

# Application of Near-Infrared Spectral Reflectance Measurements for Detection of Acid Damage to Building Stones

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## Introduction

Several methods have been tested and proven to be useful for measuring stone damage due to acidic deposition. For example, comparison of the chemical composition of incident rainwater to rainwater runoff can be used to determine changes in dissolved anionic species and pH increases due to reaction of acidic rain with carbonate building stone. Color change, weight loss, surface recession, roughness and chemical and mineralogical alteration of exposed stone surfaces are other parameters that can be measured to determine stone degradation. Many of these measurements require that a sample of the stone be collected for laboratory measurements or that monitoring apparatus be in permanent operation at the building or monument. However, diffuse reflectance spectroscopy in the near-infrared (NIR) spectral region has been found to be a useful tool for the in situ and non-destructive measurement of the mineralogical composition of stone surfaces. A NIR spectral scan requires less than five minutes and yields qualitative and semi-quantitative data on the mineral composition of the stone surface.

In southern Britain, an on-site exposure experiment demonstrated that the accumulation of gypsum on limestone samples protected from direct wet precipitation correlated with the weight loss of unprotected stone. The authors concluded that gypsum accumulation is a good indicator of stone damage (Bultin and others, 1985). Cheng and others (1987) also reported that gypsum was present in samples of deteriorated marble and determined that airborne  $\text{SO}_2$  converted the marble into the soluble gypsum resulting in erosion of the marble. Gypsum, which is the product of a complex series of reactions between  $\text{SO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_3$ , has a solubility product constant of  $2.4 \times 10^{-5}$ , several times greater than that of carbonate,  $4.8 \times 10^{-9}$ . Therefore, gypsum will dissolve earlier than carbonate when stone is exposed to rainfall, resulting in weight loss and changes in surface texture.

## Spectral Reflectance Laboratory Studies

Spectral reflectance methods permit rapid non-destructive measurements of building stone materials. These measurements can be used for future reference and comparison of changes that may occur in the mineralogical composition of the stone. This technique measures radiation that is scattered from the near surface of a material. Spectral features arise when photons have passed through a volume of the material and have been absorbed at certain wavelengths before being scattered or refracted back out. In the NIR region of the spectrum, absorption features are produced by two mechanisms: electronic processes and fundamental vibrational processes. The absorption features related to vibrational modes of  $\text{CO}_3$ , OH and HOH groups, are of particular interest here.

The  $\text{CO}_2$  group causes five distinct absorption bands in the NIR. Intense bands at  $2.35 \mu\text{m}$  and  $2.50 \mu\text{m}$  and weaker features near  $1.88$ ,  $2.0$  and  $2.16 \mu\text{m}$  are characteristic of carbonates (figs. 1 and 2). The marble bands are more intense because the optical path length of photons is greater in marble than in limestone. The spectrum of gypsum also displays a series of intense absorption bands between  $1.0$  and  $2.5 \mu\text{m}$ , including a prominent water-of-hydration band at  $1.93 \mu\text{m}$  (fig. 1 and 2).

At the U.S. Geological Survey, we have conducted laboratory experiments to determine the composite reflectance spectra of known amounts of gypsum present on limestone and marble surfaces (Kingston and Ager, 1985; Eastes and Salisbury, 1986). The experiments show that the depth of the gypsum water-of-hydration band near  $1.93 \mu\text{m}$  increases linearly with increasing amounts of gypsum on the surface (figs. 1 and 2). The lower limit of detection for gypsum on a limestone surface is  $0.043 \text{ mg/cm}^2$ , but up to  $0.114 \text{ mg/cm}^2$  of gypsum is required for detection on a marble surface in the NIR (Eastes and Salisbury, 1986). These laboratory studies demonstrated the potential for semi-quantitative and non-destructive determinations of gypsum accumulation on limestone and marble buildings and monuments.

