First Assessment of Liquid Glasses for Central Receiver CSP Applications

STERG Report

Lukas Heller*

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1 Definition of Glass

Glasses are compositions of (mostly inorganic) oxides that have been cooled to a solid condition without crystallizing. Crystallization is the building of a "[...] 'crystal lattice', in which the positions and orientations of the units of structure repeat themselves regularly[...]" (Shand, 1958, p. 9). In a non-crystallized solid, the molecules are in a definite position but not in a repeating lattice. Crystallization normally occurs when a liquid is cooled down to the liquidus temperature and solidifies into energetically ideal bonds. Glasses, however, have a very high viscosity (that is the required force to overcome the shear stress and move molecules) when they are approaching the liquidus temperature as liquids. When cooled down very slowly, they can still rearrange and build a lattice, when cooled down more abruptly, on the other hand, the molecules freeze in the unorganized positions of the liquid phase. These definitions, as most information in this report has been derived from Shand and Turkdogan (1983).

2 Compositions of Glasses and their Properties

Most commercial glasses consist mainly of silica molecules (SiO_2). Other 'glass formers' than silicon are phosphorus (P_2O_5) and boron (B_2O_3). Common constituents to the glass formers are: soda (Na_2O), alumina (Al_2O_3), potash (K_2)), lime (CaO), magnesia (MgO) and the above mentioned potential glass formers.

Silicas The simplest glass configuration is '**fused silica**', which is pure silica with minor contaminations. Fused silica has interesting optical and electrical characters and a high liquidus temperature of 1710 °C. The by far most common glas is **soda-lime** glass, which is based on silica with soda, lime, potash and potentially magnesia as major constituents.

*LukasHeller@sun.ac.za — Solar Thermal Energy Research Group, Stellenbosch University

Soda and potash significantly reduce the dynamic viscosity (from here on referred to as 'viscosity') while lime, alumina and magnesia improve the chemical durability. The effect of **boric** (B_2O_3) in lowering the viscosity and increasing the expansion factor of pure silicate is less severe than that of soda-lime. Adding lead oxide (PbO) to fused silica creates **lead-alkali silicate** glasses. They can have even lower softening points[1] than soda-lime silicas when considerable amounts are constituted. **Aluminosilicate** glasses contain at least 20 % of alumina. Typically, they have a high softening temperature and small thermal expansion coefficients.

Metal oxides are often added for changing the color of the glass, however, the physical properties are usually not influenced strongly. The photosensitive metals gold, silver or copper are introduced to acquire photosensitive glass. Figure 1 shows the compositions of some exemplary glass types.

3 Potential CSP Applications

In this report, liquid glasses are investigated for two different applications in central receiver concentrating solar power (CSP) systems. Firstly, they can act as the heat transfer fluid (HTF) between solar receiver as the heat source and thermal energy storage system (TESS) and power block as the heat sink. Secondly, they can be used as the sensible heat storage medium in the TESS. A combined use as the HTF and storage medium would be favorable.

4 Relevant Properties for CSP Applications

Some of the most important requirements on potential HTFs and storage media are given in Table 2. The importance of the respective properties is indicated by the number of exclamation marks '!'.

4.1 Upper Temperature Limits

Central receiver CSP plants are or will be used to power Rankine steam cycles or Brayton cycles with air or other potential gases, namely supercritical carbon dioxide (s-CO_2) or helium. The upper temperature limit of high-temperature supercritical steam power blocks is expected to reach 700 °C in the near future. Brayton air cycles usually operate at temperatures up to 1400 °C and s-CO_2 cycles are most practical between 500 °C and 1000 °C. The upper temperature limit of the HTF and storage medium (also accounting for corrosion with containing material) should be higher than the respective working fluid limitation. Cascaded designs with high temperature (HT) and low temperature (LT) TESSs are conceivable.

