PHYSICAL AND CHEMICAL CHARACTERISTICS OF MASONRY STONES DURING BUILDING CLEANING

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ABSTRACT
This research focused on analysing and assessing the changes of the physical and chemical characteristics of the stone surface during the cleaning process by conducting various tests. Seven masonry stones were studied, including red sandstone, yellow sandstone, limestone, marble, white clay brick, yellow clay brick and granite. The physical testing included the evaluation of the cleaning degree, the Vickers hardness test, and measurements of water absorption. Using a digital imaging analysis, the greyscale and cleanness were introduced and determined to quantitatively assess the effectiveness of stone cleaning and proved to be useful and accurate. The cleanness analysis, hardness and water absorption tests showed that a stone with a higher cleaning degree always corresponded to a brighter and harder stone surface. The chemical investigations included the micrographs of the stone façade and analysis of the chemical elements and compounds on four of the stones before and after the cleaning using the Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) techniques. In general, the physical and chemical properties were found to be largely affected by the cleaning degrees on the stone. The chemical test results showed that the chemical elements and compounds on the stone façade significantly varied after long exposures to the atmosphere, mainly due to the polluting gases and biological soiling.

INTRODUCTION

Historic buildings and monuments are precious finite asset and powerful reminders for future generations of the work and way of life of earlier cultures and civilisations. The stone cleaning and restoration of old and historic buildings is a crucial strategy in maintaining the aesthetic appearance, integrity and quality of the fine art, construction method and architecture of previous civilisations. Stone cleaning is one of the most noticeable changes a building can be subjected to, which can change its appearance, persona and environmental context (Ashurst, 1994a, 1994b; Historic Scotland, 1991, 1994; Verhoef, 1988). The stone cleaning and restoration of historic buildings has been conducted for decades in the United Kingdom due to the persistent investigations and research on physical and chemical characteristics of masonry stones for the buildings and the development of modern cleaning techniques. Millions of pounds have been spent every year on building cleaning and this is highly appraised by the public because of the significant effect on the appearance of the buildings and urban environment (Young et al, 2003; Khalaf et al, 2008). Before deciding the best method for cleaning a building preliminary investigations have to be conducted first on both physical and chemical characteristics of the surfaces of the masonry stones for the building.

In this study, the physical testing and analysis were conducted to accurately determine the hardness and water absorption and assess the efficiency on the surfaces of the masonry stones cleaned at four different stages, from dirty to clean. Seven masonry stones selected for physical testing included yellow sandstone, red sandstone, limestone, marble, white clay brick, yellow clay brick and granite. Meanwhile, the chemical analysis was also conducted to quantitatively assess the variations in chemical elements on the original dirty and fully cleaned surfaces of the masonry stones using the Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX) techniques. Four out of the seven masonry stones selected for the physical testing were adopted for chemical testing, including yellow clay brick, yellow sandstone, limestone and marble.

PREPARATION OF STONE SAMPLES

All seven types of stones were selected from those that had been used for masonry building and exposed to the open environmental conditions for decades with large amounts of heavy soiling and decay existing on the surfaces. The samples were cut into the required dimensions from the original masonry stones by using a diamond saw (Figure 1). Thereafter, the exposed surfaces of the stones were cleaned into different levels by using the abrasive cleaning method, sandblasting. Here an abrasive cleaning system selected included an air compressor, shot blasting cabinet and nozzle (Figure 2). Recycled fine glass with the particle size varying 125-1000 µm was selected for sandblasting cleaning (Figure 3). Figure 4 shows typical samples of seven selected masonry stones.

Figure 1: Cutting samples from original stones

Figure 2: The abrasive cleaning system

Figure 3: Recycled fine glass

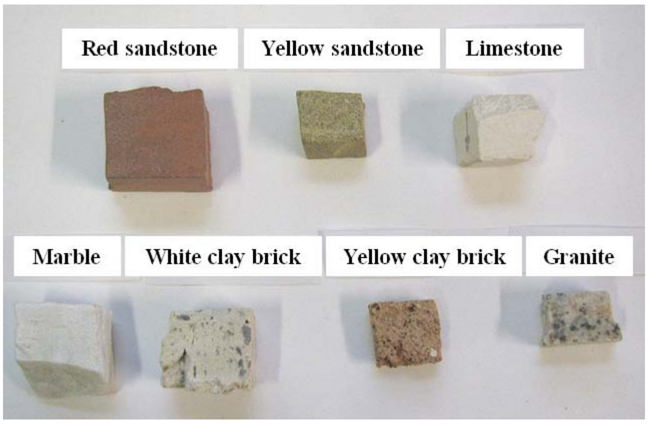
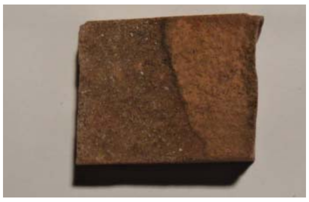


Figure 4: Typical masonry stone samples

During cleaning, the stone surfaces were gradually cleaned to four different levels by controlling the sandblasting time *t* from 0, 3, 6 and 10 sec for most stones, except the yellow clay brick and granite, with the cleaning degrees estimated as 0%, 30%, 60% and 100% (see Table 1). Granite had polished surface so only two stages were selected, fully dirty and fully clean. Figure 5 and 6 illustrate the red sandstone and limestone samples at different cleaning stages.

