Outgassing of Silicone Elastomers

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Abstract

The performance advantages of silicone elastomers are widely known. Silicone provides unique characteristics that allow it to be used in a broad range of applications, including applications serving continuous extreme conditions of temperature and pressure. One design-limiting aspect of silicone is volatile component outgassing. While outgassing is a valid concern for a number of sensitive applications, there is a broad lack of understanding about silicone outgassing, as well as much misperception and confusion. As a result, silicone is often excluded from designs.

This paper broadly addresses the topic of silicone outgassing and includes a survey of outgassing species, measurement techniques and methods, and empirical case studies targeted to reduce and/or manage outgassing.

Introduction

At high temperatures and low pressures, outgassing from silicone elastomers is inevitable. If we cannot eliminate it, at least we can understand the phenomenon and intelligently attempt to reduce the volume. In any discussion of outgassing, certain questions are evoked – What is outgassed? What is the source? How much outgassing can we expect? How do we control or reduce the amount? This paper addresses these questions for a common general-purpose rubber compound.

Objectives

- Develop a phenomenological understanding of outgassing.
- Provide factual outgassing information for typical commodity silicone rubbers.
- Furnish a benchmark for end users of silicone elastomers in production, design and fabrication.

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Post-Curing

Post-curing is one of the principal tools to mitigate outgassing. Post-cure is a process that removes the volatiles from the cross-linked silicone rubber by diffusion and evaporation and is carried out at a temperature greater than the service temperature for the part. (The post-cure process is analogous to water removal in the kiln drying of wood.) Once the volatiles are 'vaporized' they are no longer available to outgas. If the volatiles are not removed from the rubber and then exposed to elevated temperatures with poor ventilation, we can expect a reduction in strength, elongation, compression set properties accompanied by chemical decomposition. Insufficient or poor post-cure can result in 'smoke', bubbling, delamination and unsightly sticky surface deposits.

Figure 1 illustrates the key concepts of post-cure. The first 4 hours consist of a typical post–cure at 204°C (400°F). In this phase about 2.7% mass-loss occurs. The next time period from 4 to 28 hours show representative operating conditions. Even after 'operation' at 177°C (350°F) for 24 hours, mass-loss that would be observed is less than 0.5%. Without the post-cure the mass-loss at 177°C would have been in the order of 4% or about 8 times as great. It is evident that post-cure provides excellent control of outgassing.

Species Outgassed

Gas chromatography / mass spectrometry was used to identify the outgassing species from a post-cured silicone rubber (General-purpose silicone rubber compound prepared by ARLON). The principal outgassing components are displayed in table 1 in order of relative amounts. It is not surprising to see that much of the outgassed species are low molecular weight silicone oils. Silicone oils are used to incorporate pigments, additives and catalyst into the compound. In addition these oils are precursor reactants and frequently remain in the silicone gum.

Table 1. Principal outgassed species from a post-cured silicone rubber compound.

Component	Probable Source
cyclohexasiloxane	LMW silicone fluid
phenyl benzoate	catalyst byproduct
linear hexasiloxane	LMW silicone fluid
linear pentasiloxane	LMW silicone fluid
propanoic acid ester	catalyst byproduct
diethylphthalate	pigment wetting agent
Cx hydrocarbons	Silane coupling agent
cyclopentasiloxane	LMW silicone fluid
biphenyl hydrocarbon	catalyst byproduct
linear heptasiloxane	LMW silicone fluid
Cx aldehydes	catalyst decomposition product
cyclotrisiloxane	LMW silicone fluid

The information displayed in table 1 provides guidance in reducing outgassing – reduce or eliminate as much of the low molecular weight silicone oils as possible from the rubber compounds. These materials are largely unreactive and will either 'vaporize' during post-cure (best practice if possible) or during service.

Technique for the Outgassing Experiments

For all of the experiments, silicone rubber was compounded with the prescribed components on a clean 2-roll mill and then compression molded into slabs of controlled thickness. These slabs were then cured at 135°C (275°F) for 15 minutes. Circular samples of diameter 50 mm (2 inch) were punched for the slab and massed to a precision of 0.0001 g. The samples were then post-cured at the experimental temperature on flat plates in a well-ventilated forced-circulation laboratory oven for the required time. The samples were removed and massed periodically to determine outgassing by mass-loss. All efforts were made to control sample thickness and surface to volume ratio. This technique was chosen in preference to the use of a TGA instrument, as it more closely mimics work on the shop floor with similar sample geometry and diffusion distances.

