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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JULY 2009

Impact Factor: 5.33 · DOI: 10.1021/es9010527 · Source: PubMed

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Fugitive Emissions from Liquid-Charged Flange Joints: A Comparison of Laboratory and Field Data

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Received April 7, 2009. Accepted April 14, 2009.

Starting from Hagen−Poiseuille's law, we analyzed the parameters influencing fugitive emission rates. It is shown that liquid and gas emissions follow basically different mass transport mechanisms so that mathematical models available for gases are not suitable to calculate liquid emissions. The emission behavior of liquid-charged flange joints is characterized, and a model conception for the observed phenomena is presented explaining the unexpectedly high emissions of liquid-charged flange joints. Against the background of field data, the influence of maintenance on fugitive emmissions is demonstrated, and exchanging old gaskets with high-grade gaskets as a means of emission reduction in old plants is critically scrutinized. A general maintenance plan is proposed as the most effective method for emission reductions.

Introduction

Keeping the air clean is one of the most important aims in environmental protection. The ozone precursors nitrogen oxides (NOx) and volatile organic compounds (VOC) have a great impact on the quality of the atmospheric air. Therefore, a lot of countries have started activities to reduce fugitive emissions, using different approaches. The United States, for instance, has launched a mandatory leak detection and repair (LDAR) program, which has yielded major reductions in fugitive emissions from processing plants. In Germany, by contrast, measurements in operating plants are not mandatory, but as a consequence of joining several United Nations Economic Commission for Europe (UNECE) agreements such as the first and second Oslo Protocol on sulfur reductions in 1985 and 1994 and the VOC agreement in 1988 the German air pollution law (*1*) requests testing of the so-called high-grade gaskets for most plants processing organic chemicals. High-grade gaskets in this context must comply with the specific leakage rate of 10^{-4} mbar L/(m s) in a first-time test (*2*). The test procedure applied is helium mass spectrometry at a pressure of 1 bar and gasket stress of 30 MPa. Alternatively, a specific leakage rate of 10^{-2} mbar L/(m s) at a test pressure of 40 bar can be used (*3*). This requirement for high-grade gaskets holds for newly built as well as for old plants, which have to be retrofit with the new gaskets.

As a result of these efforts, the total emissions from chemical plants have been declining for the past several years. However, on closer inspection, it becomes obvious that the predominant cause for this decline has been channeled emissions leaking from sources like chimneys and flares. On the other hand, fugitive emissions emitted from sources like pumps, compressors, armatures, and flange joints nearly remained constant (*4*), leading to an increasing influence of fugitive emissions on total emissions (*5*).

In the American approach as well as the German approach, fugitive emissions are investigated macroscopically. However, even if the emission rate of a single flange joint is measured, the transport phenomena in the gasket material are not taken into account. A closer look could help understand the mechanisms that determine fugitive emission rates and thus identify remaining potentials for further reductions.

Taking into account that gases have much lower viscosities than liquids, they have been expected to have significantly less emissions (*3*). A similar statement is implied in the emission factors for oil and gas production operations prepared by the U.S. Environmental Protection Agency (EPA) in the 1995 Protocol for Fugitive Emissions Estimation, where the emission factor for gas-charged flanges is given as $3.9E-04$ kg/hr/source and for flanges charged with light oil the factor is $1.1E-04$ kg/hr/source. Therefore, in terms of a worst case estimation, leakage tests under laboratory conditions have been performed with helium for a long time. Consequently, even though most pipes in chemical plants contain liquids, most of the fugitive emission prediction models on the microscopic scale have been developed for gases.

On the basis of the capillary models published for rubber asbestos gaskets by Kämpkes (*6*) and Micheely (*7*), Hummelt (*8*) has developed an approach for the prediction of fugitive gas emissions from graphite gaskets. Knowing the respective model parameters, we can predict the emission rates from gas-charged flange joints with graphite sealings under variations of the parameters gasket stress, pipe pressure, and roughness of the sealing face.

Because of the much higher surface tensions and viscosities for the mass transport of liquids, additional effects have to be taken into account. Therefore, the models for the gas-charged flange joints cannot be used to predict the emissions from liquid-charged equipment.

Choi (*9*) found that fugitive emissions of volatile organic compounds (VOC) correlate poorly with bulk pressure. Therefore, he presents an approach that describes the total mass transport through the flange joint and packing box sealing materials as a poiseuille flow driven by capillary forces. He assumes capillaries in which mass transport is governed by constrictions called "pinch-points". Here, the pressure gradient increases due to capillary forces and determines the emission mass flow so that the emission rate is independent from the bulk pressure.

