Surface preparation of historic wrought iron: evidencing the requirement for standardisation

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Summary

The conservation of heritage wrought iron mostly relies on corrosion prevention by preparation of surfaces and application of protective coatings. In contrast to industrial and engineering treatment of modern steel, conservation practice is not regulated by accepted national and international standards or underpinned by empirical evidence. This paper presents the results of oxygen consumption rate testing (as proxy corrosion rate) of historic wrought iron samples prepared by five commonly applied surface preparation methods and subjected to high humidity environments, with outcomes assessed by use of international standards employed in industrial contexts. Results indicate that choice of surface preparation method has a direct influence on corrosion rate of the uncoated wrought iron, which impacts on performance of the protective coatings that may ultimately determine survival or loss of our rich wrought iron heritage. By implication, more extensive empirical evidence is required to underpin and develop heritage standards for treatment of wrought iron which encompass specifics of the historic material, heritage context and the ethics of conservation practice. The introduction of such standards is called for in order to bring treatment of historic ironwork in line with highly regulated engineering and industrial practices.

Key Words

heritage; iron; surface preparation; corrosion; coatings; protection; standards.

Introduction

Treatments aiming to prevent corrosion of historic wrought iron in the atmosphere normally centre on the application of protective coatings following preparation of the substrate surface to remove existing paint layers and corrosion products. Preparation methods include manual techniques, power tools, blasting with a variety of media and chemical immersion. Due to heavy reliance on tendering in this part of the heritage sector, specification for treatment of wrought iron often falls to a range of individuals whose familiarity with historic materials and structures and conservation practice and ethics is limited.

Even where treatment is by conservation specialists, sector specific research to aid their choice of paint and treatment system is sparse and quantified data is absent entirely. Consequently, conservation decisions must be made on the strength of anecdotal reports of successes and failures. This limited understanding of the effects of treatments applied to heritage material is in direct contravention of sector codes of ethics as set out in national standards which advocate evidence based treatment techniques delivered within ethical constructs [1,2,3]. For instance, the availability of empirical evidence relating selection of surface treatment methods and protective coatings to the corrosion rates of historic wrought iron is non-existent yet this information is the key to delivering evidence based management of our ferrous metal heritage. If the limited resources available for heritage preservation across the globe are to be employed to best effect, informed and predictive management strategies are essential.

This approach requires heritage specific guidance that can be utilised internationally across the sector, much as industry uses agreed international standards to dictate procedure for surface preparation, coating application and coating performance. The stringent stipulations of coating manufacturers and the existence of international industrial standards guide practice in the protection of modern steels, producing a heavily regulated industry where best practice methodologies for surface preparation and application of protective coatings are clear for practitioners [4,5]. Coating manufacturer datasheets recommend suitable coatings for steel substrates in various corrosive environments and specify appropriate surface preparation and application methods according to these standards.

In contrast to industry, heritage preservation is a poor relation with neither regulation nor its own industry focused standards. Despite offering a rich source of information, caveats prevent wholesale application of the international corrosion prevention standards and guidelines to heritage contexts. First, these international standards for surface preparation are scaled by the corrosion performance of mild steel. While this may be applicable to many heritage contexts dating from the twentieth century, mild steel having replaced wrought iron in many construction contexts, each material exhibits different composition, microstructure and corrosion mechanisms [6,7,8,9]. Second, industry as related to modern construction is not hampered by the ethical and aesthetic constraints applicable to heritage ironwork practitioners which are set out in national standards. For example, coating manufacturers regularly specify blasting to Sa2.5 or 'near white metal' to produce a surface profile promoting coating-substrate adhesion. For the heritage industry, loss of original material associated with blasting to a metal core (where this exists) conflicts with concepts of 'limitos' and preservation of original surface [10]. The perceived advantages of achieving the most suitable surface for optimal performance of new protective coatings to minimise loss of metal mass through further corrosion, must be weighed against decimation of information held within historic coating and corrosion product layers.

A recent extensive survey of references to the use of national and international standards cited in metal conservation literature, covering the period 1995-2010, revealed only two instances of citations of surface preparation standards for heritage ferrous metals [11]. Why is there a lack of engagement with existing industrial standards in heritage conservation; is it

an indication of a lack of standardisation in metal conservation practice, an indictment of standards which are not fit for purpose within heritage contexts or simply that there is limited reportage of current practices? Whatever the reason, the applicability and usefulness of the standards employed in the corrosion protection sector to heritage contexts need to be explored, if they are to be recommended as meeting the particular needs of historic ferrous metals. Research delivering quantitative data is required to fulfil these goals.

A first step towards achieving this is to use international standards to determine how surface preparation methods used in these contexts influence corrosion rates of the ferrous metal substrate. This is fundamental to evaluating the likely efficacy of a coating system, as transmission of reactants through coatings will result in corrosion related to the reactivity of the underlying surface. Corrosion will impact on the deterioration and loss of the overlying coating subject to the input of other variables such as its adhesion to the prepared surface. Clearly, a wide range of interrelating factors determine coating performance but surface preparation remains a fundamental variable within the equation.

Recognising the importance of surface preparation, this paper presents an investigation of the effect of five commonly applied surface preparation methods on surface morphology and corrosion rate of historic wrought iron samples. This produces data that contributes to developing a firm evidence base from which effective, ethical decision making can be developed for the conservation of historic wrought iron.

Aims and Objectives

This study aims to address the current knowledge gap regarding impact of choice of surface preparation method on effective corrosion prevention for wrought iron by:

- preparing the surfaces of historic wrought iron samples by five methods;
- determining the effect of these preparations on sample surface morphology, retention of existing coatings and corrosion products;
- quantifying the corrosion rates of the samples via measurement of oxygen consumption at high relative humidity;
- relating corrosion rate to surface preparation method.

Methodology

Sample material

The sample material is a wrought iron railing of unknown provenance and date but which is thought to be from the late 19th century. Vestiges of failed polymeric coating systems remain on approximately 40-50% of the surface, adhering closely in some areas and loosely in others (Figure 1). Corrosion products also cover the entirety of the railing, presumably as a result of atmospheric corrosion. These comprise closely adhering, coherent oxide layers as well as laminating and powdery corrosion products and pitting.

Figure 1. Iron railing from which sample material was sourced.

Characterisation of the sample material and standardisation of the samples for the corrosion rate determination methodology used here has been reported previously [12]. Its mean composition is typical of wrought iron with 99% iron, 0.37% silicon, 0.36% phosphorus and 0.27% manganese, with slag stringers of varied size (<10μm to >600μm). Existing corrosion products were identified by X-ray diffraction as goethite, magnetite and lepidocrocite. The presence of multiple coating layers indicates prior ad hoc painting regimes which SEM EDX investigation revealed included application of lead based coatings, layers containing barium sulphate fillers, cobalt drying agents, copper based pigments and evidence of zinc.

Wrought iron is inhomogeneous, so major compositional variation between the samples was minimised by producing samples from a continuous length of flat bar iron. Samples were cut using a hand hacksaw with white spirit lubricant to avoid heat and localised microstructural alterations that machine sawing would produce. The 40mm x 30mm x 10mm sample size was dictated by the dimensions of the bar and the diameter of the aperture of the reaction vessel used for subsequent oxygen consumption tests. The mass of each sample and minor discrepancies in overall dimensions, and hence surface area, were recorded.

Surface preparation methods

Five surface preparation methods, determined through prior testing by Historic Scotland [13], were applied to the historic wrought iron samples:

- airbrasion with glass beads;
- airbrasion with aluminium oxide;
- airbrasion with crushed walnut powder;
- immersion in sodium hydroxide solution followed by wire brushing;

- flame cleaning followed by wire brushing.

Five samples of the wrought iron railing were prepared by each method with five samples left in an as received, untreated condition acting as controls. The methodology used for each preparation method is described below.

Blast cleaning with glass beads, aluminium oxide and crushed walnut abrasive media: Blast cleaning of samples was carried out using a Texas Airsonics Model AJ-1 airbrasive unit. The airbrasive feed was thoroughly cleaned when changing between abrasive media to avoid cross contamination. The abrasive media were:

- glass beads (Grade No.9 - 44μm; hardness 6 Mohs);
- aluminium oxide (Grade No. 3 - 53μm; hardness 8-9 Mohs);
- crushed walnut shell (Grade No. 6 - 0.3-0.6mm; hardness 3-4 Mohs).

Parameters standardised during the cleaning were:

- pressure - c.4 bar (increased slightly for crushed walnut to due softness of the medium);
- powder flow/aim intensity (5);
- nozzle diameter 0.65mm;
- distance of nozzle from sample surface (50mm);
- angle of nozzle to surface (45°);
- end point [aim Sa 2.5 (near white metal)].

Post-cleaning samples were blasted with pressurised air to remove loose blast media from their surfaces.

Immersion in sodium hydroxide followed by wire brushing: Samples were immersed in a 1.25M solution of sodium hydroxide in deionised water for two hours then rinsed in deionised water until pH 7 was attained in two rinses. Vigorous manual brushing with a stainless steel wire brush removed any remaining coating and loosely adhering corrosion products until there was no further visible change in the sample surface. The samples were then rinsed again in deionised water, blotted to remove excess water and left to dry in a well-ventilated, warm area.

