

## Materials and Cultural Resources

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I am from the National Center for Preservation, Technology and Training, and many of you may have never heard of our center. So, I am going to tell you a little bit about it.

The national center was established by Congress in 1992 and is part of the National Park Service. It is a research and development facility located in Natchitoches, Louisiana. We have a mission to promote the application of science and technology to the preservation of our nation's cultural resources and cultural patrimony.

Within the center we have four main components. That includes a research component, a training component, an information management component and we have an environmental and materials research program. We also have a newly formed federal preservation institute that is under the national center.

We look at problems that are within the fields of historic architecture, historic landscapes, archeology, materials conservation and ethnographic studies and historic interpretation.

I am going to talk about a few topics today. I am going to talk about our philosophy of research. I am going to give you an overview of pollutant-caused stone decay. I will be talking about a few of our recent experiments, and then I am going to tell you what we have learned.

At NCPTT, or the national center, we talk about a knowledge continuum. What we are trying to do is to understand the universal laws of nature. That is what we are all trying to do as scientists. In order to do that, some of our highest understanding comes from what we observe, identify, describe and test.

We use that information to develop technology, the application of science to broader issues, including issues that are industrial and commercial in nature. Ultimately, we want to provide knowledge to a user for consumption.

Now, at NCPTT, we try to span this whole spectrum or continuum of knowledge, from understanding basic principles from science, developing new technologies and applications, moving to disseminating that information and

ultimately using it. You, in a sense, are some of my end users because you need to know about stone deterioration and how air pollution affects them.

When we think about the relationship between air pollution and stone decay, we know it is a complex situation. We have many of the individual pieces described, but we don't always end up with a clear picture. It is a lot like working a jigsaw puzzle.

Sometimes we have better pictures than others, depending on the amount of effort and resources that we put in place.

With a lot of energy, we can sometimes get a better picture, but we may not always have the ability to get the big picture. That is the way it is with our air pollution interactions with stone.

We know that outdoor man-made air pollution is affecting our cultural resources and it is causing decay (Figure 1). We know that sulfur dioxide is one of the most important pollutants affecting stone, and we know that combustion processes lead to the production of large quantities of sulfur dioxide in the air.

When we have a simple model, we can talk about sulfur dioxide reacting with material such as stone by two main processes. One process is through dry deposition, where the gas is deposited directly on the stone, and the second is through wet deposition (Figure 2).

Once the pollutant has deposited onto the stone, it can interact to create an alteration crust



*Figure 1. Air pollution.*

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Figure 2. Deterioration of limestone caused by wet deposition of sulfur dioxide.

on the stone, and then that alteration crust is usually calcium sulfate, which is more water soluble than the stone itself and, with subsequent rains, the alteration crusts are moved.

What we end up with is a permanently altered sculpture. We have heard a lot of talk today about recovery. When a sculpture or a building or a stone is altered, it is permanently altered. We can't talk about recovery. It is gone.

Now, we have also heard a lot today about dose response functions. I am going to talk to you just a little bit about dose response functions. This is my personal opinion. You may agree or disagree.

We are going to talk about stone as a receptor, a complex receptor. It is heterogeneous. It has many different minerals in it. It is porous. When we talk about a dose response function, we want to say, if the stone sees air pollution, such as sulfur dioxide, nitrogen oxides, ozone, or particulate matter, it is doing to have a damage response, something that we can measure.

Those changes may be chemical changes or they may be physical changes. What we want to know is, given a dose, we have a response. But we can't get a true dose response relationship because of the complexity of the system.

First of all, stone has a very long response time. It sees air pollution today. It may react 25 years from now. It may react 50 years from now. It may react 100 years from now.

I am showing you two examples of stone decay (Figure 3). The results of gypsum formation and the incorporation of pollution onto the stone can result in spalling, delamination and total loss of the stone.

On the right-hand side you see a Funerary sculpture that is located in Cahill Cemetery in Louisville, Kentucky. This sculpture was featured in an article in National Geographic in 1978. At

that time, it had a head and shoulders on it. This photograph was taken by me 20 years later and the head and shoulders are completely gone.

Now, gypsum is the resulting product of the interaction of sulfur dioxide with the calcite or calcareous materials of stone. It forms a needle-like porous structure that can trap particulate matter (Figure 4). It also acts like a sponge to absorb water and increase the surface time of wetness.

The studies that we have done in the past and are currently doing include field studies, case



Figure 3. Stone deterioration.



Figure 4. Gypsum crust formation.

studies and lab studies. The field studies were part of the NAPAP studies. We have had current research going on since 1990 on the Cathedral of Learning building, which is in Pittsburgh. This is work done by Cliff Davidson at Carnegie Mellon University. In 1936, the air pollution concentrations in Pittsburgh were much higher than they are today. By the time of the completion of the building, it was completely soiled from top to bottom.

