Engineering molten MgCl₂–KCl–NaCl salt for high-temperature thermal energy storage: Review on salt properties and corrosion control strategies

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Abstract

Conventional thermal energy storage (TES) media and heat transfer fluids (HTFs) currently used in commercial concentrated solar power (CSP) plants are nitrate-based molten salts with working temperature up to about 565°C. Current interest in raising the working temperature in next-generation CSP for higher energy conversion efficiency leads to chloride-based molten salt technology (>700°C). MgCl₂-KCl-NaCl salt is selected to be such a TES/HTF material due to its excellent salt properties, abundance and low costs. In this review, survey and evaluation of its exact eutectic composition by evaluation of the phase diagram as well as most relevant salt properties for design, construction and operation of a test loop and projection of a real TES/HTF system are presented. They include minimum melting temperature, vapor pressure, heat capacity, density, thermal conductivity and dynamic viscosity. The working temperature range 420-800°C is suggested for the TES/HTF system using this salt. Moreover, the recommended values of the heat capacity, density, thermal conductivity and dynamic viscosity in the suggested working temperature range are given. In addition, corrosion control strategies for this salt including corrosion monitoring and mitigation techniques are briefly reviewed, since controlling the salt corrosivity is one main concern of the engineering aspects using the molten chlorides at high temperatures. Overall, this review is expected to supply reliable values of the most relevant salt properties and recommend the most promising corrosion control strategies for further material studies, as well as modeling, simulation, detailed design and construction of molten MgCl2-KCl-NaCl salt TES/HTF systems.

Highlights

- Most relevant salt properties of MgCl₂-KCl-NaCl to engineer this salt are reviewed.
- A full set of their recommended temperature-dependent values are given.
- Working temperature range of MgCl₂–KCl–NaCl for TES/HTF is suggested.
- Corrosion control strategies including corrosion monitoring and mitigation techniques are briefly reviewed.
- Concept of corrosion control system integrated into TES/HTF system is introduced.

Keywords

Concentrated solar power (CSP); Thermal energy storage (TES); Heat transfer fluid (HTF); Molten chloride salts; Thermophysical and physicochemical property; Corrosion monitoring and mitigation.

1. Introduction

Global warming exacerbates the effects of climate change due to the increasing trend of the global energy demand. Efforts of the scientific community and industry have been made in the diversification of sustainable clean energy sources [1]. For instance, the developed concentrated solar power (CSP) plant uses the solar energy to produce electricity and has been an attractive option due to its facile coupling to thermal energy storage (TES) to produce dispatchable clean electricity [2]. It is estimated by International Energy Agency (IEA) that the global capacity of CSP and its TES will grow by 4.3 GW and 21 GWh_{el} from 2018 to 2023, respectively [3].

The TES technology has the advantage that it is possible to store the thermal energy for later use, thereby reducing the gap between solar energy supply and energy demand due to the intermittency during cloudy conditions and at night [4]. Among various TES systems, the most widely used is sensible thermal energy storage (STES). The materials for STES generally are liquids or solids and utilize the heat capacity due to temperature changes during charging and discharging [5], [6]. Conventional STES liquids include pressurized water, thermal oils, liquid metals and molten salts. Among them, molten salts have been successfully applied in commercial CSP plants. The commercial TES systems based on molten salts have two different configurations. One is the indirect storage system with molten salt as storage medium often used in a parabolic trough CSP plant with a lower maximum temperature level of about 400 °C. Another configuration is direct storage system often used in a tower CSP plant with molten salt as both, heat transfer fluid (HTF) and TES up to about 565°C [7], [8].

At the time of writing, virtually almost all the commercial CSP plants use nitrate-based molten salt mixtures as TES media because of their properties such as favorable melting temperatures and thermal stabilities for the given thermal application, low viscosity, high heat capacity, low vapor pressure and relatively low costs. However, the maximum working temperature of the nitrate-based molten salt mixtures is limited at about 565°C due to thermal decomposition [9]. Next-generation (next-Gen) CSP technologies with higher TES/HTF working temperature for higher energy conversion efficiency and lower levelized cost of electricity (LCOE) are being developed, e.g., in the project of U.S. Department of Energy

(DOE) - Gen3 CSP [9]. One of the main challenges for the next-Gen CSP technologies is the development of alternative HTF and TES materials with lower costs that could work at temperatures higher than 565 °C of the current nitrate-based molten salt mixtures.

1.1. State-of-the-art CSP and TES technologies

CSP technology has higher solar-to-electrical energy conversion efficiency than photovoltaics (PV) and represents an attractive energy conversion option, since the thermal energy collected from the sun is stored and later transformed into electrical energy through a conventional power block [5]. A conventional commercial CSP plant generally consists of heliostats, a solar receiver, a HTF/TES system and a power generation system [10], [11]. As illustrated in **Figure 1**, CSP technologies generally are classified into parabolic trough (PT), linear Fresnel (LF), solar tower (ST) and parabolic dish (PD).



Figure 1. Different existing CSP configurations: a) parabolic trough, b) linear Fresnel, c) solar tower and d) parabolic dish. Figures adapted from [12].

Parabolic trough (PT) technology belongs to linear-focusing CSP technologies. It is the preferred choice in working plants due to its high technology maturity and low construction costs. In 2018, ~90 % of the commercial CSP plants in operation used this technology [12], [13]. As shown in **Figure 1a**, its standard configuration includes a set of parabolic mirrors which reflect the sunlight on an absorber tube [14]. PT-type CSP plants generally have TES/HTF working temperatures below 400°C due to low solar concentration ratio (generally below 100) and thus mostly employ synthetic oils or molten nitrate salts as TES/HTF materials and water steam in the power block [7], [8], [15]. The current state-of-the-art PT-type CSP has a two-tank TES/HTF configuration using Solar Salt (a mixture of NaNO₃-KNO₃ 60-40 wt.%) with a working temperature up to about 385 °C [1], [16], which is also considered to be the most reliable and safe TES/HTF system for this type of CSP plants [17].

Some representative operational PT plants include the Solar Electric Generating Station (SEGS I-IX) located in California's Mojave Desert using Therminol as HTF without storage [18], and the Andasol plant, which is the first commercial PT plant built in Europe (southern Spain) with a two-tank indirect configuration using synthetic oil as HTF and molten salt as TES material [19], [20].

Linear Fresnel (LF) technology is another linear-focusing CSP technology. As illustrated in **Figure 1b**, it uses a series of long flat mirrors placed at different angles to concentrate the sunlight into a line on the receiver [21]. Molten salts have been utilized as TES/HTF in LF-type CSP plants [14], [22]. However, the LF-type CSP plants currently are not the mainstreaming CSP plants as the PT-type plants, although their structural simplicity offers low structural support and reflector costs, as well as long focal lengths [23]. SolarPACES (short for Solar Power and Chemical Energy Systems), which is an international cooperative network of International Energy Agency (IEA) for the development and marketing of CSP systems, presents the status of all CSP projects around the world, either operational, under construction, or under development on its official website (solarpaces.org/csp-technologies/csp-projects-around-the-world/). At the time of writing, among the total CSP capacity of about 10 GW, there is about 400 MW LF-type CSP (i.e., about 4% of the total capacity), while PT-type has more than 5 GW capacity, i.e., >50% of the total capacity.

Solar tower (ST) technology is a point-focusing CSP technology, which has much higher solar concentration ratio (in the range of 300-1000) and working temperatures (565°C or higher) compared to the linear-focusing CSP technology [7]. It is considered as a very promising alternative since higher efficiencies and lower LCOEs are achieved by converting heat into electricity at higher working temperatures [19]. The official website of SolarPACES shows that most CSP plants built recently use this technology, and more than 3 GW ST-type CSPs are either operational, under construction, or under development. This technology comprises a receiver on a tower surrounded by thousands of mirrors that can efficiently achieve high temperatures [24] (see **Figure 1c**). Some representative commercial large-scale ST plants are Solar Two and Crescent Dunes in United States, Atacama-1 in Chile, Gemasolar in Spain, and NOOR 3 in Morocco. The state-of-the-art ST CSP is working up to

about 565°C with nitrate-based molten salts as both heat transfer and storage medium (i.e., direct TES system), and the power cycle is a superheated steam Rankine cycle [25].

Parabolic dish (PD) technology is another common point-focusing CSP technology. A PD plant generally consists of a parabolic dish-shaped concentrator, a receiver set on its focal point and a power generation system (e.g., a Stirling engine). The heat from the sun radiation is transferred from the receiver to a Stirling engine for power generation with a working temperature between 700-1200°C [26]. However, although PD has higher solar-to-electrical energy conversion efficiencies owing to higher working temperatures, those systems are still at the demonstration stage due to high installation costs.

1.2. Next-generation CSP using chloride salts

Nowadays, molten salt TES technology is the most dominant commercial solution for CSP. The commercial TES capacity with molten salts (almost 17 GWh_{el}) represents about 77 % of the globally deployed TES used for electricity applications by the end of 2018 [25], [27]. The NaNO₃-KNO₃ (60-40 wt. %, non-eutectic) mixture, called Solar Salt, is used in most commercial CSP plants due to their low costs (~0.8 \$/kg [9]), high heat capacity of about 1.52 J/g °C (at 390 °C) and low liquidus temperature of about 250 °C with practical lower operation limit of about 290 °C [28], [29]. Next-Gen CSP plants are expected to operate at higher temperatures (> 700°C) than the nitrate mixtures currently in use, in order to achieve higher power cycle efficiencies by using e.g., sCO₂ Brayton power cycle, and reduce the LCOE [2] (see **Figure 2**). The selection and definition of suitable new salt mixtures is a key aspect to meet the high-efficiency target considered in the next-Gen CSP [9].

In the1950s at Oak Ridge National Laboratory (ORNL) molten chloride salts have been examined as coolants and storage media in advanced nuclear reactors [30]. Despite the first commercial application of molten nitrate salts in CSP technology occurred in 2009 in the Andasol plant [16], molten chloride salts have not been used in commercial CSP plants due to technical challenges such as extremely strong salt corrosivity at high temperatures. According to the SunShot Initiative of DOE [9], the target TES/HTF temperature in the next-Gen CSP technologies is higher than 720 °C. In principle, there are different salt classes to address this temperature. They include sulfates, carbonates, fluorides and chlorides [9].

Considering selection criteria such as melting temperature, salt price, salt density, heat capacity, vapor pressure, corrosivity, thermal stability and toxicity, chloride mixtures were selected as the most promising salt class [9], [31]-[33].



Figure 2. Concept of next-Gen CSP using chloride salts in TES/HTF system, in which a corrosion control system is integrated into the molten salt TES/HTF loop. Hot salt tank works at > 700 °C. The CSP schematic from [9] is adapted by DLR with potential installation locations of the corrosion control system (CCS).

Several authors identified a number of binary and ternary eutectic chloride salt mixtures for high-temperature TES applications. In 2010 Kenisarin [34] summarized several eutectic salts such as KCl-MgCl₂, KCl-ZnCl₂, LiCl-KCl, NaCl-MgCl₂, CaCl₂-KCl-MgCl₂, CaCl₂-KCl-MgCl₂, LiCl-BaCl₂-KCl, MgCl₂-KCl-NaCl with a melting temperature range of 320-487 °C. Wang et al. [35] proposed three different eutectic mixtures of NaCl-KCl-ZnCl₂ with a minimum temperature of about 204 °C. One of them is also known as Saltstream 700e[®], developed by Halotechnics [19]. Quaternary mixtures have been also investigated by Wei, et al. [36] with a melting temperature of 385 °C for the KCl-NaCl-CaCl₂-MgCl₂ system. Myers, et al. [37] investigated a total of 133 chloride salt systems including LiCl, NaCl, KCl, MgCl₂, CaCl₂, BaCl₂ pure salts and their mixtures using a thermodynamic database software - FactSageTM. The lowest melting temperatures are achieved with mixtures containing LiCl [38]. However, their price is a disadvantage. AlCl₃ and ZnCl₂-containing molten salt mixtures

have also low melting temperatures but the disadvantage of a relatively high vapor pressure at high temperatures (i.e., a limited maximum upper working temperature) [38], [39].

1.3. MgCl₂-KCl-NaCl for high-temperature TES in next-Gen CSP

With intensive research in the last few years [39]-[42], the eutectic MgCl₂-KCl-NaCl salt mixture has been identified by different research groups as one of the most promising TES/HTF candidates for the next-Gen CSP due to its low cost (<0.35 \$/kg [9], [39]), abundance and favorable properties (e.g., low vapor pressure at high temperatures, low melting temperature and high thermal stability). In 1978 Nemecek, et al. [43] worked on a latent TES boiler tank using the MgCl₂-KCl-NaCl mixture. Fundamental knowledge as sensible TES on this chloride mixture arises from nuclear research of Williams [44] in 2006 as well as Ambrosek [45] in 2011, who explored the use of binary KCl-MgCl₂ as HTF in nuclear systems. Since about 2015, there has been a strong renewed interest in the ternary MgCl₂-KCl-NaCl mixture as one of the most promising HTF/TES materials in next-Gen CSP due to its abundance and low price [46]-[47]. Our research group in the German Aerospace Center (DLR) in Germany started in 2015 with the MgCl₂-KCl-NaCl ternary mixture for sensible TES [31] and National Renewable Energy Laboratory (NREL) in US considered in 2017 the binary mixture MgCl₂-KCl for next-gen CSP [9]. In 2019, Australian National University (ANU) and NREL [40] explored also the MgCl₂-KCl-NaCl mixture for sensible heat storage applications in Australia and US. In 2020, Shanghai Institute of Applied Physics, Chinese Academy of Sciences (SINAP-CAS) [41] started intensive study on the MgCl₂-KCl-NaCl ternary mixture as HTF/TES in China.

