Construction and Building Materials 25 (2011) 813–822

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Deposition of particles on gypsum-rich coatings of historic buildings in urban and rural environments

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ARTICLE INFO

Article history:
Received 26 June 2009
Received in revised form 14 July 2010
Accepted 15 July 2010
Available online 11 August 2010

Keywords:
Atmospheric particles
Air pollution
Gypsum coatings
Gypsum crusts
Dust coatings
Historic mortars
Decay

ABSTRACT

Deposition of gaseous and particulate atmospheric pollutants causes decay of historic mortars to give gypsum-rich coatings by sulphation of lime mortars and blackening of gypsum mortar, resulting in gypsum coatings. Particulate pollution emitted by industrial sources and vehicular traffic is responsible for the deterioration. XRF and SEM analyses of these coatings and their comparison with both the composition of dust coatings formed by the deposition of gaseous and particulate matter in an urban and a rural locality allows assessing which pollution sources are the most damaging for these materials, knowing the elemental composition of these emissions.

1. Introduction

Atmospheric chemical constituents can precipitate by wet and dry deposition. The deposition involves a close interaction between the atmosphere and the surface. Measuring deposition by analyzing the deposits formed on rock surfaces allows knowing the real effect of the pollutants and the deposition rate on that rocks. Drawing on the surface of building façades, it has been reported that dry deposition plays a major role in the deposition of acid substances on buildings. The characteristics of individual underlying surfaces often allows determining the mass-transfer rates [1,2]. Depending on the characteristics of the surface, interaction of pollutants from the air may vary causing varied dry deposition rates [3].

The industrial atmospheric emissions have been increased in the last decades causing important changes in the conditions of conservation of stone buildings. Fossil fuel combustion by industrial facilities and vehicular engines is a major source of anthropogenic particulate emissions into the atmosphere. However, few research works on dry deposition of particles have been performed in comparison to gaseous compounds [4]. Studies on building materials have been limited to deposition of SO_2, NO_2, HNO_3 and organic pollutants [5–9]. Of all the constituents produced by this combustion, SO_2 is considered as the most important for stone decay processes. They react with calcite ($CaCO_3$) from marble, calcareous rocks and lime mortars to form calcium sulphate ($CaSO_4{\cdot}2H_2O$). Also, NO_x gases increase the acidity and thus the oxidation capability of the SO_2 to react with $CaCO_3$ and to give calcium sulphate [10]. Because the solubility of calcium sulphate is higher than that of $CaCO_3$, they are dissolved in rainwater and can penetrate into inner pores of the building materials. After evaporation, these salts give rise to stress in the building materials causing deterioration [11].

1.1. Atmospheric particles

The term 'atmospheric particles' is used to refer fine solid or liquid particles suspended in air. They may be originated by either natural or anthropogenic sources. Natural sources greatly exceed anthropogenic emissions, but anthropogenic particle emissions are frequently concentrated in urban areas. These are emitted directly into the atmosphere and are frequently mechanically transported. Their diameter ranges between 0.002 and 0.1 mm. Standards for particle concentrations have been focused on different classes of particle, based on particle diameter, but PM_{10} particles (particles of <10 μm in diameter) and $PM_{2.5}$ (particles of diameters <2.5 μm) are considered the most active portion in human health impacts [12]. PM_{10} contribute to coarse mass in the form of soil dust (mostly silicate minerals, aluminium, iron and

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[1] Financial support from FEDER.

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doi:10.1016/j.conbuildmat.2010.07.001

dust), sea spray (sodium and chloride), and plant particles. Other sources of coarse aerosols include products of reaction of gaseous nitric acid (HNO_3) on soils [13].

Anthropogenic sources of atmospheric gases and particles are very important in urban areas. NO_x, CO and lead can be generated from gasoline combustion in vehicle engines, although no lead-enriched gasoline exist at present in the EU. Estimated emissions of traffic exhaust are responsible of 10% of the CO_2 emissions globally. The combustion of diesel fuel is not a significant source of SO_2 but a major source of NO_x. These last engines produce carbonaceous particles (carbon soot or fly ash by incomplete combustion) and metals (Al, Si, Zn, Cd, Pb) [14]. Simão et al. [15] refers a study of Colebeck published in 1995 that indicates that, in the UK, on-road diesel combustion contribution to airborne elemental carbon level it is though to be between 80% and 95%. Industrial emissions are a significant source of most of these gases (SO_2, NO_x, CO_2) and particles. Among pollutant industrial facilities, thermal power stations and chemical industries produce most of these gas and particulate emissions from coal and oil combustion. For that reason, the question of which pollution sources are the most important is a key question to protect the health of the habitants and the historical buildings of urban areas from decay.

1.2. Gypsum coatings on granitic rock buildings and air pollution

Rock coatings are accretions on rock surfaces whose constituents have been transported to these from a few microns or thousands of kilometres [16]. The different types of existing coatings on rock surfaces have been classified according to their composition and attributed to different sources. However, their occurrence is not the same either on natural rock surfaces or rocks ashlars of Heritage building façades. In particular, gypsum coatings are very frequent on building stones. They have been found and studied in diverse Heritage buildings, on different rock types and have been identified from rural to urban areas in all climatic conditions.

