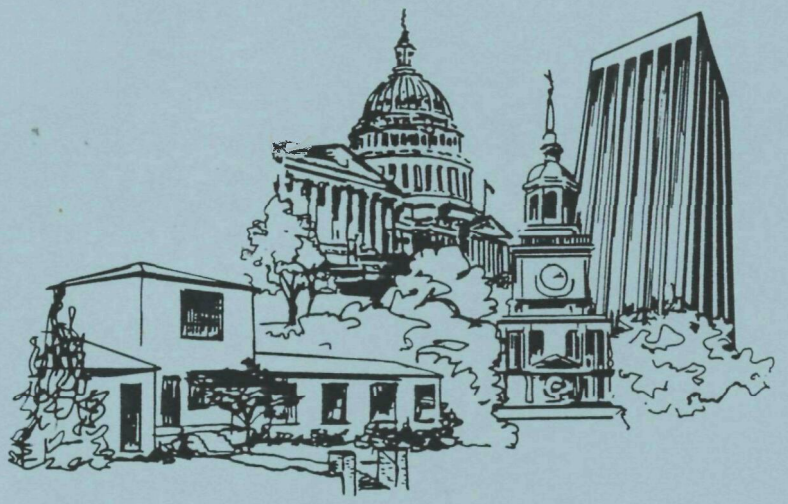
United States
Environmental Protection Agency

Research and Development

U.S. EPA Workshop on Acid Deposition Effects on Portland Cement Concrete and Related Materials

Final Report



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FINAL REPORT OF THE

U.S. EPA WORKSHOP ON ACID DEPOSITION EFFECTS ON PORTLAND CEMENT CONCRETE AND RELATED MATERIALS

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DISCLAIMER

Although the research strategies workshop described in this internal report has been funded by the U.S. Environmental Protection Agency, under Contract 68-02-3839 to Northrop Services, Inc., it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade name or commercial products does not constitute endorsement or recommendation for use.

A questionnaire was used at the workshop to stimulate discussion and was sent to foreign scientists for comment. Note that the foreign scientists who responded to this questionnaire expressed differing viewpoints and do not necessarily endorse all recommendations in this report.

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ACKNOWLEDGEMENTS

We wish to thank Dr. Geoffrey Frohnsdorff, Building Materials Division, National Bureau of Standards, for chairing and summarizing workshop discussions. The efforts of Ms. Linda Cooper, Workshop Coordinator, Northrop Services, Inc., in planning and arranging the workshop and in producing this final report are gratefully acknowledged.

SECTION 1

EXECUTIVE SUMMARY

There is no direct evidence that acid deposition has a significant economic effect on portland cement concrete and related materials. However, acid deposition may:

1. Convert the alteration layer caused by the action of CO_2 from carbonate compounds to more soluble materials.

2. Cause corrosion of the steel rebar if the alteration layer reaches the steel.

3. Increase the rate of neutralization of the matrix by adding to the effects of CO_2.

Although effects are not likely to be large, a research program is needed to determine whether they occur and to assess their magnitudes.

Acid deposition could possibly damage the ties and hangers (usually made of galvanized steel or carbon steel) that support masonry and concrete walls of building structures. Failure of these supporting elements due to corrosion could lead to catastrophic failure of the wall.

Two study programs were recommended by workshop participants:

1. Field Case Studies: to select a few structures that are located in high deposition areas and conduct microscopic and microanalytical studies of specimens from structures.

2. Laboratory Research: to determine and quantify environmental factors affecting the rate of attack of cracked and uncracked concrete and mortar by acid deposition.

SECTION 2

INTRODUCTION

The Atmospheric Sciences Research Laboratory (ASRL) program, Effects of Acid Deposition on Materials, is planned and conducted for Task Group G, Effects on Materials and Cultural Resources; this is one of several task groups within the National Acid Precipitation Assessment Program (NAPAP). One of the objectives of the NAPAP is to provide a scientific data base on the causes and effects of acid precipitation.

Task Group G has two overall areas of responsibility in developing a research program on the effects of wet and dry acid deposition on materials:

1. Develop data bases and methods for assessing the materials-related benefits of acid deposition control policies.

2. Establish guidelines for protecting individual structures from the effects of acid deposition or for restoring damaged structures.