However, MgCl₂ is a strong hygroscopic chloride salt and one of the main issues for MgCl₂-KCl-NaCl is its strong salt corrosivity due to reactions of impurities (e.g., hydrated water, O₂) with the chloride anion, which produce corrosive gases like HCl, Cl₂ and corrosive impurities dissolved in the melt like MgOHCl [47]. For this reason, a corrosion control system including corrosion monitoring and mitigation is essential in next-Gen CSP plants to use affordable structural materials (e.g., alloys used in salt tanks) and should be integrated in the molten salt TES/HTF system, as shown in **Figure 2**. Several research groups in e.g., NREL, SRNL and DLR, have developed some effective methods for corrosion control and monitoring of metallic structural materials in contact with MgCl₂-KCl-NaCl mixture in the

lab for potential use on an industrial scale [9], [48], [49]. Corrosion control strategies of MgCl₂-containing molten chlorides for high-temperature HTF/TES will be discussed in Section 3.

1.4. Test loops/facilities for engineering molten MgCl2-KCl-NaCl salt technology

There have been some test loops/facilities for next-Gen molten salt TES/HTF technologies (> 700 °C) under design, under construction or in operation to alleviate the molten salt technology risks, e.g., FASTR facility of ORNL in US for MgCl₂-KCl-NaCl [50], Avanza2 loop of Abengoa in Spain for Li₂CO₃-Na₂CO₃-K₂CO₃ [51]. Compared to Li₂CO₃-Na₂CO₃-K₂CO₃ (>1.3 \$/kg, melting temperature of ~397°C [9], [39]), MgCl₂-KCl-NaCl (<0.35 \$/kg, melting temperature of ~385°C) has lower material cost and melting temperature, but generally higher corrosivity to metallic materials [9], [48], [49]. As shown in **Figure 3**, the FASTR facility for development of the MgCl₂-KCl-NaCl TES/HTF technology is under construction, which includes two parts: (1) salt purification to reduce salt corrosivity and preparation of purified salt for the test loop (**Figure 3** left) and (2) the test loop mainly for testing corrosion control technologies (**Figure 3** right). With the molten salt test loop, the corrosion monitoring and mitigation methods, as well as performance demonstrations of major components such as flanges, heat exchangers and pumps, can be investigated and tested close to real conditions.

For design of a test loop or real TES/HTF system based on molten MgCl₂-KCl-NaCl, reliable values of the most relevant thermophysical and physicochemical properties are vital and essential. Moreover, controlling the salt corrosivity is one main concern of the engineering aspects using the molten chlorides at high temperatures. To support engineering of the molten MgCl₂-KCl-NaCl salt for high-temperature TES and HTF application, this review presents survey and evaluation of its most relevant thermophysical and physicochemical properties, as well as of the corrosion control strategies for the molten MgCl₂-KCl-NaCl salt HTF/TES system. In Section 2, different eutectic compositions of the MgCl₂-KCl-NaCl salt system are discussed according to phase diagrams from the literature and simulation using FactSage, in order to determine the exact eutectic composition and melting temperature (minimum working temperature) [52]. Moreover, the maximum working temperature is defined based on the vapor pressure data available in literature and simulated with FactSage. Additionally,

this section will review most relevant thermophysical and physicochemical properties of MgCl₂-KCl-NaCl for engineering this salt, include heat capacity, salt density, thermal conductivity and dynamic viscosity. In Section 3, the corrosion control strategies on this salt including corrosion monitoring and mitigation are briefly reviewed, since controlling the salt corrosivity is one main concern of the engineering aspects using molten chlorides. Moreover, based on the promising corrosion monitoring and mitigation techniques, a concept of a corrosion control system integrated into the chloride-based TES/HTF system is introduced. In the last section, the recommendations based on Sections 2 and 3 are summarized for further material studies, as well as modeling, simulation, detailed design and construction of molten MgCl₂-KCl-NaCl salt HTF/TES systems.



Figure 3. Facility to Alleviate Salt Technology Risks (FASTR) in ORNL for development of molten MgCl₂-KCl-NaCl salt technology, which includes two parts: salt purification and preparation for test loop (left) and molten salt test loop (right) [50].

2. Thermophysical and physicochemical properties of molten MgCl₂-KCl-NaCl salt

As given in Eq. (1), the equation for sensible heat storage Q (J) considers the density of storage material ρ (g/cm³), the volume of storage material V (cm³), the specific heat capacity c_p (J/g °C) and the temperature change ΔT (°C) [11], [53].

$$Q = \rho V c_p \Delta T \qquad \qquad \text{Eq. (1)}$$

Using molten salts with a larger ΔT (i.e., allowed working temperature range) and c_p the required material mass (i.e., ρV) and consequently the capital costs of the TES system can be reduced. Besides ΔT and c_p , the reliable value of ρ is required for volumetric flow measurement and in the design of the storage tanks, e.g., to calculate the required volume of storage material *V*. Besides these properties, the reliable thermal conductivity and dynamic viscosity are essential in the thermal design of the molten salt loop and key components in a CSP plant such as the solar receiver, heat exchangers and molten pumps.

The effort has been given to define testing procedures and data analysis criteria for the most relevant thermophysical and physicochemical properties of molten salts in TES/HTF application in some research programs such as the EU-funded research project - SFERA II [54]. However, most of the available testing procedures and methods for the molten salt properties are based on the commercial molten nitrate salts. Not all of them are suitable for molten chlorides, e.g., the determination of maximum working temperature based on thermal decomposition (this will be discussed in Section 2.2). Our recently published review paper [55] summarized the available testing procedures for the most relevant thermophysical and physicochemical properties of molten chloride salts in TES/HTF application. Recently, Wang et al. [56] reported the experimental vapor pressure, heat capacity, density, thermal conductivity and dynamic viscosity of a MgCl₂-KCl-NaCl salt mixture. Moreover, the research group in NREL summarized the results of the Gen3 CSP project in thermophysical properties, chemical optimization, and purification of a molten MgCl₂-KCl-NaCl salt mixture mixed with anhydrous carnallite and halite from industries [57]. However, the related research work, particularly the survey and evaluation work, is still limited. In this work, survey and evaluation of the most relevant thermophysical and physicochemical properties of the MgCl₂-KCl-NaCl salt mixture are presented to recommend the reliable values for engineering.

Given the high working temperature and corrosivity of molten chloride salts, experimental measurements are costly and time-consuming. For this reason, numerical simulation has been used as an alternative tool in designing the required TES/HTF materials with specific properties applicable to CSP. For example, thermodynamic simulation based on e.g. CALPHAD or Molecular Dynamics (MD) method can predict phase diagrams [42], [46] and salt properties such as heat capacity, enthalpies of mixing, dynamic viscosity and conductivity of pure molten salts and their mixtures [32], [58]. Moreover, the Dulong-Petit approximation can be used to approximate the heat capacity of a molten salt mixture [58], while the Quasi-chemical model reported by Robelin et al. [59] is used for density prediction.

In this section, a review of the most relevant properties of the molten MgCl₂-KCl-NaCl mixture is evaluated by comparing the data available in literature. Selected properties are summarized for each single chloride and the salt mixtures using the following sequence in this work: phase diagram (minimum melting temperature and exact eutectic salt composition) and minimum working temperature (2.1), vapor pressure and maximum working temperature (2.2), heat capacity (2.3), density (2.4), thermal conductivity (2.5) and dynamic viscosity (2.6). Each temperature-dependent property of the ternary chloride salt mixture involves a plot according to the best correlation found based on experimental and simulation data and, a reliable value is recommended in the relevant working temperature range for potential use of MgCl₂-KCl-NaCl mixture in the next-Gen CSP.

2.1.Phase diagram and minimum working temperature

It is well known that melting temperature is one of the main criteria to evaluate TES and HTF media. Molten salts with sufficiently low melting temperatures are preferred in CSP plants since they mark the lower working TES and HTF temperature, i.e., allow larger working temperature range (ΔT). Additionally, it is important to fix a safety margin for practical applications to avoid salt freezing events which is normally taken 30-40 °C higher than the melting temperature (or liquidus temperature for non-eutectic mixture such as Solar Salt) [29]. As mentioned before, to satisfy the requirements for next-Gen CSP, the system MgCl₂-

KCl-NaCl is chosen as a promising candidate to study due to their abundance, low cost and salt properties. Mixing of single salts to form binary eutectics and then ternary mixtures is a viable way to achieve the lower melting temperature. In terms of thermal stability, each individual salt should be thermally stable in a large temperature range. In this case, for single MgCl₂, KCl or NaCl, the boiling point is above 1350 °C, much higher than for example 732 °C for ZnCl₂ [39]. The three selected single salts i.e., MgCl₂, KCl and NaCl, have similar melting temperatures at around 750 °C (see **Table 1**). Among the three binary subsystems of the MgCl₂-KCl-NaCl system, MgCl₂-KCl has the lowest eutectic temperature at about 426°C [39], [44]. The ternary MgCl₂-KCl-NaCl mixture exhibits a lower minimum melting temperature of about 385 °C [43]. The exact minimum melting temperature and salt composition (i.e., eutectic composition) will be discussed and determined later based on the data available in literature and thermodynamic simulations. Melting temperatures of the single salts and the eutectic binary salt mixtures are listed in **Table 1**.

]	Table 1. Melting temperatures of single	salts and eutectic binary salt r	nixtures in the ternary	7
N	MgCl ₂ -KCl-NaCl salt system.			
	Salts	Melting temperature (°C)	Reference	

Salts	Melting temperature (°C)	Reference
Single salt		
MgCl ₂	714	[39], [44]
KCl	772	[39], [44]
NaCl	801	[39], [44]
Binary salt		
MgCl ₂ -KCl (33-67 mol. %)	426	[39], [44]
MgCl ₂ -NaCl (42-58 mol. %)	445	[39], [44]
KCl-NaCl (49.4-50.6 mol. %)	657	[39]

In order to determine the exact minimum melting temperature of the MgCl₂-KCl-NaCl salt mixture and its corresponding composition, their ternary phase diagram has been experimentally and numerically determined by several authors [42], [46], [60]-[62] (see **Figure 4**). To our knowledge, the phase diagram of MgCl₂-KCl-NaCl available in literature was firstly reported by Scholich [60] in 1920 and then by Jänecke [61] in 1950 with the same minimum melting temperature of 385 °C but a difference of MgCl₂ content about 3.6 mol. % (see **Table 2**). Later in 1987, Podlesnyak, et al. [62] obtained the liquidus point below 400°C with the similar minimum melting temperature composition as in [61]. Currently, Vidal, et al. [42] experimentally determined the minimum melting temperature composition, which

has the same melting temperature of about 385° C but lowest reported MgCl₂ content of 44.7 mol. %. The minimum melting temperatures and the corresponding compositions available in literature as well as from simulation with FactSage are listed in **Table 2** for better comparison. As presented in **Figure 4**, the region in the phase diagrams for the minimum melting temperature is located in the MgCl₂ content between 44.7-49 mol. % by all authors. Assuming an average value from all the work summarized in **Table 2**, the eutectic composition with the minimum melting temperature of $385\pm1^{\circ}$ C corresponds to 46.5 ± 1.7 mol. % MgCl₂-22.2±2.6 mol. % KCl-31.3±1.5 mol. % NaCl.

Discrepancies of different minimum melting temperature compositions are relatively high (about 2 mol.%) in the literature and may be due to different water content in the salt mixture used in the experiment, particularly in hygroscopic MgCl₂. Thus, special attention on salt purity as well as careful and sufficient drying is suggested for experimental determination of the exact eutectic composition and minimum melting temperature [47]. In terms of minimum melting temperature, there is good agreement in literature with a value of about 385 °C with the standard deviation of 1°C. Moreover, our experimental results via differential scanning calorimetry (DSC) on the salt mixtures listed in **Table 2**, which will be published in another paper, also confirm that the minimum melting temperature could be below 390°C. Hence, we propose to define the minimum working temperature of the eutectic MgCl₂-KCl-NaCl at 420°C for HTF/TES application (more than 30°C higher than the minimum melting temperature). However, some factors, e.g., gradual composition shift of salt mixtures during operation, may lead to other higher practical values than 420 °C for a higher safety margin in practical applications to avoid salt freezing events.

Additionally, it is concluded for the ternary MgCl₂-KCl-NaCl system that in the region of the eutectic composition, MgCl₂ is the main constituent of this system. If the application allows for a higher minimum operation temperature, then the salt could be also optimized by reducing the MgCl₂ content and/or increasing the KCl or NaCl content in order to reduce salt corrosivity due to strong hygroscopicity of MgCl₂ and the material cost as well as improve heat capacity of the salts. Such a salt mixture (non-eutectic MgCl₂-KCl-NaCl 37.51-40.92-21.57 mol. % with melting temperature of about 400°C) mixed with commercial anhydrous

carnallite and halite has been studied by NREL in the Gen3 CSP project and reported in [57]. Such optimization is considered for future work but not considered in this work.

In this work, we propose to use the eutectic composition simulated with FactSage in this work (i.e., 47.1 mol. % MgCl₂-22.7 mol. % KCl-30.2 mol. % NaCl) for simulations of other thermophysical and physicochemical properties as well as comparison with the data available in literature.

Table 2. Eutectic compositions and melting temperatures of MgCl₂-KCl-NaCl from literature and simulation in this work, as well as their average and standard deviation. E: Experiment; S: Simulation.

Authors (year)Eutectic composition (mol %)		Т	Method	Reference		
	MgCl ₂	KCl	NaCl	(°C)		
Scholich (1920)	49.0	18.5	32.5	385	Е	[60]
Jänecke (1950)	45.4	21.6	33.0	385	Е	[61]
Nemecek (1976)	47.1	22.7	30.2	385	Е	[43]
Mohan (2018)				383	S	[46]
				387	Е	[46]
Podlesnyak (1987)	46.5	22.2	31.3	<400	Е	[62]
Vidal (2018)	44.7	25.8	29.4	385	Е	[42]
FactSage	47.1	22.7	30.2	385.4	S	This work
	46.5±1.7	22.2±2.6	31.3±1.5	385±1	Average ±	
					Standard	
					deviation	



Figure 4. Measured and simulated phase diagrams of MgCl₂-KCl-NaCl in mol. % or wt. % available in the literature and obtained in this work: a) Scholich in mol. % [60]; b) Jänecke (note here bottom axis is labeled inversely in mol. % with double ions (NaCl)₂ and (KCl)₂) [61]; c) Podlesnyak, et al. in mol. % [62]; simulation by FactSage in d) Vidal, et al. in wt. % [42], e) Mohan, et al. in wt. % [46], and f) this study in mol. %. The eutectic composition with the minimum melting temperature is marked with a red circle.