Because the majority of models published has been developed for gases and the model published by Choi (*9*) cannot display all of the effects observed in laboratory measurements (*6–8*), (*10–15*), the existing models cannot completely describe the emission behavior of liquid-charge flange joints. A new model conception accounting for the influence of parameters like pipe pressure and the medium properties is indispensable for obtaining deeper insight into the transport mechanisms in liquid-charged gaskets.

Experimental Section

Investigations in Operating Plants. Considering the parameters influencing fugitive emissions of liquids, we performed field measurements on flange joints with graphite

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10.1021/es9010527 CCC: $40.75
Published on Web 05/06/2009

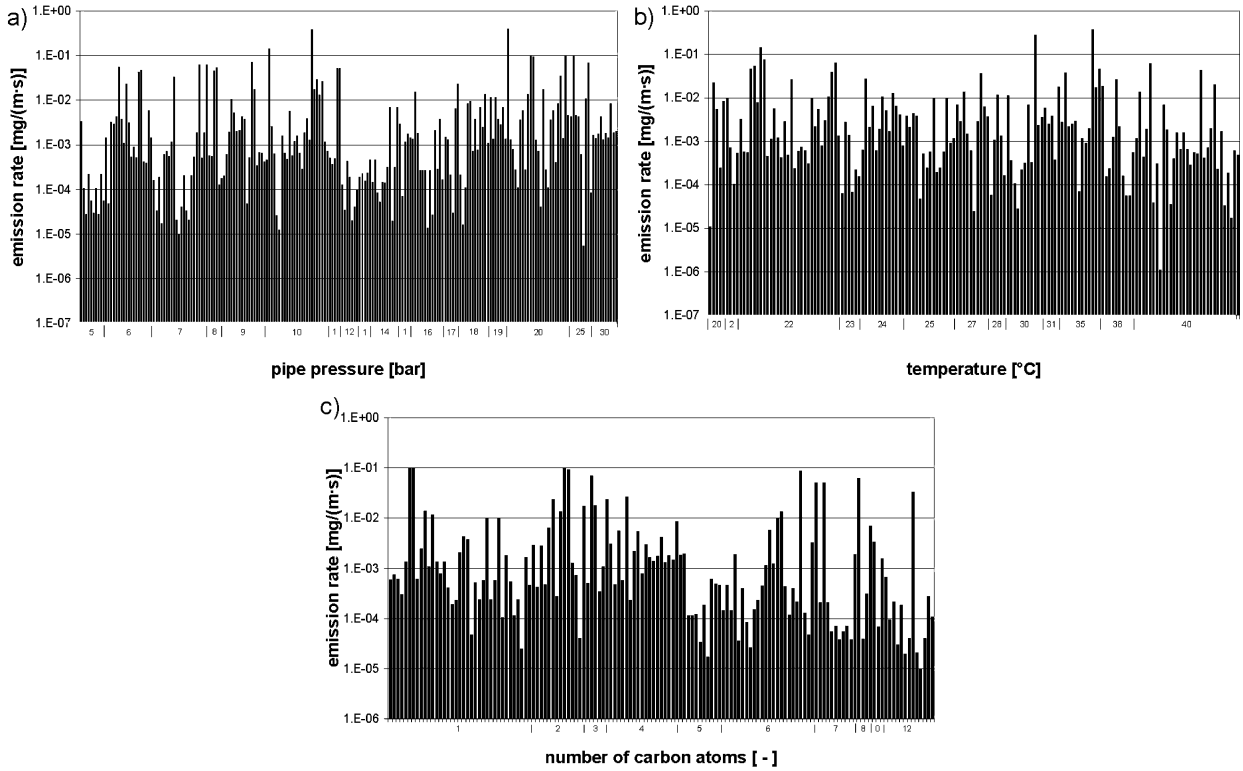

FIGURE 1. Field data of fugitive emission measurements on liquid-charged flange joints with graphite sheet gaskets as a function of pipe pressure (a), temperature (b), and molecule size (c).

sheet gaskets charged with VOCs in operating plants during the period of retrofitting to high-grade gaskets in Germany. To catch the emitted organic compound, we encapsulated the flange joint with a custom-made collar, and the cavity was rinsed with synthetic air from gas cylinders. Aspiration of secondary air was prevented by sealing the transition from the flange to the collar with putty. The carbon concentration was determined with a Compur Multi-FID 100 from Bayer Diagnostic. The sweeping gas flow rate was 70 L/h and was measured with a A5400 metal cone flow meter from Fischer & Porter. To equilibrate the gasket and reach a stationary emission rate, we used a period of 10−15 min, which was usually sufficient.

