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Numerical investigation of safety aspects of hydrogen/carbon monoxide mixture release

Boris Chernyavsky^{a*}, Pierre Bénard^a, Jake Devaal^b and Benjamin Angers^a^aHydrogen Research Institute, Université du Québec à Trois-Rivières, CP Box 500, Trois-Rivières, Québec, G9A 5H7, Canada^bBallard Power Systems, 9000 Glenlyon Parkway Burnaby, BC V5J 5J8 Canada

Abstract

Research into the performance of proton exchange membrane fuel cell (PEMFC) and its degradation ("poisoning") by the presence of carbon monoxide, a common byproduct of most common hydrogen production methods, requires storage of a large quantities of hydrogen/carbon monoxide mixture in high pressure tanks. The possibility of unintended release of the gas calls for a safety study of H₂/CO mixture leaks, as well as potential higher rate releases. This presentation covers the safety aspects of the numerical study of a H₂/CO mixture release at a wide range of release parameters, including release velocity, orientation, initial diameter, and initial gases fraction ratio. The study provides a simulation of a) the extent of flammable concentrations of H₂, corrected for the presence of CO; b) the extent of CO concentration exceeding OSHA recommended health safety limits. The presence of CO in the mixture required reassessment of hydrogen flammability limits, although the correction proved to be relatively small for the CO fractions used in the present. The maximum extents and evolution of H₂ and CO envelopes had been modeled and compared. An important conclusion is the possibility of using hydrogen detectors to predict CO concentration levels with accuracy sufficient for practical purposes.

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binary gas mixture releases, numerical modeling, gas mixture segregation, hydrogen

1. Introduction

Common methods of hydrogen production often leave a significant amount of CO present in gas mixture. The presence of CO can degrade the performance of proton exchange membrane fuel cell

* Boris Chernyavsky. Tel.: +1-819-376-5011x3432

E-mail address: boris.chernyavsky@uqtr.ca

(PEMFC) which is referred to as CO poisoning. In order to study its effects, it is necessary to store and use significant quantities of hydrogen mixed with CO in various ratios. This requirement and consequent possibility of mixture leak from storage tanks or piping has prompted Ballard Power Systems to commission the research into the characteristics of mixture release with an emphasis on the determination of the extent of gas envelope with concentration exceeding safety limits and its comparison with hydrogen flammability envelope extent.

While jet evolution and the behaviour of resulting gas concentration envelopes, including studies of hydrogen releases, is a field of active research with a number of research papers appearing in the literature, the study of binary releases had so far been much more limited, particularly in regard of releases with CO component. Meanwhile the binary releases present unique challenges for safety analysis and characterization. The first challenge lies in a dramatic change of release conditions (Mach number, flow rate, velocity, etc.) with the change of mixture gas fractions, due to a significant difference in molecular weight. This requires larger number of simulations to cover the entire possible range of release conditions in order to formulate useful safety criteria. The second challenge lies in potential segregation of gas components, causing a binary jet to exhibiting behaviour different from a single component jet. The segregation of gas components is promoted by a) difference in gases mutual diffusion coefficients with air, and b) different molecular weight and therefore buoyancy. At the same time, it is suppressed by the turbulence which promotes intensive gas mixing. The outcome of the action of these opposite effects depends on a local conditions at a given release location and presents an interesting physical problem, which has significant practical importance for successful prediction of binary gas release evolution and resulting gas envelope extents. The main objectives of the study, therefore, were to:

- Compare the extents of flammable H₂ envelope with hazardous CO concentration envelope for a variety of jet release velocities, flow rates/nozzle diameters and orientations
- Evaluate the influence of local gas mixture on flammability criteria
- Investigate the degree of gas segregation, if any

Investigation of gas segregation had an important practical objective. Most of the facilities handling hydrogen possess a well developed network of hydrogen sensors to monitor hydrogen concentrations to prevent it reaching flammable thresholds unexpectedly, for example in the result of leaks and/or emergency releases, and to plot the extent of such concentration envelopes in case of emergency. At the same time, relatively few facilities working with hydrogen possess a separate network of CO sensors. If it can be assumed that there is no segregation between gas components, or the degree of segregation is negligible, it would be possible to utilize existing hydrogen sensors network to predict the presence of hazardous CO concentrations by extrapolating from the measured hydrogen fractions and the known initial gas ratio.

