**Advanced Molten Glass for Heat Transfer and Thermal Energy Storage**

Concept paper submitted in response to DE-FOA-0000471 (HEATS)

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Abstract: Halotechnics proposes to develop a thermal storage system utilizing a low melting point molten glass as the heat transfer and thermal storage material. An advanced oxide glass represents a potential breakthrough in a low cost, earth abundant, and stable thermal storage material. This novel material will enable unprecedented efficiency with thermal energy storage exploiting sensible heat. We will develop a two-tank thermal storage system operating at a hot temperature of 1200 °C and a cold temperature of 400 °C. This project will leverage technology used in the modern glass industry, with decades of experience in handling high temperature viscous materials. Halotechnics will combine its proven expertise in combinatorial chemistry with advanced techniques for handling molten glass. The molten glass thermal storage system has the potential to reduce thermal storage costs by a factor of 10 once developed and deployed at commercial scale.

We will take a systematic approach to eliminating risk from critical components of the molten glass thermal storage system. The proposed project scope includes both the development and optimization of a novel molten glass for heat transfer and thermal storage, as well as the system to pump, heat, and store the novel material. The first aspect of this program is to develop an advanced glass with sufficiently low melting point, low viscosity, and low cost to achieve the performance targets of the program. We have identified a promising proof of concept material and measured its physical properties in our laboratory. Halotechnics is a proven leader in combinatorial chemistry and materials science and we will leverage our expertise to optimize the material for heat transfer and thermal energy storage at large scales. The second aspect of this program is to develop a prototype system to pump, heat, store, and discharge the molten glass fluid. Halotechnics staff has deep experience in thermal system design and high temperature engineering. We will leverage existing techniques borrowed from the glass industry to efficiently and reliably transfer and store heat in our prototype system.

If successful this project will be both transformative and disruptive. We propose to translate technology developed by the glass industry and use it to transform a new sector – to develop cheap thermal energy storage for concentrating solar power (CSP). If successful, our technology will provide thermal energy storage at such a low cost that it will make today’s technology obsolete. Our proposed solution reduces the cost of CSP and thermal energy storage by two routes: 1) enabling significantly higher operating temperatures in the plants and more effective sensible heat thermal storage, and 2) enabling the use of a lower cost thermal storage material.

The SunShot Initiative sets the goal of making solar electricity cheaper than fossil fuels by 2020. To achieve this vision we must push for a breakthrough in low cost thermal energy storage. We must push for significantly higher operating temperature in CSP plants in order to use more efficient power conversion technology. Halotechnics has identified a pathway to enable this vision via advanced molten glass.

Background and Impact:Current commercially deployed thermal storage systems are two-tank sensible heat designs using molten salt as the thermal storage media [[[1]](#footnote-1)].The most significant drawback of this technology is its high capital cost – up to $120/kWht [[[2]](#footnote-2)].Today’s plants using this technology have a small temperature difference between the hot tank (at 400 °C) and the cold tank (at 300 °C). Our innovation will increase by a factor of eight the temperature difference in the storage system, resulting in equal heat being stored with 1/8th the material relative to the state of the art technology. Furthermore, our advanced molten glass material could be 50% cheaper than the molten salt used for today’s technology. Based upon our estimates including the higher cost of high temperature structural materials, we anticipate a potential 10x reduction in the cost per unit energy stored with our proposed innovation – as low as $12/kWht once deployed at commercial scale.

The higher operating temperature enabled by the success of our innovation will dramatically increase the efficiency of the power block available to CSP project developers. Today’s steam turbines used for commercial CSP plants achieve a gross conversion efficiency of just 38% [[[3]](#footnote-3)], constrained primarily by their lower operating temperature (under 400 °C). A combined cycle gas turbine with an inlet temperature of 1200 °C can achieve a conversion efficiency of 52% [[[4]](#footnote-4)]. The outlet temperature of the gas from the compressor of such a turbine is just under 400 °C, setting the temperature of the cold tank in our system. We will develop an optimized glass material and thermal storage system with operating temperatures tailored to commercially available gas turbines.

