Lost Knowledge Today

Part 3: Glazes with water-soluble substances and what has become of them

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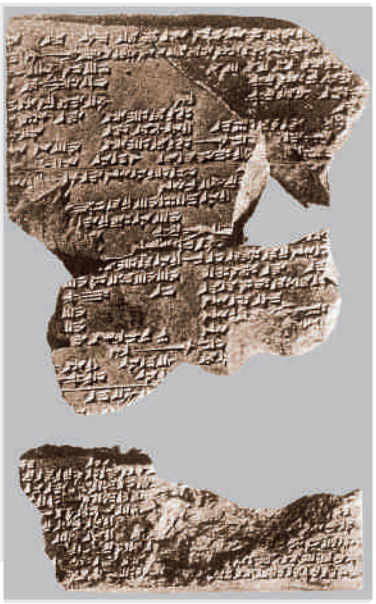
The following piece began with the interpretation by Rolf Wihr of a recipe in cuneiform script, which he actually only wanted to pass on as a practical procedure. However, the recipe pointed to evidence that led to new findings on the origins of glazes.

The ball was set in motion by Rolf Wihr visiting the Pergamon Museum in Berlin, as a consequence of which he discovered the translation of a glass recipe, from the cuneiform library of Assurbanipal in Nineveh, in A. Leo Oppenheim's book, "Glass and Glass Making in Ancient Mesopotamia". It consisted of

10 parts immanaku stone
15 parts aga plant ash
$1\,^{2}/_{3}$ parts white plant

Rolf Wihr interpreted this as a glaze recipe consisting of 10 parts = 40% glass former (probably quartz) and 15 parts = 60% of an initially indeterminate vegetable ash containing a flux. It was the "white plant" that seized his attention. In Oppenheim (p. 75) he found that the sap of the "white plant", i.e. the poplar tree, was used medicinally in the ancient Middle East. Its mention in a recipe for glass was inexplicable even to Oppenheim, one of the leading experts in the field of glass. But for Fritz Wihr, it was clear from the start that it could only be a glaze recipe. And he related the use of the vegetable gum with the solubility of the alkalis in the ash because their absorption by the clay body could thus be prevented. This insight alone would have sufficed to give contemporary potters the practical hint that a frit is dispensable by making up a glaze of water soluble substances not with pure water but vegetable gum dissolved in water. And he undertook a series of experiments in which he discovered that gum arabic is suitable for this purpose but not tragacanth.

However, historically things had developed quite differently; it was not an attempt to avoid using a frit. Rolf Wihr's assumption that this might indeed be a glaze had far-reaching consequences, beginning with the linking of this glaze with glazes made shortly afterwards in Baghdad for the Ishtar Gate and other structures. Nobody had ever done this before because the five recipes in Nineveh and more in Babylon and Bogazköj were thought to be glass recipes, which in fact they all were. At that time, 600 years before the invention of glass that could be freely shaped in Syria, glazes were not much different from glass. Glaze was a variant from the field of glass technology and had nothing to do with pottery.

