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Molten oxide glass materials for thermal energy storage

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Abstract

Halotechnics, Inc. is developing an energy storage system utilizing a low melting point molten glass as the heat transfer and thermal storage material. This work is supported under a grant from the Department of Energy's Advanced Research Projects Agency-Energy (ARPA-E). Advanced oxide glasses promise a potential breakthrough as a low cost, earth abundant, and stable thermal storage material. The system and new glass material will enable grid scale electricity storage at a fraction of the cost of batteries by integrating the thermal storage with a large heat pump device. Halotechnics is combining its proven expertise in combinatorial chemistry with advanced techniques for handling molten glass to design and build a two-tank thermal energy storage system. This system, operating at a high temperature of 1200 °C and a low temperature of 400 °C, will demonstrate sensible heat thermal energy storage using a uniquely formulated oxide glass. Our molten glass thermal storage material has the potential to significantly reduce thermal storage costs once developed and deployed at commercial scale. Thermal storage at the target temperature can be integrated with existing high temperature gas turbines that significantly increase efficiencies over today's steam turbine technology. This paper describes the development and selection of Halotechnics' molten glass heat transfer fluids with some additional systems considerations.

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Keywords: thermal energy storage; molten glass; electricity storage; oxides

1. Introduction

This paper describes progress on the development of a novel oxide glass material and fluid system for use in a thermal energy storage system. Halotechnics' combinatorial chemistry R&D has identified multiple advanced oxide glasses for use as thermal storage fluid in the range of 400 °C to 1200 °C. The selection criteria for thermal storage media are: (1) Low viscosity over a wide temperature range, (2) High heat capacity, (3) Thermal stability, (4) Low cost, and (5) Low toxicity. Halotechnics has characterized two promising proof of concept materials with suitable thermal properties. This paper will provide a comparison of these materials and discuss their relative feasibility for

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use as thermal storage materials. We will present thermal and physical properties of the materials using measurements taken in our laboratory.

2. Background

Current commercially deployed thermal storage systems are two-tank sensible heat designs using molten salt as the thermal storage media [1]. The most significant drawback of this technology is its relatively high capital cost, where molten salts such as Solar Salt (60% sodium nitrate and 40% potassium nitrate) cannot achieve a large enough difference between hot and cold storage temperatures. Accordingly, there is an industry push by project developers to increase the temperature of storage materials for more efficient, inexpensive operation. As the storage temperature increases, efficiency increases due to higher turbomachinery performance. Additionally, capital cost decreases because more heat can be stored in a given quantity of material. These are the driving forces behind Halotechnics' push for a higher temperature thermal storage material.

Glass is most commonly a mixture of oxides, the most abundant materials in the earth's crust. Oxides are typically what one digs out of a mine – raw ore. Oxide glasses have many compelling characteristics. Firstly, glass exhibits very high thermal stability, where oxides are typical end products of thermal decomposition. As such, metal oxides are stable against further decomposition at very high temperatures, far beyond molten salt. At elevated temperatures, oxides have very low vapor pressure, an important concern in designing thermal systems and storage tanks. Additionally, production of oxide ores occurs worldwide, in quantities of millions of tons annually, leading to very low cost for glass raw materials.

One of the challenges with using molten oxide glass as a heat transfer fluid and thermal energy storage material is its characteristically high viscosity. To meet pumping power requirements Halotechnics' molten glass materials must exhibit viscosity orders of magnitude lower than traditional soda-lime glasses.

3. Methodology

3.1. Experimental Design

Halotechnics owes its thermal materials testing efficacy to methods of high throughput combinatorial chemistry [2]. To that end, Halotechnics has programmed a custom-built software suite for experimental design of glass mixtures. In the standard case of a three-dimensional ternary phase diagram, the user selects three different oxide materials of interest and adjusts the compositions over the region of study. Each oxide component is varied over a set range while selecting the number of divisions within that range. An additional layer of complexity is added by linearly varying a fourth oxide material while keeping the original three components' ratios fixed on the ternary diagram. An example of such a system is depicted below in Figure 1, where each blue dot corresponds to a distinct glass composition. Using this technique, 210 experiments were designed for subsequent synthesis and screening.