Table 1: Cleaning times in seconds for four cleaning stages

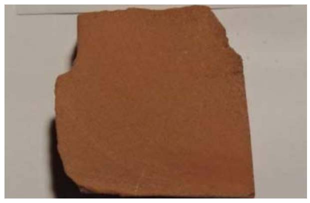
Cleaning degree	Yellow sandstone	Red sandstone	Limestone	Marble	White clay brick	Yellow clay brick	Granite
0%	0	0	0	0	0	0	0
30%	3	3	3	3	3	2	/
60%	6	6	6	6	6	4	/
100%	10	10	10	10	10	7	/



(a) t = 0 sec

(b) t = 3 sec

(c) t = 6 sec



(d) t = 10 sec

Figure 5: Red sandstone samples at different cleaning stages

(a) t = 0 sec

(b) t = 3 sec

(c) t = 6 sec

(d) t = 10 sec

Figure 6: Limestone samples at different cleaning stages

GREYSCALE AND CLEANNESS

To investigate the cleaning degrees of the surfaces of the stone samples, colour photos were taken first. A powerful lamp, used to create parallel lights, was fixed at 1.5 m above the samples. A Sony Cybershot DSC-T110 camera was used with the fixed 2.3 × optical zoom and distance of 0.5 m. All the colour photos taken were opened in the WORD files and converted to the greyscale digital images using the Photoshop software. These greyscale images were composed of shades of grey, varying from black at the weakest intensity to white at the strongest intensity. The corresponding greyscale levels could be read using Colourpad software. The greyscale (GS) is used to define the colour shades of the stone surface and ranges from 0 to 255 with 0 for pure black and 255 for pure white. An area of 1 cm^2 with a 10×10 grid including one hundred sampling points was placed on top of the greyscale photos and the GS values at the sampling points could be read in order to get the surface greyness of each stone sample by averaging these readings. Figs. 7 and 8 illustrate the sampling grids placed on the top of the greyscale photos of the red sandstone and limestone samples cleaned at different stages.

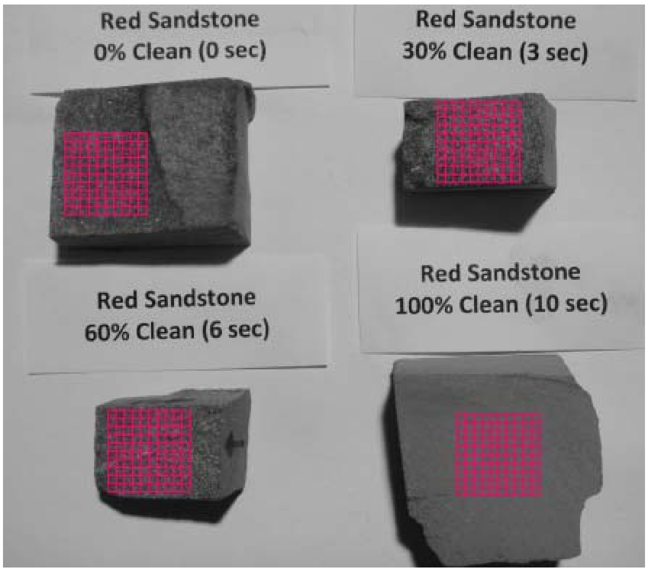


Figure 7: Grids on greyscale images of red sandstone

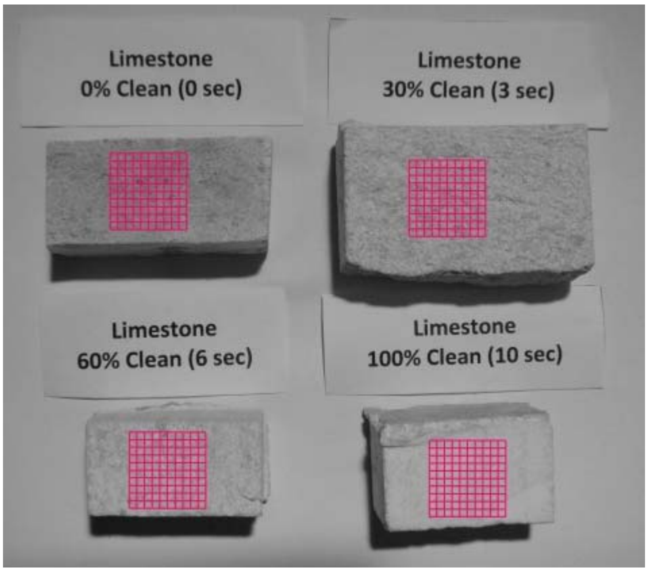


Figure 8: Grids on greyscale images of limestone

Figure 9 summarises the relationships between the greyscale and cleaning time for all seven types of masonry stones. It can be seen that the fully cleaned limestone had the brightest surface while the fully cleaned red sandstone had a darkest surface.

