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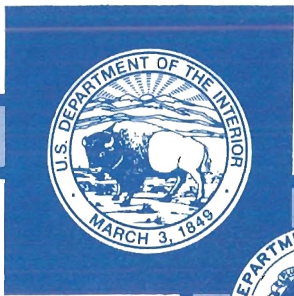
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Evaluation of the Response of Diffusion-Type Carbon Monoxide Sensors

By John C. Edwards and Gerald S. Morrow

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | | | |
|-------------------------|-------------------------------------|------------|-------------------------|
| cm | centimeter | m/s | meter per second |
| cm/s | centimeter per second | min | minute |
| cm²/s | square centimeter per second | pct | percent |
| L | liter | ppm | part per million |
| L/min | liter per minute | s | second |
| m | meter | | |

EVALUATION OF THE RESPONSE OF DIFFUSION-TYPE CARBON MONOXIDE SENSORS

By John C. Edwards¹ and Gerald S. Morrow²

ABSTRACT

Carbon monoxide (CO) sensors are used in mine fire early-warning systems. Experiments were conducted by the U.S. Bureau of Mines with six diffusion-type CO sensors to determine their response to a reference CO concentration under both static and dynamic flow conditions. Static experiments were conducted with 0.5 L/min flow of 16 ppm CO in N₂ through 8- and 12-L chambers. Dynamic flow experiments were conducted in two environmental chambers: One had directional flow capability of 1 m/s, and the second provided moderately nondirectional flow as high as 1.8 m/s. Reference CO concentrations of 13.5 to 19 ppm in air were used for the dynamic experiments. The results of the static experiments demonstrated that the sensors consistently underestimated the reference gas concentration. The dynamic experiment results showed the sensors provided reasonable agreement with the reference gas concentration when directional flow effects were not considered. Directional flow effects were evaluated for two sensors. One of the sensors showed a strong dependence upon the relative orientation of the diffusion tube with respect to flow direction. The second sensor did not show a dependence upon flow direction. The sensors' directional flow effect is significant for their proper in-mine utilization.

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INTRODUCTION

This work was initiated by the U.S. Bureau of Mines (USBM) with the objective of evaluating potential fire sensors for use in underground mines. As part of the development of a fire detection strategy to improve mine safety, it is necessary to know the response characteristics of the sensors employed in the measurements. A recent study (1)³ has shown sensor characteristics to be important for the interpretation of contaminant spread and fire location in a mine. A common type of sensor used for detection is a diffusion-type carbon monoxide (CO) sensor. The contaminant gas reaches an electrochemical cell in the sensor by diffusion. A diffusion-type sensor has advantages over a mechanical pump sensor, including factors such as less electrical energy consumption and the lack of mechanical pump maintenance. The operational principle of the sensor is based upon the electrochemical oxidation of CO at one of the sensor's electrodes (2-3) and the resultant hydrogen ion's transport to the other electrode. This creates a current that is amplified and converted to a voltage. The voltage is linearly proportional to the gas concentration. The characteristic time defined by this electrochemical conversion is much faster than the time for the CO to reach the electrochemical cell by diffusion. This time is defined as the diffusion mode time constant.

Access of CO to the electrolytic cell occurs through either a tube or a screen or a sintered disk. In most cases, the sensor combines a tube, referred to as the diffusion tube, with a screen or sintered disk. This combination not only will prevent airborne dust from clogging and blocking the cell entrance, but will create a constant diffusion rate of CO to the cell. The diameter of the tube is sufficiently large so as not to influence the diffusion process. The details of this process have not been addressed by the manufacturers. A uniform diffusion mode of CO to the cell ensures a wide range of air flow independence in the in-mine application of diffusion-type CO sensors.

In order to determine the response characteristics of CO diffusion-type sensors, the USBM investigated the response of a diffusion-type sensor from each of six distinct manufacturers to both a static and a dynamic environment containing a known CO concentration. The diffusion process will be molecular diffusion in the static mode and turbulent in the dynamic mode. Although the latter is most representative of in-mine use, the former is important for understanding the response characteristics of sensors. The specific experimental conditions investigated are not representative of all possible conditions, but do give a broad definition to the possible uses of the diffusion mode sensor.

