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Simulation investigations on the marble deterioration by sulphur dioxide*

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Abstract—This paper deals with investigations on corrosion of marble SO_2. We have simulated oxidation of SO_2 by photochemical process in the atmosphere. The experiments indicate that formation of SO_3 aerosols is related to the concentration of SO_2, the UV light intensity, the time of irradiation and the humidity of the air. The corrosion feature of surfaces of the marble and the depth profiles of sulphur were obtained by SEM (Scanning electron microscope), EDXA (Energy-dispersive X-ray analyzer) and SIMS (Secondary ion mass spectrometer). The results of experiments show the corrosive extent of marble depends on its compositions and microareas of marble, which contain lower silicon content can be easily corroded by SO_2.

Keywords: acid rain; acidification of environment; photochemical process; marble deterioration; SO_2.

INTRODUCTION

In China there are plenty of marble statues and marble forests of steles which record the Chinese civilization of long standing. But the calligraphy of the words and the shapes of the marble carvings are gradually becoming blurred. Definitely, this is a serious problem which our scientists are concerned on. As is well known that acid rain and acidification of environment have become a key environmental topic in recent years. In the previous papers (Cheng 1976; 1984; 1987), it is indicated that the marble grains are being structurally weakened by a chemical conversion process of the marble to gypsum crystals, and the possibility of a catalytic mechanism for the conversion of sulfur dioxide to sulfate. Recently we have simulated the oxidation of SO_2 by photochemical process in the atmosphere, and showed that the corrosive extent is related to the composition of marble and other factors. According to our experiments we can obtain some ideas to prevent marble statues and steles from corroding.

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EXPERIMENT

Instruments and methods

1. Ion chromatograph

The apparatus has been used for analysis of SO_2 as sulfate in solution. The ion chromatograph ZIC was produced in China and is equipped with a conductivity detector.

2. Scanning electron microscope X-ray analyser

The analyser (Hitachi X-650) consists of a scanning electron microscope (SEM), wavelength-dispersive spectrometer (WDS), and energy-dispersive spectrometer (EDS). It has been used for investigations of the surface features and microarea chemical analyses of marble. The operational parameters are as follows: The accelerating voltage is 25 kV, the electron current is 3×10^{-7} Å and the spectroscopic crystals are LiF, PET, RAP and STE. The electron beam diameter is 1000Å.

3. Secondary ion mass spectrometer

A Hitachi IMA-2A secondary ion mass spectrometer has been used for element profiles and analysis of compositions on the sample surfaces.

The primary ions are Ar^+ and the accelerating voltage is 15 kV. The accelerating voltage for the secondary ions is 3 kV. The ion beam diameter is 0.5μm. The experiments have been done at pressure of 1.3×10^{-4}Pa.

4. Apparatus for corrosion test

A simple apparatus for corrosion test is shown in Fig. 1.