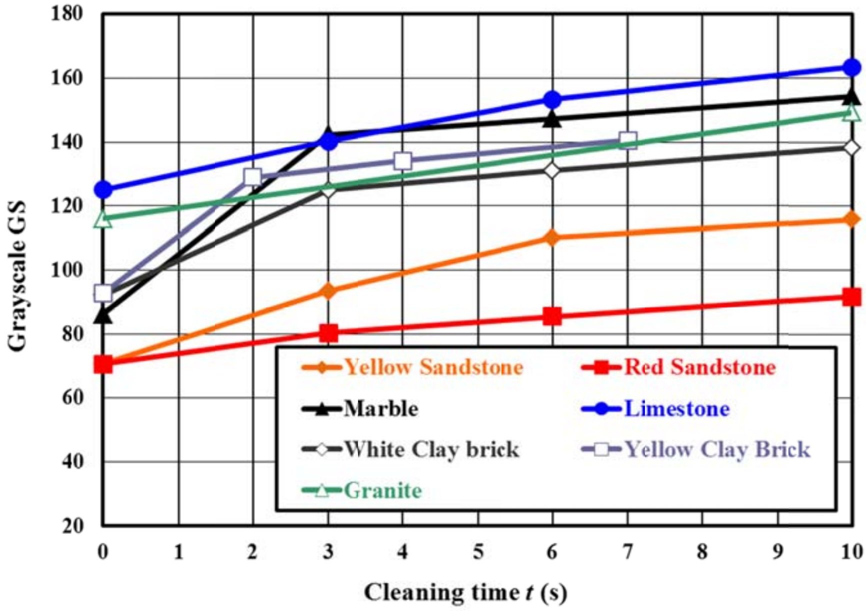


Figure 9: Greyscale versus cleaning time for various masonry stones

In general, the greyscale gradually increased with the increasing cleaning time but at a decrease rate and finally became stable when the stone surface was fully cleaned. These trends can be expressed using a parabolic or a bi-linear relationship. The differences in the greyscale between the original dirty and fully cleaned surfaces can be used to assess the dirty conditions on the stone surface. The larger the difference in greyscale, the dirtier the original stone surface. Marble had a largest difference of 68.3 and its original surface was the dirtiest. The differences in greyscale for yellow clay brick, white clay brick, yellow sandstone and limestone varied between 47.9 and 43.3 so they were relatively dirtier. The greyscale differences for granite and red sandstone were 33.3 and 21.2, respectively, which indicates that the original red sandstone was the least dirty.

In order to normalise the cleaning level for all types of the stones studied, a term of cleanness (CS) or the relative greyscale is introduced as follows:

$$\text{Cleanness (CS)} = \frac{\text{Greyscale at certain cleaning level}}{\text{Greyscale at fully cleaned level}} \tag{1}$$

The cleanness value for a fully cleaned stone surface is defined as 1.0 and the cleanness for other cleaning levels are smaller than 1.0. Figure 10 summarises the relationships between the cleanness and cleaning time for all seven types of masonry stones. It can be seen that the cleanness had similar increasing trends with the cleaning time as the greyscale. The smaller the cleanness value, the dirtier the original dirty surface. It is obvious that the original surface of marble was the dirtiest, followed by yellow sandstone, yellow clay brick and white clay brick. Red sandstone still had the least dirty original surface, together with granite and limestone. These trends match those with respect to the greyscale, which indicates that the digital imaging analysis and the two proposed parameters can be used for assessing the building cleaning degree.

SURFACE HARDNESS OF MASONRY STONES

The surface hardness of the stone samples at different cleaning stages can be used for evaluating the changes in the surface strength during building cleaning. The Vickers hardness number H_V was adopted here and can be calculated from:

$$H_V = \frac{\text{Applied load (kg)}}{\text{Contact area of indenter (mm}^2\text{)}} = \frac{2P\sin\theta/2}{d^2} \times 1000 = 1854.27\frac{P}{d^2} \quad (2)$$

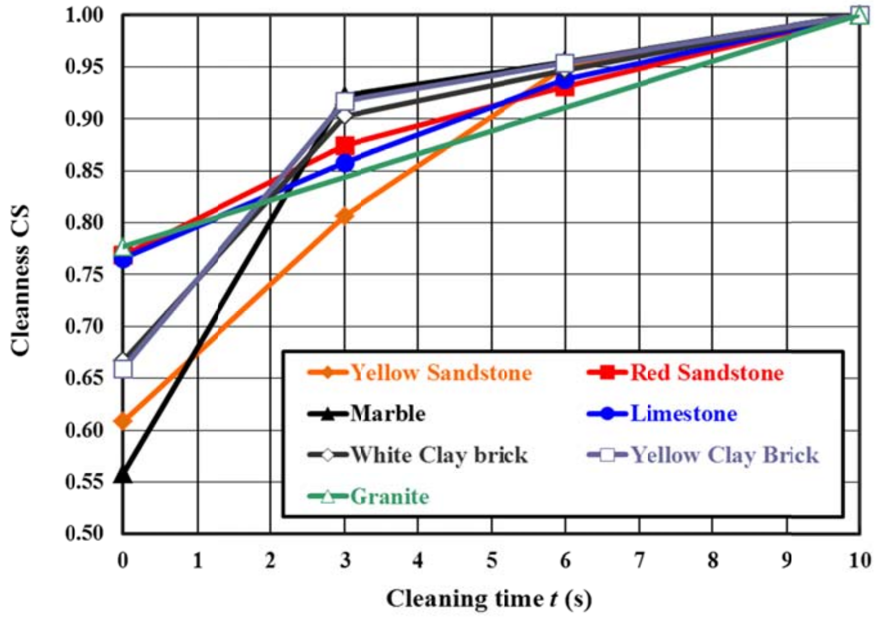


Figure 10: Cleanness versus cleaning time for various masonry stones

where

H_v Vickers Hardness Number (kg/mm^2)

P Applied load (g)

θ Angle between the opposite faces (136°)

d Diagonal of indentation (1 µm = 0.001 mm).

