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THERMAL ANALYSIS OF HERITAGE STONES

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Many of Sydney's heritage buildings and monuments were built as a result of the first European settlement in the 1800s. These buildings not only display the richness of the Australian culture, but also capture the architectural and historical values of its past. Although many of these buildings still appear to be strong and sound, many signs of deterioration have been detected in recent years. Conservators from various disciplines such as science, architecture and engineering are working closely together to develop suitable solutions to stop or at least slow down the degradation process of these precious buildings. This study demonstrates the usefulness of thermal analysis in determining the weathering mechanisms of marble and sandstone taken from two of Sydney's landmarks, the Captain Arthur Phillips Monument at Sydney's Botanic Gardens and Sydney's St. Mary's Cathedral. This paper reports the findings of the weathering behaviours of both marble and sandstone samples determined using thermal analysis techniques.

Keywords: *DSC, kaolinite, marble, sandstone, TG, weathering*

Introduction

The restoration and preservation of heritage buildings in Sydney, Australia, has received attention from various disciplines in the country. The detection of deterioration of these buildings due to the fast development of an urban environment in the city and its surroundings has pushed conservation issues to the forefront. Although the replacement of decayed stones in some of the current restoration projects may seem appropriate from the viewpoint of conservation, total replacement of stones from historic buildings remain debatable. A proper understanding of the mechanisms of decay is needed in order to develop suitable solutions to preserve the original stones. Our current research aims to first determine the degradation processes of the original building materials. Secondly, suitable materials, such as stone consolidants will be developed in order to prevent these buildings from further degradation.

The Captain Arthur Phillip Monument in Sydney's Botanic Gardens is a significant historical landmark (Fig. 1). This Neo-classical style marble monument was built in the late 19th century by a local sculptor, Archille Simonetti, and his fellow artists to commemorate the discovery and settlement of Eastern Australia by the Captain-General and first Governor of New South Wales, Arthur Phillip, of the First Fleet. The casting of the bronze statues and the carving of the marble were both carried out in Italy, where four varieties of Carrara marbles were used: Bianco Carrara Venato, Bianco Brouille, Bardiglio Carrara Scuro and Statuario Altissimo [1]. Recent inspections of the monument suggest that deterioration is rapidly proceeding. Many forms of degradation including the dissolution of bronze statue, exfoliation and the scaling of the marble surfaces and the formation of black crusts, have been observed.

Sydney's St. Mary's Cathedral, a Gothic style sandstone cathedral, is situated in Sydney's busy city centre (Fig. 2). The cathedral was constructed in the mid-1800s using entirely Sydney's unique yellow block sandstones from the Pyrmont quarries [2]. Sydney's yellow block sandstones generally contain 60–68% quartz and 16–25% clay matrix with up to 7% siderite ($FeCO_3$) and a small amount of other minerals such as iron oxide and gypsum [3]. The exposure of these newly quarried sandstones to the atmosphere results in the oxidation of iron rich minerals in the sandstones, giving them their

Fig. 1 Captain Arthur Phillip Monument

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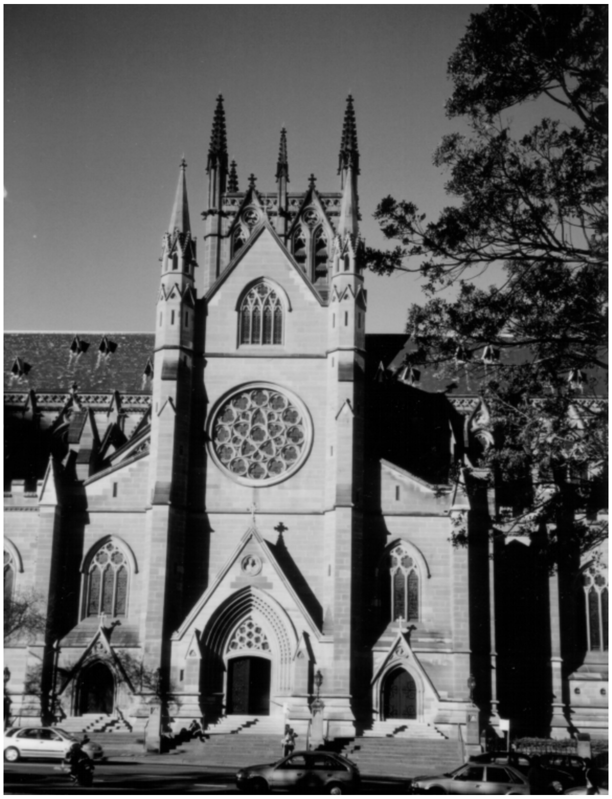

Fig. 2 Sydney's St. Mary Cathedral

rich, golden colour, and hence, their name [4]. Many of the decayed original stones in the cathedral have been replaced by new stones during its maintenance. Some of the decayed stones were used for scientific analysis in our laboratory.