Nomenclature

D	diameter of the release opening, m
Delta	difference between observed CO molar fraction and CO molar fraction predicted from hydrogen data in assumption of no segregation, $X_{CO \text{ observed}} - X_{CO \text{ predicted}}$
M	Mach number

u	axial velocity, m/s
x	distance from release origin along jet (plume) centerline, m
X_n	molar fraction of gas n

2. Methodology, results and discussion

2.1 Methodology

Numerical simulations of binary gas releases had been performed using ANSYS FLUENT [1] CFD software, using steady state solver with k- ϵ realizable turbulence modeling approach, which had been previously validated during simulations of pure hydrogen jet releases [2]. Simulations used high resolution unstructured grids clustered around projected jet expansion trajectory in order to accurately capture mixing and diffusion processes at the jet periphery. Simulations used standard hydrogen, air and CO properties as listed in ANSYS FLUENT built-in database. Mutual diffusion coefficient for hydrogen and carbon monoxide is taken from experimental results as reported in [3, 4].

Two sets of release conditions, covering high flow rate ("jet-like") and low flow rate ("plume-like") had been investigated. The first set modeled the gas mixture release from a 6.35 mm diameter round opening with release Mach numbers varied between 0.1 and 0.5, and CO molar fractions between 0 and 30%. In addition to different release conditions, simulations covered different release orientation relative to the gravity vector. These conditions simulated either uncontrolled (pipe rupture) or controlled (through emergency valve) release with a high flow rate resulting in a gas jet with significant initial velocity and extended momentum dominated region. Second set of simulations covered low rate releases more characteristic of leak scenarios, with low speed ($M = 0.01 - 0.001$) release of a mixture containing 1% of carbon monoxide from a 1 mm diameter round opening.

The primary criteria for determination of safe concentration were OSHA limits for a long term exposure (50 ppm), and a maximum short term exposure limit of 1500 ppm. Conventional 4% limit had been initially chosen for evaluation of hydrogen flammable concentration extent for pure hydrogen. The presence of CO in the mixture required reassessment of flammability limits, although the correction proved to be relatively small for the CO fraction values used in the present study (the largest correction was necessary for 30% CO case, altering lower hydrogen flammability from 4% to 5.025%).

2.2 High flow rate releases

First series of simulations covered high flow rate jet releases. Summary of the release conditions and maximum extents of gas envelopes is provided in Table 1 and in Fig. 1. Figures 2-5 illustrate the envelopes of CO and H₂ at different release conditions and orientations. It can be seen that the maximum extent of 50 ppm CO envelope significantly exceed flammable hydrogen extent for all tested release conditions, while the extent of 1500 ppm CO envelope lies between 1% and 4% hydrogen envelopes for initial CO fractions above 2%, indicating that for the high flow rate releases the hazardous CO concentration extent typically significantly exceed the extent of hydrogen flammable envelope. Figures 4 and 5 confirm that this remains the case for all jet orientations, with both 1500 ppm CO and 4% hydrogen envelopes largely confined within momentum dominated areas showing relatively little influence of buoyancy effects (compare with 50 ppm CO envelope). The difference in the flammable hydrogen envelope extent due to

the correction of hydrogen flammability limits, accounting for the presence of CO, is small (0.6 m versus 0.71 m uncorrected 4% value for the case of 30% initial CO fraction, requiring the largest correction)

Table 1. The maximum extent of practically significant thresholds of hydrogen and CO molar fractions for various high flow rate release conditions measured along jet centerline. Numbers in brackets for the horizontal release corresponds to the molar fraction extent along the horizontal axis. For all cases gas is released from an opening with D=6.35 mm.

