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MEASUREMENT OF THE TIME-OF-WETNESS

BY MOISTURE SENSORS AND THEIR CALIBRATION

by P.J. Sereda, S.G. Croll, and H.F. Slade

ANALYZED

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SOMMAIRE

Un programme d'une année impliquant plusieurs laboratoires situés dans différentes zones climatiques nous a offert l'opportunité d'évaluer la réponse de capteurs solaires miniatures (mis au point au CNRC) à l'humidité superficielle de panneaux exposés à l'air. Il a été démontré que des capteurs d'humidité placés à la surface de panneaux en métal ou en plastique réagissent à l'humidité superficielle, ou plus précisément à celle de leur surface, et que cette humidité résulte autant de l'interaction du milieu avec le matériau que des conditions ambiantes du l'HR.

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P. J. Sereda,¹ S. G. Croll,¹ and H. F. Slade¹

Measurement of the Time-of-Wetness by Moisture Sensors and Their Calibration

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ABSTRACT: A 1-year program involving several laboratories located in different climatic zones has afforded an opportunity to evaluate the response of miniature moisture sensors (developed at the National Research Council of Canada) to surface moisture on panels exposed to the atmosphere. It has shown that when these moisture sensors are placed on the surface of metal or plastic panels they respond to moisture conditions at the surface or more precisely, at the sensor surface, and that such moisture conditions result from interaction of the total environment with the material as well as with the ambient relative humidity conditions.

KEY WORDS: corrosion, metals, atmosphere, measurement, time-of-wetness, moisture sensors, calibration, sensor potential, ambient relative humidity, temperature

Time-of-wetness was first measured by Sereda with a sensor consisting of a platinum foil strip on a zinc panel [1-3].² The period during which the potential generated by this galvanic cell exceeds 0.2 V was defined as the time-of-wetness, which served as the time base for the expression of the rate of corrosion in terms of MDD_w (milligrams/square decimetre/day of wetness). Subsequent work has demonstrated the significance of this factor and its correlation with rate of corrosion [4-7]. In the early work [1-3] it was observed that the potential measured by the cell varied in the range 0 to 1 V, apparently due to changing conditions of exposure. Whether the level of potential correlated, however, with certain ambient conditions such as relative humidity was not resolved.

Some success has been achieved by other workers in measuring integrated current using a sensor involving a galvanic or electrolytic cell and correlating

¹National Research Council of Canada, Division of Building Research, Ottawa, Ont., Canada.

²The italic numbers in brackets refer to the list of references appended to this paper.

this with the rate of corrosion [8-14]. Although the monitoring of current levels above a certain value can be used as a measure of the time-of-wetness of such sensors, they are not appropriate, because of their large size, for monitoring surface moisture on exposed specimens of various materials or elements of buildings.

A new miniature moisture sensor has been developed. It monitors the presence of surface moisture in conjunction with atmospheric corrosion testing. Because of its possible usefulness, Subcommittee G01.04 on Weather of ASTM Committee G-01 on Corrosion of Metals organized a round-robin test series to evaluate its performance and to attempt its calibration in the range of 75 to 100 percent ambient relative humidity. This paper reports the results of the round-robin and the additional work carried out at the National Research Council of Canada (NRCC) Laboratories.

Experimental

The new moisture sensor was developed by NRCC in conjunction with Bell Northern Research Laboratories. It consists of a cell of alternate electrodes of zinc and gold or copper and gold on a glass-reinforced polyester (GRP) base 1.5 mm thick (Fig. 1a); the overall size is 20 by 25 mm. It was mounted on both galvanized metal and plastic bases 100 by 150 mm (Fig. 1b).

Temperature of the metal and plastic bases and that of the sensor was measured with 30-gage copper-constantan thermocouples embedded in the surface (Fig. 2). The mounted sensors were placed on a corrosion rack (Fig. 3).

At the Ottawa site, potential levels from the zinc/gold (Zn/Au) or copper/gold (Cu/Au) sensors and temperatures, including the ambient and dew-point temperatures (dew cells located in a Stevenson screen; see Fig. 3), were recorded every 10 min on magnetic tape.

