Methods for reducing copper glazes

Peter Wollwage

In this chapter, Peter Wollwage describes a method for the reduction of copper glazes at relatively low temperatures. In addition, examples of copper glazes are shown that produce a good red or other special effects.

The illustrations are explained in the texts beside or beneath the photos or in the separate sidebar.

To get a red in copper glazes, I tried to reduce them with graphite in small saggars in an electric kiln but without any lasting success. After doing a course on saggar firing with Markus Klausmann in Freiburg in spring 2007, I was motivated by the demonstrations and experiments we did and tried to continue the experiments, firstly in a woodfired kiln without a saggar. I was especially interested in the reduction of copper glazes, which tended to bubble in saggar firings to 850° and above. Success in my reductions firings in this woodfired kiln had always been dependent of luck so far.

"Saggar" firing without a saggar

If you use at least six layers of newspaper stuck together with slip, it is possible to achieve reduction effects in already-fired copper glazes. Similar experiments in an electric kiln showed that it is possible to achieve a copper red at temperatures as low as 600°C. To minimise the stench, which is unbearable in unventilated rooms, charcoal can be used. Graphite can also be used as a reduction agent, but graphite only works at higher temperatures and often causes a blackening or blistering of the glaze.

The smoke and fumes that occur when using sawdust or other organic compounds can be avoided by using charcoal because if the reduction only begins above 550-600°C, the formation of tar and fumes do not play any significant part. It has to be the charcoal which is present above 500-600°C. With barbecue charcoal, the desired effects can be achieved without the smell.

Charcoal can be used in two ways. It is easiest to put it in a tin with the glazed items and then to fire them a third time (1 = biscuit firing, 2 = glaze firing, 3 = reduction firing) to 600-700°C. Of course the expensive ceramic saggars recommended by Markus Klausmann can also be used.

The second method is to wrap the pulverised charcoal with the glazed items in aluminium foil. The charcoal should be evenly distributed around the glazed

Experiments with vases wrapped in wet newspaper and slip, fired to 1000°C showed one way to continue. However, consistent results were hardly possible with this method either.

ILLUSTRATIONS

right -
results of a "wrapped" firing after cleaning, in part with a sander. Glaze and reduction firing both happened at the same time in this instance.

far right - top to bottom-
former biscuit tin (great care must be taken with this in an electric kiln to avoid contact with the electric elements.)

Wrapped pots

Coating with slip

items and the foil should be coated in slip. This keeps it in shape better if the temperature locally exceeds 610°C, the melting point of aluminium.

Larger or awkwardly shaped items that do not fit in a tin or a ceramic saggar can be treated with reduction paste. To make this paste, grind up the charcoal in a mortar, adding water to avoid dust. The ground charcoal is mixed with wallpaper paste and bentonite to form a paste, which is then applied to the parts that are to be reduced and left to dry.

Recipe for "reduction paste"

90 gr powdered charcoal

2 gr bentonite EW (bentonite EW is montmorillonite, prevents sedimentation)

4 gr CMC (CMC is carboxymethylcellulose, available in the form of wallpaper paste)

+ 200 gr water

The package is then placed in the kiln and fired to 600°C with a 30 minute soak.

Two vases after glaze firing.
Glaze composition: test number E17/6, see chart at the end of the article

right -
wrapping a pot in newspaper, powdered charcoal and aluminium foil

the reduction paste, so it is better to aply the paste to the foil and then wrap the pots with this. In this case too, the final step is to coat the foil with slip from the outside. For safety reasons, contact with the kiln elements must always be avoided.

ILLUSTRATIONS -

far left-
the vases illustrated on the previous page after a third firing to 600°C with 20 minutes soak

Influence of glaze composition

Compared with all the other factors that influence results, only the glaze composition seems to have any significant effect on colour.

Results can be achieved that are otherwise only found in raku. The pot illustrated below was fired to 650°C. Colour and surface effect depend mainly on glaze composition. (Glaze D 78/3, see chart at the end of the article).

lefthand column

Pots before and after treatment

The white vase in the bottom picture was only coated with reduction paste on the red band.
The rather transparent red looks rather weak on a brown body.

The sample on the left (E 19/7) (see photo below) is a heavily alkaline glaze without borax. The second is a mixture of 1 and 2 (E20/2). The third from the left (E17/6) is rich in borax (23.8% molecular weight, only

7% alkali). The glaze on the extreme right has a large proportion of borax and 9.6% molecular weight of zinc (E20/3). The lighter colour is probably caused by a slight clouding due to the borax content. (For the exact composition, see chart at the end of the article.)

As soon as the paste is dry, the pots are loosely wrapped in aluminium foil, fastened with thin wire and coated with slip (I use porcelain slip).

With this method, it sometimes happens that a brownish or grey surface appears, which is hard to remove. This coating is caused by direct contact with

ILLUSTRATIONS -

right -
interesting effects with crystal glazes

far right -
composition of D64/6 (in % by weight. For oxides, cf. chart at the end of the article)

Frit A8969	*16*
Frit 90038	*7*
Vitroflux A38	*29*
Quartz	*20*
Zinc oxide	*20*
Barium carbonata	*7*
Copper oxide	*1.5*

The glazes are fired to 1250°C and then soaked for an hour at 1150°C. The reduction followed in the third firing with charcoal.
(Tests 5.5 cm in height.)

