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MP MATERIALS PERFORMANCE

CORROSION PREVENTION AND CONTROL WORLDWIDE

Surface preparation is key to a successful duplex system when painting over hot-dip galvanized steel (p. 44). Here, a worker uses aluminum/magnesium silicate to sweep-blast galvanized steel before a coating is applied. Courtesy of the American Galvanizers Association.

The Powell Building in Reston, Virginia, was studied to verify the effects of pollution on its poured concrete columns. The study included visual and tactile examination, wash-down experiments, and a quantitative examination of coarse pores (p. 64). Courtesy of the U.S. Geological Survey.

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Pollution Damage to the Powell Building, Reston, Virginia

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Concrete column segments of the Powell Building (Reston, VA) exposed to the elements and wetted by precipitation were "cleaned" and roughened, but sheltered portions of the columns retained their smoothness and pollution accumulates, similar to observations for limestone, marble, and sandstone. Weathering effects on the columns were dominated by precipitation run-off and not the acidity of the precipitation. The process may be dry deposition of sulfur dioxide (SO_2) and nitric oxides (NO_x) that formed soluble salts in the presence of humid air or dew, salts that were removed by precipitation run-off.

Exposure tests were made of limestone and marble as part of the U.S. National Acid Precipitation and Assessment Program (NAPAP).[1] Although concrete was considered for inclusion in studies of the effects of acid rain on materials,[2-3] the conclusion was that other materials (limestone, marble, metals, and paint) were more at risk. Therefore, study of concrete was not pursued. A later observation indicated that the greatest damage to limestone and marble was observed in pieces that had been turned on a lathe (columns and balusters). Publication of this information[4] led to the selection and examination of one concrete structure, the John Wesley Powell Building (Figure 1), whose columns are made by a different process (poured concrete), rather than formed by turning on a lathe. The building is the main structure of the U.S. Geological Survey complex in Reston, Virginia. It is comprised of ~1 million ft² (94,000 m²) of buildings with exteriors of unfaced Portland cement concrete, glass, and numerous columns. Bill Schmidt of the U.S. Geological Survey, retired, provided information on the construction of the Powell Building. The study was comprised of three parts: a visual and tactile examination, wash-down experiments, and a quantitative study of coarse pores.

Building Construction

The ground-breaking date for the Powell Building was July 31, 1971 with construction by the George Hyman Construction Co. It was dedicated July 12, 1974. Some people, however, began to occupy the building as early as the fall of 1973. Concrete was supplied by two divisions of the Virginia Concrete Co. and also by Sterling Concrete Corp. One division of Virginia Concrete Co. used Lehigh† Portland cement Type II and Chantilly† crushed stone, whereas the other division used Alpha† Portland cement and Virginia Sand and Gravel Co. aggregate. Both divisions used sand from the Virginia Sand and Gravel Co., Solite† lightweight aggregate, and Protex† air entraining agent. Sterling Concrete Corp. used Medusa Cement Co. Type I cement, aggregate from Fairfax Quarries, sand from the Solite Corp., and Darex† air entraining agent.

The material from the Solite Concrete Corp. is slate, crushed and heated to 2,000°F (1,093°C), producing an expanded aggregate, which then is mixed with sand and lime. This aggregate produces a lightweight concrete that facilitates pumping the mixture and the

†Trade name.

building of higher structures. Concrete made using expanded aggregate also has better insulating properties.

No records were kept on which kind of concrete was used during construction. The concrete specified that honeycomb, aggregate pockets, and voids over 1/2-in. (13-mm) diameter and holes from form ties were to be patched before the concrete dried. Patching mortar was composed of one part Portland cement and two parts fine aggregate. No finishing treatment was intended other than an application of transparent waterproofing. The architectural concrete was to be dense, smooth, uniform in color and surface texture, and free of honeycomb, cold joint discoloration, and matrix losses at form joints. The building was cleaned with minor patching during 1997.