In the hardness testing, a stone sample was indented in the Vickers hardness instrument by a diamond indenter with a load P = 1000 g for 15 seconds (Figure 11). The pyramid shaped indenter had a square base diamond and an angle of 136° between opposite faces, as shown in Figure 12. After removing the load, a diamond indentation could be found on the stone surface using the microscope. Figure 13 shows that a diamond indentation had two diagonals, horizontal and vertical ones. The diagonal dimensions, d_H and d_V, were measured separately by attaching the two mark lines in the microscope to the edges of the indentation and then reading the values of d_H and d_V which were shown on the digital encoder. The two Vickers hardness numbers (H_V) corresponding to d_H and d_V could be obtained by checking against a Vickers hardness number table. The final value of H_V was the average of the two H_V results for the horizontal and vertical directions.

Figure 11: Vickers Hardness instrument

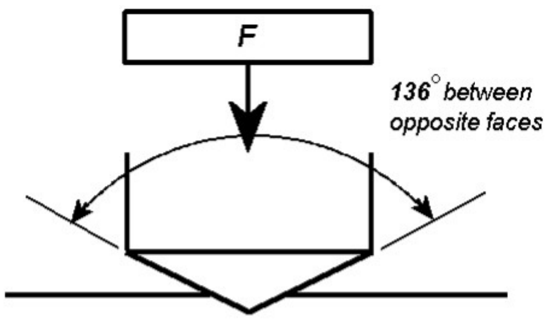


Figure 12: The pyramid shaped indenter

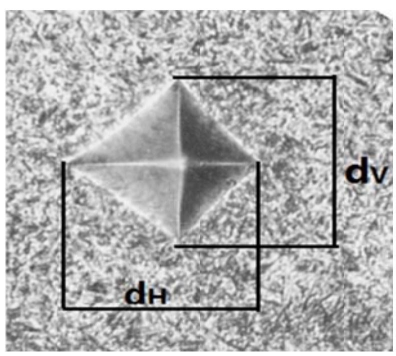


Figure 13: Diamond indentation on the stone surface

Figure 14 shows the increase trends of the surface hardness of the masonry stones with the increasing cleaning time but at a decrease rate. Similar trends could also be observed between the surface hardness and the cleanness. The granite had a hardest surface while the white clay brick had a softest surface.

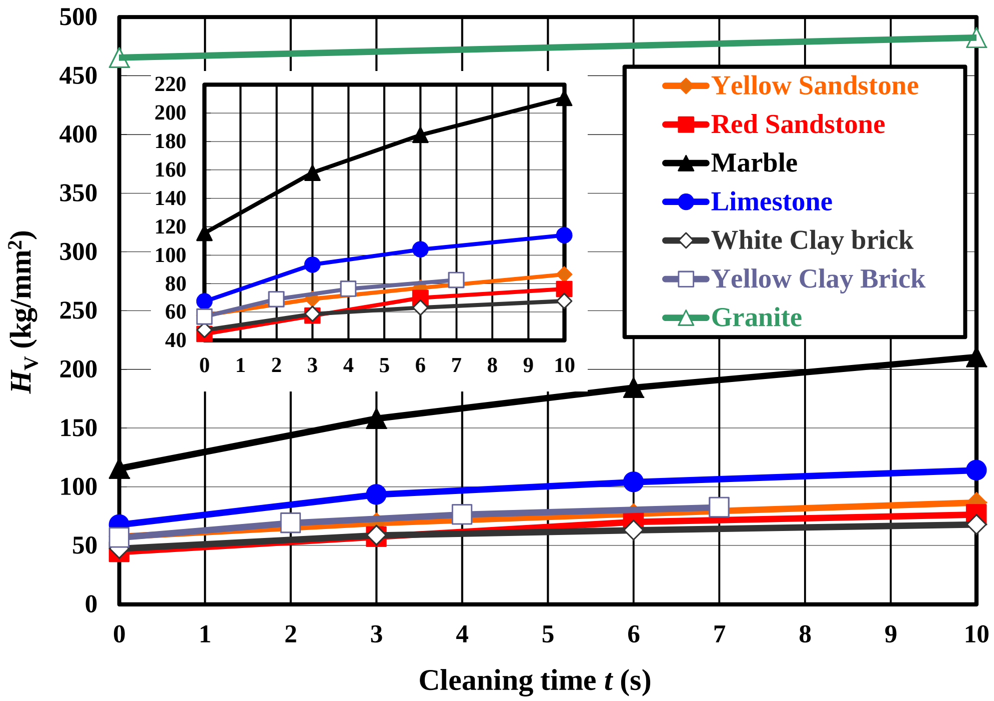


Figure 14: Vickers hardness number versus cleaning time for various types of masonry stones

WATER ABSORPTION

Water absorption, the quantity of water absorbed by a masonry stone when immersed in water for a stipulated period of time under the ambient atmospheric pressure, is another physical parameter which may largely influence the effectiveness of building cleaning. The water absorption testing was undertaken according to BS EN 13755 (BSI, 2008). The dried samples were placed in a tank after weighing, and then tap water at (20 ± 10)°C was added up to half the height of the stone samples. An hour later, tap water was added again until the level of the water reached three-quarter of the height of the samples. After another hour, tap water was added for a third time to overwhelm the samples completely. The samples were taken out of the tank after 48 hours, quickly wiped with a damp cloth and then weighed within 1 minute on a scale with an accuracy of 0.01 g. The result of the weighing was the weight of the saturated sample, $M_{\text{saturated}}$. The water absorption (WA) can be calculated from

$$\text{WA} = \frac{M_{\text{saturated}} - M_{\text{dried}}}{M_{\text{dried}}} \times 100\% \tag{3}$$

where

$M_{\text{saturated}}$ is the weight of the saturated sample
M_{dried} is the weight of the dried sample.