The first responsibility is identified primarily with the regulatory activities of the U.S. Environmental Protection Agency (EPA), whereas the second responsibility concerns the National Park Service (NPS).

Man-made and naturally occurring materials used extensively in structures such as buildings, monuments, electrical transmission towers, and highway bridges are exposed to acid deposition. ASRL's program is concerned with studying the effects of acid deposition on materials of construction such as galvanized steel, weathering steel, exterior paints, and portland cement concrete, whereas the program with the NPS is primarily concerned with studying the effects on materials found in cultural resources.

The objective of ASRL's program is to design and conduct a materials research program that will differentiate between normal expected weathering and the accelerated deterioration attributed to acid deposition, including both wet and dry deposition. Material damage functions that quantify physical damages with significant environmental parameters causing the damage will be derived for use in cost-benefit models.

The purpose of this workshop was to provide recommendations from which a research program for developing damage functions for the effects of acid deposition on portland cement concrete structures can be developed.

SECTION 3

DISCUSSION

SPECULATIONS ON HOW ACID DEPOSITION MIGHT AFFECT PLAIN CONCRETE MATERIALS

The cement paste matrix (M) consists of anhydrous cement compounds [tricalcium silicate (C_3S)*, dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and calcium aluminoferrite (F_{SS})], their hydration products [e.g., calcium silicate hydrate (C-S-H), calcium hydroxide (CH), and two phases containing aluminum and iron (AFt and AFm)], pores, and an altered layer (a) caused by weathering that contains calcium carbonate ($C\bar{C}$), and carbonate analogs of AFt and AFm as well as residues of the other phases.

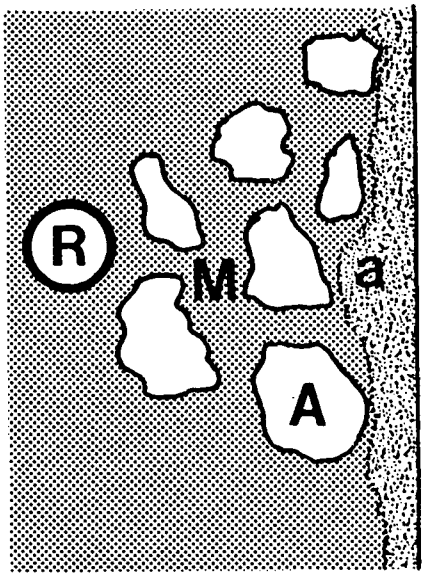

Figure 1. Cement Paste Matrix.

The aggregate particles (A), both fine and coarse, consist of either silicious and carbonate materials or both. The paste matrix (M) is known to be substantially modified close to the aggregate particle surfaces, but the effects on concrete durability have not yet been determined. The thickness of the layer of alteration products (a) increases as the square root of time ($\sqrt{t}$). The rate depends on the permeability of the concrete that varies markedly with the water to cement ratio of the original mixture. Whereas the pH water in the pores of the paste before the alteration is about 13, it drops to below 9 after alteration by CO_2. Normal cracks appear to have little effect on the rate of advance of the alteration front.

*In this cement industry nomenclature, C = CaO and S = SiO_2; other symbols used in this section are A = Al_2O_3, H = H_2O, and C = CO_2.

It is speculated that acid deposition may either:

1. convert a portion of the alteration layer from carbonate compounds to compounds of stronger acids, or
2. increase the rate of neutralization of the matrix by adding to the effects of CO_2.

In either case, the effect is not expected to be large, but research is needed to establish this.

Possible degradative effects that may result from acid deposition are as follows:

- Formation of more soluble compounds causing enhanced rate of leaching
- Expansion followed by spalling
- Discoloration
- Enhanced propensity for freeze/thaw damage.

SPECULATIONS ON HOW ACID DEPOSITION MIGHT AFFECT REINFORCED CONCRETES

Acid deposition will affect the concrete portion of reinforced concrete in much the same way as unreinforced concretes. However, when the alteration layer reaches the steel rebar (R, see Figure 1), and the pH falls to about 9 or below, the passivation of steel against corrosion will be lost. The steel would then corrode at a rate depending on factors including:

- O_2 concentration
- H_2O concentration
- Electrical conductivity of the concrete.