EXPERIMENTAL PROCEDURE

The static experiments were conducted with each sensor in a cylindrical chamber through which 16 ppm CO in N₂ was fed at a constant flow rate of 0.5 L/min with an accuracy of ± 0.05 L/min. Initially, the static chamber contained room air. As CO was fed into the chamber, the CO concentration in the chamber increased. The linear gas flow in the chamber was less than 0.05 cm/s, which is nearly a quiescent environment. The size limitations of the chamber required that several sensors be removed from their cases in order to be inserted into the chamber. For these sensors the CO detection cell with attached diffusion tube and electronics board were mounted in the chamber. Two samples of the CO supply gas were analyzed. Volume concentrations of 16.3 and 16.4 ppm were determined within an accuracy of ± 0.5 ppm. The six sensors are labeled A through F for reference. Sensors designated B₁ and B₂ differ only insofar as sensor B₂ is sensor

B₁ with a dust shield on the inlet of the diffusion tube. For sensors A and B₁, an 8-L chamber was used, and for sensors B₂ through F a 12-L chamber was used.

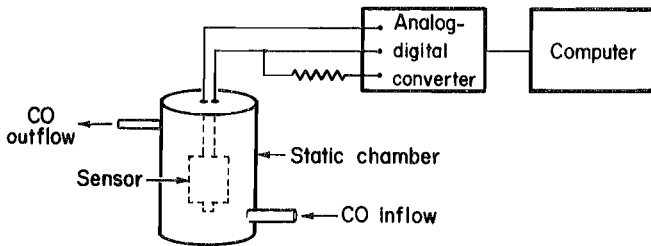
The sensors were calibrated to within 1 ppm prior to each experiment with hydrocarbon-free air and 25 ppm CO, per the manufacturers' instructions. Subsequent to each experiment the calibration was verified. Lengthy exposures to 16 ppm of CO did not appear to affect the sensors' calibration by more than 0.5 ppm. The electrolytic cell common to most of the sensors had a stated accuracy of at least ± 1 ppm, which is the controlling factor for the sensor. The static experiments were conducted for sufficient duration until a steady-state concentration was achieved. As a guide, the chamber concentration is expected to be within 94 pct of the steady-state concentration after three exchanges of gas volume. This is based upon the assumption that the increase in contaminant concentration is well mixed during each volume exchange in the chamber. For sensors B₁, B₂, and F, a video was made of the digital display of CO concentration for each

³Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

experiment. For the remaining sensors, data were acquired with an analog-to-digital data acquisition system and recorded on a mine monitoring computer system. A schematic of the experimental static test arrangement is shown in figure 1.

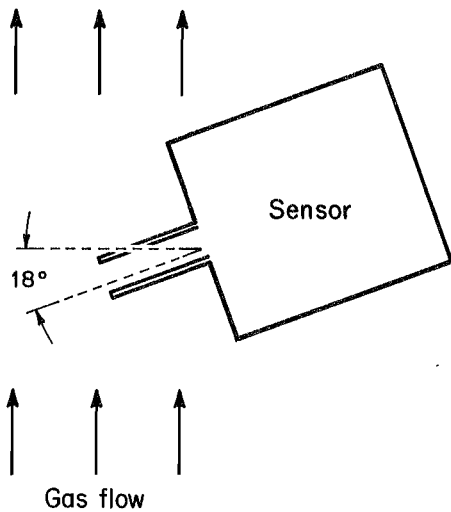
The dynamic experiments were conducted in an environmental chamber that can be used to regulate not only gas flow, but humidity and temperature. For sensors A, B₁, and B₂, the environmental chamber had dominant unidirectional gas flow control as shown in figure 2. This chamber was not available for the experiments with the other sensors. The environmental chamber used for experiments with sensors C through F did not have dominant unidirectional flow. The flow in this environmental chamber was recirculatory, as shown in figure 3.

Figure 1



Schematic of static test procedure for CO sensors.

