

Article

Oxygen Depletion Testing of Metals

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Abstract: The altered nature of archaeological metals means they deteriorate at much lower relative humidity (RH) conditions than historical metals. The study of deterioration for such materials is hampered by their complexity, variability and difficulties in measuring deterioration. Placing an object in a sealed container, controlling the RH and pollutant gases and measuring any decrease in oxygen concentration is an accessible method to measure the deterioration rate. It has been used for research into suitable environmental conditions to manage the deterioration rates of such artefacts, including the differences in the response of artefacts from different excavation sites. Some objects need the careful control of RH to low values; this is expensive to maintain and poses risks to other artefacts displayed together. Many objects are actually stable up to quite high RH values, and oxygen depletion testing has been used to identify those that can be safely displayed with minimal environmental control. The accelerated corrosion ‘Oddy’ test is frequently used to sift out unsuitable display materials. The visual assessment is widely recognized to be subjective. The test container has been modified and oxygen depletion appears to give good quantitative measurements of corrosion that correspond with both visual comparison and corrosion loss measurement with linear stripping voltametry or chemical stripping for copper, lead and steel but not for silver.

Keywords: oxygen depletion; heritage metals; corrosion testing



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1. Introduction

The measurement of corrosion rate is essential for the preventive conservation of metals. Whilst several analytical methods exist, they have drawbacks in real situations for heritage objects. Chemical or electrochemical stripping is probably the most used method [1], but the impact of aggressive chemical agents needs to be controlled, and surface finishes and materials such as mineral preserved organic remains can be lost. Other electrochemical techniques require an electrolyte and an electrical contact to metal, which requires surface cleaning. XRD and FTIR can be non-invasive and can quantify most corrosion products, but they struggle with complex surface geometries. Objects such as archaeological metals often have very complex corrosion and deposition layers as a result of burial. These are difficult to fully characterise, and much of the relevant information is below the surface. Analyses of iron artefacts often reveal several layers, from a loose surface soil and sand layer down to a dense product layer (frequently magnetite mixed with other iron corrosion products) either in the centre of or next to any remaining metal. Metal frequently does not survive the burial process.

Oxygen depletion, enclosing an object in an air-tight container and measuring any reduction in oxygen concentration, provides a convenient, non-invasive technique to determine corrosion rates on complex objects. The technique has been used or has the potential to be used in at least four main areas:

- Research into preventive conservation;
- A screening technique for archaeological iron and copper alloy stability;
- Research into interventive conservation (not researched in this work);
- A detection method for accelerated corrosion tests, such as the Oddy test.

This paper considers each area in turn, using examples from English Heritage collections gathered over the last 15 years, to illustrate the strengths, weaknesses and challenges for the conservation of heritage metals.

1.1. Research into Preventive Conservation

The atmosphere in the container can be varied to investigate its effect on the corrosion rate. Relative humidity (RH) is controlled with pre-conditioned silica gel, saturated soluble salt solutions and glycerol solutions. Temperature is normally controlled by placing the container in an oven or environmental chamber. Saturated salt solutions can be used with ethanoic acid, methanoic acid and methanal (also known as formaldehyde) to produce atmospheres with controlled carbonyl concentrations and RHs [2]. Initial work in the late 1990s used a heated zirconium oxide detection method, which required an air sample to be drawn into the instrument. The method assumes oxygen reduction is the dominating cathodic reaction and that it is rate controlling. In the presence of water, under acidic conditions, water can be reduced. This was investigated by analysing the reduction product hydrogen gas. The introduction of ruthenium fluorescent quenching sensors and fibre-optic analysers simplified the experiments as the sensors can be read through glass or clear films, removing the need to take a gas sample or disturbing the seal of the air-tight container [3]. The technique is designed for industrial applications in packaging and a number of factors need to be accommodated in the experimental method:

- Temperature compensation;
- Angle of measurement—the angle between the analyser fibre and sensor can affect the measured value; much less impact is seen on phase shift type measurements than absolute intensity measurements;
- Distance from the probe head to the sensor can affect the measured value;
- 80% maximum RH, without further calibration;
- Air pressure;
- Moving the containers appears to affect the measured value for some minutes;
- Light sensitivity of the sensors;
- Cleaning—the packaging industry practice of adhering the sensor to the inside of the glass vessel is unsuitable when cleaning of the container is required between heritage conservation experiments.

Several containers have been validated as suitable for this technique. This has usually been done by first flushing the container with nitrogen to produce a zero or very low oxygen concentration and then measuring any increases in oxygen concentration with time. Quickfit laboratory glassware, Bernardin or Bocal Mason jars, corrosion jars, borosilicate glass jars with polypropylene screw tops blocked with aluminium foil and heat-sealed Escal™ film bags (but not Escal™ bags sealed with Escal™ clips) have all been shown to be suitable [2–6].

The method has been used by several researchers, investigating the impact of RH on archaeological wrought iron and cast cannon balls [7,8]; single samples of a cast iron cannon ball, shell and rivet plate [5]; and the impact of RH and carbonyl pollutants on terrestrial archaeological iron and copper alloys [2,6]. The test has been minimized to investigate the impact of samples of akaganeite (chloride-containing β -FeOOH) from objects as small as 2 μ g [9]. The method can be extremely sensitive at low volume-to-object ratios. A series of tests investigating the impact of RH on archaeological iron are reported.