Research is needed to determine if acid deposition causes significant changes in the times to corrosion and rates of corrosion of steel in reinforced concrete. (Reinforcement in masonry poses a different problem, which is discussed in the Laboratory Research section (see Figure 2).

RECOMMENDED RESEARCH PROGRAM

Both field and laboratory research studies are recommended to determine the effects of acid deposition on portland cement concrete and related materials.

Field Case Studies

The objective of a field investigation is to seek evidence of effects of acid deposition on concrete. The effects might include the following:

- Discoloration
- Increased freeze/thaw damage

- Corrosion of reinforcing steel
- Other evidence of degradative effects.

The approach would be to select a few candidate structures believed to have a particularly high probability of attack by acid deposition.

Microscopic and microanalytical studies of specimens from the structures should be made similar to those recommended for the lab studies. It is important this work be done by an expert in concrete technology and microscopic failure analysis.

Laboratory Research

The objective of a laboratory study would be to determine and quantify factors affecting the rate of attack of cracked and uncracked concrete and mortar by acid deposition.

1. Variables to be investigated should include:

   a) Environmental parameters

      (1) Pollutants:

      SO_2
      NO_X
      HCl
      Particulate matter
      Combinations of the above

      (2) Meteorological parameters:

      Various relative humidities
      Condensation
      Water (with pollutants)
      Wetting and drying cycles (need to know time of wetness)
      Temperature (including temperature cycles)
      Wind speed and direction

   b) Materials

      Cement
      Mineral admixtures (low priority)
      Air-entraining admixtures
      Aggregates (Silicious and carbonate types)
      Various mixture proportions
      Reinforcement (exclude prestress)
      Surface-to-volume ratio
      Cover for steel
      Cracks (with steel)

      Specifically, materials recommended for use in the main study are:

      Type I cement
      White cement (for discoloration study using pastes)
      Silicious fine aggregate
      Silicious coarse aggregate

Carbonate coarse aggregate
Air-entraining agent (to obtain 6% ± 1% air).

2. Specimens

a) Pastes

Various water to cement (w/c) ratios (0.7 – 0 .4)

b) Mortar

Type N mortar with

(1) Masonry cement
(2) Portland cement/lime

c) Concrete

(1) Very porous
(2) Moderately porous

d) Reinforced concrete

(1) As for concrete, but with embedded polished steel tabs; use two depths of cover
(2) As for the above, but with the standard width of cracks (as defined by the American Concrete Institute [ACI] Standard ACI 318) and one other crack width

e) Reinforced mortar

Use simulated mortar joints (Figure 2).

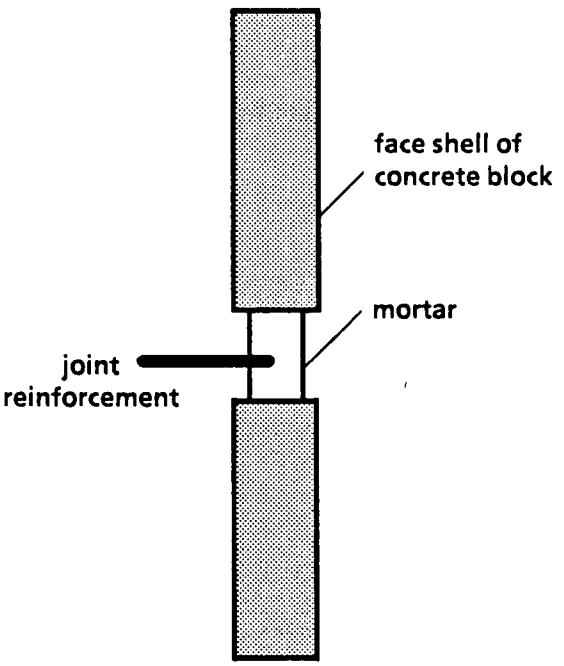

Figure 2. Simulated Mortar Joint

(This specimen to be used in studies of effect of dry deposition)

3. Exposures
    a) Dry deposition; use closed chamber
    b) Wet deposition; use
        (1) Spray with various pollutant concentrations
        (2) Spray with water at pH 5.6.

    (Requires alternate wetting and drying.)