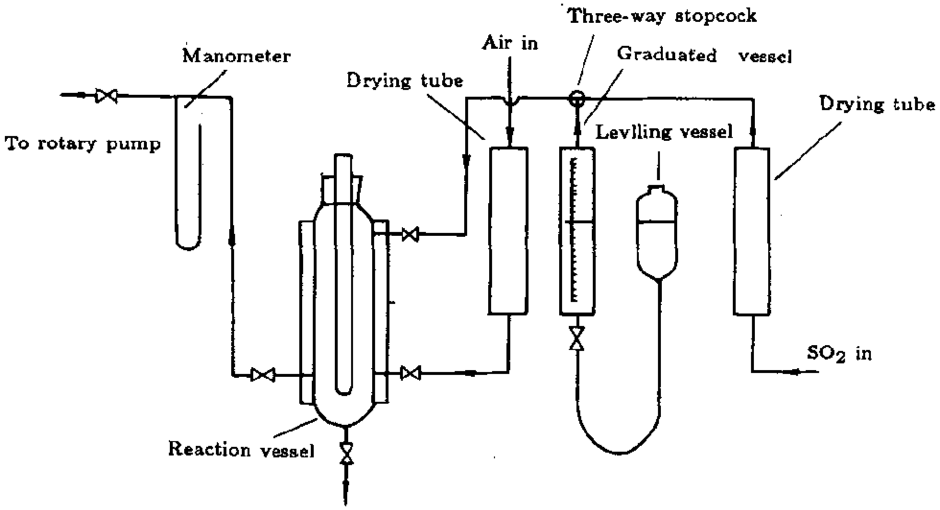

Fig. 1 Schematic of a apparatus for corrosion test

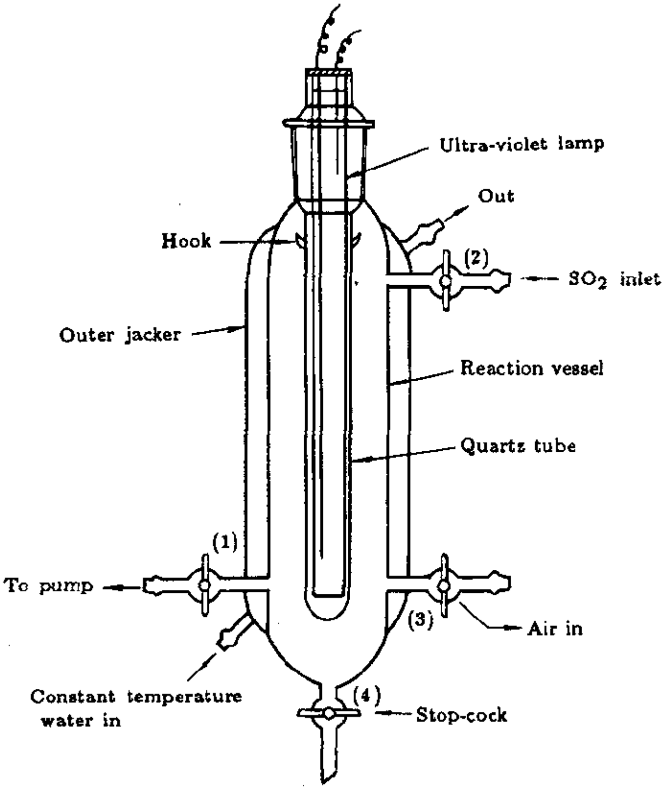

Fig. 2 Detail of reaction vessel

The detail of the reaction vessel is given in Fig. 2.

5. Operational methods

(1) Corrosion test

The marble samples (10mm wide and 2 mm thick) are adequately polished before experiments. A damp sponge is placed in the reaction vessel to provide the moisture needed to produce the acid H_2SO_4. Hang the specimens polished onto the hooks which are on the wall of quartz tube. Turn on the stop-cock 1 (Fig. 2), pump air from the vessel with a rotary pump, then turn on the stop-cock 2, a certain amount of SO_2 is introduced into it. Finally turn on the stop-cock 3, let air in until the pressure reaches one atmosphere. Close all stop-cocks. Turn on the UV lamp immediately. Several seconds later white fog appears in the vessel. After a period of time, turn off the UV lamp, take out the specimens.

(2) Ion chromatography analysis

The samples corroded were placed in 5—10 ml of distilled deionized water, washed with a ultrasonic washing machine. The resulting solution was analyzed for sulfate by ion chromatography.

(3) Scanning electron microanalysis

Three scanning modes, including spot, line and area analysis, were used for examing distribution of sulfur of the deteriorated marble.

(4) SIMS analysis

To eliminate edge effects the electron aperture technique was applied in the experiments.

RESULTS AND DISCUSSIONS

The photochemical oxidation of sulfur dioxide SO_2 to sulfate may take place heterogeneously on the wet marble surfaces. The amount of sulfate depends on experimental conditions such as pollutant concentrations, intensity of UV light, irradiation time, humidity and so on. The results are shown in Fig. 3 to Fig. 5.

