THE DEFIANT RED

A review of red coloured glazes

L.W. BAAIJ

My sincere thanks to the correctors:
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A review of red coloured glazes

This review is intended as a contribution to the common knowledge of producing so-called 'pillarbox' or 'signal red' glazes. It is commonly known that – despite the long existing ceramic tradition in various human cultures – the possibilities for successfully producing bright red glazes on an industrial scale only become apparent after further development and perfection of the systems based on the elements cadmium, sulphur and selenium.

Besides the current method, seven other methods for producing red colours are also reviewed. Some of these have long traditions like the iron and copper reds. Some of the chromium based red glazes can approximate the CdSe glazes in colour value. In general, however, one can state that for all other methods the conditions necessary to create a real red colour tone pose restrictions for applications on a large or industrial scale.

L.W. Baaij / 2010

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PREFACE

Starting this review the intention in first instance was to review and describe the existing manufacturing possibilities of the group of cadmium selenium red glazes. Although it is by far the only way which offers so many possibilities for the creation of real red colours in the various area of the ceramic field, it is not the only one.

With the idea in mind to be more complete, it became more and more obvious to also include the other existing methods' contribution towards realizing reddish colours in ceramics. Moreover, the section describing the historical aspects also grew, slowly but surely.

With admiration of what has been explored and described by numerous historians and investigators, I have tried to confine myself to the most relevant literature and available studies. Realization of the long ceramic traditions in various human cultures and their culminating points which were reached over several eras dictates the importance of mentioning these facts, albeit in more general terms.

I must admit to exploring some side roads which, in my opinion, are mentioned to complement the overall view of the genesis of some red glazes.

The eight different methods reviewed cover the important existing methods for realizing red coloured glazes. Two of them are by far the most important in respect of their industrial applications. These two are the reddish colours obtained by colour stains of the CrSn group and the CdSe glazes.

The most typical red colour, represented by a wavelength of 614 nm and a colour saturation σ of about 90, is however only possible to create when making use of the facilities offered by the system of the CdSe glazes and CdSe stains. This group of colours and glazes is well known by names such as signal red, cinnabar, scarlet, madder red, lobster red, carmine red, poppy red and pillar box red.

The importance of the CdSe glazes has increased considerably since the end of the fifties and the early sixties of the last century when improved methods were developed for the retention of the red colour under normal industrial firing conditions. The available literature, including patent literature, is somewhat limited in the area of describing the practical application and manufacture of these glazes. It is therefore hoped that this review will also contribute to this knowledge.

Red colours have something defiant in their character but that was not the only reason for this review. Under certain but different circumstances I think I might have undertaken the same exercise for blue.

With my sincere thanks to all who helped me to realize this publication.

L.W. Baaij
Gronsveld, 2010
The Netherlands

1 INTRODUCTION

Without doubt one can state that both now and in history the colour red is a colour that holds great fascination. Something of this sense can be felt when one sees the red colour gradations of an early sunrise or a sunset on a bright summer evening. Accurate reproduction of such reddish sky-colours posed great challenges for many famous artists in their wonderful paintings. These colours, caused by the fact that when the sun is low in the sky the blue and violet light is more refracted than the red light by the atmosphere, were and are in this way a continuous source of inspiration.

Red was for sure one of the first applied colours, if not the very first. The abundant use of red ochre together with yellow ochre and black for the famous prehistoric cave paintings like those of Lascaux and Altamira are in evidence of this. The red colour was often associated with blood and, more particularly, with the life-giving idea of it. This can be illustrated by the linguistic reduction of the words blood and red.[1] In Sanskrit, the oldest Indo-European language, the word for blood is *rudhira*. The first part of this word appears also in other languages like e.g. Greek and Latin: *erythros* and *rutilus* resp. for red. Also in modern languages this word shows up like in the German 'Rot', the Dutch 'rood', the English 'red' and the French 'rouge'.

From the earliest times humankind has attached strong attributes to this colour. The main attributes meant here have to do with activity, action, struggle and other strong emotions which can all be associated with this never-tranquil character. An example illustrating the power of red is the almost innumerable number of red flags. The so-called 'Oriflamme' of Charles the Great, used on the battle fields is a well-known example. Another outstanding example of the image of the red colour is the use of the red flag whenever there is a struggle or a revolution, especially when it is said to be a socialistic one. Even the red colour of the cap of Little Red Riding-Hood is in this respect not accidental, but a very conscious choice according to the explanation of psycho-analysts (Fromm), psychologists (Bettelheim) and exegetes (Hans Ritz).

This psychological impact of the red colour is nowadays frequently used in commercials and advertisements. Very fast racing cars are more associated with the colour red than with any other colour.

The bright red colour was impossible to produce in ceramics before the properties and possibilities with the cadmium, selenium and sulphur compounds were fully exploited. Although there are several ways to obtain reddish colours, not one of them has the properties as those from the CdSe reds, not even close to them.

One of these properties is expressed in the data which are obtained when measuring the colour with a filter- or tristimulus colorimeter. When measuring a colour with this type of equipment the basic principle is that the subject is exposed to a well-defined light source and that the reflected light passes at least 3 filters. The exact transmittance of the filters is prescribed by the Commission Internationale de l'Eclairage (CIE), after investigations by e.g. Guild and Wright. Modern colorimeters have more e.g. 16 filters and are connected with a computer to perform the necessary calculations. A terminal offers the possibility to visualize the reflectance curve in a diagram and a connected printer gives the curve instantly.

In these cases the colorimeter takes over the role of the human eye. This take-over has however only reference to those physical properties of colours which follow the nowadays existing laws

whereupon colorimeters are based, whilst a colour judgment with the human eye involves also the physiological-optical problems. The physical properties are more and more laid down in laws after Newton published his opinion that light can be conceived as a mixture of spectral colours. Colour measurements refer only to these physical properties such as wavelength, colour saturation, etc. A more physiological approach was first given by Goethe (*Zur Farbenlehre* 1810) while a more recent representative in this line ranks e.g. Itten (*Kunst der Farbe* 1961). It often means that colour measurements are applied as an internal support parameter in the quality control area but that for final acceptance of colours and coloured glazes the judgment of the human eye is also taken into account.

The tristimulus values X (for red), Y (for green) and Z (for blue) are concluded from the reflectance curve and one can calculate the trichromatic coordinates x, y and z according to:

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

The relative blue part is:

$$z = 1 - (x + y)$$

The x and y coordinates of the CIE system defines any position on the chromatic diagram (see Figure 1). When another variable, the Y value (lightness) is coupled with the chromaticity diagram, the combination defines the exact place in the spatial pattern of the CIE diagram. The dominant wavelength, λ_d, can be determined by lengthening the line between the neutral point and the point as located by the x and y coordinates. The point of intersection of this line and the curve of the spectral colours gives λ_d for that particular colour. The distance from the neutral point till the point as fixed by the chromatic coordinates x and y is a measure for the colour saturation σ. The colours on the spectral curve have a $\sigma = 100$.

If one measures a typical example of a CdSe glaze prepared through the method using a pigment (i) and through the melted-in method (ii), one arrives at the data as given in Table I. For this measurement a colorimeter of Zeiss, type RFC 16 was used. The colour is measured through 16 filters. With these data one can determine the λ_d and σ for these colours.

Sample	**x**	**y**	$\boldsymbol{\lambda_d}$	$\boldsymbol{\sigma}$	**Y**
CdSe sample (i)	0.637	0.327	612.0	90.50	9.67
CdSe sample (ii)	0.646	0.321	614.5	91.00	8.41

Table I: Cd · S · Se *colour measurements (Zeiss RFC 16 colorimeter)*

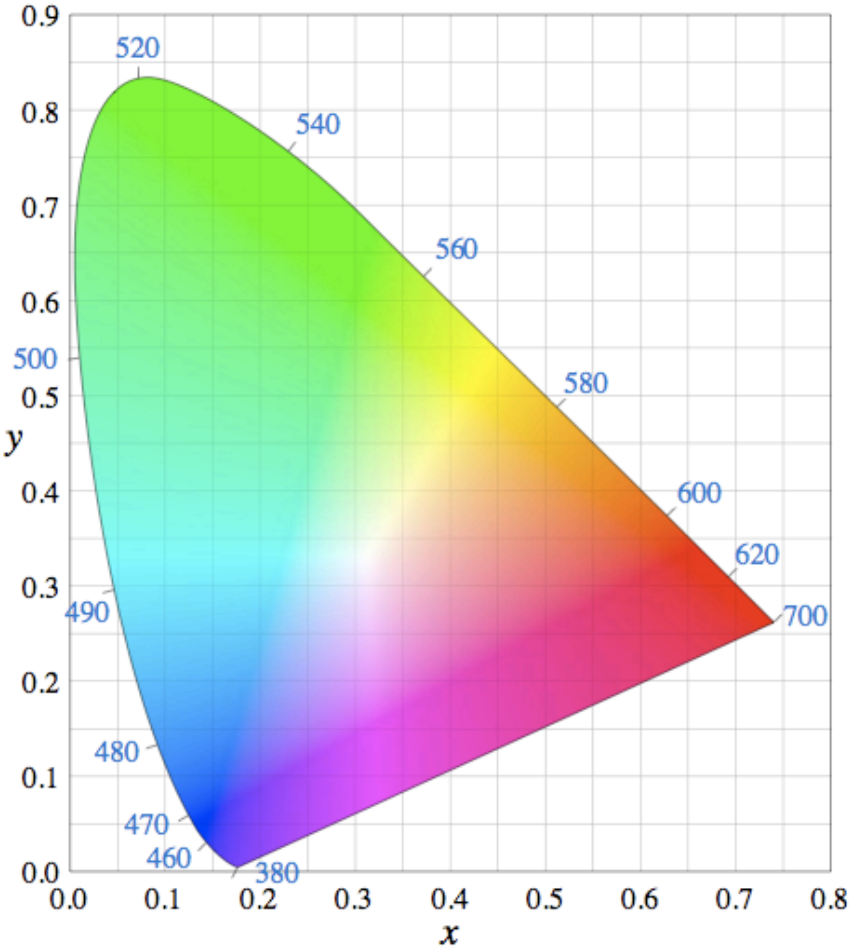


Figure 1: CIE chromatic diagram

Another type of colorimeter is the Hunterlab colorimeter, also including advanced calculation equipment. This meter gives the colour values in L, a and b and is also able to give the in-line colour difference according to the CIELAB method in a fast way. When measured the same colour samples (i) and (ii) as mentioned before with a Hunterlab type D 25 g, the data is obtained as given in Table II.