Flame cleaning followed by wire brushing: A hand held GoSystem Tech Multi Torch MT2055 using propane/butane fuel and having a 17mm burner, a power output of 1000 Watts and a flame temperature of 1350°C was used. A standard protocol for cleaning was developed ensuring samples were exposed to the same part of the flame which was constantly moving across the surfaces. The duration for which each sample was exposed to the flame was similar but with slight variation due to differing amounts of paint and corrosion product adhering to surfaces, as would be the case in practice.

Samples were then brushed vigorously with a stainless steel wire brush until there was no longer any visible change in the surface and blasted with high pressure dry air to remove any remaining loose corrosion products or paint residues.

Determination of end point

In practice, the end point of surface preparation will be guided by a range of factors. Coating manufacturer instructions may stipulate removal of all oxides and remnants of previous coatings, heritage ethics or aesthetics may prioritise maximum retention of coherent original material and availability of techniques limit possible outcomes. Surfaces would generally be blasted with glass beads and aluminium oxide where the aim was removal of oxides and existing coatings to bare metal (Sa 2.5). This was the end point aimed for here. Crushed walnut having a lower hardness than magnetite limits its use to contexts in which retention of coherent oxides is desirable. A surface free from loosely adherent oxides and vestiges of coating systems was deemed the end point for this technique. Immersion in sodium hydroxide solution and flame cleaning both rely on wire brushing for final removal of loosely adhering corrosion products and are unlikely to remove coherent oxide layers. End point in these cases was when continued brushing caused no further visible change in surface appearance. With all techniques, end point was assessed visually macroscopically as would be the case for their *in situ* use.

Examining resultant surfaces

Prepared surfaces were subjected to macro and microscopic examination and comparison with untreated control samples. Macroscopic recording was by photography and microscopically by use of a CamScan Maxim 2040 scanning electron microscope (SEM) equipped with Oxford Instruments energy and wavelength dispersive X-ray spectrometers using secondary electron imaging to examine the resultant surface topography.

Measuring oxygen consumption and corrosion rates

Samples were individually enclosed within airtight reaction vessels (250ml Mason Ball glass jars with plastic coated brass sealing discs tightened with threaded outer sealing rings of brass which create a seal by deforming a synthetic rubberised ring on the disc) containing 160g silica gel conditioned to 90% relative humidity (RH). Within each vessel was an oxygen sensor spot (World Precision Instruments (WPI) part #503090) adhered to the interior wall of the vessel using silicon adhesive (Radio Spares RTV silicone rubber compound) and a watch glass to separate the sample from the silica gel. The reaction vessels with samples were stored in a Binder KB240 climate chamber to control temperature to 20 ± 0.5°C and avoid RH changes within the vessels which would result from fluctuating temperature. Madgetech RHTemp 101A data loggers monitored the internal environment to $\pm$ 3% RH of 28 of the 31 reaction vessels. All vessels maintained humidity between 88 – 93% RH $\pm$ 3% (logger error) throughout the test period.

Using a fibre optic probe and WPI OxyMini oxygen meter (WPI OXY-MINI-AOT with cable #501644) the oxygen concentration within each vessel was measured at regular intervals

(twice weekly) over an 11 month period (338 days for prepared samples, 257 days for un-cleaned samples). The oxygen within the vessels was replenished by opening the vessel and resealing when internal oxygen pressure became depleted to 150mbar to ensure this did not influence corrosion rates and samples were photographed at this stage. The precision of the oxygen measurements is 2mbar at atmospheric oxygen pressure of 210mbar and increases proportionally with decreasing oxygen pressure. Control vessels filled with nitrogen showed a negligible ingress of oxygen over a two year period indicating very little leakage of the vessels [14]. A further control vessel containing silica gel, watch glass and sensor spot was measured alongside the sample vessels to quantify the oxygen consumption of the apparatus. This was found to be 0.03 mbar day^{-1} which was subtracted from the oxygen consumption of each vessel when results were analysed.

Identification of corrosion products

Following completion of oxygen consumption recording, corrosion products formed on the glass beads, aluminium oxide and flame cleaned samples were mechanically removed and analysed using a PANalytical X'Pert Pro (Cu) X-ray powder diffractometer.

Results

Resultant sample surfaces

The results of cleaning (Figure 2) reflect the end point goals and limitations of the methods employed as discussed above. Both aluminium oxide powder and glass beads blasting exposed the entire metal surface. Crushed walnut blasted, sodium hydroxide immersed and flame cleaned surfaces were similar in their retention of oxides but differed in colour and extent of powdery corrosion products evident.
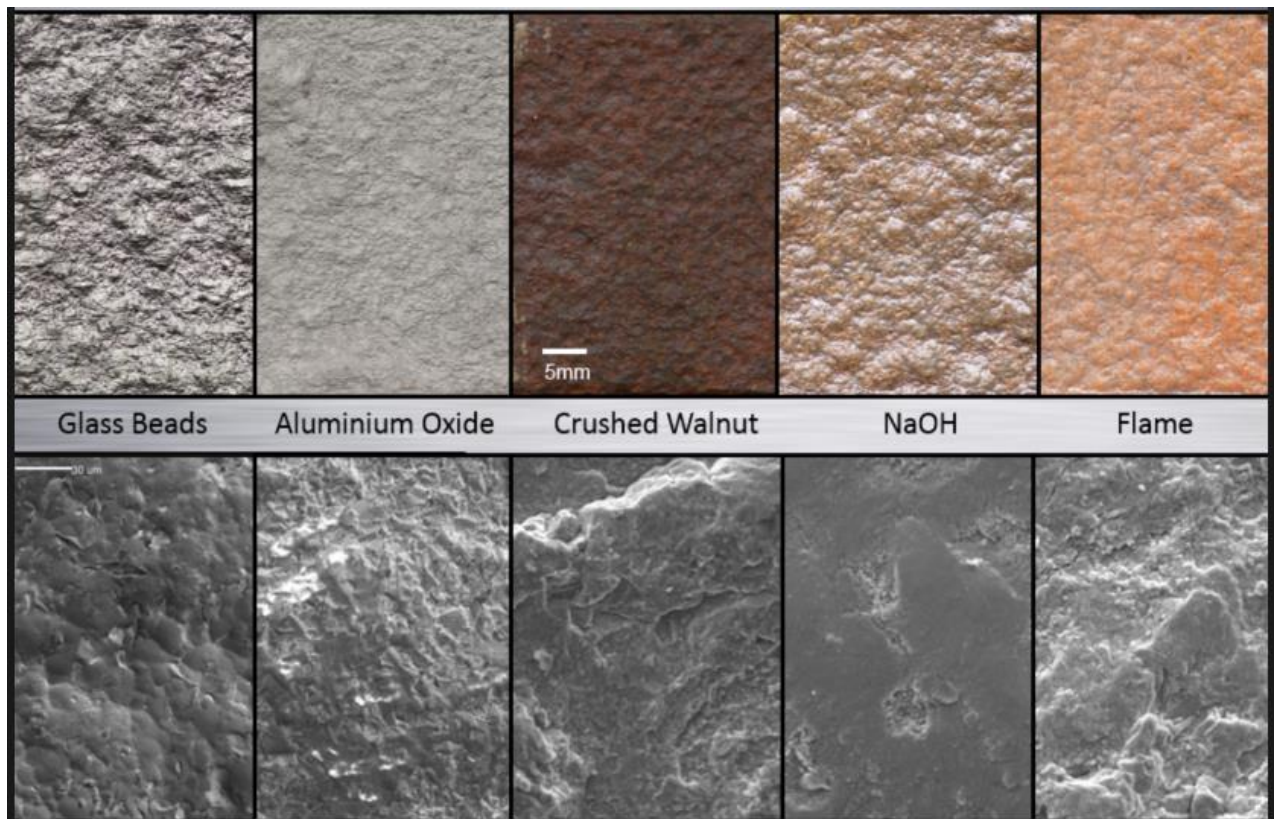
Figure 2. Morphology of metal surfaces post-preparation.

Oxygen consumption

All samples within all preparation methods, including the unprepared controls, consumed oxygen during the 350 days of testing (Figures 3–8). The rates of consumption differed according to the preparation technique used but patterns of consumption are similar; an initial fast phase followed by a steady rate. While the range of oxygen consumption rates within a treatment likely reflects the difficulty of standardisation and reproducibility for the heritage metal samples, patterns emerge for oxygen consumption according to preparation method (Figure 9). Oxygen consumption is given as a function of surface area (Figure 9, Table 2) but it should be noted that surfaces are not perfectly planar and variation in surface morphology is inherent in the preparation methods (Figures 2,10). Flame and wire brush cleaning, aluminium oxide blasting and glass beads blasting have averages that are faster than the untreated control samples, whereas both crushed walnut blasting and sodium hydroxide and wire brush preparations are significantly slower than the untreated samples. Oxygen consumption values are used to calculate moles of iron reacting to form corrosion products (Table 2) in accordance with the methodology discussed previously [12]. It is possible to calculate the corresponding loss of depth of metallic iron across sample surfaces but this is not appropriate for the localised corrosion seen on these samples (Figure 10).