If successful, our innovation would both reduce the cost of CSP and enable economic thermal storage, bringing the nation significantly closer to eliminating the use of coal and furthering ARPA-E’s Mission Areas.This will result in enhanced energy security for the United States – by enabling clean reliable solar electricity day and night. It will also enhance economic security by promoting domestic mining and manufacturing. The raw materials and components we propose to use in our prototype could come primarily from domestic sources and therefore enhance domestic economic productivity.

Key Technical Risks and Proposed Solutions: We propose to design and build a complete system prototype of an advanced sensible heat thermal storage system, shown in Figure 1. In place of a central receiver we will use a standard laboratory tube furnace to heat the molten glass as it flows through the pipes.

**1. Heat transfer and thermal storage media:** At the heart of our design is an earth abundant, stable, and pumpable molten glass. 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. A common glass such as Pyrex is a material made up of silicon dioxide, boron oxide, and sodium oxide. Oxide glasses have many compelling characteristics, such as very high thermal stability, very low cost (with production of millions of tons annually), and low environmental impact.



Figure 1: System design of prototype 1200 °C thermal storage system with system boundary denoting project scope.

We have identified a promising proof of concept oxide mixture that is suitable for further development into an advanced heat transfer and thermal energy storage material. It is a composition of sodium oxide, phosphorous pentoxide, and molybdenum trioxide (Na2O-P2O5-MoO3). See Figure 2 for a phase diagram containing this mixture, called the “moly glass.” We have synthesized this material in our laboratory using commonly available chemicals. We have measured its melting at 349 °C, very close to the literature value. The moly glass is stable to at least 1200 °C. We have heated it to this temperature and held it for over one hour, then re-measured its thermal properties after the test. The melting point results and the weight of the sample were unchanged within experimental error. The moly glass forms a clear reddish brown melt and at 700 °C has a viscosity near water based upon qualitative observations. See Figure 3 for data from melting point and stability testing of this material.



Figure 2: Phase diagram of moly glass with eutectic region zoomed in.

We have performed sufficient analysis on the moly glass to verify that as a proof of concept material, it appears suitable for heat transfer and thermal storage applications from 400 °C up to 1200 °C. We will use it as a starting point from which to begin our high throughput combinatorial chemistry work and optimize its properties. In its current form it is too expensive (molybdenum oxide is the most expensive component at over $30/kg) and is too viscous at low temperature (at 400 °C it has a higher viscosity than honey). The optimal combination of these properties with an acceptable melting point will be a primary focus of our work. Large changes in glass physical properties (hundreds of degrees in melting point, orders of magnitude in viscosity) can be induced by adding or removing components from a glass melt. Reducing the amount of molybdenum will significantly lower the cost. We will develop models for physical properties and materials cost to complement experimental work in our R&D program.

