Corroding glass, corroding metals: survey of joint metal/glass corrosion products on historic objects

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Corroding glass forms alkali(ne) surface films, which may lead to special metal corrosion products in the contact zone, for example different sodium copper carbonates or basic sodium lead carbonate. Sodium copper formate acetate was found on objects exposed to long term emissions from wood. A higher pH value may also lead to basic compounds, which normally do not form, e.g. the newly characterised $Cu_2(OH)_3HCOO$. The alkaline films also create a reactive environment for the formation of formates from formaldehyde (e.g. emitted from glues) due to the Cannizzaro reaction or possibly from the neglected pollutant carbon monoxide. Further products containing, for example, potassium or sulphate may be expected.

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Introduction

Corrosion products on ancient objects and, especially, on copper alloys have been analysed since the rise of modern analytical sciences, one of the first studies being Sage's[1] identification of cuprite on a gilded copper leg found in the Saone in 1766. Despite more than two centuries of research, there are still hitherto unknown corrosion products to be detected. Surprisingly, the eye catching occasional occurrence of green to blue efflorescences at the contact zone between corroding glass and copper alloys (and nowhere else on some objects) was nearly totally ignored until now. To inspire further research, this paper collects the few mentions in the literature together with the author's own unpublished results to picture current knowledge.

Glass corrosion

When on objects made from glass and copper alloys copper corrosion occurs in contact with glass, the latter often shows visible signs of corrosion: hazing, wet surfaces or efflorescences, cracking, roughening, pitting and the like. This gives an obvious hint to the special situation. In glass corrosion, alkali ions bonded in the glass network are leached out by humidity from the air

$$\equiv SiO^- Na^+ + H_2O \rightarrow \equiv SiOH + Na^+ + OH^- \qquad (1)$$

The alkaline surface films on corroding glass are maintaining equilibrium with the carbon dioxide content in the air

$$2Na^+ + 2OH^- + CO_2 \rightarrow 2Na^+ + 2CO_3^{2-} + H_2O \qquad (2)$$

The reaction can proceed to form some hydrogen carbonate ions as well; the pH value of an equimolar buffer is $\sim 10 \cdot 1$. The special situation of joint glass/metal corrosion is, therefore, simply metal corrosion occurring in the presence of alkali(ne) carbonate containing solutions at ambient atmosphere.

Copper alloys

From the number of observed cases, copper corrosion products outnumber all other metals by far. These are discussed here first; other metals are considered at the end.

Sodium copper carbonates

The first joint copper/glass corrosion product was apparently found by Magee[2] in 1999 on a late fifteenth century enamelled covered copper alloy cup (*tazza*) under a flaking enamel. The enamel consisted of an unstable high alkali/low lime (3·4 mass% CaO) glass composition. Chalconatronite (sodium dicarbonatocuprate(II) trihydrate, $Na_2[Cu(CO_3)_2].3H_2O$) and malachite were identified both in the raised interior and on the exterior of the lid.

Chalconatronite is quite soluble and indicative of copper corrosion in the presence of carbonate/hydrogen carbonate ions. It has first been reported and named by Gettens[3] in 1955, who found it as corrosion product on ancient Egyptian bronzes from arid soda rich soils. It can also be formed by long time immersion of bronzes in sesquicarbonate solution as treatment of 'bronze disease'.[4] Sodium copper carbonate can indeed be synthesised by pouring a copper solution into a sesquicarbonate solution (i.e. a carbonate/hydrogen carbonate buffer). Drying of objects immersed in sodium

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hydroxide (as in traditional electrolytic treatments)[5] might be another route for its formation.

In contrast to these cases, the *tazza* was never soil logged or immersion treated. Therefore, the sodium in the chalconatronite undoubtedly originates from the glass, making it a real joint corrosion product. In the meantime, another case of chalconatronite has been reported[6] together with cuprite (Cu_2O) on a copper wire inside a fractured mixed alkali lead glass figure made perhaps in Venice in the eighteenth century.