Sample	**L**	**a**	**b**
CdSe sample (i)	+30.46	+52.69	+19.05
CdSe sample (ii)	+27.98	+52.80	+17.65

Table II: Cd · S · Se *colour measurements (Hunterlab type D 25 g)*

Although these data of the colour measurements of sample (i) and sample (ii) are rather close, it is without doubt that a simple visual judgment, even by inexperienced eyes, is sufficient to distinguish the different nature of these two examples of CdSe glazes.

The typical colour characteristics of the CdSe glazes as shown in the Tables I and II are clearer if they are compared with the results of the colour measurements of some other typical representatives of components which also create reddish colours in ceramics. For these colour measurements the same Zeiss RFC 16 colorimeter was used. The results are given in Table III.

Colour sample	x	y	λ_d	σ	Y
CdSe sample (i)	0.637	0.327	612.0	90.50	9.67
CdSe sample (ii)	0.646	0.321	614.5	91.00	8.41
CrSn red	0.581	0.314	618.0	72.00	2.59
Ni red	0.437	0.330	594.0	30.00	12.04
Cr red	0.545	0.355	601.0	73.50	18.25

Table III: Comparison of reddish glaze colour data

As there are no colours which can be considered as standard colours for the various mentioned reds, the glaze examples of Table III represent a certain choice. This choice per colouring component was made in such a way that the mentioned glazes clearly can be recognized as representatives for that colour component. The glaze references as used for these colour measurements are given in Table IV.

Colour sample	Glaze reference	Firing temp. / cycle
CdSe sample (i)	Transp. frit + CdSSe stain R125AT*	1040 °C / 12 hrs c.t.c.
CdSe sample (ii)	12.95672.00**	1040 °C / 12 hrs c.t.c.
CrSn red	12.55028.00**	1020 °C / 12 hrs c.t.c.
Ni red	B0457**	1020 °C / 12 hrs c.t.c.
Cr red	12.55097.00**	940 °C / 12 hrs

* originated from BCRA., UK
** originated from Ferro (Holland) BV, Netherlands

Table IV: Glaze references for the colour data in Table III

As mentioned before, these values illustrate more or less the typical character of the CdSe colours. Only the red colour obtained through chromium can approximate these values to a certain extent. However, the special character and application possibilities of chromium red glazes mean that these types of glazes are only applicable in the field of art pottery. All other methods are unable to create the typical signal or pillar-box red colours as those from the CdSe glazes.

From the other possibilities which can be used to create reddish colours like iron, copper, nickel, gold, CrSn stains and sodium uranate, it can be mentioned that they all create a colour which is typical for that particular component. In most cases, the glaze requires a composition to such a degree that indeed a reddish colour is obtained but that the nature of the glaze is an absolute

disadvantage in respect of industrial application. Only the use of calcined stains of the CrSn type is quite often applied.

The use of Se in glass compositions is known for a long time already. The investigations of Rooksby resulting in the determination that the red colour is caused by mixed crystals of CdS · CdSe and published in 1932 were an incitement for a more intensive and scientific approach of this colour mechanism. The first application of CdSSe pigments were, besides the glass colouring, as decoration colours to be fired at rather low temperatures in a 3rd firing process. The majority of the CdSSe stains were applied in plastics and only a very small amount found an application in ceramics. Technical improvements made the pigments suitable for higher temperatures when used in specific base glazes. The use in enamel processing and low firing glazes became possible. These classic types of CdSSe pigments could be applied till about 1020 °C in a firing cycle of approximately 16 hours.

The type of glaze to be used for these CdSSe pigments was preferably a cadmium stabilized one. Several of these types of glazes are mentioned in the literature[2] and developed by the ceramic industry.

Another significant step in the development of these colours is the invention of the so-called encapsulated pigments. The first patent is filed in 1973 and published in 1974[3]. The nature of this type differs from the classic type. The real bright red colour tones are however difficult to achieve with the first generation of inclusion pigments. It is a kind of contradiction: the $ZrSiO_4$ crystals are necessary to protect the pigment but are also the reason that a too high degree of covering power (whiteness) is formed caused by the difference in refraction index between the amorphous glass and the $ZrSiO_4$ crystals.

Later developments in this sphere by the British Ceramic Research Association have shown to be an improvement of this $ZrSiO_4$ protected pigment type. Colour stains made according to this patent show a real bright red colour. This improvement is realized by a modified production process resulting in the fact that all the single zircon silicate crystals contain some of the CdSSe pigment. These types of encapsulated pigments contain therefore about 7 times as much cadmium as the first inclusion pigments[4]. This gives the pigment more firing stability while also the release of cadmium is considerably lower than its predecessor[5].

After 2000 another generation of stabilized CdSSe pigments has been developed in China. These pigments have a higher colour strength and brightness and can be applied even over 1200 °C. It is remarkable that the development of the inclusion pigments somehow stopped in the western European countries and that a new generation of much stronger and brighter pigments has been developed in China. It is generally believed that a well known supplier of inclusion pigments as e.g. the German company Broll Buntpigmente found the investments necessary to develop this new generation of very strong stains to be too high. It is not exactly known by the writer why the Peoples Rep. of China came up with these very strong stains, but it is assumed that severe laws and regulations in the western countries are very much an obstacle for the production in the western countries and that the production of these type of stains at manufacturers at e.g. China is only possible by the lack of the same severe laws and regulations regarding the working with and the production of cadmium-containing compounds.

The method of melted-in CdSe coloured glazes came to a real industrial use during the late fifties and the sixties of the former century. Through the years, an unremitting zeal has ensured that nowadays for practically each and every firing cycle a variety of CdSe glazes is available.

Due to its better firing stability this type of CdSe glaze has taken over the role of the classic pigmented CdSe glazes. The conventional pigmented type of glaze has some disadvantages: the firing temperature is limited, the colour stability is less compared to the melted-in types and the glaze is sensitive for a less favourable kiln condition. These were reasons that the improved melted-in type of CdSe glazes replaced the pigmented types for industrial applications.

Only with the latest generation of very strong and bright CdSe pigments have the earlier disadvantages been overcome. The high prices of these strong pigments are however a block for a comprehensive application.

In the dinnerware industry another advantage benefitted the melted-in types: the lower figures for metal release and far within the limits as prescribed by the standard DIN EN 1388-1/-2. As a typical representative company which produces safe dinnerware using CdSe glazes of the melted-in type counts e.g. the German company Wächtersbach now called Keramische Fertigungstaette Brachtal GmbH. This company has produced red glazed dinnerware for several decades already and it is e.g. meeting the requirements for export to the U.S. Only in those cases where an absolute lacquer-like appearance is required do the pigmented types fulfill these requirements better than the melted-in types. In this respect one can e.g. refer to the Fiesta dinnerware type called 'Scarlet' made in 2004 by Homer Laughlin (USA) which is produced with a suitable transparent glaze and a strong CdSSe pigment from the last generation.

The wall- and floor tile industry used to only apply the melted-in types of glazes. Nowadays, with the strong CdSe pigments available, these pigments are applied as well to achieve lacquer-like red colours. In particular, floor tile glazes require a special surface which can be obtained through some mill additions. The melted-in type of glazes tolerates these additions much better than the pigmented type with respect to the retention of the red colour.

It may also be stated that it is commonly known that the higher the firing temperature and the longer the firing cycle, the more difficult it becomes to retain the red colour. The fact that nowadays CdSe glazes are available for 1200 °C and over in a firing cycle of roughly 20 hrs shows how far the developments have proceeded. The trend in the ceramic industry to apply faster firing cycles is therefore less problematical with respect to stability and retention of the colouring components. However, other problems remain and therefore these types of glazes must always be treated attentively.

The peak in application of cadmium selenium glazes was in the seventies and eighties of last century when thousands of tons of cadmium selenium glazes were produced per annum by the main West European manufacturers and applied onto wall- and floor tiles, vases, dinnerware and giftware. Colours are, however, also strongly dependent on colour trends for interior textiles and follow e.g. the directions as given by the ICA (International Colour Authority) and other organisations in this field. Although today such huge quantities are not applied anymore, there will always be a place also in ceramics for the application of red glazes.



Photograph 1: Vase "Tokio" with glossy red CdSe *glaze and hand-painted decoration. The vase was in production from 1967 till 1976. Courtesy of 'Flora' (now Royal Goedewaagen).*

2 HISTORICAL ASPECTS OF RED COLOURS

Including some thoughts about colours other than ceramic red colours.

Although red is called the colour of activity it is remarkable that the ceramic industry had to wait roughly 8000 years before a more general use and application of the so-called pillar box or signal red colour was possible.

From the early glazed objects as e.g. found after the excavation of ancient Babylon (mainly from 1899 till 1917), till the first half of the 20th century, there were several possible methods of achieving reddish colours. However, none of them gave the typical bright red colours as those based on CdSe.

Most of the bright red colours which were used in the past were all based on organic combinations which made them unsuitable for ceramic applications.

In this field it was already known for a very long time how to prepare a typical clear red colour. Nowadays, only some of these old methods have survived. Most of them are replaced by the synthetic colours.

Although not directly related to ceramics it is interesting to see how some typical red colours were achieved in the past. Most of them are replaced by synthetic colours which offer almost every desirable colour possibility. An exception is of course Mother Nature: she still creates the most beautiful red colours without any human influence.

Several sources mention 'kermes' as the oldest recorded dye; a red colour stain obtained from a particular coccus.[1, page 184] Also the name scarlet has in this respect a long tradition. It is the colour of the dye cochineal, obtained from a special kind of louse. The word is present in many languages. The origin of the word is explained as being derived from the Persian word 'sakirlat' which indicated clothes dyed with this colour. This can also been said from the Arabic 'sagillat'. The word can also been found in the Latin 'scarlatum', the old-French 'escarlate', the old-German 'scharlach' and the English 'scarlet'.

A long existing class of red and purple colours is e.g. the porphyrin group (from the Greek porfyra = purple). In ancient times the old Fenician town Tyros had already a famous purple production around 1200 BC. It is said that a certain kind of 'whelks' were the source for this purple dye. This fact has also given the name to the philosopher Porfyrios (Tyros 232 – Rome 305). His real name was Malchos but he was called after the purple industry of his native town.

The basic colouring compound is metalloporfyrine. The metal ion can be Fe, Mg, Cu, Zn, Co, etc. These types of compositions are found in numerous, important organic compositions like hemoglobin (Fe containing porphyrin complex), chlorophyll (Mg containing porphyrin complex) and others.

Solutions of porphyrines have, just like those of pyrrole, the property to colour deep red in a reaction with organic solvents and mineral acids.

