

Interactive comment on “Gas adsorption and desorption effects on cylinders and their importance for long-term gas records” by M. C. Leuenberger et al.

Anonymous Referee #2

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General Comments

The manuscript is describing an experimental approach to investigate effects of sorption processes of various gaseous species on high pressure air cylinder walls. It is providing an introduction in the theoretical description of physisorption and evaluates the obtained experimental results from the perspective of this theoretical framework. The subject is of significance for high accuracy trace gas analysis as these measurements generally are based on referencing to air standards that are stored in such high pressure cylinders. Any composition change in the extracted air from these reference gas cylinders throughout the lifetime of such a standard as observed by the authors

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would introduce a bias in the measurement data. The authors conclude by raising the need for further experiments using a better defined experimental set-up. I highly welcome such efforts to quantify these phenomena and elucidate their mechanistic background.

However, I do have substantial questions on the presented data material as well as the interpretation of these data by the authors. The presented material seems insufficient to justify the conclusions drawn by the authors. I am not convinced that the interpretation of the experimental data is focussing on the correct processes but rather feel that it might be biased by the adopted theoretical framework. I would rate a revised version of the manuscript ready for publication only if the authors can exclude any ambiguity in the experimental set-up. The authors should also be conclusive in responding to questions raised to their interpretation of the data.

In addition, there are several specific comments that I would ask the authors to consider for a revision of the manuscript.

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Specific and Technical Comments with respect to the experimental data:

- The description of the material involved in the experiments is incomplete with respect to the characterization of the cylinders (p.8088, l.13-15). The volume and the supplier are not an exhausting characterization of the cylinders: the kind of steel and the aluminium alloy (probably 6061) should be mentioned and most importantly the cylinder head valve mounted on the cylinder. While Scott Marin aluminium cylinders are commonly equipped with packless diaphragm valves, steel cylinders from gas companies could have various types of valves. In packed valves or O-ring sealed valves the pressurized gas is in contact to sealing polymers (like PTFE, Viton, EPDM). We have made the experience that there are cylinders valve types with the potential to significantly

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modify the gas composition specifically for CO₂. This most likely is due to permeation and sorption effects on sealing polymers that are inappropriate. Such effects have the potential to be significantly larger than sorption on cylinder walls and therefore would completely mix up the experiment. The authors therefore should specify the valve type specifically the sealing type (O-ring/packed/packless) and wetted materials. The value of the entire study is at stake if the possibility that this component interferes in the experiment cannot be excluded.

- p.8089, l. 10f: "Unfortunately, the electronics of the Vici valve was malfunctioning after the first night and therefore we had to replace it." The reader does not get an idea what relevance this problem has for the experiment and the validity of its results: if the valve remained at one position for a longer period, or no gas was flowing during the period of the valve defect.

- In experiment 2 the CRDS instrument was calibrated measuring one external reference gas every two hours. The authors specify the set of calibration coefficients for CO₂ which I would consider as an irrelevant information because it is a characteristic of the individual instrument (and why only CO₂ and not CH₄ or CO?). More relevant would be the presentation of the reference measurement data to document the stability of the measurement throughout the experiment. Fig. 6 presents data with <0.005 ppm resolution whereas Fig. 4 (lower panel) indicates temporary fluctuations on a time scale of 20 min in the 0.03 ppm range (based on 480 min for 80 bar decrease = 8 min /bar), which raises the question what minimum signal actually can be taken as significant.

- p.8103 (Table 1): Surprisingly, the pressure drop for the cylinder described as leaky is the same as for the two other steel cylinders. The leaking cylinder has been replaced during the experiment but apparently not been excluded, as the results are listed anyhow in Table 2. This leaves the reader with the question whether the leak does not have the potential to provoke an additional drift.

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- The pressure drop for the replacement cylinder is more than double compared to the other three steel cylinders although it is stated that it was included only for part of the time.

- p. 8092, l. 19-22: "Unlike the steel cylinder, aluminium cylinder did not show any desorption effect for H₂O and CO and a hardly visible effect for CH₄ as displayed in Figure 5. However, it has to be stressed that the H₂O and CO mole fraction were very low and further experiment should be done in particular for CO including steel and aluminium cylinders." The CO and H₂O diagrams in Figure 5 show negative mole fractions (raw reading from the analyzer) which do not make physical sense. These data show that the instrument is at its limit of detection or that its precision is not sufficient at that level to make a meaningful measurement. I do not see the information content in displaying these data. They should be removed.