2.2.Vapor pressure and maximum working temperature

The study on maximum working temperatures of chloride salt mixtures at different conditions such as gas atmosphere and sample mass has not been extensively studied. Since it is believed that the MgCl₂-KCl-NaCl salt mixture without or only with a small amount of impurities such as hydrated water have high thermal stability, the maximum working temperature of this salt mixture is limited mainly by the vapor pressure of the melt or salt corrosivity (salt corrosivity will be discussed in Section 3), not as nitrate salt mixtures mainly limited by thermal decomposition [28], [54], [63].

To define the maximum working temperature of a molten salt for TES/HTF, this has been studied by different methods such as mass spectrometric (MS) analysis, long-term stability tests and thermogravimetric analysis (TGA) experiments, where the maximum working temperature is often estimated with the temperature at which the sample has lost 3 wt. % [28], [54], [63]. For instance, the maximum upper working temperature for the molten nitrate salts, which is mainly limited by thermal decomposition and affordable structural materials for high temperatures, is defined below ~565 °C partly based on this method. Concerning chloride mixtures, they could have higher maximum upper working temperatures if only considering thermal decomposition, for example a maximum value of 850 °C for the NaCl-KCl-ZnCl₂ mixture was proposed by Xu, et al. [64]. However, for ternary CaCl₂-MgCl₂-NaCl and quaternary CaCl₂-MgCl₂-KCl-NaCl mixture, which have much higher theoretical melting temperatures than NaCl-KCl-ZnCl₂, Wei et. al [36] proposed a much lower upper temperature limit of 650 °C based on mass loss in the TGA experiment [65], [66]. The experimental investigation using DSC, TGA, X-ray Diffraction (XRD) and Mass Spectrometry (MS) shows that the mass loss was mainly caused by water/salt vaporization and/or reactions of salt impurities such as hydrated water with the salts, not by thermal decomposition [66], [67]. Kipouros & Sadoway did thermochemical analysis of the production of anhydrous MgCl₂ and showed that the dehydration and hydrolysis reactions of hydrated MgCl₂ take place at <300°C [68]. Moreover, Vidal et al. reported the thermal stability up to 773°C for MgCl₂-KCl-NaCl (44.7-25.8-29.4 mol.%) mixture based on 3 wt.% mass loss in the TGA experiment considering salt vaporization, mainly associated with $MgCl_2$ high vapor pressure [42]. Since in general TGA was done using a constant flow of N_2

gas above the salt, this flow helps remove the salt vapor above the salt thus mass losses might be associated to salt vaporization in an open environment [42]. Xu et al. [69] reported an obvious mass loss (~1 wt.%) in the range of 100-200 °C due to the water vaporization but negligible in the range of 200-700 °C for the 32 mol. % MgCl₂- 68 mol. % KCl binary mixture, thus suggested a upper temperature limit of 800 °C based on experimentally determined low vapor pressure at 800°C (<10 kPa). Thus, it is concluded in this work that the conventional TGA + 3 wt. % mass loss method used for molten nitrate salts is not an applicable method for molten chloride salts, needs improvement by considering other factors. The impurities/salt vaporization and reactions of salt impurities such as hydrated water with the salts are suggested to be considered in definition of the maximum working temperature of molten MgCl₂-KCl-NaCl for TES/HTF.

Recently, Mohan, et al. [46] considered the mass loss of the chloride salt due to salt vapor pressure instead of thermal decomposition. They reported the mass loss of the ternary MgCl₂-KCl-NaCl in three different gas atmospheres (nitrogen, air and argon) at a flow rate of 50 mL/min using the DSC-TGA equipment with an initial mass loss of about 5 wt.% between 100-250 °C due to dehydration and/or hydrolysis and about 10 % mass loss at 700-800 °C for all atmospheres. The result of Mohan et al. [46] shows that the pure MgCl₂-KCl-NaCl salt has negligible mass loss below 700°C and could be used at least up to 700°C. Moreover, if the mass ratio of molten salt to cover gas is low (e.g., 10:1) in a TGA measurement without gas sweeping, the mass loss is quite low even at very high temperatures (0.5 % mass loss)after heating from room temperature to 1000°C). Thus, the mass loss of the molten chloride salt due to vaporization at high temperatures also significantly depends on the flow rate of sweep gas over the salt. It is suggested in this work that the maximum upper working temperature of molten chlorides could be defined by the salt vapor pressure and the gas atmosphere (closed or purged type, and gas composition), if corrosion is not considered. Regarding corrosion and chemical decomposition due to reactions with H₂O and O₂ in air, there is a general agreement that the molten chloride TES/HTF system in next-Gen CSP plants requires an inert cover gas. If a large amount of salt vapor is present in cover gas due to high temperatures (>700°C), a closed gas system may be beneficial to have a higher maximum working temperature.

Table 3 shows vapor pressure data for the MgCl₂-KCl-NaCl salt system at different temperatures available in literature and from simulation of this work. The vapor pressures of single NaCl and KCl have been first measured (900 to 1100 °C) by the quasistatic method of Rodebush and Dixon [70]. In the data compiled by Janz [71], vapor pressures of single salts were also reported using different methods and correlations such as the boiling point method, transpiration technique as well as the Rodebush-Dixon method, with uncertainties of 5 % for the single chlorides (see Table 3). Compared to the single KCl and NaCl, the ternary mixture and single MgCl₂ exhibit much higher vapor pressures at >800 °C (see Table 3). To avoid the problem associated to the evaporation of MgCl₂, it is likely that a chloride salt composition with lower content of MgCl₂ (20-45 mol. % MgCl₂) will be preferred [44]. Thus, besides the melting temperature, the vapor pressure is also suggested to be considered in the salt optimization in future work. In the report of Williams [44], the vapor pressure of the binary eutectic KCl-MgCl₂ chloride mixture is reported and compared with the pure KCl and MgCl₂. For the binary eutectic MgCl₂-KCl (32-68 mol. %) salt, the experimental value of vapor pressure (~10 kPa at 800°C) reported by Xu et al. [69] is much higher than the simulated value (<0.13 kPa at 800°C [44]). An in-house-developed vapor pressure test system was used to test the vapor pressures of eutectic MgCl₂-KCl at 450-800°C by Xu et al. [69]. Note that this measurement system may have a measurement error due to gases produced by the dehydration or hydrolysis reactions, as a high vapor pressure of ~4 kPa was detected even at 450°C close to the melting temperature (426°C). The actual salt vapor pressure could be much lower than that measured with this method. Thus, in this work, a correction is made based on these measurement data at different temperatures under assumption that the produced gas at 450°C by reactions e.g., dehydration, is an ideal gas with neglectable salt vapor, i.e.,

$$P_{v,corrected}(450^{\circ}\text{C}) = 0 \text{ kPa, and}$$
 Eq. (2)

$$P_{v,corrected}(T) = P_v(T) - P_v(450^{\circ}C) \times (T+273.15)/723.15,$$
 Eq. (3)

where *P* and *T* have the units of kPa and °C, respectively, while P_v and $P_{v,corrected}$ are the experimental value in [69] and corrected value of the vapor pressures, respectively. The corrected values at 450-800°C are presented in **Table 3** and **Figure 5** for comparison with simulated vapor pressures of MgCl₂-KCl-NaCl. Moreover, the authors concluded that the vapor pressure of this salt is less than 13 kPa even at the temperature at 800°C, and this low

vapor pressure implies that the mass loss of MgCl₂–KCl molten salts below 800°C is very small [69]. Based on their experimental results and conclusion, MgCl₂-KCl can be used for TES application at >800°C.

Experimental data on vapor pressures of MgCl₂-KCl-NaCl are limited in the literature, however, in recent publications some values are given from some experiments [56] and thermodynamic simulation such as FactSage and HSC software based on the data of single and binary salts [46]. The experiments by Wang, et al. [56] showed that the vapor pressure of molten MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) increases from 0.25 to 3.48 kPa at 500-725°C with the overall measurement uncertainty of 0.6 kPa (i.e., >17%), which can be fitted with $7.1320 \times 10^{-8} \times T^3 - 7.909 \times 10^{-5} \times T^2 + 0.030355 \times T(^{\circ}C) - 4.0966$ (see Figure 5). The result of the simulation using FactSage in this work is also given in Figure 5. Here, the vapor pressure of the molten MgCl₂-KCl-NaCl (47.1-22.7-30.2 mol. %) has been calculated for the temperature range between 400 and 1000 °C, and can be well fitted with

$$P_{v,sim} = 3.1 \cdot 10^{-8} \cdot e^{0.0214 \cdot T(^{\circ}C)}$$
 Eq. (4)

at 700-1000°C. It is observed that the vapor pressure increases sharply over 800°C and is <0.2 kPa below 700°C for the ternary mixture. Moreover, the simulated vapor pressure is 1 kPa and 10 kPa (i.e., 0.01 and 0.1 bar) at 804 °C and 916°C, respectively. These simulated values are comparable to (slightly lower than) the corrected value of MgCl₂-KCl (32-68 mol.%) at 800°C (4.86 kPa) based on the experimental value and its extended value to 900°C (12.2 kPa), as well as the extended value to 800°C (6.1 kPa) for MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %).

As previously discussed, it is concluded in this work that the maximum upper operation temperature of MgCl₂-KCl-NaCl is not limited by the thermal decomposition of the salt but other factors, such as salt vapor pressure or corrosivity associated with impurities in the salt. Thus, the determination of the most practicable maximum operation temperature of MgCl₂-KCl-NaCl regarding all the relevant factors related to real application is strongly suggested as future work. In this work, only considering the salt vapor, it is defined not higher than 10 kPa (0.1 bar) in the molten salt TES system to avoid the technical problems caused e.g., by salt condensation in cold region of the TES system. Thus, we suggest the maximum upper working temperature of 800 °C for the MgCl₂-KCl-NaCl salt mixture, at which the salt

vapor pressure is below 10 kPa, based on the survey and evaluation of the salt vapor pressure. However, corrosion aspects and costs of alloy materials with high strengths may lead to other lower practical values than 800 °C regarding the overall TES costs.

Table 3. Vapor pressure data for the MgCl₂-KCl-NaCl salt system at different temperatures available in literature and from FactSage data of this work. The values in brackets after experimental values are the corrected vapor pressures of MgCl₂-KCl ($P_{v,corrected}$) by the authors of this work. E: Experiment; S: Simulation, E-Ext: Extended value calculated with fitting of experimental values.