Filler, Pigment and Peroxide DOE

A design of experiments (***DOE***) was carried out to investigate the effect of ground quartz content, pigment content (with the silicone carrier) and catalyst type. With center points, 10 different compositions were utilized for these experiments. A general-purpose rubber was utilized with quantity and types of components typical for the industry. Table 2 illustrates the setup of the experiments. The materials were post-cured for 2 weeks to essentially establish the 'volatile-free' state.

Table 2. Material compositions for the Filler, Pigment and Peroxide DOE

Mat No.	Quartz Content L = Low (< 10%) H = High (> 35%)	Pigment Content L = Low (~ 2%) H = High (~ 4%)	Peroxide Type BS = Benzoyl TS = 2,4-dichlorobenzoyl
1	L	L	BS
2	L	H	BS
3	L	L	TS
4	L	H	TS
5	M	M	BS
6	M	M	TS
7	H	L	BS
8	H	H	BS
9	H	L	TS
10	H	H	TS

Figure 2 illustrates the mass-loss for the first hour of post-cure for the DOE samples. Two points of interest are immediately apparent:

1. The curves separate into 3 bands depending upon the ground quartz content. All the samples in the top band, with higher mass-loss, have low quartz loading. The low band has high quartz content and the least mass-loss while the intermediate band has middle quartz content and mass-loss. This observation is confirmed by Pareto analysis, as quartz content is the only factor that is statistically significant at an alpha of 0.10. Intuitively, more filler in the compound translates to less rubber and reduced outgassing.

2. Curves from samples that are catalyzed with benzoyl peroxide cross the respective equivalent 2,4-dichlorobenzoyl peroxide curve. In addition the benzoyl peroxide samples have a greater initial slope than the 2,4-dichlorobenzoyl peroxide equivalent. This argues strongly that the benzoyl peroxide is rapidly removed by post-cure.

Figure 3 shows the complete 2-week span of the post-cure at 204°C (400°F). This figure illustrates that silicone rubber continues to outgas at very low levels for extended periods of time.

Figure 4 portrays the instantaneous outgassing rate versus time for post-curing at a temperature of 204°C (400°F). The key point demonstrated by this figure is that outgassing is rapid initially, but quickly reduces within an hour. It should also be noted that rate is low after only 2 to 4 hours of post curing.

Based upon the 2-week vaporization, figure 5 estimates the amount of volatiles remaining in the sample as a function of cure time. After 4 hours of post cure, a substantial amount of volatile material still remains in the sample (> 40%). This estimate is on the low side.

Part Thickness and Oil Content

A quick DOE was conducted to determine the effect of silicone oil and diffusion distance upon outgassing. Silicone oils are present in all silicone rubber compounds as either a precursor or as the oil commonly used to incorporate ingredients into the rubber. Most sheet products have a high surface to volume ratio and relatively short diffusion distances. In this DOE up to 2 phr of extra silicone oil is added to the rubber, which is calendered in thicknesses of 0.5 to 1.5 mm (0.020 to 0.060 inch)

Figure 6 shows the part thickness, within the range of 0.5 to 1.5 mm, is unimportant in comparison to the oil content. The curves for the thick and thin samples essentially coincide for the respective oil content. Pareto analysis strongly confirms this casual interpretation. Adding 2 phr of extra oil, easily done when mixing in an additive, can increase the outgassing rate and the necessary post-cure significantly. The strong response of oil on outgassing may be concealing the weaker effect of part thickness.

Effect of Post-Cure Temperature and Ventilation

Figure 7 shows that post-cure temperature has a great effect on outgassing mass-loss. As would be expected, higher post-cure temperatures are more effective in volatilization, but 232°C (450°F) is considered an effective upper bound to limit thermal stress on a conventional rubber.

Ventilation is a necessary part of the post-cure process. Figure 8 compares well-ventilated samples to samples sealed in aluminum foil. It is immediately obvious that the sealed samples do not "breathe" and volatiles are trapped within the rubber. (After 15 minutes the ventilated samples have lost more volatiles than 5 hours for the sealed samples.) All of the sealed samples showed evidence of reversion (i.e., rubber degradation). If rubber 'breathing' is prevented the post-cure process is ineffective and may lead to excessive service outgassing and 'smoking'.

