An Approach to the Evaluation of Cleaning Methods for Unglazed Architectural Terracotta in the USA

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Abstract
The safe and effective removal of disfiguring atmospheric soiling from brick and unglazed architectural terra cotta is a problem well known to building specialists. While limited research has been conducted on the study and repair of glazed architectural ceramics, very little recent work has addressed the characterisation and analysis of unglazed architectural terracotta, the physicochemical nature of soiling mechanisms, or the short- and long-term effects of commercial cleaning methods currently employed. In addition, an over-emphasis on cleaning efficacy, along with the meteoric rise in the availability of untested chemical and mechanical cleaning systems, has led to the disfigurement and surface damage of many terracotta buildings, permanently altering the visual and protective qualities of the material and potentially jeorardising the overall weatherability and performance of each building's skin.

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An Approach to the Evaluation of Cleaning Methods for Unglazed Architectural Terracotta in the USA

FRANK G MATERO, ELIZABETH A BEDE AND ALBERTO TAGLE

The safe and effective removal of disfiguring atmospheric soiling from brick and unglazed architectural terracotta is a problem well known to building specialists. While limited research has been conducted on the study and repair of glazed architectural ceramics, very little recent work has addressed the characterisation and analysis of unglazed architectural terracotta, the physico-chemical nature of soiling mechanisms, or the short- and long-term effects of commercial cleaning methods currently employed. In addition, an over-emphasis on cleaning efficacy, along with the meteoric rise in the availability of untested chemical and mechanical cleaning systems, has led to the disfigurement and surface damage of many terracotta buildings, permanently altering the visual and protective qualities of the material and potentially jeopardising the overall weatherability and performance of each building's skin.

Unglazed terracotta buildings account for a large percentage of the industrial world's nineteenth-century architectural heritage and as such represent a unique and difficult cleaning problem that demands considerably more study than has previously occurred. A complex issue, their neglect and mishandling can in part be attributed to both past and current attitudes regarding the perceived durability of ceramic materials and a long-standing professional preoccupation with natural building stone and its specific decay mechanisms. This has resulted in both an ignorance of terracotta's unique problems of variability, aside from faulty installation techniques or 'glaze fit', and the misapplication of cleaning approaches designed for natural building stone.

In response to this problem, the Architectural Conservation Laboratory at the University of Pennsylvania began a phased research programme focused on an assessment of available and potential cleaning systems for unglazed architectural terracotta. Phase I of this research, conducted between August 1991 and June 1992, was generated as part of the development of a master plan for the preservation of the Brooklyn Historical Society building by Jan Hird Pokorny Architects & Planners, New York City. Conservation training and research on this project was funded in part by the Getty Grant Programme and the Graduate School of Fine Arts, University of Pennsylvania. Phase II was begun in late 1994 in conjunction with Historic Building and Site Services of Bournemouth University (HBSS) for English Heritage, Science and Conservation Services Division (Research and Professional Services Group). This work, currently underway, has focused on the replication of the UPenn-ACL research protocol on English terracotta by HBSS and the joint compilation of a bibliographic database and technical glossary on the conservation of unglazed architectural terracotta.

One primary goal of this project was to ascertain which cleaning techniques effectively removed atmospheric soiling without negatively altering the physical properties of the terracotta, especially the fireskin. Factors considered significant in assessing the cleaning of unglazed terracotta included: the manufacture, composition, and weathering of the material; the nature and age of the soiling; and the type and history of previous cleaning methods. Given the quality, significance,
and condition of the Brooklyn Historical Society Building, its availability for this research provided a first class American example appropriate for the investigation of these issues. A three-part approach was developed for the research programme outlined above:

1. Review of technical literature on the cleaning and repair of unglazed architectural terracotta;
2. Characterisation of terracotta and diagnosis of the agents and mechanisms of deterioration – in general, and for the terracotta of the Brooklyn Historical Society Building in particular;
3. Development and execution of a preliminary testing programme designed to study the physical effects of commercial and custom cleaning methods on unglazed terracotta using scanning electron microscopy.

HISTORY AND TECHNOLOGY

The Long Island (now Brooklyn) Historical Society, designed in 1878 by the American architect George B Post with facade sculptures by Olin Levi Warner, is one of North America’s great architectural treasures and a supreme and early example of the successful large-scale use of unglazed terracotta (Fig 6:1). According to James Taylor, manufacturer and early historian of the material,

The Long Island Historical Society Building was the first important or public building in New York to contain terracotta in its exterior design, and the first on the East Coast to use locally produced terracotta in an extensive way. It is not clear when Post began to consider terracotta as an alternative to the originally planned sandstone and brick building; however, by 11 November 1878 the Building Committee approved the substitution of terracotta for the proposed brownstone decorative elements. Several reasons were cited for this change, including the unavailability of the brownstone from Newark, New Jersey, that had originally been selected. More importantly, Post proclaimed that terracotta was more resistant to weather and fire than sandstone and the Society would be able to afford more ornamentation on their building if the elements were of terracotta. The Committee unanimously endorsed the change in material.

Post gave the contract to supply the terracotta to the Perth Amboy Terracotta Company of Perth Amboy, New Jersey, and enlisted the talents of sculptors Olin Levi Warner and Truman Hiram Bartlett. Warner’s ornamentation was reportedly modelled directly from the wet terracotta, so the building actually contains the original work of the artist. The total cost for the terracotta work was $11,000.

The building opened on 12 January 1881 to rave reviews. The Christian Union declared the Long Island Historical Society ‘the finest specimen of pressed brick and terracotta in this country ... the Historical Society is certainly to be congratulated on this noble building.’ The World described the building as:

... a poem in red ... a red structure of the most artistic character ... it is abundantly evident that Post knows his material, and that his decorations were designed from a wish to lovingly demonstrate the true value of terracotta ... to use terracotta justly the architect must do what Post has done ... invent, invent, invent.’
The historical and architectural significance of the Brooklyn Historical Society Building derives from the unique circumstances of its time and place. The combination of the creative genius of Post and Warner with the technological capabilities and resources of Alfred Hall and the Perth Amboy Terracotta Company together created a monument of instant and long-lived significance.

While terracotta has often been hailed as one of the oldest of building materials, prior to 1879 the material had been used in only a few buildings in the greater New York area. Objections about the durability of terracotta raged for several decades after Richard Upjohn’s introduction of the material to New York City in 1852. In the 1870s, however, terracotta manufacturers in Chicago began to improve their technical knowledge and the demand for a fireproof material to rebuild the city after the fire of 1871 stimulated new interest in terracotta as a fireproof building material. It was not until the 1880s that architects on the east coast began to use the material. During this time, the architects Stone & Carpenter employed terracotta for Brown University and the City Hall in Providence, Rhode Island; H H Richardson employed terracotta at Trinity Church, Boston; Whitney Lewis used it for a large residence on Commonwealth Avenue, Boston; and George B Post used it again at the Produce Exchange in New York City.

Thus when Post convinced the Building Committee of the Brooklyn Historical Society to use terracotta ornamentation, there was very little precedent or support for the material on the east coast. There were, moreover, no manufacturers of architectural terracotta in the vicinity to provide the material. It was on the strength of the commission for the Brooklyn Historical Society Building that the Perth Amboy Terracotta Company was incorporated in 1879 (Fig 6:2).

The Perth Amboy Terracotta Company was founded by Alfred B Hall, a brick manufacturer from Cleveland who invented a brick-moulding machine that was patented in 1842. In 1845 Hall visited England and afterwards returned to settle in Perth Amboy where he founded A Hall and Sons Fire Brick Works, which produced fire bricks and household pottery. In 1877 R Taylor, who reportedly trained in Chicago, joined the firm; with the commission of the Brooklyn Historical Society Building he converted several of their kilns to produce architectural terracotta. Thus the venture began; however, it was not without its difficulties. The Christian Union reported that ‘some of the work was so difficult to manufacture and bake without cracking it would hardly be undertaken a second time.’ Nevertheless, the Perth Amboy Terracotta Company continued in production, making 2000 tons of terracotta for Post’s Produce Exchange building in New York City between 1881 and 84 – thus assuring ‘the success of terracotta as a building material and the prosperity of the Perth Amboy Terracotta Company.’

Until 1890 terracotta was most commonly used as a stone substitute, as Herbert Croly, a noted architectural historian, stated in 1906. Terracotta when first introduced had to win its way to favour by pretending to be a cheap stone. In this form it was normally used in conjunction with bricks as a decorative element that imitated stone or was painted to look like stone. However, when George B Post commissioned the Perth Amboy Terracotta Company to introduce a new terracotta colour, ‘a burnt red, a peculiar warm shade of red ... he at once divorced the material from stone and started it upon its independent career.’ By the 1890s architectural terracotta had indeed come into its own.

Terracotta was promoted as a lightweight, inexpensive, durable and essentially fireproof material that could be manufactured in large quantities in a relatively short period of time.
without diminishing the ornamental or decorative possibilities of architectural features. Writers even went so far as to attribute the recent advances in freedom of design in the country to the use of architectural terracotta. The acceptance and widespread use of the material was due in large part to Alfred B Hall and the terracotta industry of New Jersey.

During the 1880s Alfred B Hall sold his interest in the company after a disagreement and started a new company in the Perth Amboy vicinity, called the A Hall Terracotta Company. The Perth Amboy Company remained in the Hall family and by 1898 Edward J Hall, Jr is listed as president, and William C Hall as vice-president and general manager. In 1885 the Perth Amboy and A Hall Companies reportedly manufactured 60% of the terracotta in the United States, and by 1893 the company had established offices in New York, Boston and Philadelphia. The Perth Amboy Terracotta Company was listed as the largest producer in the United States with 46 kilns — an impressive advance on the three they had converted in 1879. In 1896 The Yale Scientific Monthly reported that

the largest quantities of terracotta in the United States come from New Jersey, for the clay deposits there are the most valuable in the world. They cover an area of about 320 square miles extending across the state.

By 1898 the Perth Amboy plant itself covered 8 acres and the company owned 170 acres of clay banks — more than half the 'valuable' clay banks in New Jersey.

As the terracotta industry boomed and the technology quickly advanced, companies began to merge in order to stay competitive. The Perth Amboy Terracotta Company merged with the Excelsior Terracotta Company and with the Atlantic Terracotta Company in 1906. In 1907, the Standard Terracotta Company also merged with Atlantic. Thereafter the Perth Amboy facilities became known as Atlantic Terracotta Company Plant Two; Excelsior became Atlantic's Plant Three; and Standard, Atlantic's Plant Four.

With the development of terracotta glazes in the 1890s, a shift in taste towards lighter-coloured buildings after the Chicago Columbian Exposition of 1893, and the technological innovations that occurred simultaneously, the production and use of dark unglazed terracotta declined dramatically during the early twentieth century.

