

Chemically Reduced Copper Reds In Oxidation



Picture One.

*Tom Turner shares his
years of experience*



Picture Two.

IBELIEVE COPPER RED OXBLOOD GLAZES ARE THE MOST unique, intriguing and elusive of all high fire glazes, which is why they are praised and highly sought after by museums and collectors. They are reported to have been discovered in China in the 15th century,⁸ although ruby glass dates as early as 1500 BC. In 2009, after 45 years of gas fired reduction glazes, I began working with an electric kiln to produce Oil Spot Yuteki glazes and that led to pursuing non-running Zinc Crystal glazes and now the elusive Copper Red Oxblood. Oxblood glazes are produced when copper is reduced of its oxygen during the firing and re-oxidised in the cooling.² Oxbloods can be translucent or opaque and vary from rich deep reds, maroons, purples and red fading into clear which, on porcelain, becomes white. I learned in the 1970s that a copper red glaze must be thick enough to maintain the copper during the firing and also during the re-oxidation of cooling. *Picture One* shows the same glaze thick and thin. If the glaze is not thick enough to maintain the red in firing and cooling, the glaze goes clear and reveals the body. Too thin a glaze and the copper can vaporise out, or be re-oxidised too much and go clear. In a gas kiln the flame can burn the copper out and you again have clear over white. The copper blues and maroons are referred to as Flambés and generally result from boron in the glaze, a thick application and/or heavy reduction. These colour and surface variations are created by chemistry of the glaze, application and firing techniques. The chemistry of the glaze is crucial whether it be a reduction fired or oxidation fired. There are plenty of articles discussing formulas and the bottom line is that you will have to start testing with your chemicals, on your body, in your kiln and with your particular firing schedule. I have a list of suggested readings at the end of this article.



Picture Three.

I will also be experimenting with a process called 'striking' which has nothing to do with reduction. The term striking is being misused these days to explain post fired reduction. The term striking refers to reheating the glass or glaze to a temperature that allows the protons and neutrons to shift the molecular structure of the glass or glaze, creating copper crystals, which in turn changes the light refraction off the colloidal copper, producing a bright Oxblood Red.

I want to focus on the concept of Copper Reds in oxidation firings. Copper with oxygen is green and when the oxygen is taken away properly and cooled properly, it becomes red. It has long been known that you can reduce an electric kiln by inserting material that will burn to create carbon monoxide and free carbon, but the carbon particles shorten the life of the elements drastically. I also want to say that carbon does not reduce, carbon monoxide does and free carbon adds grey to your glaze. There is also post-fired reduction in electric kilns created by introducing combustibles, or dripping alcohol,

motor oil, or vegetable into the kiln during the cooling cycle. The crystalline-glaze potters have been doing this with stunning results. This article is about Copper Reds without any atmospheric reduction during the firing or cooling.

The process of reducing glazes chemically is not new and I have known about it for many years, but never pursued it because I gas fired all those years. I do not know when someone first tried silicon carbide to create reduction in glazes, but I do know that Catalina Pottery, off the coast of California was doing Oxbloods in oxidation firings in the 1920s. (Picture Two) There are articles on "Local Reduction", and "Artificial Reduction", listed at the end of this article, but I want to use the term "Chemical Reduction", as there is nothing artificial about it. I also want to say that I am not a chemist and whatever knowledge I have about this subject has come from reading and running thousands of glaze tests and line blend adjustments. Some of our glaze chemicals give off oxygen during the firing and some are hungry for oxygen during the firing.

Chemicals such as tin, zinc, magnesium, iron, phosphorous, sulphates and of course any material containing carbon are hungry for oxygen and will help reduce the glaze colourants as they melt. Ohio State University's famous Arthur Baggs wrote an article in 1932,⁴ in which he explains how he tried carbon black and graphite without success. Then he tried silicon carbide which held the carbon combined with the silica until glaze melt when the carbon was then able to reduce the oxides in

the molten glaze. Silicon carbide can be used as a reducing agent, but the coarseness can give many different results. Too coarse a grind will develop excessive bubbling and I believe this is possibly how the 'Lava' glazes were developed. A glaze chemist will match oxides in ratios such as 1:1 or 3:1 and it is recommended that tin to copper is 3:1, although too much tin leads to opacity. Tin is essential to the development of Copper Red Oxblood, in reduction or oxidation firing. By incorporating these chemicals into the glaze formula, in the right proportions, they can help you achieve the copper reds by stealing some oxygen from the copper during melt. Glass blowers have done this for years to help reduce Copper Ruby Red glass.