Influence of temperature

At 600-700°C, an orange to wine red appears after 10-30 minutes. If the reduction paste is applied direct to the glaze, a brownish or greyish red tends to occur. A higher temperature, i.e. 800-850°C may lead to carbon deposits forming in the glaze. The red is not as good, and bubbles may form. The sample on the left was reduced in a saggar at 850°C and the one on the right at 650°C. The composition corresponds to E17/6. the carbon deposits on the surface are very apparent if reduction has taken place at 850°C.

Influence of tin oxide (right) -

The addition of SnO_2 favourably affects the red colour. SnO_2 intensifies the colour to some extent without making a major difference to the hue. Without SnO_2 a somewhat transparent red is produced, which is rather weak on a coloured body. (cf. E17/1 and E17/3 below). The glaze on the right is E17/1, in the centre E17/2 and on the left E17/3. The colour varies more with the thickness of the glaze than with the tin oxide content.

Influence of copper oxide (right)

Glaze E17/6 percentage of copper oxide: left 4%, then 2%, 1% and to the right 0.5%. All the tests were fired to 700°C in a saggar and reduced for 30 minutes with reduction paste painted on the inside of the saggar walls.

Right: the same experiments as above; spots where the reduction paste was in direct contact with the glaze can clearly be seen. Particularly in the tests with 2% and 4% copper oxide, these spots are carbon black. With less copper oxide, (1% or 0.5%) a lustre-like sheen is appeared.

Influence of the duration of the reduction (right) -
For the colour shade, the period at reduction temperature seemed to be of no importance. Due to the slow heating and cooling, this period cannot be determined with any accuracy, but whether the soak lasted 10, 30 or 60 minutes, an almost identical red is produced with this glaze. Left 10 minutes at 600°C, right 30 minutes at 600°C.

Influence of clay and glaze (bottom right)
After bisque firing, these samples were painted with a mixture of a little copper oxide and a watery 1% solution of CMC. They were then fired to 1250°C and then reduced in a third firing for 30 minutes at 700°C without glaze in both cases!

Conclusions -
According to the book by Wolf E. Matthes, reduction should take place between 700° and 1000°C. However, at this temperature, cracks may appear in the red glaze that remain copper green. After reduction, he recommends crash cooling to 700°C, which implies that below 700°C nothing more will happen to the glaze. Werner Lehnhäuser says the glazed and fired ware should be painted with a copper rich clay mixture and then fired again to 600°-800°C with 8-10 minutes reduction.
According to the tests conducted here, suitable glazes can be reduced with the Lehnhäuser method at as little as 600°C, but the copper/clay mixture is not necessary if the glaze already contains some copper oxide. The literature contains some examples of glazes containing lead, which often produced a greyish colour in these tests, so they cannot really be recommended. In contrast, borax glazes produce a good strong red, and heavily alkaline glazes tend towards a metallic brown.

Batch	E19/7	E20/2	E17/6	E20/3	D78/3	E17/1	E17/2	E17/3
Frit 3158	—	—	70	—	—	65	65	65
Frit 2120	55	30	—	—	—	—	—	—
Frit 8969	—	—	—	—	—	—	—	—
Frit 8962	—	30	—	—	20	—	—	—
Frit 90038	—	—	—	85	—	—	—	—
Frit 3383	—	—	—	—	35	—	—	—
Frit 90209	—	—	—	—	35	—	—	—
Kaolin	—	—	10	—	—	10	5	10
Quartz	40	35	15	15	—	15	15	15
tin oxide	5	5	5	5	9	10	15	5
Copper oxide	2	1	2	1	1	1	1	0.5

Composition on % molecular weight (for D78/3, no percentage of oxides can be stated because no information is available for frit no. 90209.
All values have been rounded up or down.

No.	Li_2O	Na_2O	K_2O	CaO	BaO	ZnO	B_2O_3	Al_2O_3	SiO_2	SnO_2	CuO
E19/7	—	15.0	—	3.8	—	—	—	0.9	76.7	2.0	1.6
E20/2	—	13.3	—	2.1	—	—	9.88	0.5	71.3	2.1	0.8
E17/6	—	5.6	—	2.4	—	—	23.8	3.3	61.1	2.2	1.7
E20/3	—	—	4.1	—	—	9.6	20.6	4.1	58.4	2.3	0.9
E17/1	—	5.4	—	2.3	—	—	23	3.4	60.6	4.5	0.9
E17/2	—	5.6	—	2.3	—	—	23.4	2.1	59	6.9	0.9
E17/3	—	5.5	—	2.4	—	—	23.5	3.5	62	2.3	0.9
D64/6	2.7	2.4	1.2	—	2.5	17.9	6.4	4.9	60.7	—	1.3

The quoted glaze recipes are examples. They can be used as a starting point for your own tests but do not represent fully balanced glaze mixtures. Have fun with your own tests!