4. Damage measurements
    a) Pastes
        (1) Loss of material
            (a) Weight loss
            (b) Run-off analysis
            (c) Recession
        (2) Alteration of phases
            (a) X-ray diffraction (XRD)
            (b) Microanalysis
            (c) pH
        (3) Alteration of microstructures
            (a) Scanning electron microscopy (SEM)
            (b) Permeability
        (4) Change of mechanical properties
            (a) Surface hardness
    b) Concrete
        (1) As for pastes and mechanical properties (f_c)
    c) Reinforced concrete
        (1) Corrosion potential
        (2) Bond strength
    d) Reinforced mortar
        (1) As for reinforced concrete.

An overall diagram for determining failure mechanisms and service life predictions from the exposure study is shown in Figure 3.

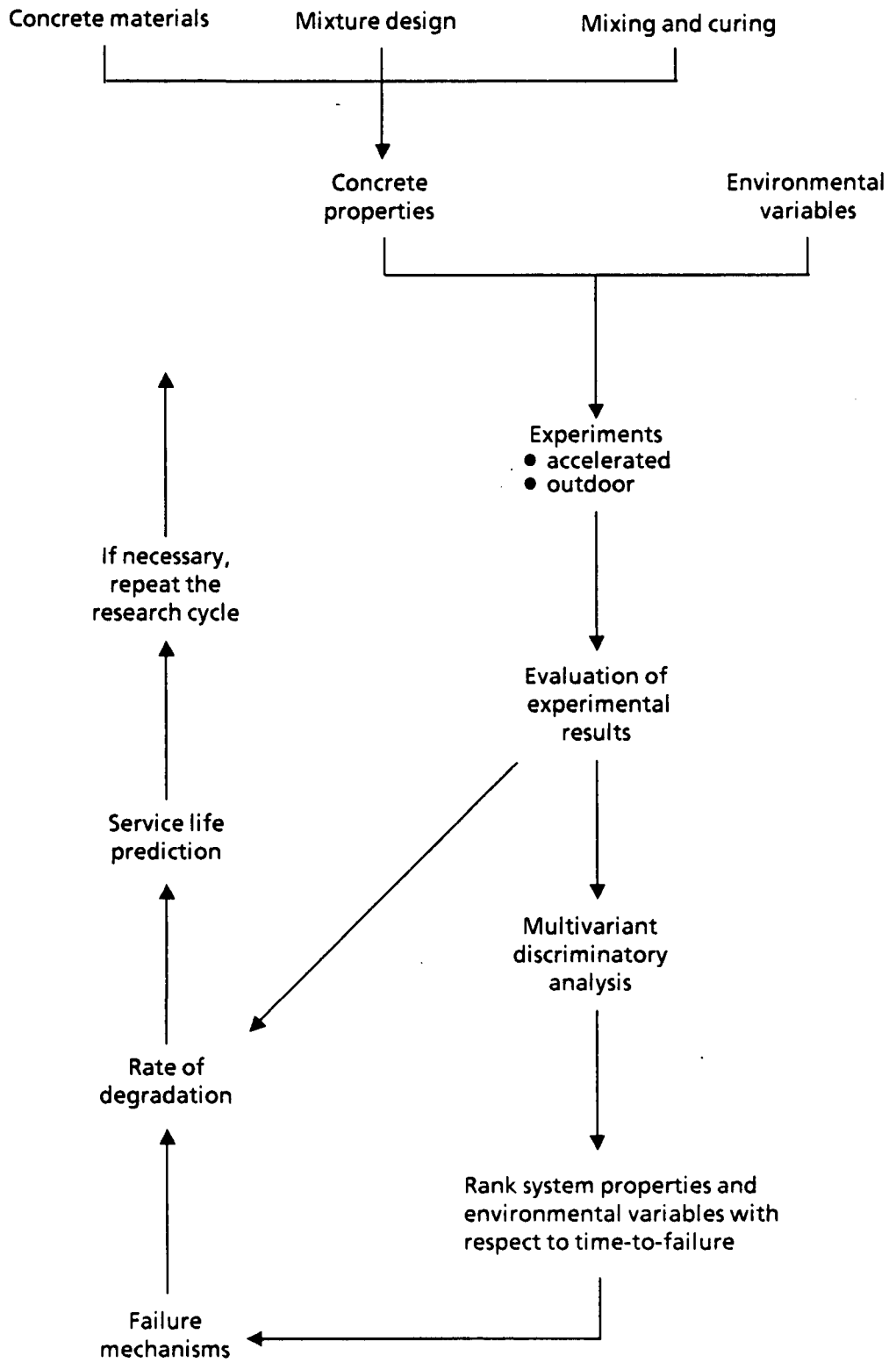

Figure 3. Diagram For Exposure Study.