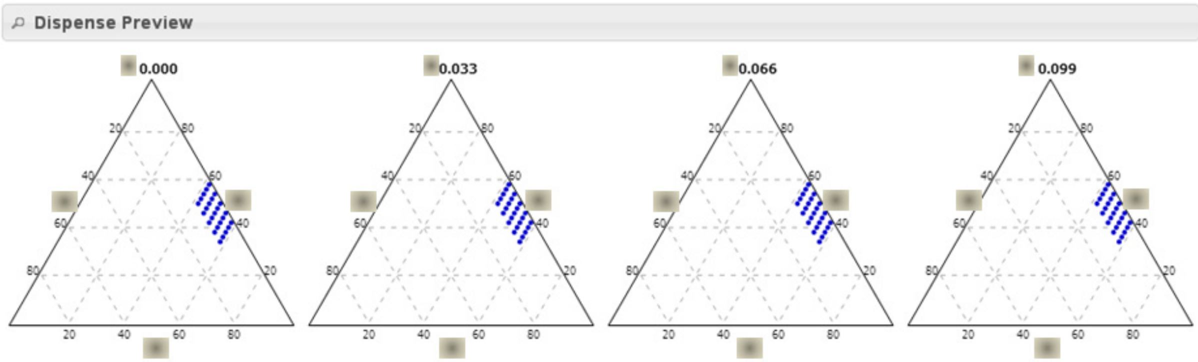

Fig. 1. Sample three-dimensional, four oxide component experimental design.

3.2. Materials Synthesis

One of the keys to the Halotechnics high-throughput glass innovation workflow is the MTM Powdernium device (Symyx Technologies, Santa Clara, CA). This robotic machinery accurately dispenses powders (within 1.0 mg) into distinct positions on a grid of wells. The Powdernium is programmed to dispense the oxide material weights outputted by the aforementioned design tool.

While Halotechnics had previously dispensed into metal or glass plates for molten salt synthesis and characterization, our molten glass screening program demanded more robust materials for high temperature applications. As such, Halotechnics designed refractory alumina plates with a 4x6 array of sample wells for this purpose. Each well is a through-hole on top of which sits a standard 1.3 or 2.0 mL porcelain or alumina crucible. The entire plate and sample apparatus sits atop an analytical balance such that each precise oxide powder weight is recorded to ensure accurate synthesis. The Powdernium was subsequently trained to dispense precise weights of numerous oxide materials into each crucible for subsequent synthesis.

Fig. 2. Powder dispensing robotic device with alumina sample carrier plate.

After the powders were dispensed into each crucible, they were well-mixed and crushed to best facilitate glass forming. This was accomplished by thoroughly mixing and twisting with a small metal spatula, followed by crushing with the blunt end of a standard glass stir rod. These steps adequately prepare the raw glass materials for synthesis in a furnace. During synthesis, the alumina sample carrier plate and 24 well-mixed glass samples were fired in a time-and-temperature programmable furnace. A typical firing cycle was as follows:

- RAMP up (500 °C/hr) to 1100 °C
- HOLD 2-4 hrs
- RAMP down (500 °C/hr) to 150 °C

Synthesis at 1100 °C sufficiently melted the samples, and subsequent cooling facilitated formation of a homogenous glass material. Fired samples are stored at 150 °C to prevent water contamination.

3.3 Thermal Analysis: Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analysis is a critical tool when screening candidate thermal energy storage fluids. This instrument is capable of measuring glass transition temperature (when available), crystallization temperature (when available), liquidus temperature (when available), enthalpy of fusion (when available), and perhaps most importantly, heat capacity.

In preparing the sample, approximately 10mg of each fused glass material was mined using a high-speed Dremel tool and diamond-tipped drill bit. The powdered, fused glass was weighed into an aluminium sample carrier pan for measurement.

An automated DSC device (Netzsch Instruments DSC 404 F1 Pegasus, Selb, Germany) was used for high-throughput analysis of glass samples. This DSC possesses a twenty-position auto-sampler, allowing the user to analyze all twenty samples under desired temperature programs without repeatedly having to monitor the instrument. The auto-sampler's robotic arm ensured exact sample placement and experimental accuracy and reproducibility. Gas flow controllers were also available to control the atmosphere around the sample by accurately blend up to four gases. A typical measurement cycle was as follows:

- RAMP up (40 °C/min) to 250 °C
- HOLD 15-20 min
- RAMP up (20 °C/min) to 550 °C - this step constitutes the measurement
- HOLD 5 min
- RAMP down (40 °C/min) to 100 °C

Every sample was subjected to this representative program for analysis of thermal events. The Netzsch DSC contains software to concurrently analyze and record these thermal events. Once melting points have been determined, Halotechnics can produce liquidus phase diagrams for high-order, multi-component, previously-unstudied oxide glass systems. Under such a protocol, Halotechnics can screen 50 samples in a 24 hour period, representing unparalleled thermal analysis capabilities.