From the measured concentration and the flow rate of the sweeping gas, we calculated the emission rate and referred to the length of the gasket to make gaskets of different diameters comparable. For a derivation of the calculation formula to determine the emission rate in units of mg/(m s) and a schematic drawing of the setup (Figure S1 of the Supporting Information), see Supporting Information.

Laboratory Measurements. Using an identically constructed experimental setup as in the field measurements, we performed laboratory measurements on methanol-charged flange joints under ideal conditions, eliminating variable disturbances that occur in operating plants. Building a database for model validation, we found these measurements display the physical transport phenomena that determine the fugitive emissions of liquids.

The methanol-charged grooved gasket inner diameter was 95 mm, and the outer diameter was 121 mm. The graphite layer was 0.5 mm on each side of the gasket in a pair of flanges, with a nominal pressure of PN40, a nominal diameter of DN80, and a surface roughness of the sealing faces of 40 μm. For the laboratory measurements, an FID from Mess- und Analysetechnik GmbH Leverkusen was used. The sweeping gas flow rate was 25 L/h and was measured with a FMA1816 flow meter from Newport Electronics. The gasket stress was applied with a calibrated torque wrench. Settling was monitored with feeler pin screws according to (*16*) and compensated after 24 h and again after 36 h by retightening the screws. The measurements were run for at least 2 days to guarantee that equilibrium was reached.

Results and Discussion

Investigations in Operating Plants. To obtain deeper insight into the transport mechanisms in liquid-charged gaskets, we analyzed field data obtained with the sweeping gas method, during the German retrofit period. The majority of the gaskets investigated were graphite sheet gaskets that had to be exchanged for high-grade gaskets in order to achieve the focused fugitive emission reduction. The data are presented in Figure 1.

Although laboratory investigations on gas-charged flange joints have shown an explicit correlation between emission rates and process parameters on the one hand and properties of the transported substance on the other hand, an influence of these parameters on the leakage rates could not be found in the field data (Figure 1).

Because the expected correlations could not be found, a very simple model can help obtain insight into the transport mechanisms in liquid-charged gasket materials. Because the soft material in the gaskets investigated was graphite, in contrast to polymeric materials, the absorption of the emitting medium into the gasket material can be neglected. Assuming the total emitted mass flow to be due to laminar flow, we derived a formula describing the emission rate.

According to (*17*), the pressure loss along a straight pipe or capillary inside the sealing material can be calculated as

$$\Delta p = \frac{\rho}{2} u^2 \lambda \frac{l}{d_{\mathrm{cap}}} \tag{1}$$

where d_{cap} is the diameter of the capillaries (m), l is the length of the capillary (length of the capillary = width of the sealing material) (m), u is the velocity of the emitting component in the pores of the sealing material (m/s), Δp is the pressure

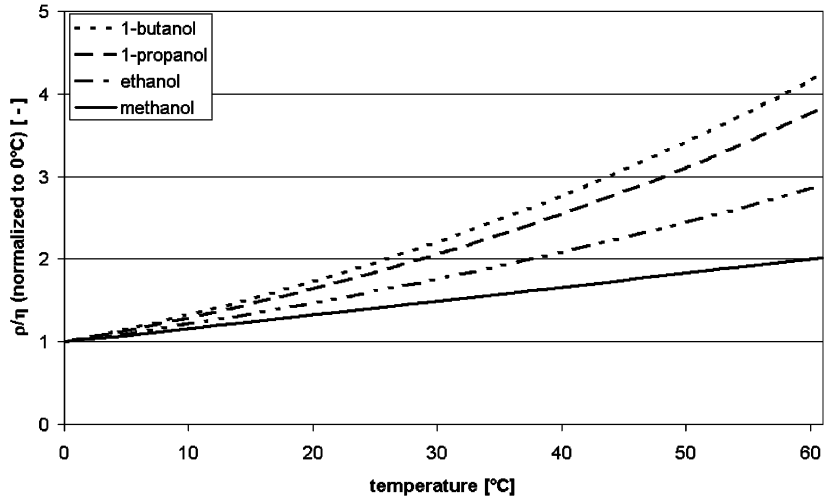

FIGURE 2. Development of the factor ρ/η with temperature for four different alcohols at a pressure of 1 bar (values calculated for 0 °C with Aspen Properties 2004.1 in units of kg/(m³ Pa s): methanol $\rho/\eta = 1.05E + 06$, ethanol $\rho/\eta = 4.52E + 05$, 1-propanol $\rho/\eta = 2.22E + 05$, and 1-butanol $\rho/\eta = 1.62E + 05$.