Statistical Study of Pores

A selection of columns was photographed. The log recorded the picture number, column number, side of building, exposed/sheltered areas, high/low pore density, height of the photograph from the column base, and the depth of the overhang. Overhangs are important in protecting a column from precipitation. In the case of the Powell Building, roughly one out of four rains was observed to wet the lower parts of the columns. The 35-mm photos were enlarged to 8 by 10 in. (20 by 25 cm) to allow pores >0.1 mm to be easily counted. A template with a narrow slit (~2 cm) was used to focus the view and minimize double counting of pores. Data were reduced to density of pores >0.1 mm. A visual separation was made on each column into high and low coarse-pore density regions for both exposed and sheltered portions of the columns.

Tables 1 and 2 give the results of the point counts. Robert P. Dosch Jr. (of Bloomington High School South, Bloomington, Indiana at the time) conducted the statistical examination of coarse pores in the concrete while he was a Rickover Fellow with one of the authors.

FIGURE 1

The John Wesley Powell Building, Reston, Virginia (taken 1978). Seven stories of unfaced Portland cement and glass comprise nearly 1 million ft^2 of office and laboratory space. Courtesy of the U.S. Geological Survey.

TABLE 1

LOW-DENSITY PORE RESULTS

Exposed			Sheltered		
Pores (no.)	Area (cm^2)	Density (pores/cm^2)	Pores (no.)	Area (cm^2)	Density (pores/cm^2)
1,925	675	2.85	240	1,030	0.23
1,440	965	1.49	652	645	1.01
1,541	840	1.83	1,231	770	1.60
1,649	675	2.44	522	1,515	0.34
1,945	965	2.02	669	805	0.83
1,575	805	1.96	751	485	1.55
1,108	775	1.43	852	775	1.10
1,056	580	1.82	494	385	1.28
—	—	—	569	970	0.59
—	—	—	176	450	0.39
—	—	—	263	350	0.75
—	—	—	660	450	1.47
12,239	6,280	1.95	7,079	8,630	0.82

Wash-Down Experiments

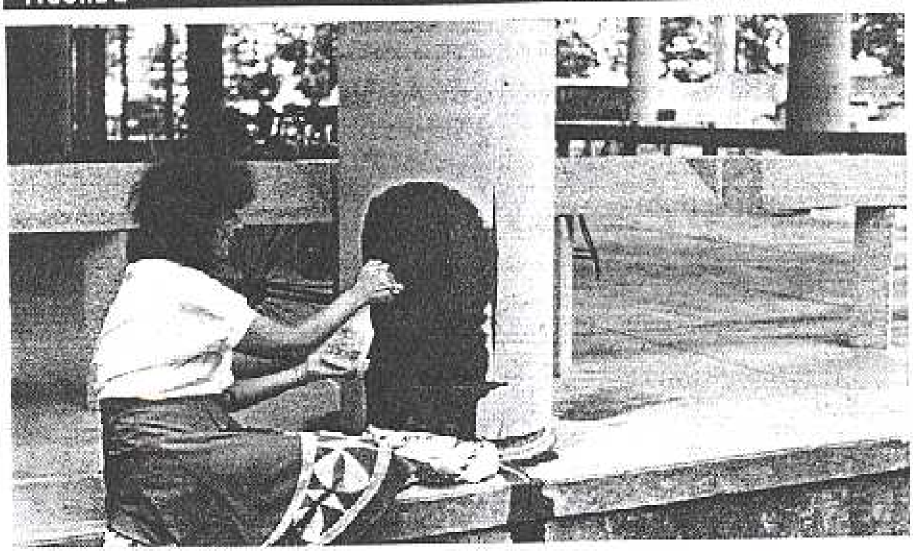
Wash downs (Figure 2) were made on parts of columns exposed to precipitation with both deionized water and acid rainwater collected in a plastic bucket on the fourth-floor atrium of the Powell Building. Water was sprayed from a plastic spray bottle at the base of a column, wetting an area ~12-in. (0.3-m) wide by 24-in. (0.6-m) high. The bottom 4 in. (100 mm) were sprayed first to wet it. Preliminary experiments showed that to get the wa-

