Mystery of the black glazes from Khorsabad (Iraq, 8th century BC)

Emmie Beauvoit†, Daniel Caurant, Odile Majerus, Yvan Coquinot, Julien Cuny, Ariane Thomas, and Anne Bouquillon

1Centre de recherche et de restauration des musées de France – Ministère de la Culture et de la Communication, Centre National de la Recherche Scientifique – France
2Institut de Recherche de Chimie Paris – Ecole Nationale Supérieure de Chimie de Paris - Chimie ParisTech-PSL, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique, Ministère de la culture – France
3Musée du Louvre – Musée du Louvre – France

Abstract

From Antiquity to the present day, black is an omnipresent color in heritage glazes. Research conducted by the ceramists have allowed the development of many techniques and recipes used to produce a more or less intense black coloring. Nevertheless, not all of them are fully understood nowadays. After a short review of the different solutions developed throughout history by the craftsmen, we will focus on the case study of black glazes from ancient glazed bricks produced in the 8th century BC in Khorsabad (Iraq). These decorated bricks were produced in huge quantities to construct monumental architectures of Middle Eastern cities.

The purpose of this paper is to gather information about the ancient brick manufacturing practices by examining the colored glazes. More specifically, we focused on black glazes used to separate different glazes or to fill colored areas. In this study, a double approach was conducted in parallel. Firstly, we characterized the well-preserved glazes of seven colored bricks representative of the decoration of the palace of Sargon II in Khorsabad (formerly Dur-Sharrukin). Secondly, and on the basis of the latter analyses, synthetized glazes were made in laboratory. The examination of both archaeological and replica glazes was performed using a combination of methods that included optical microscopy, SEM-EDX, PIXE-PIGE and X-Ray diffraction.

The analysis showed that black glazes of Khorsabad are characterized by the presence of copper sulfide and/or galena nanoparticles. This coloring technique is very rarely described in the literature, as well as the mechanism of formation of these spherical nanoparticles. Glazes produced under controlled conditions with alkali glass frit, different copper vectors (sulfide or oxide) and the presence (or not) of a reducing agent can give us some indications on the production techniques (especially recipes, firing temperature and kind of atmosphere). The different conditions experimented suggest that a reducing atmosphere is necessary to obtain sulfide-rich nanoparticles. Actually, a preparatory step of the black glaze seems required before the firing of all the glazes on the brick. The data obtained recontextualized with the published data constitute a privileged tool to support hypotheses on the evolution of the production techniques of bricks craftsmen in the Middle East in Antiquity.
Keywords: architectural brick, black glazes, Khorsabad, nanoparticles, copper, sulfide