Case	4% H2 extent, m	2% H2 extent, m	1% H2 extent, m	1500 ppm CO extent, m	Flow rate kg/s
0% CO M=0.5	2.95	5.53	8.74	n/a	1.7e-3
2% CO M=0.5	2.44	4.90	7.84	1.13	1.9e-3
5% CO M=0.5	1.99	4.23	7.04	2.98	2.22e-3
10% CO M=0.5	1.46	3.35	6.04	4.85	2.62e-3
30% CO M=0.5	0.71	1.61	3.60	7.75	3.81e-3
2% CO M=0.3	2.31	4.54	7.23	1.115	1.33e-3
2% CO M=0.3 Horizontal	2.49 (2.15)	4.72 (2.68)	6.83 (2.94)	1.105	1.33e-3

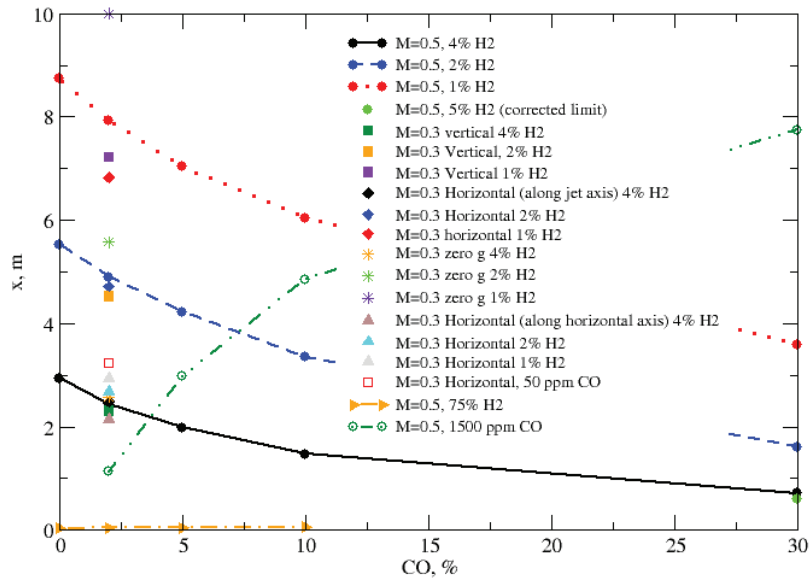


Fig. 1. Hydrogen and CO concentration envelopes extent for various initial parameters. All cases are for D=0.00635 m.

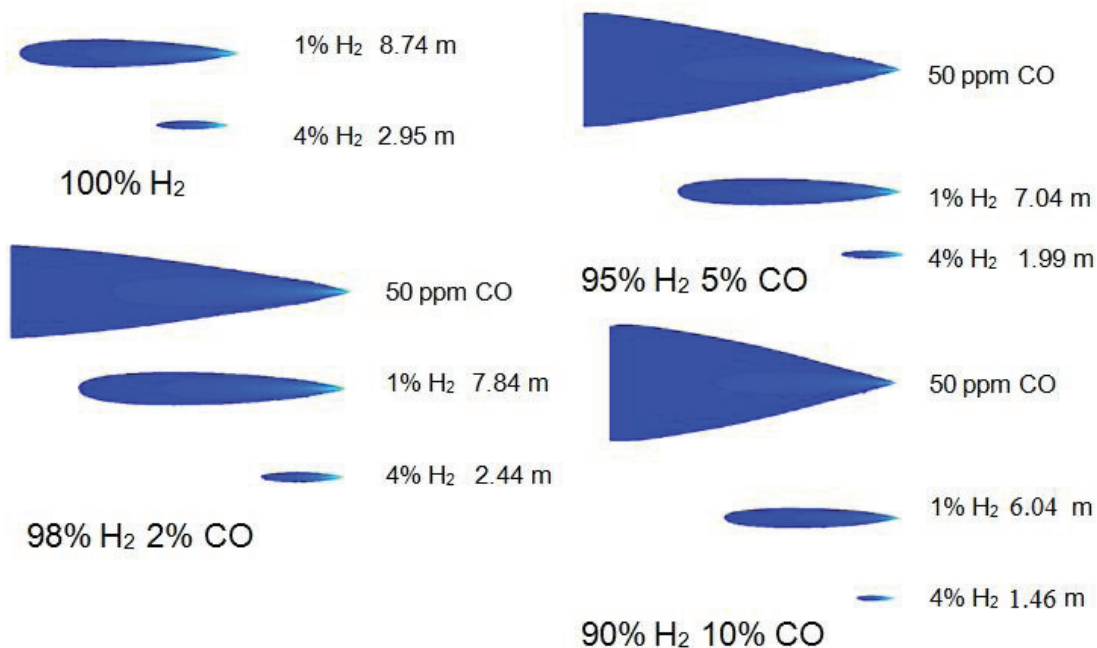


Fig. 2. Comparison of the hydrogen and carbon monoxide envelopes: the effect of initial CO volume fraction on hydrogen and carbon monoxide gas envelopes. Numbers correspond to the maximum extent of appropriate concentration envelope along the centerline.