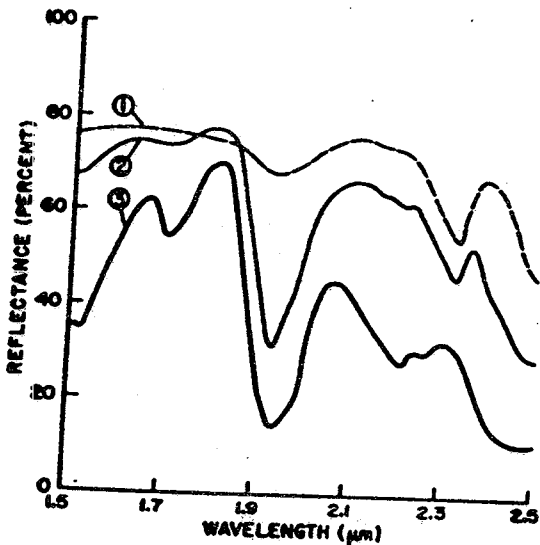


Figure 1. Near-infrared spectra of: 1) pure limestone, 2) limestone with gypsum on surface measured and 3) pure gypsum.

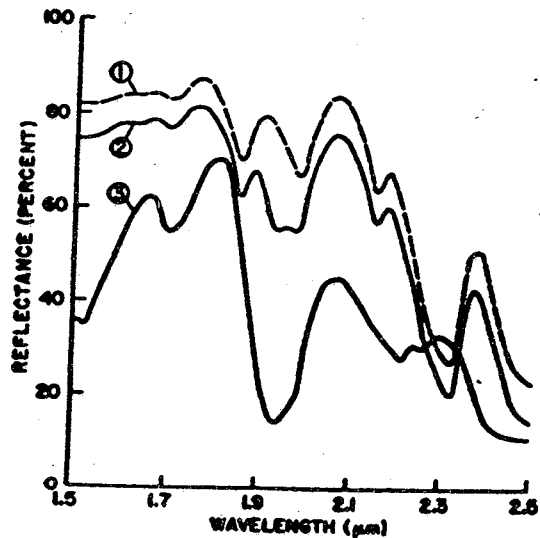


Figure 2. Near-infrared spectra of: 1) pure marble, 2) marble with gypsum on surface measured and 3) pure gypsum.

### Test Site Studies

Field data for the development of representative spectral reflectance calibration curves are being collected at four test sites in the eastern United States. Facilities were installed in late 1984 by the National Park Service under the National Acid Precipitation Assessment Program (NAPAP). The test sites are located at established meteorological monitoring sites to achieve correlation between environmental conditions and material degradation. Freshly quarried briquettes of Salem limestone

and Shelborne marble (7.3 cm by 8.3 cm) were exposed at a 30° angle on south facing racks at the following sites (Table 1).

Table 1

Site	Location	Environment
Research Triangle Park	Raleigh, N.C.	Suburban
Roof, West End Library	Washington, D.C.	Urban
Bell Laboratories	Chester, N.J.	Suburban/Rural
Huntington Forest	Newcomb, N.Y.	Rural

At each site, NIR spectra were recorded with a portable spectrometer made by Geophysical Environmental Research, Inc. (citation of commercial products does not constitute endorsement by the U.S. Geological Survey). The spectrometer scans the 0.4- to 2.5- $\mu\text{m}$  wavelength region. Each spectrum is recorded and temporarily stored on a cassette; these files are copied later to computer for data processing and storage. Both upper (skyward) and lower (protected) surfaces of the briquettes were measured. Preliminary results indicated that there was little or no measurable gypsum accumulation on the exposed upper surface, but varying amounts of gypsum were concentrated on the protected lower surfaces of both limestone and marble briquettes. Gypsum accumulates in the center of the briquette lower surface and is always associated with a brown stain. Scanning electron microscopy (SEM) has illustrated that fly ash and other dust particles may be trapped among gypsum "blades" (McGee, Ross and Ross, personal communication). Evidence from X-ray diffraction data, as well as the SEM studies, agree with the spectral data that gypsum is developed only within the central portion of the lower surfaces of briquettes.

