In Search of Frequency: Glass-induced Metal Corrosion in the Deutsches Bergbau-Museum Bochum

Alexandra Schorpp, Miriam Braun, Andrea Fischer and Gerhard Eggert

Keywords
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Abstract
Together with humidity and oxygen from the air, electrolytes that form during glass decay can induce corrosion in neighbouring metals. The presence of sodium, potassium, and formate ions on glass leads to the formation of special metal corrosion compounds. The late discovery of this phenomenon in museum collections pointed to its rarity, but a survey in the cultural history collection of the Swiss National Museum discovered the proportion of affected objects was more than 20%. The question arose whether this is a common phenomenon or if it only occurs in exceptional cases. For a new investigation and for an independent test on the frequency of this phenomenon, the collection of the Deutsches Bergbau-Museum Bochum (DBM) was selected. The museum has large collections of miners’ lamps and surveying instruments, which exhibit glass-metal contact. In fact, severe cases of corrosion have rarely been detected, but light cases are in the order of 10%. The compounds identified in the DBM technical heritage collection were the same as those found before in decorative arts collections.

Glass Induced Metal Corrosion (GIM)
Manufactured glass forms an important part of our cultural heritage. Janssen’s handbook (2013) provides details on ‘Raw materials, Recipes and Procedures Used for Making Glass’ (Janssen, 2013, Ch. 1.2, pp.23-36) and the development of ‘Glass Composition over Several Millennia in the Western World’ (Ch. 1.4, pp.67-78).

Due to its 3D network with strong Si-O-Si bonds (oxygen bridges), quartz (SiO2), the main component of sand used for glass, has a melting point of 1713°C. Such extremely high temperatures could not be achieved in ancient melting furnaces. Therefore, to produce glass, fluxes like potassium (for potash glass) or sodium carbonates from the air, mainly CO2 (now more than 400 ppm), but also pollutants like SO2 and NOx dissolve in pure water. Therefore, it becomes slightly acidic (pH ≈ 5) and traces of the anions CO3²⁻, SO4²⁻, and NO3⁻ can be detected. Depending on the metal, corrosion is quite slow under such circumstances. The situation changes totally if additional sources of electrolytes are available: Metal corrosion involves the flow of charges, and on the liquid side, a high concentration of ions means a high electric conductivity accelerating the charge flow (i.e. the reaction rate).

Only 10 years ago (Eggert, 2010) it was fully realised that decomposing historic glasses may also provide electrolyte solutions inducing corrosion in neighbouring metals. This led to the design of the GIMME (= Glass Induced Metal-corrosion on Museum Exhibits) explorative research projects 2012-2015 (Eggert and Fischer, 2012) at the Stuttgart State Academy of Art and Design (ABK) supported by Friede Springer Stiftung. It was followed by a project (2016-2019) on analysis and prevention of glass induced metal corrosion funded by the German Federal Environmental Foundation (DBU Az. 33255/01) which included the survey in the DBM reported here.

Introduction
Metal corrosion occurs when susceptible metals come in contact with oxygen, water, and electrolytes. Museum displays and stores are full of sensitive metal objects, and the air around has plenty of oxygen and humidity. However, what about electrolytes? Electrolytes are compounds like acids or salts, which dissociate into cat- and anions in water providing the conductivity necessary for corrosion reactions rates to increase. Traces of acidic gases from the air, mainly CO2 (now more than 400 ppm), but also pollutants like SO2 and NOx dissolve in pure water. Therefore, it becomes slightly acidic (pH ≈ 5) and traces of the anions CO3²⁻, SO4²⁻, and NO3⁻ can be detected. Depending on the metal, corrosion is quite slow under such circumstances. The situation changes totally if additional sources of electrolytes are available: Metal corrosion involves the flow of charges, and on the liquid side, a high concentration of ions means a high electric conductivity accelerating the charge flow (i.e. the reaction rate).

