

Oak Ridge National Laboratory M4FT:18OR110102182-Develop a new composite molten salt fluid exhibiting an increased heat capacity of 10%



Dmitriy Dolzhnikov
Sheng Dai

October 5, 2018

Approved for Public Release
Distribution is Unlimited

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via US Department of Energy (DOE) SciTech Connect.

Website www.osti.gov

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900
E-mail info@ntis.gov
Website <http://classic.ntis.gov/>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange representatives, and International Nuclear Information System representatives from the following source:

Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@osti.gov
Website <http://www.osti.gov/contact.html>

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Chemical Sciences Division

M4FT:18OR110102182 - Develop a new composite molten salt fluid exhibiting an increased heat capacity of 10 %

Author(s)

**Dmitriy Dolzhnikov
Sheng Dai**

Date Published:
October 5, 2018

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

CONTENTS.....	iii
Abstract.....	1
Experimental.....	1
Results.....	2
Conclusions.....	6
Acknowledgement	6

ABSTRACT

We were able to purify as-bought MgCl_2 by vacuum distillation and KCl by high-temperature drying. It allowed us to remove MgO and H_2O contamination and use pure salts in the heat capacity experiments. We observed that various carbon-based particles in the molten salt glow red even at temperatures as low as 800°C . We used that property to qualitatively analyze the dispersion of particles in the salt. It is clear that hollow carbon spheres disperse in the molten salt to a higher degree than any other particles. Nanodiamonds and onion-like carbon nanoparticle are heavier than the salt and without any favorable interaction they just sediment. Hollow carbon spheres on the other hand allow the salt into the cavity, leading to density-matching and their subsequent dispersion. Preliminary heat capacity measurements are being performed by Linseis Inc. and encountered unexpected delays. The measurement results will be shown later.

Molten salts have seen revival of interest in various applications. Their viscosity, stability and heat capacity make them suitable materials in energy production and storage. Specifically, chloride-based salts are an attractive medium for concentrated solar power and nuclear reactors. Unlike their fluoride counterparts, they are cheaper and create less hazardous environment. Chloride molten salts also have wider working temperature ranges with higher maximum temperatures than nitrates and carbonates. However, fluoride and oxygen-based salt technologies are well established and that brings inertia into switching to chlorides. A way to make chlorides even more attractive is to improve their heat capacity, heat transfer and working temperature range. It was suggested and shown that addition of nanoparticles to carbonate and nitrate based molten salts can alter those properties. In this work, we are investigating the addition of carbon-based nanoparticles to the magnesium chloride based molten salts and its effect on thermal properties of said salts.

EXPERIMENTAL

Magnesium chloride, due to its hygroscopic nature, was purified by distillation and kept in an oxygen- and moisture-free glovebox. Distillation was done under vacuum at 800°C in a Watlow ceramic fiber heater. Potassium and sodium chlorides were purified by drying at elevated temperatures. Carbon particles were used as received.

The scheme of the distillation setup is shown in figure 1B. MgCl_2 is loaded through a long funnel to deliver the salt directly into the bottom part of the tube bypassing the top, cold zone. The tube is connected to a Schlenk line and evacuated. The bottom part of the tube then heated in a furnace and salt sublimates in the cold zone of the tube. After no more salt evaporates, the heating is stopped, and the cooled setup is taken into the glovebox to unload purified salt. The scheme of the distillation setup is shown in figure 1B. MgCl_2 is loaded through a long funnel to deliver the salt directly into the bottom part of the tube bypassing the top, cold zone. The tube is connected to a Schlenk line and evacuated. The bottom part of the tube then heated in a furnace and salt sublimates

in the cold zone of the tube. After no more salt evaporates, the heating is stopped, and the cooled setup is taken into the glovebox to unload purified salt.

In a standard experiment, 2-5 mg of carbon-based particles were loaded into a quartz tube and sealed with a valve with two ACE threads: one connecting to the tube and the other to the Schlenk line to establish air-free conditions. After air was evacuated, the sealed tube was taken into the glovebox and 1 g of salt was added to it. The salt composition included pure MgCl_2 , MgCl_2 and KCl (with 60 or 30 mol % of MgCl_2) mixtures, as well as MgCl_2 and NaCl (with 30 mol % MgCl_2) mixtures. The tube was then heated to 800 °C and the molten salt/carbon mixture was visually examined. After 2 hours, the salt was cooled down and transferred into the glovebox to be used in further heat capacity and melting point analysis.

Scanning transmission electron microscopy (STEM) images were obtained with a Hitachi HD-2000 instrument operating at an accelerating voltage of 200 kV. Samples were dispersed on a lacey carbon grid prior to imaging. The particles were imaged in SEM, TEM and dark contrast mode.

