molten salts can be used as both thermal energy storage material and heat transfer fluid to promote synergy between energy systems. This way, thermal or electric energy from solar, nuclear and fuel cells can be integrated into chemical processes to create energy efficient hybrid industrial plants.

The role of molten salts is then explored in the processes of steam cracking of hydrocarbons and steam methane reforming for the production of ammonia and methanol. This concept was exemplified by highlighting the implications of electrifying conventional furnaces and how molten salts emerge as a viable option for heat recovery and reuse in this new process. Finally, we presented the opportunities advancing the molten salt research, such as new salt compositions and nano-enhanced mixtures, as well as exploration of similar fluids, such as ionic liquids and liquid metals. Continued investment in molten salt research will be essential for realizing their full potential in transforming industrial heat management and achieving global net-zero emissions goals within the chemical industry.

CRediT authorship contribution statement

Debora de Figueiredo Luiz: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jurriaan Boon:** Writing – review & editing, Supervision. **Gustavo Otero Rodriguez:** Writing – review & editing, Supervision. **Martin van Sint Annaland:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Debora de Figueiredo Luiz reports financial support was provided by Top Sector Energy Subsidy from the Ministry of Economic Affairs and Climate.

Data availability

No data was used for the research described in the article.

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