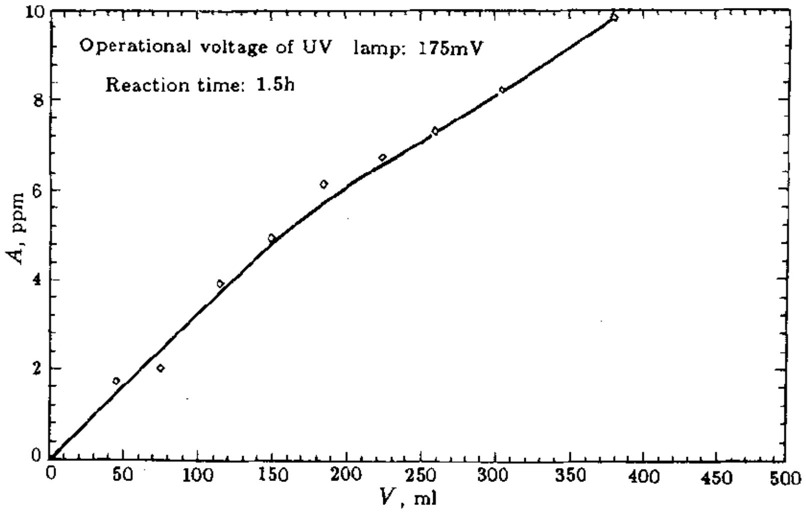

Fig. 3 Effect of SO_2 in the reaction vessel

It can be seen from Fig. 3 to Fig. 5 that the amount of sulfate is proportional to the intensity of UV light, irradiation time and the amout of SO_2.

In addition to the above influences, we find the effect of sample compositions which play a significant role. We have chosen four kinds of sample for experiments (Table 1).

