Flame cleaning of historic wrought iron: practitioner methods and their impact on oxide morphologies and post-treatment corrosion rates

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Abstract

Flame cleaning followed by wire brushing is a common treatment for wrought iron; the flame combusts existing coatings and spalls oxides while wire brushing removes any debris, producing a sound surface for recoating. Although frequently applied, little is known about the effects of the treatment on the substrate material and its post-treatment corrosion rate. This study reports scanning electron microscope backscattered electron imaging (SEM-BEI) and oxygen consumption corrosion rate testing of wrought iron flame cleaned by three practitioners.

Wrought iron samples treated by two practitioners corrode up to 4 times faster than uncleaned control samples. Samples cleaned by one practitioner exhibit no increase in corrosion rate. Torch fuel type and temperature attained by the iron are identified as parameters potentially contributing to differences in corrosion rates.

Comparing oxide morphology of treated and untreated samples reveals extensive cracking and fragmentation following flame cleaning. This offers multiple pathways for ingress of oxygen and water to the metal core to support corrosion. This data simultaneously calls into question the ethics of flame cleaning and offers evidence that a 'safe' method exists, prompting further research into this popular treatment.

Keywords

Iron; corrosion; wrought iron; flame cleaning; treatment; practitioner; oxygen consumption; SEM-BEI

1. Introduction

1.1 Conservation of historic wrought iron

Effective management of heritage assets requires that decision-making is underpinned by empirical evidence of the impact of treatments on long-term survival of materials. Historic ironwork, which occupies a niche position between heritage and engineering, is frequently exposed to outdoor atmospheric corrosion and, in the case of bridges, gates and similar structures, may be required to perform a distinct structural function. Sector guidance to direct practice is based largely on anecdotal evidence and established methods (Ashurst and Ashurst 1988; Blackney and Martin 1998; Davey 2007; Davey 2009; Mitchell 2005; Schütz and Gehrke 2008; Watkinson et al. 2005; Wilson et al. 2010). International and British Standards relate to modern steels (ASTM 2008; British Standards Institute 2000; 2007), their application to historic ferrous metals being complicated by differences in metallurgy and lack of concession to conservation ethics (Canadian Association for the Conservation of Cultural

Property 2000; American Institute for Conservation of Historic and Artistic Works 1994; International Council of Museums 1984).

Recognition that corrosion of iron degrades its functional and aesthetic properties, leading to failures of structures and objects, is long standing with treatments applied to iron historically to increase its useful lifespan. In theory, reducing the rate of atmospheric corrosion of metals is achievable by: modifying the environment to make it less corrosive; exploiting electrochemical principles to suppress anodic or cathodic reactions; or by separating the metal from the corrosive environment and introducing a large resistance to impede ion transport between anode and cathode (Scully 1990; Mayne 1954). In practice, modern techniques for corrosion prevention of historic iron continue to centre on the application of organic coatings, effectively separating the metal from its exposure environment and exploiting electrochemical principles.

Adhesion is crucial for successful anti-corrosion performance of organic coatings and can be maximised by thorough surface preparation, with clean metal surfaces or sound metal oxides ideal for wetting due to their high surface energies (Bierwagen and Huovinen 2010). Surface preparation techniques are therefore integral to conservation treatments for historic ironwork and aim to remove existing paint layers and corrosion products prior to recoating, optimising performance and longevity of protective coatings. Methods of surface preparation include: blasting at high pressure with abrasive media or dry ice; immersion in alkaline solution baths to dissolve paint layers; wire brushing or needle-gunning to abrade flaking coatings and corrosion products; and flame cleaning.

1.2 Flame cleaning

Flame cleaning uses a torch flame to combust paint layers and heat the surface of the object. The metal core expands more than the overlying corrosion products with the increased temperature, causing the corrosion products to spall from the surface. Wire brushing removes any remaining loose corrosion products. Increasing focus on ethical and environmentally friendly practices have sparked a resurgence in popularity of flame cleaning thanks to its perceived advantages over alternative techniques. These include: minimal loss of original historic material; retention of protective oxides; ease of use on-site; controllability; ready availability of equipment; minimal detritus of operation; and cost effectiveness.

Despite anecdotal treatment successes, prior research identified increased corrosion rates of wrought iron following flame cleaning (Emmerson and Watkinson 2016) as measured via oxygen consumption (Emmerson and Watkinson 2014; 2016; Watkinson and Rimmer 2014). Laboratory flame cleaned iron corroded up to four times faster than untreated, abrasive blasted or chemically stripped iron. The widespread use of flame cleaning and its potential to drive corrosion rates of ironwork, ultimately leading to loss of heritage structures, makes empirical investigation of the treatment an important issue for conservation science.

1.3 Aim and objectives

This research investigated the impact of flame cleaning on the post-treatment corrosion of historic wrought iron by:

- Recording flame cleaning of historic wrought iron samples by three historic ironwork conservation practitioners;

- Imaging oxide morphology pre- and post-treatment by scanning electron microscopy;
- Measuring oxygen consumption of individual flame cleaned and uncleaned samples at high relative humidity (RH) as a proxy corrosion rate;
- Correlating experimental results to practitioner treatment methods.