1.2. A Screening Technique for Archaeological Iron and Copper Alloy

Whilst some archaeological iron and copper alloy artefacts deteriorate frighteningly rapidly at ambient RHs, others are stable even at 70 or 80%. In display situations, several similar objects are often available from an excavation that could fulfil the interpretation narrative for a showcase. It can be possible to identify some that are stable and do not require RH control. This is financially significant given that RH control is expensive and resource intensive. Many showcases also display organic artefacts that are damaged at the

very low RHs required to preserve unstable archaeological iron and copper alloys. Oxygen depletion tests, based on likely RH levels, can determine which artefacts are stable in these conditions. The results have been assessed and compared to long term exposure for archaeological iron [2] and copper alloys [6]. It is important that the tests limit the corrosion occurring, so that minimal damage to the artefact occurs. This is achieved by controlling the artefact-to-container volume, hence the amount of oxygen available, and controlling the RH. One concern over this type of testing is the often deep corrosion layers, which slow oxygen or water vapour transport to the corrosion centres and thereby influence how long tests need to be continued for. Fourteen days was initially used as a compromise between the period for the test (in museums, displays often have short preparation schedules) and allowing sufficient time for gas phase transport. The dense product layer would be expected to have the most resistance to transport. A series of oxygen and water vapour transport tests were undertaken with samples of archaeological iron with dense product layers from object fragments due to be disposed of.

1.3. Research into Interventive Conservation

The high level of variability in reactivity for archaeological metals makes treatment trials difficult. Consequently, very large numbers of objects are typically needed to obtain statistical data. Oxygen depletion tests have been used to compare the efficiency of chemical treatments [7,10–12]. The oxygen depletion rates for untreated and treated single objects have been reported. One potential use for using the oxygen depletion technique, however, is to pre-select groups of objects reacting at similar rates for trials. The reduction in oxygen depletion rate due to coatings has also been investigated [5,13,14]. Oxygen depletion with respect to research into interventive conservation has not been investigated further in this paper.

1.4. A Detection Method for Accelerated Corrosion Tests, Such as the Oddy Test

Most archaeological metal objects are displayed in showcases. These can provide sustainable environmental control [15], but there is a risk from gases emitted from the construction and dressing materials. Most materials are tested with an accelerated corrosion test, the Oddy test, to determine those suitable for this use [16]. The test has developed many variations and its variability is an issue [17–19] however there are some moves towards materials emission testing. Beyond the variation in method used, which would be a concern for any type of testing, accelerated corrosion tests are prone to two major causes of variation: (i) in the preparation of the metal coupons used and (ii) in the visual assessment for the test. Several better methods for quantification of the amount of corrosion have been proposed [10,20,21]. Despite these drawbacks, the Oddy test probably has a future due to its accessibility; emission tests require expensive and complex gas analysis equipment and routine use will be limited to major institutions. Emission tests are a viable route to test materials used by showcase manufacturers but, in a survey of UK showcase users, over 85% used materials in their cases that were not supplied by the manufacturer. Emission tests rely on a comprehensive knowledge of which gases and at what levels these are damaging. Substantial further research is required to produce this information for the very large number of gases encountered in heritage science and display showcases. The dangers of this approach were illustrated by van Iperen et al. [22], with piperidinol secondary amine compounds being detected in large numbers of showcases despite the cases having passed emission tests. In contrast, accelerated corrosion testing is effective despite not knowing which gases are present, since if the gases emitted cause corrosion, then any corrosion will be observed on the sacrificial test metals. Modifications for an air-tight container could allow oxygen depletion to be used as a reproducible, accurate and cost-effective way to quantify the corrosion. A series of initial tests are described. The measurement by oxygen depletion replacing visual assessment also gives the potential to replace the cleaned metal coupons with metal powders. This removes the variability in cleaning procedures, although careful storage will be required in order to preserve the

reactivity of the powders. It would be possible to test all three metals in separate tubes, to give separate results similar to the present test. However, it can be argued that it is the overall result that is important (worst of the three metals tested), and this could be achieved in a single combined test.

2. Materials and Methods

2.1. Samples

Objects from a number of excavations were monitored using a range of oxygen depletion tests. Table 1 gives details of the named samples and the tests applied.

Table 1. Overview of tests on objects.

Location (Code)	Object Description	Number of Objects Tested	Test Method ¹	Storage Conditions
Billingsgate	Nails	27	as [8]	unreported, data taken from Watkinson et al. [8]
Caerleon (CPF)	Nails	30	as [8]	unreported, data taken from Watkinson et al. [8]
Camber Castle (Cam)	Cannon balls, musket fittings, swords, daggers	41	(ii)	dry silica gel
Carisbrooke Castle	Lock, chainmail, nails, knives, spear heads, arrowheads, helmets	31	(iii)	dry silica gel
Dover Castle	Horseshoes, keys, arrowheads, nails	27	(iii)	dry silica gel
Haughmond Abbey	Buckles, pins	15	(iii)	dry silica gel
Lullingstone Villa	Pin, knife, lock, nails	21	(iii)	dry silica gel
Pevensey Castle	Horseshoes, keys, arrowheads, nails, staff terminal	12	(iii)	dry silica gel
St Augustine's Abbey	Keys, nails, brackets, pins	32	(iii)	dry silica gel
Stonea (Stn)	Hook, daggers, spearheads, arrowheads, nails	32	(i)	uncontrolled conditions
Sutton Hoo (SH)	Daggers, spearheads, arrowheads, nails	29	(i)	dry silica gel
Uley	Daggers, spearheads, arrowheads, nails	21	(i)	uncontrolled conditions
Whitby Abbey	Knives, pins, bar, bracket	23	(iii)	dry silica gel

¹ Test methods are described in the experimental methods section below, see also Supplementary Materials.