Today the air pollution concentrations have lowered significantly, but we still have a deposition process competing with an erosion and a washing away. So, we see changes in soiling patterns.

We also have laboratory studies. For example, I will be talking to you a little bit today about our studies on the surface morphology and porosity of stone and how that affects deposition and what that means to ultimately trying to talk about dose response functions.

Some of our work focuses on how we can use this information to develop better treatments for buildings, sculptures and monuments, so that we can get a better handle on how to prevent the damage rather than lower the pollution (Figure 5). This is our baby, as we call it. It is an environmental exposure chamber constructed by the National Oceanic and Atmospheric Administration. It allows us to test the uptake of pollution onto materials. We can control temperature, humidity, wind speed and turbulence within the sample and can measure directly the deposition of air pollution and particularly sulfur dioxide onto materials.

One of the studies that we have done was to look at the effects of texture on pollution uptake to different types of limestone. We looked at four different types of limestone because we wanted to



Figure 5. NCPTT exposure chamber

find out if there were differences between types. We looked at several different types of textures. We looked at very smooth surfaces and we looked at very rough surfaces.

We imposed the texture on the samples by etching them and then we characterized surface parameters such as the traditional roughness values,  $R^a$  and 17 other parameters. We also used mercury porosimetry to determine porosity within the stone, and we used nitrogen absorption to determine surface area on the very surface of the stone and also on the pore network.

This is probably the most important slide that I am going to show you. That is, we took our rough and our smooth samples. We exposed them eight different times for 24-hour exposures (Figure 6).

Now, the important thing to note is that the very first exposure and the second exposure have a much higher deposition of air pollution onto the stone than subsequent runs. What that tells us is that we can get sulfur dioxide onto the stone, but we have a lot of trouble getting it off. It gets into the stone. It gets into the spongy pores of the stone and it stays there.

The reason that is important is because it ultimately leads to a memory effect. I heard someone speaking about soils earlier. He said if you took all the sulfur dioxide in the air away tomorrow, you would still have problems. With stone, if you take all the sulfur dioxide away tomorrow, you are still going to have problems.

The results of our work show that we can identify trends within each stone type. For example, with the Salem limestone, the rougher

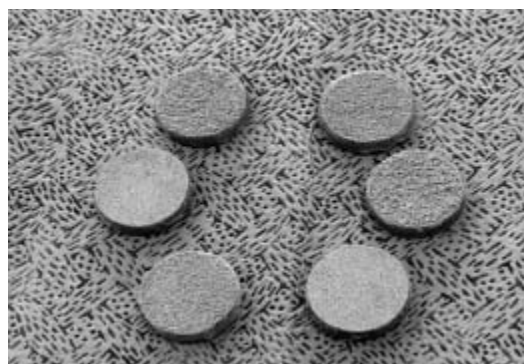


Figure 6. Texture on stone.

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stone, we will have more deposition than the smoother stone (Figure 7 and 8).

Surface roughness isn't the same across stone types. For example, a smooth Cordoba cream limestone may have a much lower deposition than a rough Salem limestone. Surface roughness itself isn't the controlling or dominant factor. It may affect the deposition but only within stone types, not across stone types.

We did learn something that was very important to us. That is, sample porosity and the number of valleys that we see on a stone surface will enhance deposition while the protruding piece will limit deposition.

Now, why is that important to us? Well, when we go out and clean our buildings, let's say we water wash them or we sand blast them or we use a chemical cleaner. Every one of those treatments changes that stone surface and ultimately sets up a different type of deposition.

What are the implications for us? Well, really,

what we are seeing is that the deposition of sulfur dioxide is a complex phenomenon that involves many environmental and material factors.

Porosity of the stone is a dominant factor within the deposition process. Once sulfur dioxide gets into the pores, it is difficult to get out. This leads to that memory effect that I talked about.

The take home message that I want you to know is that we are continuing to look at the stone systems and trying to describe the uptake of air pollution. I don't think we are going to get to dose response functions, but it just may require new approaches to increase our understanding.

Our understanding of stone decay is limited by the long response time of the stone and, to be frank with you, one of our biggest problems is that our resources are limited, there are very few scientists worldwide looking at this problem, and this limits our ability to make further progress.

I thank you for your attention and am willing to answer any of your questions.