The data demonstrates broad agreement within preparation methods, except for two anomalous results; aluminium oxide blasting (HS7) and flame cleaning (HS25) (Figures 3-8).
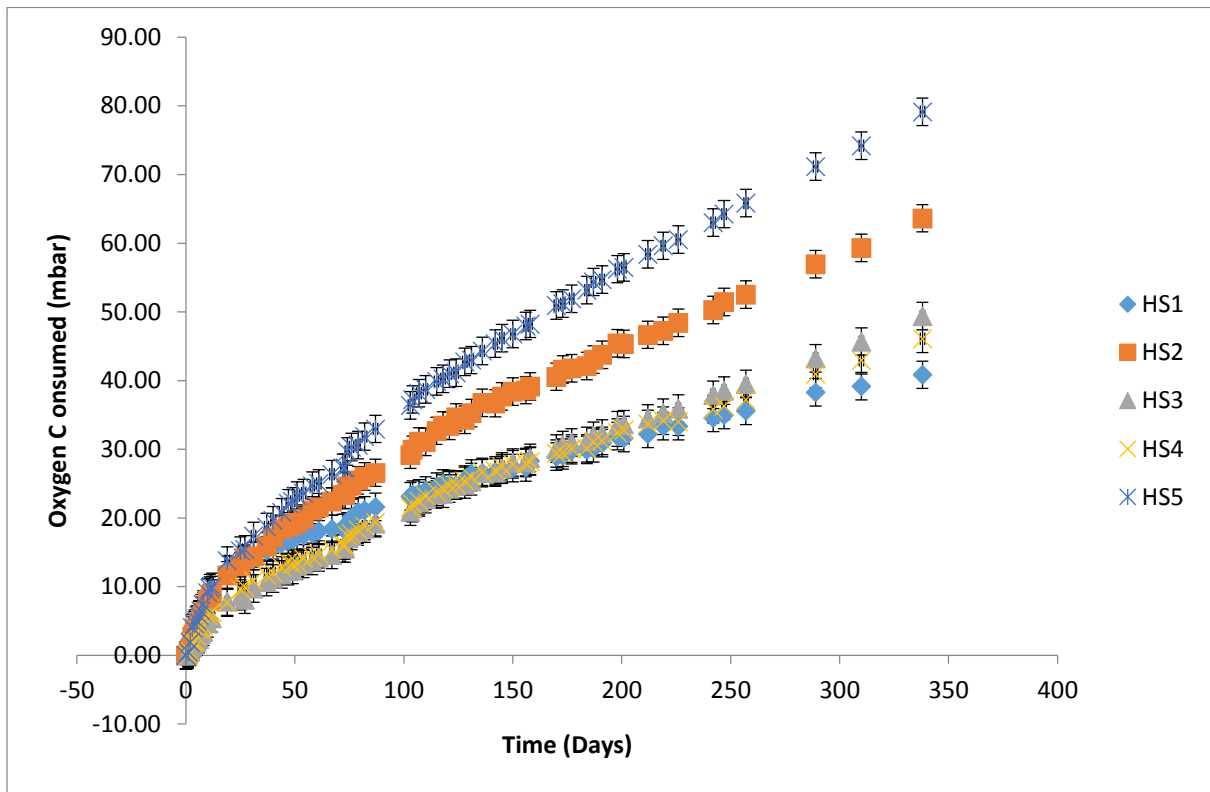
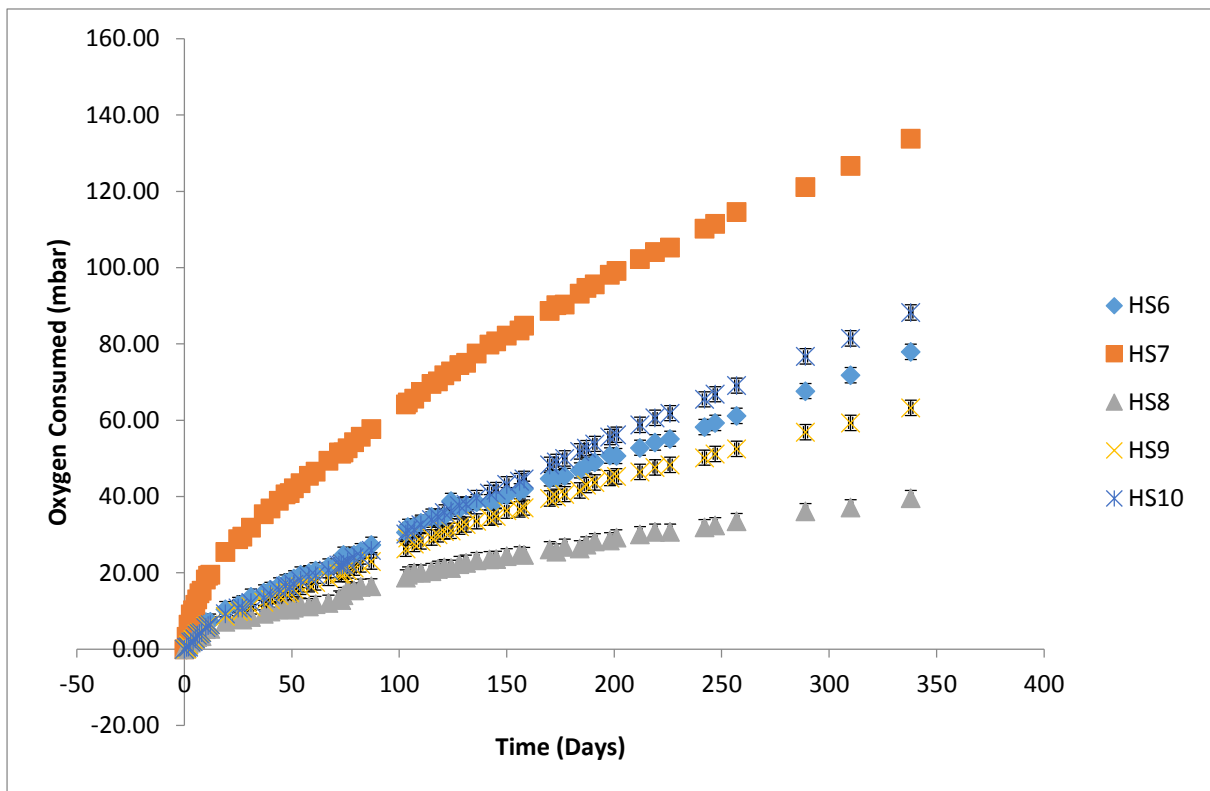*Figure 3. Glass beads oxide oxygen consumption (error ±1 mbar).*

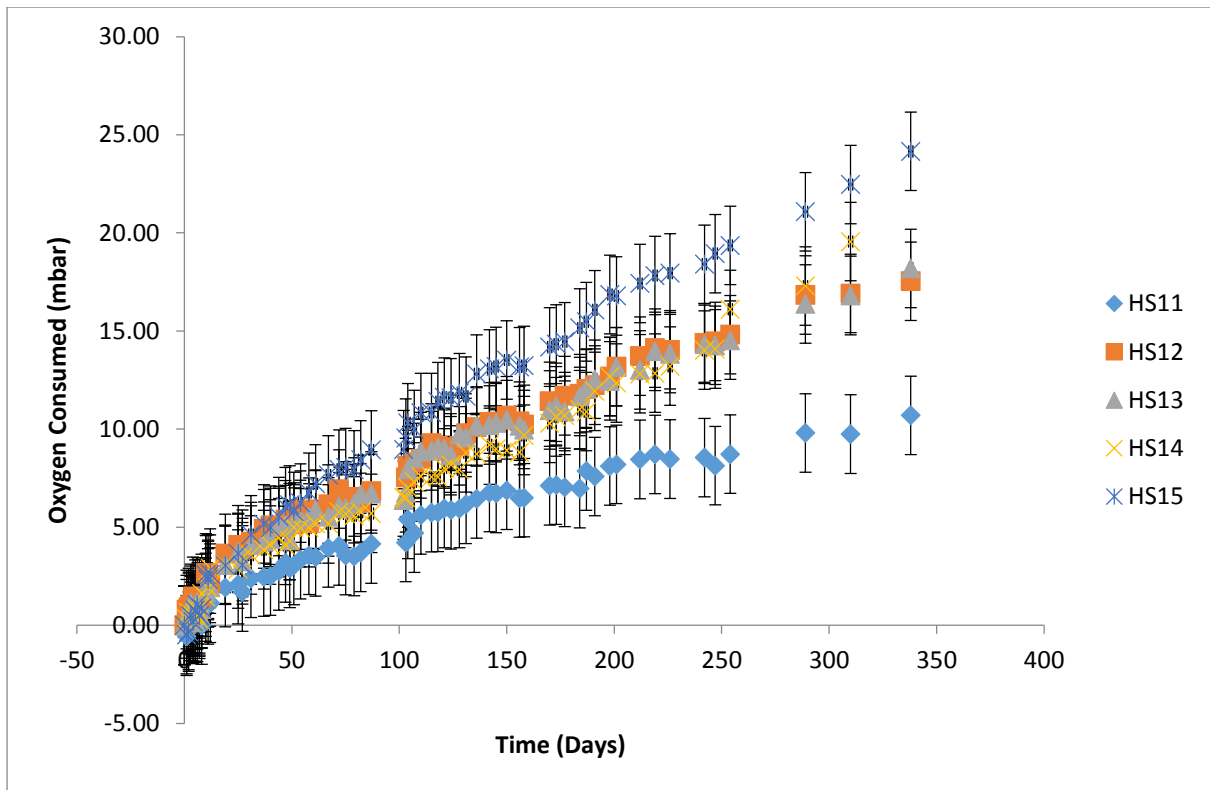*Figure 4. Aluminium oxide oxygen consumption (error ±1 mbar).*