2.2. Experimental Methods

Method (i): Oxygen depletion tests for the Stonea, Uley and Sutton Hoo objects were undertaken in 1000 mL borosilicate glass corrosion jars. A Quickfit fitting trapped a septum seal, made of a Systech Illinois self-adhesive polymer disc attached to Escal™ film, to sample through a reseal. A needle pushed through the seal allowed air sampling with a Systech Illinois Mapcheck oxygen meter. Jars flushed with nitrogen were tested and showed no oxygen ingress (<0.1% above original concentrations over 6 months and 24 measurements). No more than 10% of the air was sampled in total to comply with ISO 16000 [23]. The RH was controlled with conditioned silica gel and measured with Hanwell Humbug data loggers. Hydrogen gas was measured for the Sutton Hoo samples with a Quintron MicroLyzer.

Method (ii): Oxygen depletion tests for Camber Castle used 300 mL Bernardin Mason jars and a Presens 4 Oxygen meter with Presens Sp-PSt3-NAU-D7-YOP self-adhesive oxygen spots. The RH was controlled with glycerol solutions [24] and measured with calibrated iButton® (±2%) temperature and RH data loggers.

Method (iii): Oxygen depletion tests for objects from Carisbrooke Castle, Dover Castle, Haughmond Abbey, Lullingstone Villa, Pevensey Castle, St Augustine's Abbey and Whitby Abbey used either a Presens 4 Oxygen meter with Presens Sp-PSt3-NAU-D7-YOP oxygen spots or a Gas Sensor Systems instrument based on the same principles. Tests were undertaken in either stoppered Quickfit glassware or heat-sealed Escal™ bags with conditioned silica gel, depending upon the size of the object. The Escal™ bags also contained an RH logger.

Method (iv): The object survey used deterioration criteria described in [4] in over 100 showcases across 31 English Heritages sites. The different room environments and showcase performances gave a wide range of maximum RH values. RH was measured in each showcase for at least a year, and in some instances 15 years, using Signatrol SR002, Hanwell Humbugs data loggers or Meaco radiotelemetry transmitters with Rotronic hygroclip probes. All probes underwent annual 3-point calibrations to National Accreditation Measurement Service (NAMAS) standards.

Method (v): Eight fragments of dense product layer from object material destined for disposal (from Uley and Stonea excavations) were embedded in the centres of 20 mm diameter epoxy discs (Araldite AY753 and hardener HY956), cast in several consecutive thin layers to limit heating. Two of the samples were from the Uley excavation. These objects had been observed to exhibit pitting into the dense product layer to a depth of 2 mm, so oxygen must have permeated the dense product layer for the corrosion to occur in this instance. The discs had epoxy forming at least the outer 4 mm or more (depending on sample dimensions), but no epoxy was present in the inner 5 mm of any of the samples. The discs were trapped into the steel top of Bernardin Mason jars with a Viton™ 'o'-ring compression seal. Epoxies are reported to be oxygen impermeable [25] and this was confirmed by casting a complete epoxy disc, flushing the jar with nitrogen and measuring no oxygen ingress. The test jars were flushed with zero grade nitrogen and kept in a chamber controlled to 50% RH; see schematic in Supplementary Materials. Calibrated iButton® ($\pm 2\%$) temperature and RH data loggers were placed in the jars along with Presens Sp-PSt3-NAU-D7-YOP oxygen spots. The oxygen concentration was measured with a Presens 4 Oxygen meter, initially, and checked to be below 0.3% and then again after 14 days. The RH was also read initially and checked to be below 3% and then from the loggers after 14 days.

Method (vi): The Oddy test involves enclosing 2 g of material with cleaned copper, lead and silver coupons and 0.5 mL water. A silicone stopper is used to close the borate glass reaction vessel and the coupons are held in slots in the stopper, in the air space above the test material. The test takes 28 days at 60 °C, and any corrosion is assessed visually after this [16]. Eight showcase materials (including cotton and wool fabrics, polypropylene, polystyrene, polyethylene and polyvinyl chloride and MDF) that had previously been Oddy tested separately for silver, copper and lead and that gave a range of results (three rated as suitable for permanent use, two as suitable for temporary use and three rated as unsuitable for use) were selected for oxygen tests. Tests were also undertaken with steel, but there are very few previous test results to use to determine suitable test materials. Thirty-two materials were tested in all. Oddy-type tests were undertaken in 134 mL borosilicate GL-45 screw-top glass jars, see schematic in Supplementary Materials. A separate borosilicate glass vial filled with 0.5 mL 18.2 MΩ cm⁻¹ water was added to generate a near 100% RH. Lead, copper, silver (all 99.9% pure, Alfa Aesar), and low carbon A36 steel sheet (acquired a number of years previously from unknown supplier) were each cut into 0.8 cm × 2.5 cm coupons and abraded with 3200 grit Micromesh™ sandpaper until the surface oxidation was removed. These metals were then cleaned sequentially with HPLC grade acetone and isopropanol, then air-dried above dry silica gel. Cleaned coupons were hung from a custom-designed, 3D-printed sintered nylon coupon holder in the neck of the jar (SHAPEWAYS product/62958LYNJ). An aluminium foil circle was cut to fit the inside of the polypropylene screw top lid. A Viton™ 'o'-ring was fitted into the lid to create a seal that was tightened with a socket wrench to a torque of 4 Nm. Two replicate jars were prepared for each test.