Select samples with promising low-melting behaviour were further analyzed for heat capacity up to 1200 °C, the target hot-tank temperature for the molten glass system. In this scenario, approximately 10 mg of fused glass sample was weighed into platinum sample pans for analysis using the standard Ratio Method [3] for heat capacity measurement. Before measuring each sample, differential scanning calorimeter (DSC) methods were first completed with an empty "blank" pan followed by a sapphire calibration standard in the same pan. In this sequence, all three DSC runs were subjected to the same temperature program under a defined inert gas purge. By such methods, Halotechnics accurately measured heat capacity as a function of temperature, a critical metric when designing thermal energy storage systems.

3.4 Thermal Analysis: Viscosity

Viscosity data is of key importance in designing pump and piping requirements for Halotechnics' molten glasses. For feasible operation, our molten glass heat transfer fluids must exhibit low viscosity over their entire temperature range of functionality to limit parasitic power losses due to pumping. A molten glass viscometer (Orton Instruments RSV-16RT, Westerville, OH) was used for measuring viscosity up to 1600 °C. Because the molten glass viscometer is a low-throughput instrument, only very promising samples were screened after passing acceptable milestones for liquidus temperature and heat capacity.

Approximately 200 g of glass were melted in a platinum crucible and loaded into the viscometer's furnace chamber. Once molten, a platinum-rhodium alloy spindle was dropped into the melt, taking care to ensure that liquid level and spindle depth are consistent with previously-measured calibration standards. Using the standard rotating spindle method, the spindle was rotated while submerged in the glass melt as temperature increases. The shear torque was measured and used to calculate the viscosity of the melt. This procedure enabled viscosity measurement as a function of temperature.

4. Results

The high-throughput glass screening methods developed at Halotechnics enabled discovery of two distinct molten glass candidates for thermal energy storage. Thermal properties of these glasses are described herein, leading to the selection of Haloglass^{TM} RX as our leading candidate for thermal energy storage applications.

4.1 Haloglass CK

After screening 81 unique oxide compositions, Halotechnics arrived at Haloglass CK as its first candidate for thermal energy storage. After demonstrating resilience through repeated thermal cycling between 400 – 1200 °C, Haloglass CK's heat capacity was measured to be 1.2 – 1.3 J/g·K.

Table 1. Measured heat capacity of Haloglass CK

Temperature (°C)	Heat Capacity (J/g·K)
450	1.22
500	1.18
550	1.14
600	1.10

During viscosity testing, measurement was cut off above 600 °C due to signal deterioration at high temperature. This is a result of a non-steady sampling environment while measuring heat capacity, where the glass sample creeps up the test crucible's walls due to low viscosity.

The low viscosity of Haloglass CK is its most defining feature, where it is less than 80 cP even at 400 °C.

Temperature (°C)	Viscosity (cP)
400	78
450	44
500	30
550	24
600	16
650	12
700	9
750	6
800	3
850	0

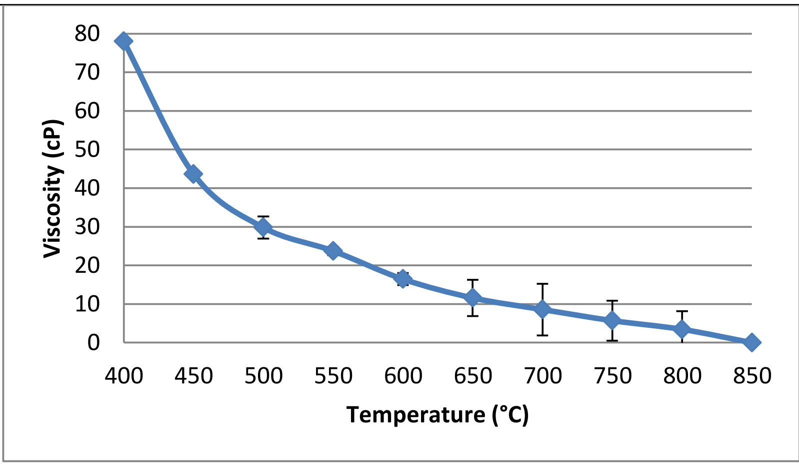

Fig. 3. Viscosity of Haloglass CK, averaged over three measurements with standard deviation error bars.