- p. 8094, l. 11f: "...which might point to a small contribution of thermal diffusion on measured CO₂ mole fraction.." It is not clear to me on what basis the argument is made that the impact of this phenomenon has a small impact on the observed small changes.

- In the caption of Table 1 the statement is made: "Note that no pretreatment of the cylinder has been applied, i.e. no steam cleaning,..". One step in the production of aluminium high-pressure cylinders is a heating and subsequent quenching using water, new cylinders are generally hydrostatically tested, there are proprietary cleaning procedures employed by manufacturers. So the quote from the caption rather states that the cylinder pretreatment is not known. The question would rather be if the cylinders had been new or what has been their filling history.

- The caption of Figure 4 explains that the Joule-Thompson cooling effect. The cooling takes place at the point of the pressure expansion of the gas, i.e. the pressure regulator; why is the regulator temperature above the cylinder temperature?

- Fig. 6: The CO₂-deviation for aluminium cylinders is between +0.01 ppm at cold

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and -0.01 ppm at warm temperatures. Despite the known precision and stability of the CRDS analyzers this is a very small signal and it would be more convincing if also the actual data and not only the linear correlation line were presented also for the aluminium cylinders, not only for steel cylinder 1 (e.g. as supplemental material - for clarity reasons, the figures could be split in a and b).

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Specific and Technical Comments with respect to the discussion of the results:

The experimental observations are directly put in the context of the theoretical framework considered in the introduction assuming that surface physisorption on a metal surface is the dominant effect:

- p. 8090, l. 22: "..where CO₂, ad corresponds to the adsorbed CO₂ molecules on the wall.."

- p. 8091, l. 3f: "These values can be compared with a monomolecular layer of CO₂ molecules on the inner cylinder wall area.."

- p. 8091, l. 22-25f: " The effect of adsorption is significantly less on aluminium than on steel surface, only about 35% of the adsorption sites are occupied. This further supports our approach to use the Langmuir model for a monomolecular layer in contrast to a multi-layer coverage."

- p. 8095, l. 12f: "The determined energy value underpins that the observed adsorption mechanism is physisorption only."

The perception of the inner surface of an aluminum cylinder as a metal surface is not appropriate. Aluminium surfaces are generally covered by a small aluminium oxide layer that may contain hydroxyl groups. Such a surface clearly has a large potential to rather form strong chemisorption (hydrogen bonds, lewis acid - base bonds) particularly

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with water molecules. Yet, these processes are not considered at all. Therefore, the following conclusion seems premature:

p. 8094, l. 18-20: " The experiments performed clearly demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO₂, CO, CH₄ and H₂O than steel cylinders."

In the introduction section, the authors have listed the assumptions that are the basis for the Langmuir model (p. 8087, l.4-7) and concede that these assumptions are often not fulfilled (p. 8087, l.15). This simplification of the Langmuir model is not at all discussed in the results section, e.g. the competition of different gas species (like H₂O and CO₂ molecules) on surface sorbent sites is not considered. The different air mixtures used in the test had varying water contents (as specified in Table 1) and this could have an influence on the CO₂ sorption in each test gas.

Such the validity of the conclusions drawn is questionable. The fact that the model provides a formula that can be used to fit the data by itself is no convincing proof.

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Further Technical Comments:

- p. 8084, l. 11: " We proved the pressure effect on physisorption..". The statement should be modified or removed as the presented evidence in the manuscript is no real proof.

- p. 8084, l. 13: Inaccurate language generates an ambiguity, either: "The CO₂ results for both aluminium cylinders ..." or "The CO₂ results for both cylinder types are in excellent agreement ..."

- p. 8084, l. 15f: The language is inaccurate: describing adsorption in units of ppm does not make sense: all quantitative statements only have a meaning in combination

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with dimensions of the used cylinders. It is disputable that there is no sorption of H₂O on the aluminium cylinder inner surface (0 ppm), and 0 ppm is not 10 times less than < 2.5 ppm.