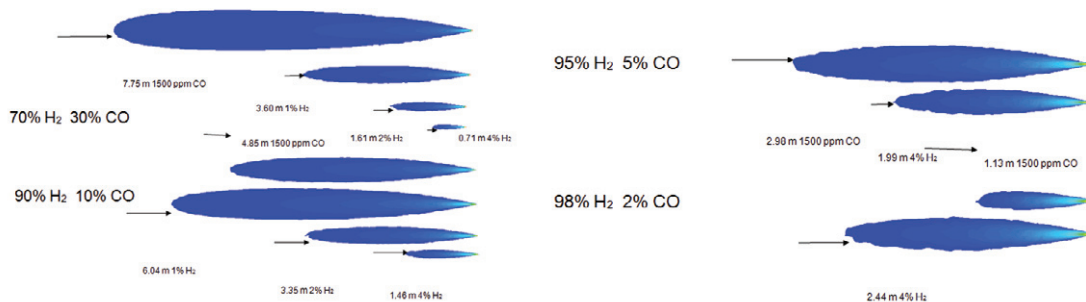


Fig. 3. Comparison of the hydrogen and carbon monoxide envelopes: the effect of initial CO volume fraction on hydrogen and carbon monoxide gas envelopes. Numbers correspond to the maximum extent of appropriate concentration envelope along the centerline.

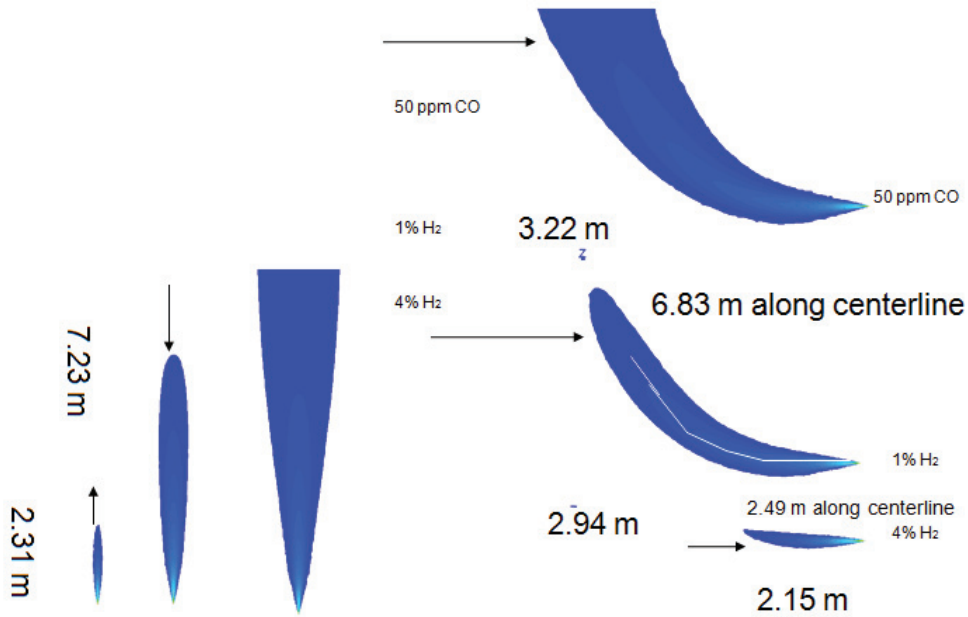


Fig. 4. Comparison of the hydrogen and carbon monoxide envelopes for the (a) vertical and (b) horizontal releases. Three envelopes represent, top to bottom: 50 ppm CO envelope, 1% H₂ envelope, and 4% H₂ envelope. Initial CO molar fraction is 2%, release velocity corresponds to M=0.5.