Figure 5. Crushed walnut oxygen consumption (error ±1 mbar).
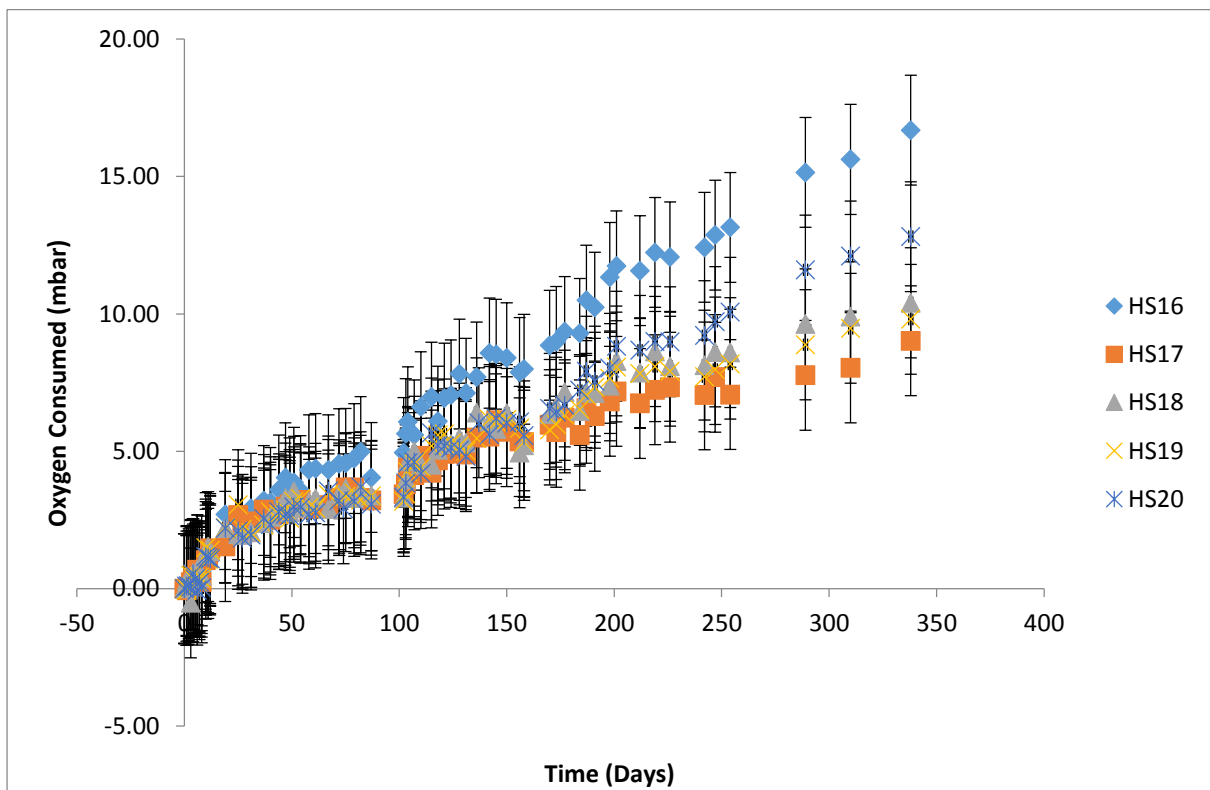
Figure 6. Sodium hydroxide and wire brush oxygen consumption (error ±1 mbar).
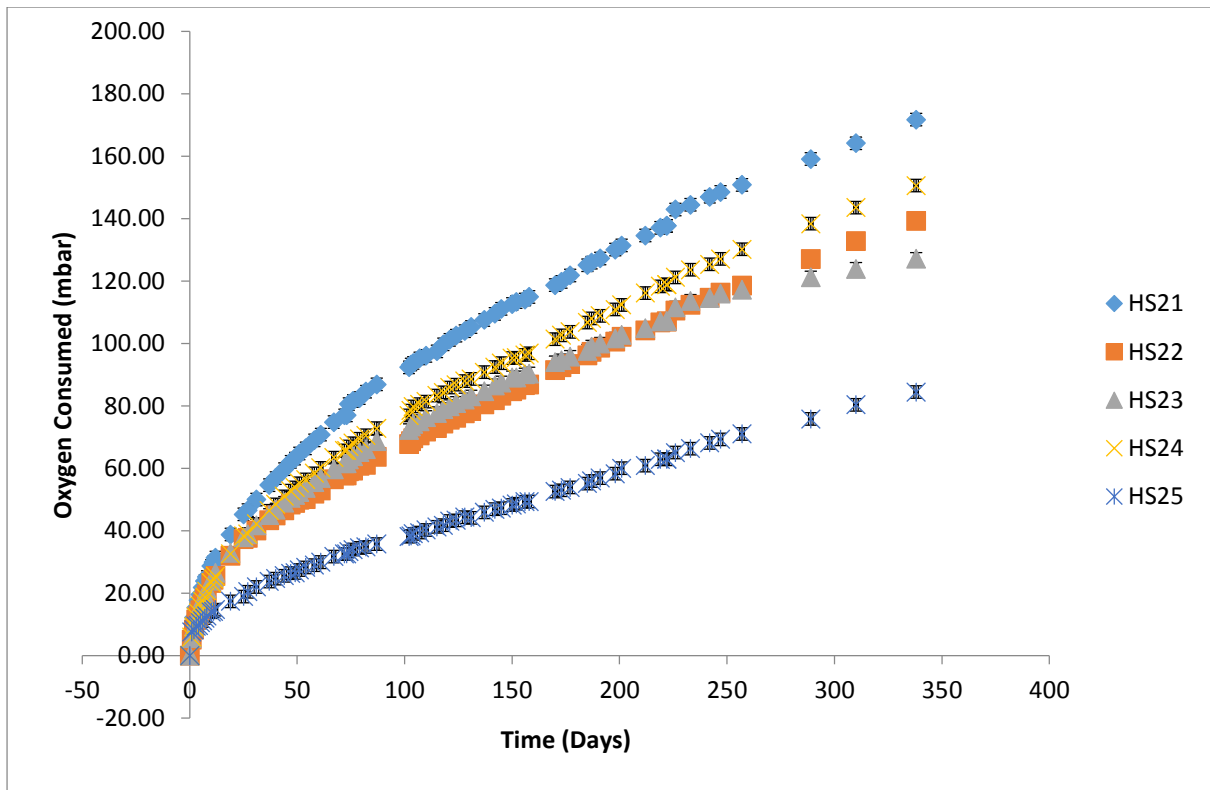
Figure 7. Flame and wire brush oxygen consumption (error ±1 mbar).
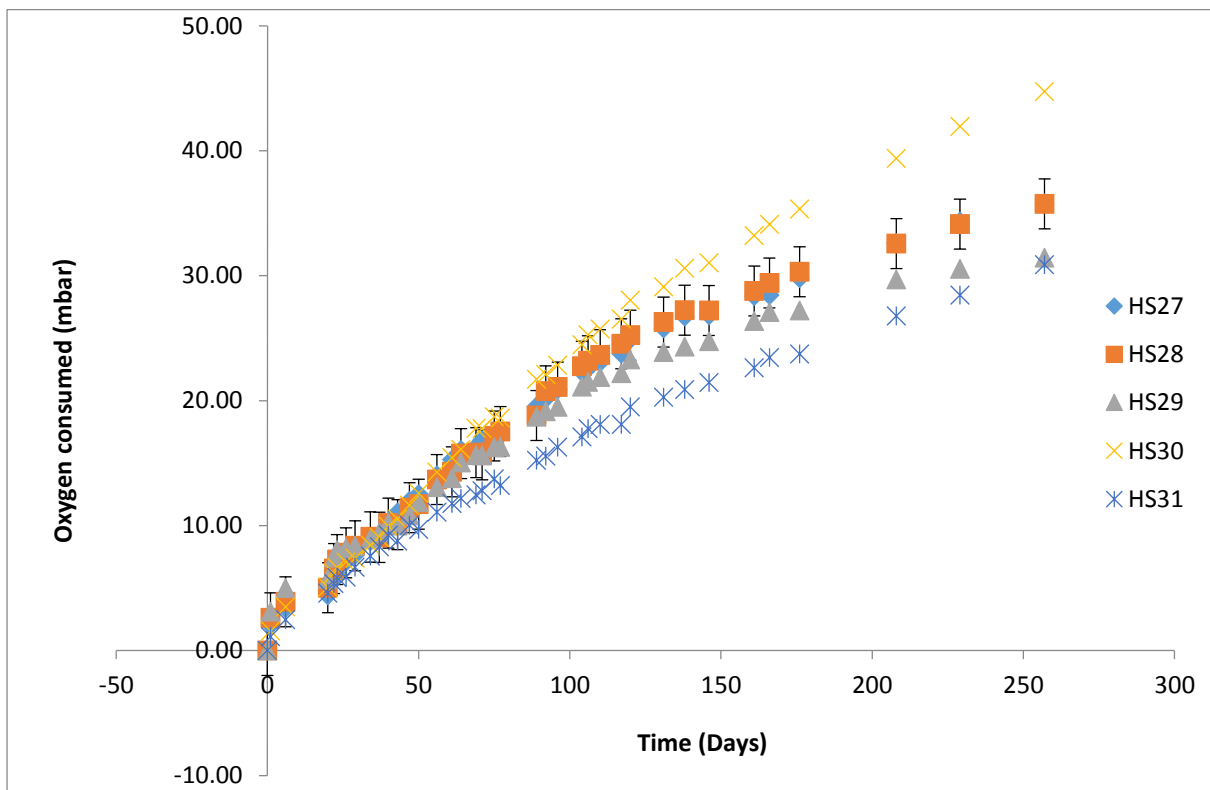
Figure 8. Un-cleaned samples oxygen consumption (error ±1 mbar).
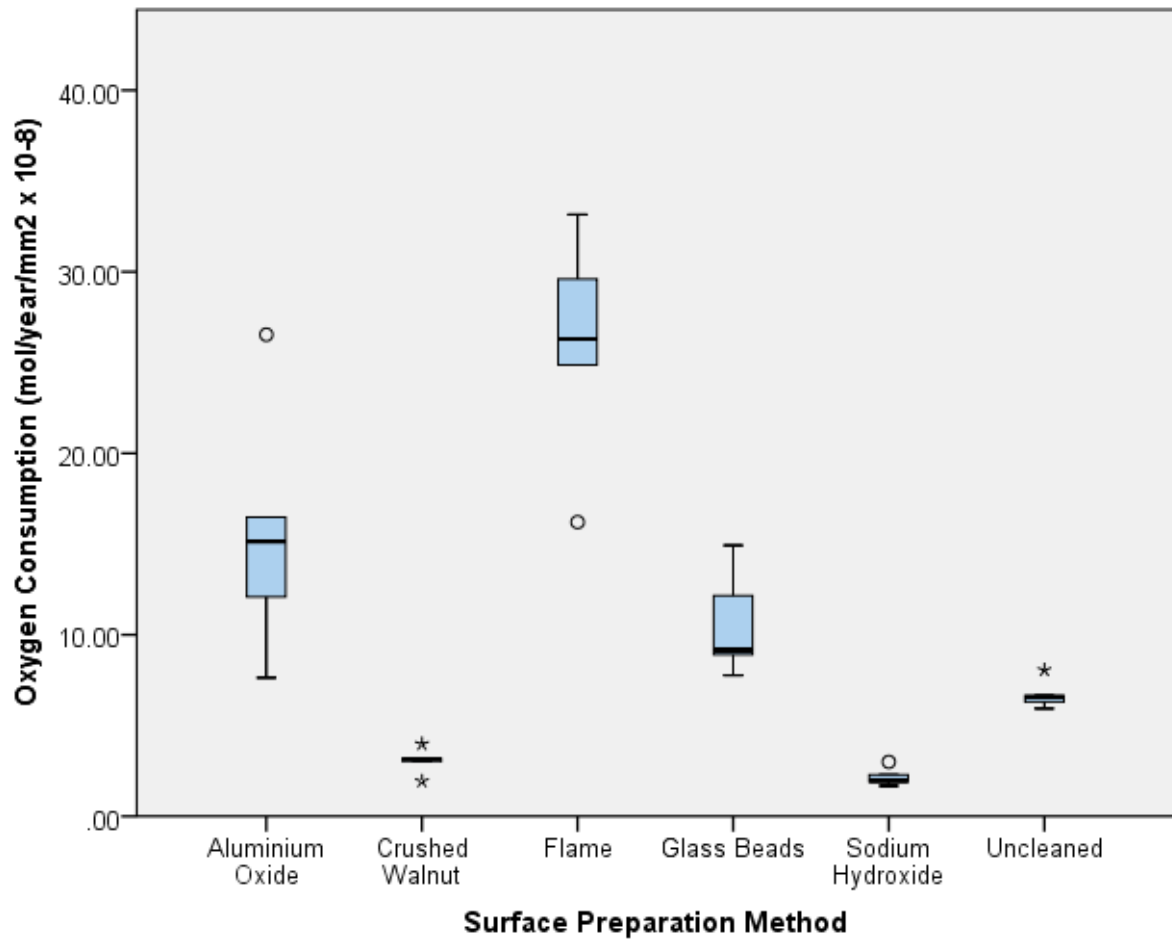
Figure 9. Boxplot showing oxygen consumed by samples prepared by each method (mol/year/mm² x 10⁻⁸) as averaged over test period. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).