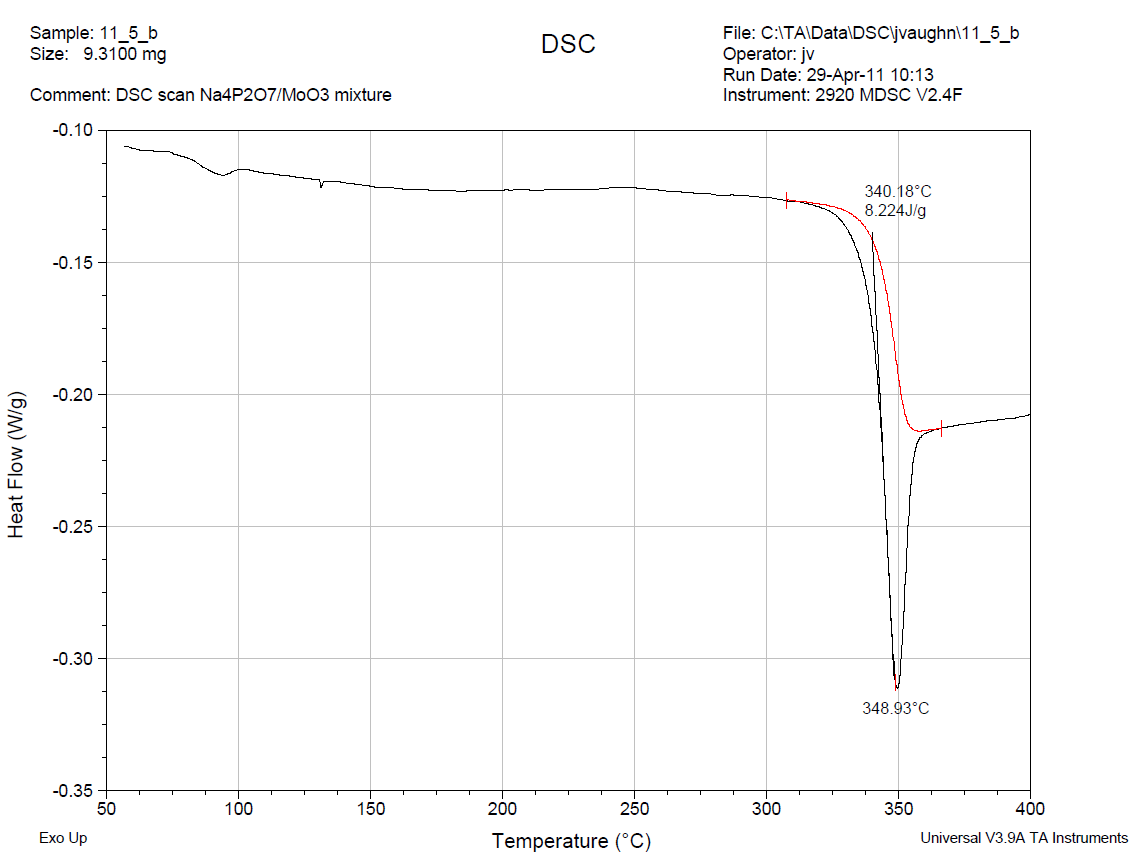
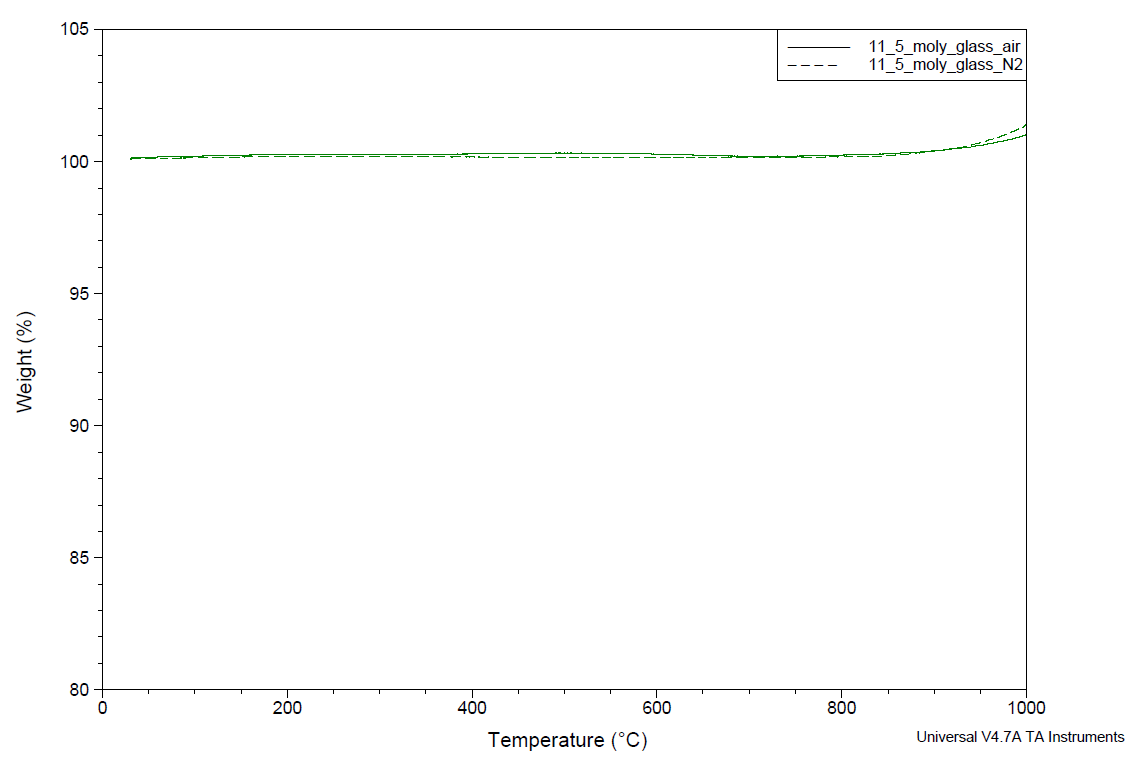