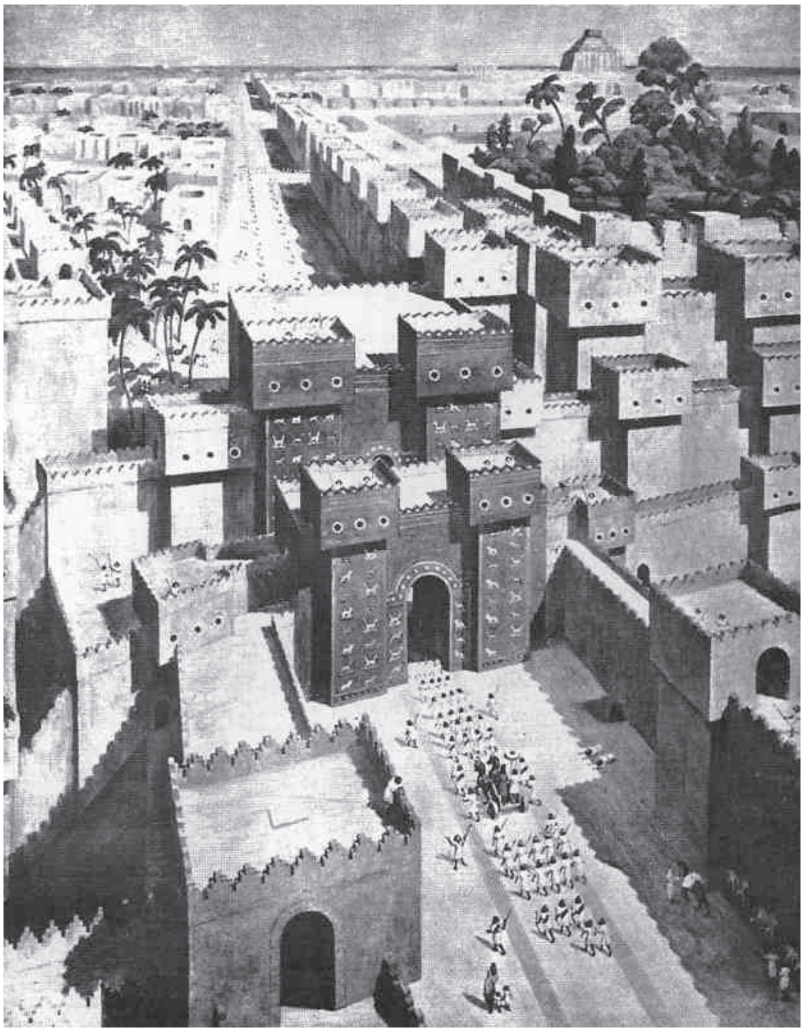


Cuneiform tablet with the glaze recipe from Nineveh, in which a white ash is mentioned. After Oppenheim.

The ingredients in the cuneiform recipe

In the chapter of Oppenheim's book on "The Chemical Interpretation of Texts", Robert H. Brill made a series of assumptions as to which raw materials could be meant. He analysed 15 plant ashes and 20 varieties of Mesopotamian glass. He also interpreted the two-stage production procedure for the glass as a sintering process at low temperature in which a frit is created that in the second stage, ground to a powder, is melted at a higher temperature in a crucible. And he smelted the glasses, finding that they melted at 1050 – 1100 °C and could be used from 700 – 1000°C. As far as the glaze is concerned, that does not leave many open questions. Nevertheless, one wonders whether the two-stage system only served to allow the glass to be coloured in the second stage. It should not be overlooked that the mixture absorbs energy which – the faster it is cooled or quenched – is retained, and that his energy contributes to a reduction in the energy requirement for the smelting in the second stage. The addition of colouring agents leads to a further reduction in temperature. Copper, cobalt, manganese and iron are all fluxes. The colouring agents often contain lead impurities. The frits from the first stage could just as easily be stuck to the clay tiles as a powder as they could be made to melt in a crucible in the second. According to this assumption, there is no need to search for any specific glaze recipe, and Brill's glass analyses can be used for further research. This led to the conclusion that zuku glass from the cuneiform tablet was largely identical to the assumed Babylonian glazes, if suitable ingredients are mixed in a ratio of 40:60.

For the ingredient with the glass forming characteristics Brill quotes



Reconstruction of Babylon with the Ishtar Gate. The smaller outer gate is in the Pergamon Museum, Berlin. In the background, right, the hanging gardens are visible and on the horizon, the Tower of Babel. After Seton Lloyd: "Building in Brick and Stone" in Charles Singer et al. (Ed.): "A History of Technology", Vol. 1, 3rd edn., Oxford: Clarendon 1956.

the cuneiform text which describes the material as "like river silt with pebbles". The sand at the mouth of the Belus River in Syria (today known as the Na'amat River) was full of shells, which may have created this impression. It was well-known for centuries. R. Campbell Thompson ("A Dictionary of Assyrian Chemistry and Geology", Oxford 1936) suggests that the Sumerians may well have used this river sand several thousand years B.C.

With the computer glaze program a comparison with zuku glass shows that a glaze batch using the shells would be far too rich in lime, thus making a dull-looking glaze. This implies that the sand alone without shells was used.