2. Method

2.1 Sample material

Historic wrought iron was used as the sample material to avoid the pitfalls of analogous samples and ensure direct applicability of results to heritage practices. Mid-19th century rolled wrought iron plate from the Kings Cross/St Pancras gasometer was sourced. Optical and scanning electron (CamScan Maxim 2040) microscopy confirmed this to be wrought iron due to the presence of stringers of slag. X-ray diffraction (PANalytical X'Pert Pro (Cu K_α)) of the corrosion products on untreated samples identified magnetite, goethite and lepidocrocite consistent with corrosion products reported on iron subjected to atmospheric corrosion (Bouchar et al. 2014).

The gasometer plates are of consistent thickness (4mm) and samples (30mm x 40mm x 4mm) were cut using a water-cooled cutting process to minimise temperature increase and associated changes in microstructure of the iron. Historic wrought iron is by nature an inhomogeneous material (Dillmann et al. 2004) and local differences in microstructure and slag distribution are possible. Producing all samples from the same rolled sheet minimised likelihood of large compositional variations.

2.2 Flame cleaning

Eight samples were flame cleaned by each of three practitioners according to their preferred method. All practitioners applied the flame to the surfaces of the samples and intermittently brushed the samples surfaces with a steel wire brush. Duration of application of the flame varied between practitioners. The colour of the metal during cleaning was recorded as an indicator of temperature. The specifics of these methods were recorded for comparison.

2.3 Examining corrosion product morphology

Samples of uncleaned and practitioner cleaned samples were embedded in Struers Epofix resin and cross-sectioned using a Struers Minitom precision cut-off machine. Sections were polished (600-0.25μm polishing cloths), carbon coated and imaged in BEI mode using a CamScan Maxim 2040 scanning electron microscope (SEM) equipped with Oxford Instruments energy and wavelength dispersive X-ray spectrometers (Oxford Link Pentafet 5518 Caesium™ 7.2.17).

2.4 Oxygen consumption corrosion rate measurement

Flame cleaned and uncleaned control samples were enclosed individually in airtight reaction vessels (250ml Mason Ball glass jars with plastic coated brass sealing discs tightened with threaded outer sealing rings of brass) containing 160g silica gel conditioned to 90% RH. To the interior wall of each vessel was adhered an oxygen sensitive spot (World Precision Instruments (WPI) part #503090 adhered with Radio Spares RTV silicone rubber compound). A watch glass separated each sample from

the silica gel. The reaction vessels were stored in a Binder KBF240 climate chamber at a constant 20 ±0.5°C to avoid RH fluctuations within vessels due to temperature change. MadgeTech RHTemp 101A dataloggers recorded internal vessel conditions confirming 90 ±3% throughout the test period for all vessels.

Oxygen concentration within each vessel was measured at regular intervals over a 108-day period using a WPI OxyMini meter with fibre optic cable (WPI OXY-MINI-AOT with cable #501644). The accuracy of the oxygen measurements is ±2mbar at 210mbar (atmospheric oxygen pressure) and increases with decreasing oxygen pressure. Negligible ingress of oxygen has been shown in control vessels filled with nitrogen over this time period, indicating a low leakage rate (Watkinson and Rimmer 2014).

3. Results

3.1 Practitioner methods and prepared samples

Examining the video recordings of practitioner flame cleaning allowed identification of parameters of operation and individual methods (Table 1). There were notable differences which centred on the variables of torch fuel, temperature of the metal and duration of flame application which is linked to determination of end point. Prepared samples show a distinct colour change to red oxides after treatment (Figure 1).