Through trial and error testing, it was learned that the silicon carbide had to be exceptionally fine, such as FFF grade, or finer. Each silicon carbide mesh size will develop different patterns and surfaces, so I cannot say one is the best, it depends upon your intent and what results you are after. (Picture Three) Arthur Baggs was doing his research at Ohio State University in the 1930s while another graduate from Alfred, Max Compton, was producing incredible reds at Catalina Island Pottery off the coast of California. These are the most successful reds I have ever seen. (Picture Four) They are all glazed inside with an oxidized green copper glaze and glazed outside with a brilliant Copper Red Oxblood. This could only happen with chemical reduction since atmospheric reduction would have reduced both inside and outside. I bought my first Catalina piece in 1973 not knowing where it was made. It took many years of antique hunting to identify the maker through observation of feet and markings on other pots. It only had a "Made In USA" stamp of black glaze on the foot, which I later saw on a Catalina Island Pottery, then a Gladding McBean vase and then a Franciscan Pottery vase. Rookwood Pottery was also producing Oxbloods during the 1920s, 1930s and 1940s, but I am not sure if it was atmospheric reduction or chemical reduction. That article is for someone else to write.

The early references listed at the end of this article, gave us an insight to possibilities and encouraged potters to experiment with chemically



Picture Four.

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Picture Five.

reduced copper reds. There may be earlier articles than what I have read, but Bagg of Ohio State University first presented his research to The American Ceramic Society in February of 1931.⁴ His paper was presented in March of 1932. Harding Black, a studio potter in Texas presented an article in *Ceramics Monthly* in the January, 1953 issue⁵ and Edgar Littlefield of Ohio State University presented his article in *Ceramics Monthly* in December, 1953.⁶ The most recent article that I have seen was in *Ceramic Review*, published in the UK, written by Michael Bailey with assistance from Dean McRaine, a studio potter in Hawaii.⁷ Prior to McRaine and Bailey's testing of different size silicon carbide powders, early research used FFF grade Silicon Carbide. I believe Bagg's article stated that it was readily available in hardware stores, used for polishing furniture.

I read these articles and Googled everything I could find and began testing. I obtained samples of silicon carbide from 500 to 1200 mesh from Brian Hauer at Washington Mills, a manufacturer of silicon carbide. I asked Hauer what the FFF grade meant and he explained that the particle sizes are more inconsistent in the F grades and that the specific mesh grades, such as 600, 800, or 1000 were more consistent in that size. My tests were similar to McRaine's tests, although I found my samples varied a little from his results. Like all of our chemicals, I am sure there is variation with the manufacturing of the silicon carbide, added to the variations of formulas, chemicals, bodies and firing techniques that determine our results. I found that as the silicon carbide size became smaller, there was more glaze melt, less surface texture from the glaze bubbling while giving off oxygen during the chemical processes and weaker reduction. (Picture Five) I settled on the 800 mesh silicon carbide from Washington Mills, the supplier of my testing material. The 800 mesh gave me a better glaze surface, reduced the copper uniformly and the reds were brighter. (Picture Six) I also found that less copper is required in a chemically reduced glaze than in an atmospherically reduced glaze, using as little as .1 to .3 percent.

Testing the smaller mesh silicon carbide led me to wonder about different types of copper. I considered smaller mesh copper carbonate but, instead, decided to test copper sulphate as did Black when he researched copper reds.⁵ Copper sulphate is soluble in water so I felt the copper would be dispersed more evenly than carbonates or oxides. Since sulphates reduce, I figured I might get a double attribution, colour and reduction. The reds were more uniform and stronger in colour. (Picture Seven)

In 2009, after 45 years of gas fired reduction glazes, I began working with an electric kiln to produce Oil Spot Yuteki glazes and that led to pursuing non-running Zinc Crystal glazes and now the elusive Copper Red Oxblood. Oxblood glazes are produced when copper is reduced of its oxygen during the firing and re-oxidised in the cooling.²



Picture Six.

People may wonder about damage to the elements from the silicon carbide, but I do not believe it will happen. I believe the 1/3 percent to 1/2 percent silicon carbide in a glaze will be totally absorbed by the melt. Oxygen is given off and will create bubbles such as with Lava Glazes, but they are miniscule from the 800 mesh silicon carbide. Many of our glaze chemicals vaporise at cone 9 and they would have more effect on the elements than the silicon carbide. Truthfully, even if it destroyed the elements sooner, getting incredible copper red oxblood glazes in an electric kiln, to me, is worth whatever it costs.