TABLE 2
HIGH-DENSITY PORE RESULTS

Exposed			Sheltered		
Pores (no.)	Area (cm²)	Density (pores/cm²)	Pores (no.)	Area (cm²)	Density (pores/cm²)
1,799	515	3.49	1,040	675	1.54
1,982	840	2.36	1,836	420	4.37
2,313	740	3.13	1,226	645	1.90
3,572	1,030	3.47	1,362	1,095	1.24
3,869	1,515	2.55	1,956	965	2.03
2,472	870	2.89	1,878	645	2.91
2,889	805	3.59	2,519	1,450	1.74
4,661	450	10.36[A]	1,617	775	2.09
1,518	1,195	1.27	1,114	550	2.03
1,640	670	2.45	1,001	905	1.11
4,026	805	5.00	911	970	0.94
2,507	580	4.32	1,111	645	1.72
3,436	740	4.64	1,616	580	2.79
3,919	905	4.33	—	—	—
2,856	580	4.92	—	—	—
2,912	805	3.62	—	—	—
41,710	12,595	3.31	19,187	10,320	1.86

[A]Sample deleted.

FIGURE 2



Wash down in progress of a column on the Powell Building.

ter to drip off the column at a notch near the base, spraying the lower inch with polytetrafluoroethylene (PTFE) was necessary. Otherwise, water tended to flow into the notch and prevent its recovery. An aluminum pan was bent to fit under the notch at the column base and covered with aluminum foil to collect as little miscellaneous spray water as possible. An attempt was made to spray the top 18 in. (0.45 m) evenly. About 150 to 200 mL of run-off were collected.

The pH was measured using a hand-held pH meter on deionized water (85DI1) (stock pH = 6.45; reserve water pH = 6.95). Run-off for experiments performed July 25, 1985 on two columns had a pH = 7.4. On August 6, 1985, a run-off experiment was done with filtered acid rain on a different column (85AR1) (pH = 4.36). The measured pH of runoff fraction 85AR1a was 7.68 and the pH of fraction 85AR1b was 7.15.

A year later (Sept. 27, 1986), the experiments were repeated using the same columns and wash-down areas as before. The stock deionized water for sample 86DI1 had a pH = 7.45; run-off fraction 86DI1a had a pH = 7.21, and fraction 86DI1b had a pH = 7.52. The acid rain sample (86AR1) had an unfiltered pH = 3.91; run-off fraction 86AR1a had a pH = 7.30, and 86AR1b had a pH = 7.36. The run-off water looked turbid in all cases but less so in Fraction b than in Fraction a.

Discussion

VISUAL AND TACTILE EXAMINATION

Parts of columns of limestone, marble, and sandstone building stone exposed to acid rain were characterized in 1985 by a clean appearance and a rough feel, whereas protected parts of columns accumulated pollutants and retained their approximate original smoothness. The roughening occurs because of differential solubility of grains and cement at the stone surface. In addition, dissolution of fine-grained material around coarser grains allows these coarser grains to be mechanically removed (i.e., fall off), further roughening the surface.

The concrete columns of the Powell Building were observed to have these same traits in 1985; however, more large pores were observed in the visual examination of the parts of concrete columns exposed to acid rain compared to more sheltered areas. Pitting rarely is seen in building stones, but pitting and grooving, when observed, has been ascribed to the mechanical removal of silicate mineral inclusions as carbonate material is dissolved from around them, examples being the south side of the U.S. Capital building[5] and Jefferson Memorial.[1] A similar process could well account for the coarse pores in Portland and Alpha cement concrete. A newer building, dedicated

~20 years after the Powell Building (particulars on the concrete are not available) has columns that are roughening and have a powdery feel, but coarse-pore formation has not begun.

STATISTICAL EXAMINATION OF COARSE-PORE DENSITY DISTRIBUTION

The distribution of coarse-pore density was examined separately for the exposed and sheltered parts of columns to assess the degree to which the coarse-pore densities approached normal distribution. Some columns were found to consistently have higher densities of coarse pores for both exposed and protected areas, which was suspected largely to be a primary feature of the columns when they were formed. The assessment of normality was necessary for determining whether a t-test or its non-parametric counterpart, the Wilcoxon Rank Sum test, would be used to test the significance of the difference in coarse-pore densities. The statistical analysis was performed by Sandra Stinnett of the Duke Clinical Research Institute, Durham, North Carolina.