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Glass Induced Metal Corrosion (GIM)
ubiquitous indoor pollutant formaldehyde1 according to:

\[ \text{Na}^+\text{CO}_2^- + \text{Na}^+\text{O}_2^- + \text{CO}_2. \]

The oxide anion \(\text{O}_2^-\) is a Lewis base (electron donor) which attacks the Lewis acid Si\(^{IV}\) (electron acceptor) and transforms an oxygen bridge into two-charged non-bridging oxygens in the structure:

\[ \text{Si}-\text{O}-\text{Si} + \text{Na}^+\text{O}_2^- + \text{Na}^+ -\text{O}-\text{Si} \]

Water molecules from aerial humidity can leach out these sodium cations forming silanol groups:

\[ \text{Si}-\text{O}-\text{Na}^+ + \text{Na}^+ -\text{O}-\text{Si} \]

Contrary to expectations, in the liquid surface films formed on the white base on glass (when the relative humidity is below the deliquescence point of the salts), formate, not carbonate, dominates (Verhaar, 2018). A likely explanation is the base catalysed Cannizzaro reaction of the ubiquitous indoor pollutant formaldehyde2 according to:

\[ \text{Na}^+\text{OH}^- + 2\text{HCO}_2^- \rightarrow \text{Na}^+\text{CO}_3^- + \text{H}_2\text{O} \]

Formaldehyde is indeed known to react on oxide surfaces (including Si\(^{IV}\)) producing formate at room temperature (Busca, et al., 1987). Like a dosimetre, the alkaline films can be used to monitor pollution levels of different types of glass.

More details on ‘Historic glass and its interaction with the environment’ are given by Römich (1999). Contrary to expectations, in the liquid surface films formed on the white base on glass (when the relative humidity is below the deliquescence point of the salts), formate, not carbonate, dominates (Verhaar, 2018). A likely explanation is the base catalysed Cannizzaro reaction of the ubiquitous indoor pollutant formaldehyde2 according to:

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Formaldehyde is indeed known to react on oxide surfaces (including Si\(^{IV}\)) producing formate at room temperature (Busca, et al., 1987). Like a dosimetre, the alkaline films absorb formaldehyde over decades and centuries and form make formate ions directly available in solution such that no aerial adsorption on particles and oxidation are required. When glasses are stored in wood-based cupboards (e.g., made from oak), the films are also exposed to traces of acetic acid and, to a lesser degree, formic acid. Acetate can, therefore, also be detected in the films.

In many objects, glass is in direct contact to metal. Metallic parts are exposed to alkaline films on the glass, which, as aqueous electrolytes, are able to induce metal corrosion in the presence of air containing some humid-
corrosion product, basic zinc copper formate ("Zinc C") (4), could also be derived from powder diffraction measurements (Bette, et al., 2019). The composition of the new corrosion product is somewhat variable, as either copper or zinc can occupy one type of sites in the lattice. A pure one-phase sample from GIM model experiments could be used. Brass coupons were dipped in alkaline carbonate solutions and then exposed to formaldehyde vapours in a desiccator for half a year. – A number of other hitherto unknown corrosion products, some containing zinc, still need further characterisation.

Copper carbonates are found much rarer than forms, although chalconatronite (5) seems to be the first definite GIM product to be reported (Mager, 1999). This corrosion product forms when copper alloys are exposed to sodium carbonate solutions. These derive here from glass deterioration (Fischer, Eggert and Stelzner, 2020). Other sources reported earlier were Egyptian soil and conservation treatments. As chalconatronite (5) was also found in GIM simulation experiments with metals soaked in soda solution and then exposed to sodium carbonate solutions, it is not clear why this compound is comparatively rarely found in GIM samples from objects. When objects containing chalconatronite are stored in wooden cupboards emitting acetic acid, sodium acetate and sodium copper acetate carbonate (6) (exact formula and structure unknown) are formed. Thieckert and Oddyha (2000) first detected this compound on Egyptian bronzes in the British Museum. The same transformation can occur with chalconatronite from glass-induced metal corrosion (Fischer, 2014).