One set of sensors having Zn/Au electrodes was distributed to a number of participating laboratories to extend the evaluation program to different climates. As various unforeseen difficulties arose, however, only two of the original six laboratories have been able to supply completed data. These are included in the present paper, along with extensive data collected at the NRCC laboratory.

Analyses of the data included determination of the frequency distributions of ambient relative humidity and the potential levels from Zn/Au and Cu/Au sensors mounted on metal and plastic panels. The distribution of surface temperature, the difference between surface temperature and ambient temperature, and surface temperature (metal or plastic) and sensor temperature were obtained for the periods when the potential from the Zn/Au cell exceeded 0.1 V and that from the Cu/Au cell exceeded 0.01 V. For the purpose of this paper these limits define the time-of-wetness. Data were collected at the Ottawa site for 1 1/2 years, and as they were reasonably

FIG. 1a—Moisture sensor.

FIG. 1b—Sensor mounted on metal base.

FIG. 2—*Thermocouples mounted on specimens and on sensors: (a) on plastic specimen; (b) on metal specimen.*

FIG. 3—*Exposure station at Ottawa.*

reproducible for comparable months of each year, only typical results are presented in this paper. Representative results reported by other participating laboratories are given to indicate the influence of different climatic conditions.

Results and Discussion

Characteristic Results for Periods of Rain, Snow, Dew, and Hoarfrost

Figure 4 presents typical data collected for a period of rainfall that occurred on 14 Sept. 1979. The ambient and sensor surface temperatures were very similar, the relative humidity was 100 percent during most of the period, and the potential recorded by the Zn/Au cell was steady at about 0.8 V and that by the Cu/Au cell was initially about 0.05 V and tended to decrease with the time-of-wetness, a characteristic of this type of cell. The increase in voltage is more rapid than the decay at the termination of rain because of the persistence of surface moisture.

Figure 5, showing a typical record of snowfall, has some similarity to Fig.

FIG. 4—Record for interval of rainfall (20 mm), Ottawa.

FIG. 5—Record for interval of wet snowfall (20.4 mm of rain equivalent), Ottawa.

4 for rainfall in having essentially equal ambient and surface temperatures. The ambient relative humidity was about 90 percent, but the surface relative humidity was assumed to be 100 percent because snow lay on its surface, probably creating a local condition of saturation under the snow cover. When the temperature rose, the snow melted and surface relative humidity was definitely 100 percent. The potentials on both Zn/Au and Cu/Au cells reached initially high values and remained fairly steady, in agreement with the assumed condition of saturation, although there was again a tendency for potential from Cu/Au cells to decrease.

Figure 6 is a typical record for a period of dew formation when the ambient temperature was falling slowly and the surface temperature continuously about 2 deg lower, in contrast with conditions during rainfall or snowfall. Consequently, the surface relative humidity was 100 percent, while the ambient relative humidity varied between 90 and 97.5 percent. Under these conditions the surface temperature is below the dew-point temperature and water vapor condenses on the surface. This represents a nonequilibrium

FIG. 6—Record for interval of dew, Ottawa.

state. Under these conditions the potential generated by the Zn/Au cell was fairly steady at about 0.8 V. The Cu/Au cell reached a high value of 0.085 V at the beginning but decreased with time to 0.04 V. In the period of dew formation a potential was recorded during most of the interval.

The results obtained for a period of hoarfrost formation are similar to those for dew formation, as shown in Fig. 7. The surface temperature was generally 2 deg C lower than the ambient temperature, but the ambient temperature decreased from -10 to -18°C . Under these conditions the relative humidity at the surface reaches 100 percent and water condenses (as hoarfrost), although the ambient relative humidity is in the range of 85 to 95 percent. During this interval, the potential recorded by the Zn/Au cell rose rapidly to a value of 0.45 V, decreasing to a value of 0.1 V in 14 h, and the Cu/Au cell recorded initially 0.095 V, decreasing to 0.025 in the same period. Under these conditions the Cu/Au cell started at nearly its highest possible potential (roughly one tenth of that produced by the Zn/Au cell). This is in contrast with what appears to happen at temperatures above freezing when

FIG. 7—Record for interval of hoarfrost, Ottawa.

dew is forming and the Zn/Au cell is relatively more sensitive (Fig. 6). This, however, has no significant effect on the measured time-of-wetness, as will be shown.