The identification of accretions of another sodium copper carbonate by X-ray diffraction (XRD) (Gandolfi camera), sodium tricarbonatohydroxodicuprate(II) tetrahydrate $Na_3[Cu_2(CO_3)_3(OH)].4H_2O$, is only mentioned in the book on daguerreotypes by Barger and White[7] but was not included in their original research paper.[8] Daguerreotypes (copper plates with a halide sensitised silver plating) are usually sandwiched airtight with a stamped brass mat and a cover glass, which often shows severe signs of corrosion on the inside. Sodium formate (see below) and sulphate have been identified as other crystalline glass corrosion products.

This basic sodium copper carbonate can be synthesised by dropping a copper acetate solution into a sodium hydrogen carbonate solution.[9] Interestingly, this compound containing a hydroxide anion forms at a lower pH value than sodium copper carbonate, which crystallises when a copper solution is added to a carbonate/hydrogen carbonate buffer. In glass corrosion in contact with copper alloys, the pH value of the humidity film on the surface will determine which of the two compounds is formed on drying. This should most likely depend on the glass corrosion rate (i.e. the production of NaOH and its consumption in splitting Si–O–Si bonds) and the deposition rate of acid gases from the environment.

Copper formates

Recently, two cases of sodium copper formate acetate (abbreviated as socoformacite) have been reported by Eggert and co-workers.[10] A green corrosion product was detected during conservation on a seventeenth century limewood box of board games made in the 1670s for Countess Hedwig-Sophie of Hesse-Kassel. Some of the turquoise enamel (made from saline plant ash, about 13–16 mass% Na_2O, wavelength dispersive X-ray microprobe) used for the decoration of the silver alloy ($\sim5\cdot5$ mass% Cu, atomic absorption spectroscopy) backgammon fields flaked off. In some of the now open silver grooves, where there was formerly enamel (and only there!), socoformacite was identified by XRD. The same holds true for an about 100 year old Chinese theatre hat (Ethnological Museum of Heidelberg, inventory no. 30406), which has long been stored in a wooden cupboard made from oak. The hat consists mainly of silk

stabilised with cardboard. Silvered copper wire and glass beads were used as decorative elements. One metal spiral was covered with a light green blue corrosion product where it was in direct contact with an apparently weathered glass bead, showing iridescence and crizzling. As wood is known to continuously emit traces of formic and acetic acid (ester bound in its hemicelluloses) into the air, this might reasonably be the source for formate and acetate in joint copper/glass corrosion products.

The identification by XRD was at first impossible, as there is no entry for it in the powder diffraction file, and the crystal structure is unknown. The match of the author's diffraction pattern with diffraction data published by Scott[11] finally tracked to the study of this compound by Trentelman *et al.*[12] (see the comparative table of data in Eggert *et al.*).[10] According to their X-ray photoelectron spectroscopy and Raman spectroscopy data, socoformacite is a mixed sodium copper (1:1) formate acetate, with the formate/acetate ratio estimated between 1:2 and 2:1. The general formula might, therefore, be given as $NaCu(HCOO)_{1+X}(CH_3COO)_{2-X}$, with $0 \leqslant X \leqslant 1$. Trentelman *et al.* observed it on a number of archaeological copper alloy artefacts containing no glass from various cultures and a number of collections. Apparently, all these finds were exposed to carbonyl pollutants in the museum atmosphere as is often the case when, for example, wood is used for building or display cases. Only one object was non-archaeological, a fifteenth century Italian leaded tin bronze statue.[12] It is not clear if socoformacite was formed by the action of acid gases on already existing chalconatronite (from soil logging or conservation treatment) or simply crystallised from solutions containing all four ions formed by corrosion in humid air. Eggert *et al.* were unable to prove either route in model experiments or even to grow single crystals.[10]

As Trentelman *et al.*[12] proved that socoformacite was not extremely rare on museum artefacts without glass, it was an interesting question to find out how rare these newly reported cases with sodium from glass corrosion would be. A call for samples in conservation conferences and newsletters lead to the identification of socoformacite in seven further combined metal/glass objects of totally different backgrounds within 3 years:[13]

(i) a traditional Black Forest *Schäppel* (girl's headdress worn on high ecclesiastical holidays and wedding) decorated with glass beads from Lauscha (many mirrored) on wires showed copper contact corrosion. *Schäppels* were of course stored at home in wooden cupboards or boxes