Haloglass CK exhibits acceptable heat capacity and excellent viscosity, but is synthesized from expensive constituents. This renders the material impractical for grid-scale thermal energy storage.

4.2 Haloglass RX

After screening 129 unique oxide candidates using high-throughput methods, Halotechnics arrived at Haloglass RX as its second and most promising candidate for thermal energy storage. Once its resilience through repeated thermal cycling between 400 – 1200 °C was confirmed, Haloglass CK's heat capacity was measured to be 1.3 – 1.5 J/g·K.

Table 2. Measured heat capacity of Haloglass RX

Temperature (°C)	Heat Capacity (J/g·K)
400	1.32
500	1.39
600	1.47
700	1.43

Measurement was cut off above 700 °C due to signal deterioration at high temperature. After 650 °C, the glass' low viscosity allows the sample to creep up the crucible walls, resulting in a dynamic (rather than constant) sampling environment. Overall, this represents a credible measurement with a loosely temperature-dependent baseline.

While exhibiting viscosity much higher than that of Haloglass CK, Haloglass RX has sufficiently low viscosity to enable pumping with acceptable parasitic power loses.

Temp. (°C)	Viscosity (cP)	Log-10 Viscosity
400	64800	4.8
450	10400	4.0
500	3540	3.5
550	1520	3.2
600	768	2.9
650	447	2.6
700	270	2.4
750	156	2.2
800	98	2.0
850	66	1.8
900	43	1.6
950	31	1.5
1000	23	1.4
1050	18	1.2
1100	13	1.1
1150	10	1.0
1200	8	0.9

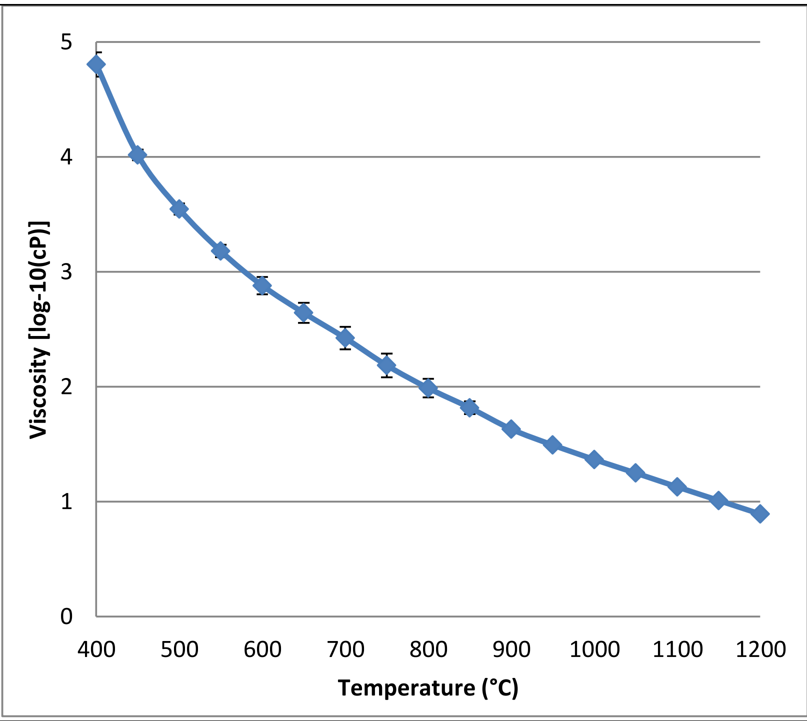

Fig. 4. Viscosity of Haloglass RX, averaged over four measurements with standard deviation error bars.

Haloglass RX shows high heat capacity and sufficiently low viscosity. Furthermore, this material is synthesized from inexpensive, non-hazardous materials. This combination of factors make Haloglass RX the best candidate for thermal energy storage applications, meeting the requirements for thermal stability, high heat capacity, low viscosity, low cost, and low toxicity.