The results in Fig. 7 and those shown in Table 1 confirm that both Zn/Au and Cu/Au cells will develop a potential whether their temperature is above or below freezing, that is, 0°C . In Table 1 it is evident that for the winter months in Ottawa over 80 percent of the time-of-wetness occurred at temperatures below 0°C . For the month of February 1979 about 5 percent of the recorded time-of-wetness occurred at or below a temperature of -30°C . These observations confirm earlier findings [15] that films of water or solution on the surface do not freeze as bulk water does, but continue to serve as an electrolyte for the galvanic cell.

In general, the surface temperature is lower than the ambient temperature for an average of 83 percent of the time, but for plastic panels this value is 95 percent (Table 1). The temperature of the surface of metal panels was 2 to 4 deg C lower than the ambient temperature for an average of 13.2 percent of

TABLE 1—Record of temperatures during time-of-wetness at Ottawa.

Year and Month	Panel Sensor ^a	% T-O-W ^b	Lowest Temperature, °C, for <5% T-O-W	% T-O-W for Interval Below 0°C	Lowest Δt °C (Panel-Air) During T-O-W	% T-O-W for Interval in Previous Column	% T-O-W for $\Delta t < 0^\circ\text{C}$ ^c
1978							
Sept.	P-Cu/Au	36.1	-2	2.5	-2 to -4	35.4	93.8
Sept.	M-Cu/Au	28.3	0	1.7	-2 to -4	15.3	86.8
Sept.	M-Zn/Au	30.5	0	1.6	-2 to -4	14.6	85.3
Nov.	P-Cu/Au	22.4	-8	38.3	-4 to -6	2.3	93.3
Nov.	M-Cu/Au	14.7	-4	19.5	-2 to -4	15.7	88.8
Nov.	M-Zn/Au	13.2	-4	15.0	-2 to -4	14.1	91.0
1979							
Jan.	P-Cu/Au	25.0	-16	88.0	-2 to -4	5.8	76.8
Jan.	M-Cu/Au	21.9	-14	84.6	-2 to -4	2.9	73.1
Jan.	M-Zn/Au	24.8	-10	87.5	-2 to -4	2.4	70.7
March	P-Cu/Au	38.2	-12	51.4	-4 to -6	4.3	89.2
March	M-Cu/Au	25.9	-12	45.6	-2 to -4	17.8	83.5
March	M-Zn/Au	20.4	-10	36.6	-2 to -4	16.6	82.2
May	P-Cu/Au	28.6	0	3.8	-4 to -6	0.8	96.6
May	M-Cu/Au	22.5	2	1.0	-2 to -4	8.9	89.6
May	M-Zn/Au	23.8	2	0.6	-2 to -4	8.3	88.2
July	P-Cu/Au	26.2	8	0	-4 to -6	4.6	97.3
July	M-Cu/Au	21.8	10	0	-2 to -4	22.6	91.2
July	M-Zn/Au	18.6	10	0	-2 to -4	23.1	90.6
Sept.	P-Cu/Au	31.1	-2	15.3	-4 to -6	11.2	96.9
Sept.	M-Cu/Au	16.5	-2	13.4	-2 to -4	36.9	88.0
Sept.	M-Zn/Au	23.7	-2	12.2	-2 to -4	37.4	89.0
Nov.	P-Cu/Au	38.2	-6	37.9	-4 to -6	0.9	92.6
Nov.	M-Cu/Au	33.9	-4	29.9	-2 to -4	2.2	79.3
Nov.	M-Zn/Au	29.6	-4	33.6	-2 to -4	3.8	85.7
1980							
Jan.	P-Cu/Au	31.2	-20	87.3	-4 to -6	2.6	78.0
Jan.	M-Cu/Au	25.5	-18	86.6	-2 to -4	4.7	84.1
Jan.	M-Zn/Au	16.8	-16	81.8	-2 to -4	3.6	70.8

^a P = clear plastic; M = metal.^b T-O-W = time-of-wetness.^c $\Delta t < 0^\circ\text{C}$ = panel temperature lower than ambient.