MANUFACTURE OF ARCHITECTURAL TERRACOTTA

Clays

The clays used for architectural terracotta are of higher quality than those used for bricks or tiles. They are usually clays which have undergone geological compaction since their deposition, with some alteration, so that they are laminated in structure, and only develop plasticity when ground and moistened. The natural colours of these clays often range from a very deep red through buff to off-white.

The primary constituents of clays used for architectural terracotta are 60%-70% silicon dioxide (SiO₂) and 20%-30% aluminium oxide (Al₂O₃) resulting in the general formula Al₂O₃·3SiO₂. The combining of silicon dioxide and aluminium oxide forms the 'cementing' or 'consolidating' matrix as the clays are heated, usually to 1100-1370°C. For terracotta clays it was generally recommended that free silicon dioxide not exceed 20% but it very often did. An excess of free silicon dioxide (that which has not combined with aluminium oxide or another base) gives the terracotta mix a 'pseudo-plastic' character and the mix may be prematurely sent to age or dry before it is actually in a proper plastic condition, which often leads to cracking during the drying and cooling phase.

Under extreme heat, aluminium oxide will react as a base or acid to yield aluminium cations or anions in salts. When combined with water in this state, it will form a hydroxide gel, which is desirable as it imparts plasticity and tenacity to the paste. An excess of free aluminium oxide may also give rise to serious trouble in drying, owing to its strong retention of water, and in firing, owing to its great and rather sudden contraction. Specifically, clays containing laterite exhibit these problems, due to their high content of hydrated aluminium oxides.
Other components usually found in architectural terracotta clays include: chemically combined water (or bound water), calcium oxide (CaO), magnesium oxide (MgO), potassium oxide (K₂O), sodium oxide (Na₂O) and iron II and III oxides (FeO, Fe₂O₃). Silicon dioxide (pure quartz) when melted (1713°C) forms a viscous liquid that cools at room temperature as a solid noncrystalline glass. When alcalis, such as sodium oxide and potassium oxide, and alkaline earths, such as calcium and magnesium oxides, are present, the melting temperature is markedly lowered. These alcalis act as fluxes but still allow the glass to form on cooling.

In architectural terracotta only the surface reaches temperatures high enough to begin to melt the silicon dioxide and fuse the clay particles. The result is a dense, non-porous glassy skin known as the 'fireskin'. Sodium and potassium oxides also stabilise suspensions and allow the finer particles to be separated by decanting off the surface layer during the washing process. These alcalis also increase drying shrinkage and lower the stiffness of the plastic mass. The alkaline earths stiffen the clay-water suspensions, firm up the plastic mass, reduce drying shrinkage, and increase workability. The iron oxides, which are present in some quantity in all clays, reportedly have 'little or no effect upon the strength or durability of the material but only act as a colouring agent.' Their presence in large or small quantities makes the difference in colour, varying from a slightly tinged buff to a dark red. The chemistry of all these components working together is complex and partially unpredictable. In the nineteenth century, and still to some extent today, desired results from a particular clay source were obtained empirically.

Additionally, clays used for the manufacture of terracotta should not contain an appreciable amount of water-soluble materials, especially gypsum. During the drying or firing process the absorbed water evaporates from the surface and a residue, soluble sulphates held in solution, is deposited on the surface. To eliminate this discoulouration or 'scumming', barium hydroxide (Ba(OH)₂.xH₂O), barium sulphate (BaSO₄), or a combination of the two, were often introduced into the clay to form insoluble barium sulphate, thus preventing the conveyance of salts to the surface as the water evaporated from the terracotta body. A specific clay seldom contained all the desired characteristics for the production of architectural terracotta. In the early twentieth century the relationship of the clay content to the desired characteristics became better understood and often particular additives were added to certain clays. However, in the late nineteenth century the desired results were obtained by trial and error of mixing various clays. The Perth Amboy Terracotta Company, however, owned some of the best clay banks in the country and their clays, reportedly, needed very little adjustment.

**Perth Amboy terracotta clay**

The clay primarily used by the Perth Amboy Terracotta Company was fine buff-coloured clay of low to medium refactoriness from the Raritan formation which straddled the Raritan River in Perth Amboy, New Jersey. The Clay Record, in 1896, stated: 'For fineness of texture and plasticity some of the clays of New Jersey have no equal' in the terracotta industry. The 1882 Annual Report of the State Geologist reported that the clays mined by the Perth Amboy Terracotta Company were also used by the Boston Terracotta Company and the Long Island Terracotta Company.

In 1904 a special publication issued by the state geologist entitled The Clays and Clay Industry of New Jersey stated that the Perth Amboy terracotta clays contained an average of 5% white quartz sand, although some clays contained as little as 0.5%. Additionally, some portions of the Raritan bed contained considerable pyrites in the form of 'sulphur' balls or nodules which were carefully picked out and rejected during mining. Furthermore, the report described the terracotta clay mix used by the Perth Amboy Terracotta Company as having a tendency to warp, requiring 34% water for tempering, with an air shrinkage allowance of 6.6%, firing shrinkage of some 7.4%, and a tensile strength of 142 lbs/square inch. A New Jersey geological survey published in 1878, entitled Clay Deposits, reported the results of an analysis of A Hall & Sons' fireclay, one year before the company became The Perth Amboy
Terracotta Company. It is not known whether the clay described here is the same as that used for the terracotta for the Brooklyn Historical Society Building, although it is consistent with the state geologist's report of 1904 cited above. The composition of this fireclay was reported as: hydrated silica 42.05%; aluminium oxide 35.83%; water (bound) 12.20%; silicon dioxide (quartz sand) 5.70%; water (moisture, free) 1.50%; titanic [titanium] hydroxide 1.10%; iron oxide 0.77%; potassium hydroxide 0.44%; magnesium oxide 0.11%; sodium hydroxide trace; lime (calcium carbonate) trace.

The analysis further stated that the clay was blue to buff coloured and contained 'some pyrites that is removed and sold to chemical works'.

**Clay preparation**

Once the clays were mined and sorted by quality they were allowed to 'weather'. Since many clays are formed under strong geological compaction, the process of breaking them down into their ultimate particle size, and thus developing their latent plasticity, occurs slowly. Exposing the clays to the weather (i.e., wet/dry, freeze/thaw cycles) increases this rate of decomposition, enabling the clays to be more readily processed. In addition, sulphides (as pyrites) are converted to sulphates and oxides through oxidation and the oxides hydrate to hydrated ferric oxide, thus minimising the potential for chemical changes during or after the manufacture of the blocks.

After weathering, the clay was ground and sieved, usually through a 5mm mesh, to remove small particles of stone and other foreign matter. Two basic types of machinery were used to accomplish this: edge runner mills and roller mills. Both types of mills consisted essentially of metal rollers set close to a metal plate. As the clay passed under the rollers, it was crushed and either fell through perforations in the plate or was pushed aside and discarded.

Next, the clay was washed. Prior to 1893, this consisted of mixing the clay with sufficient water to make a cream-like slip. Stones and other impurities settled out, and the slip was passed through a strainer into a 'drying pan'. The finer the clay desired, the longer it was allowed to remain in suspension. In the twentieth century, machines were developed to attain a higher degree of purification. The washed clay was then deposited in a receiving bin with alternating layers of grog.

An important factor in the production of any type of fired clay ware is shrinkage. Clay particles swell in water and contract as the water evaporates. In order to limit and predict the amount of shrinkage when the clay was fired, grog was added to the clay mix. Grog usually consisted of previously fired bodies such as terracotta and/or brick. Because these had previously been fired, thereby evacuating the majority of the water, they would not shrink further. The ideal grog came from the same clay that had been fired at the same temperature as the piece being produced. However, there was seldom enough of this material, and in practice, any available fired material was added to the clay mix. The quantity of the grog added depended on the quality of the clay and the amount of shrinkage desired. The usual shrinkage was approximately 8%. In the early years of manufacturing architectural terracotta, each plant would experiment with the amount of grog required for their clay to obtain consistent shrinkage; as the industry matured in the twentieth century, standard ratios for various clay beds and terracotta plants were established.

Alternating layers of weathered clay and grog were then placed into troughs. These troughs usually varied from 2–5 feet in depth. The superfluous water rose to the top and was drawn off. The paste was aged until it 'ripened' or stiffened in its stratified form and was then mixed. The mixing was done by taking vertical sections from the paste and mixing them in a pug mill. A pug mill contained projecting knives that revolved in a hollow cylinder or trough that mixed the moist stiff clay. When the material left the pug mill it possessed the desired consistency or 'temper'. It was important that proper and consistent plasticity was obtained for moulding. If one part of the clay mass was stiff, and another portion soft, the moulded piece would warp and crack while drying.

In plants which 'washed' the clay rather than simply 'cleaned' it, excess water had to be removed from the slip before further processing. In the
early years of terracotta manufacturing this was done by heating the clay in a drying pan to drive off the excess water. The result was a paste-like clay ready for aging. In later years, filter presses were used.

The paste was now ready to be aged. Aging, also called 'souring', was not always thought necessary. The clay was stored in a cool dark place for an average of 12 months (some plants aged the clay for up to two years). The aging process provided time for the moisture to become evenly distributed, for air bubbles to dissipate and for the plasticity of the clay to increase through the formation of hydrated, gellified hydroxides. The result was a much more plastic clay that was easier to mould. Many manufacturers believed this reduced cracking. If aging was not part of the process the clay was taken from the pug mill or the filter press, as the case warranted, spread out on a 'battering slab' and beaten to drive out the air bubbles. The clay was then sufficiently prepared to be worked into the moulds.

**The moulding process**

Architectural terracotta moulds were designed by the manufacturer or sometimes under the direction of an architect. Some architects would furnish the manufacturer with working drawings with each detail indicated, while others would suggest what they envisioned and permitted the company artist and draughtsman to elaborate their ideas. No working drawings of the terracotta detailing for the Brooklyn Historical Society Building have been discovered to date but the presence of the noted artists Olin Warner and Truman Bartlett at the Perth Amboy Terracotta Company, and citations suggesting that some of the decorative work was modelled in the plastic condition, indicate that the detailing may be the artists' in this case.

The architect produced 1/2 inch scale drawings, with or without detailing, and the manufacturer would then produce 1 inch scale working drawings. Shrinkage was estimated by calculating the amount of 'face area' and drawings, compensating for this shrinkage, were produced. From these drawings the plaster model was created and from the model a mould was produced. The moulds were usually made of plaster of Paris, which offered a quick set, low shrinkage and the ability to absorb large amounts of moisture from the clay cast. In so doing, the process promoted the concentration of fine colloidal clay particles to the surface in fine parallel layers, thus contributing to the formation of the fireskin.