Figure 2



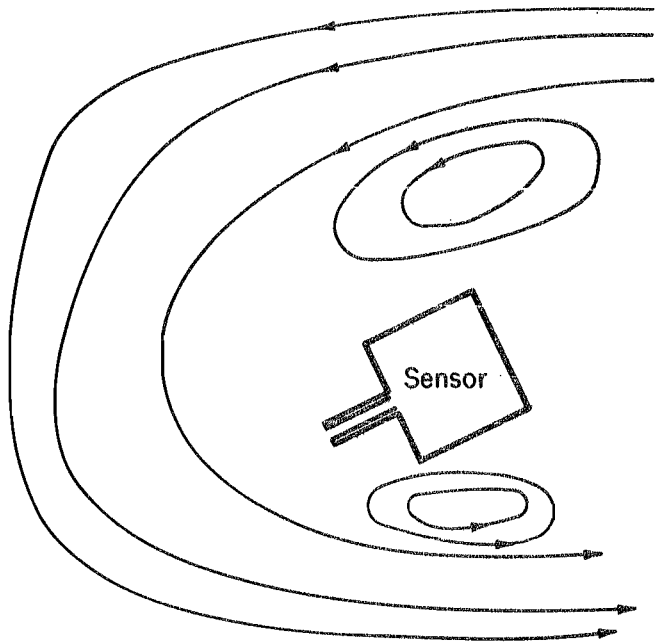
Schematic of flows in environmental chamber with unidirectional flow.

The physical dimensions, inner length L and inner diameter d , of the diffusion tube for each sensor are listed in table 1. Sensor F did not have a diffusion tube. To prevent the deposition of dust on the cell interface during in-mine utilization, each diffusion tube had either a screen or sintered metal disk in place. Sensors B₁ and B₂ had a sintered metal disk in both the diffusion tube and the calibration plug, while the remaining sensors had a screen. The screen also provided a uniform flow in the diffusion tube for calibration purposes. It was demonstrated for a sensor that the absence of a screen resulted in a calibration dependence upon the azimuthal orientation of the calibration plug through which CO enters the sensor's cell.

Table 1.—Sensor diffusion tube length (L) and diameter (d), in centimeters

| Sensor | L | d |
|-------------------------------------------|-----|-----|
| A | 5.3 | 1.9 |
| B ₁ , B ₂ | 2.2 | 2.2 |
| C | 4.4 | 3.4 |
| D | 5.2 | 2.0 |
| E | 1.9 | 1.9 |

Figure 3



Schematic of flow in environmental chamber with recirculating flow.

DIFFUSION MODEL

In order to provide an interpretation of the static experiments, a one-dimensional diffusion model was developed. Diffusion of CO along the sensor diffusion tube results in a concentration $C(x,t)$ at distance x from the open end ($x = 0$) of the diffusion tube at elapsed time t . The diffusion transport equation is as follows (4):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

where D is the diffusion coefficient.

The boundary condition at the tube inlet is the concentration of CO in the static chamber. This is approximated by an asymptotic approach to the steady-state concentration, which is exponential in time:

$$C(x = 0, t) = C_0 (1 - e^{-t/\tau}). \quad (2)$$

This represents an approximation to the actual change in concentration within the chamber with a constant inflow

and constant outflow rate. The time constant τ is the time required to flow a volume of gas equal to the chamber volume.

At the interface of the diffusion tube with the electrolytic cell ($x = L$ in the one-dimensional coordinate system), the boundary condition is

$$-D \frac{\partial C}{\partial x} = \gamma C \Big|_{x=L}. \quad (3)$$

A linear loss of CO to the cell is assumed in equation 3 at a velocity γ . The velocity parameter γ is determined from the chamber and cell final equilibrium concentrations, C_0 and C_1 , respectively.

$$\gamma = \frac{D}{L} \frac{C_0 - C_1}{C_1}. \quad (4)$$

Equation 4 is a direct result of the steady solution for equation 1.

RESULTS

Static Experiments

The static experiments were conducted for a sufficient duration until a steady-state concentration was achieved. Figure 4 shows the measured CO concentration increases with time for each of the sensors. The average steady-state concentrations, C_s , as indicated by the sensor readings, are shown in table 2, as well as the ratio of steady-state concentration to reference CO concentration, C_{REF} , which was 16 ppm. The sensor cell had an internal characteristic response time of less than 35 s to reach 90 pct of the steady-state concentration. However, the chamber fills with contaminant at a rate governed approximately by the proposed mixing equation, equation 2. This results in the relatively long time, t_s , for the sensor to reach the steady-state concentration, C_s , shown in table 2. The measured values in table 2 are reported within ± 0.5 ppm.

The results in table 2 show that, for a static environment, the sensor readings consistently underestimate the reference gas concentration in the chamber by 6 to 19 pct. Figure 4 also shows that the measured CO concentration for each sensor increases in a relatively uniform manner and follows the proposed mixing equation for the chamber.