4.3 Summary of Results

Overall, 210 unique glass samples were screened using Halotechnics' custom-built high-throughput thermal analysis methodologies. These studies resulted in two molten glass candidates, the best of which is Haloglass RX. The defining properties of each glass material are summarized below in Table 3:

Table 3. Summary of key molten glass properties leading selection of Haloglass RX

Glass System	Viscosity at 400°C (cP)	Viscosity at 1200°C (cP)	Heat Capacity (J/g·K)	Relative Cost	Relative Toxicity
Haloglass CK	78	<1	1.2 – 1.3	$$$	xxx
Haloglass RX	64,800	8	1.3 – 1.5	$	x

4.4 System Considerations and Future Work

Haloglass RX is an enabling material that will allow thermal storage applications at unprecedented temperatures. Funded by ARPA-E, all glass-wetted system components are currently under development at lab scale by Halotechnics, including molten glass pumps (400 °C and 1200 °C), piping material, storage tank designs (400 °C and 1200 °C), a glass heating furnace, and a glass to air heat exchanger. By the end of 2014 we will have demonstrated the complete system at lab scale using tanks containing approximately 250 kg of glass. The system will pump and heat the molten glass to 1200 °C at a rate of 5 kW and store 30 kWh_t of energy.

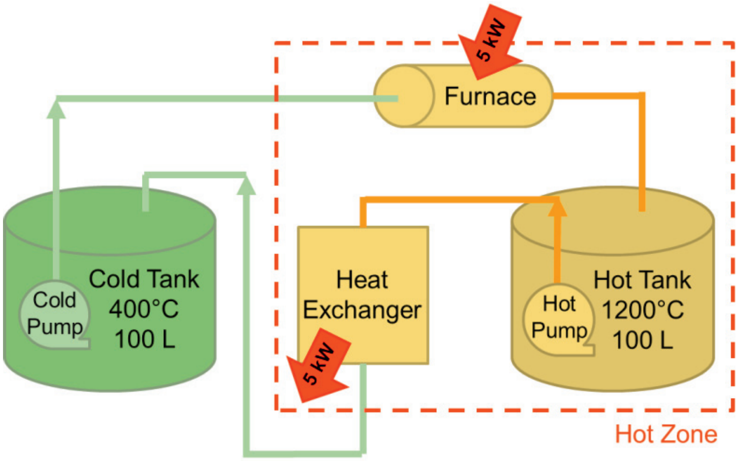

Fig. 5. System design for Halotechnics molten glass thermal storage system (target completion 2014).

With an eye towards system design, Halotechnics has completed thousands of hours of corrosion testing for our molten glass fluids. These tests were completed at both 400 and 1200 °C, the target system operating temperatures. At 400 °C, both molten glass products are compatible with common stainless steels, representing an inexpensive option for engineering systems components including the cold tank, pump, and pipes. High temperature materials compatibility studies have indicated Halotechnics molten glass heat transfer and thermal storage fluids are compatible with common refractories such as alumina, AZS composite ceramics, and graphite.

Corrosion and materials compatibility studies informed decisions for system component design. A stainless steel cold tank and viscosity pump have already been built and operated for over 300 hours at steady state. The hot tank, heater, and heat exchanger components are currently in the design and prototyping phase, with expected system completion in December 2014.

5. Discussion

Molten glass as a media for heat transfer and thermal energy storage represents a great improvement over previously-demonstrated molten salt technologies, namely Solar Salt. Thermal energy storage using molten salt at 565 °C maximum temperature has been commercially proven at various concentrating solar power (CSP) plants over the past 15 years (10 MW Solar 2 demonstration project, 20 MW Gemasolar plant in Spain, and 110 MW Crescent Dunes plant currently under construction in Nevada). Storage tanks have been deployed capable of containing 30,000 metric tons of molten salt [1]. The capital cost is approximately \$30/kWh_t [4], and when converted to electricity at 40% efficiency [5] through a Rankine cycle steam turbine power block, this results in a marginal cost of storage of \$75/kWh_e.

The temperature difference between the hot tank and cold tank in the molten glass storage system is approximately three times higher than with a molten salt system: 1200 – 400 = 800 °C for molten glass, versus 565 – 290 = 275 °C for molten salt. All things being equal, this would mean storage costs with glass would be \$10/kWh_t. Allowing for more expensive tank designs due to high temperature, we estimate a 50% increase to \$15/kWh_t.

Converting thermal energy to electricity through a conservative 50% efficiency [6] combined cycle power block at 1200 °C results in marginal storage cost of $30/kWh$_e$.

Table 4. Thermal storage cost comparison of Haloglass RX with Solar Salt.

Product	ΔT (°C)	Capital Cost ($/kWh$_t$)	Power Block	Efficiency	Storage Cost ($/kWh$_e$)
Solar Salt	275	30	Rankine, steam	40%	75
Haloglass RX	800	15	Brayton, gas cc	50%	30

For comparison, the best lithium ion batteries utilized for grid-scale energy storage cost ~$1,000/kWh$_e$ [7] at Megawatt scale.

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