The mould was then systematically filled with processed clay usually 30-35mm thick with the aid of a presser. Sections of excess clay were removed by hand from the back of the piece, creating hollow cells. Cross pieces, called 'straps', were placed where necessary to strengthen the block and help it to retain its shape in the mould. The mould was then set aside and clay allowed to dry to a stiffness that would allow the mould to be removed without damaging the work. Once carefully removed from the mould, the block was set on a board with a sheet under it. The sheet allowed for free contraction so the clay block could creep or shrink without cracking—otherwise the clay would stick to the board. The piece was left for two to three days 'till in a fit state for finishing'. Finishing work, such as the removal of seams and the texturing of the surface, was performed by experienced workmen with a knife for flat surfaces and leather or special tools for others. More detailed carving could also be done at this point, although some terracotta workers advised against working over the greenware surface, other than smoothing and trimming, because they believed that carving disrupted the microstructure at the surface and resulted in a weaker piece.

In the early years of architectural terracotta manufacturing the finished pieces were then placed in drying rooms for approximately 48 hours. These rooms were heated to 30°C by steam pipes which covered the floor. However, because the edges and corners of a piece naturally dry first and the middle last, the ends of the pieces tended to curve inward and/or crack. Thus, quite quickly, various manufacturers developed alternative methods of drying the pieces to alleviate this uneven shrinkage and resulting distortion. Some dried the pieces in two stages, first with a slow, dry heat and second with steam heat. A few even went so far as to wrap the blocks with damp cloths to allow the centres to dry first and thus encourage
the edges to contract towards the hard centres.\textsuperscript{51} Large terracotta pieces were also turned periodically to prevent uneven drying. It was also discovered that pieces that were dried too rapidly, having been exposed to draughts or excessive heat, formed a crust that prevented even drying. Moisture collected behind the surface and the crust was forced off during the first frost – if it survived the firing process. Terracotta that was not consistently dry was extremely apt to warp, twist or even explode in the kiln. Therefore, it was essential for the moulded pieces to be consistently, thoroughly, and slowly dried before being placed in the kiln for firing.

\textbf{Firing}

Firing is the process of heating the terracotta until the clay particles knit together. This degree of bonding was historically called ‘sintering’,\textsuperscript{52} ‘Vitrification’, or actual fusing of the clay particles into a single mass with closed pores, was generally achieved, to a degree, only on the outer skin of the piece that was exposed to higher temperatures than the core. This fusion, which created a thin densification zone known as the ‘fireskin’ made the terracotta impervious to moisture.\textsuperscript{53}

The majority of manufacturing plants fired their wares in round muffle kilns operated with a down-draught. While the method of construction differed from plant to plant, and the fuel varied from coal to crude oil to natural gas, all kilns operated on the same principles. Flames travelled up over the top wall of the muffle, along the crown of the kiln to the middle, where they were drawn out. Openings were constructed in the crown leading into the muffle. During the early stages of firing these were kept open so that the water vapour and products of the combustion of the organic material in the clay could escape. As the kiln became hot these openings were closed. ‘Trial-holes’ perforated the kiln in various places so that all parts of the kiln could be observed from the outside. Trial pieces were placed near these holes and were examined as the firing progressed. These slow fires were maintained until all indications of moisture disappeared, usually after 48 hours.\textsuperscript{54}

The next stage was critical and, if not executed carefully, would be responsible for many terracotta pieces becoming damaged. During this stage, the water smoking period, the heat was increased very slowly until all the combined water was expelled and any organic material burned out. Once this was accomplished, the kiln could be heated up as rapidly as desired; a too rapid rate was hardly possible because of the close setting of the large amount of ware in the kiln. Temperatures during this stage often ranged from 1100–1370°C and, depending on the size of the kiln, were maintained for 90–150 hours.\textsuperscript{55} An article in the \textit{Christian Union} implied that the Perth Amboy Terracotta Company had experienced problems during this phase of their virgin venture in the production of the terracotta for the Brooklyn Historical Society Building: ‘some of the work was so difficult to manufacture and bake without cracking.’\textsuperscript{56}

In cooling a kiln filled with terracotta a certain amount of care was necessary to avoid cracked ware. The critical stage in cooling the kiln was between the temperature of red heat and the point of darkness. As soon as the kiln was cooled to red heat, the damper in the stack and the fire boxes were tightly shut. At least a day before the kiln was emptied, the damper was drawn, the fire boxes opened and the wicket torn down. The wares were usually allowed to cool for 60 to 80 hours. In many plants a fan was connected to the kiln and cold air drawn through at this stage, in order to cool the kiln completely. On account of the long firing period, the slow cooling and the size of the kilns, firings did not occur more than two or three times a month. Once the terracotta pieces were cooled and removed from the kiln they were ready to be shipped to the site and installed.

\textbf{INSTALLATION AND POINTING}

Prior to 1885, terracotta was incorporated into a masonry building in one of two ways. In the first case, the terracotta pieces were masonry bonded into the wall and the blocks were backfilled with both brick and cement mortar to prevent crushing from the weight above. In the second method, the pieces were ‘hung’ on the wall. The hollow cells of the terracotta blocks were filled with mortar and pressed into place onto metal anchors,
which had previously been driven into the wall joints. The terracotta was held in place until the mortar hardened. These anchors, usually iron or steel, were coated with cement or asphalt in an attempt to prevent corrosion. In later years it was recommended that the pieces which were not backfilled, and thus subject to water penetration, be hung on bronze anchor rods. Bronze was chosen because of its apparent resistance to corrosion. The first system, of brick and cement backfilling, appears to have been the method used for the Brooklyn Historical Society Building. The few damaged pieces removed from the building were found to be backfilled with brick and a cementitious mortar. To date, no evidence of metallic fasteners has been observed or recorded.

Regardless of the method by which the terracotta blocks were incorporated into the masonry construction, joint location was always a major concern. There were two main reasons that prompted the careful planning of the joints. First, the majority of early architectural terracotta designs were intended to simulate stone. Since terracotta blocks were often smaller than stone, there were more joints, and efforts were made to hide as many of the extra joints as possible. Second, many designs included large sculptural areas, and in these areas all the joints were made to be as unobtrusive as possible by placing them at changes in the plane of the surface, thus hiding them behind the projecting piece. This process was referred to as ‘back-jointing’ or ‘back-checking’.

Additionally, joints were coloured so as to make them seem to ‘disappear’. Red terracotta joints were often coloured by the addition of red iron oxide pigment. Sometimes red bricks were very finely pulverised and combined with sand to obtain the requisite mortar colour.

Another consideration in the careful detailing of the joints was to ensure proper water shed from the building. For this reason, horizontal joints were given a variety of special treatments, projections were given drips, and raglets (grooves to receive flashings) were built into the blocks. In an effort to hide special horizontal joints from the ground, the outer edges of the joints might be given a cove.

The mortar used in setting terracotta was generally stronger and more waterproof than mortar for brick or stone masonry. Recommended mixes during the late nineteenth century ranged from cement:sand (1:2) to a mixture of cement:sand:lime (3:8:1). During the setting process, small wooden wedges might be placed in the joints to prevent the weight of the blocks from pushing the mortar out of the joint during set. At the Brooklyn Historical Society Building, slate shims were inserted for this purpose. After the blocks were in place, the joints were either tooled or raked out for later pointing. Joints on projections, parapets and other exposed areas were raked out and then filled with a waterproof cement following all other work on the terracotta.

The final procedure in the installation of architectural terracotta was surface cleaning. For exterior terracotta typical recommendations included: naphtha and a cloth; rinsing the facade with a dilute solution of either oxalic or sulphuric acid; or washing powder with stiff scrubbing brushes (not wire). In the early twentieth century, glazed surfaces were sometimes sandblasted to produce a matt finish.

**ANALYSIS AND CHARACTERISATION**

**Description**

The majority of the unglazed terracotta of the Brooklyn Historical Society Building is burnt red in colour and is used for the ornamental spandrels of the arcades, cornice, band courses between floors, the base course and the eight medallions from which project the various sculpted portrait heads. Additionally, a buff-coloured terra cotta was used to accent the bases and capitals of the two granite pilasters flanking the main entrance. Two previously detached samples of the red terracotta were provided for examination and laboratory treatment tests. These samples, a 380 x 150 x 150mm corner piece and its associated coping, measuring 250 x 225 x 200mm, were removed from the east corner of the pedimented clock tower on the north facade.

Exposed surfaces of both samples displayed the typical black soiling found on the brick and terracotta elements of the building. It is important to note that the terracotta on the Brooklyn Historical Society Building, outside of normal
weathering, has remained intact and virtually untouched; it has not been treated with chemicals or coatings, or experienced structural cracking or related failures. Moreover, because this terracotta is primarily, if not totally, masonry bonded, it does not exhibit the common problems and failures associated with corroding metal anchors. The terracotta itself, albeit soiled, appears to be in excellent condition.

The two pieces provided for testing revealed evidence of typical late nineteenth-century manufacturing techniques: hand-pressing the prepared terracotta clay into moulds and then removing excess material from the rear to create cells or pockets with web walls of 20-25mm thick. These cells aided in drying and firing, reduced the amount of clay used and weight of the piece, and provided a key for attachment to the building. Both sample pieces possess finger markings on their undersides, indicating hand processes. Voids ranging in size from 13-25mm appear periodically in each piece; these are the result of air pockets that were not eliminated when the clay was compacted into the moulds. A cross-hatched pattern, evidence of a final tooling before firing, textures the surface. The lines comprising the pattern are approximately 1.5mm apart and rise from the surface approximately 0.5mm. In accordance with contemporary practice, these pieces were inscribed with numbers while still wet, presumably as an aid to their correct installation. They were masonry bonded into the building; the cornice piece contains a common brick fragment embedded into five inches of cementitious mortar in the central cell. No evidence of metal anchors was observed.

Water absorption

The standard absorption value for unglazed terracotta usually ranges from 7%–11% as per tests run in accordance with ASTM C67. In this procedure, a sample is oven dried and weighed before being immersed for 24 hours in cold water and weighed again. The sample is then immersed for five hours in boiling water and weighed. The difference in weight before and after each immersion is calculated as a percentage of the original weight and indicates the amount of water absorbed. This test allows for no distinction between the water absorption of the fireskin versus the core. Since it is the fireskin that is primarily responsible for the weather protection of the material, measurement of the absorption of the fireskin alone is also important.

This was achieved by using the RILEM induction tube method developed for in situ surface measurement. The RILEM method uses a tube-like apparatus that has a flat, circular brim 25–38mm in diameter, which is affixed to the masonry. The vertical tube is graduated and the water level is periodically recorded over time and the percent absorption calculated. The average water absorption of the unsoiled fireskin was 0%; that is, no degree of water absorption could be measured in cc/min with this apparatus. The average water absorption of the core, however, was 6.2%. This figure is just below the range of water absorption cited for ASTM C67; thus indicating that the standard value is a result of water absorption primarily, if not totally, of the core.