For lead, basic sodium (Fischer, et al., 2013, 7) or potassium (Bette, et al., 2017, 8) lead carbonates form, but no formates could be detected. Other metals used in history like silver, iron, and tin are also prone to corrosion but no special corrosion products occurring in the presence of glass have been reported (Eggert, 2010).

Survey in the Deutsches Bergbau-Museum
Glass-induced metal corrosion on museum exhibits, despite being so conspicuous, has only been identified in the last decade as a general phenomenon (Eggert, 2010). From 2004 to 2012, only 13 affected objects could be identified. This lead to the tentative assumption that this phenomenon is extremely rare. This view changed completely during the full-time GIMME research projects when Fischer (2016) collected 400 samples from 250 objects between 2012 and 2015. A survey in the Swiss National Museum of some 700 objects with glass-metal contact (Keller and Fischer, 2015) showed that the frequency varies between types of objects but the frequency was astonishingly high, on average more than 20 % were affected. This led to the new hypothesis that when more than a few per cent of combined glass-metal objects are corrosion product, basic zinc copper formate ("Zinc C") (4) could also be derived from powder diffraction measurements (Bette, et al., 2019). The composition of the new corrosion product is somewhat variable, as either copper or zinc can occupy one type of sites in the lattice. A pure one-phase sample from GIM model experiments could be used. Brass coupons were dipped in alkaline carbonate solutions and then exposed to formaldehyde vapours in a desiccator for half a year. – A number of other hitherto unknown corrosion products, some containing zinc, still need further characterisation.

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Table 1. Detected GIM Compounds.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium copper formate hydroxide</td>
<td>Cu2Na3(OH)(CO3)2(OH)2·4H2O</td>
<td>Fischer et al., 2018</td>
</tr>
<tr>
<td>Copper formate trihydroxide</td>
<td>Cu4(OH)4HCOO</td>
<td>Eggert et al., 2011, Fischer, 2016</td>
</tr>
<tr>
<td>Zinc formate dihydroxide</td>
<td>Zn(COOH)2·2H2O</td>
<td>Fischer et al., 2019</td>
</tr>
<tr>
<td>Copper formate hydroxide</td>
<td>Cu3(COOH)3·H2O</td>
<td>Fischer et al., 2018</td>
</tr>
<tr>
<td>Carbonates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalconatronite</td>
<td>Na2(Cu(CO3)3)·3H2O</td>
<td>Fischer et al., 2020</td>
</tr>
<tr>
<td>Sodium copper acetate carbonate</td>
<td>NaCu(CO3)(CH3CO2)·nH2O</td>
<td>Fischer, 2016</td>
</tr>
<tr>
<td>Lead carbonate hydroxide</td>
<td>Na8Cu4(CO3)(OH)2</td>
<td>Fischer et al., 2017</td>
</tr>
<tr>
<td>Potassium lead carbonate hydroxide</td>
<td>KPb2(CO3)3·OH</td>
<td>Fischer, 2016</td>
</tr>
<tr>
<td>Unknown</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compounds containing Na, K, Cu, and/or Zn, often carboxylates</td>
<td></td>
<td>Fischer, 2016</td>
</tr>
</tbody>
</table>
The material science lab of the museum was able to select the outstanding collection of miners’ lamps, which documented the technical development in the 19th and 20th century. Lamps often contain glass cylinders in contact to metal, frequently brass. More modern ones contain electrical bulbs which were discovered as a new object type prone to GIM. In some cases, it was hard to distinguish between GIM and powder residues from earlier polishing treatment. Such residues can act as poultries for humidity and themselves can cause some corrosion, a phenomenon well known to all metal conservators. 25 miners’ lamps showed signs of GIM. Only the safety lamp DBM Inv. no. 030140115000 (Figure 1) fuelled with oil made in 1872 was classified in the highest grade GIM 3. The broken protection glass had droplets of alkali liquids from glass deterioration on the inside in- and non-destructive. If no other fluxes, such as potash or lead, are detected, a soda glass can be assumed.