(ii) a Christmas glass ball (also possibly made in Lauscha, in the collection of Badisches Landesmuseum Karlsruhe), silver mirrored inside, was decorated on the outside with silvered

Table 1 Joint soda glass/copper alloy corrosion products

Chemical name	Formula	Other names	References
Sodium dicarbonatocuprate(II) trihydrate	$Na_2[Cu(CO_3)_2].3H_2O$	Chalconatronite, sodium copper carbonate	2,6
Sodium tricarbonatohydroxodicuprate(II) tetrahydrate	$Na_3[Cu_2(CO_3)_3(OH)].4H_2O$	Basic sodium copper carbonate	7
Sodium copper formate acetate	$NaCu(HCOO)_{1+X}(CH_3COO)_{2-X}$	Socoformacite	10,13
Dicopper trihydroxy formate	$Cu_2(OH)_3HCOO$	Basic copper formate	14

copper wire. Green corrosion products (not analysed) had been stripped with a chelating agent (Na_2EDTA) in 2002. When inspected again 7 years later, the corrosion products reoccurred where the wire was in contact with the glass and were identified as socoformacite

(iii) two enamel objects made in Limoges from the Museum für Angewandte Kunst Frankfurt had socoformacite and basic copper formate (see below) efflorescences at the border between the metal and enamel. Acetate containing efflorescences ('thecotrichite') occurred also on ceramics from this collection

(iv) the brass passepartout of a glass framed daguerreotype from the 1860s (donated to the author by Pau Maynes) showed green corrosion spots. If stored flat, condensing humidity might have dropped down from the glass

(v) a small female enamel figure from a 'Handstein' (the second half of the sixteenth century, Kunsthistorisches Museum Vienna) with interior copper wire showed socoformacite efflorescences growing from fractures in the arm

(vi) a glass cabochon (imitation of gem) with a gilded silver mounting (the thirteenth century, apparently debased with copper) on the cover of the Otto-Adelheid-Evangeliar (Quedlinburg) developed socoformacite in the contact zone. It was formerly displayed in a case with high emissions of acetic and formic acid.

Undoubtedly, publication of these occurrences will lead to further identifications on combined glass/metal objects.

In the meantime, sampling in search of socoformacite has lead to the identification of another corrosion product,[14] dicopper trihydroxy formate $Cu_2(OH)_3HCOO$. The author's diffraction data (not in the PDF) could be matched with a basic copper formate given by Scott *et al.*[15] as their film 770 (Table 3). Single crystals of this compound could be synthesised during copper corrosion experiments with formic acid and ammonia, adjusted to pH 9·1, and the crystal structure could be determined.

The compound was identified on:

(i) a 200 year old glass flute with silver mounting (Rijksmuseum Amsterdam)

(ii) a Baroque silver mounted ruby glass box (Green Vault Dresden)

(iii) the enamelled Limoges objects from Frankfurt (see before).

Corrosion experiments with copper coupons over formic acid only yield neutral formates or perhaps also $Cu(OH)HCOO$.[16,17] The formation of the trihydroxy compound is due to the glass corrosion as it needs a higher pH.

Copper formates (without sodium) on historic objects are very rare; only two other cases have been found in the literature.[18,19] The connection with glass corrosion reported here might be significant, as the alkaline surface film not only absorbs formic acid but may also form it from formaldehyde (emitted, e.g. from glues) without further oxidation step by disproportionation (Cannizzaro reaction)[20]

$$2H_2CO + NaOH \rightarrow CH_3OH + NaHCOO \qquad (3)$$

Another possible source for formate is the hitherto neglected air pollutant carbon monoxide. This gas does not react in water and is not the anhydride of HCOOH (as hydrogen is bonded to carbon). However, Berthelot[21] had already discovered in 1856 that alkali hydroxide solutions can absorb carbon monoxide to form formates. The modern synthesis of sodium formate uses heat and pressure according to

$$NaOH + CO \rightarrow NaHCOO \qquad (4)$$

Currently, experiments are set up with model glasses rich in sodium exposed to CO to see how relevant this reaction is. Carbon monoxide concentrations in rooms where organic material is burnt (fireplaces, stoves, tobacco smoking, etc.) are in the order of some 10 ppm (!). Historically, this might be much more relevant for formate formation than other trace gases in the parts per billion range.

