MONITORING OF AIR CHEMISTRY AND SANDSTONE MASONRY DEGRADATION AT MESA VERDE NATIONAL PARK, COLORADO.

Task Group Project:

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IMPORTANCE

The Four Corners region of the United States contains some of this country's most ancient cultural resources, in the form of building ruins of prehistoric Anasazi civilization. The ruins have been exposed for a thousand years to a pristeen environment which was unaffected by human activities. However, in very recent years, increasing visitation of the sites by tourists, construction and operation of large industrial facilities such as power plants and smelters, and rapid population growth have changed this situation. The present decade represents a period of unprecedented growth in pollutant emissions in the area. Local air quality may be sufficiently altered as to affect the mode and rate of deterioration of the masonry of the ruins. A system has been installed for monitoring air and precipitation chemistry in coordination with observations of the deterioration of building materials found in the Anasazi ruins. Measurements are made in and near Spruce Tree House ruin at Mesa Verde National Park, Colorado. The specific materials of interest are the sandstone masonry units from which the ruins were built. The monitoring data will allow investigation of possible correlations between local air chemistry variations and the rate of deterioration of the sandstone blocks.

HYPOTHESES

(1) Inputs of acidic components accelerate deterioration by natural processes by increasing the rate of dissolution of the bonding phases in the sandstone microstructure.

(2) Correlations between the rate of deterioration of the sandstone masonry and variability in the concentrations of air pollutants, at appropriate temporal scales, can be detected.

TECHNICAL APPROACH

The monitoring objective is to conduct simultaneous materials-deterioration and aerometric measurements at one location for several years. Information from these coordinated sets of measurments will be used to describe the present rate of deterioration of the ruin, and the status of the microscale environment at Spruce Tree House. Further, the data will be used to examine possible correlations between environmental factors and the surface erosion process.

Materials Monitoring

The sandstone used as masonry material in the Anasazi dwellings in Mesa Verde National Park consists primarily of quartz grains which are loosely bonded together by an interlocking mechanism. Chemical bonding by quartz overgrowths is also involved in the mechanical stability of the stone, with minor contributions by interstital clay particles. The clay mineral bonding phase is known to be attacked by acidic environments, although at slower rates in comparison to the carbonates which are common bonding materials in eastern U.S. sandstones. Quartz, on the other hand, is essentially inert on time scales relevant to the context of this project. Consequently, deterioration of the sandstone which might be related to chemical environmental effects occurs through loosening of the grains by preferential removal of the bonding material, or lubricating of the grains, thus hastening removal.

Five masonry stones indicative of the variety of sandstones found on Mesa Verde were selected and placed in two test walls. The test walls were constructed in a manner typical of Anasazi grainaries. One wall is protected from direct exposure to rain and snow by a large rock overhang, as is most of Spruce Tree House ruin. The other wall is located on a rock ledge in a small clearing within Spruce Canyon, about 35 meters south of the ruin, and is exposed completely to precipitation. The stones were selected from rubble, identified by Park personnel as stones fashioned and dressed by the Anasazi. The materials have lost their archaeological value due to dislocation by ruins restorers in the 1930's and '40's. Nevertheless, the selected stones revealed surfaces that had been exposed to the environment for thirty or more years and appeared to be in the same physical state as stones found in the ruin walls.

The physical deterioration of the stones is monitored by optical microphotography. Photographs of stone surfaces are taken at 32X magnification (projected image on 35mm film), at monthly intervals. Those taken from successive periods are compared to detect grain removal or deposition. Because the grain shapes are equiaxed, an average recession rate can be calculated from the number and size of grains removed from the surface. This parameter can be examined with respect to environmental data, as described below. The surface analysis focusses on 300 X 600 μm areas, which means that 400 to 700 quartz grains are resolveable in the photographs.

Monitoring of chemical an microstructural changes of sandstones is also conducted, using several techniques. A series of .250 inch diameter specimen cores were taken from one stone and mounted in holders. These cores were then exposed at the two test wall sites. Four cores are removed at monthly intervals from both the exposed and the protected site. Thin sections of one core from each site are prepared for analysis by optical and backscatter - imaging electron microscopy. Another core is ultrasonically crushed and soaked in deionized water to extract soluble minerals. The third core is analyzed by secondary - imaging electron microscopy and energy dispersive x-ray methods, to detect deposition of airborne particles and chemical changes at the stone surface. The fourth core is held in reserve for possible replicate measurements.

Optical microscopy is useful in detecting gross changes in the sandstone microstructure. Because the samples represent cross sections extending from the surface to a depth of 5 mm, it is possible to observe variations which may be related to surface and subsurface processes. Events observed include the removal of interstitial material which may contribute to the overall bonding, and the alteration of accessory phases such as calcite, dolomite, rutile, feldspars, and iron compounds. Some of these materials are sensitive to acidic environments. Their decomposition and alteration are indicators of the environment to which they are exposed, even though they comprise only one to four volume percent of the stone.