TABLE 2—*Frequency distribution of levels of potential for individual sensors, July 1979, Ottawa, Ont.*

Zn/Au Sensors			Cu/Au Sensors		
Designation	0.1 V	0.2 V	Designation	0.01 V	0.02 V
B4-1	18.64 ^a	17.76	CA-1	21.86	20.66
B4-4	21.03	19.99	CA-2	21.40	20.47
B4-11	20.10	18.98	CN-2	22.25	20.42
B4-24	19.76	19.14			
Avg	19.88	18.97	Avg	21.84	20.52

^a Percent time when a given potential in volts is exceeded.

the time. The temperature of the surface of the plastic panels was 4 to 6 deg C lower than ambient temperature for an average of 5.0 percent of the time.

Although there were variations in the time-of-wetness for any one month, as recorded by a single Cu/Au or Zn/Au cell on metal, the annual time-of-wetness for the period August 1978 to August 1979 was 21.92 percent for the Cu/Au sensor and 21.89 percent for the Zn/Au sensor. For the same period, the Cu/Au sensor on plastic gave a value of 28.93 percent. To illustrate the

TABLE 3—*Monthly frequency distribution of levels of potential, using average values from 3 or 4 sensors (percent time when a given potential is exceeded).*

Month	Zn/Au Sensors		Cu/Au Sensors	
	0.1 V	0.2 V	0.01 V	0.02 V
1978				
Aug.	19.07	18.12	19.50	18.25
Sept.	29.82	29.13	27.63	26.12
Oct.	20.81	19.84	20.43	18.41
Nov.	13.82	13.15	15.96	13.70
Dec.	35.60	23.06	19.77	13.96
1979				
Jan.	25.12	18.27	21.05	14.36
Feb.	15.77	13.77	21.95	17.52
March	20.85	19.27	29.20	25.64
April	20.92	20.11	22.47	20.57
May	25.39	24.79	23.70	22.75
June	22.38	21.75	23.28	21.99
July	19.88	18.97	21.84	20.52
Aug.	28.91	27.91	30.16	28.97
Sept.	25.56	24.86	26.32	25.16
Oct.	38.27	35.06	35.80	32.58
Nov.	33.60	31.00	34.16	26.17
Dec.	28.33	25.73	25.94	19.56
Avg	24.94	22.63	24.65	21.54

reproducibility of individual sensors, data are presented from four sensors using Zn/Au cells and three sensors using Cu/Au cells (Table 2). The variation between sensors was not large, and good agreement was obtained between the two sets even on a monthly basis.

Table 3 lists the average monthly values (as percent time a given potential level is exceeded) from three or four sensors. These results show that potential levels of 0.1 or 0.2 V for Zn/Au cells and 0.01 or 0.02 V for Cu/Au cells can be used to indicate the time-of-wetness with an agreement of better than 10 percent. The variation between the two types of cells at 0.1 and 0.01 V or 0.2 and 0.02 V is between 1 and 5 percent for a period of 17 months.

Distribution of Ambient Relative Humidity, Potentials Measured by Moisture Sensors, and Resulting Correlation

The current program was designed to determine whether a simple relation exists between the potential generated by the sensors and ambient relative humidity. This assumes that the surface temperature is not too different from the ambient temperature, and that a certain pseudo-equilibrium exists between ambient and surface conditions. These assumptions are based on previous work in which it was observed that the percent time during which the potential from a platinum foil on zinc plate sensor exceeded 0.2 V corresponded to percent time during which the ambient relative humidity was above a critical value depending on site (in the range of 80 to 89 percent) [3-16].

Some results obtained from exposure sites in Ottawa, Ont., Thousand Oaks, Calif., and Cleveland, Ohio, as part of the round-robin test, are presented in Figs. 8 to 12. Each figure comprises three graphs coordinated to show the distribution of ambient relative humidity, distribution of measured potential, and the resulting correlation of potential with relative humidity. Figures 8 and 9 include data for both Zn/Au and Cu/Au cells. The characteristic distribution curves for potential are somewhat different for conditions above freezing (Fig. 8 for July) and conditions below freezing (Fig. 9 for January). These curves are also different for sensors mounted on plastic panels and metal panels.