In urban areas, there are important differences between buildings constructed with siliceous and calcareous rocks. In both cases gypsum coatings are very common. Because of the elevated air concentration of sulphates, Ca from calcium carbonate reacts with atmospheric sulphate to give crusts that deteriorate the rock surface. The catalytic effect of particles from motor vehicles exhaust emissions in the formation of gypsum has been observed in laboratory experiments with carbonate rocks [17] and silicate rocks [16], with particulate from diesel engine exhausts having a much more marked effect than particulate from gasoline ones. Therefore, gypsum has been linked to air pollution but there is the problem of the source of Ca in siliceous rocks. Some authors have specifically postulated that gypsum coatings are formed by combination of sulphates from air pollution and Ca from feldspars [18]. Sulphate origin has been attributed to the oxidation of rock pyrites [19]. For others authors, they are produced by nucleation and sulphation from clay and soil airborne particles [1] or by microorganisms [20]. However, these processes cannot explain the formation of thick and compact coatings, due to both the low proportion of Ca of granitic rocks and the low crystallization of gypsum by nucleation, even in experiments under polluted atmospheres with high sulphate concentrations [21].

Other authors have proposed alternative sources of calcium sulphate, as [22,23] the sulphation of calcium from mortars (very prone to sulphation because they are a huge source of easily soluble calcium and salts) or [24,25] the use of gypsum plaster on the granite ashlars of the buildings. A study of long-time exposure of limestones on different urban environments have shown that soiling rate, evaluated by chromatic changes, after three years was high in a busy road with high diesel traffic, low in a urban background site (around 200 m from roads) and intermediate in samples exposed in roads with low frequency of diesel powered traffic [26]. In a study of limestone façades, Schiavon et al. [27] concluded for a link between air pollutants related to vehicular traffic (such as particles from diesel motors) and sulphate crust composition.

Hélène Cachier, coordinator of the European project CARAMEL (Carbon content and origin of damage layers in European monuments) has been quoted as saying "unlike in past eras, transport is now the overwhelming contributor of atmospheric gaseous and particulate pollutants in most European urban zones." (http://ec.europa.eu/research/environment/newsanddoc/article_2387_en.htm). Grossi and Brimblecombe [28], referring data from the same CARAMEL project, indicate asymptotic lightness values (lower values correspond to darker surfaces) that in areas with high traffic intensity and in road tunnels are around half of those found in urban background sites (the authors refer elemental carbon values that in areas with high traffic intensity and in road tunnels are above three times higher than in urban background sites).

The deterioration and blackening of gypsum plasters by deposition of atmospheric particles could explain its appearance as black gypsum-rich coatings, similar to the gypsum crusts developed on limestones. A recent study has allowed identifying six different types of gypsum-rich coatings (types 1–6) on granite rock buildings [29], most of them related with previous gypsum or calcium carbonate mortars. These mortars are very prone to deposition and accumulation of atmospheric particles and, therefore, very useful to determine the mass-transfer rates of particles and gaseous substances. Thus, types referred as 1, 4 and 5 coatings have been related to previous gypsum plasters and have been formed by deterioration due to the interaction of atmospheric factors surrounding the façades of the buildings. As that study reported, type 1 coatings are remnant gypsum plasters. Since these, type 4 coatings are formed by the deposition of particles on the surface and type 5 are developed by re-precipitation of calcium sulphate dissolved on the surface from gypsum plasters or Ca-rich mortars of upper areas of the façades. On the contrary, the type 6 coatings are formed by precipitated calcium sulphate, washed from upper areas of the façades on the ashlars surface. Moreover, the type 2 coatings correspond to original lime mortar coatings that have undergone in situ sulphation processes (not necessarily connected to runoff). This fact allows developing a calcium sulphate or gypsum surface layer of variable thickness. Also, the type 3 coatings come from mixed gypsum and calcium carbonate mortars. The main characteristics of these coatings are exposed in Table 1.

After the study of composition and origin of these gypsum coatings, some questions have remained unsolved. The first one is the effect of the air pollution from both urban (from traffic exhaust) and industrial sources in the formation of gypsum and the deposition of atmospheric particles. The second one is which particles are original components of the plasters and mortars of the buildings, and which are originated from air pollution sources. Although some particles are undoubtedly originated by deposition of atmospheric particles, some others could be related with both origins. This discussion is very important to know which is the original composition of the historic mortars and which are the most important sources of air pollution.

1.3. Aim of this work

The aim of this paper is to present the diverse composition of typical particle content found in the gypsum coatings, formed, modified or deteriorated, at least in part, by deposition of atmospheric particles and gases in urban and rural environments. The comparison of these particles with the particle content of a dust coating found on one of the studied building façades, originated due to the strong air pollution could contribute to identify components that