



Molten carbonate salts for advanced solar thermal energy power plants: Cover gas effect on fluid thermal stability



Sonia Fereres^{a,*}, Cristina Prieto^{a,b}, Pau Giménez-Gavarrrell^b, Alfonso Rodríguez^a, Pedro Enrique Sánchez-Jiménez^c, Luis A. Pérez-Maqueda^c

^a Abengoa, C/ Energía Solar 1, 41014 Sevilla, Spain

^b Dept. Ingeniería Energética, ETSI Universidad de Sevilla, Spain

^c Instituto de Ciencia de Materiales de Sevilla, C.S.I.C.-Universidad de Sevilla, C. Américo Vespucio no. 49, 41092 Sevilla, Spain

ARTICLE INFO

Keywords:

Molten salts
Carbonates
Thermal energy storage
Heat transfer fluid
Thermal stability
Decomposition

ABSTRACT

The eutectic mixture $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ is investigated as a high temperature heat transfer fluid and storage medium alternative for molten salt solar thermal power plants. This salt has an operating temperature range of 400–700 °C, enabling the use of higher temperature/efficiency power cycles. However, this carbonate mixture is known to thermally decompose in air. This study evaluates the thermal stability of the salt mixture under different cover gases: air, nitrogen, carbon dioxide, and an 80/20 carbon dioxide/air mixture. Initial characterization is performed through thermogravimetric analysis (TGA), followed by larger scale testing in a custom-made reactor to simulate conditions closer to its practical use. The results show improved thermal stability with a CO_2 atmosphere. The decomposition kinetics under different cover gases are estimated from TGA data. However, larger-scale, longer duration experiments show much slower decomposition rates compared to the classical TGA approach. These findings indicate that the main contribution to mass loss in TGA is due to vaporization rather than thermal decomposition. Thus, a proper evaluation of the molten salt's thermal stability can only be obtained from reactor experiments where vaporization is inhibited. Very long induction periods (of the order of days) are observed, suggesting that the kinetic decomposition mechanism is a nucleation and growth type. Other considerations for future plants incorporating these high temperature salts are discussed.

1. Introduction

The competitive advantage of Solar Thermal Energy (STE) plants is the capability of overcoming the natural intermittencies of the sun with Thermal Energy Storage (TES) to produce electricity continuously beyond daylight hours. Current STE power plants use nitrate molten salts as their storage media and, depending of the technology, also as their Heat Transfer Fluid (HTF) in Molten Salt Tower (MST) designs. There is a constant search in the engineering community for novel HTF and TES media working at higher temperatures to be used with advanced thermodynamic cycles to improve the overall solar-to-electric conversion efficiency [1–3]. Novel MST plants with higher temperature HTF could feed both subcritical and supercritical cycles increasing the efficiency of current MST with nitrates [4].

Traditional nitrate MST power plants work in the 240–565 °C temperature range using ‘solar salt’, a 60–40%wt mixture of NaNO_3 and KNO_3 [5]. Through appropriate mitigation strategies (on the container materials and operation procedures) their upper temperature limit

could be extended by roughly 50 °C above the classical practical values. However, reaching maximum operating temperatures above 700 °C is only possible with new salt compositions. Carbonates are the natural first option to explore higher temperature molten salts, since their corrosion behavior is notoriously better than other high temperature molten salts such as hydroxides, fluorides or sulfides [6].

The ternary carbonate mixture, $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (LiNaK carbonate) has been previously proposed in the literature as a potential candidate for high temperature STE applications despite its high melting temperature. Wu et al. [6] investigated over thirty-six different compositions of LiNaK carbonate salts for sensible heat storage in STE, looking to replace molten nitrates with peak salt temperatures from 565 °C to higher values between 700 °C and 850 °C, finding melting temperatures around 400 °C. Table 1 summarizes the literature reported data for a LiNaK carbonate mixture compared to the baseline solar salt. The evaluation criteria for new salt compositions focuses on their melting point, energetic cost, thermal stability, and corrosion compatibility. A lower melting point (T_m) is desirable, as it reduces the risk of

* Corresponding author.

E-mail address: sonia.fereres@abengoa.com (S. Fereres).

Table 1

Candidate salt properties for high temperature MST: “solar salt” compared to the salt mixture presented in this study.

Fluid	Composition (wt%)			Cp (J/g-K)	Tm (°C)	Td (°C)	Energetic Cost (\$/kWh)	Refs.
Solar salt NaNO ₃ -KNO ₃	60	40	–	1.5	240	600	8.8	[7]
Ternary carbonate Li ₂ CO ₃ -Na ₂ CO ₃ -K ₂ CO ₃	32	33	35	1.7	397	662	26.1	[8–10]

frozen blockages in pipes. A higher decomposition temperature or thermal stability (Td) increases the operational temperature, with possible coupling to higher efficiency thermodynamic cycles working at higher temperatures. The energetic cost is calculated with the material's specific heat capacity over the operational temperature range.

The main handicaps associated with using this carbonate salt as a HTF in advanced MST plants are:

- 1) High melting point in the range of 400 °C [7,8]. In practice, the working temperature for carbonate salts should be even slightly higher to avoid solidification risk. However, mixing additives such as NaNO₃, KCl, or NaOH has been proposed to reduce the melting point of LiNaK carbonates by as much as 75 °C [8,11].
- 2) High cost (2.4\$/kg). Despite having a higher specific heat and a higher operating temperature range than solar salt, its increased energetic cost is essentially due to the cost of lithium carbonate (6\$/kg).
- 3) Low thermal stability in air [9].
- 4) Corrosion performance of this mixture at temperatures near or above 700 °C is relatively unknown. Recent publications are analyzing container materials for this salt to be used in solar thermal power plants [12,13].