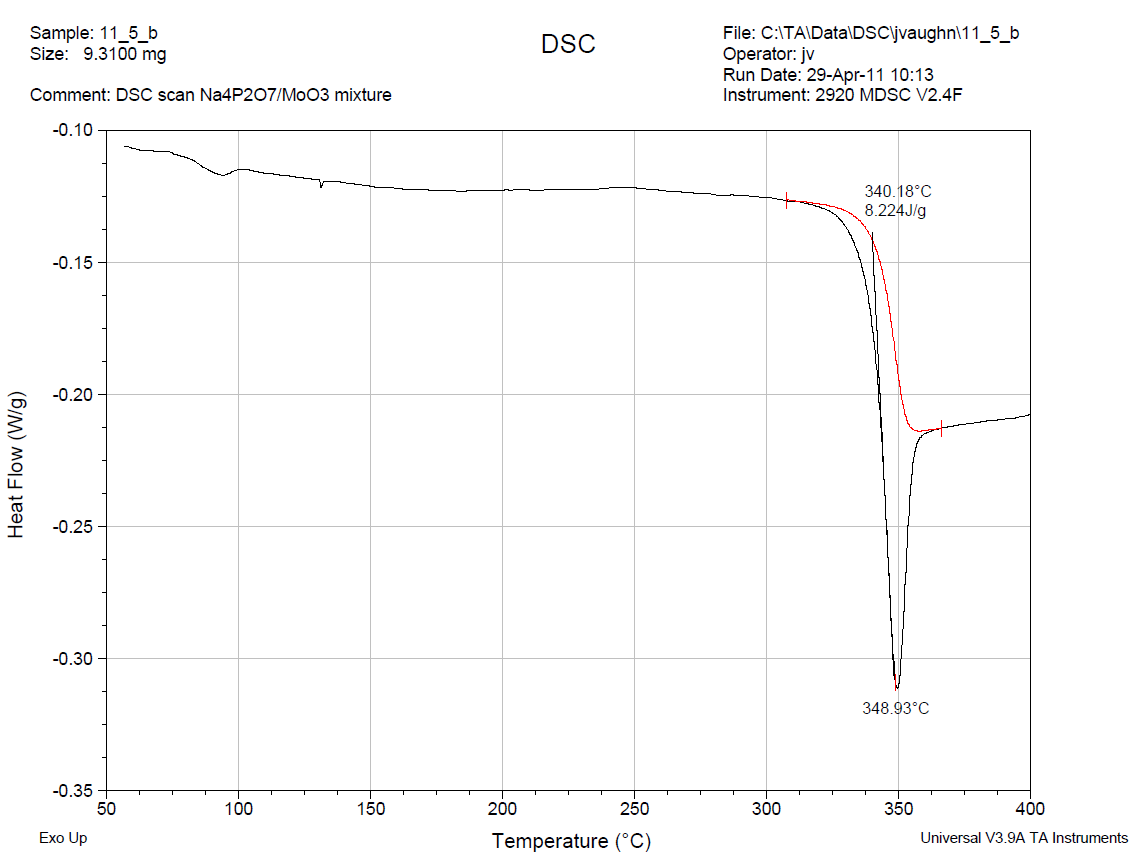