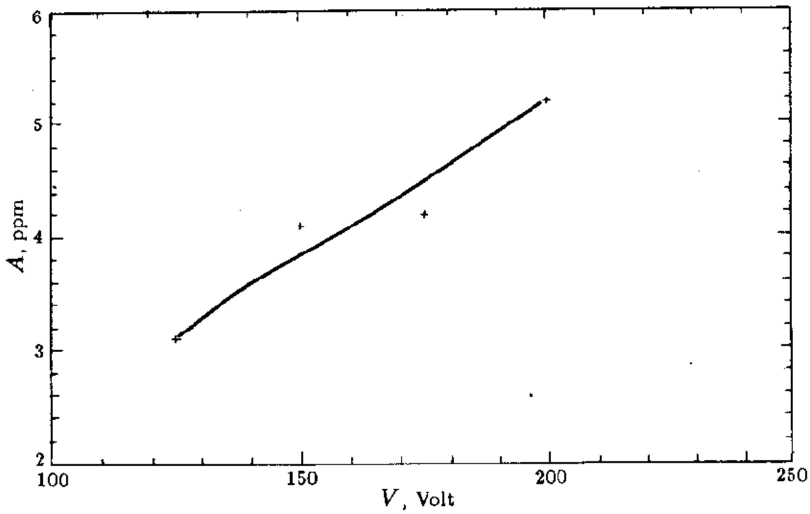

Fig. 4 Effect of irradiation intensity

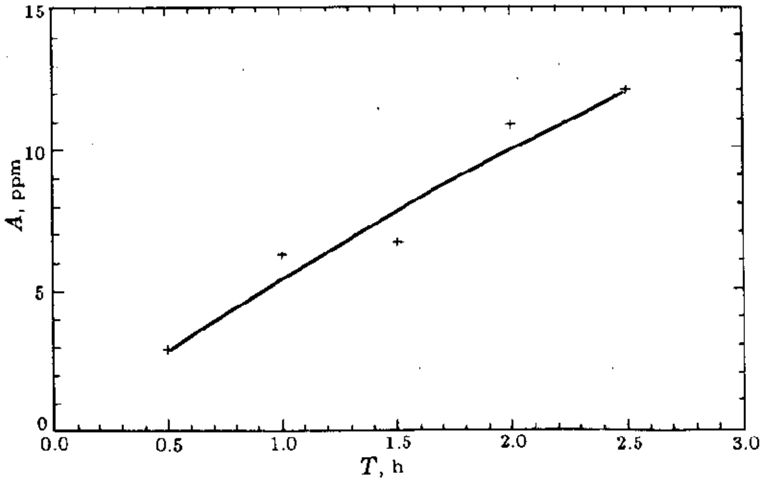

Fig. 5 Effect of irradiation time

Table 1 Names and compositions of samples

No.	Name	Major compositions
1	Serpentinite marble	Calcite ($CaCO_3$) 50—60% Serpentine ($Mg_6(Si_4O_{10})OH$)25—30%
2	Granite	Plagioclase ($NaAlSi_3O_8$)($CaAl_2Si_3O_8$)
3	Iron-limestone	Calcite ($CaCO_3$)65—70% Iron-dolomite ($CaMg(CO_3)_2$)25—30%
4	Marble	Calcite ($CaCO_3$)>95%

The results of SME had shown that the surfaces of No.1 to No.4 samples were corroded and gypsum crystals were formed on the surfaces of the samples and EDXA spectra are given in Figs. 6, 7, 8 and 9.

Concentration

	WT.%	AT.%	%S.E.
MGK	2.96	3.51	7.18
ALK	24.18	25.90	1.20
SIK	58.54	60.24	0.69
SK	0.14	0.13	102.62
CAK	14.18	10.22	1.63

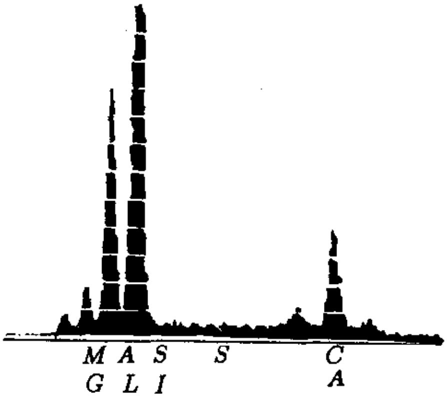

Fig. 6 The EDXA spectra of No.2 sample

Concentration

	WT.%	AT.%	%S.E.
MGK	46.44	50.05	0.93
ALK	0.00	0.00	0.00
SIK	53.33	49.76	0.79
SK	0.22	0.18	82.12
CAK	0.00	0.00	0.00

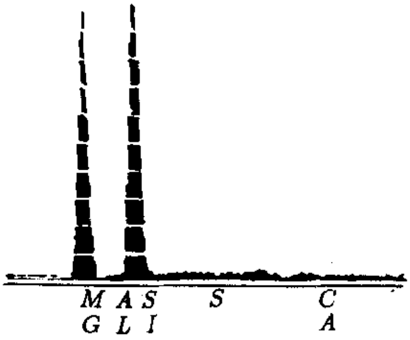

Fig. 7 The EDXA spectra of No.1 sample in the region of high silicon content

Concentration

	WT.%	AT.%	%S.E.
MGK	14.47	19.56	2.75
SIK	6.94	8.12	3.22
SK	38.44	39.40	0.97
CAK	40.15	39.92	1.02

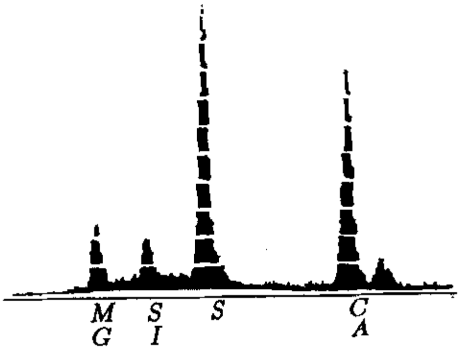

Fig. 8 The EDXA spectra of No.4 sample in the region of low silicon content

Concentration

	WT.%	AT.%	%S.E.
MGK	51.86	55.44	0.73
ALK	0.00	0.00	0.00
SIK	48.14	44.55	0.73
SK	0.00	0.00	******
KK	0.00	0.00	0.00
CAK	0.00	0.00	0.00