Experimental

Materials and methods

Samples

Both weathered and unweathered marble samples were provided by the New South Wales Department of Commerce-Offices of Government Business and Government Procurement (OGB-OGP). The unweathered sample originated from Carrara, Italy and the weathered samples were chiselled from various parts of the fountain basin of the Captain Arthur Phillip Monument. Each sample was ground into a fine powder using an agate mortar and pestle. Samples for analyses were obtained from the following locations of the monument:

- below the original water level
- from the waxed area at the inner bowl surface (a small trial area treated with waxy consolidant by OGB-OGP)
- near the joint on the outer surface

The decayed sandstone blocks mostly contained an external weathered surface of approximately 1.5 cm deep and unweathered cores. The weathered outer surfaces were separated from the unweathered part using a diamond saw. Unweathered samples were obtained from the core of the stone 10 cm from the weathered surface. Each sample was crushed by hand and the clay base cementing materials were separated from the large amount of sand grains by using an ultrasonic probe. Clay particles were collected by using a gravity settling method [5].

Experimental parameters

A Setaram Setsys 16/18 TG-DSC 15 Thermal Gravimetric Analysis instrument was used for the thermal analysis. The mass spectrometer for evolved gas analysis was a Balzers Thermo Star 300 with a capillary interface and the detector used was a Chaneltrom electron multiplier. Approximately 10 mg of either marble or clay sample was placed in a platinum crucible for analysis. The reference pan was left empty and triplicate analyses were performed on each clay sample; however, due to the limited amount of marble samples provided, only duplicate results were obtained for those samples.

Results

Marble samples

The results of the thermal analysis indicate significant differences between weathered and unweathered marble samples (Figs 3 and 4). The samples from the joint of the outer surface show similar patterns to those of the unweathered marble sample, where the peak of thermal decomposition of $CaCO_3$, the main component of marble, occurs at ~825°C. However, the samples from the waxed area and below the original water level indicate

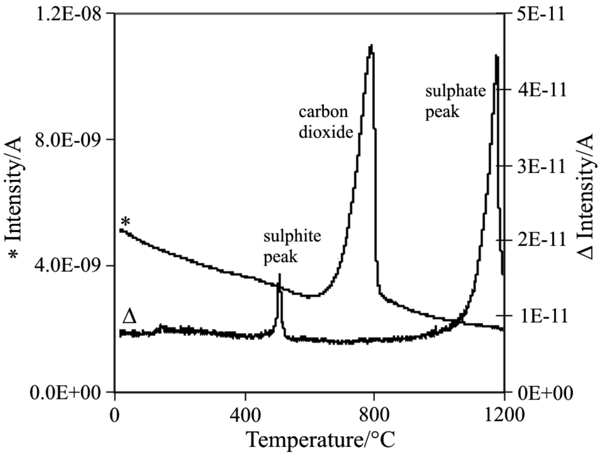

Fig. 3 Gas evolution curve of the weathered marble from the waxed area

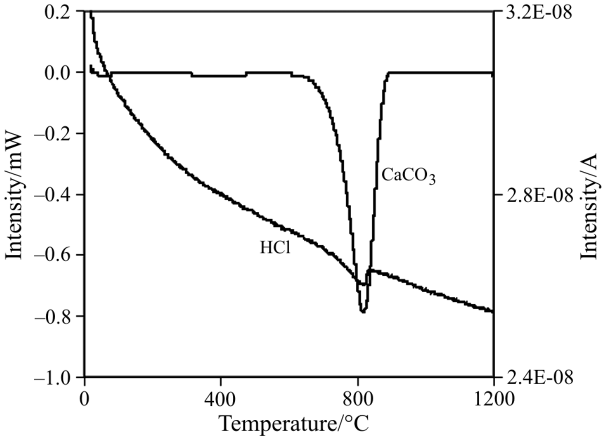

Fig. 4 Gas evolution curve of HCl and DTG curve of $CaCO_3$ from the waxed area

that both samples contain other compounds in addition to $CaCO_3$. The gas evolution curves of the waxed area show the presence of sulphite and sulphate peaks at 508 and 1179°C, respectively, as well as a carbonate peak (Fig. 3). A peak denoting the evolution of HCl was observed at the same temperature as the decomposition of the carbonate compounds (Fig. 4). In addition, the curve of the sample from below the original water level does not exhibit the sulphite peak; however, traces of chloride ions and carbonate compounds are observed.