RESPONSES TO QUESTIONNAIRE

The responses to the questionnaire that was used in the workshop to stimulate discussion and that was sent for foreign scientists are compiled below.

A. Response provided by Dr. Geoffrey Frohnsdorff, chairman of workshop discussions.

1. Please list any research on the effects of acid deposition on cement concrete materials that is in progress or that is being planned.

   The only research on the effects of acid deposition on cement concrete materials that the workshop participants believed to be in progress or being planned was:

   - The National Park Service was to support research on the effects on mortars to be carried out by a Mr. Langmuir in Colorado (this was mentioned by John Morgan).
   - The Department of Energy is supporting studies of the use of concretes for encapsulation of low-level radioactive wastes. This work, which is being carried out at Pennsylvania State University by Dr. Della Roy and colleagues, probably includes studies of acid attack of the concrete materials.

2. Are there existing experimental programs that could incorporate the study of acid deposition?

   The workshop participants mentioned a few existing experimental programs that could incorporate a study of the effects of acid deposition on concrete. These include:

   - Brookhaven National Laboratory's studies of the effects of acid deposition on crops in the field exclusion shelters.
   - Work being planned by the Waterways Experiment Station of the U.S. Army Corps of Engineers on the effect of aggressive waters on the service life of repaired and rehabilitated concrete.
   - The Portland Cement Association's (PCA) continuing studies of factors affecting the durability of concretes.
   - The National Bureau of Standards' (NBS) continuing studies of factors affecting the durability of building materials.
   - The Construction Materials Research Council (CMRC) of the ACI is planning to support research on effects of chlorides in concrete on the corrosion of reinforcing steel.
   - The National Concrete Masonry Association has a corrosion study under way on unreinforced concrete masonry walls.

3. Does evidence exist for acid deposition damage to cement concrete materials (structures)? If so, where?

   The workshop participants knew of no conclusive evidence to show that acid deposition had an effect on Portland cement concretes. However, it was mentioned that Dam and Lock No. 2 on the Monongahela River near Pittsburgh may show evidence of the effects of acid deposition.

   An excellent review paper entitled "The Effects of Neutralization of Concrete by Carbon Dioxide" was given at the Fifth International Symposium on the

Chemistry of Cement in Tokyo in 1968. The paper, which was by Hamada, included reference to surveys of actual buildings, including large chimneys. In a brief reference to neutralization of concrete in chimneys, Hamada mentioned that the neutralization was due to the effects of both CO_2 and SO_2. He also referred to studies by other workers on the effects of pollutants in chemical plants.

6. Is an experimental program needed to study the effects of acid deposition on cement concrete materials?

   Some other references that might be useful in designing an experimental program are as follows:

   - A series of papers by P.K. Mehta and O. Gjorv on Sulfate Attack of Cement Pastes by Sulfate Solution at Constant pH.
   - A paper by Paul Brown, on an extension of the work of Mehta and Gjorv to the study of sulfate attack at different constant pHs. (P. Brown, An Evaluation of the Sulfate Resistance of Cement in a Controlled Environment, in Cement and Concrete Research, Pergamon Press, Vol. II, 719-727, 1981.)
   - Proceedings of the NATO Advanced Workshop on Problems in Prediction of Service Life of Building Materials and Components.

7. How are the effects of acid deposition on cement concrete materials best assessed economically, i.e., loss of service life and repair and replacement frequency?

   - The PCA should be able to provide good information on the amount of cement going into each major use.
   - The two studies carried out by Battelle for NBS (on corrosion losses and on fracture losses in the United States) give some information on economic losses of construction materials and describe a methodology for analyzing losses.