Figure 10: Comparison of prepared and post-high RH exposure surfaces. Images show sample surfaces of 30mm x 40mm.

Corrosion products

All samples subjected to 90% relative humidity testing developed fresh corrosion products on their surfaces during the oxygen consumption tests (Figure 10). XRD analysis of samples of the fresh corrosion product identified goethite and lepidocrocite for all preparation methods and controls except flame cleaning (Figures 11,12). Both goethite and lepidocrocite are products commensurate with corrosion in the atmosphere [9], while hematite is expected at high temperature either as a transformation product or as a newly formed corrosion product

[15]. Chloride contamination of samples is thought to be low as evidenced by an absence of akaganeite in the analysis [16, 17].

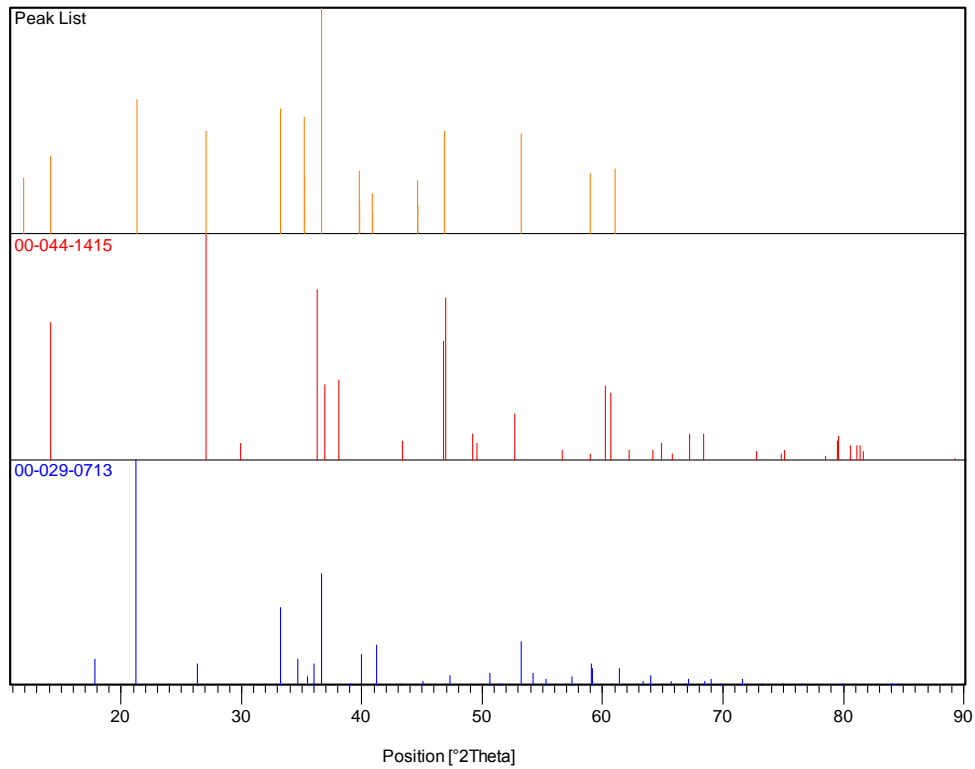*Figure 11. Diffraction pattern of corrosion products from glass beads cleaned sample (uppermost pattern) indicating presence of lepidocrocite (00-044-1415 (middle pattern)) and goethite (00-029-0713 (lowest pattern)).*
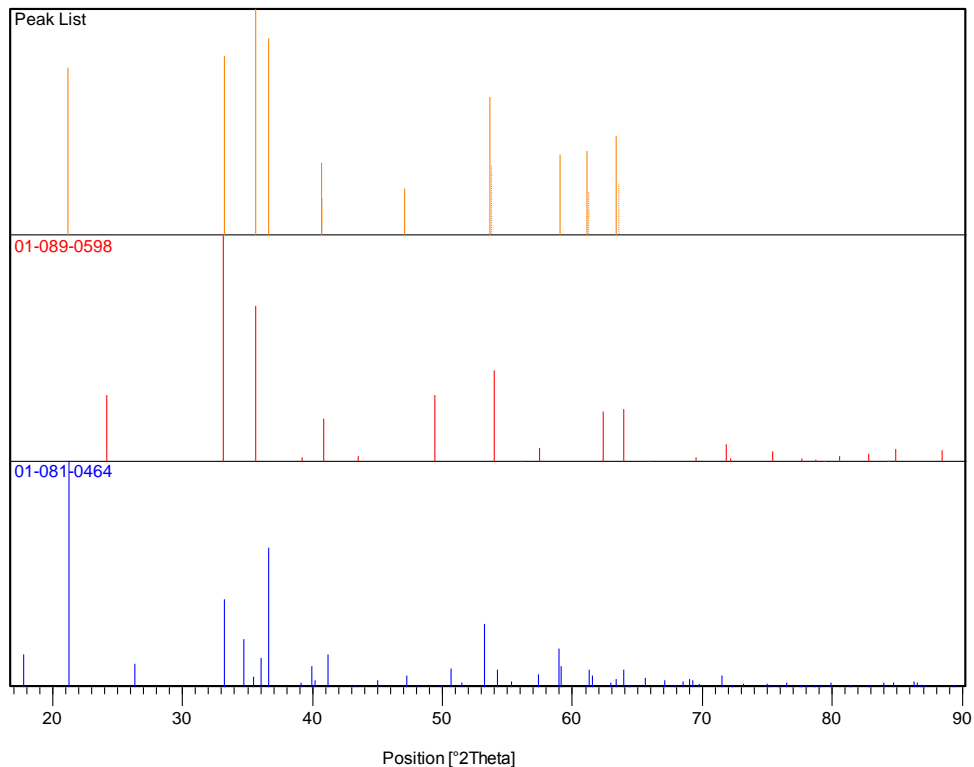
Figure 12. Diffraction pattern of corrosion products from flame cleaned sample (uppermost pattern) indicating presence of hematite (01-089-0598 (middle pattern)) and goethite (01-081-0464 (lowest pattern)).

