CCST Facilitated Expert Opinion

The Updated State of Science Regarding Maximum Permissible Siloxane Concentration

Expert Opinion Authors

Gregory Von Wald, Stanford University

Adam Brandt, PhD, Stanford University

Steering Committee Members

James L. Sweeney (Chair), PhD, Stanford University and CCST Council Chair
Charles Benson, etaPartners LLC
Fokion Egolfopoulos, PhD, University of Southern California
Charles Kolstad, PhD, Stanford University
Diane Saber, PhD, Reethink, Inc.
Jessica Westbrook, PhD, Sandia National Laboratories

California Council on Science and Technology (CCST)

Sarah E. Brady, PhD, Interim Deputy Director
Amber J. Mace, PhD, Interim Executive Director

The Steering Committee has reviewed this CCST facilitated expert opinion. We unanimously agree that this document does not change any of the findings, conclusions, or recommendations of the CCST report "Biomethane in California Common Carrier Pipelines: Assessing Heating Value and Maximum Siloxane Specifications," rather this strengthens the basis of our findings, conclusions and recommendations.

CCST Facilitated - Expert Opinion

The Updated State of Science Regarding Maximum Permissible Siloxane Concentrations

Gregory A. Von Wald, Adam R. Brandt

Department of Energy Resources Engineering, Stanford University

This note provides additional information pertaining to the treatment of siloxanes made available subsequent to the completion of the recent California Council on Science and Technology (CCST) report "Biomethane in California Common Carrier Pipelines: Assessing Heating Value and Maximum Siloxane Specifications" (Von Wald et al. 2018). CCST reports are a reflection of the body of scientific knowledge at the time of publication and are final upon completion. Therefore, this CCST-facilitated expert opinion is independent of the study.

This CCST-facilitated expert opinion was requested by the California Public Utilities Commission (CPUC) and is focused on a review of one research study; it therefore does not aim to represent a review of the full body of relevant literature. While one study may add to the broader body of scientific knowledge, it may do so only incrementally. Biogas is a renewable gaseous energy resource generated from the anaerobic decomposition of the organic components of wastes and biomass. Biogas can contain a wide range of trace constituents, which vary depending on the source of the biogas. Siloxanes are a family of silicon-containing trace constituents found in biogas from wastewater and landfill sources. It is well-documented that combustion of gas containing siloxanes results in silica (SiO_2) formation which can cause damage to appliances via clogging and reduction of airflow and/or deactivation of key sensors or catalysts (Nair et al. 2012, 2013, Gersen et al. 2013, Turkin et al. 2014). In order to protect pipeline-connected equipment, the current maximum siloxane specification in California is set at 0.1 mg Si/m^3. The California state legislature, in Bill SB 840, requested that the California Council on Science and Technology (CCST) complete a study that investigated the state of knowledge surrounding the maximum siloxane specification.

One of the major findings of the recent CCST report was the lack of data availability regarding the impact of siloxanes on combustion appliances (Von Wald et al. 2018). Only a handful of such studies have been conducted, without clear implications supporting a specific numerical standard. Since the publication of the CCST report, a new study on siloxane impacts on combustion appliances has been published (Gersen et al. 2019). Because of the paucity of data from prior studies, we review the implications of this study for the CA siloxane standard below.

Summary of new information

Gersen et al. conducted experiments on a set of seven residential gas-fired appliances. The studied appliances included one hot water heater and six natural gas boilers (two partially premixed, four fully premixed). The appliances had various heat exchanger materials and geometries. All six boilers employed an ionization safety device to detect the presence of a flame, which shuts off the gas supply when the sensor current falls below a specified threshold. The experimentation was performed in two stages. All seven appliances were tested with a natural gas containing 11.2 mg Si/m^3. In a second stage, the four most sensitive were selected for further testing at levels of 6.3, 2.8, and 1.5 mg Si/m^3. These siloxane concentrations are notably lower than previous experimental work, and therefore these data may provide a more meaningful result for understanding potential impacts of siloxanes at the levels considered for regulation. In addition, the sample size in this study is larger than in prior studies, where a total of 9 pieces of equipment have been studied across prior studies (Turkin et al. 2014, Gersen et al. 2013, Nair et al. 2012, 2013).