Catalyst Concentration – Part Thickness DOE

It is logical to believe that both catalyst concentration and thickness should have an affect upon outgassing, despite the previous results from the oil – thickness DOE. In this DOE, benzoyl peroxide catalyst concentration was set to ½ or 2 times the normal concentration for that compound and the thickness was fixed at either 1.0 or 1.9 mm (0.039 or 0.075 inch). Part thickness was found to be significant at an alpha of 0.2 (i.e., 8 out of 10). This indicates that thickness has a minor effect on outgassing for thin sheets when it is not swamped by another strong factor such as oil. Peroxide concentration was not a significant factor on outgassing for an alpha of 0.20.

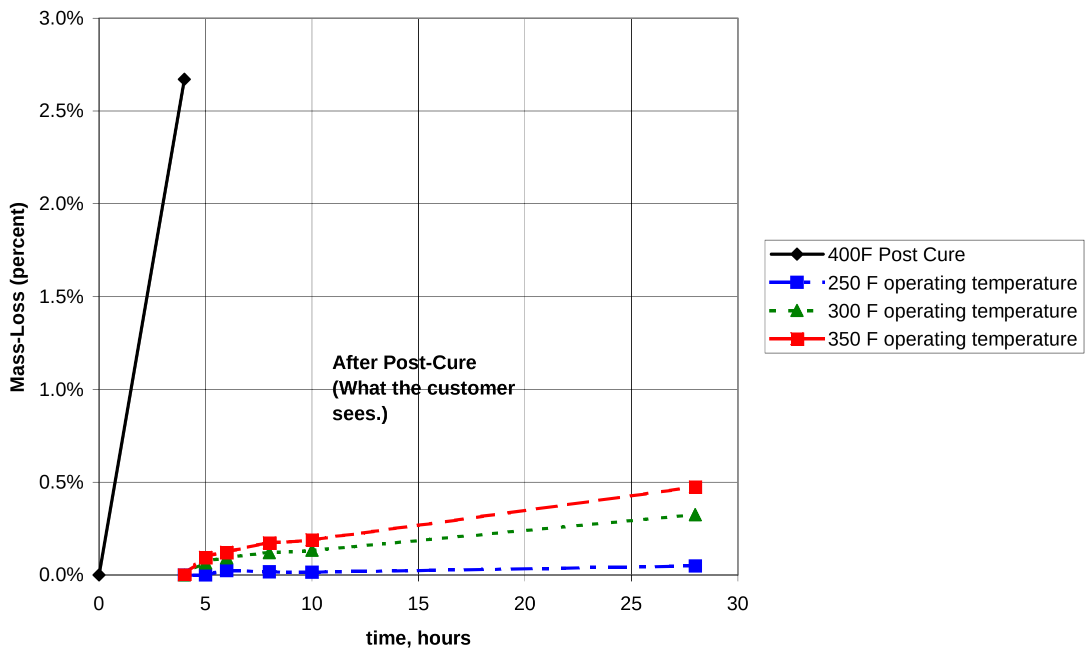
Conclusions

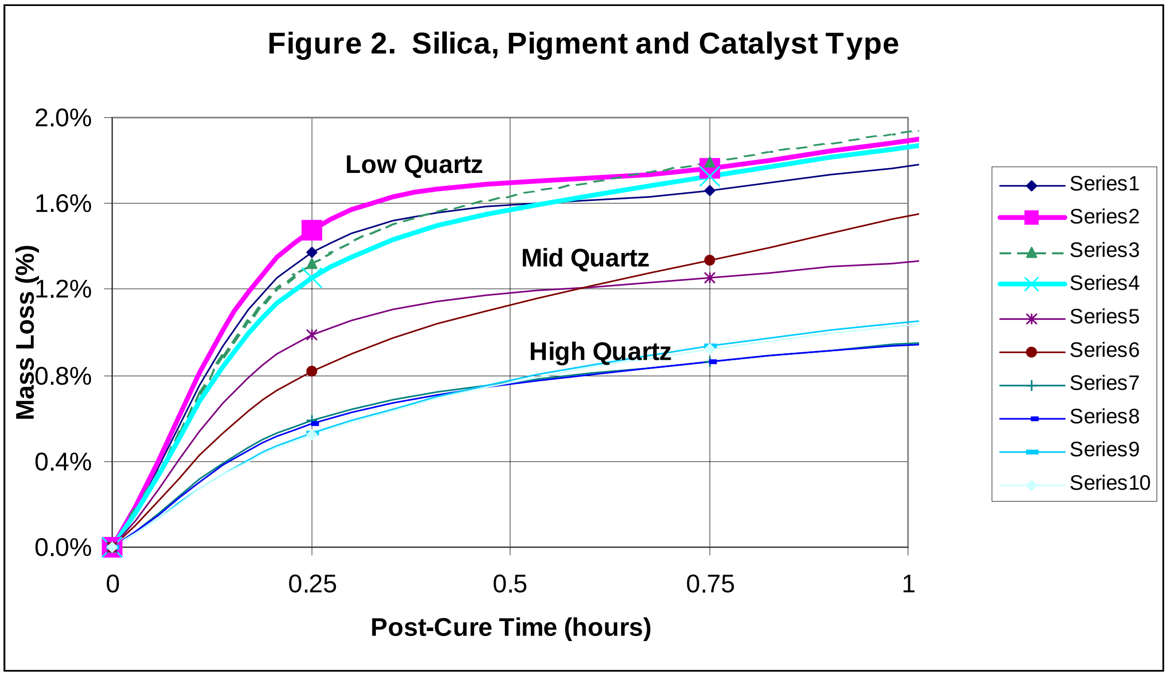
The key points to recall are:

- Post-curing is very effective in minimizing finished part outgassing.
- The rate of volatile removal during post-cure rapidly drops off after the first hour.
- Ventilate during post-cure.
- To reduce out-gassing, minimize the content of low molecular weight species in the silicone rubber compound.
- Highly filled rubbers generate less volatile material.
- Volatiles still remain after post-curing.
- Silicone material will continue to outgas for extended periods of time at elevated temperatures.
- Thickness has a minor effect, but is not a controlling factor on outgassing for thin silicone rubber sheets up to 2-mm (0.08-inch) in thickness.

Figures

Figure 1. Post Cure and Outgassing after Post-Cure





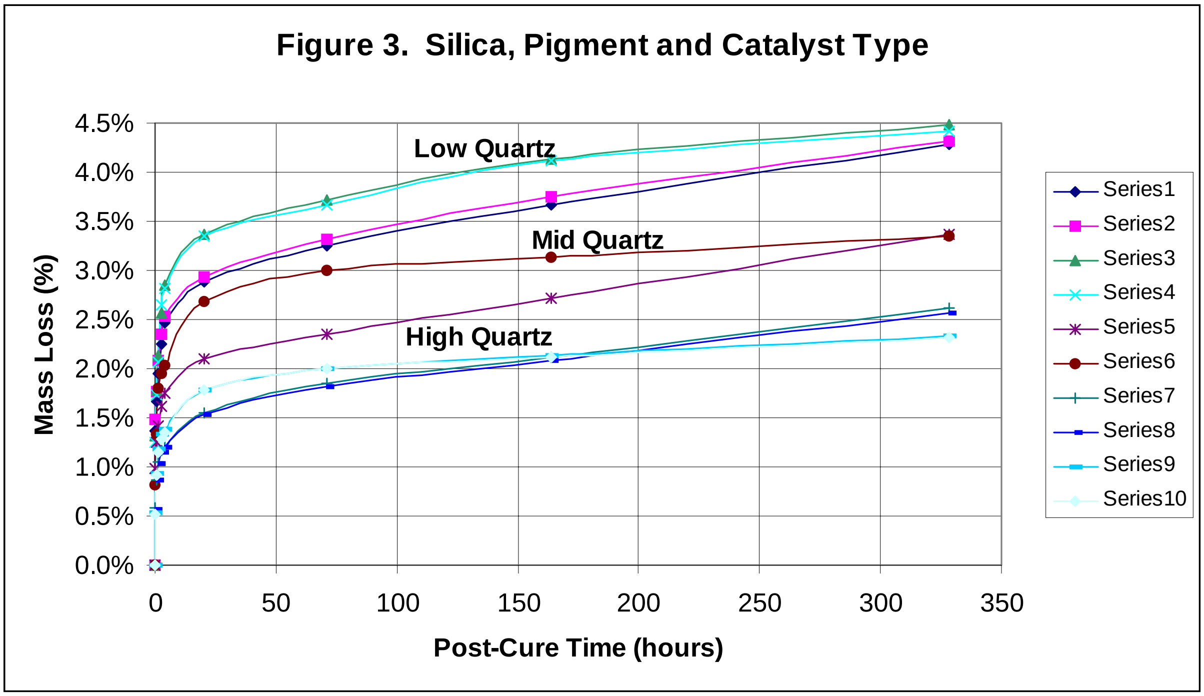


Figure 3. Silica, Pigment and Catalyst Type

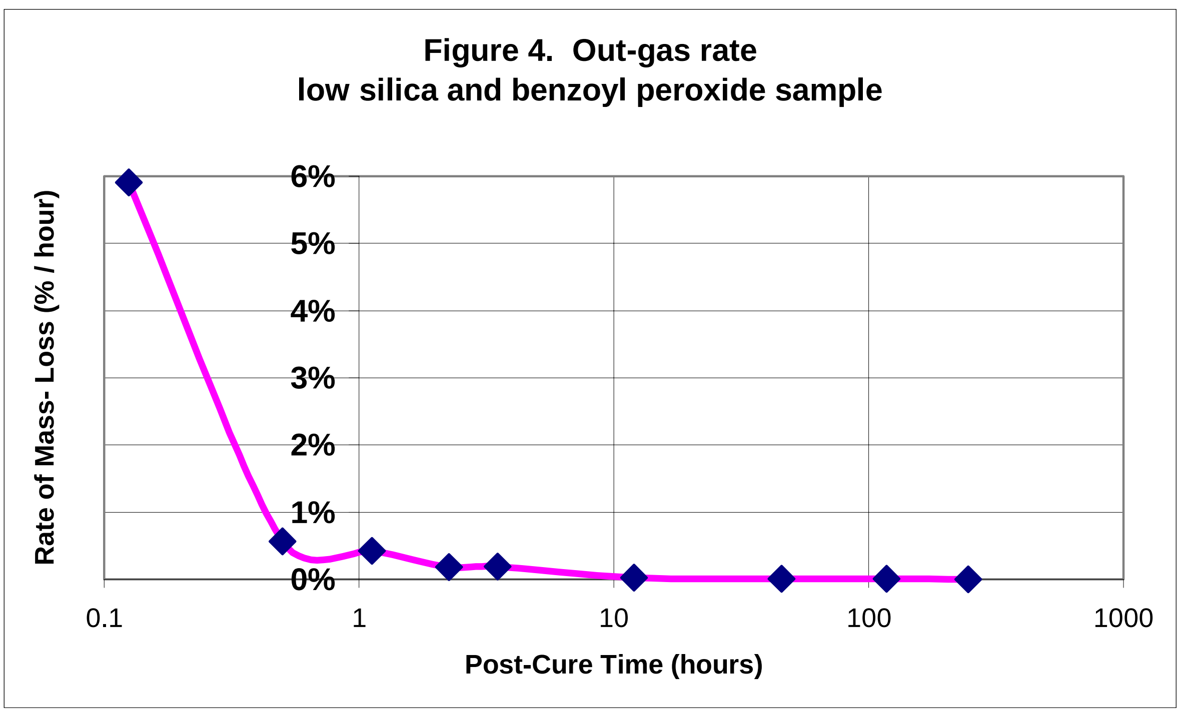


Figure 4. Out-gas rate
low silica and benzoyl peroxide sample

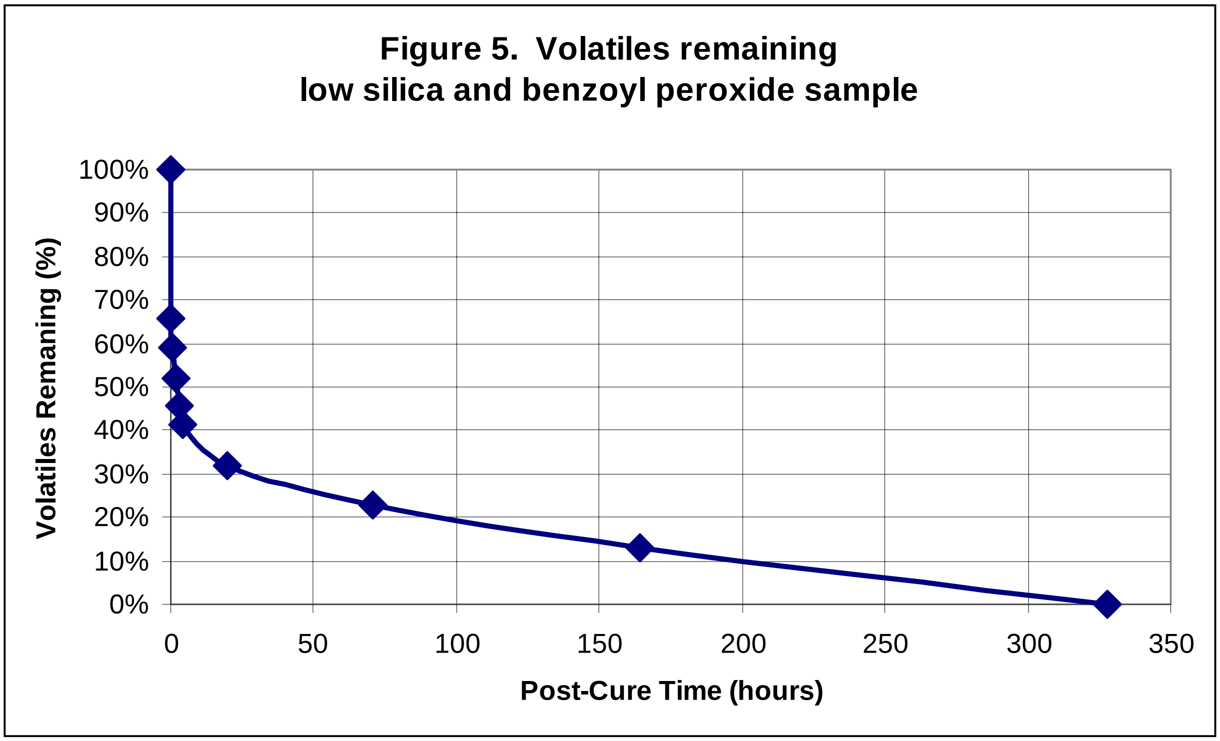


Figure 6. Thickness & Oil Content

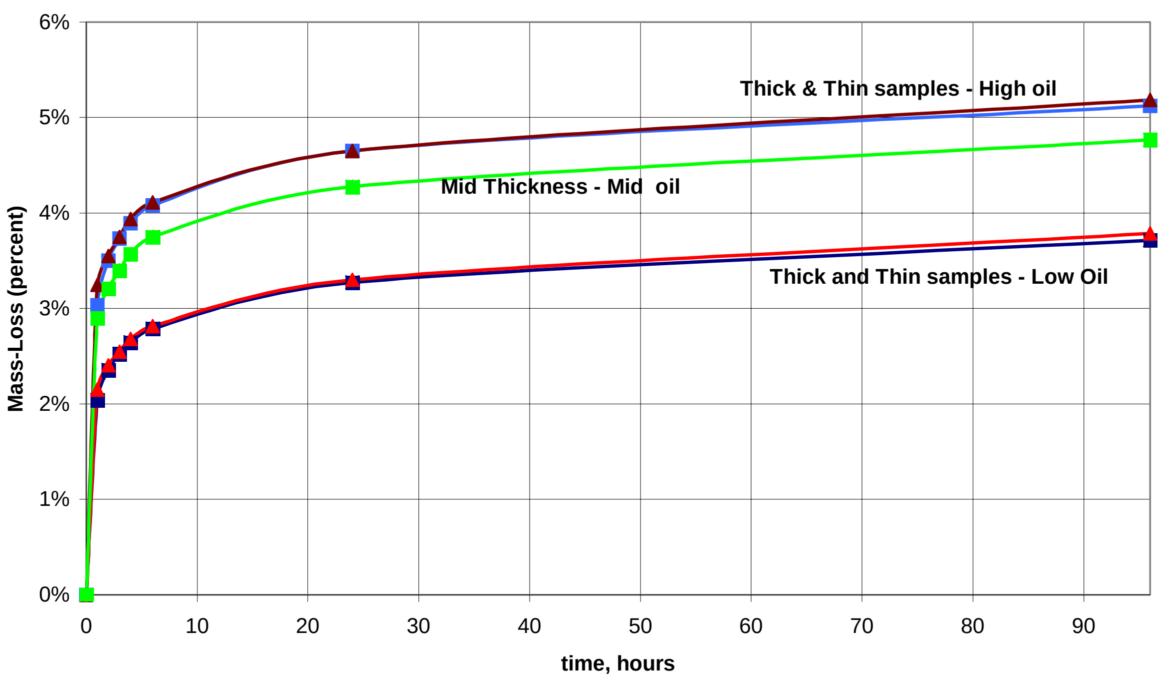


Figure 7. Temperature