From these studies we conclude that gypsum does accumulate on surfaces protected from heavy rainfall. We have also demonstrated that this gypsum deposit may be detected spectroscopically without contact with the surface of the building stone measured. As predicted by laboratory spectral studies, the band depth at 1.93  $\mu\text{m}$  is proportional to the gypsum concentration on the briquette surface. Estimates of gypsum concentration on the briquette lower surfaces are made by comparing the 1.93  $\mu\text{m}$  band depth of spectra collected annually after exposure, with spectral measurements made before and immediately after briquettes were mounted on the racks. In table 2, estimated gypsum was calculated from the calibration curve derived from laboratory experiments of Eastes and Salisbury (1986).

Table 2. Estimated gypsum in  $\text{mg}/\text{cm}^2$  on lower surfaces of briquettes. Concentrations are mean values for all briquettes measured. Value in parenthesis explained in the text.

	Limestone		Marble	
	1985	1986	1985	1986
Site 1 - N.C.	0.35	0.99	0.36	0.28 (0.43)
Site 2 - N.J.	0.40	1.51	<0.11	<0.11
Site 3 - N.Y.	<0.04	0.05	<0.11	0.35
Site 4 - D.C.	1.28	1.70	0.27	0.93

Youngdahl, of the Argonne National Laboratory has measured sulfate ion concentration of the outer layer of both upper and lower surfaces of the test briquettes using ion chromatography. He finds that gypsum on the lower surfaces increased from 1985 to 1986, with the lowest values recorded at the New York site and the highest gypsum values at the Washington, D.C. site, which is in general agreement with the results shown in table 2. These results are a function of pollutant levels as well as meteorological variables.

Seemingly non-systematic gypsum values illustrate the complex relationship between the sulfation of carbonate minerals and assessing materials damage. For example, gypsum deposition is less on briquettes located in the lower west side of the racks at all test sites. This variation explains the high gypsum value in 1985 for marble at site 1, because no marble briquettes from the west section of the rack were measured, thus effectively increasing the mean gypsum value. The site 1 1986 marble/gypsum value reported is for briquettes from all sections of the rack, but the gypsum value in parenthesis includes only those briquettes which were also measured in 1985. Variation in gypsum deposition between marble and limestone samples may be a result of porosity differences. The more porous limestone will absorb more rain water, remain wet longer and allow the accumulation of more gypsum. However, although the mechanism is not fully understood, evidence from chamber studies indicates that the rate of  $\text{SO}_2$  uptake on calcareous stone surfaces, especially marble, is catalyzed by  $\text{NO}_2$  (Johansson, 1986). Therefore  $\text{NO}_2$  pollution may result in greater gypsum accumulation on marble than limestone. Local meteorological conditions such as heavy rain or winds immediately preceding the measurement of samples, as well as seasonal weather variations may also contribute to differential gypsum buildup.

#### Spectral Reflectance of Monuments

Having demonstrated the feasibility of using spectral reflectance measurements to record the buildup of gypsum due to the sulfation of carbonate materials, we are experimenting with the use of this technique to detect gypsum on building or monument surfaces. Results of this study will also contribute to understanding the relationship between architectural detail and material deterioration.

Several modifications to the standard measurement procedure were necessary for recording reflectance spectra of monuments and buildings. The spectrometer calculates spectral reflectance by comparing the radiance of the target with the radiance of a high reflectance, non-absorbing standard that must be co-planar with the target. In the conventional operation, typically in situ measurement of rock, the target is nearly horizontal and the solar illumination impinges at a high angle. To measure nearly vertical monument and building surfaces, a more cohesive reflectance standard and an adjustable illuminating lamp must be used.

Measurements were initially made of the Jefferson Monument marble columns, where spectra typical of pure marble showed that no gypsum had accumulated. A sample of Yule marble collected from the south parapet of the Lincoln Memorial was also measured. The spectral curve contained a

slight inflection at  $1.93 \mu\text{m}$  suggesting the presence of a minor amount of gypsum (near the detection limit). Limestone which was collected from a rib on a damaged baluster (from a balustrade of the Department of Justice building, Washington, D.C.), was also measured. The deep gypsum water-of-hydration band at  $1.93 \mu\text{m}$  (fig. 3) indicated that approximately  $0.62 \text{ mg/cm}^2$  of gypsum had accumulated on this surface which was protected from direct heavy rainfall.