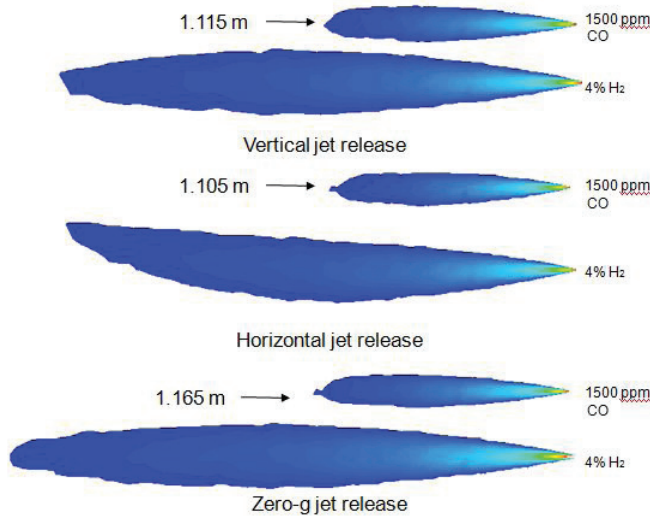


Fig. 5 Comparison of the hydrogen and carbon monoxide envelopes for the (a) vertical, (b) horizontal, and (c) zero-g releases. Two envelopes represent, top to bottom: 1500 ppm CO envelope and 4% H₂ envelope. Initial CO molar fraction is 2%, release velocity corresponds to M=0.5.

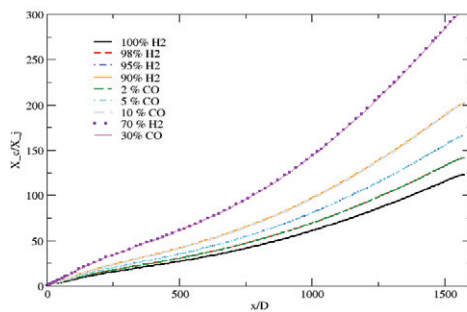


Fig. 6. Normalized molar fraction decay rates for high flow rate releases. Segregation between gases is below plot resolution

Table 2. Magnitudes and locations of maximum values of Delta (difference between predicted and observed CO molar fractions). Note that M=0.5 case had larger nozzle diameter (numbers in square brackets are recalculated for D=0.001 mm for comparison with low flow rate cases).

Case	Diameter, mm	Flow rate, kg/s	Maximum Delta, ppm	Maximum Delta location, x/D
U=1.2 m/s, vertical, 1% CO	1	91e-9	4059 (-300)	2.77
U=1.2 m/s, horizontal, 1% CO	1	91e-9	3686 (-275)	2.51
U=12 m/s, vertical, 1% CO	1	0.9e-6	889	11.9
U=12 m/s, horizontal, 1% CO	1	0.9e-6	711	13.8
M=0.5, vertical, 2% CO	6.35	1.9e-3	9.4	6.8 [43.18]
M=0.5, vertical, 5% CO	6.35	2.22e-3	20	6.8 [43.18]
M=0.5, vertical, 10% CO	6.35	2.62e-3	47	5.39 [34.22]
M=0.5, vertical, 30% CO	6.35	3.81e-3	338	3.95 [25.08]

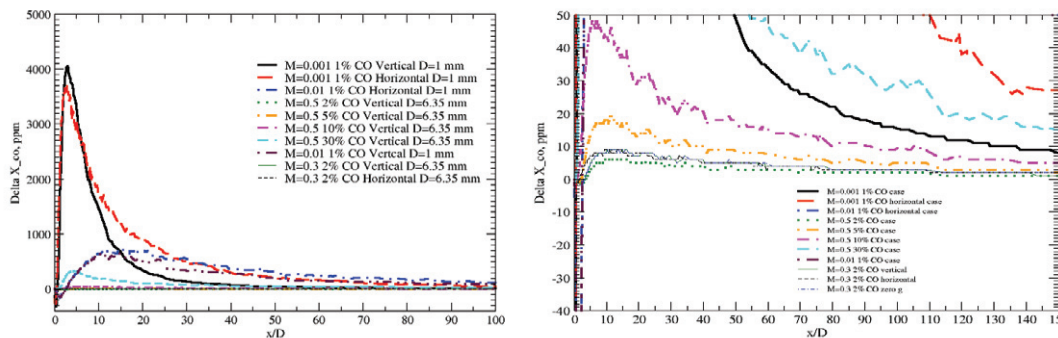


Fig. 7. Difference between CO molar fraction values predicted from H₂ and actually observed $\Delta = X_{CO \text{ observed}} - X_{CO \text{ predicted}}$ for various initial conditions (a) magnitude of Delta; (b) magnified view illustrating the extent of area with Delta > 50 ppm