In medicine the complex zinc-proto-porfyrine (zpp) is also known as a means to check a possible increase of lead in blood. However, if the zpp factor is too high it is not necessarily caused by lead poisoning. There are more factors which can lead to an increased zpp factor.

The porphyrine compounds play an important role in the hemoglobin. It is well known that hemoglobin is important for the transport of oxygen and the removal of carbon dioxide. The active group hematine forms part of the hemoglobin and this plays an important role in the binding and relinquishment of oxygen in the blood.

The carotenoids are another group of yellow, orange till red colours belonging to the group of tetraterpenes. A well known representative of this group is carotene, responsible for the orange colouring of carrots. Other representatives of this group of colours are responsible e.g. for the yellow colour of the dandelion, the orange/red colour of tomatoes and also for the yellow colour of the canary.

Another organic possibility which was used to obtain a warm red colour came from the roots of the 'Rubia Tinctorum'. This plant was first cultivated in Asia (India, Iran, Egypt), followed by the countries around the Mediterranean. From the 16th century, the plant was also cultivated on a rather large scale in France and The Netherlands (mainly the south-west part). The dried and pulverized roots were used for colouring wool and silk.[6] The important component here is alizarine (from the Arab word 'al oesara' = the sap). The chemical compound responsible for the colouring is 1,2-dihydroxyanthraquinone ($C_{14}H_8O_4$). This compound is intrinsically light coloured. When chemically bound with metal oxides (Al, Zn) the real vivid red colours become possible to produce. Similarly, clear red colours could be created (Figure 2).

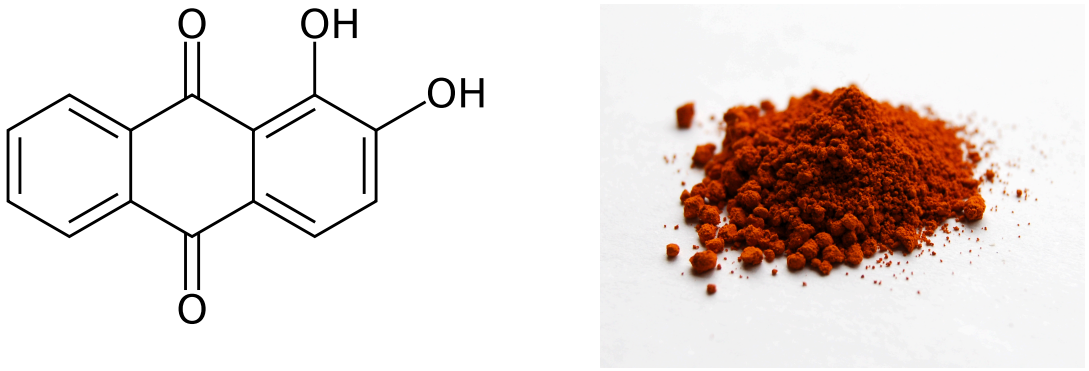


Figure 2: Alizarine

In 1868 Graebe and Liebermann succeeded in producing alizarine synthetically starting from coal tar. From that time the plant became unimportant and later on the alizarine itself also. One of the applications today of alizarine red is e.g. in the plastic industry but only to a minor extent. The reasons for this are its inferior heat resistance and its poor resistance to ultra violet light and chemicals.

Another way to obtain bright red colours was the so-called 'orseille', a vegetable colour pigment prepared through extraction of various kinds of lichen with ammonia.

The colouring component is orceine ($C_{28}H_{24}O_7N_2$). This orceine is the purified extract from the orseille. One of the families of lichen which was important in this respect was the Rocella species. It is said that the name (orceine as well as orseille) stems from Rosela, a rich traders family from Firenze. They were trading with these types of lichen pigments as early as the 14th century.[7] H. Musso[7] succeeded in decomposing the orceine in 14 components in a chromatographic way. The

main components are α-amino orceine ($C_{21}H_{18}O_4N_2$) and γ-amino orceine ($C_{28}H_{24}O_6N_6$). As a colouring agent it is almost completely replaced by synthetic colours. In the food industry it is still used on a small scale.

Litmus is very similar to orceine and is derived from the same kind of lichen.

Similarly the famous Harris Tweed is said to be coloured with a type of lichen. The reddish-brown colour is obtained with a lichen type having the local name 'crottal'. It is collected by the people living on the Hebrides who still prepare the colour in a traditional way.

'Brazil wood' is a further example. For this aim the wood of the family Caesalpinia and Haematoxylum was utilized. Its purified sap served as an ingredient by the preparation of aluminium-, chromium- and zinc paints. However, these paints were not resistant against acids, alkalines, neither were they light-resistant (UV). Today they are completely replaced by synthetic colours.

Besides these and other vegetable sources of red-making colours, there were also some animal-organic pigments in use. One on these was carmine. This was prepared from the female cochenille lice. The lice were dried and after boiling in water the colour was separated in the form of a sediment. The colouring component is mainly carmine acid. To make it more suitable as a pigment it was precipitated on a carrier, in most cases alum.

It will be clear that there are a number of disadvantages with regard to these natural colours. The production methods, the inferior resistance to chemicals and UV light can be highlighted. The situation regarding the production and application of organic colours changed completely by the discovery of aniline. Aniline (from the Arab word anil = indigo plant) is an amine derived from benzene by substitution of a hydrogen atom by an amino group with the formula $C_6H_5 - NH_2$.



Figure 3: Alinine (aminobenzene)

Aniline was discovered by Otto Unverdorben in 1826. He succeeded in isolating the component from the products obtained by a dry distillation process of indigo. The preparation nowadays is done by reduction of nitrobenzene with the help of iron filings and diluted HCl. Directly after the distillation the aniline is colourless but due to the influence of light a brownish colour appears. At temperatures as low as −6 °C the aniline solidifies. It has a slight but unpleasant smell and it is highly toxic.

Aniline is a weak base with salts which can easily be hydrolyzed. The hydrogen atoms of the NH_2 group can be replaced by alkali metals. A typical and important reaction of aniline and the other aryl amines is the formation of diazonium salts $C_6H_5N_2Cl$ by the influence of HNO_2. These salts are starting points for hydrazines and for the important azo colours.

Aniline is also the starting point for secondary bases from the type $C_6H_5 - NH - CH_3$ or $C_6H_5 - NH - C_6H_5$ and of tertiary bases of the type $C_6H_5 - N(CH_3)_2$. These are mixed bases because they are both aliphatic and aromatic. They are produced by influence of alcohols on aniline under pressure in the presence of H_2SO_4. The bases give under influence of HNO_2 paranitroso combinations $ON - C_6H_5 - N(CH_3)_2$. These are the starting points for azine and oxazine colours.

All these organic colours, based on pure chemical reactions, have now replaced the natural colours. There is no need here to point out that the development of these colours could take place thanks to their durability advantages over the natural colours.

This picture of relieving and succeeding methods for red colouring can also be recorded with regard to the methods on creating a deep red colour in ceramics.

It can roughly be stated that the oldest methods made use of red coloured clays (Fe_2O_3). Notably it is not only the use of red coloured clays, but also the development of techniques which created warm and deep red colours and which could only be duplicated after thorough investigations and a lot of trial and error work during the first half of the 20th century.

Iron is the most important natural colorant in clays. Together with some other components like CaO, MgO and TiO_2 it gives specific colours which are - among other things - dependent on the processing of the raw materials and the firing conditions. The colouring properties of iron compounds were already known and utilized before one could speak of a ceramic use or tradition. Some well known earth colours such as yellow and red ochre, sienna and umber exist in mixtures of iron hydroxide (Goethite), clays and quartz. The iron compounds in sediments are developed by weathering of iron-containing minerals. During the formation of clay materials, the iron is partially built in. The main part however is separated as iron (III) hydroxide which is rather insoluble at an acidity of 6 or 7. In a publication of Fischer[8] he indicates the following compositions of some well known earth colours:

Name	**Fe_2O_3**	**MnO_2**	**Al_2O_3**	**SiO_2**	**Moisture content**	**colour**
Yellow ochre	17 – 60	-	10 – 40	35 – 50	10 – 12	yellow / brown
Red ochre	20 – 40	-	10 – 15	35 – 50	5 – 10	red
Sienna	25 – 75	little	10 – 20	10 – 35	15 – 20	yellow / brown
Umber	37 – 60	11 – 23	3 – 13	16 – 35	10 – 15	darkbrown / black

Table V: Compositions of common natural earth pigments

These types of earth colours were applied in paintings during the late-Paleolithicum. As such they are the oldest type of paints and most probably older than ceramics. The homo sapiens living in the late-Paleolithicum have left us evidence of earth colours as can be seen in the admirable

paintings in beautiful red colours like those in the caves of Lascaux, Altamira, Font de Gaume and others. The cave of Altamira e.g. has a 'room' called the 'Sistine chapel of prehistory'[9] and the paintings of bulls, horses, deer and bison stem from the Magdalénien (± 12000 BC).

Although science cannot give an exact time or place were a society started to use clay as building material or for food storing, there are some historical clues that one of the oldest and common ceramic industries existed in the Near East countries. This dated back some 7000 to 8000 years.[10] Even before this time it was already known how to make use of the plastic properties of clay. Many human and animal figures are found at several human civilizations around the world. As one example of the existence of a kind of pottery culture at a completely different place, the so-called band-ceramic culture can be mentioned. Under the leadership of prof. dr. P.J.R. Modderman excavation and a study were made from 1950 till 1966 in Elsloo, a small village in the Dutch province Limburg. In that place an ancient settlement was found. With the active carbon method the settlement could be dated as from 4400 till 4000 BC.[11] The ceramic articles which were found were rather simple, except the decoration. The decoration in the form of engraved bands around the upper part of the pots and vases is so typical that it has given the name to the inhabitants of these settlements. The decoration of the oldest pieces was rather simple; the latest vases show a very nice game of lines and points in wavy movements around the vases. These types of settlements of the so-called 'band ceramic people' are found in central Europe along the Danube countries and in western directions following more or less the river Rhine till the south-eastern part of what now is Belgium and The Netherlands.[12]

Another place with an early and famous ceramic tradition and more close to the stream area of Euphrate and Tigris is the delta of the Nile. Archeologists have found evidence suggesting that ceramic knowledge also existed here, including special glazing techniques.

Dr. A. Berendsen[13] indicates that the oldest known type of wall tiles is found in Egypt and is dated from the 4th millennium BC. In this respect the discoveries made in the complex of Medinet-Haboe near Tell-el-Jahudi in the Nile delta are of a great importance.