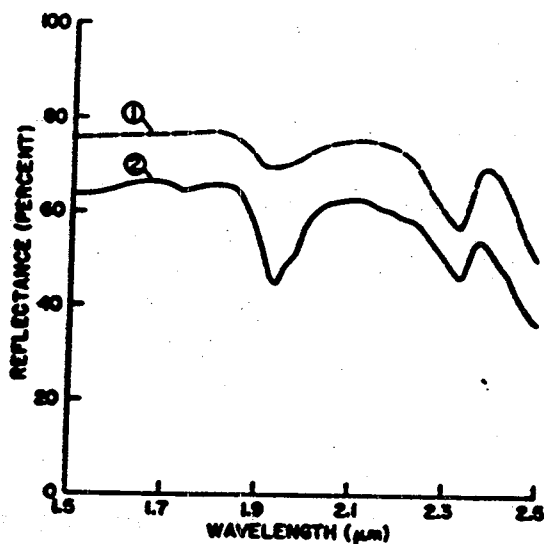


Figure 3. Near-infrared spectra of: 1) fresh limestone, and 2) damaged limestone balustrade.

### Conclusion

Diffuse spectral reflectance measurements may be rapidly collected in situ, and are non-destructive. The spectral reflectance curves are specific for limestone, marble and gypsum. A spectral mixture of gypsum and carbonate materials results in increased band depth of the gypsum water-of-hydration feature near  $1.93 \mu\text{m}$ . Laboratory studies have shown that as gypsum accumulates on marble or limestone surfaces, the  $1.93 \mu\text{m}$  band depth increases in proportion to the gypsum concentration. We have used a calibration curve determined from laboratory experiments to estimate the amount of gypsum deposited on the lower surface of briquettes exposed to ambient conditions at four test sites in the eastern United States. Because gypsum is formed by the reaction of carbonate with sulphur dioxide and water, gypsum accumulation correlates with acid deposition. Because of its solubility, gypsum tends to accumulate only on surfaces protected from direct precipitation. Dissolution of gypsum formed by acid deposition leads to stone damage, including textural changes, recession and erosion. Because gypsum has accumulated only on a specific area of the central lower surface of the test briquettes, it is evident from the NAPAP test site study that geometric configuration is also a controlling factor in gypsum deposition on calcareous stone.

the system is called VCAD, the

Measurements of limestone and marble from buildings and monuments in Washington, D.C. have corroborated these results. Exposed marble columns of the Jefferson Monument are gypsum free, but a small amount of gypsum was detected on samples of marble from a more rain-protected parapet at the nearby Lincoln Memorial.

Because small areas of a building stone surface may be rapidly measured, we anticipate that this technique will be useful for mapping gypsum accumulation on different parts of buildings or monuments. Results of these studies may also be useful in developing a damage assessment of cultural resources and understanding the role of architectural design in materials deterioration due to pollutants.

#### References

- Bultin, R.N., Cooke, R.U., Janes, S.M. and Sharpe, A.S., 1985, Research on limestone decay in the United Kingdom: in Proceedings of 5th International Congress on Deterioration and Conservation of Stone, G. Felix, Ed., Presses Polytechniques Ramandes, Lausanne, Switzerland, p. 537.
- Cheng, R.J., Hwu, J.R., Kim, J.T., and Leu, S., 1987, Deterioration of marble structures, the role of acid rain: Analytical Chemistry, vol. 59, no. 2, p. 104A.
- Eastes, J.W., and Salisbury, J.W., 1986, Spectral properties of sulfated limestone and marble: implications for in situ assessment of atmospheric pollution damage to carbonate rock building materials, Applied Spectroscopy, v. 40, p. 954.
- Johansson, L.G., Lindquist, O. and Mangio, R.E., 1986, Corrosion of calcareous stones in humid air containing SO<sub>2</sub> and NO<sub>2</sub>: Symposium on Air Pollution and Conservation, eds. Aleby, S. Lindquist, O., and Olsson, L., Rome.
- Kingston, M.J., and Ager, C.M., 1985, A spectral reflectance method to measure acid deposition effects on building stone: in Proceedings of the American Society of Photogrammetry Annual Meeting, March 11-16, Washington, D.C., p. 871.