Resistance to mechanical abrasion

Since the fireskin is the dense, water impervious barrier that protects the inner, more porous and permeable, terracotta core from many of the destructive agents of weathering, its resistance to mechanical abrasion is important. Once the barrier
of the intact fireskin is broken, the terracotta piece is vulnerable to decay. Application of the Rockwell Indentation Hardness test was attempted to measure the fireskin’s resistance to mechanical abrasion. The tests were carried out using a diamond pyramid bit as the indentor on the B scale (100kg load). The results of this test ranged from B11 to B44; the wide range of values was assumed to be due to the heterogeneous nature of the material. No further attempts were made to record or quantify abrasion resistance.

The microstructure of the core

A thin section of the terracotta surface and its associated core was prepared and its constituents examined using reflected and polarised light microscopy (Fig 6:3) and scanning electron microscopy (Fig 6:4). This examination revealed the terracotta to be a well-dispersed, multi-phased mixture of a fine-grained red clay matrix with vacuoles and larger particles of quartz, feldspar and grog, ranging from very fine to rather fine in size. A 1.6mm square area was closely examined and analysed for qualitative and quantitative characterisation using polarised light microscopy (Fig 6:3). The area was also mapped to determine the location and percentages of the major constituents and features.

Of the area examined it was determined that approximately 7% consisted of vacuoles or voids. The size of the voids was determined to be in the range of 0.3–0.8mm. The particles identified as quartz and feldspar were approximately 13.6% of the terracotta body. The particle size ranged from 0.2–0.8mm, with a few larger particles measuring approximately 0.9mm. Periodic cooling cracks were observed around the quartz particles. These cracks accommodate the change in crystalline form of the quartz that occurs at approximately 573°C. As the terracotta body cools, the partially dissolved quartz solidifies and cracks result in the material immediately surrounding the quartz particles.

The size of the grog ranged from 0.2–0.8mm with a few large pieces measuring approximately 1mm. The grog comprised approximately 16% of the material. As cited previously, the reported amounts of grog in terracotta by the industry in the late nineteenth century ranged from 10%–50%. In the twentieth century, much attention was devoted to the issue of the size and amount of grog. The optimal range of grog per mixture was determined to be generally 25–30%, although it varied slightly from clay to clay. The percentage in the sample area was lower than this prescribed range and may be due to the heterogeneous nature of the material and the sample size. Since the Brooklyn Historical Society Building was the first commission for the Perth Amboy Terracotta Company, an intimate knowledge of the clay and the manufacturing process might not yet have been established when the terracotta examined in these tests was made; hence, the contemporary report that many pieces cracked during manufacturing and much of the work had to be repeated.

The microstructure of the fireskin

It is the dense, glassy fireskin that renders unglazed terracotta impervious to moisture and thus restricts many of the deterioration mechanisms that depend on the presence of moisture. The fireskin is a rigid, coherent framework that is formed by the diffusional sintering (or vitrification) of the clay grains during firing. Diffusional sintering is defined as the process where an assembly of fine particles of a dispersed system undergoes spontaneous strain which results in a densification of the particle assembly. This usually occurs when the heated
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Fig 6:5 Terracotta, fireskin cross-section from the Brooklyn Historical Society (160x, SEM). Arrows indicate approximate thickness of fireskin (24–32 microns) visible as a densified zone.

range is 40–85% of the temperature that causes the material to melt. Densification occurs as a result of mass transfer from the grain contact points to the pores, which causes the particle centres to come closer together and a transfer of mass due to mutual sliding of the particles. The result is a change of geometry of the grains and pores. Scanning electron microscopy (SEM) was used to examine the micromorphology of the fireskin.

SEM combines the advantages of high magnification with sufficient depth of field to allow detailed examination of heterogeneous and porous materials. The terracotta samples were examined under SEM to determine specific physical characteristics believed significant for durability and performance: the extent of vitrification, the pore structure of the core and the fireskin, and the depth of the fireskin. In addition, sample surfaces were examined both before and after cleaning tests to ascertain the physical effects (if any) of the treatments on the soiling and the substrate.

The terracotta samples were also examined in polished cross-section. In the fireskin region grain-to-grain contact was observed and the density of the grains was found to be markedly higher than in the core (Figs 6:5, 6:6 and 6:7). Additionally, glassy filaments were present but the fireskin did not exhibit a continuous glassy phase, thus suggesting a low to moderate vitrification. The thickness of the fireskin ranged approximately from 24–32 microns, judging from the visible densification of the upper zone (Fig 6:5). The fireskin tended to be more homogeneous than the core: the pores of the fireskin were round and not interconnected, probably resulting from trapped gas that was not evacuated during sintering (Fig 6:6). The pores occurred more frequently in the core than in the fireskin and were amorphous and often interconnected. These pores are gaps between grains and tend to be larger than those located in the fireskin region (Fig 6:7).

Fig 6:6 Porosimetry of terracotta fireskin, cross-section (2500x, SEM). Note small, round, isolated pores and dense matrix.

Fig 6:7 Porosimetry of terracotta core, cross-section (2500x, SEM). Note larger, irregular, interconnected pores.
TEST PROGRAMME OF CLEANING SYSTEMS

Cleaning considerations

The decision to clean a building is one that needs to be considered carefully, whether it is to be performed as a single activity or as part of a larger conservation programme. While cleaning may remove soiling or staining that is unsightly and contributing to surface decay, the process of cleaning itself may cause other types of deterioration. Residual salts from chemical cleaning may be introduced into the masonry causing latent staining or spalling, excessive moisture applied to the substrate may mobilise existing soluble salts and other organic compounds, and mechanical cleaning may cause irreparable changes to the microstructure of the substrate. It is therefore imperative that before cleaning occurs, a full assessment of the problems is undertaken and both the advantages and risks of each cleaning option are considered.

The most common and valid reasons for cleaning are: to re-establish the original appearance, taking into consideration the difference between the natural aging of the surface (patina) and the undesirable soiling or staining; to allow or facilitate an inspection of the building’s condition; to assist in prevention or reduction of further chemical and mechanical deterioration; and to prepare the surface for other treatments such as consolidation, water repellents and repairs.

Development of a proper cleaning programme for any masonry building, and particularly terracotta, must include consideration of the following:

1. Building material. Physical, mechanical and chemical properties of terracotta (eg microstructure, condition of fireskin, colour, texture, glazes, production marks).
3. Cause of soiling. The soiling may only be symptomatic of the problem and will re-occur if the necessary corrective measures are not taken (eg efflorescence indicative of moisture penetration into structure).
4. History of the structure. Previous repair and cleaning campaigns, surface coatings, sealants that may affect the present cleaning campaign.
5. Building construction. Certain details inhibit the success of certain cleaning methods; embedded anchors may be susceptible to various cleaning agents.
6. Safety considerations. Waste disposal, application hazards to workers, the public and the environment.
7. Location. The structure’s location and ground plot, effect on neighbouring structures, nearby industry, weather and wind patterns that may affect application or drying procedures, etc.
8. Seasonal restrictions. Wet cleaning should be undertaken in warm, dry weather to allow for sufficient ‘dry time’ to alleviate the multitude of moisture-related decay processes (eg wet/dry, freeze/thaw cycles).
10. Feasible products and processes available. Reversibility/retractability; advantages and disadvantages; applicability on a large scale; results of laboratory and small-scale site testing; compatibility with the above cited considerations.

REVIEW OF AVAILABLE METHODS OF CLEANING

The following provides an overview of the commercial cleaning methods frequently used for historic masonry and in particular, architectural terracotta. These were all considered as potential methods for cleaning the unglazed terracotta of the Brooklyn Historical Society Building.

Water cleaning

Water cleaning is often cited as the gentlest means available for cleaning structures. The National Park Service states, “water methods generally are the simplest to carry out, the safest for the building and the environment, and the least expensive.” Water washing can consist of
water soaking, a continuous or intermittent spraying with a fine nebulised mist (for several hours) or pressure washing at low (20–100psi) or medium (100–600psi) pressures.

Water cleaning is effective on soiling that adheres to the masonry surface by secondary bonding (i.e., the soiling is not chemically bonded to the surface). Water cleaning is also effective if the soiling is soluble in water. However, this type of soiling will occur only in areas of the building not exposed to periodic washing by precipitation.

It is important to realise that although some types of masonry may benefit from frequent water washing, others do not. Frequent washing of some of the harder siliceous stones including granite and some sandstones, as well as brick and terracotta, is not beneficial, since water alone is not effective for cleaning most siliceous surfaces and it is not easily evacuated once it penetrates below the surface. The opposite is generally true of calcareous stones such as limestone and marble.

Steam cleaning

Steam cleaning, another water-based cleaning method, was used extensively during the mid-twentieth century. Reasons for its present drop in popularity vary: often cited are the increased sophistication and successful marketing of chemical methods; the reported hazards of hot steam; and the residual damage left by the caustic soda that is often used as a water softener.

The procedure involves heating the water in a flash boiler and directing the heated water at the masonry surface with the use of a low-pressure nozzle, generally with a 13mm diameter aperture. The heat of the steam swells and softens the soiling and the low pressure hot water mechanically removes the loosened soiling from the masonry surface.

Steam is useful as a support method for removing greasy deposits or organic coatings such as waxes with low melting points. It may be preceded by manual scrubbing using a non-ionic detergent or low-concentrate chemical-based cleaner. Steam provides little or no advantage when used in conjunction with an acidic masonry cleaner. It is often followed by a low-pressure water rinse for more effective cleaning results. Steam cleaning is also used to remove vines and other vegetation clinging to masonry surfaces, for cleaning building sections that are difficult to reach and highly ornamental elements.

Detergents

Detergents are defined as synthetic organic compounds that are chemically different from soaps but able to emulsify oils, hold dirt in suspension, and act as wetting agents. The surface tension of water can be dramatically reduced by the addition of a small amount of detergent or other surface active agent. Thus hydrophobic surfaces can be made to act as though hydrophilic. Most detergents are derived from carboxylic acid and contain a long hydrocarbon chain of more than a dozen carbons. A detergent generally contains polar and non-polar ends. The polar end of the molecule allows the detergent to be soluble in water while the non-polar end (the hydrocarbon chain) is soluble in 'grease' (soiling primarily formed by organic compounds). Since like substances dissolve like substances, the 'grease' becomes attached to the non-polar ends of the detergent and is pulled into solution. In other words, the concentration of detergent molecules around a soil particle helps to reduce the forces of adhesion between the particle and the masonry and insoluble soiling is held in suspension and carried away by the detergent. The detergent is important for this function but often chelating, sequestering, and complexing agents are added to improve its effectiveness.

There are four basic classifications of detergents. These classifications depend upon the nature of the electrically charged groups within their molecules. They are: anionic (electrically negative hydrophobic ions), cationic (electrically positive hydrophobic ions), non-ionic (electrically neutral), and amphoteric (electrically positive or negative, depending on the pH). Non-ionic detergents are preferred in masonry cleaning, since they generally provide better surface wetting and are more easily removed from the masonry surface. Non-ionic detergents do not leave cations or anions on the surface when removed, whereas ionic
detergents may leave a charged surface which can attract soiling. Since detergents, by nature, are polar, their removal from the surface on which they are acting can be difficult. As non-ionic detergents are polar enough to be soluble in water, they are not as difficult to remove from the surface as ionic ones.