Steinbrecht[14] mentions a discovery of a small statue at the Nile delta in 1875 which represents a hippopotamus. The statue is made from an earthenware type of body and glazed with a green coloured glaze. According to the engraved hieroglyphics, the statue could be dated as from 4000 BC.

Copper oxide was one of the main oxides used for colouring, resulting in the old 'Egyptian blue' colours. The technique of inlaid work was already applied in early times. Famous is a deep blue coloured bracelet of Amenhotep III (abt. 1411-1375 BC). Sir Flinders Petrie has found examples of faience which could be dated from the 18th dynasty (1580-1335 BC). The different parts, as e.g. light blue coloured corn flowers and a yellow coloured background, are made separately and later assembled. Other well known specimens of an Egyptian ceramic tradition are the King-cartouches. Since the reign of Seti I (abt. 1308-1298 BC) this method of making the cartouches appears popular. The engraved parts are filled with glaze giving a beautiful array of dark blue coloured parts and lines and the light blue coloured parts appeared. The cartouche in faience technique of Ramses III, dated abt. 1180 BC is in the British museum in London[13] and is a beautiful example of this technique.

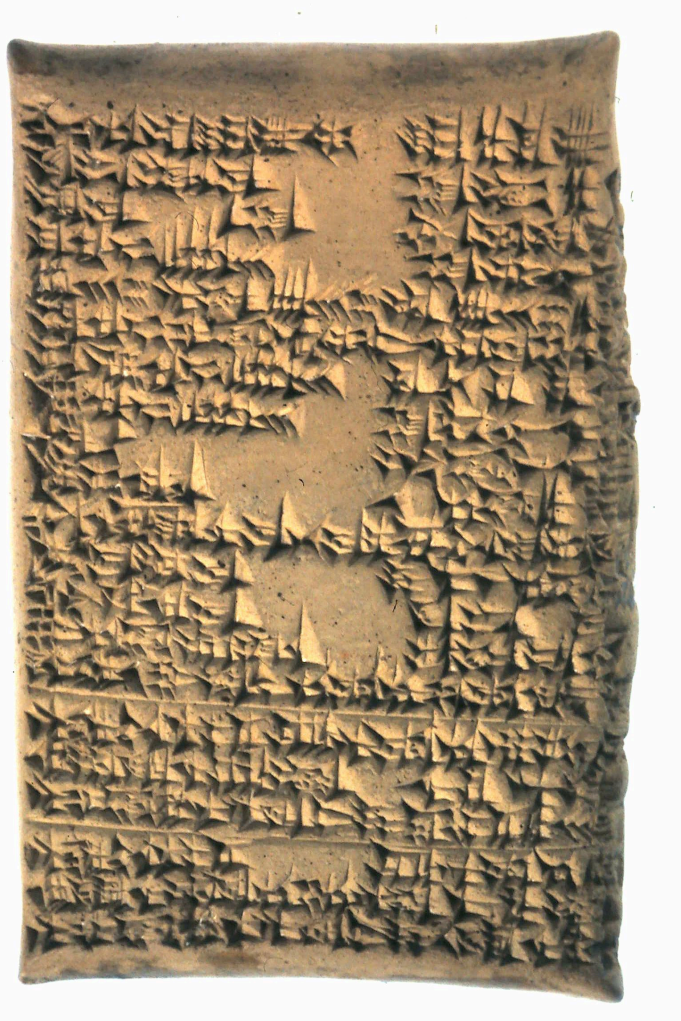
One of the explanations for the evolution of ceramic articles like pots, vessels and vases is the ongoing necessity for storing food. Besides evidence of ceramic pieces the fire places or kilns where the articles were fired were also discovered. Vertical kilns, in which the potters' ware did

not come into direct contact with the flames, are found in Mesopotamia and also in Iran.[15] These kilns could be dated $\pm$ 4000 BC. The products from that time show that one was able, by varying the thickness of one or more pigment containing layers, to obtain polychrome coloured articles. Well known examples are found in the northern part of Mesopotamia. One of the examples of this ancient art of pottery is a plate with a diameter of 12 cm. It is polychrome decorated and originated from the Tell Halaf period, found in Arpachiyah and dated from 4500 – 4000 BC. It is only one example of the multitude of data which are known today and which show clearly that from the 5th millennium BC the existence of rather high ceramic standards.

An important fact is that in the Middle East area, Assyrian power and culture reached a high degree under several rulers. One of them was King Assurbanipal (668 – 626 BC). He developed, like other Assyrian rulers, a predilection to fix and collect scientific, religious and literary texts. He also installed the famous Royal Library at Nineveh which consisted of over more than 20,000 clay tablets. These clay tablets are closely written on both sides in cuneiform. Thanks to these 'ceramic papers' and the fact that they are not completely destroyed in this ever turbulent part of the world, we know not only the famous Gilgamesh epos, but also a lot of other valuable information. Most of these clay tablets are now in the British Museum. Another clay tablet which is called the 'Glassmakers Tablet' and found in Tall'Umar (Iraq) is dated from the 17th century BC. It gives the earliest known description and formulae for making copper-lead glazes and moreover their application to earthenware articles. This famous clay tablet is also in the British Museum and is catalogued under the number BM 120960 (figure 7). The tablet measures $3\frac{1}{4} \times 2\frac{1}{16}$ in. $= 8.25 \times 5.24$ cm and is a unique writing in the history of chemistry and more in particular in the history of ceramics as it is the first known description for the preparation of a glaze. The tablet makes mention of a complete prescription for several glazes to be mixed and moreover how to apply them to biscuit fired earthenware.

Other evidence of the same kind for early ceramic cultures is found during the excavation of the Royal Library at Nineveh and dated as from the 7th century BC.

From the translation of the so-called 'Glassmakers Tablet' which are available, namely one of C. J. Gadd and R. Campbell Thomson[16] and another one of A. L. Oppenheim[17], it is possible to get a view of the then present knowledge of glass- and glaze techniques.



Photograph 2: The 'Glassmakers Tablet'. Courtesy of the British Museum

The text of the tablet is divided into five chapters. The first chapter gives the receipt for 'lead-copper' glaze; the second chapter gives a receipt for 'Akkadian-copper'. Chapter three describes the handling of the clay for the potter ware to be glazed. Chapter four mentions the glazing, while the fifth chapter gives the signature which translation reads as follows:

'Liballit-Marduk, Son of Ussur-an-Marduk, priest of Marduk, a man (native) of Babylon, Month of Tebet, 24th day, year after (which) Gulkishar (became) the king'.

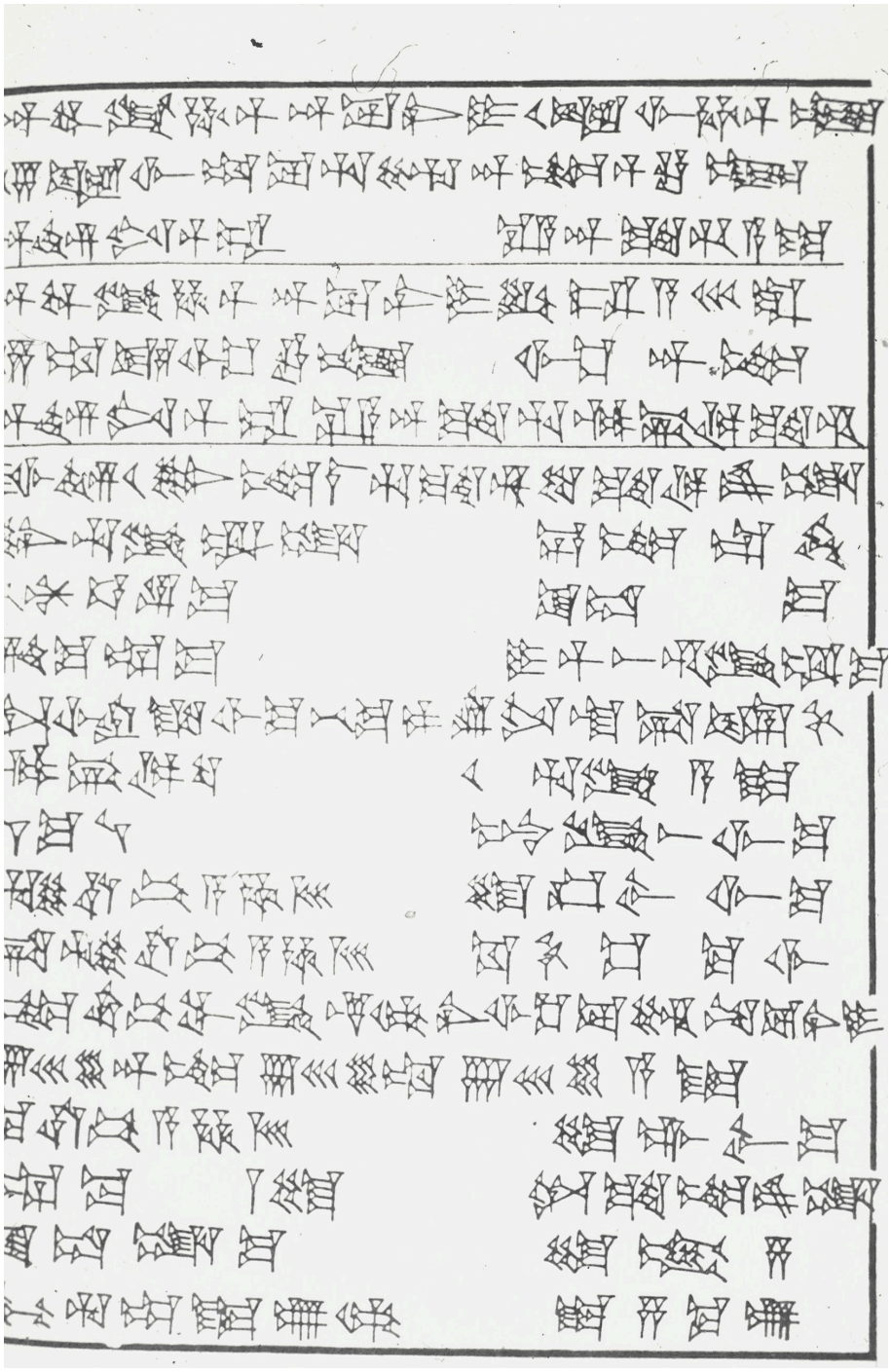


Figure 4: Chapters 1 and 2 of the Glassmakers Tablet (reproduction)

Although Assyriologists had already succeeded to unravel Assyrian cuneiform more than a hundred years ago, one can notice some differences in the mentioned translations. Where Campbell Thomson mentions salpeter, Oppenheims' translation gives anzahhu-glass. Another difference is that Campbell Thomson makes mention of lime, where Oppenheim mentions antimony. Furthermore, a striking difference is that Oppenheim states that the BM 120960 text gives 'a prescription how to produce red-stone coloured glass'. Following Oppenheim, chapter one gives the recipe for Assyrian red-stone glass and chapter two the recipe for Akkadian red-

stone glass. R. Campbell Thomson, who has done a lot of work in respect of investigation and translation of Assyrian clay tablets, speaks of green lead-copper glazes in his translation.[18]

Only the fact that the tablet BM 120960 gives the oldest known ceramic recipe makes it very remarkable, but if translations mention 'red-stone coloured glass' it is of course worthwhile to see if this is the very first recipe for a red glass or glaze ever. Therefore, some practical work has been done following the translations mentioned and further explanations as given by prof. Veenhof from the Assyriologic Institute of the State University of Leiden.