Fluids' boiling points can in most cases be raised by increasing the pressure. However, this increases material requirements on the HTF loop and the storage tank. Pressur-

[1] According to Shand (1958), the softening point is reached when the viscosity becomes $\leq 10^{10}$ mPa s

Table 1: Compositions of commercial glasses as summarized by Shand (1958).

No.	Designation	Percent								
		SiO_2	Na_2O	K_2O	CaO	MgO	BaO	PbO	B_2O_3	Al_2O_3
1	Silica glass (fused silica)	99.5+								
2	96 % silica glass	96.3	< 0.2	< 0.2					2.9	0.4
3	Soda-lime—window sheet	71–73	12–15		8–10	1.5-3.5			0.5–1.5	
4	Soda-lime—plate glass	71–73	12–14		10–12	1-4			0.5–1.5	
5	Soda-lime—containers	70–74	13–16		10–13		0–0.5			1.5–2.5
6	Soda-lime—electric lamp bulbs	73.6	16		0.6	5.2	3.6			1
7	Lead-alkali silicate—electrical	63	7.6	6	0.3	0.2		21	0.2	0.6
8	Lead-alkali silicate—high-lead	35		7.2				58		
9	Aluminoborosilicate (apparatus)	74.7	6.4	0.5	0.9		2.2		9.6	5.6
10	Borosilicate—low-expansion	80.5	3.8	0.4				Li_2O	12.0	2.2
11	Borosilicate—low-electrical loss	70.0		0.5				1.2	28.0	1.1
12	Borosilicate—tungsten sealing	67.3	4.6	1.0		0.2			24.6	1.7
13	Aluminosilicate	57	1.0		5.5	12			4	20.5

Table 2: Requirements on HTFs and storage media (depending on working fluid).

Property	Desirable value HTFs	Desirable value storage media
T_{max} [°C]	high (!!!)	high (!!!)
T_{min} [°C] (operation)	low (!!!)	low (!!!)
T_{min} [°C] (freeze protection)	low (!!)	low (!)
p_{req} [bar]	low (!!)	low (!!!)
c_p [kJ/kg K]	high (!)	high (!!!)
ρ [kg/m^3]	high (!)	high (!!!)
λ [W/m K]	high (!!!)	high/low[a] (!/!![a])
μ [mPa s]	low (!!)	low (!)
cost [USD/kg]	low (!)	low (!!!)
chemical compatibility	high (!!)	high(!!)
toxicity	low (!!)	low (!!)

[a]for thermocline storage

ized tanks are considered non-viable in this study, which means that the temperature limitations of storage media are given for ambient pressure.

To the author's knowledge, the evaporation/degradation temperatures of organic oxide salts are all at least 1200 °C and therefore only limiting in air Brayton cycle systems. Chemical compatibility of the glasses with pipe, heat exchanger and tank materials has to be investigated.

4.2 Lower Temperature Limits

Ideally, HTFs and storage media stay in the liquid phase throughout the cycle (except for designs in which the HTF is also the working fluid). During operation, the lowest temperature in CSP cycles is, therefore, usually dictated by the solidification or degradation temperature of the HTF/working fluid (lower temperature limit). The design of receivers, pipes, valves and tanks is additionally simplified if the HTF's/storage medium's lower temperature limit is below minimum ambient temperatures, so that freezing is not an issue.

One of the determining properties of glasses is the continuous increase in viscosity during solidification over a temperature range. The lower temperature limit is therefore not abrupt but rather expressed by the increasing viscosity, accompanied by increasing difficulties in and energetic work of pumping. The upside of this is that solidification happens gradually and thermal expansion shocks should be reduced (also because thermal expansion of most glasses is low).