- The collection was terra incognita, no GIM cases were known to its staff so far. Therefore, any bias in selecting a collection with special very sensitive types of objects was avoided.
- From 2012 to 2015, the search for GIM cases was mainly focused on the decorative arts. Technical heritage objects provided a new challenge with more modern items.
- The movement of the collection from display to storage during renovation in summer 2016 gave a welcome opportunity of access (but with considerable time constraints for the survey).

As methodology for the survey of the collection it was decided to follow this sequence of steps:
1. To select suitable classes of objects with metal-glass contact to ensure that a large number of items could be examined.
2. Visual inspection of all these items (including magnifying glasses) for signs of corrosion.
3. Classification of the extent of corrosion into the grades GIM 1 (little, barely visible), GIM 2 (advanced, clearly visible) and GIM 3 (strong, big loss and danger for the whole object), as has proven successful in the Swiss National Museum.
4. Characterisation of the materials of affected objects with p-XRF and sample any corrosion product, whenever it was possible.
5. Analytical investigation of corrosion samples with μ-Raman spectroscopy. Additional analyses of the elemental composition with EDX-SEM for those compounds which could not be safely identified (for experimental details, see Fischer, et al., 2018).

The largest group of objects (370 examples) selected was the outstanding collection of miners’ lamps, which documents the technical development in the 19th and 20th century. Lamps often contain glass cylinders in contact to metal, frequently brass. More modern ones contain electrical bulbs which were discovered as a new object type prone to GIM. In some cases, it was hard to distinguish between GIM and powder residues from earlier polishing treatment. Such residues can act as poultries for humidity and themselves can cause some corrosion, a phenomenon well known to all metal conservators.

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These storage conditions might have caused the highest proportion (20%) of GIM compared to the other groups. Glass-metal contact was not only found at optical lenses, but also at cover glasses of compasses and glass levelling gauges/vials. The repetition theodolite (Figure 5) DBM Inv. no. 030150288000 showed the most severe GIM case: A glass levelling gauge (Figure 6) with ca. 8% K2O (possibly a mixed soda-potash glass) was mounted in brass (p-XRF: CuZn32Pb1). The corrosion product was identified by its Raman spectrum as sodium copper formate (1), the most frequently found in GIM research.3

Objects with cover glasses in contact to metal are prone to GIM as prior observations in other collections have shown, e.g. daguerreotypes, miniatures with metal frames and watches (Fischer, 2016). Therefore, pocket watches (62 pieces) were also selected. Only four showed visual signs of GIM. The different Raman spectra of the two samples which could be taken could not be attributed to any compound. Typical products for glass-induced metal corrosion (1) can be excluded.

Pewter of the lids of glass tankards may contain some lead. On a vessel from the Veste Coburg we could identify – a hitherto unique discovery – basic potassium lead carbonate (2) on the metal mounting of the potash glass (Bette et al., 2017). Therefore, we added this small group.

dicating advanced glass corrosion. As the p-XRF could not detect any traces of potassium, it apparently consists of soda glass. The shiny white nickel silver reflector (p-XRF: ca. 60% Cu, 24% Zn, 13% Ni) showed strong blue-turquoise corrosion in contact to glass (Figure 2). In both samples from the left and right hand side (Figure 3), particles of chalconatronite (5) and basic zinc copper formate (4) were identified by Raman spectroscopy. There was no evidence for nickel compounds.

The collection of instruments for mine surveying (‘Markscheidewesen’) encompassed 162 objects. They have been stored before 2010 in a basement room with periods of high humidity. A photograph of 2003 shows instruments in wooden cupboards (Figure 4).

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in the DBM (6 pieces) to the survey but could not identify any special corrosion product.

Raman analyses confirmed sodium copper formate ① and copper formate trihydroxide ② as most frequent GIM corrosion products, as was found previously in other collections. The presence of zinc in brass gave rise to the formation of zinc formate dihydrate ③ and the basic copper zinc formate ④. All these compounds are formates, but, interestingly, the carbonate chalconatronite ⑤ was also detected. As was found in a previous study (Fischer, 2016) a considerable number of compounds could still not be identified due to the lack of reference data in the literature.