Detergent cleaning of non-polished surfaces is often assisted by scrubbing the surface with a non-metallic soft bristle brush. This will ensure that the detergent solution gains access to all portions of the textured surface and assists in lifting the soiling into suspension. It is vital that the surface be thoroughly rinsed clean of the detergent solution. If a detergent film is left on the surface, it will attract dirt to the surface by nature of its polarity.

**Chelating agents**

While detergent polarity is exploited to break the bond between the soiling and the surface, complexing (or co-ordinating) agents are used to break other bonds. These bonds are the primary bonds between the metallic atoms and the organic molecule in the soiling compounds. Complexing agents can form a soluble complex from an insoluble compound. One type of complexing compound is a chelating agent. Chelating agents contain polar molecules with two strong negative parts that tie electrostatically onto particular metallic ion types and still remain soluble in water. Therefore a chelating agent can be used to break the bonds of insoluble soiling involving metals and form a soluble complex that can be washed away with water. However, technically the breaking of atomic bonds is a simple definition of a chemical reaction, and one must ensure that the chemical reaction is directed only at the soiling, and not at the substrate.

One of the most popular chelating agents used by conservators is ethylene diaminotetra-acetic-acid (EDTA). EDTA is a white anhydrous crystalline solid which is almost insoluble in water (0.5g/L), and readily soluble in alkaline solutions. EDTA forms strong complexes with almost all di- and trivalent atoms and with calcium and magnesium complexes, depending on the pH of the solution which determines the free anions and the type of complex which is preferred.

Chelation is the formation of a complex involving a multidentate organic anion and a metallic atom. These reactions on solid soiling are slow because they must generally pass from solid to liquid through hydration, dissolution, migration through diffusion, etc, and that takes time. Most treatments must remain on the surface for a minimum dwell time of several hours. As a result, most chelating-based cleaners are formulated to contain suitable fillers to produce a paste or gel. Sodium carboxymethyl-cellulose (Na CMC) is one such filler, widely used to produce gel formulations. In addition to thickening the solution, it holds the lifted dirt and thus prevents resoiling of the surface. Resoiling due to redeposition of the dirt can often be more difficult to remove than the original soiling.

**Acidic cleaners**

Acidic cleaners are aqueous solutions that chemically react with the soiling and masonry to affect the interface between the soiling and the substrate. Acidic cleaners may contain varying combinations of acids which include hydrofluoric acid (HF), phosphoric acid (H₃PO₄), Hydrochloric acid (HCl), sulphuric acid (H₂SO₄) and nitric acid (HNO₃); and organic acids such as citric, acetic and oxalic acid. Acidic cleaners should never be used on masonry materials containing carbonates. These are highly reactive to acids, which will damage the masonry by dissolving the surface and widening pores, cracks and joints.

The acid most commonly used in commercial cleaners designed for siliceous masonry is hydrofluoric acid. Since this removes soiling by dissolving the silicates on the surface, effective cleaning depends on dilute concentrations and short dwell times to alleviate extensive attack to the masonry. 80

Acetic acid is also commonly used in masonry cleaning products. This is a weak organic acid and it is commonly used as a neutralising agent following alkaline treatments. Diluted, it has been used to clean carbonate stones and other masonry. It attacks and dissolves more slowly than strong mineral acids.
Alkaline cleaners

Alkaline solutions are used for soiling, paint and other organic coating removal. Alkalis can be used on materials that contain carbonates, such as marbles and limestones, that are readily dissolved by acidic cleaners. Alkaline cleaners usually consist of two ingredients: a detergent (or surfactant) and an alkali, usually potassium hydroxide or sodium hydroxide. Most alkalis neutralise acidic soils and saponify greasy materials.

Sodium hydroxide (caustic soda, lye) is typically used as a primary ingredient in alkaline cleaners. Sodium hydroxide is an extremely strong base and can effectively hydrolyse oil stains, (ie break the bonds of the oil molecules and introduce water molecules). Often, however, it cannot be effectively neutralised, especially when used on porous materials. The main concern with sodium hydroxide is its high solubility and the introduction into the masonry of sodium ions which can react with the substrate and cause destructive salt efflorescences. This efflorescence or subflorescence is extremely difficult, if not impossible, to remove. Therefore, the use of sodium hydroxide is recommended only on relatively non-porous materials.

Mechanical/abrasive cleaning

Most cleaning techniques termed 'mechanical' remove soiling from the substrate by abrading its surface. This usually involves arranging a collision between the soiling and some other material to produce a force which will break the adhesion between the soiling and the substrate and move the soiling away from it. It is important that the break occur at the interface between the surface and the soiling, and not below the surface. Thus the problem with mechanical cleaning is essentially one of control. Since it is often difficult, if not impossible, to distinguish the interface between the soiling and substrate at the macroscopic level and then to control the equipment to this precise degree, mechanical cleaning techniques are generally not recommended for overall cleaning of historic masonry, and especially for fired materials such as brick or terracotta with their thin, vulnerable, fireskins or glazes.

SOILING CHARACTERISATION

Much of the exterior masonry of the Brooklyn Historical Society Building is blanketed by a black, pollution-related carbon soot soiling. These deposits are heaviest in protected areas, such as in the relief work and under projecting elements. Heavy guano deposits also occur on the second-storey portrait heads, architrave keystones and the second-storey cornice ledge, these being favourite roosting areas for pigeons. Isolated patches of efflorescence are visible on the brickwork, especially where the head joints are open and the water has penetrated the building envelope.

A review of historical photographs of the exterior of the building suggests that as early as 1882 the terracotta on the north and east elevation already displayed efflorescence and by 1926 the terracotta exhibited dark differential staining, especially on the string course, archivoltas and cornices. A comparison of views taken in 1926 and 1991 (65 years apart) and 1981 and 1991 (10 years apart) suggests that the soiling patterns on the building were established early on and have naturally and gradually worsened.

The majority of the soiling present on the unglazed terracotta of the Brooklyn Historical Society Building is predominantly a carbonaceous surface deposit produced by the combustion of fossil fuels (Fig 6:15).81 The pH of the soiling on the surface of the terracotta samples was found to be neutral (7.0–7.1). Recent comparative analysis of urban grime conducted in six major cities82 has yielded similar results.

The existing literature suggests that the safe removal of such soiling from brick and unglazed terracotta surfaces is notoriously difficult. This difficulty may be attributed to a residue of reactive silica left on the surface during the long burn in the manufacturing process, which bonds with the airborne particulates associated with pollution-related urban grime.83 As a result, the soiling becomes chemically bonded to the terracotta surface. Removing all of the soiling evenly without damaging the terracotta is a difficult task at best, and perhaps an impossible one.84 One primary goal of this project was to ascertain which cleaning techniques effectively removed hydrocarbon soiling without altering the physico-mechanical properties of the terracotta, especially the fireskin.
Plate 1. Severe decay due to salt crystallisation and frost damage on this poorly fired bracket has caused surface exfoliation, powdering and loss of integrity. See also Fig 1:7, p14

Plate 2. In areas of heavy wear the coloured clay inlays of encaustic tiles are eventually worn away. This raised walkway at St George's Hall, Liverpool, has taken wear from foot traffic for 140 years. See also Fig 4:1, p40
Plate 3. Terracotta, core cross-section from the Brooklyn Historical Society (25x, cross-polarised light). Microstructure contains voids (1), quartz/feldspar (2) and grog (3) within a fine red clay matrix. See also Fig 6:3, p66.

Plate 4. Typical Moderate soiling conditions of samples before all cleaning tests. See also Fig 6:8, p74.

Plate 5. Results after commercial hydrofluoric acid-based aqueous cleaning. Note immediate removal of soiling after first application (numbers indicate applications). See also Fig 6:9, p74.

Plate 6. Results after commercial alkaline aqueous cleaning. Note poor soiling removal. See also Fig 6:10, p75.
Plate 7. Results after steam cleaning. Note poor soiling removal. See also Fig 6:11, p75

Plate 8. Results after dry glass powder and air abrasion. Soiled areas masked during test. See also Fig 6:12, p76

Plate 9. Before detergent-chelating gel cleaning. See also Fig 6:13, p76

Plate 10. Results after detergent-chelating gel cleaning (Formulation C). Note good removal after first application (compare with Plate 9). See also Fig 6:14, p77
Plate 11. Tile with Italianate design. See also Fig 11:5, p115

Plate 12. Lincolnshire College of Art: detail of carved brickwork tympanum and part of frieze. See also Fig 13:2, p123
TESTING PROGRAMME

In addition to the obvious visual and aesthetic evaluation of commonly-used cleaning methods, the effect of cleaning materials and techniques on the fireskin has been a primary focus of this cleaning treatment evaluation programme. Since buildings are often cleaned several times during their lifespan, the laboratory testing programme was also designed to evaluate the effects of the cleaning systems on the fireskin after repeated applications. To evaluate these effects, examination was conducted before and after each application of each cleaning system. Techniques were chosen that provided a means of observing and recording alterations in what were identified as critical physical and mechanical properties of the unglazed terracotta surface. These were: visual changes in colour and light reflectance, changes in surface water absorption, resistance to mechanical abrasion, and pore structure and density.

Only the observed alteration of the microstructure and density using scanning electron and light microscopy are reported in this paper.55

CLEANING SYSTEMS TESTED

After an extensive literature search and interviews with technicians in the building cleaning industry as well as architects and conservators, five typical and current cleaning systems designed for or used on terracotta were chosen for testing. They were:

Commercial acidic cleaners

Research suggested that many unglazed terracotta buildings56 have been cleaned with commercial hydrofluoric acid-based cleaners as recommended by the cleaning industry. This is the system most commonly used.

Commercial alkaline cleaners with acidic afterwash

The alternative system also recommended by the industry uses a strong alkaline salt, usually sodium hydroxide, with a hydrofluoric or acetic acid afterwash.

Steam cleaning

The use of steam cleaning for terracotta elements has been reported in the literature, albeit infrequently.57 Steam has also been used to clean unglazed terracotta objects and archaeological artefacts.58

Abrasive cleaning

Abrasive cleaning using a wide range of natural and synthetic aggregates and applied in a stream of pressurised air or water, has been used both to clean and to factory-finish terracotta since the late nineteenth century. Although abrasive cleaning has generally been found to be damaging to brick and terracotta, a patented abrasive cleaning process developed by Thomann-Hanry Inc59 was included in the test programme.

This system is based on a low pressure, air-driven powder of pulverised neutral glass gauged at 15, 25 or 50 microns. Cleaning is done by ‘buffing’ rather than impactive abrasion as the steady mix of powder and air circulates against the building surface. This system is relatively new on the US market but has been employed for over 25 years in Europe. However, no specific information concerning the cleaning of unglazed terracotta was available from the manufacturers.