The water absorbing capacity of the seven types of stones was determined. Figure 15 illustrates that the two types of clay bricks showed the highest water absorptions among all the stones, at 13.09% and 8.66%, respectively. The water absorptions for the limestone, yellow sandstone and red sandstone were also quite high, at 5.40%, 5.09% and 2.96%, respectively. However, the marble and granite had absorbed little water, with the water absorptions of 0.32% and 0.23% only. It could also be observed that a larger value of water absorption corresponded to a softer masonry stone, while a smaller value of water absorption corresponded to a harder masonry stone.

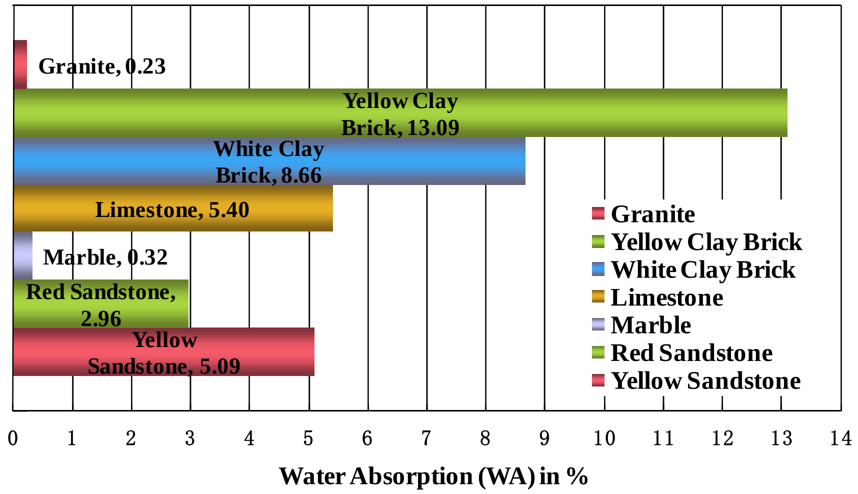


Figure 15: Water absorption for various types of masonry stones

CHEMICAL ANALYSIS

As the soiling and decay have the ability to affect the chemical substances on the stone surface, the chemical characteristics of the original dirty surface are largely different to the fully cleaned surface. In the cleaning process, the chemical substances on the stone surface continually change. Some elements and compounds may increase and some compounds may decrease or even disappear during building cleaning. The chemical analysis was conducted by using the instrument containing the Scanning Electron Microscope (SEM) and the Energy-Dispersive X-Ray Spectroscopy (EDX), as shown in Figure 16. The SEM was used to image a sample on a liquid crystal display (Figure 17) by scanning it with a beam of electrons in a raster scan pattern. It could produce the signals containing the information about the surface topography and composition of the sample by the interaction between the electrons and atoms. The EDX was used to analyse the chemical elements and compounds of the sample. EDX relies on the investigation of an interaction of some source of X-ray excitation with a sample. Its characterisation capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. It would be possible to find out the elements on the different parts of the sample. The instrument used in this study was the Scanning Electron Microscope (SEM) LEO S 430 I, U.K., coupled with ISIS EDD detector from Oxford Instrument, U.K.

Figure 16: SEM and EDX instrument

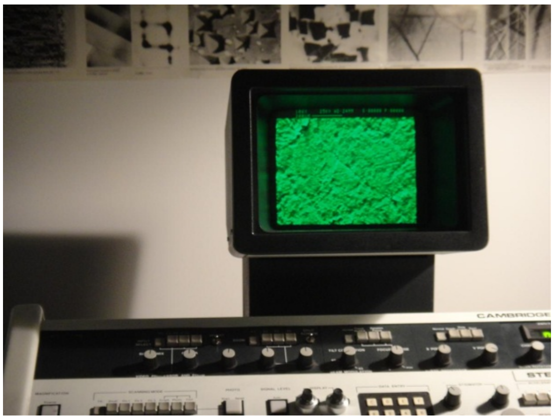


Figure 17: LCD for SEM

Sample preparation is a vital stage in the field of Electron Microscope. The insulation materials require a thin layer of conducting coating (~100 Å) to avoid charging. For the EDX in this study, carbon coating was adopted. The materials could also be observed at low primary energy, at which the coefficient for secondary emission was ~1 and the charge build-up was negligible. Entire sample preparation consisted of mounting the sample on a metallic platform via a conducting path.

Four out of seven types of masonry stones were tested:

- Yellow clay brick: Samples 1 (original dirty) and 2 (fully clean)
- Yellow sandstone: Samples 3 (original dirty) and 4 (fully clean)
- Limestone: Samples 5 (original dirty) and 6 (fully clean)
- Marble: Samples 7 (original dirty) and 8 (fully clean).

The surfaces of the clean samples were polished and cleaned in acetone. The original samples were rinsed in acetone. All the samples were dried under an IR lamp and coated with a thin layer of carbon to make them conductive. The samples were then mounted on the SEM stubs for the micro-structural and compositional analysis.