Figure : Moly glass testing (a) DSC with melting point, (b) TGA data showing stable behavior. Inset shows view inside furnace heating moly glass at 1200 °C.

*Target: Low cost, low melting point, low viscosity* Halotechnics has developed world class experimental techniques, software tools, and data handling capabilities for combinatorial chemistry R&D. We have successfully used our techniques for a variety of applications in developing patent-pending heat transfer fluids [[[5]](#footnote-5)]. shows the high throughput workflow we will utilize for rapidly screening thousands of candidate glasses for desirable properties and narrow the candidates down to one optimal material. As components to add to the moly glass we will select from a wide variety of earth abundant alkali, alkaline earth, and transition metal oxides, such as silicon dioxide, iron oxide, manganese oxide, vanadium oxide, and many others. We will also consider additional non-oxide components, such as fluorides, chlorides, nitrides, or sulfides, which may have desirable effects on the physical properties of the fluid. We will target a melting point of 350 °C or below in order to achieve our desired cold tank temperature of 400 °C.



Figure : Screening workflow for advanced molten glass

Some components increase the glass viscosity when used in higher proportions in the melt, others dramatically lower it [[[6]](#footnote-6)]. We have identified a list of glass components that tend to lower the viscosity when used in larger proportions and will use these materials as possible candidates with which to formulate our glass.

**2. Tank design:** Glass melting furnaces, operating for extended periods up to 1800 °C, are constructed of a refractory ceramic material known as “Monofrax.” This material contains zirconium oxide, fusion cast in graphite molds. It costs as low as $9/kg when purchased in bulk. Our concept for the hot tank is an internally insulated design [[[7]](#footnote-7)] using Monofrax in direct contact with the molten glass and surrounded by a low-cost insulation material. The exterior of the tank can be constructed of a steel or nickel alloy since it will be thermally isolated from the hot interior. We have had discussions with the staff of the leading U.S. supplier of refractories, RHI Monofrax in Falconer, New York. RHI is capable of custom designing the shape and composition of its Monofrax material. Halotechnics will work with RHI to procure the necessary materials for the construction of the hot thermal storage tank.

**3. Molten glass pump:** The high viscosity of glass can be used to the designer’s advantage with a device called a “viscosity pump.” [[[8]](#footnote-8)] This device uses a roller, clad with a thin layer of refractory alloy, that sits partially immersed in a pool of molten glass. As the roller spins the high viscosity of the glass causes it to be dragged along in the direction of rotation. The glass is skimmed off the roller by a wiper and directed into a passageway. In this manner a high pressure flow can be generated with a simple elegant design that minimizes the use of expensive materials. We will design a small viscosity pump and demonstrate its functionality for both the hot tank and cold tank in our prototype system.

**4. Tube material:** Molten glass is corrosive to nickel and iron based alloys especially at high temperatures [[[9]](#footnote-9)]. Furthermore, the creep resistance of common alloys is not sufficient for applications at 1200 °C. To solve this problem we will use commercially available molybdenum tubing and surround it with insulating ceramic, which will be in turn surrounded by an airtight sleeve. The whole assembly will be purged with inert gas to prevent oxidation of the molybdenum. Inside the tube furnace the molybdenum tube will be surrounded by a quartz sleeve, sealed, and filled with argon or other inert gas.

**5. Heat exchanger:** We propose to develop an internally insulated direct contact heat exchanger [[[10]](#footnote-10)]. This type of device is used at large scale in the chemical industry and once validated with our prototype could be scaled up to commercial size for CSP applications. The direct contact design facilitates an extremely high heat transfer coefficient between the molten glass and the working fluid, and allows a compact design that minimizes the use of expensive construction materials. The design is a vertical column of Monofrax bricks with an internal passage for the glass/gas cross flow. Glass flows down in droplets, gas flows up. The Monofrax is surrounded by low cost ceramic insulation, which is in turn enclosed by a steel column. In this manner the steel housing provides rupture strength but is insulated from the high temperature inside the column.

The Halotechnics Advantage: Founded in 2009 by Dr. Justin Raade as a spin-out from pioneer Symyx Technologies, Halotechnics draws upon a rich heritage in combinatorial chemistry extending back to 1996. Halotechnics staff members have deep experience in the critical risk areas of this project. We have assembled a multidisciplinary team with experts from the glass industry, physical chemists, and thermal/fluids engineers to develop a solution to the proposed targets. Receiving an ARPA-E award would be instrumental in making our vision a reality, since the project’s risk cannot justify venture investment or traditional corporate R&D funds. We must prove that the system *works* before securing traditional funding to scale it up for commercial deployment.