The static chamber experimental results were analyzed with the static diffusion model presented in equations

1 through 4. A molecular diffusion coefficient, $D = 0.15 \text{ cm}^2/\text{s}$, was used as an approximation for low-density gases (5). The results of the diffusion model analysis are shown in figure 4 for sensors A, B₁, C, D, and E. The sink term proportionality factor, γ , was varied according to equation 4. The factor γ includes not only a CO loss in the cell, but the diffusion through any membrane surface that guards the cell.

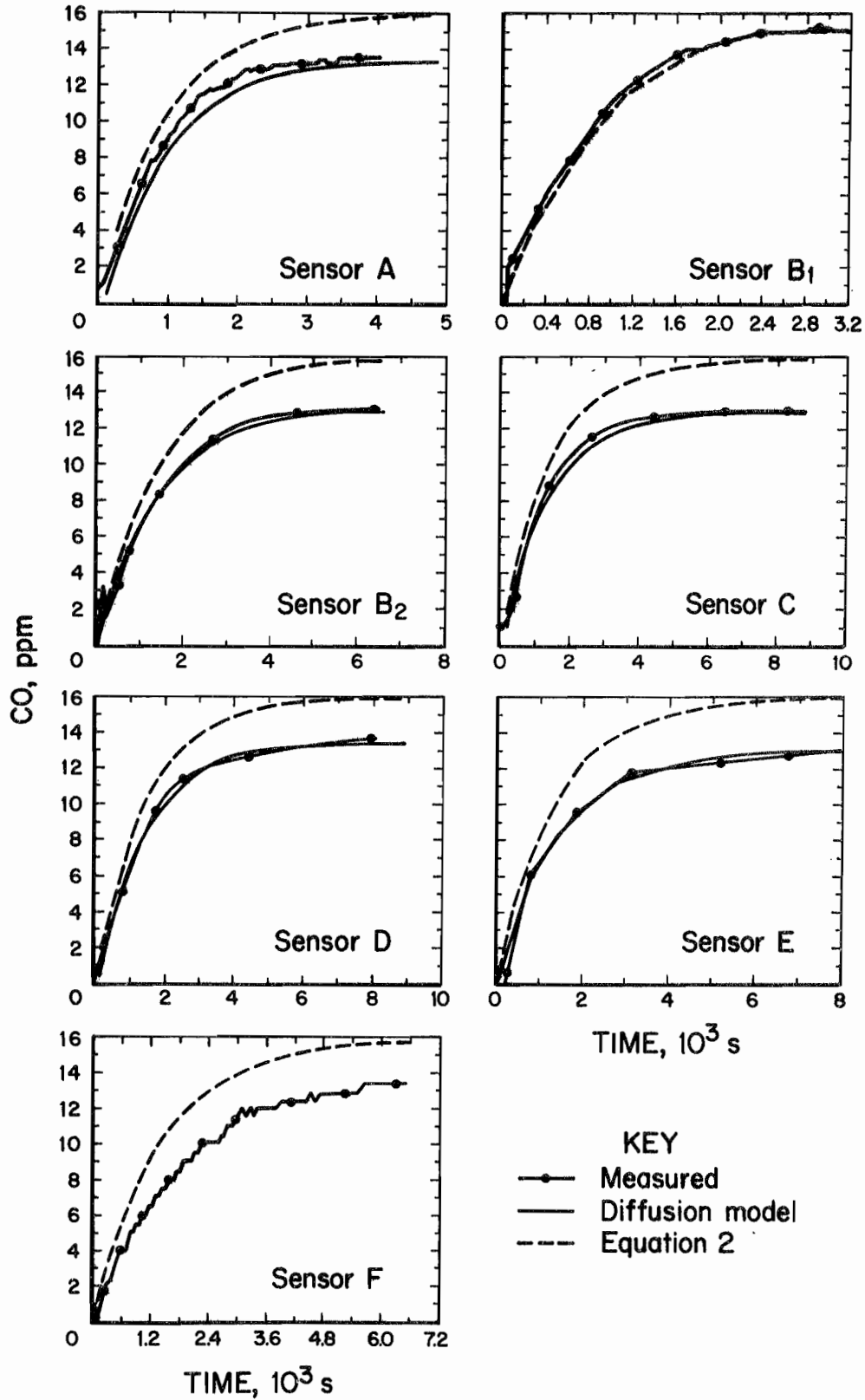
Table 2.—Steady-state CO concentration for static experiments

| Sensor | C_s , ppm | t_s , 10 ³ s | Ratio of C_s to C_{REF} ¹ |
|----------------|-------------|---------------------------|------------------------------------------|
| A | 13.5 | 4.0 | 0.84 |
| B ₁ | 15.0 | 3.0 | 0.94 |
| B ₂ | 13.0 | 6.5 | 0.81 |
| C | 13.0 | 9.0 | 0.81 |
| D | 13.5 | 8.0 | 0.84 |
| E | 13.0 | 7.5 | 0.81 |
| F | 13.5 | 6.6 | 0.84 |

