



Physical Adsorption of H₂S Related to the Conservation of Works of Art: The Role of the Pore Structure at Low Relative Pressure

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Abstract. The adsorption isotherms of H₂S in selected adsorbents were determined at 298 K, at relative pressures up to about 0.005, aiming the use of these materials in the removal of that pollutant from the museums atmosphere. The Dubinin-Astakhov equation adjusts very well the experimental results, although one cannot interpret the pre-exponential factor w_0 as the limiting adsorbed amount. The parameter E , related with the adsorption energy, and the parameter n , that can be associated with the surface heterogeneity of the adsorbents, are correlated and the first is also correlated with the adsorbed amounts. It was not found any expectable relationship between the adsorbed amounts and textural parameters of the adsorbents such as the specific surface area or the microporous volume. This points out that the adsorption of H₂S is highly specific. In general, 13X and Y sodium zeolites seem to be the most effective adsorbents, but at lowest tested pressures, near the concentrations found at museums, a pillared clay prepared from a Wyoming montmorillonite seems to be more efficient.

Keywords: adsorption, zeolite, activated carbon, pillared clay, hydrogen sulfide, museum, conservation

Introduction

The hydrogen sulfide present in the atmosphere is one of the factors that leads to the alteration of works of art conserved in museums or shown in exhibitions in other places. One well-known problem is the silver tarnishing that gives a dark gray color to silver works due to the formation of the black silver sulfide on its surface (Costa, 2001). Another problem, less frequent but with major consequences, is the blackening of paintings and drawings as a result of a reaction between H₂S and some pigments of copper or lead and the consequent formation of the black coppers and lead sulfides, respectively (Smith and Clark, 2002). Copper resinate (a transparent green pigment composed mainly of the copper salts of resin acids) and white lead (a basic lead carbonate) are the pigments more susceptible to this

changes but other examples are also known. Although copper resinate is not one of the pigments most used in paintings, white lead is, undoubtedly, the most important pigment in easel painting until the beginning of the 20th century. At least until the middle of 19th century, it is rare to find an easel painting without it (Gettens and Stout, 1966). Silver and pigments are examples of materials that may suffer specific attack by the H₂S in the atmosphere; but several others materials, namely those that are more sensitive to the pH, like paper, can suffer damages due to the acidic properties of this atmospheric pollutant.

Contrary to what happens to other museum pollutants, such as organic volatile compounds, the H₂S found in a museum gallery generally has its principal origin outside the building. Some materials may be a significant source inside, but just in special circumstances: when these materials are in closed environments, that is, in showcases or in rooms with

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poor gaseous exchange to outside. Wool is one of these materials, as H_2S may be released from sulphur amino acids, particularly cystine, that makes wool proteins (Brimblecombe et al., 1992). This potential source of problems is already identified in the literature related to museology and preventive conservation and, accordingly, it can be expected that wool materials are not to be used in the museums equipment or in the museums buildings, for instance in floor carpets. Mineral specimens, namely sulfide minerals (Waller et al., 2000), may represent another possible source of H_2S inside showcases. Of course, this is a specific problem of museums with mineralogical collections.

Therefore, the H_2S concentration in the museum atmosphere is usually related with its concentration in the museum surrounding, the gaseous exchange between inside and outside, and the air purification systems that may exist. The first of these factors is not controlled by the museum, as soon as the building is already established in one location. The second factor is linked to the architecture and the air circulation system and, at the best, only occasionally can be improved. The last variable, that is, the air purification, may be associated to an air-conditioned system, but can also be independent of that. In this case, in principle, it is the variable more easily managed, a situation that relies on the possibilities provided by adsorbent materials.

In fact, solids with adsorbent properties are used in museums, or they can be used, for the removal of pollutants from the atmosphere and, consequently, to protect the collections. With that purpose, adsorbents may be employed in one of two ways: in active mode, the air is forced through the adsorbent; in passive mode, the air is diffused naturally across the adsorbent. In the former situation, with the adsorbent embedded in an air-conditioned filter, for example, it is possible to control the atmospheric composition in a space like a room. The passive mode is more adequate for smaller spaces such as the interior of a display case. It has the advantage that results from the fact that it does not involve any equipment, since it is enough to place the solid inside the space that one wants to purify or near the works that can be attacked by the pollutants. This advantage is really important as many museums or, at least, many rooms in museums, do not have air-conditioned systems (Bradley, 1996). In the specific case of the H_2S , the passive solution is much more important since this gas, accordingly to some studies, does not seem to be

controlled by the filtration system associated to the air-conditioned at all (Cassar et al., 1999). It must be pointed out, however, that other studies claim that some adsorbents, like activated carbon and zeolite 13X, have an excellent efficiency in the H_2S removal from atmosphere when used in active mode (Pasmara and Grojean, 1991). Probably, the opposite conclusions derive from the different pollutant concentrations involved on those studies, lower in the former, higher in the later.

The H_2S concentration in museum atmospheres varies significantly. On one side, it depends on the museum. On the other hand, for a certain museum, the concentration varies along the year. The measurements done in some museums seem to show lower concentration values in Summer and Fall than in Winter and Spring. Nevertheless, the values are frequently below the 0.1–0.3 ppb range, although they can go up to 1 ppb (Brimblecombe et al., 1999; Cassar et al., 1999; Ankersmit et al., 2000).

The studies done in museum contexts have been made with a H_2S source and a sample of the solid adsorbent on test in a closed space and through direct measurement of the pollutant concentration in this atmosphere (Pasmara and Grojean, 1991) or, indirectly, through the measurement of the tarnishing effect on a silver sensor also present (Bradley, 1985).

The problem of H_2S and its removal from atmosphere is not exclusive of museums. The same situation, although with other consequences, arises in relation with the air purification from odorous and toxic compounds in water treatment facilities (Bandosz, 2002). In this case, however, the levels of H_2S are much higher.

In spite of these diversified interests in the adsorption of H_2S by adsorbents materials and in spite of the value of several other methods and techniques used in studies with relation to that process, to our knowledge, a lack of some fundamental data exists about those systems, namely adsorption isotherms and parameters that can be obtained from these through the application of theoretical models. The principal objective of the work presented here is, precisely, to provide some fundamental data about the adsorption of H_2S at low pressures by selected adsorbent materials, amongst them activated carbons and zeolites, which can be useful in the museum conservation contexts. Besides, the analysis of the isotherms was made in order to investigate the nature of the adsorptive process and to proceed to a useful generalization of the results. This study is related to a