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Summary

In situ measurements of near-infrared (1.0-2.5  $\mu\text{m}$ ) spectral reflectance provide a rapid, non-destructive method for monitoring gypsum deposition on limestone and marble buildings and monuments. The presence of gypsum causes the intensity of the  $\text{H}_2\text{O}$  absorption band at 1.93  $\mu\text{m}$  to increase. Laboratory measurements of the 1.93  $\mu\text{m}$  band indicate that as little as 0.048  $\text{mg}/\text{cm}^2$  of gypsum is detectable on limestone.

Analysis of in situ reflectance spectra recorded on Salem limestone slabs at four test sites in the eastern United States shows that gypsum is deposited on the lower surfaces. The following amounts ( $\text{mg}/\text{cm}^2$ ) of gypsum were estimated at these test sites using the laboratory calibration curve: New York - 0.05 (limestone) and 0.35 (marble); North Carolina - 0.99 and 0.28; New Jersey - 1.5 and <0.11; and Washington, DC - 1.70 and 0.93.

Although the laboratory calibration curve was useful for making these estimates and demonstrating the feasibility of this approach, field calibration curves are needed for more accurate in situ determinations. Chemical analysis of gypsum concentration on the lower surfaces of test stones by ANL will be used to relate spectral reflectance to the amount of gypsum present. Then, these data will be compared to physical (ANL) and chemical (USGS) measurements of deterioration of the upper surfaces to relate spectral reflectance to stone damage.

Development of a method to rapidly map spectral reflectance variations caused by gypsum on carbonate rock building and monument surfaces is being studied. An adequately calibrated mapping method would permit quantitative studies of the spatial distribution of gypsum on building surfaces.

L'Application de Mesures du Coefficient de Réflexion  
Proche-Infrarouge et Spectrale à la Détermination  
des Effets due Dépôt d'Acide sur les Pierres pour la Construction/

de

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Résumé

Les mesures in situ du coefficient de réflexion proche-infrarouge et spectrale fournissent une méthode rapide et non-destructrice pour observer le dépôt de gypse sur les bâtiments et sur les monuments de calcaire et de marbre. La présence de gypse cause une augmentation de l'intensité du ruban de l'absorption de  $H_2O$  à  $1.93 \mu m$ . Des mesures du  $1.93 \mu m$  ruban, faites au laboratoire indiquent que même le petit somme de  $0.04 \text{ mg/cm}^2$  discernable sur calcaire.

L'analyse des spectres du coefficient de réflexion in situ marqués sur des dalles de calcaire "Salem" à quatre emplacements aux Etats-Unis de l'Est montre que le gypse se dépose sur les surfaces inférieures. Les quantités de gypse ( $\text{mg/cm}^2$ ) qui suivent ont été calculées à ces emplacements en employant la courbe de calibration du laboratoire: New York - 0.05 (calcaire) et 0.35 (marbre); North Carolina - 0.99 et 0.28; New Jersey - 1.5 et  $<0.11$ ; et Washington - 1.7 et 0.93.

Bien que la courbe de calibration du laboratoire fût utile pour le calcul de ces estimations et pour la démonstration de la praticabilité de cette méthode, des courbes de calibration du terrain sont nécessaires afin de faire des estimations in situ plus précises. Une analyse chimique de la concentration de gypse sur les surfaces inférieures des pierres d'essai sera utilisée pour rapporter le coefficient de réflexion spectrale à la quantité de gypse présente. Ensuite, on comparera ces données aux mesures physiques (ANL) et chimiques (USGS) de la détérioration des surfaces supérieures afin de rapporter le coefficient de réflexion spectrale à l'endommagement de pierre.

Actuellement, on fait des recherches afin de développer une méthode de tracer rapidement des variations du coefficient de réflexion spectrale causées par le gypse sur les surfaces de bâtiments et de monuments de pierre carbonate. Une méthode de cartographie suffisamment calibrée permettrait des études quantitatives de la distribution spatiale de gypse sur les surfaces de bâtiments.