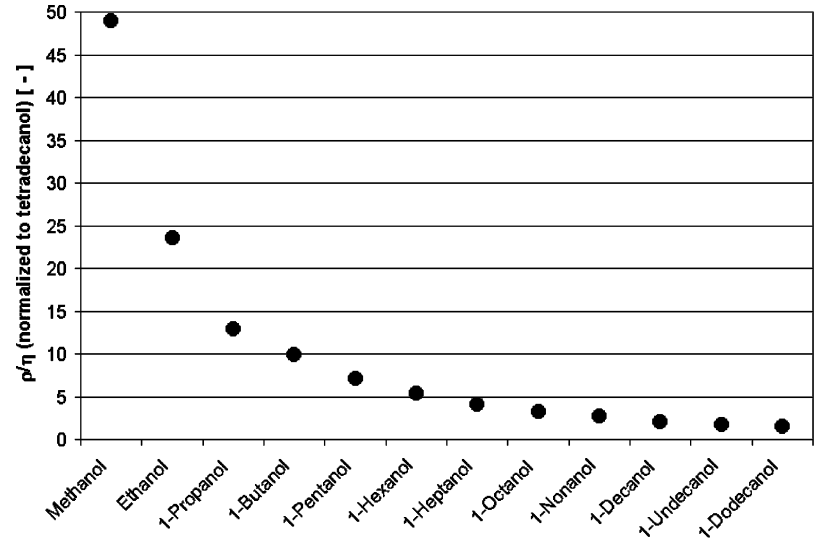

FIGURE 3. Development of the factor ρ/η with the molecule size normalized to 1-tetradecanol at 1 bar and 20 °C (reference value for 1-tetradecanol is $\rho/\eta = 2.79E + 04$ (kg)/(m³ Pa s); values calculated with Aspen Properties 2004.1).

loss along the straight pipe (Pa), λ is the pressure loss coefficient (−), and ρ is the density of the emitting liquid (kg/m³).

With laminar flow in the pores of the sealing material ($Re < 2320$), the pressure loss coefficient λ can be calculated as

$$\lambda = \frac{64}{Re} \tag{2}$$

with Re as the Reynolds number so that the mass flow emitted by a single capillary can be calculated by Hagen−Poiseuille's law

$$\dot{m}_E = \frac{\rho}{\eta}\frac{\pi d_{cap}{}^4}{128l}\Delta p \tag{3}$$

The geometry of the gasket, the factor $(\pi d_{cap}{}^4)/(128l)$, only depends on the gasket stress, which determines the diameter of the capillaries. Because the gasket stress applied on the sealing material cannot be determined without knowing the exact assembly conditions, the influence of the gasket stress cannot be taken into consideration for measurements in operating plants. Thus, the effect of the pipe pressure on the emission rate can be found in the factor Δp, which leads to an emission rate increasing linearly with pipe pressure. The influence of temperature and medium properties is determined by the factor ρ/η, where ρ is the density and η is the dynamic viscosity of the emitting medium.

In Figure 2, the factor ρ/η is plotted against the temperature for the components methanol, ethanol, 1-propanol, and 1-butanol at a pressure of 1 bar. For each component, the values presented are divided by the respective value at 0 °C to make the progressions comparable. It can be seen that the value of the factor ρ/η increases with temperature for each component, so the emission rate is expected to also increase with constant pressure. The influence of temperature on the emission rate increases with molecule size.

The impact of the molecule size on the emission rate is presented analogically in Figure 3. It shows the value of the factor ρ/η for alcohols with a terminal hydroxyl group and a length of up to 10 carbon atoms. The values presented are calculated for a pressure of 1 bar and a temperature of 20 °C. For each component, the value is divided by ρ/η for 1-tetradecanol ($C_{14}H_{30}O$) as the reference. As can be seen in Figure 3, the expected emission rate decreases with increasing molecule size for a constant pressure difference and temperature.