Salt	p_v (kPa)	T (°C)	Method	Reference
Single salt				
MgCl ₂	0.015	714	E	[71]
_	0.93	900	S	[44]
	0.57	900	S	This work
	100	1358.3	S	This work
	100	1412	E	[69]
	100	1418	S	[44]
KCl	0.055	770	Е	[71]
	0.27	900	S	[44]
	0.51	900	E	[71]
	100	1475.3	S	This work
	100	1420	E	[69]
	100	1407	S	[44]
NaCl	0.039	800	E	[71]
	0.33	900	S	[44]
	0.29	900	E	[71]
	100	1515.6	S	This work
	100	1465	S	[69]
Binary salt				
MgCl ₂ -KCl (33-67 mol. %)	< 0.13	800	S	[44]
	< 0.26	900	S	[44]
MgCl ₂ -KCl (32-68 mol. %)	4.0-10.8 (0-4.86)	450-800	E	[69]
	(12.2)	900	E-Ext	
MgCl ₂ -NaCl (42-58 mol. %)	< 0.33	900	S	[44]
Ternary salt				
MgCl ₂ -KCl-NaCl	0.25	500	Е	[56]
(38.2-41.3-20.5 mol. %)	3.5	725	E	
	6.1	800	E-Ext	
MgCl ₂ -KCl-NaCl	1	804	S	This work
(47.1-22.7-30.2 mol. %)	10	916	S	using
`````	100	1052	S	FactSage



**Figure 5.** Vapor pressures of MgCl₂-KCl-NaCl (47.1-22.7-30.2 mol. %) simulated with Equilibrium module in FactSage in this work (empty points) with an exponential fit, compared with those of MgCl₂-KCl (32-68 mol. %) measured experimentally (solid points) with a polynomial fit (corrected based on experimental data in [69]) and MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) measured experimentally (solid points) [56]. The error bars represent the overall measurement uncertainties of about 2 kPa and 0.6 kPa for MgCl₂-KCl (32-68 mol. %) and MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %), respectively.

One of the important reasons for the exclusion of some low melting temperature chloride salts in next-Gen CSP plants is that they exhibit high vapor pressures at target temperatures  $> 700 \,^{\circ}C$  (for instance ZnCl₂ containing salts) and thus e.g., pressurization of the tanks and salt evaporation and condensation at cold spots can occur. In commercial CSPs using molten nitrates, the safety limit of vapor pressure in the CSP system accepted by the CSP society is typically below 100 kPa to avoid additional requirements on containers and pipes [72]. As discussed previously, we recommend the accepted vapor pressure to be lower (< 10 kPa as defined above) for system safety, since the high vapor pressure of chloride salts in combination with oxidative gaseous compounds (e.g., HCl, O₂ and H₂O) will produce an aggressive atmosphere to the containment materials [73]. Moreover, when the TES system is purged with gas, additional challenges such as a significant salt loss have to be overcome.

#### 2.3. Heat capacity

The heat capacity  $c_p$  is an important thermal property of the molten salt mixture since the heat storage capacity can be enhanced by an increased  $c_p$  value. Heat capacity of molten salts has been measured experimentally by different methods such as drop calorimetry and DSC following for example the ASTM E1269 standard [74]. Some calculations are based upon pure-component heat capacities and the empirical Dulong-Petit equation as shown in Eq. (5) [44]:

$$c_p\left(\frac{J}{g^{\circ}c}\right) = 33.45\left(\frac{J}{mol^{\circ}c}\right) \bullet \sum X_i N_i / \sum X_i M_i , \qquad \text{Eq. (5)}$$

where  $c_p$  is the heat capacity (J/g °C),  $X_i$  is the molar fraction of salt *i* (-),  $N_i$  is the number of atoms per salt constituent (-) and  $M_i$  is the molecular weight of each salt (g/mol).

The heat capacity of the ternary chloride mixture was experimentally measured using a drop calorimetry method by Janz [71]. In his data compilation, the  $c_p$  value for the composition 45.4 mol. % MgCl₂- 21.6 mol. % KCl- 33 mol. % NaCl at 400 °C is 1.01 J/g °C with an uncertainty of about 2 %. Later, Xu, et al. [64] measured  $c_p$  with DSC and reported a value of 1.12 J/g °C for the mixture of 40 mol. % MgCl₂- 32.5 mol. % KCl- 27.5 mol. % NaCl in the range from 480 to 520 °C. Williams [44] reported a heat capacity value of 1.08 J/g °C for the binary mixture of 42 mol. % MgCl₂- 58 mol. % NaCl and 1.15 J/g °C for the binary mixture of 33 mol. % MgCl₂ - 67 mol. % KCl, both at 700 °C. Xu et al. presented the measured value of 1.00 J/g °C with a slight increase with increasing temperature for the binary mixture of 32 mol. % MgCl₂ - 68 mol. % KCl at 550-700 °C [69]. Recently, Wang et al. [56] reported the experimental heat capacity value of MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) decreases from 1.09 to 0.99 J/g °C at 450-628°C with the overall uncertainty of 0.04 J/(g °C), which can be fitted well with 1.30138-0.0005*T(°C). However, this result does not agree with the theory that the heat capacity of a molten salt is constant or increases when the temperature increases. After reviewing the literature, the variation of  $c_p$  of molten chlorides with temperature generally is quite small [76].

**Table 4** and **Figure 6** summarize the heat capacity data for the ternary MgCl₂-KCl-NaCl salt system with different compositions at different temperatures available in literature and from

simulation of this work. Due to the small variation, the heat capacity can be considered to be constant for engineering the ternary chloride mixture in the defined working temperature range of 420-800 °C. Moreover, it can be concluded that the typical simulated  $c_p$  value for the ternary chloride mixture is about 1.04 J/(g °C) with a small change of < 2% at 420-800 °C, while the typical experimental value is  $1.10\pm0.10$  J/(g °C) in the defined operation temperature range, which significantly depends on the salt composition. In general, for halide salt mixtures, heat capacity values are similar [77], for example, the  $c_p$  value for the quaternary CaCl₂-MgCl₂-KCl-NaCl mixtures is 1.19 J/g °C with melting temperature of 385 °C [36] and 1.16 J/g °C at 700 °C for the binary KCl-MgCl₂ mixture [65]. The Dulong-Petit method represented in Eq. (5) is considered as a good prediction to the heat capacity of molten halide salts [58], [78]. For simplicity, one may assume a constant value of 1.10 J/(g °C) (with the discrepancy of about 9%, i.e., 0.10 J/(g °C), of the available data) for the ternary mixture in the defined working temperature range of 420-800 °C.

Salt	$C_p(J/(g \circ C))$	Trange (°C)	Method	Ref.
Single salt		1	1	
MgCl ₂	0.98	720-1230	E	[79]
KCl	0.99	780-800	Е	[79]
NaCl	1.20	800-1000	E	[79]
Binary salt				
MgCl ₂ -KCl (32-68 mol. %)	1.00	500-700	E	[69]
MgCl ₂ -KCl (33-67 mol. %)	1.15	700	E	[44]
	0.96	700	S	
MgCl ₂ -NaCl (42-58 mol. %)	1.08	700	E	[44]
MgCl ₂ -NaCl (42-58 mol. %)	1.10	700	S	[44]
Ternary salt				
MgCl ₂ -KCl-NaCl (45.4-21.6-33.0 mol. %)	1.01	400	E	[75]
MgCl ₂ -KCl-NaCl (40-32.5-27.5 mol. %)	1.12	480-520	Е	[64]
MgCl ₂ -KCl-NaCl (45.4-21.6-33.0 mol.%)	1.18	455-600	Е	[58]
MgCl ₂ -KCl-NaCl (38.2-41.3-20.5 mol. %)	1.09-0.99	450-628	E	[56]
	0.90	800	E-Ext	
MgCl ₂ -KCl-NaCl (50-20-30 mol. %)	1.04	500-800	S	[46]
MgCl ₂ -KCl-NaCl (47-23-30 mol. %)	1.04	420-800	S	This
MgCl ₂ -KCl-NaCl (44.7-25.8-29.4 mol. %)	1.03	420-800	S	work

**Table 4.** Heat capacity data for the ternary MgCl₂-KCl-NaCl salt system at different temperatures available in literature and from simulation of this work. E: Experiment; S: Simulation, E-Ext: Extended value calculated with fitting of experimental values.



**Figure 6.** Heat capacities of MgCl₂-KCl-NaCl with different compositions at 400-800°C, available in literature and from simulation of this work. Empty points: Simulation values; Solid points: Experimental values. Error bar: overall measurement uncertainty.

#### 2.4. Density

For design of the storage tanks, the reliable value of  $\rho$  is required to calculate the required volume of storage material V. The effort has been given to determine the value of  $\rho$  as a function of temperature for the ternary MgCl₂-KCl-NaCl chloride mixture experimentally or theoretically. Density of molten salts has been measured by different techniques such as Archimedean technique as well as using the method of additive molar volumes and simulated with the Quasi-chemical model [58]. Generally, the density of liquids can be adjusted to a simple linear equation  $\rho = a - bT$  where a and b are characteristic parameters for each fluid.

The density correlations of single molten MgCl₂, KCl, NaCl as a function of temperature were reported by Janz et al. [79], [80] based on experimental data from literature. Li, et al. [58] predicted density values for different salt systems containing MgCl₂, KCl, NaCl and/or ZnCl₂ based on four different methods where the density value for the ternary MgCl₂-KCl-NaCl (50-20-30 mol. %) chloride mixture decreases from 1.75 g/cm³ to 1.65 g/cm³ by increasing temperature in the range of 350-850 °C. Robelin, et al. [59] developed a density

model for the ternary mixture with a constant ratio of KCl-NaCl in which it is observed that the density linearly decreases from 1.53 g/cm³ to 1.46 g/cm³ with increasing temperature between 775 °C and 875 °C. Williams [44] reported the density at 700 °C for the eutectic binary chlorides NaCl-MgCl₂ and KCl-MgCl₂ 1.68 and 1.66 g/cm³ respectively. Xu et al. [69] measured the density of the eutectic binary KCl-MgCl₂ at 450-800°C, and obtained the linear correlation of  $1.9037 - 5.52 \cdot 10^{-4} T(^{\circ}C)$  with an overall measurement uncertainty of 4.5709 x 10⁻⁴T  $\left(\frac{g}{cm^3}\right)$  for the binary system KCl-MgCl₂. Recently, Wang et al. [56] reported the experimental density value of MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) decreases from 1.707 to 1.565 g/cm³ at 450-700°C with an overall measurement uncertainty of 0.015 g/cm³, which can be fitted well with 1.95884 -  $5.6355 \times 10^{-4} T(^{\circ}C)$ . Table 5 shows the selected density values from literature and calculation. The calculated density of molten MgCl₂-KCl-NaCl (50-20-30 mol.% and 47.1-22.7-30.2 mol.%)  $\rho_{mix}$  as a function of temperature is plotted in Figure 7, which was calcualted with the correlation in Eq. (6) using the additive molar volume method and the single salt data of Janz et al. [79], [80]. Density of molten MgCl₂-KCl-NaCl  $\rho_{mix}$  is given in (g/cm³), where  $X_i$  is the mole fraction of the salt i,  $M_i$  is the molecular weight of each salt (g/mol) and  $V_i$  is the molecular volume of the salt i (cm³/mol) depending on temperature T (°C).

$$\rho_{mix}(T)(\frac{g}{cm^3}) = \sum X_i M_i / \sum X_i V_i(T)$$
 Eq. (6)

Comparing relevant literature and calculation results, we proposed that a typical density value for the eutectic ternary MgCl₂-KCl-NaCl (47.1-22.7-30.2 mol. %) mixture is 1.76-1.60 g/cm³ (with the discrepancy of <6%, i.e., about 0.1 g/cm³, of the available data) in the defined working temperature range of 420-800°C with the correlation:

$$\rho\left(\frac{g}{cm^3}\right) = 1.94 - 4.2 \cdot 10^{-4} \cdot T(^{\circ}C)$$
 Eq. (7)

Salt	Density (g/cm ³ )	T (°C)	Method	Ref.
Single salt				
MgCl ₂	1.66	800	E	[82]
KCl	1.47	870	E	[82]
NaCl	1.55	807	Е	[79]
	1.49	900	E	[82]
	1.44	1017	E	[64]
Binary salt				
MgCl ₂ -KCl	1.68-1.47	450-800	Е	[69]
(32-68 mol. %)	$1.9037 - 5.52 \cdot 10^{-4} T(^{\circ}C)$			
	1.54-1.48	750-900	S	[81]
	$1.875 - 4.5709 \ge 10^{-4}T$ (°C)			
Ternary salt		·	·	
MgCl ₂ -KCl-NaCl	1.71-1.57	450-700	E	[56]
(38.2-41.3-20.5 mol. %)	$1.959 - 5.264 \cdot 10^{-4}T(^{\circ}C)$			
MgCl ₂ -KCl-NaCl	1.75-1.65	380-850	S	[58]
(50-20-30 mol. %)				
MgCl ₂ -KCl-NaCl	1.76-1.60	420-800	S	This
(47.1-22.7-30.2 mol. %)	$1.94 - 4.2 \cdot 10^{-4} T(^{\circ}C)$			work

**Table 5.** Density data for MgCl₂-KCl-NaCl salt system at different temperatures available in literature and from simulation of this work. E: Experiment; S: Simulation.



**Figure 7.** Selected density data for binary MgCl₂-KCl (32-68 mol. %) (experimental: Xu et al. [69], simulated: [81]) and ternary MgCl₂-KCl-NaCl (experimental: Wang, et al. [56]; simulated: [58] and this work) molten salt over temperature. Empty points: Simulation values; Solid points: Experimental values. Error bar: overall measurement uncertainty.

#### 2.5. Thermal conductivity

Thermal conductivity is a fundamental transport property since heat transfer design aspects are important in developing the new molten salt TES/HTF applications. For example, the design of the key components of CSP such as solar receiver and heat exchanger are intrinsically dependent on accurate and reliable thermal conductivity data. Typically thermal conductivity values for molten salts are between 0.1 and 0.6 W/(m °C) [83] with a very weak dependence on temperature [84]. The most common techniques for measuring the thermal conductivity of molten salts include laser flash analysis (LFA), Forced Rayleigh scattering method and transient hot-wire method [85]. The LFA method determines the thermal diffusivity and thermal conductivity can be calculated with the thermal diffusivity, heat capacity and density [56]. Palacios et al. [83] have performed a review of the measurement protocol for TES conductivity measurements, in which the LFA technique and guarded plate are most accurate for high temperature thermal conductivity measurements.