Table 1: Parameters of flame cleaning by practitioners A, B and C

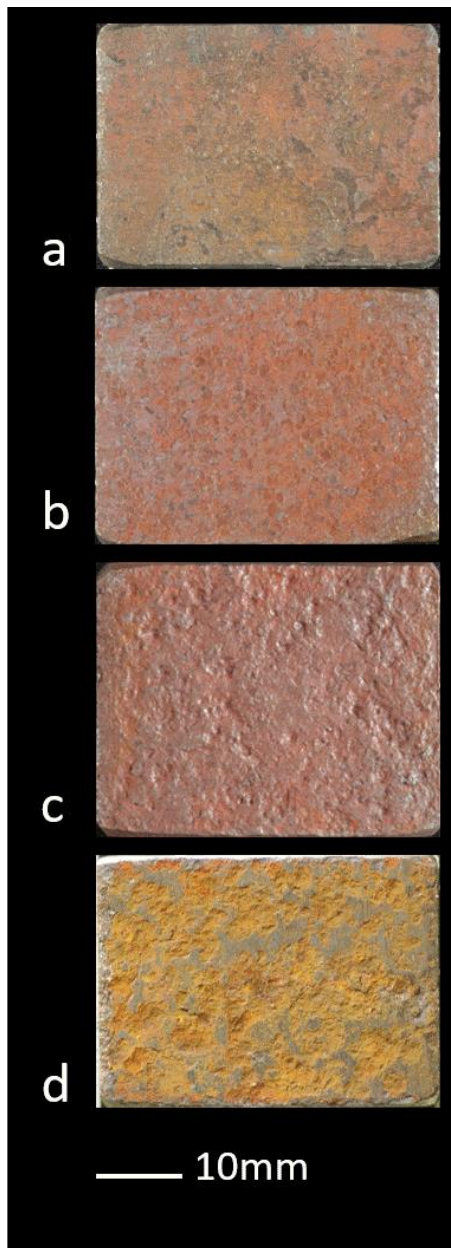| PRACTITIONER	TORCH	METAL COLOUR DURING CLEANING	ESTIMATED MAX. TEMPERATURE OF THE METAL (^{o}C)	DURATION OF FLAME APPLICATION TO SURFACE (SECONDS)	DETERMINATION OF END POINT
A	Oxypropane (oxygen cutting boost)	Dull red	500	c.20-30	Visual cleanliness
B	Oxypropane (oxygen cutting boost)	Grey	<150	<10	Cessation of luminescence of coatings and oxide vestiges under flame
C	Oxyacetylene (no oxygen boost)	Dull/ cherry red	700	c.50-60	No further corrosion removable or coating visible

Figure 1. Samples after preparation by practitioner A (a), practitioner B (b) and practitioner C (c) and uncleaned sample (d)

3.2 Post-treatment oxide morphologies