Discussion

Grading rust by pictorial standards within heritage contexts

Within heritage conservation it is challenging to define end points for cleaning methods that can be applied across the sector for specifying treatment methodologies to contractors. Swedish Standard SIS 05 59 00 and BS EN ISO 8501-1:2007 specify surface preparations necessary for the protective performance of coatings by determining the preparation end point visually using pictorial grading relative to the original condition of the metalwork. Since they are based on modern steels, pre-treatment surfaces are categorised according to their degree of pitting corrosion. These standards can be used to classify test samples since they employ preparation methods that match those used here: blast-cleaning, hand and power tool cleaning and flame cleaning from four pre-preparation rust grades. However, their use offers challenges for practitioners treating historic wrought iron which is likely to display more advanced corrosion that is lamellar rather than the pitting normally evident in the modern steels used to create the standards. How an untreated rusted surface is graded using the standard will have a direct impact on judging the surface aesthetic used to decide the end

point of a preparation method [18]. While this undermines the value of the pictorial references provided in the standard because of their limited relevance to wrought iron, in practice, application of an international standard is expected of contractors fulfilling specifications for treatment of wrought iron within the heritage sector.

The importance of using visual comparators to describe the level of preparation attained is underlined by the broad similarity in appearance of the samples prepared here. Differentiation is clearly difficult using only written descriptors therefore an internationally accepted standard provides a base line that can be used comparably across the heritage sector. Despite its limited relevance to the wrought iron, it enables clear specification for contractors and offers comparability between experimental studies carried out within the heritage sector. The grade within the standard that offers the best match for historic wrought iron is D *'Steel surface on which the mill scale has rusted away and on which general pitting is visible under normal vision'* [18]. The severe limitations of using BS EN ISO 8501-1:2007 illustrate that employing a dedicated classification based on wrought iron in heritage contexts would be preferable. Developing such a standard may be a consideration for the future, since the wrought iron heritage bank is growing and presents ever greater preservation problems that require predictive management.

Classification and comparison of prepared surfaces

Using the un-cleaned control sample as a comparator to identify the end point of the surface preparation methods, macro and microscopic investigation of surfaces reveals significant changes have occurred (Table 1). Glass beads and aluminium oxide blasted surfaces produce the most change by removing the oxide layer entirely. This correlates to grade D Sa 2.5 *'very thorough blast-cleaning'* or D Sa 3 *'blast-cleaning to visually clean steel'* being free of visible oil, grease, dirt, mill scale, rust, paint coatings and foreign matter and having a more or less uniform metallic colour [18].

Preparation Method	Coherent oxide layer	Powdery corrosion products	Micro-cracks in oxide	Surface profile	Corresponding surface preparation grade (BS EN ISO 8501-1:2007)
Un-cleaned control	Yes	Yes	No	Rough	Rust Grade D
Glass beads blasting	No	No	N/A	Undulating	D Sa 2.5
Aluminium oxide blasting	No	No	N/A	Rough	D Sa 2.5

Crushed walnut blasting	Yes	No	No	Rough (ice floes)	D Sa 1
Sodium hydroxide/ wire brushing	Yes	No	No	Smooth	D St 1
Flame cleaning/ wire brushing	Yes	Yes	Yes	Rough (ice floes)	Fl (approx.)

Table 1. Classification of surface preparation outcomes using BS EN ISO 8501-1:2007

Crushed walnut blasted surfaces are noticeably darker in appearance than the un-cleaned controls due to exposure of the dense, coherent magnetite (diffraction code 01-080-0390) layer following removal of overlying loosely adhering and powdery corrosion products and any vestiges of coatings (Figure 2). The outcome corresponds to D Sa 1 *'light blast-cleaning'* being free from visible oil, grease, dirt, poorly adhering mill scale, rust, paint coatings and foreign matter but retaining the closely adhering mill scale [18].

Samples prepared by sodium hydroxide immersion followed by manual wire brushing are markedly more polished and lustrous than the un-cleaned samples (Figure 2). Powdery corrosion products and remains of coatings have been removed and a coherent corrosion product layer is the end point. The surface preparation level corresponds to D St 2 *'thorough hand and power tool cleaning'* being free from visible oil, grease, dirt, poorly adhering mill scale, rust, paint coatings and foreign matter [18].

Flame cleaning causes the least change in some respects (Figure 2). No residues of coatings remain but the surface retains powdery corrosion products. A change in colour is noticeable; the corrosion products have gained a brighter, orange-red hue. The preparation level cannot be said to correlate to D Fl as it is not free from mill scale and rust, possibly due to wire-brushing being manual rather than by the specified power tool procedure in the standard [18].

Morphological interpretations

Blasting techniques: Spherical glass bead media peen surfaces to produce a satin finish with undulations that are visible at high magnification (Figure 2). Both glass beads and aluminium oxide removed all oxide that was visible to the naked eye. This contrasts with the matte surface of the aluminium oxide blasted samples caused by the angular roughness that is evident under high magnification. The crushed walnut blasted surfaces retain a coherent oxide layer but have lost their paint residues. This oxide layer shows a degree of surface roughness and some angularity which is due to plate-like laminations rather than a micro roughness produced by the cutting abrasive action of impinged media, as with aluminium oxide blasting. Since the hardness of glass beads on the Mohs scale (6) is similar to magnetite (5.5-6.5), corrosion product removal occurs at a slower rate than with aluminium oxide media, providing less danger of underlying metal removal. This degree of control is attractive for

heritage practitioners but is less cost effective in terms of operator time and materials. In contrast, the hard, angular aluminium oxide (8-9 on Mohs scale) cuts the surface of the corrosion products on impact, creating a more roughened, angular surface profile. This requires control and vigilance to prevent it removing underlying metal substrate. Despite their angular profile, the low hardness (3-4) of crushed walnuts limits their effect to removal of unsupported laminations, powdery corrosion products and polymeric coatings. The controlled and less aggressive nature of crushed walnut is reflected in its industrial use for polymer preparation and in heritage conservation for surface cleaning of copper alloys [19].

Sodium hydroxide immersion with manual wire-brushing: The sodium hydroxide solution (1.25M) solvated the polymeric coatings on the surfaces of the samples but the corrosion products remained insoluble at this pH [15]. Immersion facilitates the removal of powdery and loosely adhering oxides by wire-brushing, producing a surface that appears polished to the naked eye and relatively flat and smooth under high magnification. The areas of slight roughness bear some similarity to the plate-like laminations visible on the crushed walnut and flame cleaned samples with minimal disruption of the surface.

Flame cleaning with manual wire-brushing: The polymeric coatings adhering to the samples were removed by combustion during flame cleaning. Removal of large laminations of corrosion products by the abrasive action of vigorous wire-brushing was possible but both powdery and adherent corrosion products remain clearly visible. Under high magnification the surface appears rough in a manner similar to the crushed walnut blasted surfaces. The oxide layers are fractured, possibly by differential expansion of metal and oxides during heating leading to loss of laminations. Micro-cracks are visible in some areas.

Suitability of surfaces for application of protective coatings

Removal of corrosion accelerating contaminants and creation of a mechanical key for adhesion through roughening of the surface are critical for performance of protective coatings on prepared substrates [20, 21]. Of the treatments tested here, blasting with glass beads or aluminium oxide either to Sa 2.5 or Sa 3 is likely to advantageously remove the most contaminants, due to the thorough removal of corrosion products. The angular roughening of the surface profile evident on aluminium oxide blasted surfaces offers better adhesion relative to the undulating profile of glass beads peened surfaces. Pull-off testing of coatings on blasted and un-blasted surfaces report un-blasted surfaces had the lowest adhesion strengths, with failure of coating adhesion on blasted surfaces occurring between or within coating layers rather than between coating and substrate [22]. However, large peak-to-trough height differentials on surfaces allow rogue peaks to penetrate the coating leading to holidays [20]. Clearly, the dry thickness of a coating and its application rheology will be of importance in relation to the impact of peak height on coating performance. For aesthetic reasons, the heritage sector often utilises thin, low concentration and transparent acrylic coatings to protect surfaces [23], which means the deep keying supplied by aluminium oxide may prove a challenge to producing a continuous coating with an even thickness, as relatively peak height will be large in proportion to coating thickness. This merits further study as it has major

impact on matching coatings to surface preparation and is an area that has received no research in heritage contexts.