The effect of silica deposition was investigated for three modes of appliance failure: (1) increase in carbon monoxide (CO) emissions, (2) decrease in thermal output of the appliances and (3) failure of the ionization safety device.

CO emissions of the hot water heater were found to increase considerably over time due to clogging of the heat exchanger and decreased airflow through the device. Decreased airflow leads to incomplete combustion which results in CO formation. No increase in CO emissions was observed in the two partially-premixed boilers, due presumably to a different geometry of the heat exchangers. The CO emissions of the four fully-premixed boilers were found to remain constant as the control system for these appliances adjusts the flow of fuel to ensure a proper fuel/air ratio and avoid incomplete combustion.

Similarly, the thermal output from combustion in the appliances was governed by airflow. As mentioned above, the four fully premixed boilers adjust the fuel flow to maintain the desired fuel/air ratio. As such, rather than produce CO emissions, these appliances will decrease the flow of gas and reduce thermal output. This feature is uncommon in the U.S appliance population.

Experiments on the boilers confirmed that deposition of silica can deactivate the ionization safety device. However, one notable result of this work was that the relationship between the concentration of siloxane and the time to failure of the flame sensor is nonlinear. The time to failure is shown to increase exponentially as the siloxane concentration decreases. This nonlinearity is confirmed by thermodynamic calculations for equilibrium of siloxane combustion. At lower concentrations of siloxane, the equilibrium state at high temperatures will retain more of the silicon in the gas phase, thus reducing the solid deposition on surfaces and sensors near the flame zone (such as the ionization probe).

The experimental results of Gersen et al. (2019) were used to develop a mathematical relationship between the volume of gas burned over the lifetime of an appliance and the maximum concentration of silicon that would be allowable to avoid premature failure. These models are given in eq. 1-4 of Gersen et al. (2019). The models are based on experimental data from the most sensitive appliances of the set, so that results would be appropriately conservative for the other tested appliance geometries. Gersen et al. estimate that, for the studied appliances, in order remain below recommended CO emissions (0.02 CO/CO_2 ratio, approximately 2,000 ppm CO air-free), the siloxane concentration ought not exceed 0.44 mg Si/m^3. In order to avoid thermal input reductions exceeding 10%, the results recommend a siloxane concentration of less than 0.23 mg Si/m^3. Finally, to avoid failure of the ionization safety device, siloxane concentrations should be below 0.45 mg Si/m^3. These concentration results are specific to the thresholds applicable in that study region.

We can apply these models to typical California gas consumption volumes for a residential boiler (1500 m^3/year) and water heater (400 m^3/year) assuming lifetimes of 15 years. The models were modified to conform with U.S.-specific requirements. The recommended Weaver thermal input reduction maximum is 5% per Kelton (1978), while the CO emissions standard is 400 ppm air-free per Gas Consultants Inc (2009). As the relationship between CO emissions and mass of silica build-up is nonlinear, the model for this failure mode was adjusted to the new emissions threshold using the data available in Figure 3 of Gersen et al (2019). The results of applying these models under these conditions are displayed in Table 1 below.

Table 1. Result from applying Gersen et al. (2019) failure models to California-specific conditions to estimate a maximum siloxane concentration.

Failure mode	Maximum Siloxane Concentration
Exceed CO emissions guidance (water heater)	0.30 mg Si/m^3
Reduce thermal input by 5% (boiler)	0.14 mg Si/m^3
Ionization safety device failure (boiler)	0.47 mg Si/m^3

Table 1 shows that the results of applying the Gersen et al. (2019) equations confirm the order of magnitude of the current California siloxane specification (0.1 mg Si/m^3).

By testing seven residential appliances at siloxane concentrations as low as 1.5 mg Si/m^3 this study has increased the number of relevant data points available for informing regulation of siloxane concentrations in gaseous fuels. Its results also require less extrapolation to generate estimates of failure time for appliances under regulated gas quality. However, there remains significant uncertainty about the implications for real-world conditions in California due to the small sample sizes of all studies to date.