However, experimental data for molten chloride salts are limited. It is known that pure halide salts and their mixtures exhibit the trend of decreasing thermal conductivity with increasing formula weight of the salt [44]. The thermal conductivities of pure molten chlorides were reported by Janz et al. [79] using a coaxial cylinder steady state with uncertainties of about 20 %. Polimeni [65] reported a value of 0.39 W/(m °C) at 700 °C for the binary molten salt mixture MgCl₂-KCl in comparison with 0.55 W/(m °C) at 700 °C for the same mixture reported by Serrano [81]. Xu et al. [69] used LFA technique to measure the thermal conductivity of MgCl₂-KCl (32-68 mol. %) at 450-800°C, which decreases from 0.465 to 0.424 W/(m °C) with the overall uncertainty of 0.027 W/(m °C) and can be fitted well with  $0.505-10^{-4} T(^{\circ}C)$ . Tian et al. [86] reported a thermal conductivity of eutectic molten NaCl-CaCl₂-MgCl₂ of 1.17 W/(m °C). Recently, Wang et al. [56] reported the experimental thermal conductivity of MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) using the LFA method. The value decreased from 0.47 to 0.41 W/(m °C) at 450-700°C with the overall uncertainty of 0.037 W/(m °C), which can be fitted well with  $0.5822 - 0.00026 \times T$ (°C). Gheribi [87] modeled thermal conductivity for the ternary LiCl-NaCl-KCl between 900 and 1300 °C and obtained values of 0.4-0.6 W/(m °C). Li, et al. [58] surveyed five different models for the ternary MgCl₂-KCl-NaCl mixture in which the thermal conductivity values are between 0.38-0.48

W/(m °C) at 360-860 °C. Chliatzou et al. [88] established thermal conductivity reference correlations for the pure NaCl and KCl single salts and predicted thermal conductivity of molten salt mixtures using the linear mixing rule as:

$$\lambda_{mix} = \sum_{i=1}^{n} x_i \lambda_i \; (W/(m \circ C)), \qquad \text{Eq. (8)}$$

where *n* is the number of salts and  $x_i$  is the mole fraction of the *i*th salt (assuming as liquid), and  $\lambda_i$  the thermal conductivity of the *i*th salt.

From comparison of literature data summarized in **Table 6**, NaCl has higher thermal conductivity than MgCl₂ and KCl, while MgCl₂ and KCl have the similar thermal conductivity. Since reports on the thermal conductivity of single MgCl₂ are rare, we used a constant value of 0.4 W/(m °C) for MgCl₂, which is obtained from the thermal conductivity correlation in one-component molten halide salt [44] and Peng, et al. [89] for calculation of the ternary MgCl₂-KCl-NaCl (47.1-22.7-30.2 mol. %) system at 420-800°C using the linear mixing rule (Eq. (8)) in this work. For the single NaCl and KCl chlorides we recommend using the data supplied by Nagasaka with an estimated error of  $\pm 5$  % [90], since the data is comparable to that from Chliatzou et al. [88]. Data from literature review and calculation are presented in **Table 6** and **Figure 8**. The simulated values for binary MgCl₂-KCl and ternary MgCl₂-KCl-NaCl mixture using the linear mixing rule in this work compare well with the data available in literature. Thus, we recommend the thermal conductivity of MgCl₂-KCl-NaCl (47.1-22.7-30.2 mol. %) to be 0.42-0.47 W/(m °C) (with the discrepancy of <10%, i.e., about 0.04 W/(m °C), of the available data) in the defined working temperature range (i.e., 420-800°C) with the correlation of 0.53 - 1.32×10⁻⁴T (°C).

Salt	$\lambda_l (W/(m \circ C))$	T (°C)	Method	Ref.
Single salt				
MgCl ₂	~0.40	~714	E	[44], [89]
KCl	0.40-0.33	780-970	E	[90]
	$(0.687 - 3.7 \cdot 10^{-4}T)$			
	0.39-0.32	783-1062	E	[88], [91]
NaCl	0.52-0.48	900-1180	Е	[90]
	$(0.649 - 1.38 \times 10^{-4}T)$			

**Table 6.** Thermal conductivity data of MgCl₂-KCl-NaCl salt system at different temperatures available in literature and from simulation of this work. E: Experiment; S: Simulation.

	0.50-0.44	897-1166	E	[88]		
Binary salt	Binary salt					
MgCl ₂ -KCl (32-68 mol. %)	0.40	700	S	[44]		
MgCl ₂ -KCl (32.4-67.6 mol.	0.39	700	Е	[65]		
%)						
MgCl ₂ -KCl (26.9-73.1 mol.	0.55	700	E	[81]		
%)						
MgCl ₂ -KCl (32-68 mol. %)	0.465-0.424	450-800	E	[69]		
	$(0.505-10^{-4}T)$					
MgCl ₂ -NaCl (42-58 mol. %)	0.43	700	S	[44]		
MgCl ₂ -KCl (32-68 mol. %)	0.48-0.40	450-800	S	This		
				work		
Ternary salt						
MgCl ₂ -KCl-NaCl	0.47-0.41	450-700	E	[56]		
(38.2-41.3-20.5 mol. %)	$1.959 - 5.264 \times 10^{-4}T$					
MgCl ₂ -KCl-NaCl	0.47-0.42	380-830	S	[58]		
(40-32.5-27. 5 mol. %)	$0.51 - 1.11 \times 10^{-4}T$			_		
MgCl ₂ -KCl-NaCl	0.47-0.42	420-800	S	This		
(47.1-22.7-30.2 mol. %)	$0.53 - 1.32 \times 10^{-4}T$			work		



**Figure 8.** Comparison of thermal conductivity data of MgCl₂-KCl-NaCl system, available in literature and calculated using the linear mixing rule in Eq. (8) and available single salt data in this work. Empty points: Simulation values; Solid points: Experimental values. Error bar: overall measurement uncertainty.

#### 2.6. Dynamic viscosity

By calculating the dynamic viscosity of the molten salt, it is possible to obtain the flow behavior when the salt is flowing through the pipes, pumps and solar collectors [92]. Molten chloride salts have, in general, very low dynamic viscosity in the working temperature range, which is in the range of water at room temperature [93]. The dynamic viscosity can be measured by different methods such as capillary viscometers, torsional vibration method, rotational method and oscillating cup viscometer, in which most effort is focused on study of the dynamic viscosity near the crystallization point due to the operational risk [29]. In general, binary and ternary chloride systems exhibits a Newtonian behavior and their dynamic viscosities significantly decrease with increasing temperature. Values for single salts and binary systems have been reported by Janz [79] and Brockner et al. [93] using an oscillating cylinder. The values for molten NaCl and KCl in literature are comparable. The values for single salts are presented in Table 7. The dynamic viscosity of the binary mixture KCl-MgCl₂ was reported by Polimeni with a value of 1.44 mPa s at 700 °C [65]. Xu et al. [69] also measured this binary mixture and reported dynamic viscosity values below 4 mPa s at temperatures higher than 600 °C and in the range of 6-7 mPa s around 430 °C. Williams [44] reported a value of 1.36 and 1.4 mPa s at 700 °C for the binary NaCl-MgCl₂ and KCl-MgCl₂, respectively. Recently, Wang et al. [56] reported the experimental thermal dynamic viscosity value of MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) decreases from 3.79 to 2.5 mPa s at 450-700°C with the overall uncertainty of 0.09 mPa s, which can be fitted well with:

$$\eta = 0.706 * e^{1204/(T^{\circ}C + 273.15)}$$
. Eq. (9)

Wang, et al. [32] calculated dynamic viscosity of molten NaCl-KCl at different temperatures using molecular dynamic simulation and the dynamic viscosity increases slightly at a certain temperature of 680-930 °C along with a gradual increase of NaCl content. For the ternary MgCl₂-KCl-NaCl composition, it is recommended in [94] to estimate the dynamic viscosity using the mixing rule based on an ideal-mixture theory by the correlation:

$$\eta_{mix} = \left[\sum_{i} (X_i \ \eta_i^{1/3})\right]^3, \qquad \text{Eq. (10)}$$

where  $X_i$  is the mole fraction of the salt *i* and  $\eta_i$  is the dynamic viscosity of component *i*. Five different models were surveyed by Li, et al. [58] as well as the above polynomial expression,

in which the dynamic viscosity values are lower compared to the dynamic viscosity obtained by the rough-hard-sphere model (RHS). Results of dynamic viscosity as a function of temperature for the different compositions mentioned above are shown in **Figure 9** and Table 7 with an uncertainty of  $\pm 5$  % for the correlations.

Comparing relevant literature and calculation results, the simulated dynamic viscosity values using RHS or FactSage using the data for MgCl₂ from [79] and for KCl and NaCl from [93] are similar, and they compare well with the experimental data for binary MgCl₂-KCl (32-68 mol.%) and MgCl₂-KCl-NaCl (38.2-41.3-20.5 mol. %) mixture. Thus, we proposed that a typical dynamic viscosity value for the ternary MgCl₂-KCl-NaCl (47.1-22.7-30.2 mol. %) mixture is 6.01-1.51 mPa·s in the defined working temperature range (i.e., 420-800°C). The equation:

$$\eta$$
(mPa s) = 27.728  $e^{-0.00364 T(^{\circ}C)}$  Eq. (11)

**is suggested to calculate the temperature-dependent dynamic viscosity.** Note that the value decreases significantly with increasing temperature in this temperature range, particularly in the temperature range close to the melting temperature. Moreover, the dependency of dynamic viscosity on temperature and salt composition is strong. Thus, future experiments on the recommended salt mixture are suggested for more accurate values, particularly at the temperatures close to the melting temperature due to large discrepancy of the available data (see Figure 9).

Salt	η (mPa s)	T (°C)	Method	Ref.
Single salt				
MgCl ₂	$\begin{array}{r} 2.14 - 1.57 (14.903 - \\ 2.039 \times 10^{-2} (T + \\ 273.15) + 7.625 \times \\ 10^{-6} (T + 273.15)^2) \end{array}$	727-867	E	[79]
KCl	1.020-0.815	781-838	Е	[79]
KCl	$\frac{1.07-0.93}{10^{-2}} \frac{(6.168 \times 10^{-2} e^{3012.4/(T+273.15)})}{10^{-2}}$	781-838	Е	[93]
NaCl	1.008-0.807	811-930	Е	[79]
NaCl	$\frac{1.01-0.81}{10^{-2}e^{2641/(T++273.15)}}$	811-930	E	[93]

**Table 7** Dynamic viscosity data of MgCl₂-KCl-NaCl salt system at different temperatures available in literature and from simulation of this work. E: Experiment; S: Simulation.

Binary salt	Binary salt						
MgCl ₂ -KCl (32-68	5.8-3.0	450-800	Е	[69]			
mol.%)							
Ternary salt							
MgCl ₂ -KCl-NaCl	3.79-2.5	450-700	Е	[56]			
(38.2-41.3-20.5 mol. %)	$(0.706 \times e^{1204/(T+273.15))}$						
MgCl ₂ -KCl-NaCl	6.00-1.74	400-850	S (RHS)	[58]			
(50-20-30 mol. %)	$18.007 \times e^{-0.00275 T}$						
MgCl ₂ -KCl-NaCl	6.01-1.51	420-800	S	This work			
(47.1-22.7-30.2 mol. %)	$27.728 \times e^{-0.00364 T}$		(FactSage)	based on			
				[94]			



**Figure 9.** Comparison of dynamic viscosity data for binary MgCl₂-KCl and ternary MgCl₂-KCl-NaCl mixture, available in literature and calculated using RHS model or FactSage in this work. The data for MgCl₂ from [79] and for KCl and NaCl from [93] used in the simulation is also presented. Empty points: Simulation values; Solid points: Experimental values. Error bar: overall measurement uncertainty.

#### 3. Corrosion control of molten MgCl₂-KCl-NaCl salt

Molten salt corrosion is one of the main challenges to be faced by using chloride mixtures in CSP plants since compared to nitrate mixtures they are strongly corrosive to structural

materials (e.g., metallic alloys) at high working temperatures [9], [47]. In order to ensure long lifetime and economy of the molten chloride TES system, an effective and affordable corrosion control system (CCS) including corrosion monitoring and mitigation is essential and should be integrated in the TES system [55]. In this section, the main corrosion mechanisms and behaviors of conventional metallic structural materials in molten MgCl₂-KCl-NaCl salt are reviewed briefly, as the corrosion behavior of metallic alloys in molten chloride salts for thermal energy storage has been discussed in our previous review paper [47] in detail. Emphasis is given on the corrosion control system integrated into the molten chloride TES system as well as the promising online corrosion monitoring and mitigation techniques used in the corrosion control system. The salt pre-treatments before using in the molten salt TES system (e.g., stepwise heating to remove the most residual water in the salts and reduce salt corrosivity) and modifications of metallic materials (e.g., coating a protective layer on the metallic materials) have been reviewed in our recently published review paper [47], [55], and thus are not discussed in this work.

#### 3.1. Corrosion mechanisms and behaviors

In theory, the pure MgCl₂-NaCl-KCl salt mixture cannot chemically corrode the conventional metallic structural materials such as Cr-Fe-Ni alloys, since MgCl₂, NaCl and KCl salts are thermodynamically more stable than FeCl₂, CrCl₂ and NiCl₂ [55]. Moreover, it is believed that physical corrosion of metallic structural materials in pure molten halide salts due to friction and dissolving/leaching could be at a very low level, e.g., the long-term (9 years) corrosion tests using a molten salt convection flow loop between 560°C and 700°C show that the corrosion rate of Hastelloy N in pure LiF-BeF₂-ThF₄-UF₄ molten salt is below 6  $\mu$ m/year at 700°C [95]. It is well accepted that **the corrosive impurities** such as hydrated water in the molten salt or moisture and O₂ in gas atmosphere [9], [47], [49]. For salt mixtures containing strongly hygroscopic MgCl₂, it needs additional salt purification to remove the hydrated water in the salt. It can fast combine with the moisture in air and thus the corrosivity of the MgCl₂-containing molten salts increases due to corrosive impurities such as MgOHCl and HCl produced by hydrolysis during the heating to high temperature according to Eqs. (12) and (13) [47], [49]. Upon melting, MgOHCl dissolves in the molten salt according to

Eq. (14) and thereby corrodes the metallic structural materials at high temperatures. It is thermally stable up to about 555°C and gradually decomposes to MgO precipitates and HCl gas at higher temperatures according to Eq. (15) [47], [68].

$$MgCl_2 \cdot H_2O_{(s)} \to MgOHCl_{(s)} + HCl_{(g)}$$
 Eq. (12)

$$MgCl_2 \cdot 2H_2O_{(s)} \to MgOHCl_{(s)} + HCl_{(g)} + H_2O_{(g)}$$
 Eq. (13)

$$MgOHCl_{(l)} \to MgOH^+ + Cl^- \qquad \qquad \text{Eq. (14)}$$