Six micrographs were recorded at different magnifications for each stone sample by using the SEM and six sampling points were selected for determining the chemical elements and compounds. Figure 18 shows a typical micrograph of the surface structures of the clean yellow clay brick with the corresponding spectrum diagram shown in Figure 19. Table 2 presents the percentage chemical elements and the corresponding compounds they formed.

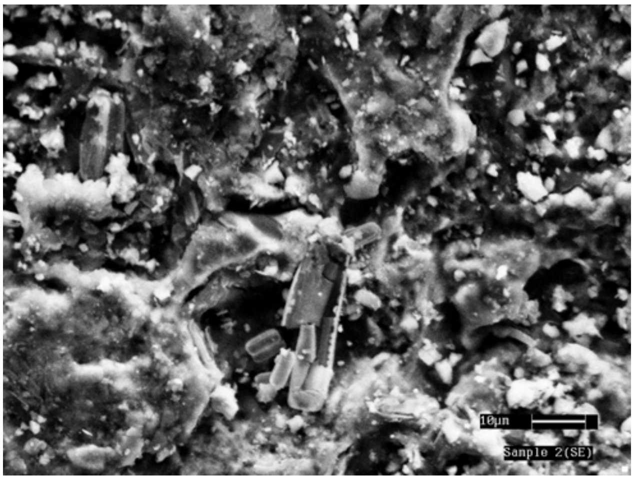


Figure 18: Micrograph for clean yellow clay brick

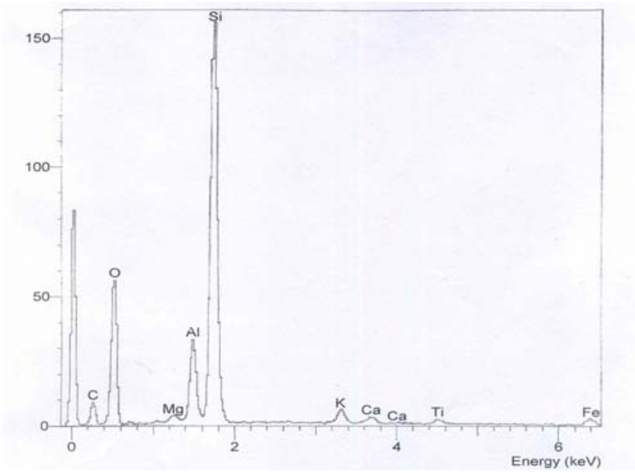


Figure 19: Spectrum diagram for clean yellow clay brick

Table 2: Typical EDX results for the clean yellow clay brick

SEMQuant results		Ref: Demonstration data SiLi detector		Spectrum label: Sample 2(1)	
System resolution = 61 eV		Quantitative method: ZAF (6 iterations)		Analysed all elements	
Element		Spectrum Type	Element (%)	Atomic (%)	Compound
C	K	ED	19.31	28.22	$CaCO_3$ 01/12/93
O	K	ED	47.14	51.70	Quartz 01/12/93
Mg	K	ED	0.46	0.33	MgO 01/12/93
Al	K	ED	4.66	3.03	Al_2O_3 23/11/93
Si	K	ED	24.14	15.08	Quartz 01/12/93
K	K	ED	1.28	0.58	MAD-10 02/12/93
Ca	K	ED	0.65	0.28	Wollas 23/11/93
Ti	K	ED	0.67	0.25	Ti 01/12/93
Fe	K	ED	1.69	0.53	Fe 01/12/93
Total			100.00	100.00	

Figure 20 shows the quantities of chemical elements on the original dirty and fully cleaned surfaces of the yellow clay brick samples. The main elements in the original yellow clay brick were C, O, Si and Al at 23.50%, 45.26%, 16.42% and 8.97%, respectively, which indicates that the main compounds in the yellow clay brick were $CaCO_3$, SiO_2 and Al_2O_3. By viewing the 50% dividing line, it can be seen that C slightly increased to 28.80% after cleaning while Si and Al decreased to 14.12% and 4.39%. As the samples were coated with carbon, it is hard to quantitatively analyse the changes of C. However, the decrease in Si and Al which represent Quartz (SiO_2) and Aluminium oxide (Al_2O_3) through the cleaning process indicates that these two compounds were formed in the original yellow clay brick. Similarly, the decrease of the rare elements in the yellow clay brick such as Mg and Fe which represent Magnesium oxide (MgO) and Iron disulfide (FeS_2) may be caused by polluting gases like O_3 and H_2S.

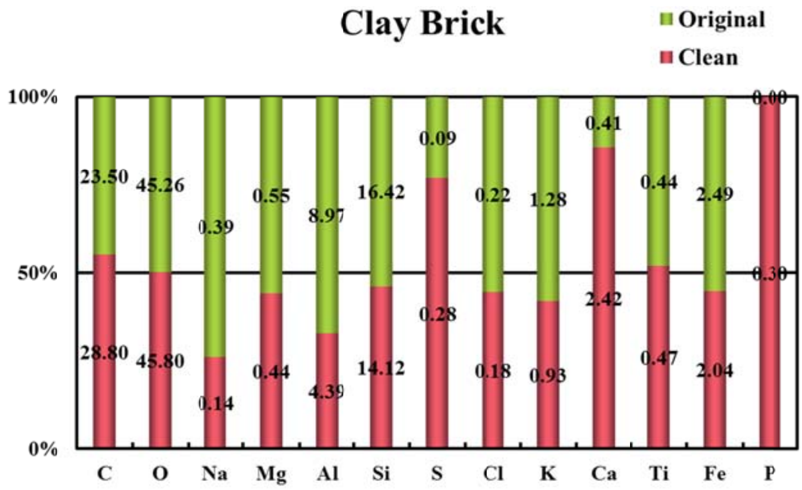


Figure 20: Chemical elements for the original dirty and fully clean yellow clay brick samples