Oppenheim assumes that the plant in the cuneiform recipe is a type of glasswort (salicornia), in which he follows Thompson ("On the Chemistry of the Ancient Assyrians", Merton College, Oxford, n. d.). It had to be a sodium plant as the finished glazes show little or no potassium content. Halophytes – plants that thrive on salty soils – store sodium and chlorine from the soil in their cells. A number of plants would be usable in the cuneiform recipe: of the goosefoot species (chenopodium) especially haloxylon salicornicum from the Jezazi Desert in Iraq and the tamarisk, tamarix meyerii from the banks of the Belus River.

R. H. Brill analysed these and other varieties of salicornia and published the results in 1999. It must be taken into account that the components of the ashes of these plants are involved in glass forming as oxides, whereas in the plant they are present as chlorides or sulphates. Chlorine and sulphur would spoil the quality of the glass and must be driven off before the glaze melts. Haloxylon has 38% of such volatile components, the tamarisk 43% so that of the 60 parts of ash in the recipe only 38 or 34% respectively are involved in the glass forming process and appear in the chemical analyses of the final glaze. An examination with the computer programme shows that the haloxylon ash mixed 40:60 would give the glaze too little silica for it to be comparable to zuku glass. Thus in all probability, tamarisk from the Belus River will have been used.

Stefan Fitz, who analysed the colours of the glazes at the Pergamon Museum, demonstrated among other things that the lions' manes matched in outline, but that in the emission spectrochemical analysis, the glazes revealed clear differences in the secondary materials. This indicates materials with various impurities, i.e. that they are from differing locations. Analyses of the glazes also demonstrated remarkably that as an opacifier not tin had been used as was long assumed but antimony. Antimony ore is rarely pure, however. With lead impurities it produces opaque yellow glazes (Naples yellow) as lead antimonate stains yellow. Lead antimonate of this kind with copper and small quantities of cobalt produced opaque green glazes. From lead-free antimony ore, calcium antimonate could be obtained that produced an opaque white. With copper and cobalt, this produced a pale blue to turquoise opaque glaze. That firings for certain colours had to be in reduction is proved by iron green and copper red, where according to Brill, lead and traces of tin and antimony were also present.

The production process

With regard to the way the mixture of raw materials was prepared and used, various pieces of evidence indicate that once a procedure had been developed, it was adhered to for many centuries and it spread over a wide area. In the book of stones by Abulqâsim (published in Kashan, Persia in 1301 A.D., in the translation by Ritter, Ruska, Sarre and Winderlich), it states that glaze batches made up of one part "sugar stone" (quartz) and one and a half parts of ash from Tebriz or Baghdad, referred to as potash, (i.e. in a ratio of 40:60) were "roasted" for eight hours in a metal pan, continually stirred with an iron spoon, and then quenched in a pit of water. The correct temperature is indicated by the powder forming a slag – 840°C. The kiln atmosphere in such firings alternated between oxidation and reduction with the stoking (clear flame = oxidation, smoky flame = reduction), which is important for the decay of the sulphur compounds. The resultant product was powdered on a long, narrow rubbing stone and "applied with gum". A. Houtum-Schindler describes a pottery in

Qamsar thus in "Eastern Persian Iraq", London 1897, p. 115 f.

Aside from this method of preparing glaze borrowed from glass technology, applying slips of the terra sigillata type led to the development of applying water-based glazes. With the disappearance of casting glass over sand moulds and the advent of freely formed glass in the last century B.C., glazes began to develop separate from glass, following the ceramic terra sigillata tradition, now in the form of lead glazes. On the clay body, the lead glazes did not have so many hairline cracks as their alkaline forerunners. Lead oxide in a glaze only produces a third of the thermal expansion of the alkaline glazes made with sodium oxide. Until the mid-twentieth century, lead glazes were the norm. The dominant producers of terra sigillata were not interested in glazes, however. They could not become established in Rome but they did in Byzantium. An influence from China then followed - a white glaze said to resemble porcelain. For this, the potters from Baghdad under the 9th century khalifs remembered the old two-stageprocess described above, this time using tin and lead in a 2:1 ratio, as it was later described in the book of stones. The resultant product was then added as a pigment to the glaze batch, a procedure that survived in the West until the 20th century for the production of faience glazes.