Table 3. The maximum extent of the region where Delta values (CO molar fraction difference between observed and predicted from H₂) exceed long (1500 ppm) and short (50 ppm) term exposure limits. Beyond these distances CO molar fraction values estimated from H₂ values are within 1500(50) ppm from actually observed. Note that M=0.5 case had larger nozzle diameter (numbers in square brackets are recalculated for D=0.001 mm for comparison with low flow rate cases).

Case	Diameter, mm	Maximum extent Delta>1500 ppm, x/D	Maximum extent Delta>50 ppm, x/D
U=1.2 m/s, vertical, 1% CO	1	9.8	49
U=1.2 m/s, horizontal, 1% CO	1	12.05	110
U=12 m/s, vertical, 1% CO	1	-	148
U=12 m/s, horizontal, 1% CO	1	-	151
M=0.5, vertical, 30% CO	6.35	-	54 [342.9]

Examination of gas molar fraction evolution along the centerline did not initially revealed significant segregation between the gases, as illustrated by Fig. 6 which shows that the decay rates (inverted molar fraction normalized by the initial value at release origin X_j/X_c , where X_j is initial molar fraction and X_c is molar fraction at a centerline at a given distance from the release origin) of both gases plotted against distance from the release origin essentially coincide within plotting accuracy. In order to resolve and quantify the segregation, we introduced parameter Delta, defined as the difference between CO molar fraction observed at a given location, and the molar fraction predicted from hydrogen molar fraction in the assumption of no segregation (i.e., constant hydrogen/CO ratio equal to initial value),

$$\Delta = X_{CO \text{ observed}} - X_{CO \text{ predicted from H}_2}$$

When applied to the results of the simulations, it revealed the presence of relatively small degree of gas segregation close to the release origin, summarized in Fig. 7a and Table 2. The maximum Delta value observed for the high flow rate release was 338 ppm (positive value indicates that no segregation assumption underestimated CO molar fraction), which was obtained at 3.95 diameters from the release origin in the case with M=0.5 and initial CO molar fraction of 30%. While this value exceeds the long term health hazard threshold of 50 ppm, it should be noted that the high Delta values were restricted to immediate vicinity of the release origin, and quickly dropped to below 50 ppm level (see Fig. 7b and Table 3 for maximum extents of practically significant Delta values). The maximum distance from the release origin at which Delta values above 50 ppm had been observed was at $x/D=54$, corresponding to 343 mm from the release origin, beyond which point the estimate of CO molar fraction made in assumption of no gas segregation produced errors below 50 ppm. Other cases with lower initial CO fraction demonstrated correspondingly smaller maximum Delta values, leading to the conclusion that CO concentration estimate from observed hydrogen molar fraction will be within practically acceptable tolerances for high flow rate releases with exception of close vicinity of release origin.

2.3 Low flow rate releases

Second series of simulations covered low flow rate releases characteristic for slow leaks, resulting in a plume-like releases, with a very short or absent momentum dominated region. Release velocity for this set of cases was in a range of 1.2-12 m/s ($M=0.001-0.01$), release opening diameter of 1 mm and initial CO molar fraction of 1%. Molar fraction decay rates for this release mode, illustrated in Fig. 8a clearly show a difference between two gases evolution. Delta values, as listed in Table 2 and illustrated in Fig. 7a are significantly larger, and in fact exceed 1500 ppm short term exposure threshold. Closer examination, however, indicates that the regions of high Delta values are once again restricted to the very close vicinity of the release origin (Fig. 7b, Table 3), with rise and subsequent decay of Delta being much faster than for the high flow rate releases. It can be seen that the maximum segregation is observed very close to the release point and it quickly falls off toward small values. Similar to high flow rate case, higher release velocity results in a lower segregation stretched further from the release point. From a practical point of view, it is seen that the maximum segregation (and therefore maximum errors in evaluation of CO concentrations from H_2 values) lies at a very close distance (10-50 diameters - 1-5 cm for this case) from the release point, and the absolute error falls below 50 ppm value beyond 50 diameters (~30 cm) in all high speed cases and ~ 150 diameters (15 cm) in all low speed cases. Maximum observed Delta exceeded 4000 ppm (4059 at 2.77 mm from the release origin for 1.2 m/s release), with the maximum extent of the region with Delta exceeding 50 ppm being 148 mm for vertical release (at $M=0.01$) and 151 mm (measured along the plume centerline) for horizontal release.