B. Response provided by Dr. John Morgan, National Park Service, USA.

1. Please list any research on the effects of acid deposition on cement concrete materials that is in progress or that is being planned.

   The National Park Service (NPS) has an interest in mortar, both Portland cement and lime mortar. There have been discussions concerning laboratory studies to investigate reaction rates with very dilute acids.

2. Are there existing experimental programs that could incorporate the study of acid deposition?

   NPS has a stone exposure program that may have aspects that could be applied to concrete. Stone is exposed for periods from three months up to several years. Runoff is collected and analyzed for cations and anions. Surface recession and roughness as well as color change is measured. A variety of surface techniques are used: ion and electron probe, SEM Auger spectrometry etc. Surfaces of whole specimens and individual grains are analyzed.

3. Does evidence exist for acid deposition damage to cement concrete materials (structures)? If so, where?

   There appears to be no definitive evidence.

4. How does acid deposition affect cement concrete materials (structures)?

   Two types of effects: a. general acid reactions, e.g., H_3O^+ and OH^-; b. sulfate effects - expansion. Also two types of materials: a. cement; b. aggregate in cement - three main phases: C_2S, C_3S, C_3A. Carbonate aggregate may be attacked, but may also provide additional buffering.

5. Will acid deposition affect reinforced cement concrete?

   Needs to be investigated. Three possible effects:

   1. Chemical corrosive attack
   2. Loss of bond
   3. Reaction with $CaCO_3$

6. Is an experimental program needed to study the effects of acid deposition on cement concrete materials?

   Yes

   If so, please make recommendations on the following:

   a. Laboratory exposure, field exposure, or survey, etc.

      Three stages: 1. Field case studies, 2. Experimental studies (e.g., natural exposure, runoff, chamber studies), 3. Derivation of damage function.

   b. Environmental variables to be measured, etc.

      Presumably the standard EPA monitoring covers most possibilities.

   c. Specimen composition and size, etc.

      Somewhat controlled by aggregate size, and the problem of reinforcement.

   d. Damage measurement, etc.

      For cement itself, it can be measured as an analog of stone, but the question of reinforcing adds complexity.

7. How are the effects of acid deposition on cement concrete materials best assessed economically, i.e., loss of service life and repair and replacement frequency?

   If we know a. the total cement production, and b. amount going into roads and below ground purposes, and can guess c. the amount going into new construction, then one can estimate an upper limit from the replacement cost. Some percentage (small-large) of this number can be ascribed to acid rain - perhaps, try several scenarios.

C. Response provided by Frances P. Bradow, U.S. EPA.

1. Please list any research on the effects of acid deposition on cement concrete materials that is in progress or that is being planned.

   The United Kingdom's building research establishment has long-term exposure studies of quite a variety of building materials. It would be useful to get access to those data.

3. Does evidence exist for acid deposition damage to cement concrete materials (structures)? If so, where?

   Refer to the Durability of Building Materials bibliography in which articles relevant to concrete and cement damage are highlighted. (Durability of Building

Materials, Ed. P.J. Sereda, Elsevier Science Publishers B.V.: Amsterdam, The Netherlands, 2, 297-349, 1985.)

D. Response provided by Dr. Gunnar Morten Idorn, Consultant, Denmark.

1. Please list any research on the effects of acid deposition on cement concrete materials that is in progress or that is being planned.

   In general, examination of concrete structures with evidence of damage incorporates (within my field of knowledge) analyses of depth of carbonation. No specific research is in progress within my regions of activity. I am not aware of studies of a potential impact of SO_2 deposition. I believe that such studies must face a problem with the abundance of sulphate originally present in concrete.

2. Are there existing experimental programs that could incorporate the study of acid deposition?

   I am not aware of any which could or ought to.

3. Does evidence exist for acid deposition damage to cement concrete materials (structures)? If so, where?

   Not to my knowledge, whereas damage to natural stone with no protective alkalinity is a considerable problem.

4. How does acid deposition affect cement concrete materials (structures)?

   To my knowledge, by carbonation in concrete of insufficient denseness. I have examined concrete of 137 years' age with only 5-mm carbonation inwards from the surface (Cement and Concrete Research, **13**, pp. 739-743, 1983), and am satisfied that with available technology, incorporating mineral admixtures, equally dense and durable concrete can be produced today.