Backscattered - imaging electron microscopy is sensitive to the chemical nature of the phasic components of the sandstone. The resolution capabilities of a typical instrument allow observation of microchemical and microstructural features smaller than 1000 angstroms. The technique is useful on smooth surfaces, such as thin sections prepared for optical microscopy. The method's primary application here is to detect phase changes of sandstone components, which may be induced by chemical influences. It is most useful in examining changes in the accessory phases.

Water extractable components are analyzed by ion chromatography for principal inorganic anions such as chloride, nitrate, and sulfate. Comparisons are made between the amounts of these species associated with surface and subsurface layers. These results, together with the secondary - imaging electron microscopy analysis, can be used to deduce periodic fluctuations in the chemical exposure of the materials.

Aerometric Monitoring

The aerometric monitoring system was configured to provide adequate temporal resolution in observations of atmospheric factors that drive the hypothesized mechanisms of accelerated sandstone deterioration. Hourly averages of most environmental parameters are recorded, as well as peak wind gust velocity and maximum and minimum temperatures each hour. This is done to allow the investigation of variations in sandstone deterioration rates with respect to not only long-term averages of the aerometric data, but also shorter-term averages, peak values, and the ranges of diurnal variations experienced by the masonry in the test walls.

An electronic environmental-monitoring station was installed at the exposed test wall site. Wind speed and direction, temperature, relative humidity, solar radiation, and vertical wind speed are measured at the top of a 6 meter tower. At this height, the sensors are located within Spruce Canyon, about 20 meters below the canyon rim. This exposure is similar to the elevation of the ruin itself. In addition, both test walls have embedded temperature sensors and surface moisture sensors that are connected to the electronic datalogger. Rainfall rate is also measured at the exposed site, about 1 meter above ground level. The environmental parameters are recorded on digital tape as hourly averages. In addition, a continuous-recording hygrothermograph and mechanical anemometer are used as a "low-tech" backup system.

An active air sampling system is located on the meteorological tower. A four-stage series filtration method is used to collect aerosol and gas samples. The first filter is 8.0 μm pore diameter Nuclepore, to collect large particles (diameter > 2.5 μm) (Cahill, et al, 1977). The second filter is 1.0 μm Teflon, to collect the remaining small particles. Third, a 1.0 μm Nylon filter selectively adsorbs nitric acid vapor (Goldan, et al, 1983). The sum of particulate nitrate from the first two filters and nitric acid from the third filter represents the total ambient nitrate concentration. The fourth filter is a double layer of cellulose fiber paper which has been treated with glycerol and potassium carbonate, to absorb sulfur dioxide (Johnson and Atkins, 1975). Loading of clean filters and extraction of exposed samples is done at the ISWS laboratory. The filter holders are sealed in several layers of polyethylene bags during shipments between the field site and laboratory. Analysis of aqueous filter extracts is done by ion chromatography. About twenty percent of the project's total sample load is devoted to a thorough quality assurance protocol. Precipitation chemical composition data are obtained from the National Atmospheric Deposition Program, which operates an acid rain monitoring site about 1.5 km north of Spruce Tree House. A passive air-quality monitoring method was used initially, to be used with the hygrothermograph and mechanical anemometer as a non-intensive environmental measurement system. After 16 months of sampling with the sulfation- and acidic gas-plates (SERCO, Inc.), this effort was abandoned because of unreliable results.

RESULTS

As part of the early design phase of the project, the vulnerability to attack by acids of typical sandstone masonry was characterized. Specimens of six sandstones were examined. The following features are typical, except where differences are noted. The primary crystalline phase is alpha quartz (SiO_2), consisting mainly of grains ranging from 80 to 150 m in diameter. Abundances ranged from 80 to 90 volume percent, (v/o). Secondary phases include clay minerals (3 to 14 v/o), iron based opaques (1 to 10 v/o), carbonates (0 to 2 v/o), feldspars (1 to 2 v/o), and accessory phases (zircon, rutile, chert, mica, and kaolinite and muscovite particles; 0.5 to 1 v/o). The primary bonding phase in all cases was clay minerals. Secondary bonding phases were either silicate or opaques. Carbonate bonding was rarely found to be significant.

The vulnerability of the various stones to acid attack was crudely assessed by soaking 1 cm diameter cores in aqueous acid solutions (10 percent sulfuric acid). The diametral strength of the cores was then measured. In all cases, measureable strength reduction was noted although most specimens retained their structural integrity (shape). Others completely disintegrated. Specimens were also exposed to vapors of sulfuric, nitric, and hydrochloric acids in varying concentrations. Chemical analysis demonstrated that the sandstones did pick up the corresponding components, although no definite trends with respect to acid strength were noted.