¹ $C_{REF} = 16$ ppm, CO concentration in the chamber.

Figure 4 shows the evaluation of equation 2 with $C_0 = 16$ ppm, $\tau = 960$ s for sensors A and B₁, and $\tau = 1.44 \times 10^3$ s for sensors B₂, C, D, E, and F. This equation

Figure 4



Response of diffusion-type CO sensors to CO in static chamber.

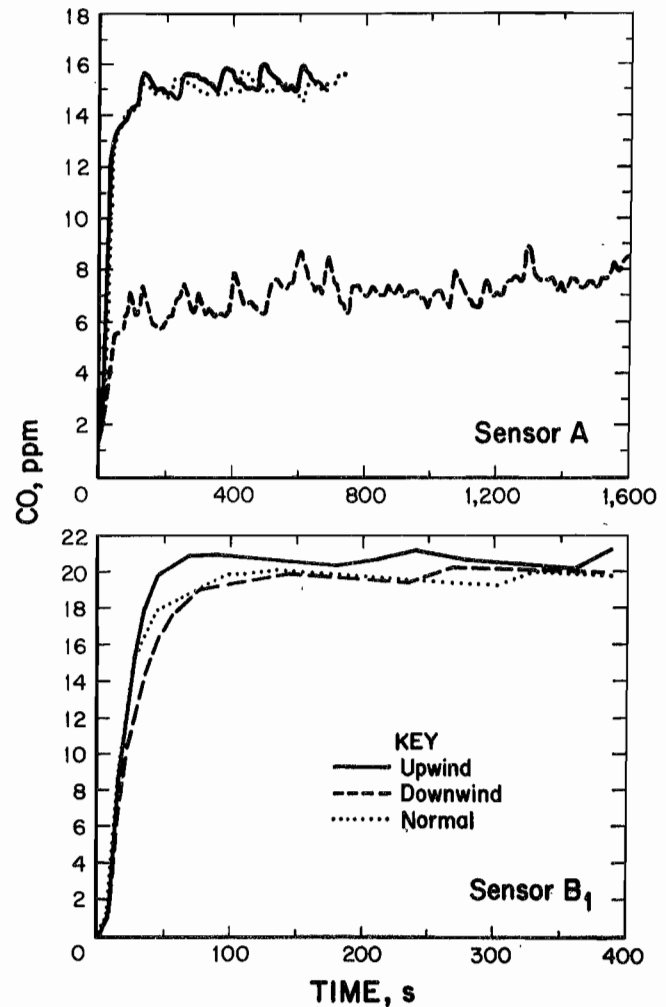
represents the CO concentration in the chamber if instantaneous mixing occurred throughout the chamber.

Dynamic Experiments

In a mine entry, dynamic flows are encountered. For this reason, dynamic experiments were conducted. The first sequence was for sensors A, B₁, and B₂ in an environmental chamber that had controlled directional gas flow. The second sequence of experiments was conducted for sensors C, D, E, and F in an environmental chamber that provided a turbulent recirculating gas flow with lack of strong directionality. For each sensor, excluding sensor B₂, a small piece of tape was placed over the diffusion tube during the mixing of CO and air in the dynamic chamber until a steady-state reference concentration was reached in the chamber. When the steady-state reference concentration was achieved, the tape was removed, and the sensor response was recorded. For sensor B₂, this was not possible because of the structure of the dust shield. In this case only the sensor's steady-state concentration could be measured. Each experiment was conducted once. Figure 5 shows the dynamic response of sensor A to three different orientations of the diffusion tube's longitudinal axis with respect to the gas velocity. The diffusion tube was tilted 18° upwind and downwind with respect to the normal to the gas flow direction, as well as being positioned normal to the gas flow. The orientation of the diffusion tube with respect to gas flow is shown in figure 2. The average gas flow was 1 m/s. The CO reference gas concentration was 17 ppm in air. The response of sensor B₁ to directional gas flow is also shown in figure 5. The measured degree of upwind and downwind tilt with respect to the gas flow was 17°. Figure 5 shows that the strong dependence of CO sensor response upon orientation of the diffusion tube with respect to gas flow exhibited for sensor A is not shown for sensor B₁. This was probably due to the presence of a sintered disk in the diffusion tube of sensor B₁, which creates a diffusion mode independent of the turbulent gas flow past the diffusion tube entrance. Table 3 lists the steady-state CO concentration, the time to reach 90 pct of the steady-state value, and the ratio of steady-state concentration C_s to reference concentration (C_{REF} = 17 ppm) for sensors A, B₁, and B₂. The values in table 3 are reported to within ±0.5 ppm.