The correlation curves for potential versus relative humidity are different for each month and for each type of panel. Attempts to obtain a single relation were not successful. The records from Thousand Oaks, Calif., for June and August (Fig. 10) and for October, November, and December (Fig. 11) and those from Cleveland, Ohio, for January, April, and June (Fig. 12) demonstrate how the monthly changes in ambient relative humidity conditions influence the distribution of potential generated by the Zn/Au sensor mounted on metal panels. These are major changes that greatly influence the apparent correlation of potential versus relative humidity. In Cleveland the sensor indicated a potential for the month of June at an ambient relative

FIG. 8—Record for July 1979, Ottawa.

FIG. 9—Record for January 1980, Ottawa.

FIG. 10—Record for June and August, Rockwell International Science Center, Thousand Oaks, Calif.

humidity below 70 percent, whereas in January it indicated a potential only when the ambient relative humidity was over 95 percent (Fig. 12). A similar result was obtained for November in Thousand Oaks, Calif. (Fig. 11).

The explanation of these results can be found in the distribution of relative humidity for each month. In January in Cleveland the relative humidity was above 97 percent for 40 percent of the time, and in November in Thousand Oaks it was above 95 percent for 30 percent of the time. Under such conditions the surface temperature would be nearly the same as the ambient, as shown in Figs. 4 and 5. Atmospheric conditions for the month of June in Cleveland dictated that the ambient relative humidity was above 80 percent only 5 percent of the time, as may be seen in Fig. 12. Under such dry conditions it is expected that most of the potential recorded represented periods of dew formation (Fig. 6), when the surface temperature is lower than ambient by as much as 2 deg (this is often below the dew-point), representing non-equilibrium conditions resulting in condensation. Thus a potential was recorded although the ambient relative humidity was below 70 percent. The two correlations of potential versus relative humidity for the months of January and June in Cleveland represent the two extreme atmospheric conditions encountered in this program. Otherwise, the conditions were intermediate, with a mixture of periods of high ambient humidity (for example,

FIG. 11—Record for October (1-18), November, and December 1978, Rockwell International Science Center, Thousand Oaks, Calif.

during rainfall) and conditions of surface condensation during lower levels of ambient relative humidity owing to surface temperatures lower than ambient temperatures.

Surface Temperature of Base Panel and That of Sensor

It is clear that surface temperature relative to ambient is a very important parameter in determining time-of-wetness. Temperature differences between sensor and base are given in Table 4. The temperature of the sensor was, on the average, higher by 0 to 0.5 deg C for 13 percent of the time on a metal base and lower by 0 to 0.5 deg C about 84 percent of the time. For this reason, condensation usually occurs first on the sensor. The temperatures plotted in Figs. 4 to 7 are those for the sensor since they are more directly related to the recorded time-of-wetness. This could not be done for all the data given in Table 1 because the thermocouples were installed on the sensors only during the latter part of the program.

When a sensor was mounted on a plastic base, the sensor temperature was lower by 0 to 0.5 deg C with respect to the temperature of the base for 57 percent of the time and higher for 43 percent of the time. This was so because the thermal characteristics of the sensor are similar to those of the plastic base on which it was mounted, and the net gain or loss of heat for the system

FIG. 12—Record for January, April, and June 1979, Republic Steel Research Center, Cleveland, Ohio.

was nearly equal. This is in contrast with the case where the sensor is mounted on a metal plate, as discussed earlier. It is desirable that the sensor not disturb the thermal regime of the surface, an objective that can be approached when the sensor is very thin. New sensors are now made only 0.1 mm thick and should respond quickly to surface temperature changes, decreasing to a minimum any temperature difference between sensor and base.

Conclusions

1. New miniature sensors provide a reasonable indication of surface wetness; sensors using Zn/Au and those using Cu/Au cells are equally effective.
2. Temperature of an exposed surface may be different from that of air; if it is lower, condensation can occur when the relative humidity of the air is not at saturation. The temperature difference depends on the character of the surface and the weather conditions.
3. The time-of-wetness of a surface will vary not only from one locality to another and from one month or year to another, but also with type, size and orientation of specimen exposed to a given atmosphere.
4. When sensors are used to indicate surface conditions, they must be small and thin to minimize temperature difference.
5. There is no unique relation between the potential developed by these sensors and ambient relative humidity.