Although no impacted particles of blast media were identified on SEM images of prepared samples, this effect has been noted in unpublished tests commissioned by Historic Scotland. Blasting angle was modified here to minimise occurrence of impacted media but were this not possible in practice, residual blast media may have a negative effect on coating adhesion.

Problems arise with the techniques which retain the oxide layer, as they are incapable of producing the minimum Sa 2.5 preparation level generally required by manufacturers of coatings that are not formulated specifically for surface tolerance. Removal of the coherent oxide layer is not always either ethically or aesthetically desirable in a heritage context and its retention is not an uncommon requirement. Of the three techniques retaining oxides within this study, blasting with crushed walnut and flame cleaning appear to produce surfaces offering more mechanical keying for adhesion, although this effect may be reduced by the powdery oxides remaining on the flame cleaned samples producing future failure in adherence of the corrosion layer. The smooth and polished surfaces of the sodium hydroxide immersed samples have little potential for mechanical keying but removal of powdery corrosion products may mean fewer contaminants to promote corrosion under coatings and adherence of the corrosion products subjectively appears to be better than for flame cleaning. The un-cleaned surfaces of the controls with powdery, laminating corrosion products and vestiges of previously applied coatings are inappropriate for direct application of a coating due to a plethora of disadvantages that include: unevenness, poor intra surface adhesion, residual contaminants, hydration of oxide layers and ongoing corrosion.

The pictorial standard for flame cleaned surfaces states that flame cleaning must be followed by power tool wire-brushing to remove the products of flame cleaning, as hand wire-brushing does not prepare the surface satisfactorily to receive protective paint coatings [18]. For reasons of practicality, manual wire-brushing after flame cleaning was investigated here, since it has anecdotally been found to be common practice in heritage ironwork conservation. The presence of powdery corrosion products on surfaces after such cleaning lends weight to the assertion that this is not satisfactory preparation before application of paint.

Practical considerations in application of preparation methods: heritage context

Blasting with glass beads, aluminium oxide and crushed walnut shell: These three blasting techniques were similar in their application, equipment needs and practical considerations. Blasting within a cabinet is a relatively controlled process with detritus of operation largely contained, as is blasting of large objects in a workshop. *In situ* blasting requires a system by which spent media, corrosion products and paint are collected and cleared from the site. The cost, practical and financial considerations of *in situ* blasting often exclude their use in heritage contexts where resources are often very limited.

Control of parameters such as angle of nozzle to and distance from surfaces is readily achievable with small, flat samples in the blasting cabinet, making this method ideal for

portable heritage structures. It would be difficult to accomplish *in situ* for large, complex structures within heritage, although garnet blasting to Sa2.5 was successfully used to prepare the surface of Brunel's ship ss Great Britain [24]. Additionally, the morphology of heritage objects may make it difficult to remove paint layers and corrosion products from intricate and inaccessible areas of a structure by blasting, although this is equally true for other preparation methods. The pressures involved have potential to buckle material of thin section or destroy heavily corroded and weakened heritage iron that it is normally desirable to retain.

Health and safety concerns exist relating to exposure of the operator to airborne particulates and to disposal of blasting detritus. Crushed walnut shell has the potential to cause allergic reaction and the larger, angular particles require use of heavier weight protective gloves. Considering these factors it appears that blasting is an ideal preparation method for use on smaller heritage objects, where total removal of coatings, corrosion and surface finish is acceptable, with execution occurring in controlled workshop environments. Its use in the field may be suitable or even essential on large projects such as ss Great Britain but this is at the expense of high cost and less controlled application, making it appropriate for large, well-funded *in situ* projects. Cost of the method may be a movable point when the input of operator time is considered.

Immersion in sodium hydroxide solution and wire-brushing: Immersion of samples in sodium hydroxide is a simple, controlled process in the laboratory but this technique requires disassembly of structures, removal from site and access to a sufficiently large dipping tank for immersion. *In situ* application may occasionally be possible and techniques employing poultices could be considered but rinsing to remove sodium hydroxide solution is necessary and must be planned for from financial, disposal and health and safety viewpoints. Similarly to blasting techniques, sodium hydroxide seems to be better suited to the controlled environment of the workshop for heritage contexts.

Flame cleaning: This is a far less controlled and more operator dependent preparation method when compared to other techniques examined here. Maintaining surface temperatures, torch to surface distance and even equal distribution of heat, along with assessing the end point of the process, are entirely qualitative decisions with large operating parameters based on operator experience and interpretation. How reproducible this preparation technique could be for heritage objects requires further research that examines how differing temperatures, time of treatment, operator identity, surface morphology and oxide transformation influence the consistency of the preparation end point. The importance of form in heritage metalwork and often inherent object fragility mean flame cleaning is not suitable for iron of section less than 5mm, due to deformation risks (heritage ironworkers *pers. comm.*). This is clearly not a technique to be applied by inexperienced operators. Major advantages for contractors are its portability for *in situ* work, low cost and conformation to an international standard and the assurance that this appears to offer; disadvantages include hazards from large scale combustion of existing paint layers, especially as lead based paints are often present within heritage coatings.

Oxygen consumption rates

All samples consume oxygen and show a decrease in oxygen consumption rate over time (Figures 3-8, Table 2). Oxygen consumption rates can be examined via the changing gradient of the average trendline for each preparation method (Figure 13). This is done by using visual analysis of consumption graphs based on dividing the trend line into an initial period of 0-12 days (0-20 for un-cleaned samples), secondary period of 19-103 days (20-104 days un-cleaned) and final period of 103-338 days (104-257 days un-cleaned). Un-cleaned sample corrosion rate testing was conducted separately, hence discrepancies in gradient analysis periods. As might be predicted, all surface preparation methods show highest average consumption rates during the initial exposure period when the maximum area of freshly exposed metal is present.

Preparation Method	Sample	O_2 Consumption (mol/year/mm^{2}x10^{-8})	Average O_2 Consumption (mol/year/mm^2 x10^{-8})	Fe Converted to FeOOH (mol/year/mm^2 x10^{-8})	Average Fe Converted to FeOOH (mol/year/mm^2 x10^{-8})
Glass Beads	HS1	7.76		10.35	
	HS2	12.16		16.22	
	HS3	9.16		12.22	
	HS4	8.90		11.87	
	HS5	14.93	10.58	19.91	14.11
Aluminium Oxide	HS6	15.14		20.18	
	HS7	26.54	15.58 (12.84 without anomalous result)	35.38	20.77 (17.11 without anomalous result)
	HS8	7.64		10.19	
	HS9	12.09		16.12	
	HS10	16.47		21.97	
Crushed Walnut	HS11	1.94		2.58	
	HS12	3.18		4.24	
	HS13	3.03		4.04	
	HS14	3.17		4.22	
	HS15	3.98	3.06	5.31	4.08
Sodium Hydroxide	HS16	3.00		4.00	
	HS17	1.67		2.23	
	HS18	1.96		2.61	
	HS19	1.90		2.53	
	HS20	2.29	2.16	3.05	2.89
Flame	HS21	33.16		44.21	
	HS22	26.30	26.03 (28.48 without anomalous result)	35.06	34.70 (37.97 without anomalous result)
	HS23	24.86		33.15	
	HS24	29.60		39.47	
	HS25	16.21		21.61	
Un-cleaned	HS27	6.66		8.88	
	HS28	6.57		8.76	
	HS29	5.93		7.91	
	HS30	8.06		10.75	8.94