The BM 120960 glazes consist for the main part of a basic material, called zukû-glass. It is generally supposed that the level of glass and glass manufacturing was already that high that a further description of this basic glass could be omitted.

Another explanation is also given, saying that the scribe did not speak the true mind. A reason for the supposition that the zukû-glass had most probably a simple composition is found in its philological connection with 'zakû' which means 'clear'. Investigations to the compositions of early Babylonian glazes[19] has shown that for copper coloured transparent glazes a simple alkaline silicate glass was used as basic material. As main alkaline component, sodium has been determined via emission spectral analyses.

From the history of glass[20] it is also known that the first type of glass as applied in Egypt as well as in Mesopotamia had the same compositions, namely the three basic components natural soda (called nitrum by Pliny), calcium containing sand and the ash of the marsh plant salicornia. It is also generally assumed that a deliberate separation between glass and glazes for ceramic use appeared from the middle of the 16th century BC. Therefore, it can be supposed that the basic components for glass as well as for glazes were generally the same.

Hecht[21] has determined the influence of glaze components in relation with the colour development in this type of glazes. From this survey it is shown that pure alkaline silicate glazes with 3 mol SiO_2 developed the most beautiful blue colours. Besides the glaze itself, the body used is also important. This influence of the body composition with regard to this type of glazes, often called Egyptian or Persian blue, is described by M.M. French.[22] From these investigations the conclusion was drawn that quartz-rich and calcium-poor bodies were favourable for the development of the blue colour. W. Henze[23] reports also that just alkaline silicate compositions render good results. Also an alkaline-lead-silicate with 18% PbO develops a good 'well-melted Turkish blue'.

From the before mentioned examinations, it is plausible to suppose that the base glass from the Glassmakers Tablet, mentioned as zukû-glass, could have consisted of an alkaline silicate, e.g. in the mole ratio alkaline : SiO_2 = 1 : 3 and where the alkaline is singly represented by sodium. Presuming this, the glaze composition should have been read as mentioned in Table VI:

Oxide composition		**Seger formula**
Na_2O	25.62 %	1.00 Na_2O : 3.00 SiO_2
SiO_2	74.38 %	
	100.00 %	

Table VI: Calculated composition of zukû glass from the Glassmakers Tablet

	According to Campbell T.		According to Oppenheim	
Oxides	**Ch. 1 glaze (%)**	**Ch. 2 glaze (%)**	**Ch. 1 glaze (%)**	**Ch. 2 glaze (%)**
Na_2O	18.28	18.44	18.23	19.06
CaO	0.35	1.41	—	—
PbO	12.48	12.38	12.45	12.88
CuO	12.03	11.24	12.00	8.21
SiO_2	56.86	56.53	56.70	58.60
Sb_2O_3	—	—	0.62	1.25
	100.00	100.00	100.00	100.00

Table VII: Comparison of base glaze compositions from the Glassmakers Tablet

The colour of the glazes of Table VII do not show much difference in appearance and colour development when applied to several bodies. A greater difference than that between the glazes is noticed for the same glaze applied on different bodies as shown by Photograph 3. For these three articles the same glaze was used, namely the chapter one glaze according to Campbell Thomson. The most beautiful blue colour, reminiscent of the colour of Lapis Lazuli, was achieved using a body with a composition as mentioned in Table VIII:

White burning clay 1001	30 %
White burning clay nr.2	22 %
Quartz	28 %
Feldspar (Na/K)	16 %
Lime	4 %
	100 %

Table VIII: Lapis Lazuli-like blue body composition

Although series of trials were also performed in a gas-heated kiln (natural gas) under reducing conditions, it was not possible to obtain (copper) reduced glazes with a reddish colour. Only the blue colour as well known from the ancient times showed up. Based on these facts it may be supposed that the glaze as prescribed on the BM 120960 tablet may have looked like the glaze on Photograph 3. The BM 120960 Glassmakers Tablet, some 3700 years old, may therefore be considered as one of the first written ceramic recipes (although not a red glaze) and the start of publishing and collecting of ceramic data.



Photograph 3: Blue alkaline copper glaze based on the oldest known records

3 IRON

The element with many-sided possibilities.

The techniques of making warm and deep red coloured ceramics ware reached another culminating point during the Greek and Roman civilizations.

Ir. A.J. Rijken[24] correctly observed that in this respect there is a lot of confusion about the designation of the slibs used for this process. Besides the group of glazes and engobes he named the group of layers necessary to create the typical red and black glazes 'slip glazes'.

As an example of slip glazes Rijken mentioned the Terra Sigillata, the mostly red earthenware of the Romans which is covered with a very thin glossy layer.

This Terra Sigillata was first made in Arezzo, mainly from 50 BC till 70 AD. This special way of manufacturing founds its way through several Gallic districts till the regions along the river Rhine. It took a long time before one could clarify the manufacturing of this typical earthenware product. One of the difficulties was the very thin cover layer (0.015 mm). With the possibilities of more modern investigation methods one could finally approximate the manufacturing of Terra Sigillata.

Neumann published in 1932 the attempts which were undertaken so far. The glossy surface indicated that fluxing materials must be present. Analyses revealed that the glossy layer contained principally less SiO_2, more Fe_2O_3, more Al_2O_3 and more alkaline materials than the surrounding body. No boron could be found. The firing temperature was determined to be 850 °C till 1000 °C.

Progress was made by Nuissl who performed trials by slibbing up the red coloured clays and separated the coarse particles from the fine particles.

Schumann continued in this way and made trials with peptisators to accomplish a better separation of the fine clay particles. With the finest clay particles he succeeded in making a good approximation of the original Terra Sigillata. With the help of X-ray diffraction analyses it could be determined that only clays of the muscovite type, $KAl_2(OH)_2AlSi_3O_{10}$ were suitable to obtain the real effect. This type of clay minerals has K in its structure[25], a point differentiating it from kaolinite and montmorillonite.

Adam Winter[26] named these ancient surface-layers 'Glanztonfilm' with the typical remark that there is no melting flux added. The gloss should be caused by the 'parallel geschichtete Anordnung der blättchenformigen Tonminerale'.

By slibbing-up one could obtain the finest particles and applied to a suitable and well treated body it was possible to reach a good looking copy of the Terra Sigillata. An oxidizing atmosphere resulted in the beautiful bright red colours, while a reducing atmosphere resulted in dark brown to black colours.

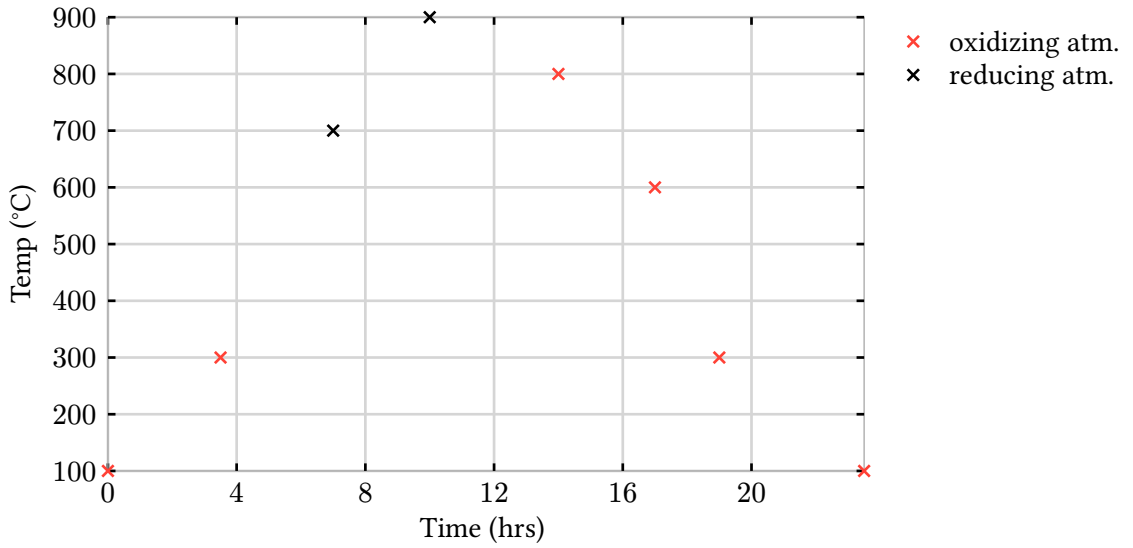


Figure 5: Typical firing curve for Terra Sigillata (oxidizing and reducing atmospheres)

This is also the explanation for the red and black colours of the Greek ceramic vases.

Durand-Gréville was the first who discovered in 1891 that the black layer remained black after heating in the absence of oxygen. When oxygen was added during the heating process, the black colour turned red.

Attempts of Charles Binns and Fraser, published in 1929 in the American Journal of Archaeology, lead to the following hypothesis: the Greek heated their ceramic ware to roughly 600 °C in an oxidizing atmosphere. After reaching this temperature they continued the firing till about 950 °C in a reducing atmosphere. After obtaining this temperature one started cooling in a reducing atmosphere till approximately 850 °C after which oxygen was admitted. The black iron oxide parts which were enclosed by the glassy material could not change anymore in the oxidizing atmosphere. The porous body itself however (the places not treated with the slib glaze) turned again into red during the oxidizing cooling from about 850 °C till room temperature. In this way one could obtain both black and red colours in one and the same firing. It is determined that the oldest Greek vases show black figures against a red background. Lateron, red figures against a black background were also made.

Interesting investigations to clarify the processes which deal with Terra Sigillata making and firing are done among other things by A. Winter[27] and F. Oberlies and N. Köppen[28].