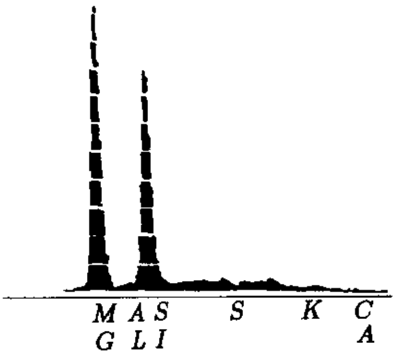

Fig. 9 The EDXA spectra of No.4 sample in the region of high silicon content

From the above experimental results one can see:

1. The corrosion extent varies clearly with compositions of specimens. For instance, the material of No.4 specimen is called "White marble" in China, which has been used for buildings, statues and other carvings from ancient time. It consists of calcite basically, and is corroded easily by acid rain. Whereas, No.2 sample contains a large amount of silicon in it, and is not easily attacked by acid rain.

2. From our experimental data it also can be found that the microregion which has a lower content of silicon usually contains higher calcium, inversely the higher silicon microregion has lower calcium.

3. Corrosion processes start from microregions of lower silicon and penetrate into the inner of specimens. From our experiments it can be seen that sulfur distribution is not uniform and from linear scanning for sulfur the same results can be also obtained. So one can see that corrosion processes continue along paths of lower silicon and gaps can be formed, therefore, marble buildings and others can be damaged.

The results of linear scanning were gained. From the linear scanning results it can be obtained that the corrosion depth are 50 μm and 300 μm, respectively. The former corresponds to microareas of higher silicon of No.1 sample and the latter corresponds to microareas of lower silicon of No.2 sample.

The results shown in Fig. 10 and Fig. 11 have been done by point analysis of EDXA and SIMS, respectively. They show the relationship between sulfur depth and intensity. Fig. 11 shows corrosion depth in different areas as well, and the area 1 corresponds to the area with higher silicon content but the area 2 corresponds to the lower one.

From Fig. 12 to Fig. 13 are mass spectra in area 1 and area 2 of No. 1 specimen. From Fig. 11 to Fig. 13 it can be obtained that the corrosion depth is much deeper for the area 1 which contains lower silicon, whereas the corrosion depth is much shallower for the area 2 which