- p. 8084, l. 16: "The CO₂ amount adsorbed..."

- p. 8084, l. 20: Inaccurate language: the reference for "latter dependence" is not clear

- p. 8084, l. 25-28: "The reversed temperature dependence for aluminium cylinders point to significantly lower desorption energies than for steel cylinders and might at least partly be due to temperature and gas consumption induced pressure changes."

I was confused why there would be a difference in temperature and gas consumption induced pressure changes between aluminium and steel cylinders and therefore suggest to re-phrase this like e.g.:

"The reversed temperature dependence for aluminium cylinders may point to significantly lower desorption energies than for steel cylinders that are covered by temperature and gas consumption induced pressure changes within the experimental set-up."

- p. 8089, l. 19: "Both CRDS instruments were frequently calibrated.."

- p. 8091, l. 8f: "It is interesting to note that the adsorbed water amount is about five times bigger.."

- p. 8090, l. 22: "CO_{2, ad} corresponds to the adsorbed CO₂ molecules on the wall, expressed as CO₂ mole fraction times the occupied adsorption sites."

The description of the term CO_{2, ad} is confusing; if this quantity means a number of molecules but is expressed as mole fraction any number can only be referred to a particular point of time within the decanting experiment. So the statement p. 8091, l. 22 has to be specified:

p. 8091, l. 22: "derived values of 0.047 ppm for CO_{2, ad} at the start of the experiment ..."

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- p. 8093, l. 5f: "Hence no influence on the temperature dependencies is expected for steel cylinders."

I was confused why the physical processes described in p. 8092, l. 29 - p. 8093, l. 8 should depend on the metal. A rephrasing could help: "The relative influence on the temperature dependency observed for steel cylinders is expected to be minor."

- p. 8095, l. 1-2: "The community is generally aware of this influence but it has not yet been quantified properly." There has been an evaluation of this effect by the WMO central calibration laboratory (Huilin Chen: Long-term stability of calibration gases in cylinders for CO₂, CH₄, CO, N₂O, and SF₆; <http://ggmt-2013.cma.gov.cn/dct/page/70029>). This evaluation did not find a generally very large increase in CO₂ mole fractions in cylinders vented to low pressures.

- Table 1: Are two decimals in bar for the pressure meaningful?

- Figure 1: The definition of "actual temperature" and "set temperature" is not self-explaining; re-phrasing the caption would make it easier to understand: "the actual temperature follows the set temperature with a delay of 2.75 h (bold blue line accounting for the time shift)"

- Figure 4 last line of caption: "...cannot be determined.."

- Figure 5: The displayed uncalibrated data for CO and H₂O are partly negative mixing ratios (raw reading from the analyzer); the relative precision of the analyzer at these mole fractions is on the order of tens of percents compared to 0.01% relative for CO₂ and 0.02% relative for CH₄. Therefore the statement "CO and H₂O show no ...desorption effect" should be replaced by "no effect of CO and H₂O can be detected given the limitations of the analyzers signal-to-noise at that level". There appears to be a pretty similar increase of CH₄ and CO₂ below mole fractions of 404.4 ppm CO₂ i.e. for the first 80 bars of pressure release. It is when venting the last 20 bar where the CO₂ increase is decoupled from the CH₄ trend.

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- Figure 6: The CO₂-deviation for aluminium cylinders is between +0.01 ppm at cold and -0.01 ppm at warm temperatures. Despite the know precision of the CRDS analyzers this is a very small signal and it would be more convincing if also the actual data and not only the linear correlation line were presented also for the aluminium cylinders, not only for steel cylinder 1 (for clarity reasons, the figures could be split in a and b).

- Figure 7, caption I. 3: "The slopes are corresponding.."

- Figure 8, caption I. 6-8: Suggestion for re-phrasing: "The correlation is rather bad ($r^2 = 0.6$). Part of the variability might be due to temperature induced effects that are independent of adsorption/desorption phenomena."

- Figure 8, caption I. 8: "Hence desorption energies have to be taken with care." This should be reflected in the number of decimals of the slopes that are displayed.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 8083, 2015.