RESULTS

Magnesium chloride is an extremely hygroscopic salt and must be kept in a dry environment. As bought truly anhydrous MgCl_2 is very expensive and hardly available due to challenges with production and storage. It was decided to buy readily available MgCl_2 and dry it ahead of time as needed for experiments. On a smaller scale it is feasible to dry MgCl_2 , and remove MgO impurity at the same time, by distillation. Magnesium chloride's vapor pressure is relatively high at temperatures slightly above melting (Fig. 1A). That is not the case for MgO , making vacuum distillation a great way to separate the two.

After distillation of MgCl_2 there is a significant amount of contaminant left behind. It is not surprising and does not only depend on the initial amount of MgO contaminant in the salt but also the amount of water. Moisture is important because of the mechanism by which MgCl_2 losses water. At room temperature, as-bought MgCl_2 that has not been properly dried is usually present in the form hexahydrate: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. With increasing temperature, the hexahydrate loses water until it forms the monohydrate $\text{MgCl}_2 \cdot \text{H}_2\text{O}$. Decomposition of the monohydrate is accompanied by hydrolysis and formation of MgOHCl that at higher temperatures decomposes to MgO and HCl .

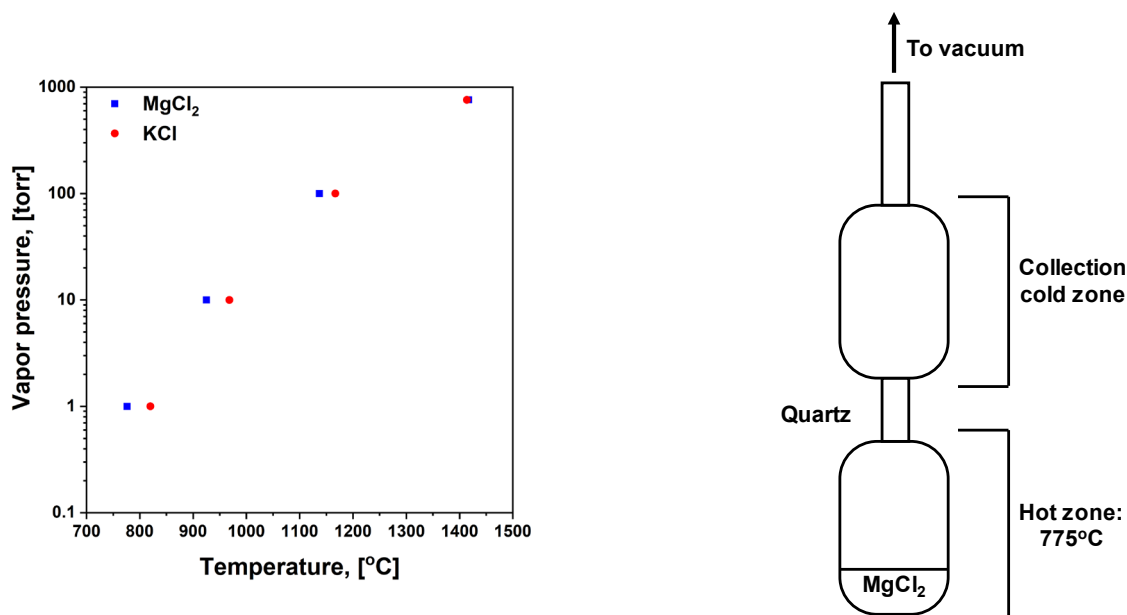


Figure 1. (A) Temperature dependence of MgCl_2 (squares) and KCl (circles) vapor pressure. (B) The distillation setup.

In principle distillation would also work for KCl since its vapor pressure is on par with MgCl_2 (Fig. 1A). However, we choose to dry it at lower temperatures. Water removal still occurs, but there is no oxide formation to contaminate dry salt.

Between experiments dried salts are stored in the glovebox. In the glovebox, we load carbon-based particles first and then load the salt, because most of carbon-based particles used here are less dense than the salt we are trying to disperse them in. Various particles were used in the experiments (Table 1)

Table 1. Results of suspending carbon-based particles in molten salts.