This technique with the slib glazes reached an absolute culminating point during the Greek period roughly from 550 BC till 400 BC and the Roman manufacturing of Terra Sigillata. After the 3rd century this application disappeared completely as far as the civilizations under Roman influence were concerned. In other early civilizations like those of the Indus-dale it was and still is quite common to make use of coloured, engobe-like layers, besides the use of the very same copper blue glazes of Sindh in northern India and the ceramic ware as found in Mohendscho-Daro and Harappa (abt. 3000 BC) are evidence for the existence of an important and also well-developed and regularly ceramic production.[29]

Besides these still beautiful red colour of the Terra Sigillata from the past there are also today iron red colours used in ceramics. One of them is as onglaze decoration colour also called Venetian

Red. This is a red onglaze colour for application at about 780 °C – 800 °C in a cycle of 5 to 6 hours also known as the classical porcelain onglaze firing. The Venetian Red is in most cases built up with one or more suitable fluxes and an iron compound which in most cases is an iron oxide.

The fluxes are composed in such a way that they develop the colour as good as possible and also have good properties with regard to gloss and acid resistance. Of course, one may call this colour red but compared to the CdSe red colours it has a clearly brown component. The famous Japanese Imari colours (see Photograph 5) are an example and a representative of this type of iron red onglaze colours.



Photograph 4: Greek vase in Terra Sigillata technique, showing red and black colours from a single firing

For a leaded onglaze iron-red colour one can use fluxes with compositions like:

(i)	Na_2O	0.074	B_2O_3	0.197	SiO_2	1.480
	PbO	0.781			ZrO_2	0.050
	CdO	0.072			TiO_2	0.076
	NaF	0.073				

In combination with a flux like:

(ii)	Na_2O	0.535	Al_2O_3	0.150	SiO_2	2.533
	K_2O	0.055	B_2O_3	0.548	ZrO_2	0.040
	CaF_2	0.060			TiO_2	0.077
	PbO	0.212				
	ZnO	0.082				
	CdO	0.056				

These fluxes can be used together in a formulation to obtain the best possible firing range. Combination e.g. can be between 50 and 70 for flux (i) and between 40 and 20 parts for flux (ii).

Together with a specific type of iron oxide in a weight percentage of 10% one obtains a good iron-red colour.

These iron-red colours are also available in an unleaded composition. In those cases one can use a flux composition like:

Li_2O	0.325	Al_2O_3	0.155	SiO_2	2.555
Na_2O	0.460	B_2O_3	0.985	ZrO_2	0.015
K_2O	0.095			TiO_2	0.010
BaO	0.035				
ZnO	0.085				

Together with e.g. 10 to 12 parts of a suitable iron oxide one obtains a reddish/brown colour which is in fact far away from the real CdSe red colours. Unleaded iron red colours are even more brownish compared to the leaded versions.

This type of iron red decoration colours are commercially available and cost-wise more attractive compared to gold-containing or CdSe based red colours.

Also on roof tiles one still applies iron-red coloured glazes today, often called ‘wine red’ glazes. The various roof tile companies in The Netherlands and Germany still manufacture these iron-red colours which all have a more maroon-like appearance instead of a clear red colour.

For a leaded composition one can use a lead-aluminium-silicate like e.g.

PbO	1.000	Al_2O_3	0.244	SiO_2	2.052

or in combination with the following frit:

PbO	1.000	Al_2O_3	0.300	SiO_2	2.200
		B_2O_3	0.600		

and e.g. 6 to 8 parts of a suitable red iron oxide type together with some quartz, a clay with good setting-up properties and some bentone EW.

As leaded glazes, also for roof tiles, become less and less popular due to various health and environmental regulations, the tendency to apply unleaded glazes is also increasing here.

For an unleaded type of iron-red glaze one can use an unleaded frit composition like: (see also Yulia Shteinberg 'Strontium Glazes')

Na_2O	0.370	Al_2O_3	0.244	SiO_2	3.300
K_2O	0.110	B_2O_3	0.390		
MgO	0.135				
BaO	0.115				
SrO	0.270				

and e.g. 12 to 16 parts of a suitable red iron oxide together with some quartz and a clay with good setting-up properties. These types of unleaded wine-red glazes will always have more covering power and somewhat less brilliance compared to the leaded compositions.

Another application for iron red glazes is e.g. as floor tile glazes which were used especially during the 70ties and 80ties of last century. The trend in those days was very much for leather-like glazes in all kinds of colour variations, applied in various layers. In most cases these floor tile glazes were applied by (double) disc and fired in roller kilns (e.g. Sacmi) in a cycle of 1150 °C - 50 minutes total firing time.

A good iron red composition in this respect is e.g.:

frit 37080 (Ferro)	30 parts
frit 37025 (Ferro)	20
frit 35310 (Ferro)	10
quartz	6
zircon silicate	17
titanium oxide	10
zinc oxide	3
iron oxide red	4

This glaze has a clearly iron-red appearance[30]. It can be turned into a matt glaze by adding a combination of 5 parts of wollastonite and 5 parts of barium carbonate. Exact quantities depend on the required colour and mattnes of the glaze.

Red coloured glazes were also used for a very long time in Japan for their small mosaic tiles. The use of these tiles was popular in the whole Far East region. One of the reasons was that Japanese technicians (for kilns, glazes, etc.) brought this technique over to countries such as Malaysia, Indonesia and Thailand. The colour is not as brilliant as the colours obtained with CdSe glazes and also not with the colours of CrSn based stains. However, the cost price was significantly lower which was an important factor in choosing Fe based glazes.

For floor- and wall tiles a glaze like

frit 34670 Ferro	85 parts
bayferrox 130M	10
sodium feldspar	7
kaolin	8

was used for firing in a Riedhammer tunnelkiln at 1060 °C – 1070 °C for 24 hours.

As a general rule here one can state that a longer firing cycle results in a more clear and brilliant red colour. This is especially the case for the small mosaic tiles which were fired at e.g. 1280 °C for 28 hours. As the manufacturers tried to decrease the firing temperatures for economical reasons to e.g. 1190 °C, it was not possible to obtain the very same clear bright Fe red colour. Important parameters in this respect are the presence of barium and magnesium in the glaze and the type of iron oxide which must be very fine[31].

Nowadays, these types of glazes are not as popular anymore. Especially, the tile manufacturers and more specifically the workers on the glazing lines do not regret this. Anyone who has worked with iron-red glazes in production knows that it is a ‘dirty’ part of ceramic production, although even the famous American writer John Updike has said: ‘Ceramic, muddy Queen of Human Arts’ in his poem ‘Dance of the Solids’[32].



Photograph 5: Imari porcelain plate with iron red onglaze decoration, flower decoration, Qianlong period (1736–1795)

4 COPPER

A wonderful red through ceramic conversion.

As mentioned before, a completely different group of red coloured glazes are the reduction glazes. This type of glazes is achieved using copper as the main colorant while the glaze composition, and even of more importance, the specific firing conditions, are decisive for the final colour tone.

These glazes are mainly indicated with the name 'oxblood' glazes, 'sang-de-boeuf' glazes, 'copper reduction reds' and also 'Chinese reds'. It is generally assumed that the origin of these types of glazes must be searched for in certain parts of China and more in particular the north-eastern part of China, viz. the province of Honan where the Imperial Honan potters during the Sung dynasty made already beautiful copper-red glazed ceramic vessels.

The available literature[33] is very positive that copper reds were not made occasionally at that time, but that it was the result of a deliberated effect and control of the kiln atmosphere.

'Copper reds' is the collective noun for all glazes where colloidal copper is responsible for the red colouring of the glaze. In these groups, however, one can distinguish different types which clearly vary from each other. The main types are the 'sang-de-boeuf' glaze or 'lang yao', the 'flambé glaze', the 'onglaze red glaze' and the so-called 'peach-bloom' glaze.

In respect of the development of Chinese ceramics one often holds over the following scheme:

Hsia dynasty (⊠) ± 2000 BC. Many specimens are found from this early period also known as 'the painted pottery culture'. Black and red coloured earthenware.

Shang dynasty (⊠) 1766 BC – 1122 BC. Mainly low fired earthenware but also grayish type of hard pottery with engraved decorations derived from cast bronze.

Chou dynasty (⊠) 1122 BC – 225 BC. Grayish-brownish ceramics with sometimes a rather rough surface.

Ch'in dynasty (⊠) 225 BC – 206 BC. The so-called small dynasties. A decline from scientific point of view also regarding the ceramic development.

Han dynasty (⊠) 206 BC – 220 AD. First important period for the ceramic development. Red coloured earthenware with brownish-green lead glaze. A turning point was reached as appears from excavated vitrified stoneware vessels and glazed with what is called the forerunner of the later celadon glazes.

The "6 small dynasties" 220 – 618. Development of celadon like the Yüeh ware. Influences of the near east countries can be noticed. During this period the precursor of the porcelain showed up thanks to the addition of kaolin to the body material.

T'ang dynasty (⊠) 618 – 906. Techniques with white glazes and engobes were added to the already existing ceramic knowledge. Some specimens are found of white porcellanous ware.

The 5 dynasties 906 – 960. During this period the potters of Yüeh reached their highest level regarding their grayish-green celadon glazes.

Sung dynasty (□) 960 – 1279. A culminating point for the Chinese ceramic development. During this period the white burning porcelain body came to development. Very admirable copper red glazes are made in this period.

Yüan dynasty / Mongol period (□) 1279 – 1368. Continuation of the Sung development. Development of the application of cobalt blue under glaze decoration technique. These were indications for a technique which was fully exploited during the Ming period.

Ming dynasty (□) 1368 – 1644. A 2nd flourishing time for the Chinese ceramics. This period is well known in the western European countries. The trading activities of the Portuguese and later on the Dutch resulted that these porcelain products became very popular. It is known that ships, fully loaded with this porcelain products[34], provided the western countries with the most beautiful porcelain. Shaping of jars, vessels, etc. reached a peak of excellence. Well known examples of this period are e.g. white porcelain painted in under glaze blue and the development of polychrome overglaze decorations.

Ch'ing dynasty (□) 1644 – 1912. A period of refinement. During the reign of K'ang Hsi (1662 – 1722) the several polychrome paintings known as famille rose, famille verte and famille noire originated. Copper red sang-de-boeuf glazes were made of a particularly deep and homogenous colour tone. Also so-called peach-bloom copper reds are dated from this period.