Other metals

With copper forming up to now four different identified corrosion products (and some still unidentified!) in contact with corroding glass, what about the other ancient metals? Gold and the pre-Columbian platinum objects of course do not corrode at all in the museum. Observed corrosion on silver alloys was always due to the minor copper content. There is no stable silver carbonate, and the formation of Ag_2O needs such a high pH value not likely to occur even in contact with the corroding glass in the presence of carbon dioxide from air. Tin also does not form a stable carbonate but corrodes to (hydr)oxides even at normal pH value, so special products from glass corrosion are unlikely. From the potential–pH stability diagrams, the same holds true for iron in the presence of oxygen, siderite [iron(II) carbonate] is found only under strongly reducing conditions in the soil.[22] Steel tends to passivate at higher pH value and is used for containers of alkali carbonate solutions. The mutual influence of glass and steel corrosion is of special interest for the long term storage of vitrified nuclear waste.[23]

However, the chemistry of lead corrosion products is as rich as that of copper. Basic sodium lead carbonate $NaPb_2(OH)(CO_3)_2$ has recently been reported as white pigment,[24] possibly formed by a non-traditional attempt to synthesise lead white (basic lead carbonate, hydrocerussite) by precipitation of a soluble lead salt (nitrate or acetate) with sodium carbonate. Solutions containing more than ~ 0.15 mol L^{-1} Na^+ form this compound, not hydrocerussite.[25] Such conditions may occur during

Table 2 Possible ions and their sources in joint glass/copper alloy corrosion products*

Source	Agents/precursors	Cations	Anions
Copper alloys		Cu^{2+} (Cu^+)	
Glass		Na^+ (K^+) (Ca^{2+}) (Mg^{2+}) (H^+)	OH^- (O^{2-})
Wood, glue, etc.	H_2CO, HCOOH CH_3COOH		$HCOO^-$, CH_3COO^-
Air	O_2, H_2O, CO_2 SO_2, NO_x CO		CO_3^{2-} (NO_3^-)(SO_4^{2-}), $HCOO^-$?

*( ) ions so far not observed in joint corrosion products; ? hypothesis needing expert verification.

Table 3 Powder diffraction data for dicopper trihydroxy formate (*I*=relative intensity, ‰)

Calculated from single crystal structure[14]		Sample from baroque ruby glass box (see text)		Scott *et al.* synthetic compound[15]	
d, Å	*I*	*d*, Å	*I*	*d*, Å	*I*
				7·35	30
6·6659	1000	6·6970	1000	6·64	1000
5·3745	7	5·3837	9	5·39	50
4·4824	1	4·5030	4	4·52	50
4·0198	19	4·0316	22	4·08	100
3·8049	14	3·8034	13	3·82	50
3·7154	7	3·7401	10	3·71	30
3·3330	158	3·3485	250	3·37	600
3·2616	7	3·2563	6	3·31	20
3·1669	21	3·1861	15	3·19	50
3·0280	3				
2·9200	10	2·9335	8		
2·8716	4				
2·7698	106	2·7695	18		
2·7569	7	2·7637	136		
2·6872	21	2·6918	30		
2·6381	150	2·6483	199		
2·5745	27	2·5804	30		
2·5377	6	2·5560	12		
2·5188	<1	2·5162	5		
2·4563	2	2·4616	16		
2·4454	122	2·4366	180	2·48	100
2·3472	207	2·3598	245		
2·3405	<1	2·3564	56		
2·2869	4	2·2961	32		
2·2844	23	2·2876	8	2·28	200
2·2675	1	2·2515	3		
2·2412	5	2·2323	26		
2·2220	16	2·2228	71	2·22	100
2·2191	57				
2·1394	<1				
2·1374	4				
2·0860	<1				
2·0437	3				
2·0099	<1				
2·0035	64	1·9979	94	1·99	200
1·9450	124	1·9568	178	1·93	50
1·9320	<1	1·9408	6		
1·9025	<1	1·8977	<1		
1·8898	<1	1·8924	3		
1·8794	<1	1·8722	1		
1·8660	<1	1·8700	30	1·87	50
1·8630	<1	1·8610	5		
1·8577	24	1·8326	5		
1·8249	45	1·8282	61	1·82	100
1·8237	1				
1·7970	1				
1·7949	<1				
1·7914	<1				
1·7806	1	1·7796	4	1·76	50
1·7760	2				
1·7738	<1				
1·7318	<1				
1·7267	<1				
1·7227	<1				
1·7179	1	1·7186	6		
1·7165	<1				
1·6709	<1				
1·6665	13	1·6743	26	1·68	100
1·6651	1	1·6699	2		
1·6314	<1	1·6349	5		
1·6308	19	1·6289	9		
1·6303	1	1·6282	23		
1·6140	1	1·6244	10		
1·6068	<1	1·6197	11		
		1·6142	8		
1·5968	40	1·6068	47	1·61	100
		1·5931	7		
1·5867	61	1·5875	99		
1·5834	<1				