As can be seen from Fig. 7a, as the release flow rate (and velocity) decreases, the maximum magnitude of Delta sharply increases, but both its rise and fall-off becomes faster, resulting in a shrinking extent of the region where prediction of CO molar fraction value based on no segregation assumption is significantly inaccurate, even as the magnitude of error grows. Figure 8b illustrates relative Delta values (Delta normalized by observed CO molar fraction). It can be seen that the relative error falls off much more gradually, remaining at ~ 10% level at 500 diameters from release origin and only gradually decaying beyond that distance; however the absolute values of Delta for CO molar fraction at these distances become significantly smaller than health hazard threshold for a long term exposure. This allows us to conclude that the estimate of CO concentration based on hydrogen molar fraction measurements and no-segregation assumption produce reasonably accurate for practical applications results. More detailed investigation of the nature of gas segregation and its primary driving forces is the subject of work in progress, with preliminary results indicating the dominance of the difference in diffusion properties over buoyant forces as a primary segregation driver [5].

3. Conclusions

Numerical simulation approach had been used to investigate the extent of hazardous CO concentration envelope for the gas mixture releases at a variety of initial conditions and to compare it with the extent of the envelope of hydrogen in flammable concentrations. Additional study had been conducted to characterize the extent of segregation between components of released gas mixture and investigate its evolution. The primary conclusions are:

- For high flow rate releases, dangerous long term exposure (> 50 ppm) CO envelope extent always exceeds flammable hydrogen envelope extent, while dangerous short term exposure (> 1500 ppm) CO envelope extent is comparable to the flammable extent of hydrogen
- Segregation of hydrogen and carbon monoxide is relatively small for the purpose of safety analysis through the entire range of tested parameters

- Maximum gas components segregation is observed close to the release point within less than 20 diameters, with Delta values falling below 50 ppm close to the release origin: within $\sim 60 x/D$ for a worst case scenario of a high flow rate release (~ 36 cm from origin) and $\sim 150 x/D$ (~ 15 cm from origin) for a low flow rate release. Only the lowest velocity release shows the segregation resulting in Delta above 1500 ppm, and only within first ten diameters from the release origin. Delta values fall below 50 ppm at.
- CO concentration can be predicted with sufficient accuracy from the hydrogen concentration readings for practical purposes, except for the immediate vicinity of release origin (within ~ 0.5 meter, or ~ 200 diameters)

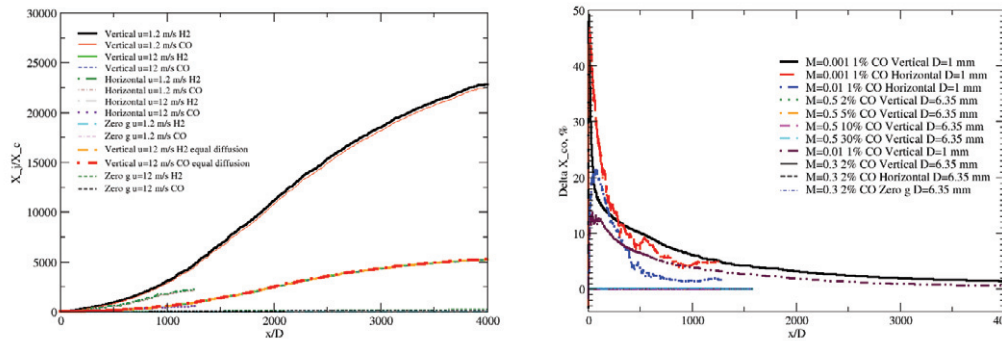


Fig. 8. (a) Normalized molar fraction decay rates for low flow rate releases. The segregation between gases is clearly visible (b) Relative Delta (Difference between observed and predicted CO molar fraction normalized by observed molar fraction)

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