EXAMINATION OF PORE DENSITY DISTRIBUTION FOR ALL EXPOSED AND SHELTERED AREAS

The results (Table 3[a]) for all exposed and all sheltered column areas indicated that the mean density was much lower and less variable in the sheltered columns than in the exposed columns. Both groups had distributions that were fairly normal, as seen in stem and leaf plots (not shown). However, the numbers in each group were small, and there was an outlier in the sheltered group. Thus, both the independent sample t-test and the Wilcoxon Rank Sum test were used. The strategy was to use the results of the Wilcoxon test if the results from the two tests differed.

The test of equal variances in the two groups was not rejected. Thus the t-test (parametric) for equal variances was used. The difference in pore density between the exposed and sheltered parts of columns was highly significant ($p < 0.001$).

The result of the Wilcoxon Rank Sum test (non-parametric) was consistent with that of the t-test; the difference in pore densities was highly significant ($p < 0.001$).

TABLE 3(a)

DESCRIPTIVE STATISTICS FOR DENSITY OF ALL EXPOSED AND ALL SHELTERED COLUMNS

Statistic	Type of Column Area: Exposed	Sheltered
Number of areas studied	23	25
Mean density (pores/cm^2)	2.95	1.50
Standard deviation	1.15	0.91
Median density (pores/cm^2)	2.85	1.47
25th, 75th percentile	1.96, 3.62	0.94, 1.90
Min./max. density	1.27/5.00	0.23/4.37

TABLE 3(b)

DESCRIPTIVE STATISTICS FOR DENSITY OF EXPOSED AND SHELTERED COLUMNS, SEPARATELY FOR LOW- AND HIGH-DENSITY PORES

Statistic	Type of Column Area: Exposed		Sheltered	
	Low	High	Low	High
Number of areas	8	15	12	13
Mean (pores/cm^2)	1.98	3.47	0.93	2.03
Std. deviation	0.47	1.06	0.48	0.91
Median	1.90	3.49	0.92	1.90
25th, 75th	1.66, 2.23	2.55, 4.35	0.49, 1.38	1.54, 2.09
Min./max.	1.43/2.85	1.27/5.00	0.23/1.60	0.94/4.37

EXAMINATION OF DENSITY DISTRIBUTION SEPARATELY FOR LOW- AND HIGH-PORE DENSITY COLUMNS

A similar analysis was carried out separately for those densities classified as "low" and "high," although the numbers in each comparison group were diminished (Table 3[b]). The results of testing exposed vs sheltered columns separately for low- and high-density pores were:

- Low-Pore Density–t-test (p-value) <0.001, Wilcoxon Rank Sum Test (p-value) <0.001.
- High-Pore Density–t-test (p-value) <0.001.
- Wilcoxon Rank Sum Test (p-value) <0.001.

Thus, results of testing with both the parametric t-test and the non-parametric Wilcoxon Rank Sum test indicated that there was a highly significant difference in pore densities between exposed and sheltered parts of columns independent of whether the pore densities are classified as low or high.

WASH-DOWN EXPERIMENTS

In the wash-down experiments (Table 4), the wash water had similar pHs (7.2 to 7.7) in all cases even though the starting water was quite different: deionized water had a pH of 6.5 and 7.5, whereas the acid rain samples had a pH of 3.9 and 4.4. Thus, there was a rapid reaction of the H^+ ion in the water with the column surface.

Marilyn Werner, U.S. Geological Survey (Denver, Colorado), performed the chemical analyses. Of the more

TABLE 4

CHEMICAL ANALYSES OF COLUMN WASH-DOWN EXPERIMENTS[A]