Because the model is very simple, the correlations presented do not necessarily have to be found exactly but can be anticipated to be in accordance with the model by trend. In Figures S2−S4 of the Supporting Information, expected progressions are plotted as a function of pipe pressure (Figure S2 of the Supporting Information), temperature (Figure S3 of the Supporting Information), and molecule size (Figure S4 of the Supporting Information) for an average emission rate of 10^{-3} mg/(m s).

Even though it is indisputable that gas and liquid emissions follow different transport mechanisms, the parameters influencing the emission rates should be similar. As none of the investigated parameters, temperature, pipe pressure, and molecule size of the emitting component had an influence on the emission rate, the effects on the microscopic scale are obviously superposed by a random influence of assembly and maintenance such as the state of the gasket, clean sealing faces, coplanar flanges, uniform gasket stress, or external forces induced into the flange joint.

The assembly conditions are especially important for modern high-grade gaskets that have a very low amount of soft material. On the one hand, this reduces the free area permeable to the emitting component and thus decreases the total emitted mass flow. On the other hand, a gasket with a higher amount of soft material can more easily compensate for unfavorable assembly conditions. Thus, high-grade gaskets are much more prone to defective mounting than graphite sheet gaskets (*18*), and the sensitivity to maintenance is increased when using high-grade gaskets.

The high roughness of the sealing faces of the old flanges is an aspect of special interest. Investigations in operating plants show that exchanging the gaskets did not lead to the reductions in emission rates that could have been expected given the very low leakage rates from laboratory investigations (*19*). Though there is no doubt about the general effectiveness of modern gaskets, the success of installing high-grade gaskets in flange joints with very rough sealing faces seems disputable.

Investigations by the American Petroleum Institute (API) (*20*) state that 1.3% of the equipment with sniffing test readings above 10000 PPM for methane caused about 77% of the total fugitive emissions in seven United States refineries. These very few pieces of equipment can very well be located with sniffing tests. Because only mechanical damage or a malfuction can lead to such high emissions, the respective equipment must be repaired as soon as possible, which is already required by regulations.

All of these findings demonstrate that assembly and maintenance have a major impact on fugitive emissions so that the only method to exactly determine fugitive emission mass flows is to survey the emission rate of every single emitter. As this involves a cost of about $400−$650 per test point, this technique is obviously not feasible. Therefore, according to the guidance of the U.S. EPA provided in the 1995 Protocol for Fugitive Emissions Estimation (*21*), empirical correlations can be used to estimate fugitive emissions. An opportunity to increase the accuracy of the estimation and to account for the conditions in the specific plant investigated is to use empirical correlations based on screening data.

Measuring emissions to detect damaged equipment is obviously a reasonable method for reducing fugitive emissions. However, an enforcement alert published by the U.S. EPA in 1999 (*22*) has shown that sniffing tests are quite prone to error. This implies that a lot of emitters may pass the maintenance test, although they should be serviced if the measurements were conducted thoroughly. Therefore, a general maintenance plan independent from the results of sniffing tests seems to be a very effective approach. Simply retightening the screws of a flange joint, which is a justifiable effort, can often reduce the emission rate by more than an order of magnitude (Figure S2 of the Supporting Information). Precondition for the success of this activity is that the gasket material is still flexible and that the maximum gasket stress is not exceeded.

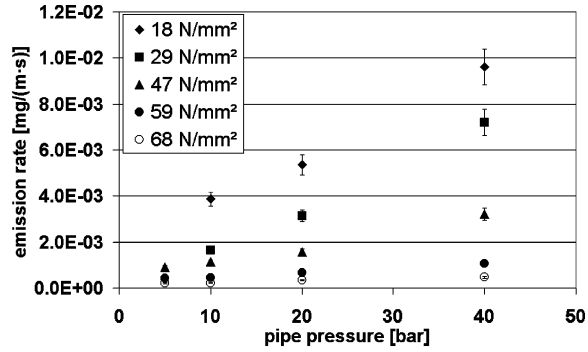

FIGURE 4. Influence of pipe pressure on emission rate.