Two control jars containing no sample were also assembled for each round of experiments. The jars were placed in an oven at 60 °C for 28 days, and the oxygen concentration was then read with a Presens 4 oxygen meter when the jars had cooled to room temperature. One test for each metal had three Presens Sp-PSt3-NAU-D7-YOP oxygen spots at different heights to check that no concentration gradients were formed. The metal coupons were removed and electrochemically stripped. The coupon was immersed in electrolyte solution (0.1 M sodium nitrate for silver, 0.1 M sodium acetate for copper, 0.1 M sodium sesquicarbonate for lead) and potentiodynamically stripped using a Palmsens 3 potentiostat and silver/silver chloride reference electrode [26,27]. Steel was chemically stripped with hydrochloric acid and hexamethylene tetramine [28].

Schematics of the experimental equipment are available in Supplementary Materials.

3. Results

3.1. Research into Preventive Conservation

Figure 1 shows the oxygen depletion rate measurements for Stonea objects taken in 2002 (18–22 years after excavation) and more recently for Camber Castle in 2016 (35–52 years after excavation).

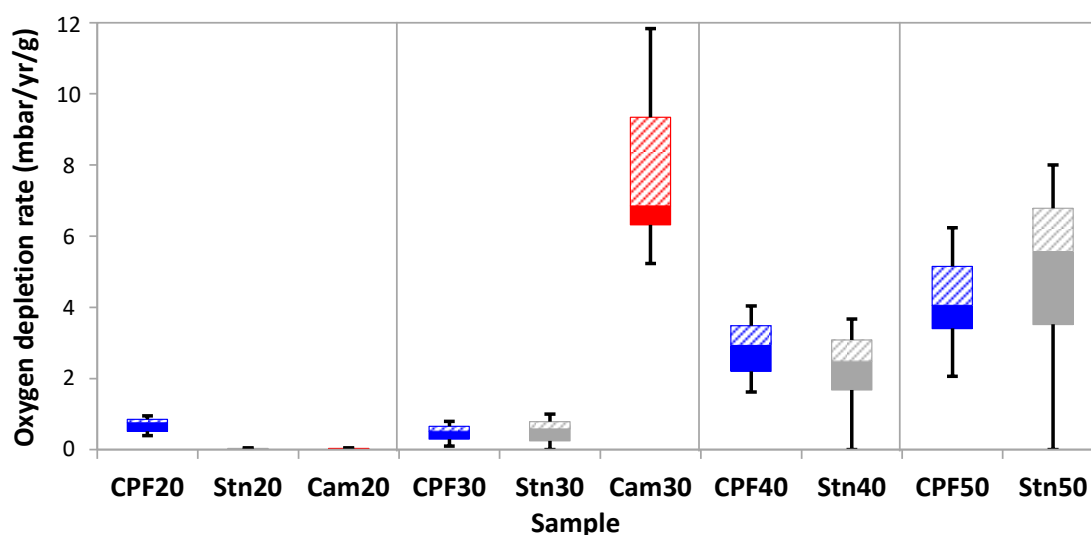


Figure 1. Oxygen depletion rates for selected samples examined at 20, 30, 40 and 50% relative humidity. Interquartile ranges and minimum and maximum values are shown. Excavated samples are from Caerleon (CPF, data taken from [8]; blue), Stonea (Stn; grey) and Camber Castle (Cam; red).

The difference in reactivity to RH is pronounced, with the Camber Castle material reacting very rapidly at 30% RH, but not at all at 20%. The Camber Castle experiments were halted at 30% in order to avoid damage as the reaction rate was so high. The Stonea material was representative of most of the other measured sites (21 so far, with 11 reported in this work) and does not show a reaction at 20%, reacts slowly at 30% and then reacts increasingly rapidly as %RH increases. The Caerleon material reported by Watkinson et al. [8] shows a reaction at 20% that then increases in rate with the increasing RH in a similar manner to the Stonea sample.

Figure 2 shows the oxygen depletion rate results from 13 sites measured at 50% RH. The data for Billingsgate and Caerleon were taken from Watkinson et al. [8]. The Camber Castle data collected at 30% RH are also included, as this is the only material tested by the author that shows all objects from the site depleting oxygen.

Objects excavated from 10 of the 13 sites showed a bimodal distribution, with several objects consuming no oxygen and the rest grouped over an 8 mbar/yr/g wide band, centred on the 4–8 mbar/yr/g range.