Sensors A and B₂ consistently underestimated the reference CO concentration in the environmental chamber. This was also a characteristic of the static chamber experiments. Table 3 shows that sensor B₁ overestimated the actual CO concentration. For both the static (table 2) and dynamic experiments (table 3), sensor B₁ achieved a steady-state concentration that was greater than that for sensor B₂. The reason is that the physical structure of the dust shield on sensor B₂ apparently increases the diffusion time through an increase in the effective diffusion path.

Figure 5



Dynamic response of sensors A and B₁.

Table 3.—Steady-state results for dynamic tests in directional flow chamber

| Sensor | Orientation of diffusion tube | C _s , ppm | Time to 90 pct of steady-state value, s | Ratio of C _s to C _{REF} ¹ |
|----------------|-------------------------------|----------------------|-----------------------------------------|----------------------------------------------------------|
| A | Upwind | 16.0 | 90 | 0.94 |
| | Downwind | 8.5 | 90 | 0.5 |
| | None | 15.5 | 90 | 0.91 |
| B ₁ | Upwind | 21.0 | 40 | 1.24 |
| | Downwind | 20.0 | 60 | 1.18 |
| | None | 20.0 | 50 | 1.18 |
| B ₂ | Upwind | 16.0 | NAP | 0.94 |
| | Downwind | 15.0 | NAP | 0.88 |
| | None | 15.0 | NAP | 0.88 |

NAP Not applicable.

¹C_{REF} = 17 ppm, CO concentration in the chamber.

Experiments for sensors C through F were conducted in an environmental chamber that had recirculating flow, as illustrated in figure 3, as opposed to unidirectional flow. Gas flow measurements indicated moderately nondirectional flow as high as 1.8 m/s. Three experiments were conducted for each sensor with 20° variations in the orientation of the diffusion tube with respect to the dominant flow direction. For sensor F, which had no diffusion tube, the measured angle is between the normal to the sensor screen and the flow direction. Because of the nature of the recirculatory flow, average values are reported for each sensor.

Table 4 lists the average steady-state concentration, C_s , the average reference gas concentration, C_{REF} , and the average time to reach 90 pct of the steady-state concentration for sensors C through F. The values in table 4 are reported to within ± 0.5 ppm.

Table 4.—Steady-state CO concentration for recirculatory flow experiments

| Sensor | C_s , ppm | Time to 90 pct of steady-state value, s | C_{REF} , ¹ ppm | Ratio of C_s to C_{REF} |
|-------------|-------------|-----------------------------------------|------------------------------|-----------------------------|
| C | 15.0 | 45 | 13.5 | 1.11 |
| D | 18.0 | 88 | 16.0 | 1.12 |
| E | 15.0 | 29 | 16.0 | 0.94 |
| F | 19.0 | 66 | 19.0 | 1.0 |

¹CO concentration in the chamber.

CONCLUSIONS

As a result of the measured responses of six diffusion-type CO sensors to both a nearly static flow of CO and a dynamic flow of CO in air, the following characteristics of the sensors were observed.

1. In a static environment, the CO sensors consistently underestimated the gas concentration, with variation in the underestimation between 6 and 19 pct. For the static experiments conducted with a reference gas concentration of 16 ppm and an electrolytic cell accuracy of ± 1 ppm, the experimental error is ± 6 pct.

2. A simple diffusion model with a linear loss term at the cell yields a reasonable prediction of the sensor response in a static environment.

