Pollution-derived heavy-metal enrichment on building stones

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Introduction

Decay of calcareous building stones has been extensively related to precipitation and growth of gypsum due to SO_2 urban pollution, aided and/or catalyzed by metals (Ross *et al.*, 1989). The main sources of these pollutants are oil-derived fuel combustion (Cheng *et al.*, 1987), mainly power plants and car engines. The latter, generate large amounts of both gaseous (SO_2, CO_2, and NO_x) and solid (soot, flying ash, and metallic particles) pollutants. Many works have pointed out that gypsum crusts develop on building stones, and have referred to all the above-mentioned solid particulates, but no clear relationship between these particulates and gypsum growth has ever been established (i.e. Camuffo *et al.*, 1983). This work, however, provides new data on gypsum crust anomalous enrichment of heavy metals (especially chalcophilic) and, supported by experimental data, points out the tremendous catalytic role of these metals in SO_2 fixation as sulphates on calcareous building stones.

Materials and methods

Samples collected from different historical buildings located in Granada and Jaén (southern Spain) with differential decay due to gypsum growth have been analysed via polarising microscopy, XRD and SEM with coupled EDX. Chemical analyses have been carried out by means of atomic absorption (AA), XRF, and ICP emission spectrometry.

Samples from the ancient quarries (taken as blanks), as well as particulate emissions from different pollution sources in these towns were also analysed.

Catalytic activity of metals in SO_2 fixation on building stones as sulphates was determined in an SO_2 chamber with 100 ppm SO_2 concentration, 32°C temperature, and 95% relative humidity. Different calcareous slabs were placed in the chamber. One set was used as a blank and a second was covered with solid oil-derived combustion exhaustion byproducts from both diesel and gasoline fuel (Rodriguez-Navarro and Sebastian, in press). 24 and 48 hours after the start of the experiment, slab surfaces were studied with XRD and SEM-EDX.

Results and discussion

Tables 1 and 2 show the metallic composition of both quarry and building (decayed) materials from Granada Cathedral and Jaen Cathedral respectively.

These data show a strong increase in heavy-metal content in the decayed materials, where gypsum was systematically observed. The main changes were detected in chalcophilic elements such as Cu, Pb, and Zn, as well as Fe.

These very same elements were detected in high proportions in the solid residue from oil-derived combustion generated by gasoline and diesel engines (Table 3).

There is a clear relationship between the decay

TABLE 1. Metallic-element concentration (in ppm) of calcarenite samples from Granada Cathedral (Gr) and the ancient quarry (Quar). Concentrations in ppm

Sample	V	Cr	Co	Ni	Cu	Zn	Pb	Fe
Quar-1	13	13	2	10	12.7	15.5	4	629
Quar-2	14	15	2	9	4.2	15.8	4	489
Gr-6	22	15	2	32	7.4	24.4	4	1713
Gr-15	14	13	2	10	9.6	18.6	26	1258
Gr-20	18	17	2	10	7.3	30.8	18	1538
Gr-21	17	18	2	11	10.5	40.8	29	1608
Gr-35	22	22	4	10	27.7	70.0	130	2308
Gr-40	14	15	3	6	12.2	54.8	37	1503

TABLE 2. Metallic-element composition (in ppm) of calcareous materials from Jaen Cathedral

Stone Type	Sample	V	Cr	Co	Ni	Cu	Zn	Pb	Fe
	Quar-a	19	15	1	5	5.8	13.0	2	1398
Limestones	Ja-37	20	13	2	5	11.7	27.6	23	1049
	Ja-38	11	8	1	4	5.1	10.3	11	804
	Ja-50	16	8	2	4	10.6	28.8	21	804
	Quar-b	10	7	1	3	3.5	3.6	2	629
Dolostones	Ja-9	12	6	1	4	17.1	18.2	17	979
	Ja-44	14	12	2	5	11.9	30.3	59	1503
	Ja-63	18	9	1	5	13.1	112.0	58	489
	Quar-c	14	9	2	7	7.0	9.4	4	1119
	Ja-24	11	9	3	6	10.0	23.7	235	1363
Calcarenites	Ja-26	12	10	3	6	11.9	25.7	35	1818
	Ja-62	32	25	4	10	14.2	24.0	27	4196

TABLE 3. Metallic composition of gasoline and diesel exhaust solid residue (in ppm)

Sample	V	Cr	Co	Ni	Cu	Zn	Pb	Fe
Gasoline exhaust	94	527	2	285	62.3	717.5	85450	24360
Diesel exhaust	58	419	6	128	1581.0	3128.0	301	68530

level of a particular building element (expressed as the concentration of gypsum in it) and the amounts of these metals. A positive linear correlation can be observed (Fig. 1). This fact is in agreement with laboratory decay simulation in an SO_2 chamber. After 24 hours of attack, stones covered with powder from both diesel and gasoline exhausts, develop large amounts of gypsum crystals; blanks show no gypsum formation. After 48 hours, large quantities of blade-shape gypsum-crystal intergrowths were observed on slabs covered with solid pollutants (more developed on those covered with diesel exhaust than on those covered with gasoline exhaust); none appeared on the blanks.

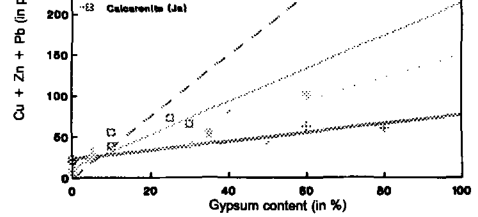

FIG. 1. Chalcophile metal content *vs.* gypsum concentration in samples from Granada Cathedral (Gr) and Jaen Cathedral (Ja).

Thus, pollutants with high proportions of metallic particles composed of Fe, Cu and Zn, operate as efficient catalyzers on SO_2 oxidation to SO_3, which in contact with humidity is hydrolized to form SO_4H_2. This, in its turn, dissolves $CaCO_3$ and/or $MgCa(CO_3)_2$ to form gypsum. This composition mostly corresponds to the metallic pollutants emitted by diesel combustion. In contrast, gasoline exhaust is rich in Pb and thus has less catalytic activity.

In the buildings, decayed stones contain all these metallic pollutants, which creates a very reactive surface producing large amounts of gypsum, which is to say, significant decay.

References

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