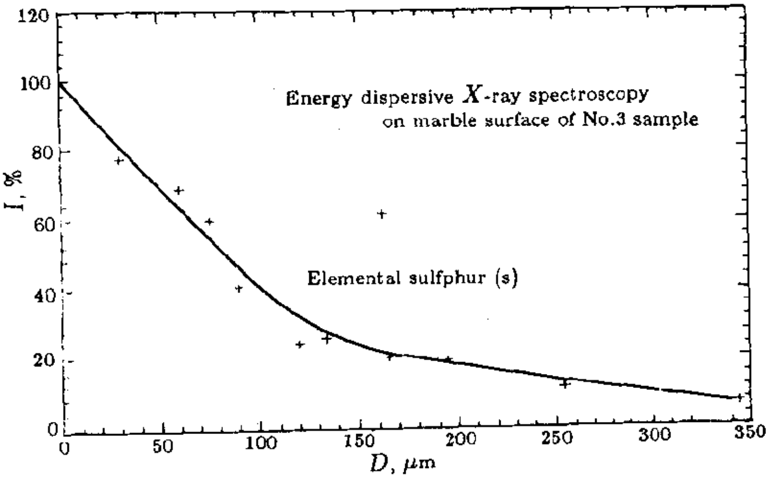

Fig. 10 Relationship between sulfur depth and intensity

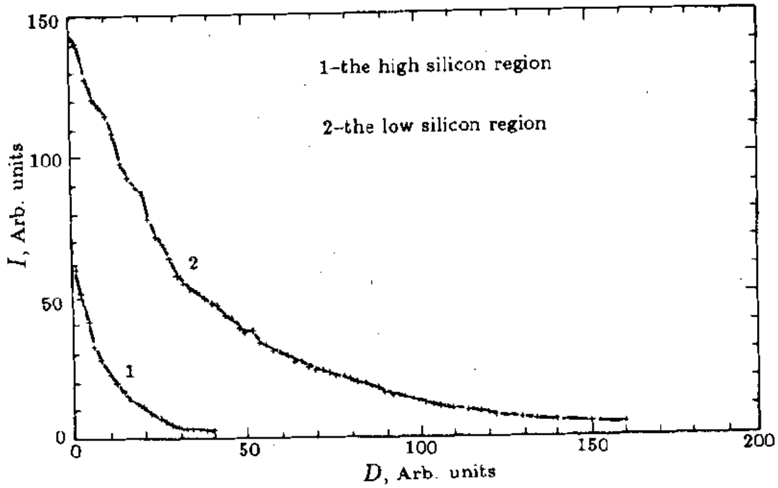

Fig. 11 Relationship between sulfur intensity and depth in different regions of No.1 sample

has higher silicon. The experimental results are in good agreement with the results obtained by EDXA and SEM.

CONCLUSIONS

Based on the above experimental results we can draw the following conclusions:

1. All kinds of marble can be attracted by sulfur dioxide in the atmosphere.

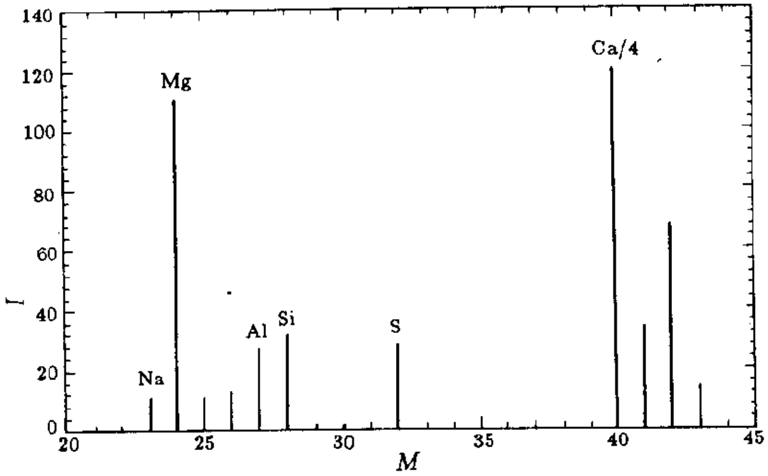

Fig. 12 Mass spectra of the low silicon region of No. 1 sample

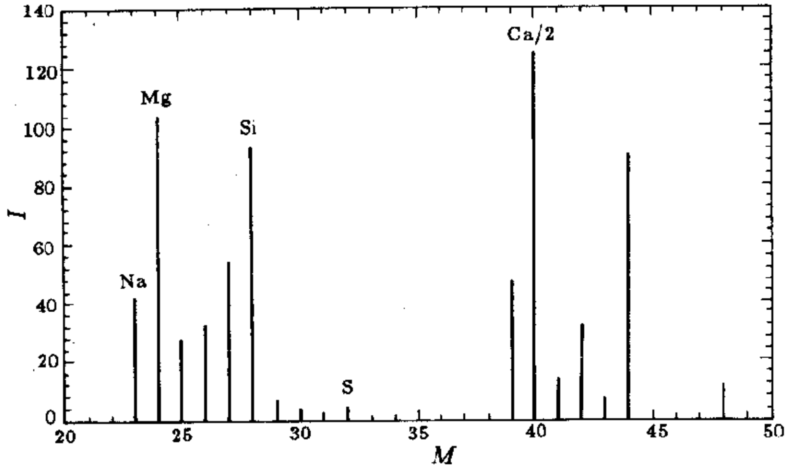

Fig. 13 Mass spectra of the high silicon region of No. 1 sample

2. The compositions of marble affect directly on corrosion effects of SO_2. In general, high silicon marble are resistant to corrosion. According to our experiments we find that silicon distributions are not uniform in marble, usually calcium content is higher in the microarea where silicon content is lower, and vice versa. Low silicon microareas of marble can easily be corroded by SO_2 and gypsum forms on the marble. The corrosion of SO_2 continue along low silicon high calcium paths into the inner of the marble.

3. We would like to suggest to use materials containning silicon, such as silicon resin, silicane and the like to spray onto the marble surfaces to prevent them from corroding.

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