$$MgOH^+ + Cl^- \to MgO_{(S)} + HCl_{(g)}$$
 Eq. (15)

It has been confirmed by individual study in different research groups including our group at DLR, NREL in US and SINAP-CAS in China that  $MgOH^+$  is the main corrosive impurity in the molten  $MgCl_2$ –KCl–NaCl due to high solubility and thermal stability [47], [96]-[99]. Thus, the molten chlorides, particularly containing the hygroscopic salt like  $MgCl_2$ , are suggested to be covered with an inert gas (e.g., N₂) to avoid the oxidizing species such as oxygen and moisture entering in the molten salt TES system [47].

The main corrosion behaviors of Cr-Fe-Ni alloys in molten chlorides include preferential depletion of the main alloying elements Cr and Fe in the alloys and intergranular corrosion [47], [100]. Moreover, different from air atmosphere, the Cr oxide layers on the Cr-Fe-Ni alloys are not protective to corrosion of molten chlorides as they can dissolve in the molten chlorides [47], [101]. The corrosive impurities in the molten salt corrode the alloys by reacting with the alloying elements [47]. It is well accepted that the alloying elements e.g., Cr, Fe, Mn and Si, react with the corrosive impurities like MgOH⁺ preferentially than Ni due to their higher electromotive forces (EMFs) [42], [47], [96]. Generally it is believed that Nickel-based superalloys such as Incoloy (In), Inconel (IN) and Hastelloy (Ha), which have higher Ni contents but also higher prices, typically have better corrosion resistance in molten chloride salts than stainless steels (SS) [47], [102], [103]. In our previous work [96], the corrosion rates of SS 310, In 800H and Ha C-276 in MgCl₂-KCl-NaCl (60-20-20 mol. %) salt mixture were measured via a static immersion test at 700°C for 500 h under Ar atmosphere. As shown in Figure 10, the Ni-based superalloy, i.e., Ha C-276, which has most Ni (~57 wt.%) and least Cr (~16 wt.%), exhibits the best corrosion resistance (~500 µm/year), while the high-temperature stainless steel SS 310 (Ni 19-22 wt.%, Cr 24-26 wt.%) has the highest corrosion rate of  $>1700 \mu$ m/year. The corrosion rates of all the tested alloys (even the Ni-based Hastelloy C-276) were much higher than the acceptable

level (typical acceptable corrosion rate:  $10-30 \mu m/year$  for 30 years in a real storage system [47]) when the salt corrosivity was not controlled.

In order to ensure the safety of the test facility FASTR of ORNL for development of hightemperature molten chloride salt technology, the expensive Ha C-276 (~20 000 \$/Metric Ton [47]) has been considered as the structural material that requires operations at >700°C or greater due to its excellent corrosion resistance and high-temperature mechanical properties [50], [104]. However, Ni-based alloys have unacceptable high prices for large-scale application in a commercial TES system [9]. Thus, the corrosion effects should be controlled and maintained at acceptable levels in order to reduce the construction costs by using non-Ni-based alloys and provide the long lifetime of materials for e.g., piping systems, storage tanks, valves, heat exchangers [28], [105].



**Figure 10**. Corrosion rates of commercial alloys (SS 310, In 800H and Ha C-276) in the molten MgCl₂-KCl-NaCl at 700°C under Ar atmosphere as well as mass fractions of Ni, Cr and Fe alloying elements in these alloys [96]. Higher Ni content in the alloy generally leads to better corrosion resistance but higher cost.

#### **3.2.** Corrosion control system (CCS)

In order to ensure long lifetime and safety of the TES system using molten chlorides, a corrosion control system including corrosion monitoring and mitigation is essential and should be integrated in the TES system. In Figure 11, a concept of such a corrosion control system is proposed. It could be used to control the salt corrosivity at different locations of the TES system in CSP (see Figure 2), e.g., 1) before entering the hot salt tank from the solar receiver to avoid severe corrosion of the tank, 2). in the tank to avoid severe corrosion of the tank due to the air leakage in operation, and 3) before entering the heat exchanger of the power block to avoid its damage, when it is detected by the corrosion monitoring devices that the salt has unacceptable high corrosivity, i.e., the structural materials in contact with the salt has an unacceptable high corrosion rate. In our currently published review paper [55], the corrosion monitoring and mitigation methods available in literature are reviewed and discussed in detail. Moreover, a research group at Queensland University of Technology also currently published a review on solubility, monitoring, and purification of impurities in molten salts including molten chlorides for energy storage in concentrated solar power plants [106]. In this work, the online corrosion monitoring and mitigation techniques available in literature, which have large application potential in CCS, are reviewed in the following subsections.



**Figure 11.** Concept of a corrosion control system (CCS) with different control locations in the molten chloride TES system (e.g., inlet and outlet of the hot salt tank). This CCS system mainly consists of online corrosion monitoring and mitigation parts.

#### **3.2.1.** Corrosion mitigation

To overcome the corrosion challenge, some salt pre-treatment methods (such as thermal salt purification [57], carbochlorination [107]) and online corrosion mitigation methods (such as salt purification via electrolysis [49], [108] and adding corrosion inhibitor [47]) to control salt corrosivity (see Figure 12). In [48], [57], [109], a promising method by adding Mg corrosion inhibitor is presented to effectively mitigate the corrosion of metallic materials, such as SS 310, Incoloy 800H and Hastelloy C276 in MgCl₂-KCl-NaCl molten salt under inert atmosphere. By adding Mg corrosion inhibitor, the corrosion rates of these commercial Cr-Fe-Ni alloys were reduced to ~10% compared to those in the molten salt without corrosion inhibitor [109]. In recent work [49], [108], we used the electrolysis for online purification of the molten MgCl₂-KCl-NaCl to reduce the concentration of the main corrosive impurity MgOH⁺. The purified molten chloride salt shows significantly reduced corrosiveness (corrosion rate of Incoloy 800H was reduced to ~7%). Currently, some important progress has been made under the projects of Gen3 CSP, for instance, the corrosion rates of SS316 and Hastelloy-N in purified MgCl₂-KCl (32-68 mol. %) mixture with low impurity level (~ 4 mg MgOH⁺/kg salt), which was purified through the carbochlorination method, are similar, and both below 20 µm/year under inert atmosphere at 700°C [107]. This reveals that the affordable SS316 could be used for molten chlorides even at high temperatures such as 700 °C, when the corrosive impurities in the melt are controlled below an acceptable level. Using molten MgCl₂-KCl-NaCl chlorides as TES material and stainless steels as main structural material, the TES cost could be reduced to <27 (kWh_{th} [9].

Compared to thermal salt purification, chemical salt purification using toxic gases and protective coatings on metallic structural materials, the methods of Mg metal corrosion inhibitor and salt purification using electrolysis are preferred in the corrosion control system, since they can be integrated with online corrosion monitoring for an automated corrosion. All the corrosion mitigation methods mentioned above are suggested to be tested under conditions close to real applications, e.g., in a test loop as described in Section 1.4.



**Figure 12.** Promising monitoring and mitigation techniques available for controlling the molten chloride salt corrosivity or corrosion of the structural materials, considering the impurity-driven corrosion mechanism.

## 3.2.2. Corrosion monitoring

The salt corrosivity can be monitored with different methods, e.g., Cyclic Voltammetry (CV) and Raman and Infrared Spectroscopy (RIS) to monitor the concentration of corrosive impurities, Open Circuit Potentiometry (OCP) to monitor the redox potential, Potentiodynamic Polarization (PDP), Electrochemical Impedance Spectroscopy (EIS) and Fiber-Optic Sensor (FOS) to online monitor the corrosion rate. In our previous work, several methods such as titration and CV [49], [99] have been investigated to measure or monitor the concentration of corrosive impurities such as MgOHCl in the MgCl₂-containing molten chlorides. Skar [110], our previous work [99] and Choi et al. [111] show the CV method to be a promising in-situ monitoring method for the MgOH⁺ impurity with the measurement limit of below 100 ppm in weight MgOH⁺. Our previous work [39] reveals that other impurities in the molten salt like corrosion products Cr, Fe ions can also be monitored by CV. Other methods like the Raman and Infrared Spectroscopy can be also used to measure or monitor the MgOH⁺ impurity [97]. Besides monitoring the impurities, the OCP was used to monitor the redox potential of molten MgCl₂-KCl-NaCl [111], while the PDP and FOS have been investigated to online monitor the corrosion rate of an alloy immersed in the molten chloride salt [39], [112]. As shown in Figure 13 from Choi, et al. [111], the not treated

molten MgCl₂-KCl-NaCl has a high open circuit potential of above -1.4 V vs. Cl⁻/Cl₂ (i.e., redox potential) due to corrosive impurities, which implies that the Cr-Fe-Ni alloys can be corroded in contact with the molten salt. By adding Mg, the open circuit potential (i.e., redox potential) of the molten MgCl₂-KCl-NaCl was significantly reduced to below -1.9 V vs. Cl⁻/Cl₂, i.e., the salt corrosivity was reduced. This confirms the corrosion inhibition of the Mg metal inhibitor [109]. When NaOH was added, the open circuit potential of the molten salt was increased to above -1.5 V vs. Cl⁻/Cl₂ due to increasing corrosive impurities like MgOH⁺, i.e., the salt corrosivity was increased. Currently, Sweeney, et al. (ORNL) developed a corrosion sensor based on a pressure-driven Fabry-Pérot cavity (FPC) and FOS [112]. Compared to the chemical post-analysis methods like titration, the in-situ monitoring methods can be developed to an online monitoring technique, which is integrated with the corrosion control methods mentioned above to build up an automated corrosion control system for the molten cloride TES system.



**Figure 13.** Open circuit potentiometry (OCP) to monitor the redox potential (i.e., corrosivity) of molten MgCl₂-KCl-NaCl [111].

#### 4. Summary and recommendations

The MgCl₂-KCl-NaCl salt mixture has shown to be a promising TES/HTF material in next-Gen CSP plants with large working temperature range of 420-800°C, excellent salt properties and low material cost of <0.35 USD/kg. By reviewing literature and comparison with the thermodynamic simulations, this work gives recommendations on the exact composition of the eutectic MgCl₂-KCl-NaCl salt mixture (47.1-22.7-30.2 mol. %) and its salt properties relevant for engineering this salt. The properties include melting temperature, vapor pressure, heat capacity, density, thermal conductivity and dynamic viscosity. **Table 8** summarizes the recommended values of these properties in the suggested working temperature range. These recommended values are very comparable to those experimental values summarized in the Gen3 CSP report of NREL [57] for a non-eutectic MgCl₂-KCl-NaCl salt mixture (37.51-40.92-21.57 mol. %) mixed with anhydrous carnallite and halite from salt industries. The main conclusions and suggested future work on the salt properties are:

- Discrepancy of available minimum melting temperature compositions is relatively high (about 2 mol.% for each salt compoment). This is mainly attributed to the impurities such as water in the salt mixture used in the experiment, particularly in the strongly hygroscopic MgCl₂.
- The minimum melting temperature of the MgCl₂-KCl-NaCl salt mixture is 385±1°C. Considering a safety margin for practical applications, the minimum working temperature is defined to be 420°C (more than 30°C higher than the minimum melting temperature).
- To define the maximum upper working temperature, the TGA + 3 wt. % mass loss method used for commercial molten nitrate salts needs improvement for molten chloride salts. It is suggested to consider other factors such as the salt vapor pressure, gas atmosphere over the salt (closed or purged type, and gas composition), salt corrosivity and structural materials.
- The maximum upper working temperature of 800 °C is suggested for the MgCl₂-KCl-NaCl salt mixture considering a low salt vapor pressure (this work below 10 kPa).

- The data of heat capacity, density and thermal conductivity for the MgCl₂-KCl-NaCl salt mixture available in literature and from the simulations agrees well, and has a low discrepancy of <10%.
- However, due to a high discrepancy of >10% of the available data, more experiments
  or improvement in experiments are suggested as future work to have accurate values
  of salt vapor pressure and dynamic viscosity for the recommended eutectic ternary
  mixture, particularly for salt vapor pressure at high temperatures and dynamic
  viscosity at temperatures close to the melting temperature.