Figure 21 shows the quantities of chemical elements on the original dirty and fully cleaned samples of the yellow sandstone. The main elements in the clean yellow sandstone were C, O and Si with 13.10%, 53.51% and 24.67%, respectively, and the corresponding compounds were $CaCO_3$ and SiO_2. By viewing the 50% dividing line, it can be seen that the main elements in the sandstone did not change much during cleaning. However, some metallic elements such as Na, Al, Fe and Ti which represent Albite, Aluminium oxide (Al_2O_3), Iron disulfide (FeS_2) and Titanium (Ti) largely increased after cleaning, which indicates that these elements were the original elements of the yellow sandstone. The biological soiling on the stone surface such as bacteria which has the ability to largely dissolve a range of components of the stone may lead to the loss of these compounds on the original stone. On the contrast, the decrease of Mg, S and Cl which represent Magnesium oxide (MgO), Iron disulfide (FeS_2) and Potassium chloride (KCl) through the cleaning indicates that these compounds were the naturally formed soiling on the façade of sandstone, probably due to the reactions with the polluting gases such as O_3, SO_2 and H_2S in the atmosphere.

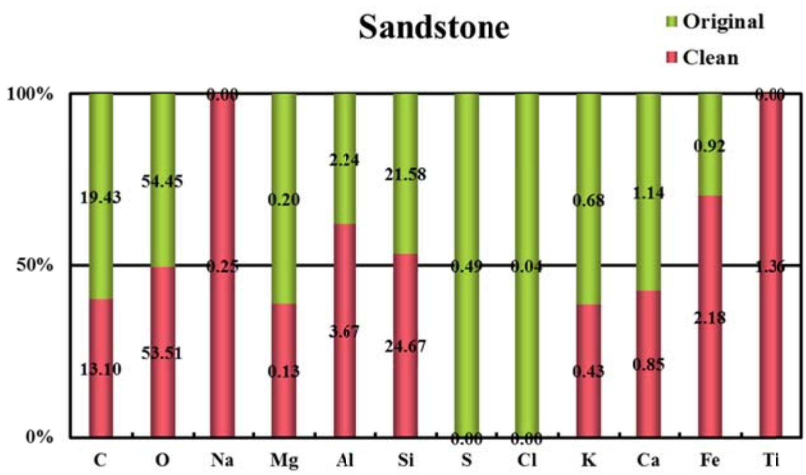


Figure 21: Chemical elements for the original dirty and fully clean yellow sandstone samples

Figure 22 shows the quantities of chemical elements on the original dirty and fully cleaned limestone samples. The main elements in the clean limestone were C, O and Ca with 12.80% 49.92%, and 36.87%, respectively, and the corresponding main compounds were $CaCO_3$, SiO_2 and Wollas. By viewing the 50% dividing line, it can be seen that the main elements in the limestone did not change largely by the cleaning. However, some rare elements such as Na, Al and Si which represent Albite, Aluminium oxide (Al_2O_3) and Quartz (SiO_2) disappeared after cleaning, which indicates that these compounds were not the original elements of the limestone but the dirty soiling.

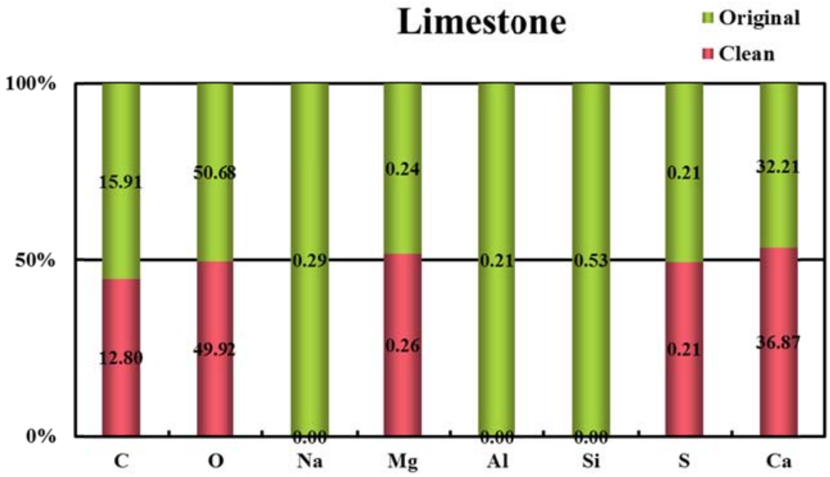


Figure 22: Chemical elements for the original dirty and fully clean limestone samples

Figure 23 shows the quantities of chemical elements on the original dirty and fully cleaned marble samples. The main elements in the clean marble were C, O and Ca with 12.70%, 51.27%and 35.49%, respectively, and the main compounds in the marble were $CaCO_3$ and Wollas. By viewing the 50% dividing line, it is found that the rare compounds in the marble were all largely decreased after cleaning, which indicates that the surface condition of the original marble was poor as large amounts of soiling formed on the surface. In addition, since Mg, Al and Si still existed after cleaning, the clean marble likely contained small amounts of Magnesium oxide (MgO), Aluminium oxide (Al_2O_3) and Quartz (SiO_2).