My one hour hold firing cycle for my Oil Spot and non-running Zinc Crystal glazes worked perfectly for the reds. If you are going to hold at the end of the firing, you must shut off at a lower temperature because during the hold, you will continue to get melt from what we call 'heat soak'. Through creative testing you need to find the shut off temperature for your controller that will give you the desired 'glaze melt' at the end of your planned hold. Some books suggest dropping an Oil Spot glaze to 1800°F and holding, but it is my guess that by then the cone 9 glaze has solidified and the hold will do little. I had no reference temperatures, so I guessed at a 50°F drop as fast as the kiln could drop (3 minutes) and an hour hold which gave me the best results for my Yuteki-Oil-Spot, my non-running Zinc Crystal and now my Copper Red Oxblood glazes. My thought was to drop two cones and see what happened and it turned out to be just the right temperature for the holding period. In programming your controllers, you also have to take into consideration thermocouple protection tubes. If your kiln has protection tubes, you may have to shut off at even a lower temperature. I can only share with you what I do but realise it is my kiln and my controller, yours will be different. My porcelain and my glazes are formulated to be completely mature at cone 9 with cone 10 at two o'clock, which for me is a solid cone 9. You cannot fire to cone 9 (2336°F), drop and hold, because you will have too much melt. Once your controller is set for 'the finished result' you are after, forget about cones and numbers. It is all about the melt. Naturally, use cones during the creation of your firing schedule and, once the cycle gives you the results you are after, the controller is in charge. It is no longer about specific numbers and

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Picture Seven.

cones because the numbers may vary with each desired result. This may be a little confusing because my controller numbers do not match cone numbers, but this is the program I have worked out for my glazes.

Ramp One – 200°F per hour to 250°F, hold 20 minutes. This hold dries all moisture in the bisque from glazing.

Ramp Two – 350°F per hour to 1800°F, hold 30 minutes. This hold allows out-gassing

which can eliminate bloating, especially if you re-fire.

Ramp Three – 350°F per hour to 2295°F, controller shuts off.

Ramp Four – 1000°F per hour down to 2245°F, (about 3 minutes) hold one hour, shut off. I fire and cool with the fan on and this gives me a perfect cone 10 at two firing. This hold allows Oil Spot glazes to ‘lay down’ and crystal glazes to grow. It works as well with copper red oxblood glazes relative to the re-oxidation of cooling.

After hundreds of tests, here is my most successful Oxidation Copper Red Oxblood. It is my gas fired Oxblood altered slightly for the oxidation firing. At the same cone, there is less melt in oxidation than reduction so I had to flux it a bit more. (Picture Eight). The test tile on the left is my gas reduction red fired in oxidation, which shows entrapped bubbles and a matte skin over the glossy red using FFF silicon carbide, whereas the tile on the right is the same glaze fluxed a little and 800 mesh silicon carbide. I have also found by testing that a good copper red, gas or electric, benefits from calcium, magnesium, barium, zinc and tin.¹⁰ For testing, I mix close to a 200 gram batch, as seen in the sidebar.

I will also be experimenting with a process called ‘striking’ which has nothing to do with reduction. The term striking is being misused these days to explain post fired reduction. The term striking refers to reheating the glass or glaze to a temperature that allows the protons and neutrons to shift the molecular structure of the glass or glaze, creating copper crystals, which in turn changes the light refraction off the colloidal copper, producing a bright Oxblood Red. Glass blowers have done this for years and I first saw Fritz Driesback do this in the 1970s and have never forgotten the instantaneous and dramatic change of colour from clear to a brilliant ruby red simply from reheating the glass. To my knowledge, potters just have not pursued this process. Glass blowers have the exact temperatures for striking glass, but the perfect strike temperature for a cone 9 glaze will have to be found. Here is an example of simply refiring a cone 9 chemically reduced glaze in a cone 08 bisque firing. (Picture Nine) In the early 1970s I fired gold lustre on a Copper Red Vapour glaze^{10, 11} at cone 019 and got a darker red indicating that