One must bear in mind that the Chinese, together with the inhabitants of two other river delta (from the Indus in India and from the delta's in the Near East) are said to be the carriers of the oldest human cultures. As far as the Chinese culture is concerned the literature[35] makes mention of a start, most probably at the delta area of the river Hwang Ho, the Yellow River. The then inhabitants start moving inland, occupying the fertile stream area of the Hwang Ho, moved further mainly in western and southern directions and started settlements with an agricultural character. It did not take a long time before these settlements started producing ceramic objects. In this respect, but without having the intention to be complete, it is worthwhile to mention the following towns which all developed a strong tradition of ceramic production: Ting-chou, Tz'ŭ-chou and Chi-hsien in the province Hopei; Chang-an, Loyang and Lin-ju in Honan; Kaifeng in the province Kiangsu; Chin-tê-chên in the province Kiangsi; Lung-ch'üan and Yüeh-chou in the province Chekiang and others.

Several Chinese cultures were of great importance in respect of ceramic developments. The rulers at those specific periods seemed to have contributed a lot to these developments. In many cases the upper class instructed the ceramic artists to make the most beautiful types of vases, vessels and all kind of tableware. Illustrative for this is the story of T'ung, the God of the potters. The story is said to be derived from an old Chinese legend. During the reign of Wan-Li (1573-1619) a potter threw himself into his kiln for reasons that he could not fulfill an Imperial order for a particular glaze effect. Following the legend, these self-sacrifices resulted through that miraculous way that the required effect was obtained.

From the early times there were two main important oxides used for colouring by the Chinese potters. These two oxides were the iron- and copper oxides. Later on, other oxides became more important like cobalt oxide (first imported from Persia) during the Ming dynasty.

Although the ultimate intention of the iron and the copper oxide was and is a complete different one, they had the resemblance that reducing firing conditions were of great importance both for celadons and for copper red glazes.

It is ascertained that the iron oxide is responsible as the colour causing component in the several types of celadon glazes. The name celadon is said to be derived from Saladin, a sultan of Egypt who sent a number of pieces of this particular ceramic ware to Nur-ed-din, the sultan of Damascus in 1171. Another story for the derivation is from the shepherd Celadon, a character in a romance called l'Astrée and written by Honoré d'Urfé in the 17th century. The shepherd Celadon was wearing a coat in distinctive grayish-greenish colours.

Studies[36] have demonstrated that the soft and warm appearance of the early celadons is caused by the fact that a relatively large number of air bubbles and non-dissolved glaze particles exist in the glaze. These are reasons for the scattering and reflection of light sources. Later dated celadons, e.g. from the Ming dynasty, differ from the earlier ones in that they usually have a more clear appearance. The so-called 'kinuta' celadons (Japanese name) are celadons with a blue colour tone. The presence of P_2O_5 in these ferrous glazes is said to be responsible for these blue colour tones. In this respect one also makes a comparison with the mineral vivianite: $Fe_3(PO_4)_2 \cdot 8H_2O$. Another famous type is the spotted celadon, also called buckwheat celadons. For these types of glazes it seems to be a precondition that both Fe and Cu are present in the glaze.

During these processes the firing conditions were of a great importance in respect of the required glazes. Reducing conditions were absolutely necessary for the creation of these glazes. The way in which the Chinese potters were able to achieve those conditions could easily be reconstructed as these particular kilns still exist today. The kilns were usually built on a hillside where the slope of the ground furnished the necessary draught. Wood was mainly used as fuel. The wood smoke, which consisted of finely divided particles of carbon, was conducted into the kiln together with a limited quantity of air. In this way, a strong reducing atmosphere was created which was necessary to reduce the copper oxide to the finely divided metallic copper in a colloidal state. In a later stage, more in particular during the Ch'ing dynasty, a more sophisticated method was employed to obtain a reducing atmosphere. The well skilled potters developed a special type of saggers. The inner sagger in which the ware was placed was perforated. This in contrast with the outer sagger which was completely closed. The space between the saggers was filled up with charcoal. This method enabled them to exercise a better control in respect of the firing under reducing conditions. A.L. Hetherington[37] indicates that only one-half percent of copper must be present for the development of the best copper reds. Under well-controlled conditions and carried out by well-experienced potters, these reds were created. These Chinese reds, known as the famous 'lang yao', thank their colour to cupric oxide which has been reduced to copper. This metal is then present in a very finely divided and colloidal state. Good representatives of this type of copper reduced glazes have a uniform deep red coloured glaze all over the vase or vessel.

Another type of copper reduced glazes is the so-called flambés. Many examples are dated from the 18th century. A general impression of these flambés is the always fascinating game of vertical

lines composed on one hand by the dark copper red and on the other hand by a bluish coloured opalescense glaze.

The red copper glaze as an onglaze effect is from a different nature. In this case the red colour is not resulting from copper in the transparent glaze. The effect is mostly realized by the vaporization of copper salts like copper chloride. During the firing in a reducing atmosphere these copper vapours condense on the surface of e.g. a white glazed vase or vessel. It is rather difficult to obtain a homogenous and thin layer of condensed copper on the surface of the ceramic substrates. This technique is said not to be a Chinese one from origin.

A famous and one of the most beautiful and also rare groups of copper red glazes are the so-called peach-bloom glazes. As a characteristic of those glazes one can mention a soft pink coloured glaze with, in many cases, a lot of deeper red coloured spots. Sometimes a certain opalescense is quite common, while also green spots often appear. These green spots are explained as being caused by the oxidation of spots of metallic copper formed by the flocculation of the colloidal metallic copper particles. Ceramic vases showing the peach-bloom effects are remarkable for their rarity. This rarity is mostly explained by the fact that even well-skilled Chinese potters could not always find the way that all fits in.

It can be stated that some natural circumstances were a cause that the Chinese community was rather closed. The old silk route however provided that an exchange of various merchandise could take place between the products from the Far East countries and the Western Asiatic and Eastern European countries. Several towns thanked their growth and prosperity to the fact that they were a stop on the silk route. In such bargain-towns like Samarkand and Boechara in Oezbekistan, the Arabic influence can still be seen today in several buildings. Evidences for a trade vice versa along this silk route are also found during the excavation of Samarra on the Tigris in Mesopotamia. During the excavations in 1914 important fragments of Chinese porcelain was found in the ruins.

However, of greater importance in respect of the spreading of Chinese ceramics were the traders' activities of the Portuguese, soon followed by the Dutch. Especially the Dutch, after the establishment of the VOC (Vereenigde Oostindische Compagnie), had a great part in shipping an important amount of Chinese porcelain to the West European countries. These trading activities made the various manifestations of Chinese porcelain well known and also very popular in the Western world. The Portuguese Jesuit priest Père d'Entrecolles lived at Ching-tê Chên during the reign of the emperor K'ang Hsi of the Ch'ing dynasty. He wrote several letters in 1712 and 1722 describing the potting techniques at that time[38].



Photograph 6: Copper reduced peach-bloom glaze

'This vase of apparently simple shape swells slowly as it rises from its foot. At the shoulder it contracts sharply, and at the neck there are three sharp-edged collars punctuating a point of union and breaking the glassy smoothness of the body of the vessel; the mouth spreads slightly. Beneath the glassy surface, one can detect subtle modulations from dull pink to red to grayish green — the whole offering a seemingly infinite variety of nuances. In Chinese, the color is sometimes called kidney-bean red, and the shape is that of a "three-string vase" (after the rings on the neck). The vase was made as one of a set of eight different vessels, all intended for the scholar's table. There were flower vases of different shapes, together with vessels used for washing brushes and holding red seal-paste. The glaze is now thought to be the result of sandwiching a layer of copper pigment between two layers of clear glaze — the end-product of a period of experimentation with copper red glazes that began in the late 17th century. The shape of the vase is an intellectualized and refined version of Sung Dynasty wares. Evidently there

was court patronage; this vase may once have been owned by the first Prince I (1686-1730), thirteenth son of the K'ang-hsi emperor and ancestor of its 19th-century owner'.

It took till 1709 before Tschirnhaus / Böttger succeeded in making that kind of porcelain that could compete with the Chinese porcelain[39]. From that time the developments in the western countries, mainly in Germany and France, went rather fast. The realization of the Chinese copper reds however requires a great experience and are to a great extent dependent on kiln conditions. Moreover, they are rather sensitive for temperature deviations and influences on the kiln atmosphere. For these reasons this type of glazes never reached a high production level. The realization, or maybe better the creation was and still is a specific challenge for the artist.

It is said that Ebelmen and Salvetat[40] were the first Europeans who were able to reproduce these type of glazes. Their examinations were published in 1851.

Other important investigations were undertaken in the 1880ies at Sèvres. Analyses were made of copper reds and published by G. Vogt[41]. According to these investigations, a typical analysis for a (fired) copper red glaze should read as follows:

Na_2O	2.71 %
K_2O	4.79 %
CaO	9.00 %
MgO	1.65 %
PbO	3.90 %
CuO	0.54 %
Fe_2O_3	0.91 %
Al_2O_3	6.57 %
SiO_2	70.18 %
	100.25 %

Glazes according to this composition were fired at 1280 °C under reducing conditions. In this way a fairly good approach of the original Chinese reds was realized.

At the end of the 19th century and the beginning of the 20th century many publications appeared dealing with Chinese copper red glazes. There was even a tendency to produce porcelain more according to the analyses made from ancient ceramics. It is however understandable that in many cases they did not reach the richness and the originality of the old Chinese copper red glazes. Reasons for this are e.g. the methods of analyzing. Now, roughly a hundred years later, it may be stated that analyses made in that time did not had the certitude as they have nowadays. With the actual possibilities with regard to silicate analyses the final results can be more trusted.

Another reason is that one made use of the Western raw materials which are available in almost pure form. In many cases minerals were used where the Chinese potters used rocks (petuntse). Just the impurities as present in the latter play also an important role for the final appearance of the glaze. It is published many times that the way of firing can even be of more importance than the composition as such. At the same time this is one of the most difficult obstacles to tackle.

Important contributions in respect of the development, the realization and the chemistry behind the copper red glazes are published by e.g. Herman A. Seger[42], C. M. Harder[43], E. Breitenfeldt[44], J. W. Mellor[45], Brown and Norton[46] and C. W. Parmelee[47].

All these investigations have contributed to a better knowledge and understanding of Chinese reds made through reduction of copper oxide. This offers the present artists a lead in their experiments but it is hardly imaginable that they will reach a higher level than the Chinese potters of the Sung dynasty. An example of copper red glaze can be seen on Photograph 7:



Photograph 7: Chinese copper red water pot, Guangxu period (1875–1908), Ch'ing dynasty. Created through copper reduction.

5 GOLD

The noble red.

Gold is often called the oldest known metal which was and still is used to express a particular richness and also as a standard of value. Specimens are found which could be dated from ancient human civilizations. The occurrence of the metal in pure form and the easy way of manufacture made it possible that it became one of the oldest known and applied metals.