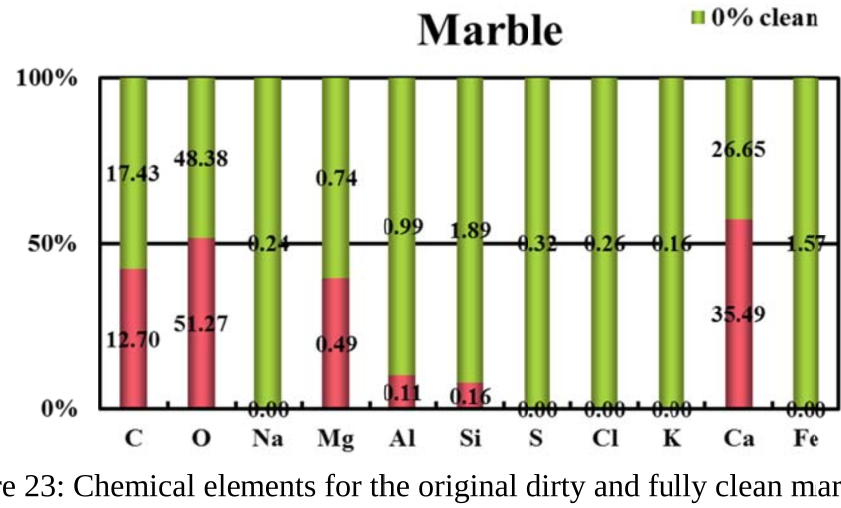


Figure 23: Chemical elements for the original dirty and fully clean marble samples

The test results showed that the chemical substances on the stone surface were quite different for different types of stones. Some chemical elements and compounds largely decreased or increased after cleaning, but the chemical elements C and O always remained at large proportions of all the chemical elements in the stones. As the stone façade was always exposed to the open environment for a long time, chemical reactions would occur, which would nevertheless form various chemical compounds or multi-components on the stone surface from the polluting gases in the air such as SO_2, H_2S, NH_3, O_3 and NO_X.

CONCLUSIONS

1. In this study, a series of tests were conducted to investigate the changes in physical and chemical characteristics of seven different types of masonry stones during the cleaning process, i.e. red sandstone, yellow sandstone, limestone, marble, white clay brick, yellow clay brick and granite. The physical investigations included the evaluation of cleaning degree, the Vickers hardness test, and measurements of water absorption. The chemical investigations included the micrographs of the stone façade and the analysis of the chemical elements and compounds on the stone façade before and after cleaning using the combined Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX) techniques.

2. The cleaning degrees of the samples were assessed by introducing a parameter, the greyscale, using the digital image analysis method. A lower greyscale corresponded to a dirtier stone surface. It was observed that the greyscale continuously increased with the increasing cleaning time and would finally stop when the surface became fully cleaned. In addition, another parameter, the cleanness which was defined as the ratio of the greyscale at certain cleaning stage to the one when the stone was fully cleaned or the relative greyscale, was introduced for assessing the effectiveness of the cleaning. For a dirty surface, the cleanness was small, while for a fully cleaned surface, the cleanness was equal to one. A larger cleanness value corresponded to a better cleaning level. The comparison of the cleanness values at different cleaning stages indicated that the original surface of the marble was extremely dirty while the surface of the granite was the cleanest among all the stones studied. This digital image analysis method together with applying the greyscale or cleanness was proved to be useful and efficient for quantitatively assessing the effectiveness of building cleaning.

3. The surface hardness of all seven types of stones studied at different cleaning levels was assessed by conducting the Vickers hardness tests. A larger hardness value corresponded to a harder stone surface. The harness test results showed that the surface hardness continuously increased with the increasing cleaning time and would finally become stable when the surface was fully cleaned. Most of the increasing trends of the surface hardness could be approximately expressed using bi-linear relationships. The granite was found to be the hardest stone among all the stones studied, and followed by the marble and limestone. However, there were no big differences in the surface hardness between the yellow clay brick, yellow sandstone, red sandstone and white clay brick.

4. The water absorbing capacity of the seven types of stones was also quantitatively determined. Two types of clay bricks showed the highest water absorptions, and water absorptions for the limestone, yellow sandstone and red sandstone were also quite high. However, the moisture absorption of the marble and granite was found to be very low, which indicates that they could hardly absorb water. It was also observed that a larger value of water absorption corresponded to a softer stone, while a smaller value of water absorption corresponded to a harder stone.

5. The chemical investigations by using the SEM and EDX techniques showed that the chemical substances on the stone surface were quite different for different types of stones. Some chemical elements and compounds largely decreased or increased after cleaning, but the chemical elements C and O always remained at large proportions of all the chemical elements in the stones. As the stone façade was always exposed to the open environment for a long time, chemical reactions would occur, which would also form various chemical compounds or multi-components on the stone surface from the polluting gases in the air such as SO_2, H_2S, NH_3, O_3 and NO_X. This may also lead to the formation of the soiling on the stone surface.

6. In summary, the investigations in this study indicated that the physical and chemical characteristics on the stone surfaces were all significantly influenced by the cleaning degrees. A stone with a higher cleaning degree always corresponded to a brighter and harder surface. Because an appropriate stone

cleaning method could not only improve the appearance of the building but also protect the stones from decay and damage, in this way, the present study could help to pave the way for selecting more appreciate, economical and effective methods of stone cleaning for existing listed masonry stone buildings.

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