Detergent emulsions60

The following detergent emulsions were custom-formulated for the removal of the hydrocarbon soiling:51 alkaline with an abrasive filler; acidic; chelating agent (EDTA ‘Versene’) with alkaline additives.

Once the evaluation techniques were determined and the cleaning methods to be tested chosen, the necessary terracotta samples were prepared.

SAMPLE PREPARATION

Two pieces of exposed and variably soiled unglazed terracotta from the Brooklyn Historical Society Building, a cornice segment and its coping, were provided for testing. The cornice segment was used for preliminary testing. One half of the
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Fig 6.8 Typical moderate soiling conditions of samples before all cleaning tests (Colour Plate 4)

coping was cut into eleven pieces using a large, stone-cutting saw at the Geology Department, University of Pennsylvania. Each piece contained approximately 70mm² of fireskin surface area. The other half of the coping became the control (Fig 6:8). Each sample was numbered according to its place of origin, its number in the sample series, and the method by which it was cleaned (eg BHS-01-ST. Origination of sample: BHS = Brooklyn Historical Society; sample number (01-11): 01 = first sample; cleaning method tested: ST = steam)

The samples were distributed and numbered as follows:

- Control: BHS-control
- Steam: BHS-01-ST
- Acid: BHS-02-AC, BHS-03-AC, BHS-04-AC
- Alkali: BHS-05-AK, BHS-06-AK, BHS-07-AK
- Detergent: BHS-08-DT, BHS-09-DT, BHS-10-DT
- Dry powder: BHS-11-DP

Initial measurements of absorption, resistance to mechanical abrasion, and pH readings were recorded. Two pieces of each sample, approximately 6mm cubes, were mounted in epoxy for scanning electron microscopy. The first piece intended for surface viewing was mounted exposing its fireskin surface and coated with a thin layer of gold. The second piece, intended for cross-section SEM examination, was embedded in epoxy, cross-sectioned perpendicular to the fireskin surface, polished and gold-coated.

CLEANING TESTING PROGRAMME PROCEDURES

Once the samples were prepared the following testing procedures of the five cleaning systems to be evaluated were conducted.

Commercial hydrofluoric acidic cleaner (Fig 6.9)

Samples Tested: BHS-02-AC, BHS-03-AC, BHS-04-AC

Each sample was divided into three sections. The first section of each sample was subjected to one application of the acidic cleaner (see below for procedure). The second section was subjected to two applications and the third section subjected to three applications. This was accomplished by using a strippable masking manufactured to protect glass and other building materials from masonry cleaning solutions. The entire surface of each sample was treated on the first application. Prior to the second application of the acidic cleaner, the first section was covered with the strippable masking. The second application of the acidic cleaner was applied to the remaining two-thirds. Prior to the third application, section two was masked with the strippable masking and
Fig 6:10 Results after commercial alkaline aqueous cleaning. Note poor soiling removal (Colour Plate 6)

the third application applied to the remaining one-third of exposed surface. After the completion of the third application, the strippable masking was removed and visual differences between the campaigns were noted.

Samples for SEM surface examination and cross-section examination were taken after each application.

Commercial alkaline cleaner (Fig 6.10)

SAMPLES TESTED: BHS-05-AK, BHS-06-AK, BHS-07-AK

The samples were divided into three sections. The first section was subjected to one application of the alkaline cleaner (see below for procedure), the second section to two applications and the third section to three applications. The masking method was the same as outlined previously.

The product literature recommends that the sodium hydroxide-based cleaner, when used on terracotta, brick, and sandstone, be neutralised with a hydrofluoric acid-based afterwash. When using the sodium hydroxide-based product on limestone, cast stone or cementitious material the recommended neutralising product is an acetic acid-based product. Since samples BHS-02-AC, BHS-03-AC and BHS-04-AC would give a clear indication as to the effectiveness of the hydrofluoric acid cleaner, it was decided not to use a hydrofluoric acid-based neutraliser but rather the acetic acid-based neutraliser. There were two reasons for this choice: to ensure that the sodium hydroxide (and not the hydrofluoric acid-based afterwash) was the primary cleaning agent, and also to compare the effect of an organic acid (acetic acid) on the terracotta surface with that of a mineral acid (hydrofluoric acid).

Samples for SEM surface examination and SEM cross-section examination were taken after each application. After the third application the strippable masking was removed and visual differences between campaigns were noted.

Steam cleaning (Fig 6.11)

SAMPLE TESTED: BHS-01-ST

The sample was divided in half and two methods of steam cleaning were tested at the Conservation Department at The Philadelphia Museum of Art. The first test was carried out using a small, hand-held 240 volt steamer. The maximum pressure of the steam was 5 bar (approx. 75 psi) and the steam reached temperatures of 130°C. The second system was a large industrial hot water and steam cleaner manufactured for cleaning buildings. The maximum operating pressure was 3000 psi with temperatures reaching 93°C. Both systems were tested since they each offered different advantages. The hand-held steamer allowed for a closer working distance and more control, as well as higher temperatures, while the industrial steamer offered higher water pressure.

The first half of the sample was cleaned with the hand-held steamer. It was subdivided into
three sections for dwell times of 15 minutes, 30 minutes and one hour with a working distance of 25–50mm.

Samples for SEM surface examination and cross-section examination were taken and visual differences in campaigns were noted.

Before the industrial steamer was tested, the half of the sample tested with the hand-held steamer was masked with a monofilament adhesive tape. The remaining half of the sample was divided into three sections. The sample was clamped to a table. The high pressure hot water and steam was applied for 10 seconds, 30 seconds and 45 seconds. The working distance was approximately 1m.

Samples for SEM surface examination and cross-section examination were taken and visual differences in campaigns were noted.

Patented ‘dry powder’ abrasive cleaning (Fig 6:12)

Sample tested: BHS-11-DP

The sample was given to Thomann-Hanly Inc for testing. The sample was divided into five sections. Two areas were taped in order to provide two uncleaned control areas. The sample was cleaned using a 40 micron glass powder applied at 50 psi.

Additionally, samples were taken from various areas for both surface and cross-section SEM examination.

Detergent-based cleaners (Figs 6:13 and 6:14)

Samples tested: BHS-08-DT, BHS-09-DT, BHS-10-DT

As indicated previously, three detergent formulations were developed for testing specifically to meet the needs of removing the soiling. These formulations were as follows:

A. Sodium Hydroxide (NaOH) (Fisher)
   - alkaline reagent
   - CARBOPOL 954 (B.F. Goodrich)
   - gelling agent
   - Sodium Metasilicate, Anhydrous (Na₂SiO₃) (Aldrich) — mildly alkaline pH stabilizer
   - Aluminium Oxide, 5.0 Micron (Al₂O₃) (Leco) — abrasive filler
   - Triton X-100 (Sigma) — non-ionic detergent; releasing agent

B. Hydrochloric Acid (HCl) (Fisher)
   - acidic reagent
   - Methyl cellulose, 4000 cp (Sigma)
   - gelling agent; suspends soiling
   - Sodium Metasilicate, Anhydrous
   - alkaline pH stabiliser
   - Triton X-100 — non-ionic detergent; releasing agent

C. Sodium Hydroxide (NaOH) (Fisher)
   - strong alkali reagent; slightly abrasive
   - Sodium Tetraborate(Na₂B₄O₇(10H₂O)) (Fisher)
   - alkaline reagent
   - Versene (EDTA) (Dow) — chelating agent
Sodium Metasilicate, Anhydrous
- mildly alkaline pH stabiliser
Triton X-100 – non-ionic detergent;
releasing agent
Polyacrylamide/polyacrylic acid (40% Acrylic acid; 1x107 MW)(Poly Sciences Inc)
- gelling agent

Initial testing of these formulations was performed on the cornice piece. Dwell times of 2 minutes, 20 minutes, 1 hour, and 24 hours, with scrubbing for one minute before removal, were tested. In all cases formulation C proved to be the most effective. Therefore further testing with formulation C was executed as follows.

Samples BHS-08-DT and BHS-09-DT were divided into three sections. The first section was subjected to one application of the detergent cleaner (see below for procedure), the second section to two applications and the third section to three applications. The masking method was the same as outlined previously for the acidic and alkaline applications. After the completion of the third detergent application, the strippable masking was removed and visual differences between campaigns were noted.

Since the detergent gel formulation tended to creep on vertical surfaces, the thickening agent, Polyacrylamide/polyacrylic acid, was eliminated and the solution applied to sample BHS-10-DT in a poultice form using kaolin clay.

Scanning electron microscopy was used to study the microstructure of the terracotta before and after the application of the various cleaning systems. Specifically, any changes in the micromorphology and density of the fireskin were examined both on the surface and in cross-section. The results were compared against a control sample displaying typical soiling (Fig 6:15) and were observed as follows:

Commercial acidic cleaner
1st application (Fig 6:16)
- some soiling particulates still visible on the surface
- chemical abrasion of the fireskin evident
- partial dissolution of the glassy plate structure of the fireskin
- pore size increased and became irregular in shape
- some pores became interconnected.
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Fig 6:16 Results after commercial hydrofluoric acid-based aqueous cleaning, 1st application. Surface (2500x, SEM). Note reduction of soiling, partial erosion of glassy plates, and interconnection of pores (compare with Fig 6:15)

2nd application (Fig 6:17)
- fewer soiling particulates visible on the surface
- obvious chemical abrasion of the surface
- increased dissolution of the glassy plates
- pores larger and more irregular
- new pores created.

3rd application (Figs 6:18 and 6:19)
- no soiling particulates observed
- increased dissolution of the glassy plates

Fig 6:17 Results after commercial hydrofluoric acid-based aqueous cleaning, 2nd application. Surface (2500x, SEM). Note further reduction of soiling, greater erosion and etching of glassy plates, and increase in pore size and interconnection

Fig 6:18 Results after commercial hydrofluoric acid-based aqueous cleaning, 3rd application. Surface (2500x, SEM). Note continued erosion and etching of glassy matrix and cracking around pores (arrows)

- pore size greatly increased, more irregular, interconnection of pores
- pore structure interconnected to core
- cracks developed around pores
- optical surface of the fireskin modified.

The commercial acidic cleaner removed soiling, altered the optical properties of the surface to give a flat, dead appearance; caused dissolution of the substrate and pitting and cracking of the

Fig 6:19 Results after commercial hydrofluoric acid-based aqueous cleaning, 3rd application. Surface (640x, SEM). Note overall enlarged and interconnected pores (arrows) (compare with Figs 6:15 and 6:31)
Fire skin; increased and significantly changed the pore structure of the sample.

*Commercial alkaline cleaner*

1st application (Fig 6:20)
- even layered particulate soiling still visible
- slight surface change of soiling particulates
- soiling obviously attacked, rough texture.