Table 3   Continued

Calculated from single crystal structure[14]		Sample from baroque ruby glass box (see text)		Scott *et al*. synthetic compound[15]	
d, Å	*I*	*d*, Å	*I*	*d*, Å	*I*
1·5798	<1				
1·5747	<1				
1·5742	<1				
1·5669	<1				
1·5568	<1				
1·5453	29	1·5456	36	1·55	50
1·5418	38	1·5437	64		
1·5198	15	1·5307	17		
1·5140	24	1·5209	9		
1·5134	<1	1·5199	28		
1·5033	35	1·5066	46		
1·4941	<1	1·5010	6		
1·4809	<1	1·4907	3		
1·4764	34	1·4831	48	1·48	30

soda glass corrosion in contact with lead (e.g. leaded windows). In tiny gaps between lead and glass, corrosion solutions are not washed away and could easily develop higher sodium concentrations. Indeed, lead foil (Merck, Darmstadt, Germany; p.a., 1·07365·000, Cu<0·002%) immersed into a 1 mol L^{-1} solution of sodium carbonate (Merck, p.a., 1·06392·0500) in the presence of air developed a brownish green (!) corrosion. A sample analysed by XRD after 3 days contained basic sodium lead carbonate as the only crystalline corrosion product as expected; a spot test for copper was negative. Currently, a corrosion experiment is performed with lead foil in contact with soda glass over half a year.

Corroded old leadings of historical soda glass windows need to be systematically analysed to prove whether basic sodium lead carbonate is formed on them under natural weathering conditions.

Conclusions

Since the start of this research on joint metal/glass corrosion products in 2006, already four copper (Table 1) and possibly one lead compound have been identified. Glass corrosion leads to an alkali(ne) environment which provides (Table 2) the following aspects.

1. Alkali cations, which may be precipitated in mixed corrosion products. So far, only sodium compounds have been identified, but there is no reason why potash glasses, which tend to be even more unstable than soda glasses, could not react similarly. Earth alkaline ions like Ca^{2+} are known to occur in glass corrosion products and, therefore, might also occur in joint products.

2. An alkaline pH, which could result in basic compounds not observed under more neutral conditions.

3. Alkaline surface films, which readily absorb acid gases like carbon dioxide, formic and/or acetic acid and may result in the precipitation of carbonates, formates and/or acetates on drying. Although sulphates form during glass corrosion, e.g. on church windows [gypsum, $Ca_2SO_4.2H_2O$, and syngenite, $K_2Ca(SO_4)_2.H_2O$], due to air pollution with SO_2, no mixed glass/metal sulphates have been detected so far. On objects where corrosion products are not washed away by rain or cleaning, even nitrates (from NO_x in the air) might be a possibility.

4. A reactive environment for the formation of formates from formaldehyde due to the Cannizzaro reaction or possibly from carbon monoxide.

As, so far, only few of the possible combinations of ions (Table 2) have been found in joint corrosion products and some compounds could not be identified yet, sampling of corrosion products on historic objects in the contact zone between metal and glass will be continued. Raman microscopy will aid in the identification of ions and compounds. Corrosion products contain some otherwise unavailable information to what conditions artefacts were exposed over centuries.

Acknowledgements

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