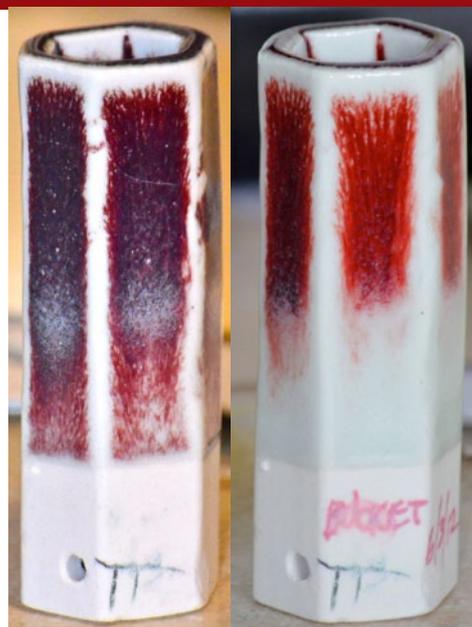
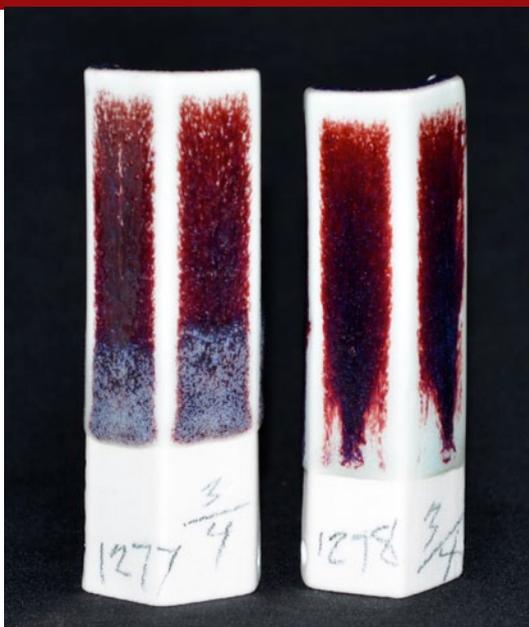
Tom Turner's Oxidation Fired Copper Red Oxblood Cone 9.

Custer Felspar	100
325 Silica	40
Pfizer Vicron Whiting	40
EPK	3.2
Magnesium Carbonate	5.6
Barium Carbonate	5.6
Zinc Oxide	5
Tin Oxide	2
Frit 3110	10
800 mesh Silicon Carbide	1
Copper Carbonate or Sulphate	1
Bentonite	4

it had 'struck' at that low temperature. The striking temperatures will vary with each different glaze formula and firing sequence. I feel the Catalina Copper Red Oxblood glaze was a cone 06 lead glaze that was struck in cooling.

So to summarise I would like

to say that much testing is required to get optimal results; our bodies and chemicals are different; each glaze formula will yield different results; each mesh silicon carbide will give different results; each type of copper will yield different results and, of course, each firing schedule will yield different results. During this search for beautiful glazes, certainly work on making beautiful pots. Too often the energy goes to the glaze research and the pot gets ignored. My research on chemically reduced glazes has just begun and I challenge everyone to think outside the box that was created by our teachers and early books and "See What Is Really Possible."



Left: Picture Eight.
Above: Picture Nine.
Below: Copper Red, Oil Spot and Crystal Glazes in Tom Turner's Electric Kiln.

1. Pere d'Entrocolles' letters 1712-1722
2. "The Chemistry of the Chinese Copper-red Glazes", Part 1, Dr. Mellor, Transactions. Ceramic Society, vol. Xxxv 1936.
3. A L Hetherington. "Chinese Ceramic Glazes". 1937.
4. "The Production and Control of Copper Reds in an Oxidizing Kiln Atmosphere", Arthur Baggs and Edgar Littlefield, presented at the Annual meeting, American Ceramic Society, February 1932.
5. "Opening The Door To Copper Red Glazes", Harding Black, *Ceramics Monthly*, January, 1953.
6. "Local Reduction Copper Reds", Edgar Littlefield, *Ceramics Monthly*, December, 1953.
7. "Copper Reds in the Electric Kiln", Mike Bailey and Dean McRaine, July / August 2010
8. "Chemical States of Copper and Tin in Copper Glazes Fired under Various Atmospheres", *Journal of American Ceramic Society*, 72, (1), 1989, Cuba University, Kyoto Institute of Technology. Mitsuru Wakamatsu, Nobuyuki Takeuchi, Hiroki Nagai, Shingo Ishida.
9. *Red Glass Coloration*, Torun Bring, Stockholm, Sweden, 2006.
10. *Ceramics Monthly*, February, 1974, page 23.
11. *Studio Potter*, Volume 8, Number 1, page 19.



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