SEM-BEI images of cross-sectioned treated and untreated samples (Figure 2) evidence a reduction in oxide layer thickness for all treated samples relative to untreated. Reduction in thickness is least evident in the sample prepared by Practitioner B (Figure 2c,g) and most evident for Practitioner A (Figure 2b,f). Oxides remain in pits on all treated samples. Whilst a small degree of oxide layer micro-cracking can be observed for the uncleaned sample (Figure 2a,e), cracking and fragmentation is extensive for oxide layers on all treated samples. Cracks have increased in both number and size post-treatment.
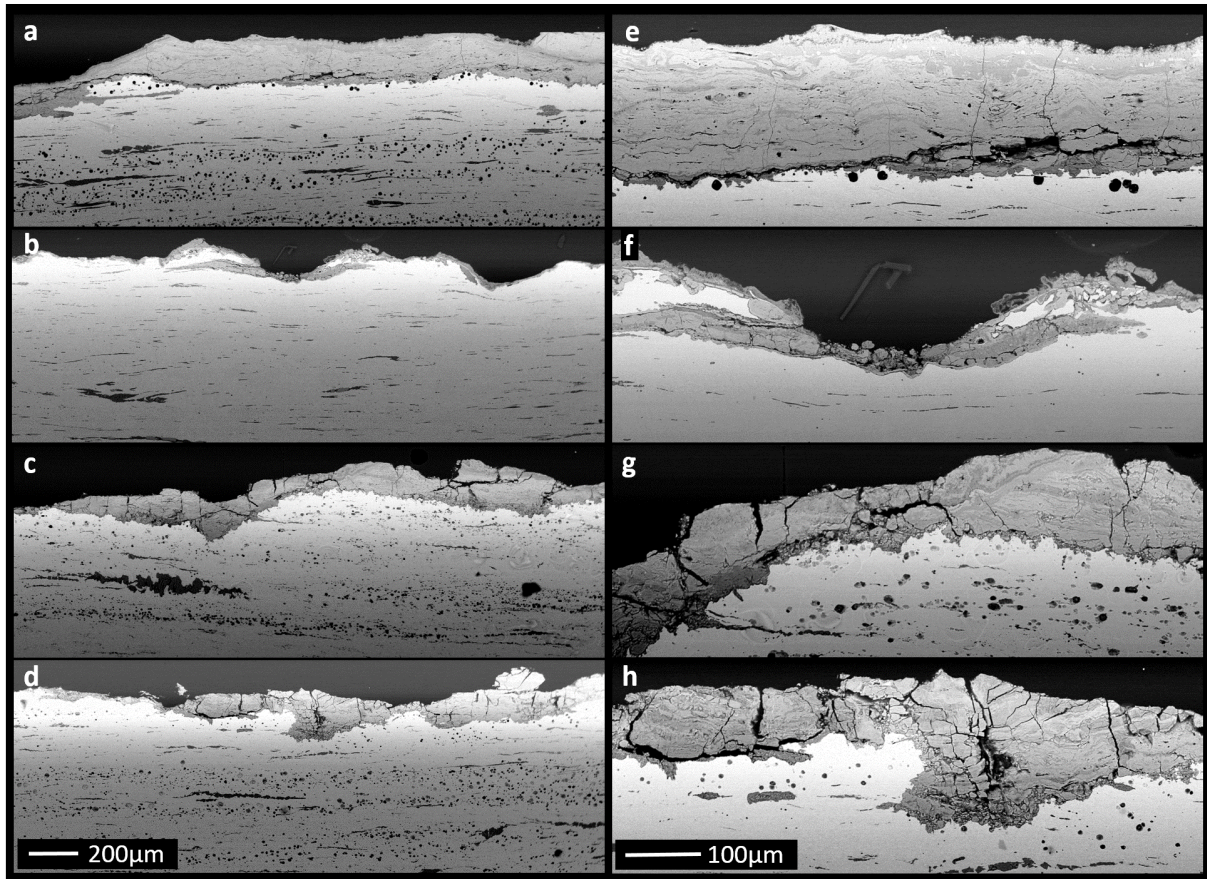
Figure 2. SEM-BEI of untreated (a,e), and practitioner A (b,f), practitioner B (c,g) and practitioner C (d,h) cleaned samples at 50x (a-d) and 150x (e-h) magnification