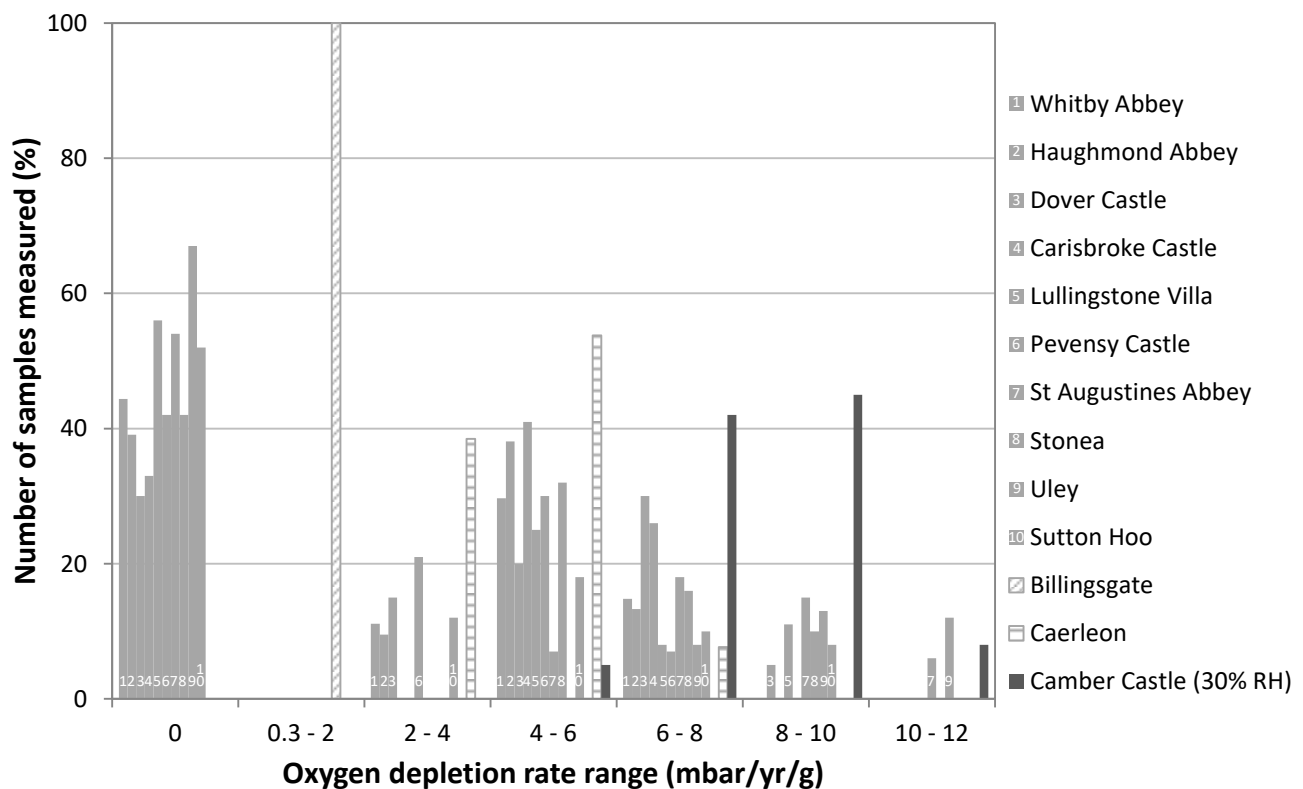


Figure 2. Oxygen depletion rate ranges measured at 50% RH for selected samples. Solid data are from English Heritage, hatched data is from Watkinson et al. [8]; note Camber Castle data was only collected at 30% RH as this already showed corrosion—as illustrated in Figure 1.

Figure 3 shows the oxygen consumption and hydrogen evolution above three uncleaned archaeological iron objects excavated during the year 2000 at Sutton Hoo (labelled SH1, SH2 and SH3). Measurements were taken in 2002, 16 months after excavation.

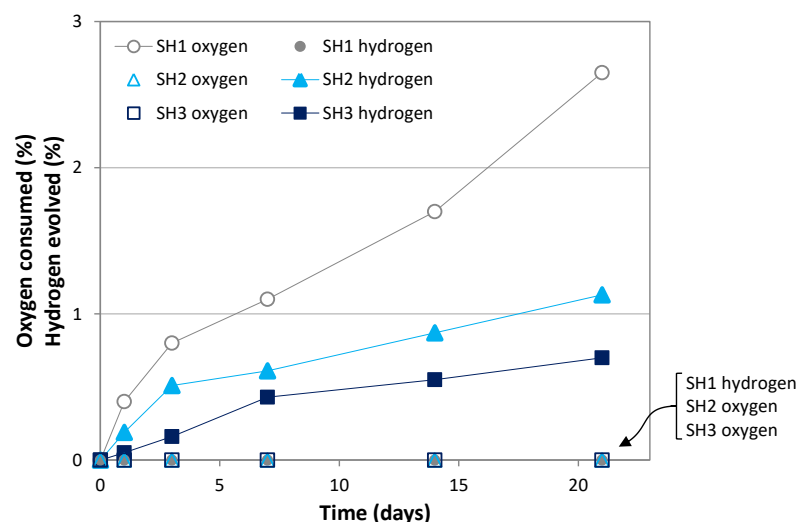


Figure 3. Selected samples from Sutton Hoo (SH) showing oxygen consumption and hydrogen evolution characteristics.