	HS31	6.30	6.70	8.40	

Table 2. Oxygen consumption averaged over test period (mol/year/mm²x10⁻⁸) and conversion of metallic iron to FeOOH (mol/year/mm²x10⁻⁸) of all samples giving averages by preparation method. All consumption values are given with blind consumption of the control vessel removed. Calculations of metallic iron conversion assume that all oxygen consumed reacts directly with metallic iron to form FeOOH and as such is an estimate of the iron consumed since some oxygen will be involved in redox reactions within the corrosion process.
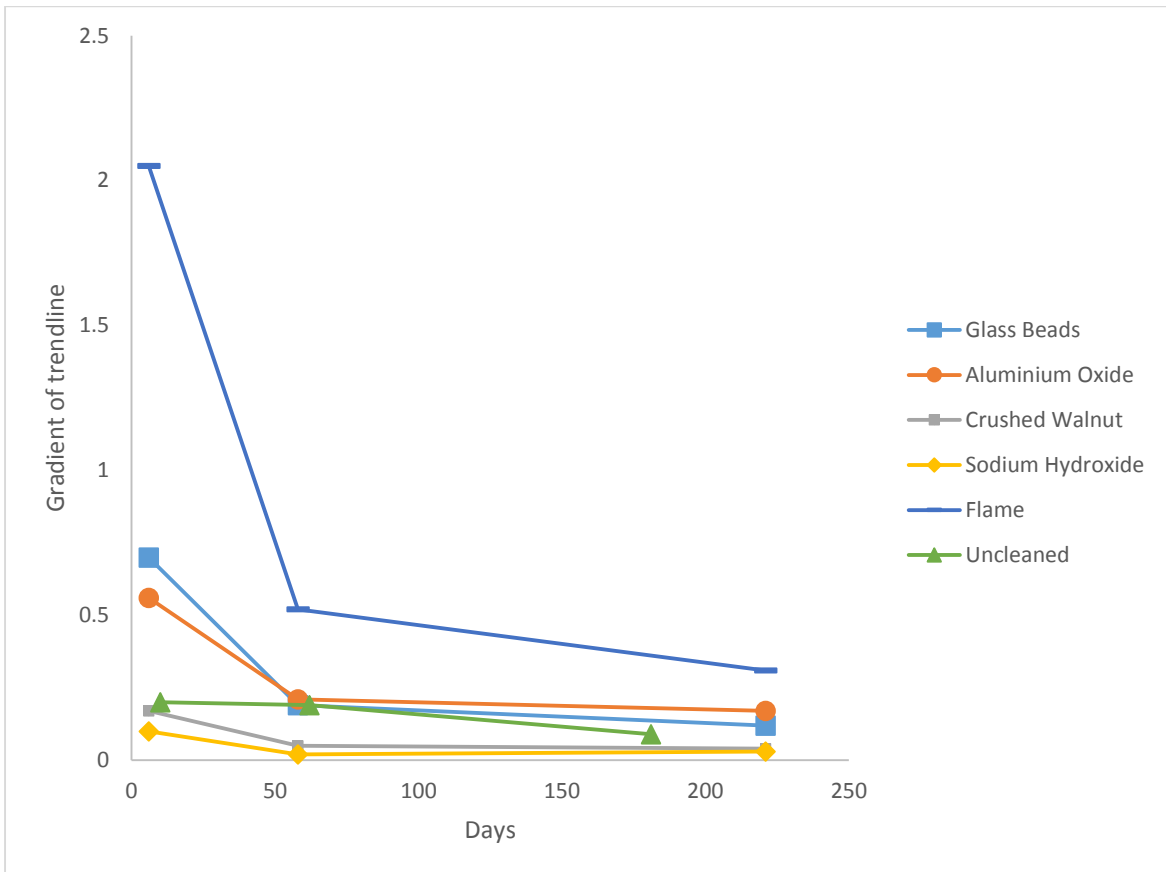

Figure 13. Change in gradient of trendline (i.e. rate) for average oxygen consumption of samples by surface preparation method. Points denote midpoint of gradient period.

Total consumption over study period: Clear and significant differences in oxygen consumption rate can be identified between a number of preparation methods using average oxygen consumption per year per gram of sample for each preparation method, with the un-cleaned samples as a baseline for comparison (Table 3). No significant difference could be determined between aluminium oxide and glass beads blasting methods or sodium hydroxide and crushed walnut blasting methods, which is evident when examining box plots (Figure 9). Removal of oxide layers to reveal the metal surface, using glass beads or aluminium oxide blasting, produced higher average oxygen consumption than the un-cleaned control. This is likely due to the exposure of the metallic surface and its unevenness offering a relative increase in surface

area and a large reaction platform of exposed metal still populated by corrosion accelerators. In contrast, there is a closely adhering, coherent oxide layer overlying the metal surface of the untreated sample but this also retains all corrosion accelerators. Initial high oxygen consumption of exposed metal surfaces is expected and is followed by slowing as corrosion products develop (Figure 13). The higher average oxygen consumption of aluminium oxide blasted samples, relative to those blasted by glass beads, may be due to a larger surface area produced by the rougher surface finish on the aluminium oxide samples. Upon termination of the tests both aluminium oxide and glass bead sample sets had developed new corrosion products concentrated in areas previously pitted during atmospheric exposure of the railing and along slag planes (Figure 10). This is likely due to the low pH anodic centres expected within pits and the potential difference between slag and iron [25].

Significantly different oxygen consumption (mol/year/mm^2)
Sodium Hydroxide / Aluminium Oxide
Sodium Hydroxide / Flame
Crushed Walnut / Flame

Table 3. Significantly different oxygen consumption per year per mm^2 of iron between surface preparation methods (calculated by Kruskal-Wallis and with a significance level of 0.05). Sodium Hydroxide / Glass Beads and Flame / Uncleaned results are close to significantly different but do not fall within the 0.05 significance level.

Both crushed walnut blasting and sodium hydroxide immersion with wire brushing decrease average oxygen consumption relative to the un-cleaned samples average. They show negligible oxygen consumption beyond 50 days (Figures 5,6,13). Treatment with sodium hydroxide solution has long been reported to inhibit iron corrosion [26,27,28], which may explain the reduction in corrosion rate recorded. For crushed walnut it may be that the impact of the blast media further compacts the coherent corrosion product layer visible on the sample surfaces post-cleaning, enhancing protection of underlying metal substrate and delivering hydrophobic effects from the drying oils in the nut shells. These oils cross link to produce films [29], whose hydrophobicity is evidenced in their traditional use for paint media. Developing even a thin non continuous drying oil layer offers potential to hinder moisture and oxygen ingress to anode sites at the metal surface. The dark colour of the surface post-preparation may be due to oils and disappears post-corrosion due to formation of new corrosion products (Figure 10). Despite, or because of, the retention of closely adhering corrosion that must also retain contaminants beneath it, both these preparation techniques reduce corrosion rate relative to the un-cleaned control (Figure 9). However, their lower oxygen consumption rate may simply relate to the arithmetic of there being a smaller reactive surface area due to retention of coherent corrosion product layers that hinder ingress of oxygen and moisture. The potential impact of a drying oil layer could be examined by using aluminium oxide blasting to remove all corrosion products, then impinging crushed walnut shells onto the surfaces of the samples. Oxygen consumption rates could then be compared

to those of aluminium oxide prepared samples which were not subsequently subjected to crushed walnut blasting.

Flame cleaned samples show a considerably higher oxygen consumption rate than the un-cleaned samples (Figures 7-9, 13). While macroscopically the extent and form of corrosion product on flame cleaned samples was least changed relative to un-cleaned surfaces, showing only colour difference, at high magnification a fractured and microcracked surface is evident (Figure 3). While differential expansion of oxides and metal substrate are used to describe the mechanism by which oxides are removed from the surface, it may also cause fracturing and cracking, which then offers pathways to oxygen and water ingress and subsequently corrosion.

Context for the heritage sector

By linking the morphology of the surfaces produced by the selected preparation methods to their oxygen consumption rate in high humidity, defined as a proxy for corrosion, a more informed approach to devising coating systems for heritage iron is possible. Whilst no tests examining the adhesion of coatings to surfaces were carried out, it is possible to use the surface morphology to predict that aluminium oxide and glass bead blasting potentially offer the best keying surfaces for coatings. There is little to choose in terms of keying morphology for the walnut blasted samples and the flame cleaned samples, with both offering less keying opportunity than either aluminium oxide or glass bead blasting. Sodium hydroxide appeared to offer the fewest keying opportunities but this must be balanced against the often powdery finish on the flame cleaned samples, which is likely to interfere with adhesion. Similarly, the possible impact of oils delivered by walnut media on adhesion of coatings must be considered.

Linked to these predictions of coating performance relative to keying onto surfaces must be the response of the surfaces themselves to high relative humidity. Should a coating applied to each surface offer exactly the same transmission of moisture and oxygen then sodium hydroxide and walnut blasted surfaces can be expected to corrode more slowly than glass bead blasted surfaces, which will corrode more slowly than aluminium oxide blasted surfaces with flame cleaned surfaces offering the worst corrosion rate of the five treatments. It is tempting to translate this into an estimation that slower corrosion rate of the samples tested here mean that a coating would remain fit for purpose for a longer time period on the less reactive substrate surfaces, thus offering better cost benefit. However, there are multiple variables that relate to coating performance. In this instance, the degree of disruption to the coating caused by the corrosion forming on the metal surface may influence its performance and adhesion at an early stage of the corrosion process. This may cause corrosion rates at the metal surface to diverge from those identified when testing surfaces without applied coatings. Also, the initial adhesion of the coating to the surface may have a major influence on how any corrosion impacts on the coating above it. Only further testing could examine these factors and other variables to add to understanding that could build a clearer picture of the complex relationships between coatings and surfaces.

Conclusion

These tests have identified the end morphology produced by five commonly used heritage conservation surface preparation methods applied to historic wrought iron corroded in real time in the atmosphere. From this, the conservation practitioner can better predict the nature of the surface that cleaning will produce and understand its likely benefits for adhesion of coatings. By comparing the corrosion rate of prepared but uncoated surfaces in high humidity, using a quantitative measurement technique, it is now possible to predict the relative impact of surface preparation on corrosion rate of wrought iron. This offers insight into the potential effect of oxygen and moisture passing through coatings that are permeable or damaged on corrosion of the metal substrate and, subsequently, the likely impact on the longevity of the coating above it. While these are unrefined measures that are not quantitative, their existence does offer some degree of prediction and insight into coating performance where previously none existed. In doing this the study provides a platform for further testing to refine and expand the results produced, which can then be used to build a quantitative data base to support predictive management of coating performance on heritage wrought iron. Overall, this will contribute to better cost benefit calculation and more efficient use of the scant resources available for heritage preservation.

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