Commercialization Strategy: Halotechnics is focused on developing the most advanced heat transfer fluids in the world for high temperature industrial processes. We have secured government research funds from DOE and NSF and are currently in the process of commercializing the advanced molten salt products resulting from those projects. Our business model is to develop novel materials and the know-how involved with procuring and utilizing the materials, then license the technology to partners. We have filed patents covering the composition and use of our materials and will partner with customers or suppliers in order to see our products commercialized. Our strategy with the proposed project will be to eliminate the science risk associated with our advanced molten glass thermal storage concept. We will obtain data validating the performance of the novel material and thermal storage system by successfully completing the project. At the conclusion of the ARPA-E project we will seek venture funding to build a pilot scale system and develop the full-scale engineering design for deployment at commercial CSP facilities. After proving the technology at pilot scale we will enter the full scale commercial market as a thermal storage system technology provider. We intend to become a reliable partner for CSP project developers seeking to build low-cost, high temperature plants. We will partner with large companies in order to make our technology bankable.

We believe that the sun is the ultimate energy source. By leveraging government funds for high risk, high reward R&D, followed by private investment directed toward commercialization, we aim to make the biggest commercial impact possible in order to achieve the vision of the SunShot Initiative and reduce the nation’s dependence on imported energy.

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| **Cost Category** | **Total** |
| Personnel | $1,520,000 |
| Consultants | $555,000 |
| Travel | $24,000 |
| Equipment | $190,000 |
| Materials | $432,000 |
| Other direct (software) | $46,000 |
| Indirect | $1,368,000 |
| **Total** | **$4,135,000** |
| ARPA-E share | $3,229,435 |
| Halotechnics share | $905,565 |
| Cost share percentage | 21.9% |

Table : Overall project budget.

Cost Summary: The cost share source will be Halotechnics funds. Some cost share will be in cash in the form of unrecovered indirect costs, cost share patent costs, and other costs ($805,565). Additional cost share will come from in-kind contributions from employees and consultants working on the project objectives ($100,000).

The advanced molten glass thermal storage system is currently at TRL 3. At the conclusion of Phase 1 of the project (months 1-12) we will have progressed the technology to TRL 4. At the conclusion of Phase 2 of this project (months 13-24) we will have advanced the technology to TRL 5.

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| --- | --- |
| **Position** | **Hours on project** |
| PI (materials science and engineering, program management) | 1040 |
| physical chemist (glass chemistry) | 2080 |
| mechanical engineer (thermal systems) | 2080 |
| mechanical engineer (thermal fluids) | 2080 |
| mechanical/electrical technician (fabrication) | 2080 |
| research associate (lab management) | 1040 |
| research associate (analytical) | 1040 |
| research associate (experiment execution) | 2080 |
| supply chain analyst (glass component logistics) | 1040 |

Table : Key positions involved on project and approximate hours of effort.

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| --- | --- | --- |
| **Equipment** | **Cost** | **Description** |
| Differential scanning calorimeter | $120,000 | Discovery DSC by TA Instruments (New Castle, DE). Rapid screening of melting point of glass mixtures. |
| Glass viscometer | $50,000 | RSV-1600 by Orton (Westerville, OH). Measures viscosity of full operating range of molten glass. |
| Tube furnace (1500 °C) | $20,000 | Blue M tube furnace by Lindberg/MPH (Riverside, MI). To be used as heat input to molten glass. |

Table : Major equipment purchases.

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| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Phase 1** | | | | **Phase 2** | | | |
| **Task** | **Q1** | **Q2** | **Q3** | **Q4** | **Q1** | **Q2** | **Q3** | **Q4** |
| Screening workflow development |  |  |  |  |  |  |  |  |
| Optimize glass material |  |  |  |  |  |  |  |  |
| Validate critical components |  |  |  |  |  |  |  |  |
| Milestone 1: Achieve TRL 4 |  |  |  |  |  |  |  |  |
| Full system design |  |  |  |  |  |  |  |  |
| Assemble prototype system |  |  |  |  |  |  |  |  |
| Full system testing |  |  |  |  |  |  |  |  |
| Milestone 2: Achieve TRL 5 |  |  |  |  |  |  |  |  |

Table : Project timeline (24 months).