Object SH1, in addition to 26 other objects excavated from Sutton Hoo that were measured, consumed oxygen with no hydrogen evolution detected. Objects SH2 and SH3, meanwhile, both evolved hydrogen and did not consume any oxygen. The detection of hydrogen indicates that water reduction can occur in some wet objects. The object drying

was followed by mass loss over 2 years and was found to be losing weight almost to the end of that period [29] including the point at which these measurements were made. This indicated that the objects were not fully dry.

3.2. A Screening Technique for Archaeological Iron and Copper Alloy

The analysis of over 1000 objects on display at English Heritage sites, when grouped into four criteria-anchored deterioration categories, reveals the impact of RH within showcases, Figure 4. The four categories, one (none; no deterioration detected) to four (heavy; significant loss, cracking or powdering), enable assessment with respect to the maximum RH experienced in the showcase.

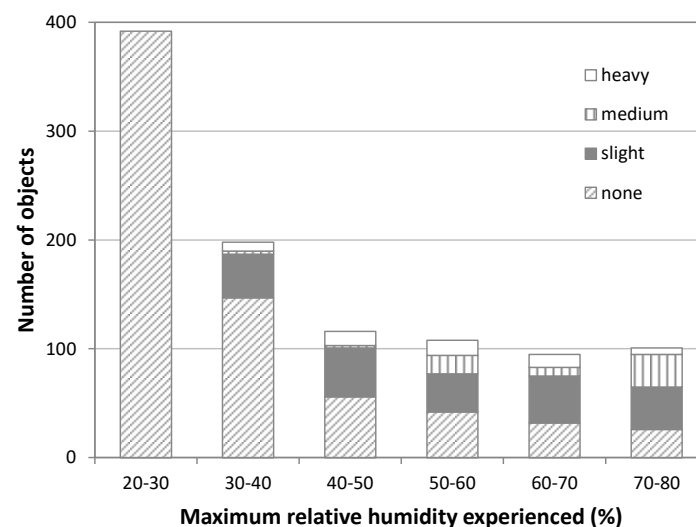


Figure 4. Deterioration categorization of over 1000 English Heritage archaeological metal objects on display with respect to the maximum relative humidity ranges that they have experienced.

Even in showcases experiencing high RH values, a significant proportion of archaeological iron objects remain in condition 1 or 2 after, in some instances, decades on display.

Results from experiments investigating the time taken for oxygen and water vapour to penetrate dense product layers from Uley and Stonea are shown in Figure 5. Two of the samples came from the Uley excavation.

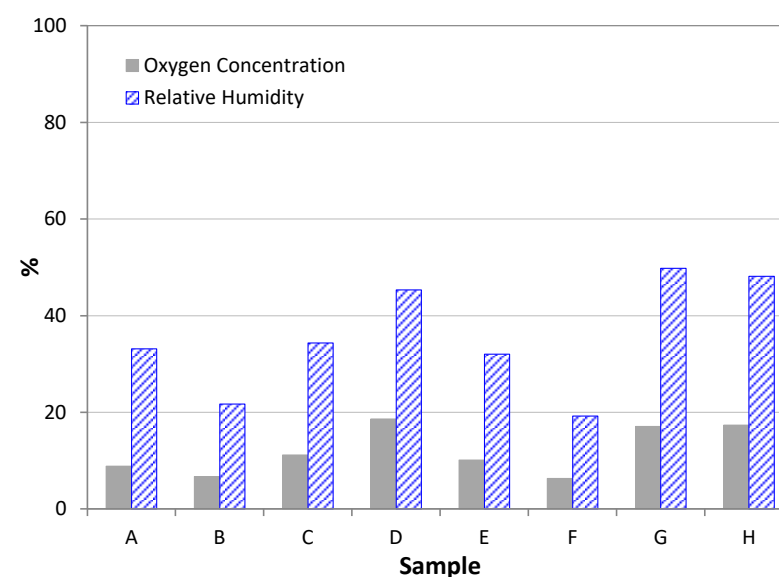


Figure 5. Amount of oxygen and water vapour penetrating dense product layer samples after 14 days. Initial oxygen concentration was below 0.3%, initial RH below 3%.

Oxygen penetrated all the layers within 14 days, indicating that the test period was sufficiently long to allow for the reaction of cleaned objects from in or below the dense product layer. Iron objects for display would almost always be cleaned down to the dense product layer. Some screening experiments were run with much longer tests, and no instances of oxygen depletion starting after 14 days were observed.

3.3. A Detection Method for Accelerated Corrosion Tests, Such as the Oddy Test

Figure 6 shows Oddy test results for each of the 8 separate showcase materials (32 in total) tested in the presence of lead, copper, silver or steel. The amount of oxidised metal from stripping is shown along with the amount of oxygen depleted during the 28 day test.