3.3 Oxygen consumption measurements

All practitioner flame cleaned and uncleaned samples consumed oxygen during the test period (figures 3-6). Consumption is characterised by a faster initial rate which slows over time for all flame cleaned samples (figures 3-5). Uncleaned samples exhibit a more constant oxygen consumption rate over the test period (Figure 6).
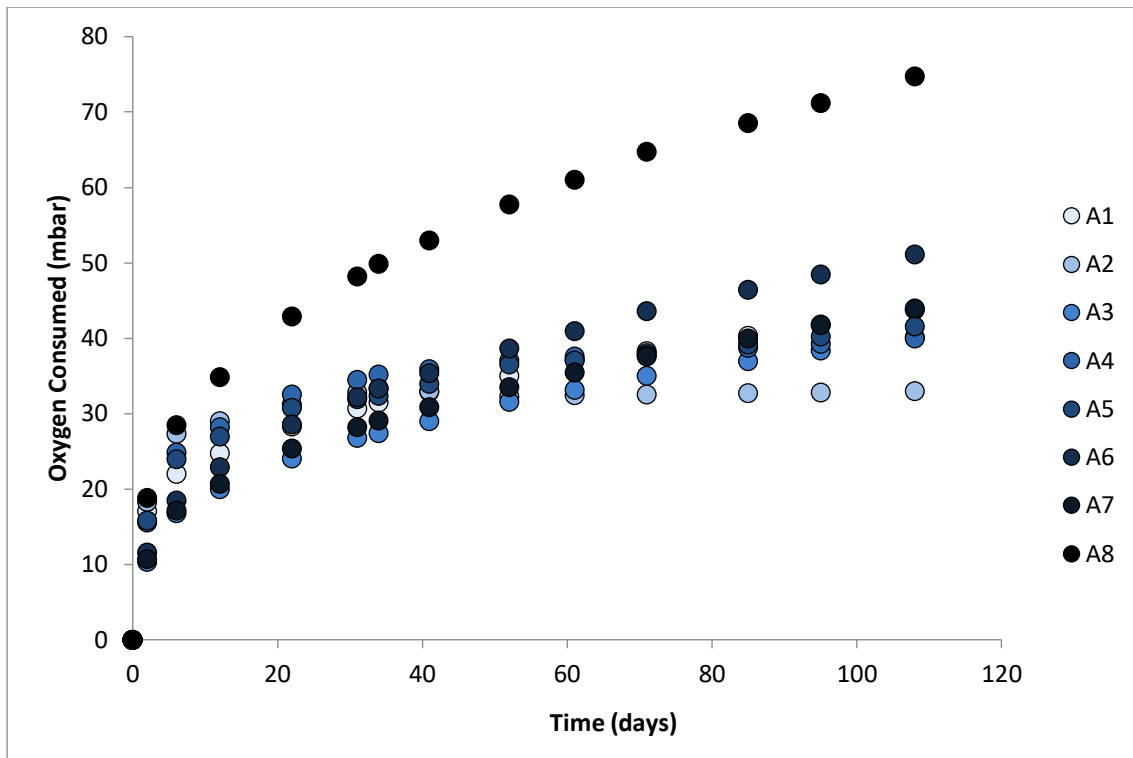
Figure 3. Oxygen consumption of wrought iron samples flame cleaned by practitioner A over the test period of 108 days. The shape of the plot for sample A2 indicates failure of the reaction vessel seal
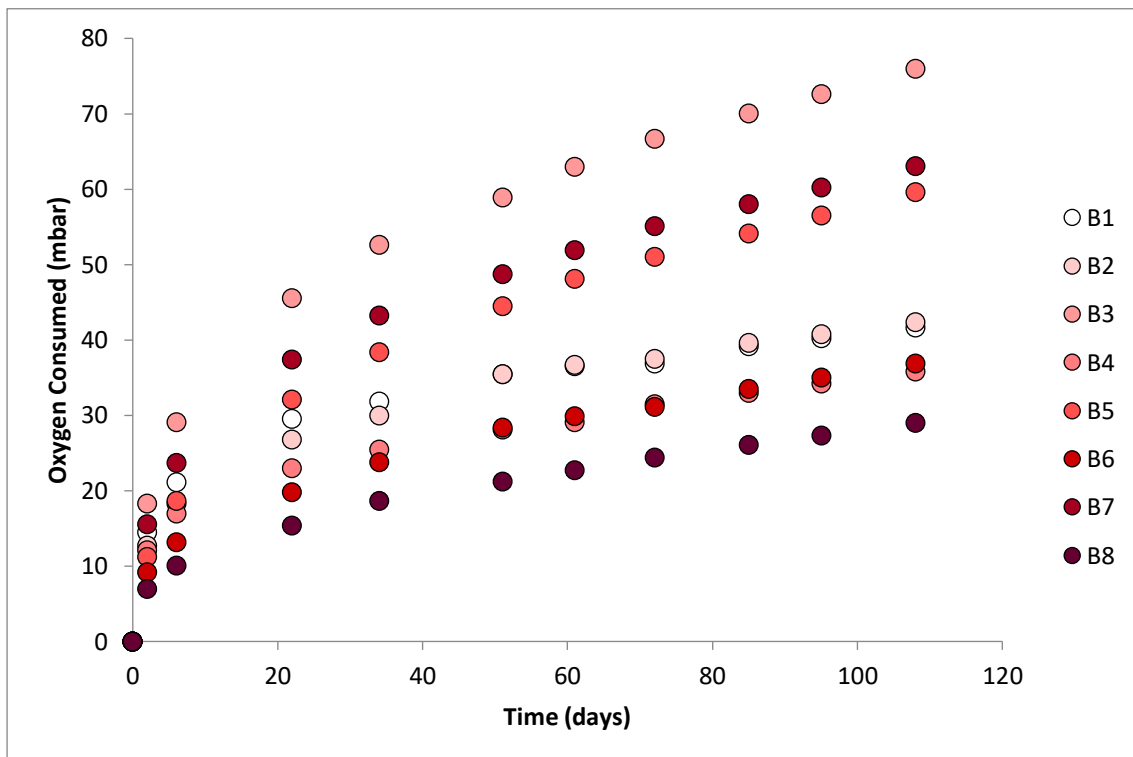