## End of Project Targets

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| --- | --- | --- | --- |
| *Primary Technical Targets* | | | |
| **ID Number** | **Category** | **Program Desired Value** | **Halotechnics End of Project Target** |
| 1.1.1 | Temperature for power generation in the down-stream power cycle | ≥ 600 °C | 1200 °C |
| 1.1.2 | Exergetic efficiency | ≥ 95% | 98% |
| 1.1.3 | Charging time for storage | ≤ 6 hours for full charge | 6 hours for full charge |
| 1.1.4 | Stored energy for technology demonstration | ≥ 30 kWht | 30 kWht |
| 1.1.5 | Technology demonstration (peak delivered thermal power from storage) | ≥ 5 kWt | 5 kWt |

|  |  |  |  |
| --- | --- | --- | --- |
| *Secondary Technical Targets* | | | |
| **ID Number** | **Category** | **Program Desired Value** | **Halotechnics End of Project Target** |
| 1.2.1 | Cost of storage system including charging and discharging devices | ≤ $15/kWht | $12/kWht a |
| 1.2.2 | Volumetric energy density | ≥ 25 kWht/m3 | 170 kWht/m3 |
| 1.2.3 | Operational lifetime | 20+ years, 10,000+ cycles | 10,000 cycles b |

aProjected cost at commercial scale. Cost for developing first of a kind prototype will be higher.

b Estimate from measured corrosion rate (TBD) of refractory tank lining.

**Discussion:** Our innovation will achieve a high exergetic efficiency when charged and discharged. The thermal storage tanks at Andasol lose approximately 1 °C per day when full [1]. For our prototype we estimate 10 °C lost per day in the hot tank due to the higher storage temperature and smaller volume and 3 °C per day in the cold tank. This results in a round trip exergetic efficiency of 98% after storing heat for one day.

Parasitic pumping losses are expected to be small at commercial scale, likely less than 1% of gross plant output [10], since molten glass has a high volumetric heat capacity and therefore will have low volumetric flow rates.

We estimate capital costs of storage by first assuming we can develop an advanced molten glass that costs $500/ton (50% less than currently used molten salts). We estimate capital costs for the tank and balance of plant by scaling to 1/8th in volume (vs. Andasol) but 50% higher unit costs due to more expensive construction materials. This estimate results in $12/kWht, a 10x reduction in costs vs. today’s technology.

We estimate approximately 88 kg of molten glass to achieve 30 kWht of energy storage with our prototype. Assuming a low density for glass (2 kg/L) and allowing for generous insulation and pump volumes results in an estimated volumetric energy density of 170 kWht/m3.

1. [] S. Relloso and E. Delgado, “Experience with molten salt thermal storage,” SolarPACES, 2009. [↑](#footnote-ref-1)
2. [] J. Stekli, “Thermal Energy Storage Research,” ARPA-E Thermal Storage Workshop, 2011. [↑](#footnote-ref-2)
3. [] “Concentrating Solar Power Projects: Andasol-1,” NREL, 2011. [↑](#footnote-ref-3)
4. [] D series combined cycle efficiency, from “Gas Turbine Efficiency and Power Output,” MHI, Ltd., 2011. [↑](#footnote-ref-4)
5. [] J. W. Raade and D. Padowitz, Journal of Solar Energy Engineering, 2011, in press. [↑](#footnote-ref-5)
6. [] A. Fluegel, European Journal of Glass Science and Technology Part A vol. 48 no. 1, 2007. [↑](#footnote-ref-6)
7. [] R. Gabrielli, C. Zamparelli, Journal of Solar Energy Engineering, vol. 131, 2009. [↑](#footnote-ref-7)
8. [] T. H. Jensen, “Glass forehearth having a viscosity pump,” U.S. Patent 4,083,711, April 1978. [↑](#footnote-ref-8)
9. [] J. Di Martino et al., Corrosion Science vol. 46, 2004, pp. 1865–1881. [↑](#footnote-ref-9)
10. [] A. P. Bruckner et al., “Heat transfer and storage system,” U.S. Patent 4,727,930, 1988. [↑](#footnote-ref-10)