- In future work, special attention on salt purity and sufficient salt purification is suggested to give in experimental determination of the exact eutectic composition and minimum melting temperature, also in measurements of other salt properties.
- DSC measurements considering salt purity and sufficient salt purification are suggested as future work to determine the more exact eutectic composition.

Besides the salt properties, the overview and progress on corrosion mechanisms and online corrosion control of metallic structural materials in contact with the molten MgCl₂-KCl-NaCl chloride salt are briefly reviewed and discussed. The main conclusions are:

- The corrosion is mainly driven by the impurities, mainly hydrolysis products like MgOHCl.
- The main corrosion behaviors of Cr-Fe-Ni alloys in molten chlorides include preferential depletion of the main alloying elements Cr and Fe in the alloys and intergranular corrosion.
- Nickel-based superalloys with higher Ni contents but also higher prices typically have better corrosion resistance in molten chloride salts than stainless steels. In order to use affordable alloys like stainless steels as structural materials, the corrosion control is essential for the molten chloride TES/HTF system.

The corrosion control system integrated into the molten chloride TES/HTF system is introduced, which is used to online control the molten chloride salt to a low level of corrosivity and protect the structural materials from corrosion during operation at high temperatures. The promising corrosion monitoring and mitigation techniques for the corrosion control system are suggested:

- Promising monitoring methods include cyclic voltammetry (CV) and Raman and Infrared Spectroscopy (RIS) to monitor the concentration of corrosive impurities in the molten salt, open circuit potentiometry (OCP) to monitor the redox potential of the molten salt, potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and fiber-optic sensor (FOS) to monitor the corrosion rate of the alloys.
- Promising mitigation methods include online salt purification via electrolysis and adding corrosion inhibitor like Mg metal to efficiently and affordably control salt corrosivity.

As future work in corrosion control, we recommend to build a test loop to develop and test these corrosion mitigation and monitoring techniques for the real molten chloride TES/HTF system with affordable structural materials such as stainless steels, which fulfill the requirements on a long lifetime in the next generation CSP. Moreover, based on the progress of materials research, the research on key devices like molten salt pump and exchanger is suggested to increase the technology readiness level (TRL) of this technology for commercial application.

**Table 8.** Summary of recommended working temperature range and values of salt properties for the eutectic MgCl₂-KCl-NaCl ternary mixture as TES/HTF materials in next-Gen CSP, compared to the data of a non-eutectic MgCl₂-KCl-NaCl studied by NREL.

Recommendation	Symbol	MgCl ₂ -KCl-NaCl		Remark on results in this
		This work	NREL [57]	work
Salt composition		Eutectic	Non-eutectic	Discrepancy of each salt
		47.1-22.7-30.2 mol. %	37.51-40.92-21.57 mol. %	component <2.6 mol.%,
		(56.5-21.3-22.2 wt.%)	(45.31-38.70-15.99 wt.%)	more exact composition
				will be determined by DSC
				measurements
Min. melting temperature (°C)	T _m	385	<400	Discrepancy <2°C
Min. working temperature (°C)	T _{min}	420	450	More than 30°C higher than
				T _m
Max. working temperature (°C)	T _{max}	800	700 (mainly limited by	$p_{v,max} < 10 \text{ kPa}$
			corrosion)	
Vapor pressure (kPa)	$p_v$	700-1000°C:	500-730°C:	More experiments are
		$3.1 \times 10^{-08} \cdot e^{0.0214 \cdot T(^{\circ}C)}$	$e^{11.246-9932.1/(T(^{\circ}C)+273.15)},$	recommended for more
		400-700°C: <0.1	standard deviation (SD):	accurate values due to large
		800°C: 1	$\sim 30\%$ -15% of the average	discrepancy of the available
			value (AV)	data (>10%)
			400-700°C: <2.9	
			800°C: 7.3	
Heat capacity (J/g °C)	$c_p$	1.10 (420-800 °C)	1.09-1.00 (450-700°C), SD:	Discrepancy <9% (about
			7%-8% of the AV	0.10 J/g °C)
Density $(g/cm^3)$	ρ	1.76-1.60 (420-800°C),	1.71-1.57 (450-700°C), SD:	Discrepancy <6% (about
		$1.94 - 4.2 \times 10^{-4} T(^{\circ}C)$	≤1% of the AV	$0.10 \text{ g/cm}^3$
Thermal conductivity (W/(m	$\lambda_l$	0.47-0.42 (420-800°C),	0.48-0.42 (450-700°C), SD:	Discrepancy <10% (about
°C))		0.53-1.32×10 ⁻⁴ · <i>T</i> (° <i>C</i> )	8%-12% of the AV	0.04 W/(m °C))
Dynamic viscosity (mPa s)	$\eta$	6.01-1.51 (420-800°C)	3.75-2.43 (450-700°C)	More accurate values are
		27.728 $e^{-0.00364 T(^{\circ}C)}$	$0.689e^{1224.73/(T(^{\circ}C)+273.15)}$	needed due to large data
			SD: 2%-6% of the AV	discrepancy (>10%)

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#### References

- M. Papaelias, L. Cheng, M. Kogia, A. Mohimi, V. Kappatos, C. Selcuk, et al. Inspection and structural health monitoring techniques for concentrated solar power plants. Renew. Energ. 85 (2016) 1178-1191.
- [2] S. Kuravi, J. Trahan, D.Y. Goswami, M.M. Rahman, E.K. Stefanakos. Thermal energy storage technologies and systems for concentrated solar power plants. Prog. Energ. Combust. 39 (2013) 285-319.
- [3] Market Report Series: Renewables 2018 Analysis and Forecasts to 2023. International Energy Agency (IEA), (2018).
- [4] L. Miró, E. Oró, D. Boer, L.F. Cabeza. Embodied energy in thermal energy storage (TES) systems for high temperature applications. Appl. Energy 137 (2015) 793-799.
- [5] L.F. Cabeza, C. Sole, A. Castell, E. Oro, A. Gil. Review of solar thermal storage techniques and associated heat transfer technologies. Proceedings of the IEEE 100 (2012) 525-538.
- [6] H. Zhang, J. Baeyens, G. Cáceres, J. Degrève, Y. Lv. Thermal energy storage: Recent developments and practical aspects. Prog. Energ. Combust. 53 (2016) 1-40.
- [7] G. Alva, Y. Lin, G. Fang. An overview of thermal energy storage systems. Energy 144 (2018) 341-378.
- [8] G. Alva, L. Liu, X. Huang, G. Fang. Thermal energy storage materials and systems for solar energy applications. Renew. Sustain. Energ. Rev. 68 (2017) 693-706.
- [9] M. Mehos, C. Turchi, J. Vidal, M. Wagner, Z. Ma, C. Ho, W. Kolb, C. Andraka, A. Kruizenga. Concentrated solar power Gen3 demonstration roadmap. National Renewable Energy Laboratory, (2017).
- [10] U. Pelay, L. Luo, Y. Fan, D. Stitou, M. Rood. Thermal energy storage systems for concentrated solar power plants. Renew. Sustain. Energ. Rev. 79 (2017) 82-100.
- [11] M. Liu, N.H.S. Tay, S. Bell, M. Belusko, R. Jacob, G. Will, et al. Review on concentrated solar power plants and new developments in high temperature thermal energy storage technologies. Renew. Sustain. Energ. Rev. 53 (2016) 1411-1432.
- [12] How CSP Works: Tower, Trough, Fresnel or Dish. SolarPaces, (2018).
- [13] P. Gauché, J. Rudman, M. Mabaso, W.A. Landman, T.W. von Backström, A.C. Brent. System value and progress of CSP. Sol. Energy 152 (2017) 106-139.

- [14] Y. Tian, C.Y. Zhao. A review of solar collectors and thermal energy storage in solar thermal applications. Appl. Energy 104 (2013) 538-553.
- [15] F. De Luca, V. Ferraro, V. Marinelli. On the performance of CSP oil-cooled plants, with and without heat storage in tanks of molten salts. Energy 83 (2015) 230-239.
- [16] S. Relloso, E. Delgado. Experience with molten salt thermal storage in a commercial parabolic trough plant. Andasol-1 commissioning and operation. Proceedings of 15th International SolarPACES Symposium (2009) 14-18.
- [17] U. Herrmann, D.W. Kearney. Survey of thermal energy storage for parabolic trough power plants. J. Sol. Energy Eng. 124 (2002) 145-152.
- [18] M. Liu, W. Saman, F. Bruno. Review on storage materials and thermal performance enhancement techniques for high temperature phase change thermal storage systems. Renew. Sustain. Energ. Rev. 16 (2012) 2118-2132.
- [19] K. Vignarooban, X. Xu, A. Arvay, K. Hsu, A.M. Kannan. Heat transfer fluids for concentrated solar power systems – A review. Appl. Energy 146 (2015) 383-396.
- [20] Desideri U, Campana PE. Analysis and comparison between a concentrated solar and a photovoltaic power plant. Appl. Energy 113 (2014) 422-433.
- [21] N. Kincaid, G. Mungas, N. Kramer, M. Wagner, G. Zhu. An optical performance comparison of three Concentrated solar power collector designs in linear Fresnel, parabolic trough, and central receiver. Appl. Energy 231 (2018) 1109-1121.
- [22] G. Morin, M. Karl, M. Mertins, M. Selig. Molten salt as a heat transfer fluid in a linear Fresnel collector – Commercial application backed by demonstration. Energy Procedia 69 (2015) 689-698.
- [23] R. Aringhoff, G. Brakmann, M. Geyer, S. Teske. Concentrated solar thermal power -Now. Amsterdam (Netherlands): Greenpeace International; 2005. p. 48.
- [24] M.R. Rodríguez-Sánchez, C. Marugan-Cruz, A. Acosta-Iborra, D. Santana. Comparison of simplified heat transfer models and CFD simulations for molten salt external receiver. Appl. Therm. Eng. 73 (2014) 993-1005.
- [25] M. Aneke, M. Wang. Energy storage technologies and real life applications A state of the art review. Appl. Energy 179 (2016) 350-377.
- [26] T. Wang, D. Mantha, R.G. Reddy. Novel high thermal stability LiF–Na₂CO₃–K₂CO₃ eutectic ternary system for thermal energy storage applications. Sol. Energy Mater. Sol. Cells 140 (2015) 366-375.
- [27] REN21. Renewables 2019 Global Status Report. (2019).
- [28] A.G. Fernández, J. Gomez-Vidal, E. Oró, A. Kruizenga, A. Solé, L.F. Cabeza. Mainstreaming commercial CSP systems: A technology review. Renew. Energ. 140 (2019 152-176.
- [29] A. Bonk, S. Sau, N. Uranga, M. Hernaiz, T. Bauer. Advanced heat transfer fluids for direct molten salt line-focusing CSP plants. Prog. Energ. Combust. 67 (2018) 69-87.
- [30] D. LeBlanc. Molten salt reactors: A new beginning for an old idea. Nucl. Eng. Des. 240 (2010) 1644-1656.

- [31] L. Maksoud, T. Bauer. Experimental investigation of chloride molten salts for thermal energy storage applications. 10th International Conference on Molten Salt Chemistry and Technology. Shenyang, China, (2015).
- [32] J. Wang, C.L. Liu. Temperature and composition dependences of shear viscosities for molten alkali metal chloride binary systems by molecular dynamics simulation. J. Mol. Liq. 273 (2019) 447-454.
- [33] C. Murphy, Y. Sun, W.J. Cole, G.J. Maclaurin, M. Mehos, C. Turchi. The potential role of concentrated solar power within the context of DOE's 2030 solar cost targets. National Renewable Energy Laboratory, UNITED STATES, (2019).
- [34] M.M. Kenisarin. High-temperature phase change materials for thermal energy storage. Renew. Sustain. Energ. Rev. 14 (2010) 955-970.
- [35] K. Wang, E. Molina, G. Dehghani, B. Xu, P. Li, Q. Hao, et al. Experimental investigation to the properties of eutectic salts by NaCl-KCl-ZnCl₂ for application as high temperature heat transfer fluids. Proceedings of the ASME 2014 8th International Conference on Energy Sustainability collocated with the ASME 2014 12th International Conference on Fuel Cell Science, Engineering and Technology. Volume 1, Boston, Massachusetts, UNITED STATES , (2014).
- [36] X. Wei, M. Song, Q. Peng, J. Ding, J. Yang. Quaternary chloride eutectic mixture for thermal energy storage at high temperature. Energy Procedia 75 (2015) 417-422.
- [37] P.D. Myers, D.Y. Goswami. Thermal energy storage using chloride salts and their eutectics. Appl. Therm. Eng. 109 (2016) 889-900.
- [38] S. Linsinger, T.J. Radtke, S. Ku. Entwicklung von niedrigschmelzenden Salzmischungen auf Basis von NaCl/KCl zur Anwendung in solarthermischen Kraftwerken (Development of Chloridic Molten Salt for use as Heat Transfer and Heat Storage Medium in Thermal Power Plants). Kali & Steinsalz 2013/3 (2013) 28-37.
- [39] W. Ding, A. Bonk, T. Bauer. Molten chloride salts for next generation CSP plants: Selection of promising chloride salts & study on corrosion of alloys in molten chloride salts. AIP Conference Proceedings 2126 (2019) 200014.
- [40] G. Mohan, M.B. Venkataraman, J. Coventry. Sensible energy storage options for Concentrated solar power plants working above 600 °C. Renew. Sustain. Energ. Rev. 107 (2019) 319-337.
- [41] X. Li, N. Li, W. Liu, Z. Tang, J. Wang. Unrevealing the thermophysical properties and microstructural evolution of MgCl2–NaCl–KCl eutectic: FPMD simulations and experimental measurements. Sol. Energy Mater. Sol. Cells 210 (2020) 110504.
- [42] J.C. Vidal, N. Klammer. Molten chloride technology pathway to meet the U.S. DOE sunshot initiative with Gen3 CSP. AIP Conference Proceedings 2126 (2019) 080006.
- [43] J.J. Nemecek, D.E. Simmons, T.A. Chubb. Demand sensitive energy storage in molten salts. Sol. Energy 20 (1978) 213-217.
- [44] D.F. Williams. Assessment of candidate molten salt coolants for the NGNP/NHI heat-transfer loop. ORNL, UNITED STATES, (2006).

- [45] J.W. Ambrosek. Molten chloride salts for heat transfer in nuclear systems. The University of Wisconsin Madison, ProQuest Dissertations Publishing, (2011).
- [46] G. Mohan, M. Venkataraman, J. Gomez-Vidal, J. Coventry. Assessment of a novel ternary eutectic chloride salt for next generation high-temperature sensible heat storage. Energ. Convers. Manage. 167 (2018) 156-164.
- [47] W. Ding, A. Bonk, T. Bauer. Corrosion behavior of metallic alloys in molten chloride salts for thermal energy storage in concentrated solar power plants: A review. Front. Chem. Sci. Eng. 12 (2018) 564-576.