2nd application (Fig 6:21)
- soiling broken up and more loosely attached but still visible.

3rd application (Figs 6:22 and 6:23)
- layered, film-like soiling evenly covering surface still visible
- rounded edges of soiling indicate soiling barely altered
- fire skin (what could be examined through the remaining soiling) not affected.

The use of commercial alkaline cleaner achieved minimal, ineffective removal of soiling, with no apparent alteration of the fire skin.
Steam cleaning (Figs 6:24 and 6:25)

- soiling remained packed onto the surface
- fireskin could not be evaluated (too much soiling still present)

Steam cleaning resulted in very little, if any, movement of soiling; the condition of the fireskin could not be evaluated, but was probably unaffected.

Fig 6:24 Typical soiling before steam cleaning. Surface (2500x, SEM)

Fig 6:25 Results after steam cleaning. Surface (2500x, SEM). Note soiling eroded but still present, obscuring terracotta (compare with Fig 6:24, 6:18 and 6:22)

Patented 'dry powder' abrasive cleaning (Figs 6:26, 6:27 and 6:28)

- majority of soiling removed except in pits
- severe abrasion of surface and particulates
- pitting and cracking of the surface
- residue and embedding of dry powder and abraded particles
- fireskin matrix displayed sharp and broken edges

Fig 6:26 Results after dry glass powder air abrasive cleaning. Surface (2500x, SEM). Note all soiling removed and the creation of sharp-edged fractures and pitting (compare with Figs 6:18, 6:22 and 6:25)

Fig 6:27 Results after dry glass powder air abrasive cleaning. Surface (160x, SEM). Note overall abraded and pitted surface
Fig 6:28 Results after dry glass powder air abrasive cleaning. Cross-section (80x, SEM). Note impacted glass fragment from cleaning

- pore size increased
- new pores created
- optical qualities of the fireskin significantly altered

'Dry powder' abrasive cleaning removed the majority of soiling but caused severe abrasive damage to the fireskin and modified the optical properties of the surface.

Detergent-based cleaner with chelating agent

1st application (Figs 6:29 and 6:30)

Fig 6:29 Soiling condition before detergent-chelating gel cleaning. Surface (2500x, SEM)

Fig 6:30 Detergent-chelating gel cleaning. 1st application. Surface (2500x, SEM). Note soiling reduction (compare with Fig 6:29)

- modest removal of soiling
- surface even and undamaged
- pores round, isolated and not enlarged.

2nd application

- increased removal of soiling
- glassy plates intact (rounded and undamaged)
- pores intact, rounded, isolated, not enlarged.

3rd application (Fig 6:31)

- majority of soiling removed
- glassy matrix of fireskin visible and intact
- particles rounded and intact

Fig 6:31 Detergent-chelating gel cleaning. 3rd application. Surface (640x, SEM). Note intact glassy matrix of the terracotta (compare with Figs 6:19, 6:23 and 6:27)
- pores rounded, isolated, not enlarged
- optical surface of fireskin not altered.

The detergent-based cleaner with EDTA effectively removed the soiling with repeated applications. The glassy matrix, pore structure and thickness of the fireskin remained intact; the optical properties of the terracotta remained unchanged.

*Site tests*

In addition, site testing was conducted to evaluate the response of the cleaning methods deemed most appropriate as a result of the laboratory study. Three methods were employed on site: a commercial alkaline cleaner, and the custom-formulated detergent chelating gel.

The site tests corroborated the results observed in the laboratory cleaning tests. Satisfactory and even removal of typical soiling was achieved only with the detergent chelating gel formulated from the following: Water; 50% NaOH (ml); Polyacrylamide/polyacrylic Acid (40% Acrylic Acid. 1x10^6 MW) (g); Na Tetra Borate (g); Na Meta Silicate (g); Versene (39% EDTA) (ml); Triton X-100 (ml).

**SUMMARY CONCLUSIONS**

Any assessment of cleaning techniques based solely on the criterion of visual improvement through the removal of unwanted soiling, no matter how carefully measured, must be considered inconclusive, especially as it relates to the potential alteration and possible damage to the substrate. Most chemical and mechanical cleaning techniques affect physico-chemical alterations to porous materials; yet issues of alteration have been insufficiently studied or reported in general, especially as they affect long-term appearance, durability and overall performance of the masonry substrate. This has been particularly true for brick and terracotta substrates, whereby the use of poorly assessed cleaning methods has resulted in irreversibly altered and damaged surfaces. As a result this study has focused on the physical effect of cleaning techniques on unglazed terracotta rather than on the more commonly considered issues of soiling removal efficacy.

It is evident from scanning electron micrography that the microstructure of the fireskin of unglazed terracotta undergoes definite alteration with commonly recommended commercial hydrofluoric acid-based cleaners and low-pressure mechanical cleaning techniques, both marketed for general masonry conservation use. The morphological changes in the terracotta microstructure – increased pore size and interconnection – that these systems produced suggest a potential increase in water absorption which could lead to greater mechanical and chemical damage as a result of repeated applications of these cleaning techniques and/or prolonged weathering, such as freeze-thaw cycling. Repeated cleaning using these systems could immediately or eventually lead to material failure, largely from the infiltration of water and chemical agents through the damaged fireskin and with it the formation of destructive soluble salts, ice, and biological growth. Given the lack of conclusive data obtained from the physical test programme during this study, further studies are under way to quantify these predicted changes before and after cleaning, especially in terms of water absorption and surface hardness, as a result of microstructural alteration.

Nevertheless, the present study suggests that the widespread use of commercial hydrofluoric acid-based cleaning methods for terracotta should be carefully reconsidered. Micro-cracking, pore enlargement, and an increase in surface area with the reduction of the thickness of the fireskin could spell future disaster under even normal weathering conditions. Other techniques, namely aqueous alkaline and detergent-based systems, did not appear to alter surface structure; however, varying degrees of soiling removal were observed. Whereas effective cleaning with alkaline systems alone was limited, cleaning with a custom-formulated detergent-chelating gel produced good results with effective removal of particulate soiling and no observable physical change to the protective fireskin.

In order to better understand and differentiate between benign or acceptable surface alteration (patina) and soiling and surface decay of terracotta, further research is urgently needed. Quantification of changes in both physical and mechanical
properties as related to the observed alterations to the microstructure should be pursued, as well as chemical studies of surface reactivity and chemical alteration of the substrate before and after cleaning. In addition, natural and artificial weathering tests on a variety of soiled and unsoiled terracotta samples of known composition, firing temperature and modelling techniques should be conducted before and after cleaning, to fully evaluate and interpret the complex relationship between manufacture, weathering, treatment, and durability.

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NOTES

2. Ibid. p 144. Post first used terra cotta in his residence in New York City in the north side of West 36th Street near Madison Avenue. The terra cotta was imported from Chicago.
3. A letter dated 21 February 1878 to C.F. Butler, Esq. states that a brick and terra cotta design for the building under discussion would be much more cost-effective than the previous sandstone and brick design. Although it is not clear to which house or building the Brooklyn Historical Society project corresponds to the time period and the profile of the proposed brick and stone building.
4. Minutes of the Building Committee, Brooklyn Historical Society Archives. 11 November 1878.
5. Brief biography of Warner in Small, Herbert. The


7. Sullivan, Beth. The History of Terracotta in New York City, p114, states that George B. Post’s first venture in architectural terracotta, the Smith residence, 1877, was carved when partially dry and not modelled in the plastic condition. However, no primary source indicating the same was true for the Brooklyn Historical Society Building has been located to date.
8. Report of the Long Island Historical Society for the Years 1878-81. The Brooklyn Historical Society, 10 May 1881, p 12. The budget reflects payment for terracotta, granite and iron work. It does not list brick. This may be because the Perth Amboy Terracotta Company also manufactured the brick.
9. Christian Union, XXIII, no 4, 20 January. 1881, p 79 (Note: also called New Outlook).
11. Greer, Walter, The Story of Terracotta. New York: Tobias Wright, 1920, p17. Greer states that nearly all the ‘ancient’ civilisations – Etruscans, Greeks, Romans, Persians, Indians, Chinese and Central American Indians – left large numbers of works in sun-baked or burned clay Roman architecture even contains examples of commercial reliefs that appear to have been pressed into moulds. From the twelfth to sixteenth centuries terracotta was used as an ornamental building material in various parts of Europe. During the eighteenth century the use of terracotta was revitalised in England; however, it was very little used in the US before the mid nineteenth century.
12. The first important building that used this material in New York was Richard Upjohn’s Trinity Building in 1852. The terracotta pieces included an elaborate cornice and ‘grotesque animal heads which formed the keystones and window arches’. As was often the case in early terracotta ornamentation, the terracotta was painted to simulate brownstone. The earliest extensive use was by James Renwick for the Tontine Building, New York. See James Taylor, The History of Terracotta in New York City, Architectural Record, 2. October-December 1892. p158
13. Ibid. pp 137-138. The overall opinion was that terracotta would not withstand the rigours of the American climate and that American architects and builders would refuse to make any further experiments with the material. It should be noted that many of the earliest attempts at architectural terracotta were by ceramic manufacturers, rather than by builders. The ceramic manufacturers were accustomed to curved
thin shelled forms and did not understand that as a building product terracotta must have strength to carry weight and must be preferably formed into rectangular shapes. This lack of understanding led to many failures due to the lack of durability. See Mack, Robert C. 'The Manufacture and Use of Architectural Terracotta in the United States', The Technology of Historic American Buildings. Jandl, H. Ward ed. Washington DC: Foundation for Preservation Technology, 1983, p 118.

14. The architects often credited as the pioneers of architectural terracotta include: W Boyington, John Van Ox, Burling & Adler, Carter, Drake & White, W L B Jenney, and Burnham & Root. Most of their work was in the Chicago area.


21. Ibid.

22. Burnham and Root of Chicago also employed and promoted non-imitative red terracotta in conjunction with red brick in their commercial work from 1879–1890.

23. For a good summary of the practical reasons for using terracotta as proclaimed during the 1890s, refer to the editorial in The Brickbuilder, vol II, June 1893, pp 57–8.


25. Ibid.

26. 25% was produced by firms in Boston. 15% by firms in Chicago and Baltimore American Architect and Building News, vol XVII, June 1885, p 226.

27. Ibid.


30. The manufacturing process outlined discusses typical early techniques used during the nineteenth century. As the architectural terracotta industry gained momentum during the early twentieth century the processes became quite sophisticated and changed quickly. The following are a few journals (in which the majority of articles between 1890–1930 are related to terracotta) that together provide the most complete overview of the progression of the twentieth-century terracotta industry: American Ceramic Society Journal: Ceramic Age; The Brickbuilder; Brick and Clay Record.