All details of the survey can be found in the final report to DBU (Braun and Schorpp, 2017) which is archived in Bochum and Stuttgart.

In only about half (or less) of the sampled objects the GIM-phases were identified (Table 2). Other identified phases are only a few: calcium sulfate, sodium sulfate, atacamite, lead carbonate. We used visual observations for the calculation of frequency and assume that the corrosion samples are due to GIM. The somewhat surprising high number of unknown phases was also found before (Fischer, 2016). Even the formulas for the two most frequent products ① and ② were unknown before our research. Unfortunately, the DBM survey did not provide pure crystalline samples of ca. 1 mg suitable for XRPD and crystal structure determination of unknowns. According to Raman analyses, samples most often contained more than one compound.

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The hypothesis that every large collection of glass-metal objects contains GIM cases could be confirmed for the DBM collection. Severe cases are indeed rare, but the order of magnitude for the overall frequency lies in the range of 10 %. Therefore, measures of preventive conservation need to be taken for such objects. The results from the DBU project and its model experiments advise to remove any source of formaldehyde. Therefore, wood-based materials should strictly be avoided in museum storage and display. If unavoidable, e.g. when sources of carbonyl pollutants like wood are part of the object itself or the ensemble which is displayed together, absorbents proved to be useful in model experiments. In objects without firm contact of glass and metal (e.g., glass beads on metal wire) separation layers (foils, lacquers) can be introduced for prevention of contact. The relative humidity should be lowered to those values recommended for ‘sick’ glasses, i.e. 35-42 % (Kunicki-Goldfinger, 2008). Lower values would even be better to decelerate corrosion, but the decomposition zone on the glass surface (gel layer) is prone to cracks (‘crizzling’) when it dries out. The absolute lower values for storage of glass (and if there is just one value for all types of glass) are still a matter of discussion and need more experimental corroborator. With now more than 500 samples from 350 objects in 40 collections analysed in Stuttgart, the existence of GIM as a frequent phenomenon has been established.
beyond reasonable doubt. The identification and characterisation of new corrosion products provided reference data useful for the whole conservation science community. Others will start their own investigations (see e.g. Hollstein et al., 2019) which will lead to the much-needed improvement of knowledge. The temporal behaviour, i.e. the dynamics/kinetics of GIM are nearly unexplored. The frequent use of p-XRF will give better ideas on the influence of the composition of glass and metals on GIM. Still too many corrosion products are simply unknown. With the software based crystal structure evaluation from high precision XRPD measurements, we now have an extremely useful tool at hand to overcome earlier limitations. Therefore, it is no risk to predict that GIM will stay in the conservation science news.

Acknowledgements

We are grateful to Stefan Brüggerhoff (Director, DBM) for granting access to the DBM collection, to Michael Prange (DBM) for performing the on-site p-XRF measurements of glass and metals, and to Jörg Stelzner (ABK) for the Raman and EDX-SEM identification of corrosion products. The GIMME projects I and II (2012-2015) were funded by Friede Springer Stiftung. The surveys of glass and metals, and to Jörg Stelzner (ABK) for performing the on-site p-XRF measurements, were funded by the German Federal Environmental Foundation (DBU), Az. 33255/01. The crystal structures of \( \mathbf{3} \) and \( \mathbf{4} \) were determined within the ‘in search of structure’ project funded by DFG (grant EG 1379-1).

Notes

1 for an overview of possible sources, see Salthammer, 2019.
2 Of 29 affected glasses, 11 contained more than 5% K.
3 The study focused on frequency. We do not have composition data for unaffected objects, therefore, we cannot say if potash glasses are more prone to this phenomenon.
4 As mentioned above, we owe the determination of formula and crystal structure of \( \mathbf{3} \), \( \mathbf{4} \), and \( \mathbf{5} \) to data evaluation of XRPD. Hopefully, it is next.

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