The presence of sulphite and sulphate peaks detected by thermogravimetric analysis of the waxed area samples of marble confirms findings by other researchers [6–8]. Two degradation mechanisms for the marble fountains can be proposed. Firstly, the conversion of atmospheric SO_2 to H_2SO_4 [9] as follow:

$$S_{(s)}+O_{2(g)}\leftrightarrows SO_{2(g)}$$

$$2SO_{2(g)}+O_{2(g)}\leftrightarrows 2SO_{3(g)}$$

$$SO_{3(g)}+H_2O_{(l)}\leftrightarrows H_2SO_{4(l)}$$

$$CaCO_{3(s)}+H_2SO_{4(l)}\leftrightarrows CaSO_{4(s)}+H_2O_{(l)}+CO_{2(g)}\uparrow$$

The Captain Arthur Phillip monument is situated in the middle of a heavy traffic area and relatively close to the industrial complexes of the city. The burning of sulphur-containing materials such as coal, petrol and refined oil releases considerable amounts of sulphur compounds into the atmosphere. Together with the water in the fountain and the atmospheric oxygen, the formation of H_2SO_4 is detrimental to the fountain since marble is a relatively alkaline material and is prone to be attacked by H_2SO_4 to form the more porous gypsum, $CaSO_4{\cdot}2H_2O$. Evidence of honeycomb-like gypsum was observed in other parts of the fountain, where samples were not able to be removed. Dissolution of the bronze statue, evident by the blue green appearance of many parts of the white marble, further confirms the presence of acid in the environment.

The second mechanism involves the direct conversion of marble to gypsum which occurs in the presence of water, oxygen and catalysts (soot particles from the pollution) as follows [10]:

$$CaCO_{3(s)}+SO_{2(g)}\xrightarrow{H_2O}CaSO_{3(s)}{\cdot}2H_2O+CO_{2(g)}\uparrow$$

$$CaSO_{3(s)}{\cdot}2H_2O+1/2O_{2(g)}\xrightarrow{\text{catalysts}}CaSO_4{\cdot}2H_2O_{(s)}$$

The detection of HCl in the sample of the waxed area suggests that HCl may have come from the chlorinated water in the fountain. By comparison, samples from below the original water level only show the presence of carbonate compounds and small amounts of sulphate and chloride ions. These findings indicate that the degradation products such as $CaSO_4$ and HCl from the water were preserved by the waxy material used as a trial stone consolidant. On the other hand, degradation products of the samples from below the original water level have been washed into the water in the fountain.

The formation of gypsum in this marble monument causes adverse effects as the fountain is situated in the vicinity to Sydney's coast, where soluble salts are abundant and can be brought to the monument via rain water, sea spray and ground water [11]. These soluble salts can crystallise on the stone surface to form unsightly efflorescence during dry seasons [9], or the salt solution may migrate into stone structures via capillary action through the more porous gypsum or microcracks. The recrystallisation of salt crystals within the stone pores exerts high pressure against the pore walls. As a result, more microcracks and blisters are formed, which makes the stone even more vulnerable to degradation.

Sandstone samples

Figures 5 and 6 are DSC and TG curves of both weathered and unweathered clay-based cementing materials of sandstones. Both traces are similar to typical patterns of kaolinite clay [12], where the three regions of dehydration, dehydroxylation and the formation of thermal products, are evident. At ~100°C, denoting the dehydration of kaolinite clay, the loss of adsorbed water is observed in both weathered and unweathered samples. The typical endothermic peak of dehydroxylation of structural water in the kaolinite clay binder occurs at ~580°C and the relative intensity of this peak decreases upon weathering. Unlike pure kaolinite clay, an additional peak also denoting dehydroxylation activity is detected at ~680°C in both weathered and unweathered samples. The relative intensity of this peak is observed to increase upon weathering. At ~1000°C, the formation of mullite, a high temperature phase transformation of kaolinite clay, is observed. In addition, a peak attributed to the dehydration of iron impurities, $FeO(OH)_x$, is detected in all weathered clay samples at ~250–300°C.