Ion Chromatography (mg/L)									
Sample No.	Lab. pH	Conductivity	Alkalinity[B]	Ca	Mg	Na	NO_3	SO_4	Cl
86DIIa	6.69	280	33.9	23.6	0.84	9.36	16.74	40.1	3.0
86DIIb	7.07	152	29.0	11.92	0.40	4.34	8.06	27.2	3.5
86AR1a	6.79	143	21.5	11.12	0.39	4.83	9.49	27.6	2.9
86AR1b	7.11	75	17.9	6.33	0.21	2.00	5.27	11.8	0.7
86RAIN	3.91	—	—	—	—	—	—	—	—
85DIIa1	7.4	—	—	—	—	—	6.05	25.3	5.9
85DIIa2	7.4	—	—	—	—	—	5.21	25.9	5.8
85AR1a1	7.68	—	—	—	—	—	6.13	24.5	0.90
85AR1a2	7.68	—	—	—	—	—	6.39	24.4	0.92
85AR1b1	7.15	—	—	—	—	—	3.72	8.60	0.35
85RAIN	4.36	—	—	—	—	—	0.96	2.01	0.50

Inductively Coupled Plasma-Atomic Emission Spectroscopy (mg/L)							
Sample	pH	Ba	Ca	Mg	Na	SiO_2	Sr
85DIIa1	7.4	0.004	11.50	0.478	3.38	5.84	0.013
85DIIa2	7.4	0.002	11.12	0.467	3.31	6.84	0.012
85DIH_2O	6.95	—	0.012	0.0006	0.33	—	—
85DIH_2O	6.95	—	0.007	0.0004	0.22	—	—
85AR1a1	7.68	0.0022	10.76	0.327	4.08	1.53	0.014
85AR1a2	7.68	0.0017	10.60	0.323	3.75	2.44	0.013
85AR1b1	7.15	0.0001	4.21	0.134	1.32	1.19	0.002
85AR1b2	7.15	0.0001	2.56	0.145	1.49	2.46	0.003
85RAIN1	4.36	—	0.1044	0.014	0.24	—	—
85RAIN2	4.36	0.0004	0.0938	0.013	0.19	—	—

[A]Ion chromatography and inductively coupled plasma.
[B]Alkalinity is expressed as HCO_3.
Note: Samples 85DIIa1 85AR1a1 were analyzed on 8/23/85; 85DIIa2 and 85AR1a2 were analyzed on 10/4/85. Sample 85RAIN was rainwater collected on 7/26/85 and 7/27/85.

major elements in the wash-down experiments, Ca, Mg, Na, nitrate (NO_3), sulfate (SO_4), and Cl all were less abundant in the second wash down than in the first wash down. Conductivity and alkalinity also were lower in the second wash down than in the first. The same observation applied to the less common elements, Ba and Sr. Chemical values in wash-down water from deionized water and from acid rain, used in experiments done on the same day, can be remarkably similar (e.g., SO_4 or NO_3 contents in 85DIIa and 85AR1a on the one hand and 86DII and 86 AR1 on the other).

In the wash-down experiments a year after the initial investigation, the anion (NO_3, SO_4, and Cl) concentrations were even higher in some cases than in the earlier study, and some values for deionized water exceeded the values for acid rain wash downs. Again the concentrations in the second wash down were less than in the first. Thus, the soluble components on the column surface were regenerated over the intervening year. The ratios, however, of SO_4/NO_3 in the wash-down water for both years always were higher than in the acid rain itself (up to twice the acid rain ratio), as were the values of Ca/Mg (about four times the acid rain ratio). As with the pH, the difference between the deionized water and acid rain wash-down water experiments is within experimental error.

Thus, the pH of the incident water within the observed range did not appear to be the controlling factor in the "cleaning," roughening, and coarse-pore formation of the concrete columns, but rather the incident water dominated. Perhaps the responsible mechanism yielding the soluble salts was dry deposition of SO_2 (or NO_x) on the concrete, which reacted with the column in the presence of moisture drawn from the humid air or from accumulation of dew. Experiments conducted on marble suggested that the transformation of the dry deposition of SO_2 to gypsum (and NO_x to nitrates) was rapid at the stone surface,[6] and a similar process may apply to concrete.

Conclusions

Concrete in exposed parts of the Powell Building pillars was "cleaned" and roughened by the elements with formation of coarse pores >0.1 mm, whereas smoothness was retained and pollution gathered on sheltered parts. These weathering effects on parts of the columns exposed to the elements were not caused by the acidity of the precipitation, but were dominated by precipitant-carrying water. The water quickly reacted with soluble products on the column surfaces that were generated during dry periods, such as SO_2 (and NO_x).

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