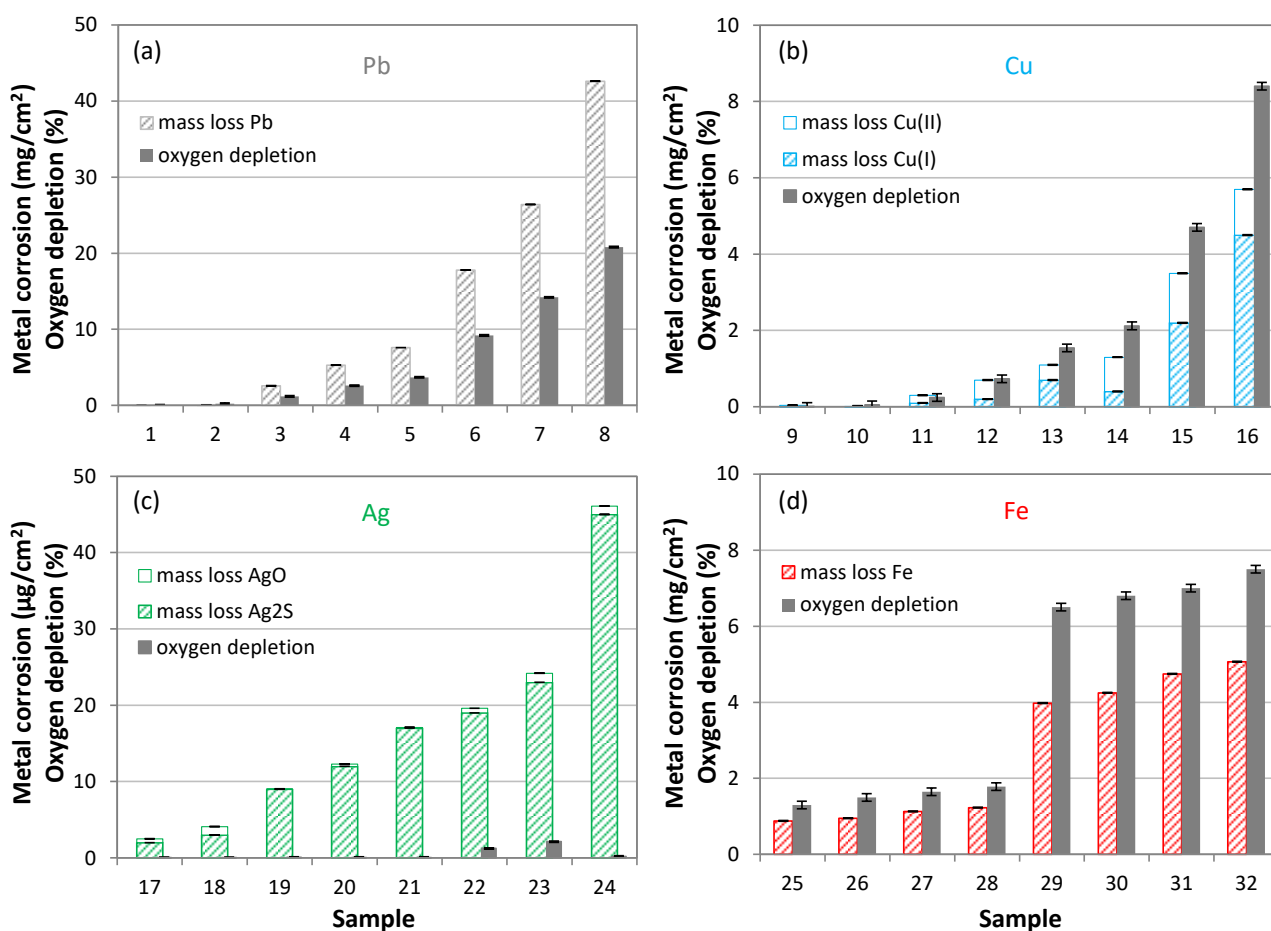


Figure 6. Accelerated ageing Oddy tests for (a) lead (Pb), (b) copper (Cu), (c) silver (Ag) and (d) steel (Fe) showing results for 32 individual samples (8 samples per Oddy test) as metal corrosion mass loss ($\text{mg}/\text{cm}^2 \pm 0.01$ or $\mu\text{g}/\text{cm}^2 \pm 0.01$) and % oxygen depletion ($\pm 0.1\%$); error bars are shown.

Figure 7 shows that there is a good correlation between the lead, copper and iron corroded and the oxygen consumed. In several of the silver tests there does not appear to be a relationship between oxygen consumption and the tarnish level measured or observed. The raw data for all figures are available in Supplementary Materials.