Figure 4. Oxygen consumption of wrought iron samples flame cleaned by practitioner B over the test period of 108 days
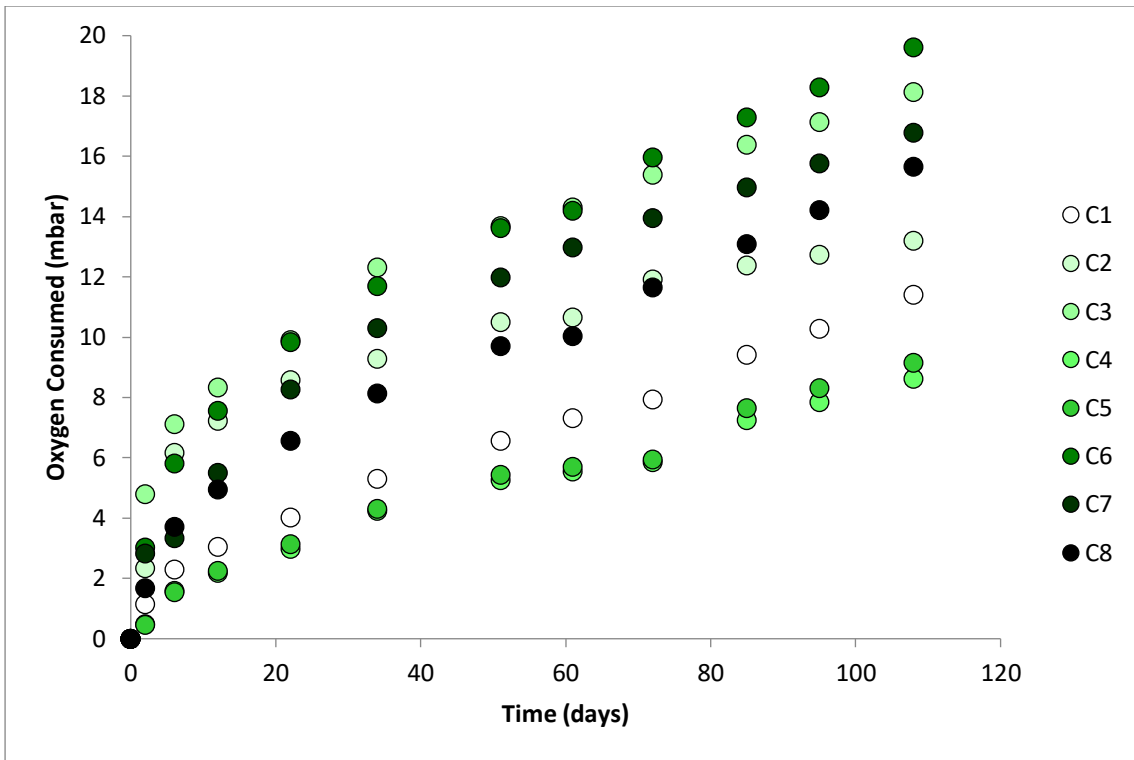
Figure 5. Oxygen consumption of wrought iron samples flame cleaned by practitioner C over the test period of 108 days
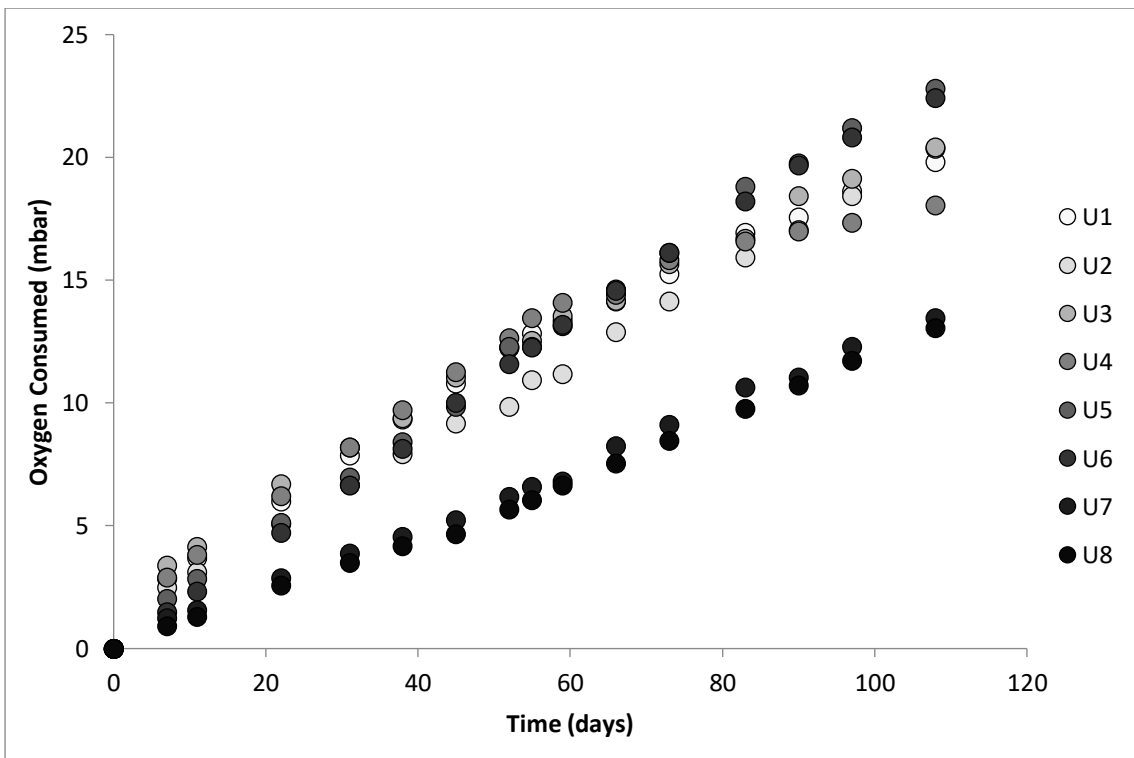