- [48] B.L. Garcia-Diaz, L. Olson, M. Martinez-Rodriguez, R. Fuentes, H. Colon-Mercado, J. Gray, High temperature electrochemical engineering and clean energy systems. J. South Carol. Acad. Sci. 14 (1) (2016) (Article 4).
- [49] W. Ding, J: Gomez-Vidal, A. Bonk, T. Bauer. Molten chloride salts for next generation CSP plants: Electrolytical salt purification for reducing corrosive impurity level. Sol. Energy Mater. Sol. Cells 199 (2019) 8-15.
- [50] K.R. Robb, P.L. Mulligan, G.L. Yoder, K. Smith, J. Massengale. Facility to alleviate salt technology risks (FASTR): Preliminary design report with failure modes and effects analysis. Oak Ridge National Laboratory (ORNL), UNITED STATES, (2019).
- [51] C. Prieto, S. Fereres, F.J. Ruiz-Cabañas, A. Rodriguez-Sanchez, C. Montero. Carbonate molten salt solar thermal pilot facility: Plant design, commissioning and operation up to 700 °C. Renew. Energ. 151 (2020) 528-541.
- [52] C.W. Bale, E. Bélisle, P. Chartrand, S.A. Decterov, G. Eriksson, A.E. Gheribi, et al. FactSage thermochemical software and databases, 2010–2016. Calphad. 54 (2016) 35-53.
- [53] C. Villada, F. Jaramillo, J.G. Castaño, F. Echeverría, F. Bolívar. Design and development of nitrate-nitrite based molten salts for Concentrated solar power applications. Sol. Energy 188 (2019) 291-299.
- [54] S. Sau, A. Tizzoni, N. Corsaro, E. Veca, M. Navas, A. Martinez-Tarifa. Deliverable N. D15.1: Report on protocols for standardized testing procedures and data analysis criteria. SFERA II Project: Solar Facilities for the European Research Area, (2015).
- [55] W. Ding, T. Bauer. Progress in research and development of molten chloride salt technology for next generation concentrated solar power plants. Engineering. 7(3) (2021) 334-347.
- [56] X. Wang, J.D. Rincon, P. Li, Y. Zhao, J. Vidal. Thermophysical properties experimentally tested for NaCl-KCl-MgCl₂ eutectic molten salt as a next-generation high-temperature heat transfer fluids in concentrated solar power systems. J. Sol. Energy Eng. 143(4) (2021) 041005.
- [57] Y. Zhao. Molten chloride theromophysical properties, chemical optimization, and purification. National Renewable Energy Laboratory (NREL/TP-5500-78047), UNITED STATES, (2017).
- [58] Y. Li, X. Xu, X. Wang, P. Li, Q. Hao, B. Xiao. Survey and evaluation of equations for thermophysical properties of binary/ternary eutectic salts from NaCl, KCl, MgCl₂,

CaCl₂, ZnCl₂ for heat transfer and thermal storage fluids in CSP. Sol. Energy 152 (2017) 57-79.

- [59] C. Robelin, P. Chartrand, G. Eriksson. A density model for multicomponent liquids based on the modified quasichemical model: Application to the NaCl-KCl-MgCl₂-CaCl₂ system. Metall. Mater. Trans. B. 38 (2007) 869-879.
- [60] K. Scholich. Neues Jahrb. Mineral., Geol., Palaontol., Beil. 43 (1920) 251-262.
- [61] E. Jänecke. Über das Schmelz-und Erstarrungsbild des doppelt-ternären Systemes (K2 · Na2 · Mg)(Cl2 · SO4). Zeitschrift für anorganische Chemie. 261 (1950) 213-225.
- [62] N.P. Podlesnyak, A.I. Orekhova, E.N. Dieva. Izv. Vyssh. Uchebn. Zaved. Tsvet. Metall. 4 (1987) 105-106.
- [63] J.W. Raade, D. Padowitz. Development of molten salt heat transfer fluid with low melting point and high thermal stability. J. Sol. Energ. Eng. 133(3) (2011) 031013.
- [64] X. Xu, G. Dehghani, J. Ning, P. Li. Basic properties of eutectic chloride salts NaCl-KCl-ZnCl₂ and NaCl-KCl-MgCl₂ as HTFs and thermal storage media measured using simultaneous DSC-TGA. Sol. Energy 162 (2018) 431-441.
- [65] S. Polimeni, M. Binotti, L. Moretti, G. Manzolini. Comparison of sodium and KCl-MgCl₂ as heat transfer fluids in CSP solar tower with sCO₂ power cycles. Sol. Energy 162 (2018) 510-524.
- [66] L. Du, J. Ding, H. Tian, W. Wang, X. Wei, M. Song. Thermal properties and thermal stability of the ternary eutectic salt NaCl-CaCl₂-MgCl₂ used in high-temperature thermal energy storage process. Appl. Energy 204 (2017) 1225-1230.
- [67] L. Maksoud, T. Bauer. Experimental investigation of chloride molten salts for thermal energy storage applications. In: Proceedings of 10th International Conference on Molten Salt Chemistry and Technology, Shenyang, China, (2015), 273–280.
- [68] J. Kipouros, D.R. Sadoway, A Thermochemical Analysis of the Production of Anhydrous MgCl₂. J. Light Metals 1(2) (2001) 111–117.
- [69] X. Xu, X. Wang, P. Li, Y. Li, Q. Hao, B. Xiao, et al. Experimental test of properties of KCl–MgCl₂ eutectic molten salt for heat transfer and thermal storage fluid in concentrated solar power systems. J. Sol. Energ. Eng. 140(5) (2018) 051011.
- [70] E.F. Fiock, W.H. Rodebush. The vapor pressures and thermal properties of potassium and some alkali halides. JACS 48 (1926) 2522-2528.
- [71] G.J. Janz, R.P.T. Tomkins, C.B. Allen, J.R. Downey, G.L. Garner, U. Krebs, et al. Molten salts: Volume 4, part 2, chlorides and mixtures—electrical conductance, density, dynamic viscosity, and surface tension data. J. Phys. Chem. Ref. Data 4 (1975) 871-1178.
- [72] K. Vignarooban, X. Xu, K. Wang, E.E. Molina, P. Li, D. Gervasio, et al. Vapor pressure and corrosivity of ternary metal-chloride molten-salt based heat transfer fluids for use in concentrated solar power systems. Appl. Energy 159 (2015) 206-213.
- [73] J.C. Gomez-Vidal, A.G. Fernandez, R. Tirawat, C. Turchi, W. Huddleston. Corrosion resistance of alumina-forming alloys against molten chlorides for energy production. I: Pre-oxidation treatment and isothermal corrosion tests. Sol. Energy Mater. Sol. Cells 166 (2017) 222-233.

- [74] ASTM E1269-11. Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry. West Conshohocken, PA: ASTM International (2011).
- [75] G.J. Janz, R.P.T. Tomkins. Physical properties data compilations relevant to energy storage. IV. molten salts: data on additional single and multi-component salt systems. National Bureau of Standards (1981).
- [76] A.D. Pelton, P. Chartrand. Thermodynamic evaluation and optimization of the LiCl-NaCl-KCl-RbCl-CsCl-MgCl₂-CaCl₂ system using the modified quasi-chemical model. Metall. Mater. Trans. A 32 (2001) 1361-1383.
- [77] A.A. Redkin, Y.P. Zaikov, I.V. Korzun, O.G. Reznitskikh, T.V. Yaroslavtseva, S.I. Kumkov. Heat capacity of molten halides. J Phys Chem B. 119 (2015) 509-512.
- [78] D.F. Williams. Assessment of candidate molten salt coolants for the advanced high temperature reactor (AHTR). ORNL, UNITED STATES, (2006).
- [79] G.J. Janz, C.B. Allen, N.P. Bansal, R.M. Murphy, R.P.T. Tomkins. Physical properties data compilations relevant to energy storage. II. Molten salts: data on single and multi-component salt systems. UNITED STATES, 1979.
- [80] G.J. Janz. I.B Density. In: G.J. Janz, editor. Molten salts handbook. Academic Press; 1967. p. 39-51.
- [81] R. Serrano-López, J. Fradera, S. Cuesta-López. Molten salts database for energy applications. Chem. Eng. Process. Process Intensification 73 (2013) 87-102.
- [82] Y. Marcus. Volumetric behavior of molten salts. Thermochim. Acta 559 (2013) 111-116.
- [83] A. Palacios, L. Cong, M.E. Navarro, Y. Ding, C. Barreneche. Thermal conductivity measurement techniques for characterizing thermal energy storage materials – A review. Renew. Sustain. Energ. Rev. 108 (2019) 32-52.
- [84] A.E. Gheribi, J.A. Torres, P. Chartrand. Recommended values for the thermal conductivity of molten salts between the melting and boiling points. Sol. Energy Mater. Sol. Cells 126 (2014) 11-25.
- [85] J.J. Healy, J.J. de Groot, J. Kestin. The theory of the transient hot-wire method for measuring thermal conductivity. Physica B+C. 82 (1976) 392-408.
- [86] H. Tian, W. Wang, J. Ding, X. Wei, M. Song, J. Yang. Thermal conductivities and characteristics of ternary eutectic chloride/expanded graphite thermal energy storage composites. Appl. Energy 148 (2015) 87-92.
- [87] A.E. Gheribi, P. Chartrand. Thermal conductivity of molten salt mixtures: Theoretical model supported by equilibrium molecular dynamics simulations. J. Chem. Phys. 144 (2016) 084506.
- [88] C.D. Chliatzou, M.J. Assael, K.D. Antoniadis, M.L. Huber, W.A. Wakeham. Reference correlations for the thermal conductivity of 13 inorganic molten salts. J. Phys. Chem. Ref. Data. 47 (2018) 033104.
- [89] Y. Peng, R.G. Reddy. Density, dynamic viscosity, vapor pressure and thermal conductivity of MgCl₂+Mg salts. Advances in Molten Slags, Fluxes, and Salts:

Proceedings of the 10th International Conference on Molten Slags, Fluxes and Salts, (2016).

- [90] Y. Nagasaka, N. Nakazawa, A. Nagashima. Experimental determination of the thermal diffusivity of molten alkali halides by the forced Rayleigh scattering method. I. Molten LiCl, NaCl, KCl, RbCl, and CsCl. Int. J. Thermophys. 13 (1992) 555-574.
- [91] M.Z. Hossain, M.H. Kassaee, S. Jeter, A.S. Teja. A new model for the thermal conductivity of molten salts. Int. J. Thermophys. 35 (2014) 246-255.
- [92] N. Ren, Y. Wu, C. Ma, L. Sang. Preparation and thermal properties of quaternary mixed nitrate with low melting point. Sol. Energy Mater. Sol. Cells 127 (2014) 6-13.
- [93] W. Brockner, K. Toerklep, H.A. Oeye. Dynamic viscosity of molten alkali chlorides. J. Chem. Eng. Data. 26 (1981) 250-253.
- [94] J.W. McMurray, T.M. Besmann, J. Ard, B. Fitzpatrick, M. Piro, J. Jerden, et al. Multiphysics simulations for molten salt reactor evaluation: Chemistry modeling and database development. United States, (2018).
- [95] K. Sridharan, T.R. Allen, Corrosion in molten salts (Chapter 12), Editor(s): F. Lantelme, H. Groult, Molten Salts Chemistry, Elsevier, 2013, pp. 241-267.
- [96] W. Ding, H. Shi, Y. Xiu, A. Bonk, A. Weisenburger, A. Jianu, et al. Hot corrosion behavior of commercial alloys in thermal energy storage material of molten MgCl₂/KCl/NaCl under inert atmosphere. Sol. Energy Mater. Sol. Cells 184 (2018) 22-30.
- [97] H. Sun, J. Wang, Z. Tang, Y. Liu, C. Wang. Assessment of effects of Mg treatment on corrosivity of molten NaCl-KCl-MgCl₂ salt with Raman and Infrared spectra. Corr. Sci. 164 (2020) 108350.
- [98] Y. Zhao, J. Vidal. Potential scalability of a cost-effective purification method for MgCl₂-containing salts for next-generation concentrated solar power technologies. Sol. Energy Mater. Sol. Cells 215 (2020) 110663.
- [99] W. Ding, A. Bonk, J. Gussone, T. Bauer. Electrochemical measurement of corrosive impurities in molten chlorides for thermal energy storage. J. Energy Storage 15 (2018) 408-414.
- [100] B. Liu, X. Wei, W. Wang, J. Lu, J. Ding. Corrosion behavior of Ni based alloys in molten NaCl-CaCl₂-MgCl₂ eutectic salt for concentrating solar power. Sol. Energy Mater. Sol. Cells 170 (2017) 77–86.
- [101] J.W. Wang, H.X. Zhou, C.Z. Zhang, W.N. Liu, B.Y. Zhao. Influence of MgCl₂ content on corrosion behavior of GH1140 in molten NaCl-MgCl₂ as thermal storage medium. Sol. Energy Mater. Sol. Cells 179 (2018) 194–201.
- [102] J.C. Gomez-Vidal, R. Tirawat. Corrosion of alloys in a chloride molten salt (NaCl-LiCl) for solar thermal technologies. Sol. Energy Mater. Sol. Cells 157 (2016) 234–244.
- [103] J.W. Wang, C.Z. Zhang, Z.H. Li, H.X. Zhou, J.X. He, J.C. Yu. Corrosion behavior of nickel-based superalloys in thermal storage medium of molten eutectic NaCl-MgCl₂ in atmosphere. Sol. Energy Mater. Sol. Cells 164 (2017) 146–155.

- [104] W. Ren, K. Robb. Alloy selection and C-276 code design value extension for advanced molten salt technology test facilities experimentation. ASME 2020 Pressure Vessels & Piping Conference, (2020).
- [105] J.C. Gomez-Vidal, A.G. Fernandez, R. Tirawat, C. Turchi, W. Huddleston. Corrosion resistance of alumina forming alloys against molten chlorides for energy production. II: Electrochemical impedance spectroscopy under thermal cycling conditions. Sol. Energy Mater. Sol. Cells 166 (2017) 234-245.
- [106] T.C. Ong, M. Sarvghad, K. Lippiatt, L. Griggs, H. Ryan, G. Will, T.A. Steinberg. Review of the solubility, monitoring, and purification of impurities in molten salts for energy storage in concentrated solar power plants. Renew. Sustain. Energ. Rev. 131 (2020) 110006,
- [107] J.M. Kurley, P.W. Halstenberg, A. McAlister, S. Raiman, S. Dai, R.T. Mayes. Enabling chloride salts for thermal energy storage: implications of salt purity. RSC Advances 9(44) (2019) 25602–8.
- [108] W. Ding, F. Yang, A. Bonk, T. Bauer. Molten chloride salts for high-temperature thermal energy storage: Continuous electrolytic salt purification with two Mg-electrodes and alternating voltage for corrosion control. Sol. Energy Mater. Sol. Cells 223 (2021) 110979.
- [109] W. Ding, H. Shi, A. Jianu, Y. Xiu, A. Bonk, A. Weisenburger, et al. Molten chloride salts for next generation concentrated solar power plants: Mitigation strategies against corrosion of structural materials. Sol. Energy Mater. Sol. Cells 193 (2019) 298-313.
- [110] R.A. Skar. Chemical and electrochemical characterisation of Oxide/Hydroxide impurities in the electrolyte for magnesium production. Norwegian University of Science and Technology (NTNU), (2001).
- [111] S. Choi, N.E. Orabona, O.R. Dale, P. Okabe, C. Inman, M.F. Simpson. Effect of Mg dissolution on cyclic voltammetry and open circuit potentiometry of molten MgCl₂–KCl– NaCl candidate heat transfer fluid for concentrated solar power. Sol. Energy Mater. Sol. Cells 202 (2019) 110087.
- [112] D. C. Sweeney, A. M. Schrell and C. M. Petrie. Pressure-driven fiber-optic sensor for online corrosion monitoring. IEEE Trans. Instrum. Meas. 70 (2021) Art. no. 9510310 1-10.