The lower temperature limit, or the high viscosity at relatively high temperatures, poses the biggest problem of glass as an HTF and as the exclusive storage medium of a TESS. According to Dyer et al. (2013), a viscosity of 10 000 mPa s represents today's pumpability limit. Engine oil at 20 °C, for reference, has a viscosity of ≈ 3800 mPa s

(Cengel and Boles, 2010). As can be seen in Figure 1, standard glasses only undergo this limit at temperatures above 1200 °C. However, Halotechnics (2013) announced the commercialization of ***Haloglass^{TM} RX***, a glass composition with a lowered softening temperature for large scale application. Some of its properties are given in Table 3.

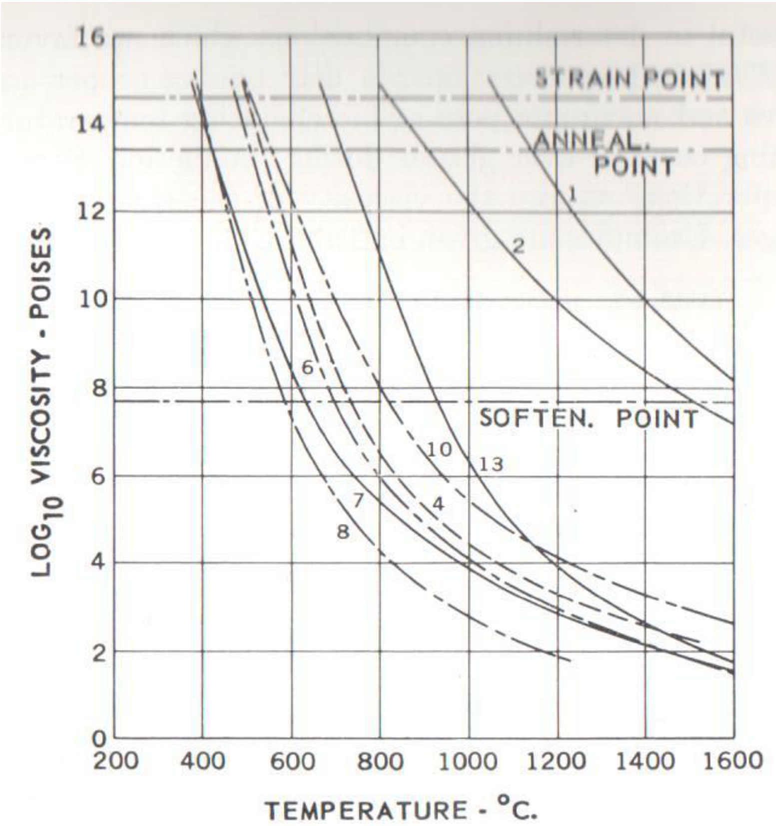


Figure 1: Viscosity curves of commercial glasses. The numbers refer to Table 1 (Shand, 1958).

4.3 Dynamic Viscosity η

The dynamic viscosity influences a fluid's pumpability and heat transfer characteristics. Low values allow for low pumping power demands and a more turbulent flow.

The viscosity of glasses is strongly influenced by the temperature. Between solid state and melting point, which can cover hundreds of kelvins, the viscosity passes through several orders of magnitude. Glasses, therefore, reach non-pumpability within their liquid phase and not abruptly at the solidification point. Viscosities of glasses consisting of different formers and constituents can be found, for example, in Turkdogan (1983).

Table 3: Some properties of *Haloglass™ RX*.

Property		Value
Melting Point		450 °C
Maximum Operating Temperature		1200 °C
Density		2400 kg/m^3
c_p at	450 °C	1.362 kJ/kg K
λ		0.8 W/m K
μ at	450 °C	10 064 mPa s
	600 °C	600 mPa s
	800 °C	84.3 mPa s
	1000 °C	23.6 mPa s
	1200 °C	11.1 mPa s

4.4 Specific Heat Capacity c_p

The specific heat capacity c_p determines how much thermal energy can be stored in a certain mass of a substance by increasing its temperature by a defined step. For HTFs, it mainly influences the required flow speeds and/or receiver pipe diameters and therefore pumping power. For storage media, it directly influences its required mass to store a certain amount of energy and indirectly, by multiplying it with the medium's density, the required tank volume. These two properties play an important role in minimizing TESSs' costs.