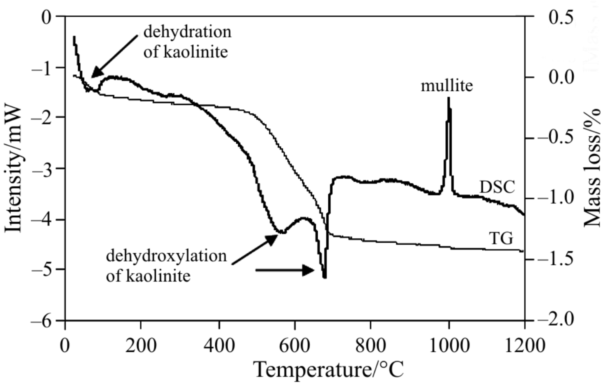

Fig. 5 DSC and TG curves of unweathered clay samples

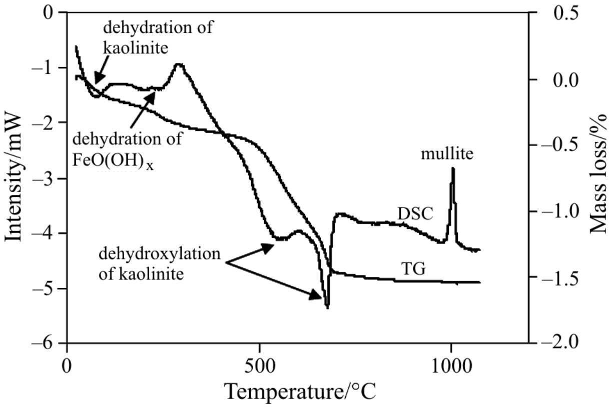

Fig. 6 DSC and TG curves of weathered clay samples

Discussion

The thermal analysis results of the weathered and unweathered cementing clay of the sandstones from Sydney's St. Mary's Cathedral confirm that the major component of the binder of the 'yellow block' sandstones is kaolinite clay. The three typical regions of dehydration, dehydroxylation and mullite formation of kaolinite are evident on the patterns of the binding clay samples. However, the detection of an extra peak at ~680°C in both weathered and unweathered samples, also denoting the dehydroxylation of kaolinite, indicates a structural change in the aluminosilicate crystal structure of the original kaolinite. This change contributes to the thermal stability of the newly formed structure, where it can withstand temperature up to 700°C. This finding was supported by hot stage X-ray diffraction analysis. The increase in thermal stability of binding materials has been attributed to the cation substitution of Al^{3+} and/or Si^{4+} in the aluminosilicate structure mainly by Fe^{3+} [13]. Apart from the Fe^{3+} found in the clay structure, Fe^{3+} also exists as iron impurities (or non-structural iron), shown in greater abundance in the thermal analysis of the weathered sample (~250–300°C). The thermally more stable clay, however, significantly increases the brittleness of the sandstone due to the cation substitution, where the crystal structure of the binding clay was destabilised upon substitution. In addition, the decrease in intensity of the original kaolinite peak at 580°C and the increase in intensity of the peak at 680°C in the weathered sample suggest a greater substitution of Fe^{3+} in the clay structures upon weathering.

Conclusions

Thermal analysis, together with other analytical techniques, has been used to characterise the weathered and unweathered stone samples from both the Captain Arthur Phillip Monument and Sydney's St Mary's Cathedral. Thermal analysis is a particularly useful tool in the conservation field where sample quantities are generally scarce. Compared with other analytical techniques such as XRD where larger amounts of samples are usually needed. Thermal methods are capable of producing significant information on both crystalline and amorphous phases. In this study, the thermal data have provided significant insight into the degradation processes of stones in our heritage buildings. The causes of their deterioration are mainly due to the urban environment, where pollution and harsh climate play a large role in the destabilisation of the stone structures. For example, the degradation of marble is largely due to the acidic environment created by the emission of SO_2 and CO_2 from motor vehicles and industry. The dissolution of $CaCO_3$ in marble by H_2SO_4 formed from SO_2 to produce $CaSO_4$ is a detrimental degradation phenomenon where the damage is totally irreversible. In addition, the formation $CaSO_4$ encourages further attacks from environmental pollutants due to the increase in porosity of the stone surfaces. Sandstone degradation, on the other hand, resulted from the destruction of the crystal structure of the clay base binding material. Although the effects of the cation substitutions into the structure of clay may seem to be negligible, the destabilisation of the structure eventually destroys the binding ability of this cementing material. As a result, exfoliation and disintegration of the sandstone in our heritage buildings are sometimes observed. The authors are continuing research not only to further understand the degradation mechanisms of the building stones, but also to develop suitable consolidants to inhibit or slow down the rapid degradation process of these precious buildings.

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