Figure 6. Oxygen consumption of uncleaned wrought iron samples over the test period of 108 days

Examining boxplots of oxygen consumption calculated by sample mass (to minimise influence of minor discrepancies in sample dimension) over the test period for all flame cleaned and uncleaned samples (Figure 7) indicates that uncleaned samples and those prepared by practitioner C share similar, lower oxygen consumption rates, with smaller consumption ranges between samples. Samples prepared by practitioners A and B exhibit comparable oxygen consumption ranges if outlier A8 is included (sample numbers argue for this) with practitioner B samples having a slightly larger range around a similar median value and particularly above it.
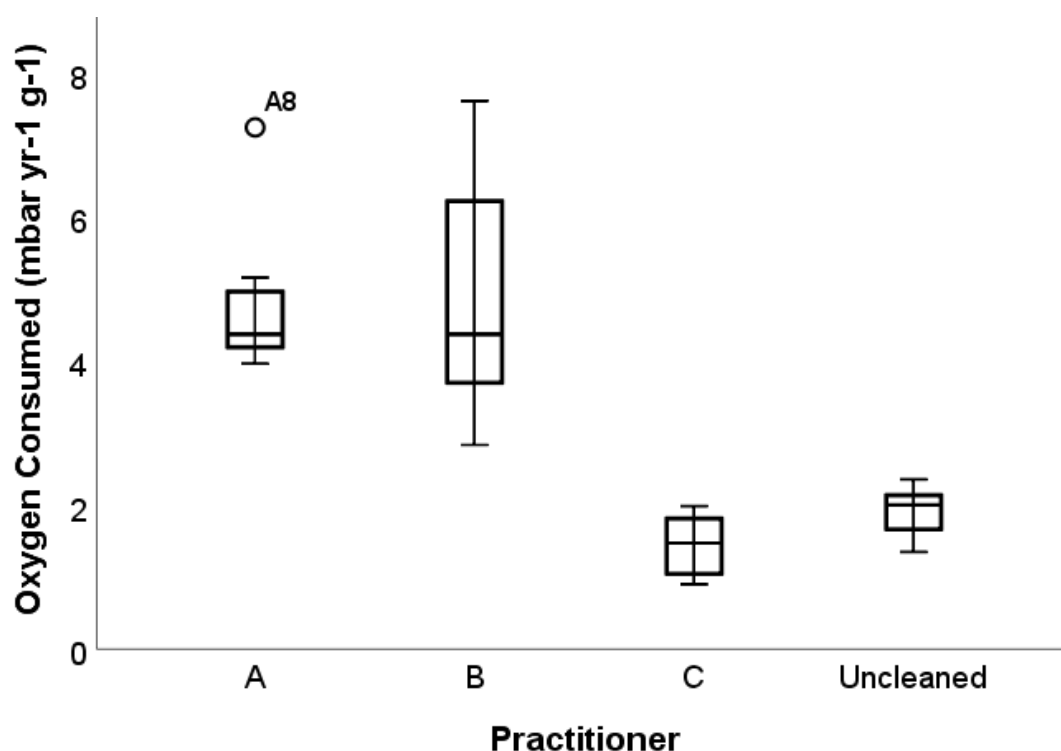

Figure 7. Boxplot showing the oxygen consumption rate of the wrought iron samples flame cleaned by practitioners A, B and C and of uncleaned samples over the test period of 108 days calculated as *mbar yr^{-1} g^{-1}* **for all samples. Sample A2 has been removed from the dataset as leakage of the reaction vessel was identified (Figure 3)**

4. Discussion

4.1 Corrosion product morphology

Macroscopically, the extent and form of corrosion products on wrought iron surfaces is not altered greatly by flame cleaning, a colour change (to brighter orange/red) being the most noticeable aspect (Figure 1). At high magnification, an extensive fragmentation of corrosion product layers is evident relative to uncleaned samples (Figure 2). While differential expansion of oxides and metal substrate describes the mechanism by which loosely adhering corrosion products are spalled from the surface of wrought iron, it has likely also caused this fracturing and cracking of closely adhering oxide layers.

This then offers pathways for ingress of oxygen and water to the metal surface which allows corrosion to occur. Capillaries of small diameter increase corrosion risk by reducing the RH at which condensation can occur (down to 50% RH in capillaries of 1.5nm) (Garverick 1994), hence increasing the number of micro-cracks may increase corrosion in treated samples.

4.2 Oxygen consumption and corrosion rates

As tests have shown that nothing in the experimental set-up consumes oxygen (Emmerson and Watkinson 2014; Watkinson and Rimmer 2014; Emmerson and Watkinson 2016), any oxygen consumed during the test period may be attributed to corrosion. Thus, rate of oxygen consumption is a proxy measure for corrosion rate. Samples cleaned by practitioners A and B showed a considerably higher corrosion rate than uncleaned samples and those cleaned by practitioner C (Figure 7). This indicates that the flame cleaning methods employed by practitioners A and B have increased the corrosion rate of the wrought iron relative to leaving the material untreated. Corrosion rates of uncleaned samples and those cleaned by practitioner C are not significantly different, with ranges overlapping and practitioner C cleaned samples having a slightly lower median value. The clear implication is that the flame cleaning method employed by practitioner C has not increased the corrosion rate of the wrought iron samples beyond their uncleaned corrosion rate.

4.3 Influence of practitioner methods on post-treatment oxide morphologies and corrosion rates

Temperature attained during cleaning is likely more important than duration of flame application. No practitioner could state with confidence the metal temperature during cleaning but there were noticeable differences between methods. Samples cleaned by practitioner B did not exceed 150°C and oxides are unlikely to have been affected beyond the influence of differential thermal expansion. Samples cleaned by practitioner A and C reached approximately 500 and 700°C respectively. It is unlikely that changes in the microstructure of this wrought iron would arise from heating to these temperatures (North et al. 1976).

Corrosion product transformations may occur at elevated temperatures; goethite to haematite has been reported at 240-250°C (Ruan et al. 2002) and lepidocrocite to maghemite at c. 200°C which is metastable and transforms again to haematite at 500°C (Gehring and Hofmeister 1994). Transformation of oxides may explain the characteristic bright red/orange colour of the corrosion products observed within c.60 seconds of flame cleaning a sample (Figure 1). Decomposition of chloride-containing iron oxides at temperatures above 380°C has been reported (North and Pearson 1977; Kanungo and Mishra 1996). It is not expected that these samples contain large quantities of chloride and the duration of high temperature exposure during flame cleaning may not be sufficiently long to support decomposition. Should this be a factor influencing corrosion rates of these samples, the increased corrosion rate of practitioner A samples suggests that the temperature required is perhaps towards the 700°C attained by practitioner C samples.