Salts/particles	HCS (100nm wall)		HCS (20nm wall)		Nanodiamond	Onion-like nanoparticles	OLC/MnO _x	MWNT-OH	HCS/TiC
	Ar	Vacuum	Ar	Vacuum					
MgCl_2	Floats	Disperses	Disperses	Disperses(+)	Sinks	Sinks	Slight mixing	Large clusters	Disperses(-)
$\text{KCl}(70\text{mol}\%)+\text{MgCl}_2$	No mixing	No mixing	No mixing	No mixing		No mixing	Cloudy with ppt		
$\text{KCl}(40\text{mol}\%)+\text{MgCl}_2$	Floats	Disperses(-)	Floats	Disperses		Sinks			
$\text{NaCl}(70\text{mol}\%)+\text{MgCl}_2$			No mixing	No mixing					

We observed that carbon particles turned bright red in the furnace (Figure 3) and slowly turned black, when they were removed from the furnace for inspection. The color change is due to black

body radiation of the particles that had higher local temperature than the salt. This color change works as a qualitative tool for seeing if particles are dispersed in the salt. The best dispersion of the carbon particles in the salt mixture was achieved with hollow carbon spheres (HCS). Applying vacuum to the molten salts with HCS particles seemed to increase the number of dispersed particles. Other particles either did not disperse in the salt or reacted with it like onion-like carbon (OLC)/ MnO_x particles did (figure 3).

We used HCS of various wall thickness (20-200 nm) for our experiments (Figure 2). After their initial success in MgCl_2 we suspended HCS particles in the mixtures of MgCl_2 and KCl (or NaCl) (Figure 4). Addition of KCl reduced the concentration of particles in the salt mix under argon atmosphere. However, applying vacuum helped disperse more particles. It should be noted that mixtures with excess of KCl had lower concentration of particles, even after evacuation. The same trend was observed in the mixtures with NaCl, which indicates that the dispersivity is dependent on the acidity of the salt and not ionic size of cations in the molten salt.

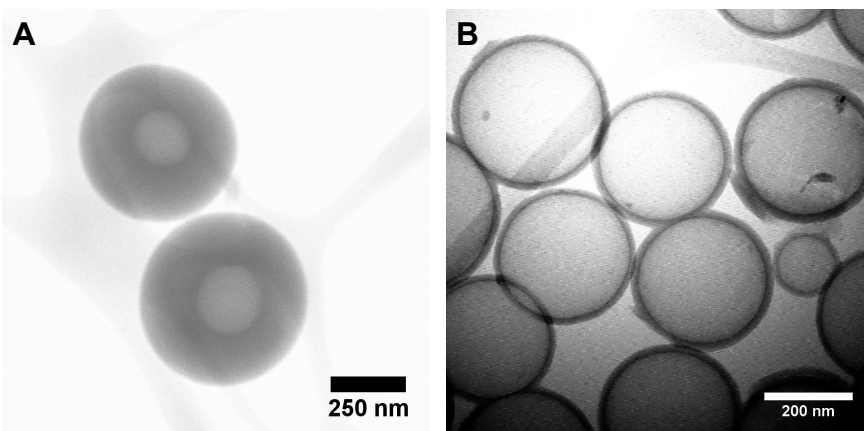


Figure 2. TEM images of HCS particles

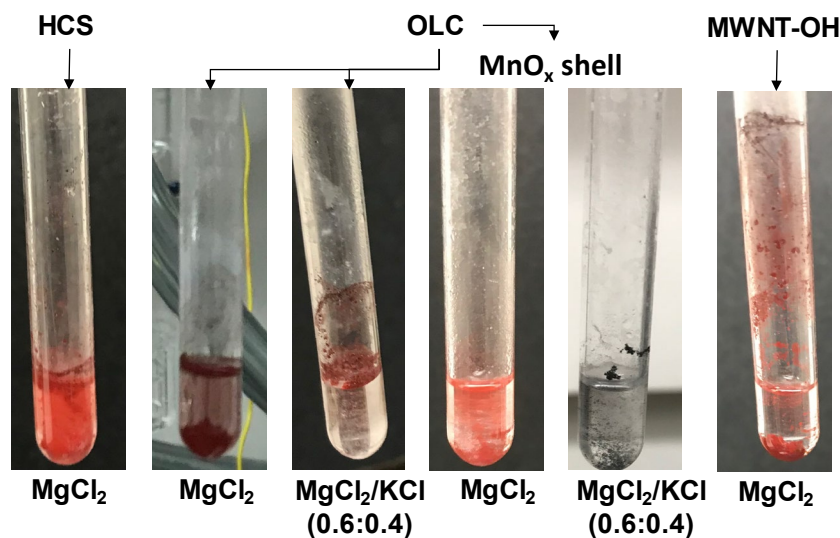


Figure 3. Various carbon particles in chloride salt mixtures. HCS = Hollow Carbon Spheres, OLC = Onion-Like Carbon particles, MWNT-OH = Multi-Wall NanoTubes functionalized with hydroxyl groups.