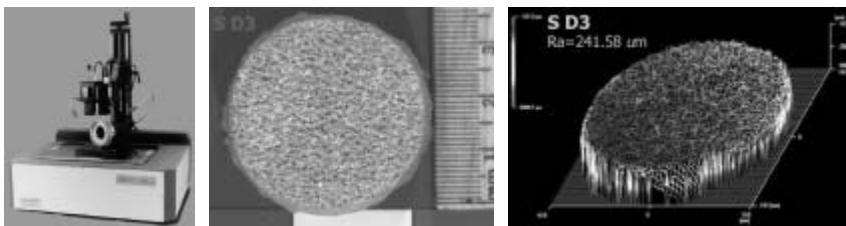


Figure 7. 3-D laser profilometry.

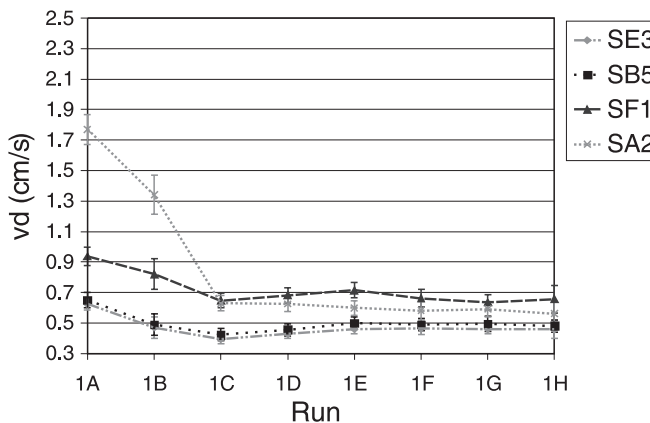


Figure 8. Salem limestone.

## QUESTIONS

MR. WHITE: I am Jim White from the Center for Environmental Information. I understand that in Europe in old buildings such as cathedrals there is a lot of deterioration of stained glass windows. Have you done anything at all with glass?

MS. STRIEGEL: I haven't been working with glass, but there are groups in Germany and in Austria that are looking at the effects of air pollution on glass.

There is a group sponsored by the UNECE on long-range transboundary air pollution and they have been looking at material effects. The last meeting that I know of was in Berlin and they reported some work on stained glass there.

MS. BAUM: I am Ellen Baum from the Clean Air Task Force. I have seen the work that has been done in D.C., where buildings have been affected, and the National Park Service believes this due to acid deposition. I understand you're saying that there are very limited resources to study this.

Is this just bits and pieces or is there a bigger piece of information so that we can understand where these impacts are being felt outside of Washington?

MS. STRIEGEL: From the early 1980s until about 1995, the work was done in Washington, D.C. and was supervised by Susan Sherwood, who some of you may well know. In 1995, the program was transferred to Natchitoches, Louisiana. We have approximately 45 projects that we have operated, but not all of them are focused on understanding deposition.

We have turned our resources to focusing on treatments and mitigation and how to prevent the damage to the stone. We know the damage is going to happen. We just don't know the time frame and we also don't know at what level.

We think there is not a threshold, that any sulfur dioxide is ultimately going to lead to some problems.

MR. OOTEN: My question is this. Do you have data, or has anyone aggregated data on the economic aspects of this materials degradation, the

cost of replacement or however you would go about measuring it. .

MS. STRIEGEL: Some of the early efforts were to look at a national inventory of stone material and then look at the cost of replacing component parts within a building. So, for example, what would it cost to replace a lintel, what would it cost to replace a door frame. Those efforts didn't lead to good evaluation.

There was a study about 1996 or 1997 out of a group from Colorado, I think from Boulder, Colorado. They decided they would survey the general public. They took a recognizable sculpture and they digitally manipulated it to age it. They had it in about four or five stages of deterioration.

They asked the general public how much they would pay to keep it pristine, to keep it at each of the different stages. That has probably been the most successful method of valuing the cultural resource.

MR. LIPPMANN: We had a prime example here in Washington. The Washington Monument was recently restored. That is clearly an example of stone deterioration that needed fixing. Do you have an idea of how much was spent on that?

MS. STRIEGEL: Unfortunately, I don't know what the cost of that project was. I can try to find that information and get back to you.

MR. LIPPMANN: I am just raising it as an example. We probably spent a lot of money.

MS. STRIEGEL: There was also a lot of money spent on the Statue of Liberty in 1986. If any of you recall that, that was a national campaign to raise the money for that restoration effort.

MR. LIPPMANN: The Lincoln Memorial, too.

MR. PENNINGTON: When I build my cabin on the top of the Blue Ridge Mountains, what should I build it out of? There is sandstone and limestone up there and some granite down the road.

MS. STRIEGEL: The granite might be nice. If you are going to choose a limestone, I recommend Salem limestone from Indiana, and polish it smooth.

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