The diversity of degradation products underlines the need for further analytical studies with a wider range of instrumentation (XRF, SEM-EDX, XRD, LA-ICP-MS and XPS) in the forthcoming NICAS project to rationalize the variations in the behaviour of the various enamel decorations present. Experimentation will involve the reconstruction of Chinese enamel recipes together with modelling and reconstruction of the micro-biological deterioration process in the laboratory. The potential for recuperation of the original glaze colours will also be explored by means of exposure to light and high temperature.

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The reversal of lead sulfide blackened earthenware glazes by means of outdoor exposure to sunlight

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SUMMARY: Lead glazes on earthenware can undergo blackening in anaerobic environments as a result of the formation of black lead sulfide within the glaze due to microbiological activity by sulfate-reducing bacteria over many decades. In this article the results of a recent campaign of roof exposure in Lisbon, incorporating environmental data, give a better understanding of the factors which bring about the glaze transformation. Accordingly, the potential for optimising the efficacy of this novel, eco-friendly treatment in the future is enhanced.

KEY-WORDS: Blackened ceramics, Lead sulfide, lead sulfate, Glaze, Earthenware

It is well established that lead glazes on earthenware undergo blackening in anaerobic environments such and canals and cesspits as a result of the formation of black lead sulfide within the glaze due to microbiological activity by sulfate-reducing bacteria over many decades (1, 2). Conservation treatments can result in successful recovery of the original glaze appearance by transformation of the lead sulfide (PbS) into white lead sulfate ($PbSO_4$), but chemical treatments are often only moderately effective and at other times aggressively deleterious. It has been shown that exposure to strong summer sun over several weeks can result in an even more impressive recuperation of the original state of the glaze (3), as illustrated in Figure 1.

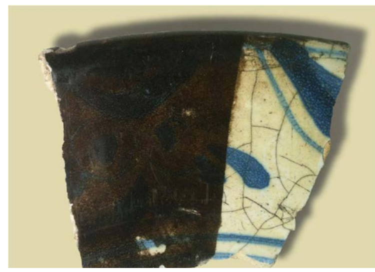
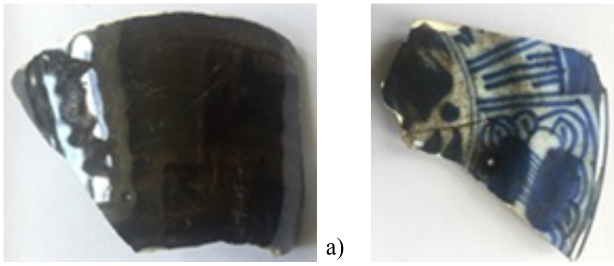


Figure 1. Fragment of blackened Delftware (c. 1660-1680, found in Amsterdam) illustrating recovery of the original glaze design in the right-hand portion which was exposed to Lisbon summer sun for 12 weeks.

More recently, a colour science rationalisation has been presented to explain how transformation of black lead sufide particles to white lead sulfate results in recuperation of a transparent lead glaze, thereby resulting in the reappearance of the coloured glaze design which had been obliterated by the formation of lead sulfide during burial (4). In this GlazeArt2024 contribution, the efficacy of the recuperation of the glaze appearance by sunlight is further scrutinised. The results of a recent campaign of roof exposure in Lisbon, incorporating the environmental data for ultraviolet light, visible light and temperature at the weathering station, give a better understanding of the factors which bring about the glaze transformation and, as a consequence, can be optimised for maximum efficacy of this novel, eco-friendly treatment process in the future. This research concerns the roof exposure of two fragments of lead sulfide blackened Delftware ceramics (Figure 2) to the strong sunlight of the roof site of the National Civil Engineering Laboratory (LNEC). These fragments illustrate the range of blackening which occurs; ultimately it can obliterate the glaze design.



a) b) **Figure 2.** Delftware ceramics blackened by lead sulfide prior to strong sunlight exposure. (Fragment samples courtesy of Owen Ooievaar.)