33. Fluxes serve as an added source of oxygen, so that there are too many oxygen atoms for all the silicon-oxygen units to be bonded at every corner. As a result, the network is weakened, becomes more open, and is liquefied at a lower temperature. However care must be taken that the alkali content is not too high since an excess of alkalis will break up the network thereby becoming soluble in water.


35. Buff and dark red are the two colours of the terracotta on the Brooklyn Historical Society Building, as was common in the early days of manufacturing when the colour was dependent solely on the composition of the clay and the firing temperature. As the industry developed, colourants were added and by the 1890s glazes were commonly applied to achieve a specific colour.


37. Ibid, p 270.

38. ‘How Terracotta is Made’, Clay Record, vol 5, 14 May 1896, p 27.


43. Ries, op cit, p 274.

44. As stated previously, the firing shrinkage of the terracotta produced by the Perth Amboy Terracotta Company was approximately 7.4%. In 1895 Davis cites adding grog to the ‘extent of 40%–60%’ of the mix (Davis, Charles Thomas, A Practical Treatise on the Manufacture of Brick, Tiles and

In 1896 Jelke states that ‘in some cases the grog used is equal to the fresh unfired clay’ (Jelke, William F, ‘Terracotta’, Yale Scientific Monthly, vol 3, no 3, December 1896, p 83).

In 1913 a standard published by Brick and Clay Record cited the use of 25%-30% grog to control shrinkage to 1 inch per foot (Heubach, AR ‘How Architectural Terracotta is Made’, Brick and Clay Record, vol 43, 4 November, 1913, p 904).


56. Sullebarger, op cit, pp 20, 23.


58. Mack, op cit, p 134.

59. Ibid.

60. Such warping has been observed in the terracotta elements of the Century Club, New York City (1889) also supplied by the Perth Amboy Terracotta Company.

61. Greer, op cit, p 25; see also ‘How Terracotta is Made’, p 26.

62. McIntyre, op cit, p 11.

63. In present-day ceramic technology, the terms ‘sinter’, ‘vitrify’ and ‘fuse’ are used interchangeably; historically they were not. See ASTM Standard Definitions of Terms Relating to Structural Clay Products, Designation C43-89, 25. For a unique discussion of ‘Fireskin’, see Salmang, Hermann, Ceramics: Physical and Chemical Fundamentals, London: Butterworths, 1961, pp141-142.


65. Heubach, op cit, p 907


68. Hasluck, op cit, p 206.

69. Ibid, p 16.

70. Ibid, p 15; Mack, op cit, p 137.

71. Hasluck, op cit, p 16.

72. Ibid.

73. The cornice piece was used for laboratory testing and returned for re-installation on the building. The coping piece was sacrificed and cut into samples for the testing programme.


77. Since terracotta is a heterogeneous material, 15 different test sites were chosen on the core and the reading averaged. The readings ranged from 4%-11.3%.

78. The polarising microscope used was a LABOPHOT-POL manufactured by Nikon Inc, Instrument Group, 623 Stewart Avenue, Garden City, New York 11530, Tel (516) 547-4200.

79. SEM P 500 scanning electron microscope was used at the Laboratory for the Research of the Structure of Matter, Scanning Electron Microscopy Lab, at the University of Pennsylvania. Samples were sputter-coated with gold to make them conductive.

80. For petrographic analysis the division of particle sizes used are as follows: 0.2-0.4mm – very fine; 0.3-0.8mm – fine; 0.5-1.2mm – rather fine; 1.0-2.5mm – medium; 2.0-4.0mm – slightly coarse; 3.0-7.0mm – coarse; 5mm and over – very coarse (Stockbridge, Jerry G, ‘Techniques for Evaluating the Conditions of Masonry Buildings’, paper presented at International Conference, Materials, Science and Restoration, Esslingen, Federal Republic of Germany, September 1983, p 383).

81. This section was chosen as representative. However, since terracotta is a heterogeneous material, the percentages should be viewed accordingly.

82. Quartz and feldspar are both white and translucent and not always easily distinguishable from one another without further chemical testing (Kingery, W David and Vandiver, Pamela B, Ceramic Masterpieces, New York: Free Press, 1986, p 291). As will be described later, cracking may occur around quartz particles. For the purposes of this analysis a distinction between the two was not pertinent.


85. Christian Union, 26 January 1881
76. Pampuch, Roman, ‘Constitution and Properties of Ceramic Materials’, Materials Science Monographs, vol 58, New York, Elsevier, 1991, p 194. Note: as stated previously, the melting point of silicon dioxide is 1713°C. The typical firing temperature of architectural terracotta during the nineteenth century was 1100–1370°C. The range of 40–85% of 1713°C is 675–1453°C. The usual firing temperature is well within this range.


79. Soaps have the same general properties as detergents but are formed from alkaline salts of an organic acid. Soaps are generally not used in architectural conservation since they are rendered insoluble by calcium ions often present in masonry materials and hard water.


81. Infrared Spectroscopy was conducted by Richard Wolbers, Associate Professor, Art Conservation Program, University of Delaware.

82. Pittsburgh, Detroit, Cleveland, Buffalo, St Louis and Boston.


84. Ibid.

85. A PSEM 500 scanning electron microscope was used at the Laboratory for the Research on the Structure of Matter, Scanning Microscopy Lab, at the University of Pennsylvania. The PSEM 500 is manufactured by NV Philips’ Gloeilampenfabrieken, Endhoven, The Netherlands.

86. Furness Library, University of Pennsylvania, Philadelphia, Pennsylvania; National Building Museum (Pension Building), Washington DC; Wainwright Building, St Louis, Missouri; Rookery, Chicago, Illinois, to name a few.


89. Thomann-Hanry Inc, 555 Madison Avenue, New York, New York 10022, USA. Tel (212) 755-5551. The headquarters of Thomann-Hanry Inc is in Paris, France.

90. According to Ashurst, the most successful and least harmful chemical method of cleaning unglazed terracotta is with detergent emulsions (in particular formulation C).

91. The emulsions were formulated by Richard Wolbers, Associate Professor, University of Delaware, Art Conservation Department.

92. Epo-Kwick Fast Cure Epoxy, manufacture by Buehler, Microstructural Analysis Division, 41 Waukegan Road, Lake Bluff, Illinois 60044, USA. Tel. (708) 295-7979.


94. Isomet Low Speed Saw, manufactured by Buehler.

95. The samples were hand-polished with 240, 400 and 600 wet sandpapers, followed by Texmet polishing cloth coupled with a diamond polishing compound. Final fine polishing was accomplished with a microcloth polishing cloth and a 0.05 micron diamond powder. All are manufactured by Buehler.

96. SURE KLEAN Restoration Cleaner is manufactured by ProSoCo Inc., PO Box 171677, Kansas City, Kansas 66117, USA. Tel (913) 281-2700.

97. SURE KLEAN strippable masking (White) contains toluene, acetone and chlorinated paraffin and is manufactured by ProSoCo Inc.

98. SURE KLEAN 766 Masonry Prewash is manufactured by ProSoCo Inc.

99. SURE KLEAN Limestone Afterwash is manufactured by ProSoCo, Inc.

100. The Derotor Steam cleaner Model GV6 is manufactured by The John Quayle Dental Manufacturing Co Ltd, Derotor House, Dominion Way, Worthing, West Sussex BN14 8QN, UK. Tel (01903) 204427/8/9.

101. The Landa PGHW5–3000 Hot Water Washer is manufactured by Landa Inc, 13705 NE Airport Way, Portland, Oregon 97230, USA.

102. The previous experience with this machine, by Philadelphia Museum of Art conservators, indicated that dwell times of a minute or more would probably remove the fireskin and damage the core of the terracotta dramatically. Therefore, dwell times of less than one minute were tested.

103. EDTA (ethylene diaminetetra-acetic-acid) is commercially available under the following trademark
104. Formulation (all % by weight): 2% Sodium Hydroxide (NaOH) (Fisher) - strong alkali reagent; slightly abrasive; 2% Sodium Tetraborate (Na2B4O7(10H2O)) (Fisher) - alkaline reagent; 2.5% Versene (EDTA) (Dow) - chelating agent; 2.5% Sodium Metasilicate, Anhydrus - mildly alkaline pH stabiliser; 0.5-1.0% Triton X-100 - non-ionic detergent; releasing agent; 0.5-1.5% Polyacrylamide/polyacrylic acid (40% Acrylic acid; 1x107 MW) (Poly Sciences Inc) - gelling agent; Water (up to final volume).


SELECTED BIBLIOGRAPHY

Brooklyn Historical Society Building

Architectural Record, 'The History of Terracotta in New York City', vol 2, October-December 1891, p144
Atlantic Terracotta, '1879-1891', vol 8, no 7, April 1926
The Christian Union, 26 January 1881, vol XXIII, no 4, p79

Long Island Historical Society scrapbooks 1877-1883, unpubl, Brooklyn Historical Society, 1877-1883

Sturgis, Russell, 'A Review of the Work of George B Post', Architectural Record, Great American Architects Series, no 4, June 1898, p3
Sullebarger, Beth, 'The Long Island Historical Society', unpubl, Brooklyn Historical Society Archives, 1984
Taylor, James, 'The History of Terracotta in New York City', Architectural Record, vol 2, October-December 1892, p144
Wontner-Smith, C, 'In Praise of Terracotta', Claycraft, vol 2, 1947, pp 340-1

Perth Amboy Terracotta Company

Cook, Henry B, Annual Report of the State Geologist for the Year 1882, Camden: FF Patterson, 1882
Geological Survey of New Jersey: Report on the Clay Deposits of Woodbridge, South Amboy and other Places in New Jersey, together with their uses for firebrick, pottery, etc., Trenton: Naar, Day & Naar, Printers, 1878

Terraotta

'Terracotta and Faience as Materials for Architectural and Decorative Application', The Brickbuilder, vol 2, 1893, pp 34-6, 48-9, 57-8
Ceramic Age, 'Terracotta Sessions Bring out Valuable Data', vol 13, February 1929, pp 65-67
Clay Record (reprinted from The New York Times), 'How Terracotta is Made', vol 5, May 14, 1896, pp 26-28
An Approach to the Evaluation of Cleaning Methods for Unglazed Architectural Terracotta in the USA

Heubach, A R. 'How Architectural Terracotta is Made', *Brick and Clay Record*, vol 43, 4 November, 1913, p 904
Meeks, Nigel. 'Backscattered Electron Imaging of Archaeological Material', unpubl, Courtesy of the Conservation Analytical Laboratory, Smithsonian, Washington, DC, nd
Plusch, Herman A. 'The Ceramic Chemical Development of Architectural Terracotta'. *The Brickbuilder*, vol 2, no 5, 1893, pp 83–85
Spurrier, H, 'Some Important Points in the Manufacture of Terracotta'. *Fuels and Furnace*. vol 8, 1930, p 707
Spurrier, H, 'Some Fundamentals of Terracotta'. *Journal of American Ceramic Society*, no 9, 1926