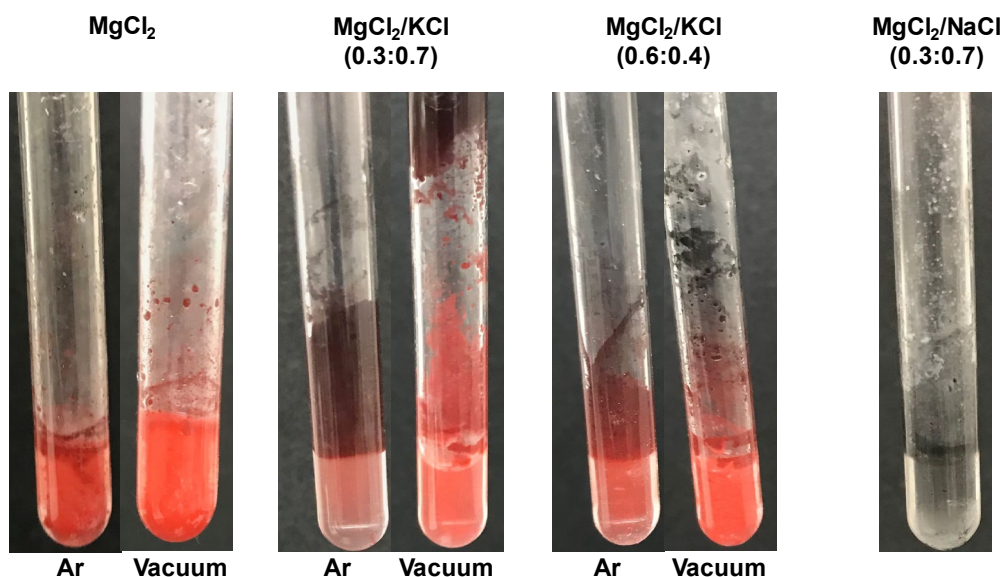


Figure 4. Thin-walled (20 nm) HCS in various MgCl_2 -based salt mixtures.

We suggest that particle suspension improves after applying vacuum due to salt diffusion into particles after atmosphere removal. We attempted to image the particles after suspending them in the salt. For that we had to remove the salt by dissolving it in water. That process led to full salt dissolution from outside and inside thin-walled particles. However, we had success with thick-wall particles (figure 5). Some of the particles retained MgCl_2 in them even after washing with water. From figure 5A we can see darker core of the particle than was visible before (figure 2A). Bright field imaging (figure 5B) shows a brighter center than the shell. Both point towards the core

containing MgCl_2 . We will study MgCl_2 , KCl:MgCl_2 (40:60 mol) and thin-walled HCS in each molten salts with DSC to understand how particles affect the heat capacity of the molten salts.

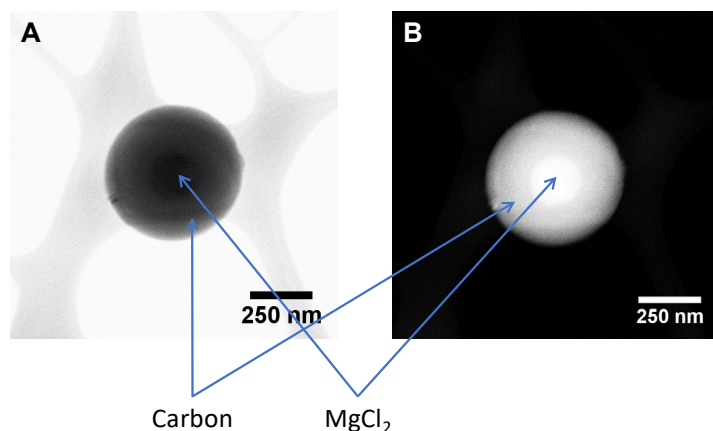


Figure 5. TEM (A) and bright field TEM (B) imaging of thick-walled HCS after suspension in the molten salt

CONCLUSIONS

We were able to purify as-bought MgCl_2 by vacuum distillation and KCl by high-temperature drying. It allowed us to remove MgO and H_2O contamination and use pure salts in the heat capacity experiments. We observed that various carbon-based particles in the molten salt glow red even at temperatures as low as 800°C . We used that property to qualitatively analyze the dispersion of particles in the salt. It is clear that hollow carbon spheres disperse in the molten salt to a higher degree than any other particles. Nanodiamonds and onion-like carbon nanoparticle are heavier than the salt and without any favorable interaction they just sediment. Hollow carbon spheres on the other hand allow the salt into the cavity, leading to density-matching and their subsequent dispersion. Preliminary heat capacity measurements are being performed by Linseis Inc. and encountered unexpected delays. The measurement results will be shown later.

ACKNOWLEDGEMENT

This work was supported by the U. S. Department of Energy, Office of Nuclear Energy.