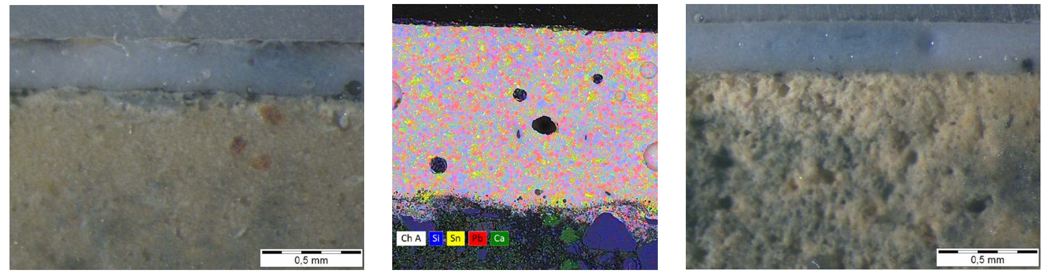
The programme ran for a total of 105 days, from 28 July to 9 November 2023, with approximately monthly photographic documentation. Half each ceramic fragment was covered by aluminium foil and the samples were exposed on a south-facing rack at an angle of 45 degrees to the horizontal. The results of this exposure period are shown in Figure 3.

Several fascinating features concerning the glaze recuperation process are evident. Most significantly, the glaze appearance on the portion not covered by foil has been very successfully

a) b) c)

Figure 3. Effect of strong sunlight on blackened Delftware ceramics. a) and b) recovery of the original glaze design in the right-hand and lower half, respectively, where sunlight was not occulted by an aluminium foil layer, c) reverse of the second fragment where the effect of the transparent tape which was securing the aluminium foil can be observed.

recuperated with the recovery of the vibrant blue and white glaze colours and the retention of the smooth, glossy surface sheen. (After 39 days the reduction of the blackening had almost reached that of the full exposure period.) More unexpected, and in contradiction to the previously-reported example (Figure 1), is the observation that the glaze blackening under the foil has also been somewhat ameliorated (Figure 3a). Even more intriguing are two additional observations. Firstly (and not illustrated), the glaze blackening on the uncovered area of the reverse side, which was not receiving direct sunlight, has also reverted to a considerable extent. Secondly, the Scotch adhesive tape, which haphazardly covered the reverse side to secure the metal foil, has clearly inhibited the reversion process (Figure 3c). This effect is also partially visible under the narrow strip of adhesive tape adjacent to the foil on the upper surface of the first fragment glaze (Figure 3a).



a) b) c)

Figure 4. Cross section images of the first fragment. a) Optical microscopy of the blackened glaze surface; b) SEM-EDS map of the blackened glaze layer; c) Optical microscopy of the sunlight exposed glaze surface.

The optical microscopy of the embedded, polished cross-sections reveal a distinct black line not only at the glaze surface but also at the glaze/body interface (Figure 4a), both of which disappear after sunlight exposure (Figure 4c). Though two zones of glaze conversion to lead sulfide are present, no clearcut confirmation by SEM-EDS was obtained; the thinness of the sulfide layer and the dominance of lead as a major glaze component result in no confirmatory sulfur signal from within the thin degradation layers (Figure 4b). Nonetheless, the uniform glaze composition indicates that in both these fragments no superficial high lead 'coperta' (in Dutch, *kwaart*) secondary layer, sometimes applied, is present in these samples.

These observations, in conjunction with the environmental data obtained during the exposure period, give rise to some preliminary conclusions on the oxidation process. Photochemical oxidation is clearly involved, but the role of temperature is now also apparent and needs to be taken into account. In addition, the inhibiting effect of the clear adhesive tape requires further investigation in order to pinpoint its role; it could be acting as a filter to light or as a barrier to atmospheric oxygen and/or moisture.

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