Addressing limitations and caveats

One limitation of this approach is that these models were developed for a specific set of seven residential appliances, based on the experimental data from the most sensitive appliances. The appliances tested were new, whereas in-place appliance populations may have existing degradation that increases their susceptibility to damage by silica deposition. Furthermore, it is unclear how generalizable the tested appliances are to the stock of California residential combustion appliances, as inventories of appliance type and vintage would be needed. There remains imperfect information for other end-users that may be more sensitive to siloxanes than the residential customers. However, it is generally assumed that larger consumers of gas will also have more robust protocols in place for system monitoring and maintenance.

Conclusions

While data on the impact of siloxanes are still limited, the Gersen et al. (2019) study gives evidence that supports the current California specification of 0.1 mg Si/m^3. Gersen et al. (2019) has nearly doubled the number of data points available regarding the modes of failure in residential combustion appliances, and tested gas with lower siloxane concentrations than previous studies. Testing of gas with lower concentrations is useful because the results require less extrapolation than prior studies. Importantly, in direct experiments at 1.5 mg Si/m^3 (no extrapolation required), short term damage was observed in residential appliances.

Applying the Gersen et al. (2019) models to California conditions supports the order of magnitude of the existing California siloxane specification of 0.1 mg Si/m^3. The above numerical results appear to represent a slight relaxation of the existing California specification. However, 0.1 mg Si/m^3 is within the margin of uncertainty introduced by temporal extrapolation and generalization from small sample size. Additional studies would be needed to determine whether relaxing the current siloxane specification is safe. This CCST-facilitated expert opinion does not supersede the siloxanes recommendation in the full report (Von Wald et al. 2018). Rather it provides an additional body of evidence to be considered by the CPUC.

The Steering Committee has reviewed this CCST facilitated expert opinion. We unanimously agree that this document does not change any of the findings, conclusions, or recommendations of the CCST report "Biomethane in California Common Carrier Pipelines: Assessing Heating Value and Maximum Siloxane Specifications", rather this strengthens the basis of our findings, conclusions and recommendations."

Works cited

Gas Consultants Inc., (2009). *Gas Interchangeability Testing Report*. Prepared for Air Conditioning, Heating, and Refrigeration Institute, American Gas Association, and Association of Home Appliance Manufactures.

Gersen, S., Visser, P., van Essen, V. M., Dutka, M., Vainchtein, D., de Hosson, J. T. M., & Levinsky, H. B. (2013). Effects of silica deposition on the performance of domestic equipment. In *Proceedings of the European Combustion Meeting* (pp. 25-28).

Gersen, S., Visser, P., van Essen, M., Brown, M., Lewis, A., & Levinsky, H. (2019). Impact of silica deposition on the performance of gas-fired domestic appliances caused by the combustion of siloxanes in the fuel. *Renewable Energy*, *132*, 575-586.

Kelton, K., (1978). Appliance performance and changes in gas composition (Paper 78-D-52). Operating Section Proceedings: American Gas Association, Arlington, Virginia, American Gas Association, pp. D-107–D-111.

Nair, N., Zhang, X., Gutierrez, J., Chen, J., Egolfopoulos, F., & Tsotsis, T. (2012). Impact of siloxane impurities on the performance of an engine operating on renewable natural gas. *Industrial & Engineering Chemistry Research*, *51*(48), 15786-15795.

Nair, N., Vas, A., Zhu, T., Sun, W., Gutierrez, J., Chen, J., ... & Tsotsis, T. T. (2013). Effect of siloxanes contained in natural gas on the operation of a residential furnace. *Industrial & Engineering Chemistry Research*, *52*(18), 6253-6261.

Turkin, A. A., Dutka, M., Vainchtein, D., Gersen, S., van Essen, V. M., Visser, P., ... & De Hosson, J. T. M. (2014). Deposition of SiO2 nanoparticles in heat exchanger during combustion of biogas. *Applied Energy*, *113*, 1141-1148.

Von Wald, G. A., Brandt, A. R., Rajagopal, D., Stanion, A. (2018). *Biomethane in California Common Carrier Pipelines: Assessing Heating Value and Maximum Siloxane Specifications.* Sacramento, CA: California Council on Science and Technology.