Clear differences in the extent of oxide remaining post-treatment are evident between practitioners (Figure 2). Least reduction in oxide thickness is evident on samples treated by practitioner B, likely due to low treatment temperatures and short duration of cleaning. Higher temperatures and longer treatment durations for practitioners A and C led to greater reduction in oxide thickness. There is no direct correlation between these parameters and the extent of oxide removal (being greater for practitioner A than practitioner B despite slightly reduced treatment time and temperature). It is

worth noting that the treatment variable not considered here is length and vigour of wire brushing which probably influences removal of oxides.

The treatment parameter which separates practitioners A and B from C, possibly accounting for corrosion rate differences, is the nature of the torch and its fuel. Practitioners A and B used oxypropane torches with oxygen boost settings to increase flame temperature. Practitioner C used an oxyacetylene torch with no oxygen boost. Oxyacetylene flame temperature is generally higher than oxypropane although the temperature of the oxypropane torches with oxygen cutting boost is not known. The combustion reaction equations for acetylene **[1]** and propane **[2]** support anecdotal reports from practitioners that propane burns with a 'wetter' flame which is feared to introduce water to oxide layers and increase post-treatment corrosion.

$$2H_2C_{2\,(g)} + 5O_{2\,(g)} \rightarrow 4CO_{2\,(g)} + 2H_2O_{(g)} \hspace{4cm} \textbf{[1]}$$

$$C_3H_{8\,(g)} + 5O_{2\,(g)} \rightarrow 3CO_{2\,(g)} + 4H_2O_{(g)} \hspace{4cm} \textbf{[2]}$$

4.4 Flame cleaning in practice

Examining practitioner methods reveals that flame cleaning is carried out in an ad hoc manner with a range of methods employed and different philosophical approaches. Torch choice may be based on availability and cost; oxyacetylene is more expensive than oxypropane. Use of the oxygen boost flame with the oxypropane torch was deliberate to increase flame temperature and burn off paint layers more quickly. Flame application time must relate to extent of corrosion product and amount and nature of existing coatings but also to the philosophy of the practitioner. Practitioner B was concerned with conservation ethics, preserving historic evidence within the metallographic structure and the concept that the metal last attained red heat during forging. This concern led to the shortest treatment duration and lowest metal temperature. Practitioners A and C did not express concern over the heating of the historic iron in relation to the material or conservation principles. This divergence, one practitioner using ethics to dictate end points and two others using appearance, apparently ignores any interpretation or conception of physical or chemical outcome for the metal and relation to subsequent application of coatings.

A high level of experience and knowledge of the materials and their properties does not prevent a 'technician' approach to work. Unless an agreement is in place for maintenance work by the same practitioner, an individual may never be in situ to judge long-term implications of decisions and practices. Training directs practitioner thought processes; conservation trained practitioner B was more thoughtful regarding impacts of decisions on retention of historic evidence, for example. It may be through training that a synergy of practical experience and understanding of chemical and physical processes can be produced to improve both practice and researcher knowledge. Practitioners are an invaluable source of information regarding wrought iron, its properties and responses to treatment.

Flame cleaning is a precursor to application of protective coatings. Although it is important to understand the corrosion rate of the substrate material, what is missing from this study is investigation of the performance of coatings applied to the flame cleaned substrates. Differences in adhesion of coatings to these sample surfaces pre- and post-treatment, plus measurement of their corrosion rates once coated, is required.

5. Conclusion

The popularity of flame cleaning is due to numerous practical and ethical advantages over other surface preparation techniques for historic wrought iron. This study has demonstrated that practitioner methods are variable and are highly influential when considering post-treatment oxide morphology and corrosion rates of uncoated material. It has been shown that there is a method by which flame cleaning can be applied without increasing the corrosion rate of the iron but as yet the parameters of this method cannot be identified. Results reported here indicating an increased post-treatment corrosion rate must introduce a note of caution to recommendations for use of flame cleaning. With the support of the practitioners, work continues at Cardiff University to identify optimal treatment parameters for flame cleaning and produce guidelines for the safe treatment of historic wrought iron.

Acknowledgements

Biographies

Nicola Emmerson lectures in conservation science at Cardiff University. Her research focuses on the management of corrosion prevention strategies for metallic cultural heritage artefacts.

David Watkinson teaches and researches conservation at Cardiff University. His work on the corrosion rate of iron underpins the preservation of Brunel's iron steamship ss Great Britain.

Johanna Thunberg has held conservation and teaching roles at Cardiff University where she is undertaking an AHRC-funded PhD. Her research centres on controlled microclimate storage protocols for archaeological metals and identification of instability in copper alloy artefacts.

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