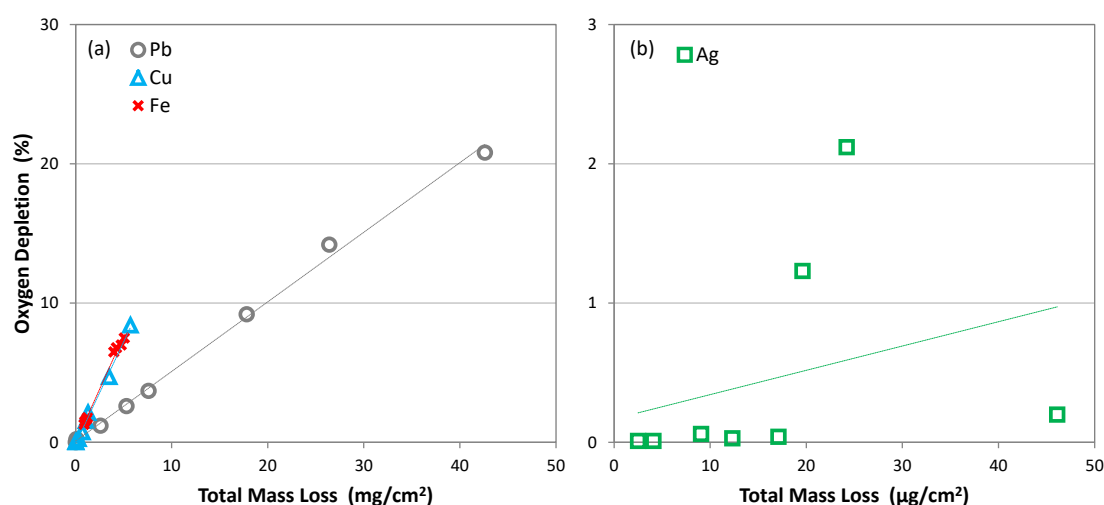


Figure 7. Correlation of oxygen depletion versus total mass loss for the four types of accelerated ageing Oddy test: (a) lead (Pb), copper (Cu) and steel (Fe) and (b) silver (Ag).

4. Discussion and Conclusions

The concept of assessing oxygen depletion has clearly been demonstrated to be a valuable tool for determining the reaction curves for archaeological metals against RH, temperature and carbonyl gases (reported in [2,6]). As no methods have yet been developed to generate ozone, nitrogen dioxide or sulfur dioxide in a closed container, it is of limited use to assess the gases present in ambient air, external to the showcase. For archaeological iron, initial experiments with iron chloride/iron powder mixtures indicate that the carboxylic compounds (formic and acetic acids and formaldehyde) accelerate the deterioration reactions to a much more significant degree than these gases [2]. Reactions for archaeological copper alloy have been found to be much less affected by the presence of carbonyl gases than iron [6]. Tests could be run with air from a particular room or generated environment, but the low levels of pollution and water vapour may limit the results. The RH control methods used presently (soluble salts, silica gel, glycerol) could absorb pollution and affect pollution levels if used with room air. The very high sensitivity of the technique may make this approach viable, but testing would be required. Using oxygen depletion experiments to non-invasively measure corrosion rates for complex objects is extremely useful, however, great care is required to generate reliable results. The container needs measurement for both airtightness and any effects due to the oxidation of polymers present in the experimental set-up or the presence of undesirable solvents [6,14]. In freshly excavated material, water reduction can occur, which can adversely affect the oxygen measurements, misleading the final interpretation. The results can be extremely useful in designing display environments for archaeological metals. At Camber Castle, the carefully designed and procured showcases keep the iron objects at an RH below 20%, in a room that frequently exceeds 75% RH. It is worth remembering that hydrogen evolution is an alternative cathodic reaction, and this will limit the method's application to freshly excavated material, which is frequently wet. Hydrogen measurements should be taken concurrently when measuring the corrosion rates of a material that is not fully dried.

These results show that oxygen depletion screening tests are appropriate and effective in assessing corrosion rates of heritage metal objects, and as a technique, it has been successfully used in over 20 exhibitions to date. Whilst the resource savings for not having to provide low RH environments are useful, the ability to safely display mixed collections (archaeological iron or copper alloys and organic artefacts) in the same showcase has been of great benefit. The 14-day test period appears to be sufficient with oxygen and water vapour transport confirmed even through iron dense product layers; longer tests have validated this. Furthermore, when examining a much larger corpus of tests for archaeological iron, other researchers found no instances where an object had not consumed oxygen after

14 days but did consume oxygen later. Their tests ran up to 6 months [30,31]. Concerns about alternative cathodic reactions were confirmed with some objects still containing water. At English Heritage, however, the vast majority of the archaeological iron and copper alloy collection has been stored in environments below 16% RH for decades, so this has not been an issue. Care will need to be taken with other collections.

The initial tests with oxygen depletion to measure and quantify Oddy tests are promising for lead, copper and steel. Steel or iron tests are not normally run as the control corrodes heavily at the near 100% RH and quantification of the amount of corrosion is needed to observe acceleration, as has been demonstrated in this work. The large amount of ferrous metallic cultural heritage makes this an important application. Many more materials obviously need testing to verify the strong correlation observed. Silver clearly tarnishes without a strong correlation to oxygen depletion in some instances. However, the silver test results are mainly applicable to a small range of artefacts: silver, objects with accessible lead white pigment (many paint layers and varnishes stop the reaction) and some photographs. In terms of costs, the sensor spots are not excessively expensive and could be readily added to the equipment at many larger museums. Oxygen measurement is already being used for anoxic storage and display in a number of museums. With proper calibration (which the manufacturer offers) the sensors could be read during the tests. This would allow for more rapid results and the opportunity for pro-active action to be taken for those materials that fail. If, however, the objects are for permanent display, the full 28 day Oddy test is still required in line with museum protocols. Even with the very high sensitivity of the oxygen detection sensors, the gases causing corrosion may not be yet present (many are degradation products of the materials) after only 14 or 21 days. Until they are emitted, corrosion cannot occur, and no oxygen depletion will be detected.

The oxygen depletion method has not yet been reported in preventive conservation for non-buried metal objects (beyond coating test), but its high sensitivity, reproducibility and ease of use are of obvious utility to the field.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/heritage4030134/s1>, Supplementary Section S1: Schematics of the experimental equipment; Supplementary Section S2: Raw Data for all Figures.

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Conflicts of Interest: The author declares no conflict of interest.

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