5. Will acid deposition affect reinforced cement concrete?

   Carbonation will affect bad concrete, see above.

6. Is an experimental program needed to study the effects of acid deposition on cement concrete materials?

   I do believe that an experimental program would meet with considerable problems concerning identification of specific acid deposition effects if reasonably attempting to model natural exposure conditions. Atmospheric acidity may, though, be more severe in places I have not been dealing with, than where my experiences originate. To provide advice I would need specific exposure data of an alarming character.

7. How are the effects of acid deposition on cement concrete materials best assessed economically, i.e., loss of service life and repair and replacement frequency?

   I don't know how the effects, if any, of acid deposition may be assessed separately, distinguished from other causes of concrete degradation - except by estimating a "percentage cause" of the total?

E. Response provided by Dr. Peter J. Sereda, National Research Council, Canada.

"I find the questionnaire difficult to answer because it does not ask the most important questions, such as:

- What percentage of exposed concrete is at risk?
- What is the rate of deposition of acid as gas and as liquid corresponding to the various concentrations in the air?
- What is the nature of the distribution of concentrations in urban areas, and how does it change with height.
- Since concrete is subject to a number of processes of deterioration, acid deposition is certain to act synergistically and for this reason it is not possible to determine the effect of one without including the study of all. I suspect that any process that causes surface cracking will expose the cement-aggregate bond to attack by acid deposition.

Concrete has a large capacity for neutralizing acid, therefore, only in the cases where surface texture and appearance is important, concrete may be able to tolerate many years of acid deposition."

F. Response provided by Dr. T. Skoulikidis, National Technical University of Athens, Greece.

5. Will acid deposition affect reinforced cement concrete?

Yes, refer to T.N. Skoulikidis, Atmospheric Corrosion of Concrete Reinforcements, Limestones, and Marbles, in Atmospheric Corrosion, Ed. William Ailor, 1982.

APPENDIX A

AGENDA

Wednesday, December 18, 1985

8:30 a.m.	**Registration**
9:00 a.m.	**Welcome and Opening Remarks** John Spence, U.S. EPA
9:15 a.m.	**Workshop Objectives** John Spence, U.S. EPA
9:30 a.m.	**Survey Results** Larry Kukacka, Brookhaven National Laboratories
10:00 a.m.	Break
10:20 a.m.	**Field and Chamber Exposure Studies - Existing Capabilities** Ed Edney and David Stiles, Northrop Services, Inc.
11:00 a.m.	**Development of Material Damage Function** Fred Haynie, U.S. EPA
11:30 a.m.	Lunch
1:00 p.m.	**Review of Questionnaire**
2:45 p.m.	Break
3:00 p.m.	**Workshop Discussion** Geoffrey Frohnsdorff, National Bureau of Standards
5:00 p.m.	Adjourn for Dinner
8:00 - 10:00 p.m.	**Discussion**

Thursday, December 19, 1985

9:00 a.m. **Opening Remarks**
Fred Haynie, U.S. EPA

9:15 a.m. **Workshop Report**
Geoffrey Frohnsdorff, National Bureau of Standards

10:15 a.m. Break

10:30 a.m. **Resume Discussion**

11:30 a.m. **Meeting Summary**
Fred Haynie, U.S. EPA

12:00 p.m. Adjourn

APPENDIX B

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APPENDIX C

QUESTIONNAIRE

1. Please list any research on the effects of acid deposition on cement concrete materials that is in progress or that is being planned.

2. Are there existing experimental programs that could incorporate the study of acid deposition?

3. Does evidence exist for acid deposition damage to cement concrete materials (structures)? If so, where?

4. How does acid deposition affect cement concrete materials (structures)?

5. Will acid deposition affect reinforced cement concrete?

6. Is an experimental program needed to study the effects of acid deposition on cement concrete materials?

   If so, please make recommendations on the following:

   a. Laboratory exposure, field exposure, or survey, etc.

   b. Environmental variables to be measured, etc.

   c. Specimen composition and size, etc.

   d. Damage measurement, etc.

7. How are the effects of acid deposition on cement concrete materials best assessed economically, i.e., loss of service life and repair and replacement frequency?