Reliable information on the deterioration rate of the sandstone has been collected over a continuous period of some ten months. Since the objective is to compare the deterioration information to fluctuations in air and precipitation chemistry, there is as yet far too little data to perform statistically meaningful analyses. The project has thus far established baseline conditions which might be compared to future results. With those qualifications in mind, a number of observations can be made on the results of the monitoring effort. First, it is eveident that the physical deterioration as determined by microphotography experiences cycles as might be expected, related to seasonal changes in meteorological conditions and air quality. The summer months reveal little or no deterioration activity, whereas the winter period, i.e. October to January, take the heaviest toll. The average recession rate in the most damaging month noted thus far (January) was 0.26 μm per month. This is roughly equivalent to 1,200 grains per square centimeter of surface.

Optical and electron microscopy reveal little variation in the sandstone chemistry. The aqueous extraction samples indicate that chloride and sulfate concentrations are slightly elevated near the surface, while nitrates are more uniformly distributed. The influence of atmospheric deposition on these observations remains speculative.

The hourly observations of environmental parameters are audited and checked for unreasonable values before being added into the overall database. Thus far, continuous data is available for over 95 percent of the time the project has been in operation. This data are being used to provide information on temperature and moisture cycles in the atmosphere and in the test walls. For example, the exposed wall experiences diurnal temperature cycles which are 2.0 to 10.0 $^{\circ}C$ larger than for the protected wall. Other deterioration - related factors can be calculated from the data, such as time of surface wetness, number of freeze - thaw cycles per time period, peak wind gusts, and so on.

Air chemistry data reveal a highly variable chemical environment at the Spruce Tree House ruin site. Minimum detectable concentrations of nitrate nitrogen and sulfate sulfur using the series filtration method, with weekly integrated samples, are less than 10 ng/m^3. Nitrate, sulfate, and sulfur dioxide all range from below detection up to several hundred ng/m^3 during the course of the year. Further, all of these species show marked seasonal trends. The character of sulfur in the air is also quite variable. In some weeks, virtually all of the sulfur is present as particulate sulfate; in other weeks, no particles are collected, and all of the sulfur is present as sulfur dioxide. The dependence of this variable partitioning on prevailing meteorological conditions is being examined. Precipitation data have also been added to the database, and, while rain pH is also quite seasonally variable, the mean volume - weighted field measured pH of rain at Mesa Verde is 4.60.

Finally, an early effort in this project to validate the use of passive gas - absorber plates as a practical and low - cost method of air quality monitoring was abandoned. The plates were exposed as quadruplicate samples of each of the two types (PbO_2 and K_2CO_3), for one month periods. In all cases, no correlation was observed between the amount of sulfates and nitrates extracted from the plates and the airborne concentrations measured by the active filtration system. Morevover, very little agreement among the quadruplicte samples was observed.

DISCUSSION AND CONCLUSIONS

The current operating plan for this monitoring phase of the project is to continue gathering additional observations, to build a sufficient database for the application of multivariate statistical analyses. Describing the influences of seasonal variations in environmental parameters on observed deterioration rates will require several years of continuous data collection.

REFERENCES

Cahill, T.A., Ashbaugh, L.L., Barone, J.B., Eldred, R.A., Feeney, P.J., Flocchini, R.G., Goodart, C., Shadoan, D.J., and Wolfe, G.W., 1977: Analysis of respirable fractions in atmospheric particulates via sequential filtration. J. Air Poll. Control Assoc., 27, p. 675.

Goldan, P.D., Kuster, W.C., Albritton, D.L., Fehsenfeld, F.C., Connell, P.S., Norton, R.B., and Huebert, B.J., 1983: Calibration and tests of the filter-collection method for measuring clean-air ambient HNO3. Atmos. Environ., 17, p. 1355.

Johnson, D.A. and Atkins, D.H.F., 1975: An airborne system for the sampling and analysis of sulphur dioxide and atmospheric aerosols. Atmos. Environ., 9, p. 825.

DELIVERABLES

An interim data summary report will be delivered to NPS in Spring, 1986, covering all monitoring results through March, 1986. A Final Project Report to NPS will be prepared about six months from the end of the present monitoring program, in March, 1987.

RELATIONSHIP TO OTHER WORK

Development and testing of this prototype monitoring system can be viewed with interest for a wide range of applications in other environments and other irreplaceable materials. The methods developed here will provide a cost-effective means of routinely monitoring deterioration processes at sites where a non-destructive, non-invasive technique is mandatory. Thus, this project is complementary to laboratory studies or field studies in which artificial "specimen" samples are expended in destructive analyses.

ACTIVITIES

Routine monitoring was initiated in December, 1984, and is planned to continue at least through October, 1986.

SUPPORT

National Park Service: $118,500; 1982-1986; CX0001-2-0039.

PERSONNEL

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