The specific heat capacity of a glass at a given temperature is mainly influenced by the heat capacities of the components. The temperature-dependent values of some commercial glasses can be derived from Figure 2.

Shibata et al. (2005) investigated six glasses' main thermal transport properties (heat capacity, density and thermal conductivity). The glasses contained between 58 % to 75 % by mass of Si_2O and differing quantities of Al_2O_3, B_2O_3, Na_2O, K_2O, MgO and CaO as well as some other constituents. The measured properties were almost independent of the temperature in the range of 800 °C to 1400 °C.

4.5 Density ρ

Just like the specific heat capacity, the density of a glass at a given temperature is mainly influenced by the heat capacities of the components. Glass densities range between 2.13 kg/m^3 for borosilicates and more than 6.00 kg/m^3 for glasses with a high mass fraction of lead oxide. Most commercial silicate glasses range between 2.2 kg/m^3 and 3.0 kg/m^3.

4.6 Thermal Conductivity λ

For an HTF, the thermal conductivity is one of the most important thermodynamic properties. A good heat transfer to and inside of the fluid means effective heat removal

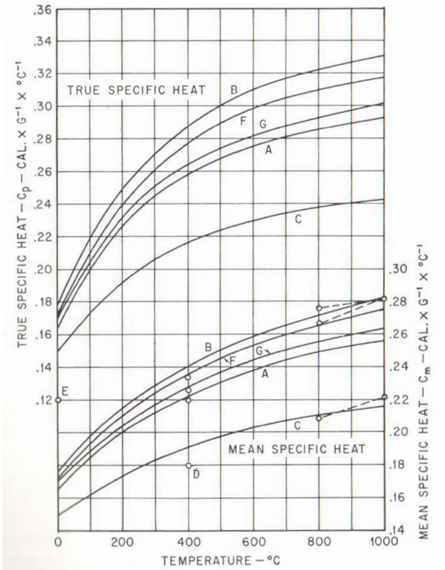


Figure 2: Specific heat capacity curves of commercial glasses. A — silica glasses. B — soda-lime glass. C — lead-alkali silicate glass 22.3 % PbO. D — Lead-alkali silicate glass 26.0 % PbO. E — Lead-alkali silicate glass 46.0 % PbO. F — low-expansion borosilicate glass. G — Aluminosilicate glass Shand (1958).

from the receiver pipes and, therefore, a minimal over-temperature of them as compared to the mean fluid outlet temperature, causing higher receiver efficiencies.

Storage media should have a high thermal conductivity to simplify the heat transfer from/to the HTF and minimize the heat exchanger area. On the other hand, when the TESS incorporates a single-tank thermocline tank, low thermal conductivity is necessary to efficiently separate the hot from the cold phase.

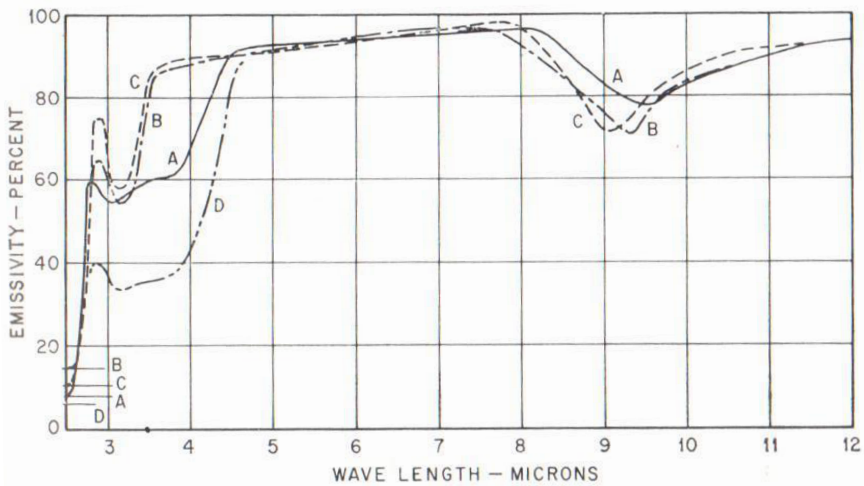
A fluid's thermal conductivity λ determines the heat transfer trough it's lattice, that is not through the fluid's movement (convection) or photon waves (radiation). However, because of the transmitting character of liquid glasses for radiation in parts of the thermal spectrum (diathermancy), conduction and radiation *through* the fluid can practically be seen as a combined *effective* thermal conductivity λ_{e} of thermal and radiative conductivities, λ_{t} and λ_{r} (Turkdogan, 1983):