TABLE 4—Percent time when value of temperature difference between sensor and base is in range denoted.

1979	Zn/Au Sensor on Metal Base		Cu/Au Sensor on Metal Base		Cu/Au Sensor on Plastic Base	
	0 to +0.5°C	0 to -0.5°C	0 to +0.5°C	0 to -0.5°C	0 to +0.5°C	0 to -0.5°C
June	13.7	86.0	14.4	85.1	37.9 ^a	45.0
July	12.7	86.7	11.0	88.8	35.4	50.2
Aug.	10.4	88.5	10.5	88.2	27.2	60.2
Sept.	21.8	70.9	23.1	71.5	33.9	49.4
Oct.	9.6	89.3	10.0	88.7	21.4	70.6
Nov.	15.3	82.1	18.7	77.7	23.3	66.5
Dec.	14.7	84.0	15.8	83.3	23.2	62.1
1980						
Jan.	12.8	82.8	7.1	89.7	29.5	58.0
Feb.	9.0	89.7	8.4	87.6	40.8	48.4
Avg	13.3	84.4	13.2	84.5	30.3	56.7

^aThe remainder of time the difference was greater than +0.5°C.

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DISCUSSION

*S. C. Byrne*¹ (*written discussion*)—The time-of-wetness gage should be drastically affected by hygroscopic or other properties of corrosion products which, in turn, should be affected by atmospheric composition. Has any work been planned to further define the role of atmospheric composition in determining time-of-wetness?

P. J. Sereda (authors' closure)—The time-of-wetness, as defined by a minimum level of potential (representing the current generated by the galvanic cell) is affected by surface contaminants resulting from deposition of atmospheric pollutants on the sensor. However, the surfaces where corrosion is being monitored are also exposed to the same contaminants, which, in turn, affect the deposition of films of moisture to foster the process of corrosion. Work is needed to measure the microenvironment at corroding surfaces.

*F. Mansfeld*² (*written discussion*)—1. The difference in the response of your sensor and our ACMs could be related to the different sensitivity of the device. You measure the voltage drop across a very large resistor which is due to galvanic current flow. However, this voltage drop separates the two electrodes and you cannot measure the maximum galvanic current which one would measure with a zero resistance ammeter.

2. Another reason for different sensitivity is that the gold electrode in your sensor does not form corrosion products which would condense moisture and lead to current flow. The zinc electrode could be wet, while the noble electrode (Pt/Au) is still dry.

3. Despite the fact that different designs of time-of-wetness t_w sensors measure different t_w -values at a given test site, do you think that one could use a sensor of constant design to compare different test sites?

P. J. Sereda (authors' closure)—1. The statement is true, but what is significant is to have adequate sensitivity to detect films of moisture which correspond to or foster practical rates of corrosion.

2. This paper presents results showing that sensors detect condensing films of water because the surface temperature is often below the ambient and at or below the dew point. Under these conditions, corrosion products are not required to condense water on any surface. Furthermore, it is not the corrosion products only, but more likely the deposited contaminants from the atmosphere (ions of Cl^- , SO_4^{2-} , etc.) deposited on all surfaces which would depress the vapor pressure of water and form solutions below 100 percent relative humidity that contribute to galvanic current, and are detected as the time-of-wetness.

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3. Conclusions 3 and 5 of the text are an answer to this question. Whatever sensor is used, provided it is small enough to respond to ambient temperature changes in the same way as a given specimen surface, it will give different values for the time-of-wetness for different type, size, and orientation of specimens exposed to a given atmosphere. In other words, there is not a unique value of the time-of-wetness for a given site; thus comparison of the time-of-wetness of different sites is valid only for identical specimens exposed in the same way at the different sites. Recent work by our institute has shown that two identical plastic specimens exposed side by side, one oriented vertically and the other horizontally, recorded the time-of-wetness (using our miniature sensors described in the paper) in the ratio of 1 : 1.7.

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