The viscosity of commercial grade LiNaK carbonate is nearly 40 mPa·s at 400 °C (just above its melting point) and 6.2 mPa·s at 700 °C, following an exponential dependency [14]. This viscosity is comparable yet still higher than the viscosity of commercial solar salt, which has a viscosity of approximately 4.6 mPa·s at 250 °C (above its melting point) and 1.8 mPa·s at 400 °C [14].

It is known that carbonate salts are unstable in air [8,9], but they can be stabilized in a carbon dioxide atmosphere by establishing an equilibrium with the CO₂ gas. LiNaK carbonates are being widely investigated for other low carbon or carbon sequestration energy related technologies. Waste disposal, gas cleaning processes, CO₂ concentration and fuel cells are some of the most common applications [6]. For example, Deng et al. [15], investigated the carbonation of Li₂O in this ternary carbonate mixture for CO₂ capture and electrochemical conversion via electrolysis with molten salts. Others, such as Ren et al. [16] have recently synthesized carbon nanofibers by electrolysis of the CO₂ dissolved in Li₂CO₃ molten carbonates. In all these cases, the molten carbonate is in certain equilibrium with dissolved atmospheric CO₂. Thus, it should not come as a surprise that gaseous CO₂ can stabilize this molten salt.

Olivares et al. [9] investigated the thermal stability of the LiNaK (32.1–33.4–34.5 wt%) mixture under three different cover gases: CO₂, argon, and air using conventional thermogravimetric analysis. The cover gas was found to have very little effect on the melting temperatures, which were between 400 and 405 °C. However, the onset temperature of the decomposition reaction did change significantly with cover gas, reaching values of 601 °C, 715 °C, and 1000 °C with air, argon, and CO₂ respectively. The main objective of the present study is to quantify the thermal decomposition of ternary carbonates under conditions similar to those in a MST plant, studying the effect of different cover gases (air, nitrogen, carbon dioxide) and evaluating if an air leak in a CO₂ tank is an assumable risk. Thus, the LiNaK carbonate salt is also tested with cover gas mixtures of different CO₂ + air proportions comparing it to its behavior under pure CO₂ atmospheres.

Thermogravimetric analysis (TGA) experiments provide a good first

approach to understand the thermal stability of new salt mixtures. In these experiments, a small sample of the salt is heated in an open crucible at ambient pressure with overflow of the cover gas to measure the mass evolution with time and temperature. These tests are usually employed to estimate the kinetics of the thermal decomposition reactions and, from there, estimate a reliable maximum operation temperature for a given process. However, they are not very representative of the actual working conditions in a molten salt TES tank in a solar plant, which operates with several tones of salt over 10–15 years. Consequently, the TGA results presented here are complemented with experiments performed with more relevant, custom-built tests. Larger size samples over longer duration tests are designed to evaluate the salt mixture behavior under a static atmosphere avoiding mass loss due to evaporation and cover gas flow renewal inside the TGA equipment. Also, longer duration tests allow the development of slower decomposition reactions appearing over long term high temperature exposure. To the best of the authors' knowledge, it is the first time that the limitations from standard laboratory scale TGA for molten carbonate salts systems are compared with long term decomposition tests, indicating important implications in practice.

A detailed characterization of this ternary carbonate mixture has been carried out to assess its performance in a large scale pre-commercial demonstrator. The following properties have been analyzed: a) heat capacity, heat of fusion and melting point, and b) thermal stability and cover gas dependency in both a standard commercial TGA equipment and in a large-scale custom-made reactor. These results lead the path for new engineering considerations for future MST and other energy related systems using molten carbonates.

2. Materials and methods

The ternary eutectic carbonate salt (Li₂CO₃-Na₂CO₃-K₂CO₃ (43.5–31.5–25 mol%)) was prepared using technical grade Li₂CO₃, Na₂CO₃ and K₂CO₃ (99.95% purity by Panreac Química S.L.U., Barcelona, Spain). The salt mixture was weighed dry, melted in an oven at 450 °C, and grinded in a manual mortar to ensure a homogenous powder mixture. This mixing procedure was compared to dissolving the dry components in the appropriate proportion in water in a glass vial, sonicating for 200 min, and evaporating the solvent water over a hot plate at 150 °C inside a laboratory hood for 5 h to obtain a powder form salt mixture following the process described in detail in [17].

2.1. Differential scanning calorimeter

A Q2000 Differential Scanning Calorimeter (DSC) from TA Instruments is used to measure the melting point, latent heat and specific heat capacity of the LiNaK carbonate. The calibration procedure is performed by using the melting temperatures and latent heat of standard certified reference materials (In, Zn). Salt samples weighing 7–12 mg are introduced in Tzero standard aluminum crucibles.

The melting temperature and latent heat are determined using a standard linear DSC procedure at a heating rate of 5 °C/min, pre-melting the samples to ensure a good contact between the sample and the crucible. Good contact between the bottom of the crucible and the sample is necessary for reliable results [18]. This first pre-melt was performed at 20 °C/min from 80 °C to 560 °C and discarded for the analysis. The samples are kept isothermally for 2 min, then cooled down to 300 °C at the same rate, followed by another isothermal segment.

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