$$\lambda_{\mathrm{e}} = \lambda_{\mathrm{t}} + \lambda_{\mathrm{r}}$$

The heat flux $\dot{q}$ can then be calculated through a modified formulation of *Fourier's law*:

$$\dot{q} = -\lambda_{\mathrm{e}} \frac{\partial T}{\partial z}$$

According to Shand (1958), radiative heat transfer becomes dominant above approximately 800 °C for glasses that are diathermanous in the relevant spectra. On the one hand, this is caused by thermal energy emissivity being dependent on the emitting body's temperature to the fourth power. On the other hand, most glasses have a low spectral transmissivity for thermal radiation with wavelengths of more than approximately 4.5 µm. Figure 3 shows the spectral emissivity, which is equivalent to the spectral absorptivity, for some commercial glasses. Figure 4 shows the wavelength and spectral emission of thermal radiation (NB: The results are plotted on a logarithmic scale).



Glass	Thick, In.	Total Emissivity, %
A—Soda-lime container	1/8	72
B—Aluminoborosilicate	1/8	75
C—Borosilicate low-expansion	1/8	77
D—Light chrome-green container	1/16	65

Figure 3: Spectral emissivity of different glasses (Shand, 1958).

The effective thermal conductivity of some commercial glasses for the high temperature range can be found in Figure 5. Above 550 °C, it ranges in between approximately 2.1 W/m K and 42 W/m K. However, this combined effective value — which is the one that is stated in most of the literature (Mann et al., 1992) — is meased through and aimed at the heat transfer *through* a medium and not *into* it. In a receiver, it is questionable whether it would create as strong of an advantage as the high purely thermal conduction λ_t of, for instance, liquid metals. Nevertheless, it could improve the circumferential heat distribution of receiver pipes, which are heated from the front only.

4.7 Cost

Due to the high production capacities and abundant base materials, glasses can be produced at low costs. However, standard glasses' melting points are too high or their

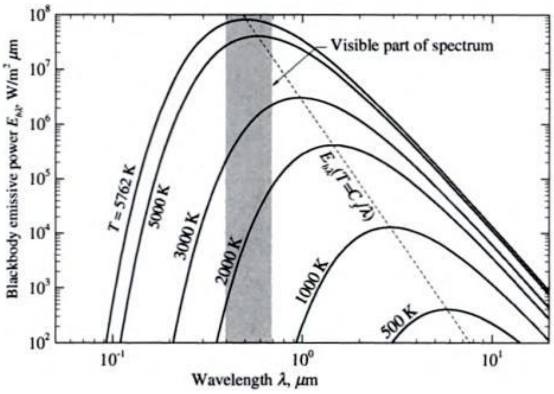


Figure 4: Blackbody emissive power spectrum (Modest, 2003).