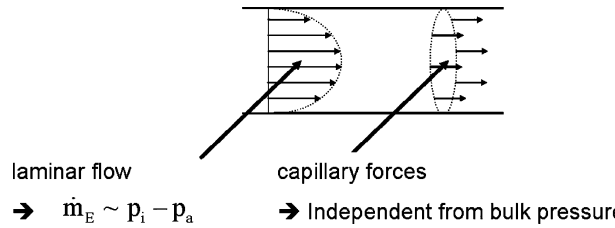

FIGURE 5. Graphical presentation of the mass transport model for liquid-charged gaskets.

Laboratory Investigations. To explain the impact of process parameters on emission rates, we performed laboratory experiments on methanol-charged grooved gaskets with the following parameters: inner diameter, 95 mm; outer diameter, 121 mm; graphite layer, 0.5 mm on each side of the gasket in a pair of flanges, with nominal pressure of PN40, nominal diameter of DN80, and a surface roughness of the sealing faces of 40 μm.

Figure 4 shows the emission rates of methanol-charged flange joints in the pressure range of 5−40 bar at five different gasket stresses from 18 to 68 N/mm^2. It can be seen that bulk pressure as well as gasket stress have a major influence on the emission rate. These two parameters have already been found to have a major impact on the emission rates of gas-charged flange joints. This affirms that the major influencing parameters are similar for gas- and liquid-charged gaskets.

It is seen in Figure 4 that, even for negligible pipe pressure, a certain minimum emission occurs that still depends on the gasket stress. This supports the hypothesis that the mass transport in liquid-charged flange joints is dominated by a combination of capillary forces and laminar flow.

Although the capillary flow mechanism proposed by Choi (*9*) can explain capillary effects, the effect of bulk pressure must additionally be taken into consideration. Modeling the entire emission behavior of liquid-charged flange joints as a laminar flow intensified by capillary forces thus seems viable. Figure 5 presents the model conception graphically.

The driving force for the mass transport must therefore be described as

$$\Delta p_{\text{driving}} = \Delta p_{\text{bulk}} + \Delta p_{\text{capillary}} \quad (4)$$

This leads to a linear correlation between emission rate and pipe pressure. Additionally, the relief of the load due to the pipe pressure has to be taken into account so that the correlation between the emission rate and the pipe pressure is no longer a straight line but a slightly convex curve, which can be found in the experimental results (Figure 4). Furthermore, the capillary forces cause a driving force inde-

pendent from bulk pressure; therefore, the emission occurring without a difference in bulk pressure can be explained.

Technical literature does not give conclusive evidence whether fugitive emissions from liquid-charged flange joints are expected to be above or below gas emissions. On the one hand, liquids have much higher viscosities than gases, but on the other hand, liquids, besides having higher densities, have much higher surface tensions. Therefore, capillary forces must play a superior role in the mass transport in liquid-charged sealing materials. By the model conception presented, it can be explained why liquid-charged equipment can cause emission rates in the same range as gas-charged equipment, even though liquids have by far higher viscosities than gases. This implies that capillary forces have a bigger influence on the emission rate than is usually thought and confirms that liquid emissions are dominated by basically different physical phenomena than are gas emissions. A prediction of liquid emissions on the basis of gas emission data is therefore not yet possible.

Because of the long periods of measurement, the database of laboratory investigations on fugitive emissions for liquids is very small in comparison to that for gases. Therefore, further measurements are inevitable to develop an experimentally verified model for the prediction of fugitive emissions from liquid-charged flange joints, including parameters like gasket stress or surface roughness of the sealing faces, which is a current research issue.

Here, two approaches are reasonable to be pursued. First, the prediction based on experiments with liquids will give a hint on the influence of medium properties so that a model can be developed. Second, helium measurements under equal conditions will provide the opportunity to determine parameters for validated models. Thus, the inner structure of the sealing material can be described so that fewer of the very time-consuming measurements on liquid-charged flange joints are necessary.

Acknowledgments

The authors thank Mr. Nottar and Mr. Skoda from Industrie- und Dichtungstechnik GmbH for providing the gaskets used in the experiments and for the technical as well as the scientific support in the course of the investigations presented. Furthermore, a very special thanks goes to the German Federal Environmental Foundation for sponsoring this research project with a scholarship and additional financial means, which made the realization of the project possible.

Supporting Information Available

A schematic drawing of the apparatus used for the laboratory investigations, expected progressions of fugitive emissions as a function of pipe pressure, molecule size and temperature, an example for the effect of retightening screws of flange joints on the emission rate, and the characteristics of the emitter concentration in the sweeping gas measured at a gasket installed dryly are available as Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org.

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ES9010527