3. Directional flow experiments with two of the sensors demonstrated that it is important to construct the diffusion tube to compensate for the preferential turbulent diffusion into the diffusion tube associated with the spatial orientation of the tube axis with respect to the flow direction. One of the sensors underestimated the reference gas concentration by 50 pct when oriented 18° downwind from the

The ratios C_s/C_{REF} in table 4 are closer to unity than ratios for the static experiments reported in table 2. Inclusion of the two unidirectional flow experiments for sensor A with the diffusion tube tilted upwind and with no tilt, as well as the experiments for sensor B₂, with the results in table 4 shows the steady-state concentrations are within 12 pct of the reference CO concentration. With an experimental error of ± 1 ppm for the sensors, the ratio C_s/C_{REF} for sensor E is unity within the experimental error. The results in tables 3 and 4 show the response times, the times to reach 90 pct of steady-state, are not greater than 90 s for the dynamic experiments. Because the static experiments were conducted with the sensors in a changing CO concentration, a conclusion cannot be made with regard to sensor response under static conditions. Although the experimental sample size is too small for definite conclusions to be drawn with regard to reproducibility of absolute concentration values, the experiments conducted show significant trends with regard to the static case versus the dynamic case for agreement of indicated steady-state concentration with reference gas concentration for the six sensors evaluated, if the directional flow effect is not considered. It was not possible to make a direct comparison of flows between the two environmental chambers because they possess different flow characteristics.

normal to the flow, while the other sensor showed no dependence upon diffusion tube orientation at a 17° angle.

4. Four of the diffusion-type sensors that underestimated the reference gas concentration in the static environment showed markedly better agreement with the reference gas concentration in the environmental chamber with moderate nondirectional gas flow.

5. Any modifications to the diffusion tube will alter the response of the sensor. This was demonstrated for sensor B₁ when a dust shield was added without altering the diffusion tube length.

A suggested consideration for sensor development is that diffusion-type CO sensors undergo testing for both static and dynamic flow conditions to determine the steady-state response of the sensor. A significant component of the dynamic testing is the necessity for directional gas flow evaluation. Except for the directional flow effect noted for sensor A, the sensors gave reasonable agreement with the reference gas concentrations for both static and dynamic evaluations. The gas flow velocities considered in

the dynamic testing were limited. Although it would be useful to evaluate the sensors at other flow velocities in a future study, there was no indication, based upon the current study, of sensor flow dependence with respect to

the magnitude of the gas flow. Mine safety could be significantly improved if diffusion-type CO sensors are deployed in a mine consistent with optimal utilization of their response characteristics.

REFERENCES

1. Edwards, J. C., G. F. Friel, and G. S. Morrow. Effect of Dead End Crosscuts on Contaminant Travel Times in Mine Entries. Paper in Proceedings of the 6th U.S. Mine Ventilation Symposium (Univ. UT, Salt Lake City, UT, June 21-23, 1993). Soc. Min., Metall., and Explor., Littleton, CO, 1993, ch. 39, pp. 259-264.

2. Bay, H. W., K. F. Blurton, J. M. Sedlak, and A. M. Valentine. Electrochemical Technique for the Measurement of Carbon Monoxide. Anal. Chem., v. 46, No. 12, Oct. 1974, pp. 1837-1839.

3. Venkatesetty, H. V. Understand the Potential Uses of Electrochemical Sensors. Chem. Eng. Prog., July 1992, pp. 63-66.

4. Jost, W. Diffusion in Solids, Liquids, Gases. Academic Press Inc., New York, 1960, p. 3.

5. Bird, R. B., W. E. Stewart, and E. N. Lightfoot. Transport Phenomena. John Wiley and Sons, Inc., New York, 1966, ch. 16, pp. 503-507.

APPENDIX.—NOMENCLATURE

| | | | |
|------------------------|-------------------------------------------|----------------------|---------------------------------------------------------|
| C | concentration, ppm | L | diffusion tube length, cm |
| C_{REF} | reference concentration, ppm | t | time, s |
| C_s | steady-state concentration, ppm | t_s | time to reach steady-state concentration, s |
| C_o | chamber equilibrium concentration, ppm | x | distance, cm |
| C₁ | cell equilibrium concentration, ppm | γ | velocity parameter, cm/s |
| d | diffusion tube diameter, cm | τ | time constant for one gas volume exchange in chamber, s |
| D | diffusion coefficient, cm ² /s | | |