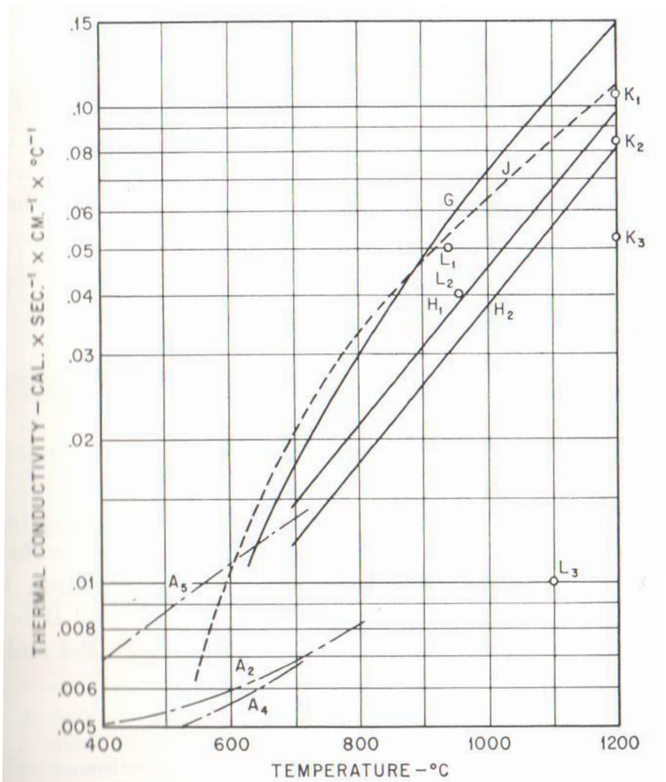


Figure 5: Effective thermal conductivity curves of commercial glasses. A — silica glasses. H — soda-lime container glasses. J — low expansion borosilicate. K_1 — soda-lime 0.015 % Fe_2O_3. K_2 — soda-lime 0.16 % Fe_2O_3 oxidized. K_3 — soda-lime 0.16 % Fe_2O_3 reduced. L_1 — soda-lime container glass. L_2 — amber glass 0.2 % Fe_2O_3. L_3 — pale blue glass 0.6 % Fe_2O_3 Shand (1958).

viscosity at the operating temperatures of CSP plants is too high. Therefore, additives or other formers than silicate have to be used. At this stage, no quantitative values for appropriate glasses' costs can be presented but these could possibly compete with typical HTFs and storage media in terms of economic viability.

4.8 Chemical Compatibility & Toxicity

Glasses are, in general, inert and chemically durable. In glass production, they are in contact to ambient air, metals and ceramics at elevated temperatures. Therefore, insurmountable problems are not expected in the use of molten glasses as HTF or storage medium. Studies on corrosion of molten glasses exist. For example, in Di Martino et al. (2004*a*) and Di Martino et al. (2004*b*), the corrosion behavior of pure metals in contact with molten borosilicate glass at a temperature of 1050 °C was investigated. They came to the conclusion that metals with high chromium content should be used to contain the glass because the cromium sample built a protective Cr_2O_3 layer prohibiting further corrosion.

5 Conclusion

Liquid glasses have the potential to enable the use of high-efficiency working cycles in CSP plants. (A-)USC Rankine steam and Brayton air/s-CO_2/helium cycles have upper operating temperatures between 620 °C and 1500 °C, raising plant efficiencies above 50 % in single or combined working cycles. These high temperatures can be generated by concentrating solar energy if the generated heat is removed efficiently from the receiver, can be stored and the fluids and materials are able to withstand them. Operating temperatures in excess of 1000 °C are possible with different glasses, however, high melting temperatures and high viscosities at lower temperatures prove problematic. The glass composition, which is pumpable up to the lowest temperature, that could be found cannot be pumped below 450 °C and that only with special pumps.

For the use as an HTF, most liquid glasses are limited by their mediocre thermal conductivity (compared to, for example, liquid metals) and their high viscosity, which prohibits highly turbulent flows and therefore significant convection. However, liquid metals are more problematic in terms of hazard and corrosion.

As a storage medium, liquid glass could be used in the high temperature storage of a cascaded TESS. The low-temperature medium could be *Solar Salt*™ or high-temperature concrete in a passive system.

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