The faience of the age of the manufacturies was followed in Europe by the earthenware of the industrial age. Lead borax glazes were typical of this type of ware, which consisted mainly of frits. The frit was now of a more complex composition: it was heated until of very low viscosity and then quenched in water. Ten percent kaolin or white "glaze clay" were added to the 90% frit at the end of the grinding process in the ball mill to keep the powder in suspension in the water and to stick it to the clay body. This was an entirely different technology from in ancient times. But the complex experience that led to this procedure lives on today and is part of the tradition.

Attempts at Reconstruction

To reconstruct the glazes of the Ishtar Gate and the Processional Way, the two-stage technique must be used if the temperatures are to be determined. As a reconstruction today is only possible with pure raw materials containing no chlorine or sulphur, 40 parts Belus sand must now be calculated with only 34 parts tamarisk ash instead of 60. That makes a glaze consisting of

32.61 calcinated soda
4.66 potash
9.93 chalk
5.37 magnesite, caustic
4.63 kaolin
0.56 iron oxide
42.24 quartz

This mixture was calcinated in this experiment to 840°C in an electric kiln with a 30-minute soak, a part being allowed to cool and a part being quenched in water, crushed, mixed with 2% copper oxide and cobalt oxide respectively, applied to a raw yellow firing clay containing 30% lime ($CaCO_3$ corresponding to 9% CaO, in analogy to clays in the Middle East) with 4.6% gum arabic and then fired in a gradient kiln.

It is remarkable that in the cuneiform text, referring to zuku glass, it is stated that to obtain copper oxide, pure metallic copper must be melted. Theoretically this means 1083°C, in practice somewhat more. The melting point of copper could have been a guideline for the firing, just as the melting point of silver was used to indicate a firing to 960°C for pottery glazes. This is the principle upon which Hermann Seger based his pyrometric cones.

A clear influence of the cooling process became visible in the gradient kiln: the following maturing temperatures were found for the material quenched in water: a) without a soaking period 1100°C, b) after soaking for 30 minutes 1070°C, c) after 1 hour's soak, 1030°C. This will have corresponded to the facts, if we consider that the white glazes opacified with calcium antimonate contain diantimonate according to Stefan Fitz's studies, which is only stable to 1050°C. To melt the mixture to form glass in a crucible the viscosity must be lower and the temperature correspondingly higher. This is why the melting point of copper may be assumed to be appropriate, i.e. 1080°C. This is especially the case as calcium pyroantimonate, which is stable at high temperatures, is present in the glass. The soaking times may well have been even longer: in a fragment of fired glaze that Eva Marie Schulz reheated, so much energy was contained that it melted at 630 and 650°C. But this is not the production temperature. One reason why the soak

The glaze made from the heated and quenched ingredients with 2% copper oxide and 0.1% cobalt oxide after the cuneiform recipe, applied with gum arabic to a raw, lime-rich body fired to 1030°C and soaked for 1 hour. The differing circumstances that stem from using an electric kiln and pure ingredients have been taken into consideration as far as possible. In such archaeological experiments, there is no guarantee that the actual processes from the past have been reproduced.

matches practical conditions in a woodfiring is that it is difficult to reach higher temperatures in spite of continued stoking, especially if the kiln is poorly insulated.

In recent years, many scientists have gone into the secrets of these first glazes from Mesopotamia. They have reached partly contradictory conclusions which are now being resolved by resorting to ceramic experience.

Independently of this, Rolf Wihr has shown through his research mentioned at the start that glazes with water-soluble fluxes do not need to be fritted because they can be applied with gum (especially gum arabic), and applied to the raw pots, achieving very beautiful results. In this way, it is possible to avoid alkaline Egyptian paste glazes settling rock hard, which makes it difficult to work with glazes of this type as a glaze slop. This method is appropriate if a new glaze is to be applied on top of a fired one.

In the field of art and crafts, this technique clearly offers obvious benefits and attractions, because for one thing newly developed glazes can be tested without the need to frit them. For practical work, it goes without saying that this technique cannot be recommended for production in series because of the inherent risks. Classic frit glazes cannot be avoided here.

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