In the 2nd millennium BC gold started to compete with copper and silver as a standard of value. The first coins from gold and gold-alloys are known from the seventh century BC but remain rare. This scarceness applied specifically to the European countries (Roman Imperium) as there were no gold mines in the European area. The oldest known golden Roman coin, called Aureus, was first made around 217 BC and bears the portrait of the God Janus. This belated use was in contrast with the more eastern area where the use of gold had already a longer existing tradition as metal as such but also in glass.

Gold is another possibility to create red colours when brought into molten glasses. Its application in conjunction with glass is old just as well. The specific application of gold for the preparation of ruby-red glass has also a long existing history. Clay tablets from the time of Assurbanipal (668 – 626 BC) give already descriptions for the use of gold for the preparation of gold-ruby glass[48]. The transliterations of R. Campbell Thomson have in that respect very much contributed to give a better picture of the existing developments at that time.

A famous example of gold-ruby glass and at the same time evidence of the high level of the art of glass manufacturing during the Roman civilization, is the so-called Lycurgus bowl. It is dated as from AD 300 and shows the legendary king Lycurgus from Thracia who is completely and fatally entangled by vine-tendrils. A general explanation for this representation is that Dionysus had turned the nymph Ambrosia into a vine-tendril after she was assaulted by Lycurgus. It is peculiar that the colour of the bowl is changing from olive-green to deep ruby-red, dependent of the amount of light which is fallen onto it (Photograph 8). Analyses of a shiver showed that the glass contains gold in a quantity of 3 till 5 ‰. This game of colours, changing with the amount of light, did presume that it was a magic bowl which could change water into wine. Now, almost 2000 years later, the Lycurgus bowl is the subject of studies about nanotechnology.

After a peak in glass manufacturing high standards were reached e.g. in Egypt, Mesopotamia and in Syria (from where the invention of the glass-workers blow-pipe is originated, 1st century BC), there followed a period of decline of roughly 1000 years. Glass manufacturing experienced a certain revival starting roughly in the 10th century. The powerful position of the church, particularly some monasteries, has without doubt contributed with regard to these developments.



Photograph 8: The Lycurgus bowl (c. AD 300), an example of dichroic gold-ruby glass

The monasteries, especially some Benedictine ones, could be seen as the defenders of the antique heritage and the guards of the transmitted literature, including those about glass manufacturing. In this respect the books in question from the bishop of Sevilla (7th century) and the bishop of Mainz (Hrabanus Maurus 'De universo', abt. 845) are dated back to Pliny, one of the main 'technical-encyclopaedists' of the ancient world.

The 'Codex Luccencis' (abt. 800) was based on Byzantine experiences. Another well known compilation of recipes from the 10th century was mainly based on this codex and is known as 'Mappae Clavicula'.

The recipe-collections of Heraclius, based on these two books, consist of three books. The first two books are dated as from the 10th century while the third book is dated from the 12th–13th century.

One of the more important books in many respects is the book of the Presbyterian priest Theophilus and is called: 'Schedula diversarum artium' and is dated from the 10th century. In this book the priest describes the than existing methods for all kinds of crafts, including e.g. how to produce leaded windows.

With the start of the Renaissance there appeared several compilations describing again the gold ruby colours of which the 'Secreti per colori' stems from the beginning of the 15th century. It mentions the following recipe:

> *'Take 3 parts of the white material (is lead-crystal glass), 1 part of Goldchalk, 1 part of Brasilash and 3 parts of fine rock salt. These ingredients must be mixed properly in the described ratio and put into a kiln. After four or six hours one must take it out and one shall have red coloured glass'.*

The Goldchalk was prepared through a solution of gold in aqua regia.

Another important book was published in 1612 and was written by the Florentine priest Antonio Neri and called 'L'arte vetraria'. The book of Neri gives more or less a status about the situation

of the art of glass manufacturing in the Renaissance. Neri mentions also raw materials such like lime and also lead containing materials. As commonly accepted, he was ahead of his time as with these recipes he already indicated the invention later on of the Bohemian lime-glass and the English lead-glass. His compilation was translated into the English language by the doctor Christopher Merret in 1662. In 1674 Ravenscroft required his patent for the lead crystal glass. The publication of Neri covered most of the experiences and recipes known at that moment. His book was published in several Italian editions, an English-one in 1662, two Latin-ones in 1668 and 1686 resp., while Kunckel made a German translation in 1679.

An important development in respect of gold-based ruby red colours was made through the Purple of Cassius. Andreas Cassius graduated in 1632 in London and lived later on as a doctor in Hamburg. His son was the first who published the discoveries of his father ('De Auro', Hamburg, 1685).

According to this publication the preparation was the following:

> *'English tin, the purer the better, must be solved in aqua regia until a yellowish or red wine-like solution appears. This solution must be kept for some days in order to give the gases the possibility to escape. Next to this one must prepare a solution of gold in aqua regia "in the normal way". After this one must take a large glassy container with a wide opening and put water into it. One must add somewhat of the tin solution, directly followed by an addition of a same quantity of the gold solution. One shall than remark a gold precipitation which will, under influence of the air, turn into a beautiful purple coloured powder'.*

This invention is still the basis for the gold-ruby decoration colours. The variation in this type of colour is from soft clear rose till dark plum pink but all have in common that they are based on gold colours made through the Purple of Cassius concept. More details regarding these onglaze and inglaze decoration colours follow later.

From great influence on the further development were the investigations of J. Kunckel. Kunckel, a German chemist, was not a compiler but he investigated the existing theories of his time. He worked as a chemist and as a pharmacist for the German elector Johann Georg II. Friedrich Wilhelm von Brandenburg leased him the 'Christallinen-Glashütte zu Drewitz', a glass factory in Berlin. At this factory he investigated the recipes as given by Neri. Among these recipes are those for the preparation of gold-ruby red glass. Neither Kunckel, Neri nor Ravenscroft were inventor of this red ruby glass. However, the publications of Kunckel were very important in respect of sieving the then existing information. His work at the Berlin glass manufacturing became of great importance for the further development of ruby red glass, above all that he distinguished the property of the final colour development after reheating of the, in first instance, colourless glass.

During the 18th century however the ruby red glass and the making of it became less popular. The demand disappeared and with that the knowledge and the experience how to produce it. In 1834 it was necessary to hold a contest 'how to prepare ruby red glass in the most economical way'. This was done by "Der Verein Zur Förderung des Gewerbefleisses in Preussen". From the result of this contest it became clear that it was not an absolute precondition to start from Purple of Cassius, but that metallic gold or any gold solution could do the job.

From the above it may be clear that gold was and still is used to prepare gold ruby red glass. For red glazes gold is not a way for manufacturing but besides the typical nice and bright ruby red gold colour in (crystal) glass there is also a gold application for red colours in ceramics. The application meant here in particular is the one of decoration colours e.g. for porcelain. For a traditional onglaze decoration firing for porcelain one applied since long time abt. 780 °C to 820 °C in a cycle of several hours (traditional cycle). After the invention of the Purple of Cassius, one succeeded in making onglaze decoration colours based on gold, creating the typical red colours. This happened especially after the invention of how to make porcelain (Böttger). By varying the amount of the Purple of Cassius and the addition of other components one succeeded in making a range of gold colours ranging from light rose till dark plum red. Until today, some well known manufacturers of decoration colours like Johnson Matthey, Ferro and also manufacturers of Japan, Taiwan and China are offering these gold colours which are applied in the manufacturing of decals or by direct application. The manufacturing principle is still the same although the processing differs between the manufacturers.

Gold colours are manufactured in light pinks (rose shades), mid-colours (fuchsia shades) till dark red (plum) colours. The light colours have a gold-base part of roughly 2 till 4 parts, the mid-colours between 7 till 10 parts and the dark red colours even up to 20 parts. A gold base exists normally of a gold component (e.g. gold chloride), stannous chloride, stannic chloride, potassium aluminium compound and an ammonium compound. Besides the gold base the compositions of the final colours exists also of suitable fluxes, in most cases two to achieve a good and wide firing range and to obtain the necessary chemical resistance.

Kenneth Shaw[49] mentions the following flux composition for use with gold colours:

Na_2O	10.29 %
K_2O	3.64 %
PbO	20.54 %
B_2O_3	23.28 %
SiO_2	42.25 %
	100.00 %

Other suitable fluxes can be compositions like:

Na_2O	14.02 %	and/or	Li_2O	1.35 %
PbO	33.47 %		Na_2O	3.92 %
Al_2O_3	5.01 %		K_2O	2.98 %
B_2O_3	5.28 %		PbO	29.69 %
SiO_2	42.22 %		CdO	3.01 %
			Al_2O_3	2.76 %
			B_2O_3	7.80 %
			SiO_2	47.51 %
			ZrO_2	0.98 %
	100.00 %			100.00 %

One way for the production of these gold pink colours is that the powders of gold base and fluxes are sintered followed by milling to the application fineness. Fineness of these type of colours is e.g. (PSD curve) $D_{10} = 0.4\mu$; $D_{50} = 2.8\mu$ and $D_{90} = 10.9\mu$. Application of the colours is done manually (painting) or by method of screen print transfer. The numerous examples of red, lilac and dark red floral decors (mainly roses) started already in the early times of European porcelain production and continued till these times. UK had always a strong reputation for these types of floral designs as well as the famous German porcelain factories. The transfers with these gold pinks have always been very popular in the UK but also in East European countries like Russia and Ukraine where huge amounts of porcelain are used by tradition. Examples of some gold pinks are shown in Photograph 9 and Photograph 10.

From the above it may be clear that only gold onglaze decoration colours are developing the nice pink red colours but that no glazes can be made in a similar way.

Without doubt one can state that during the last 10 – 15 years the (gold) decoration decreased dramatically in the European countries. The closing down of many porcelain factories in (Western) European countries and outsourcing production to Asian and other countries have a dramatic effect on screen-print transfer manufacturers particularly in Western Europe as well as decoration departments of porcelain factories. Now, it is very rare to see the rich and exuberant floral designs on porcelain which were a tradition in many households only some decades back.



Photograph 9: Gold-based onglaze decoration via screen print transfer. "Lavender Rose" pattern by Royal Albert.



Photograph 10: Gold-based onglaze decoration applied manually. Plate by the Herend Porcelain Manufactory, Hungary.

6 CHROMIUM TIN STAINS

Red shades through calcination.

A completely different way to obtain reddish colours in ceramics is making use of calcined stains e.g. of the chromium tin calcium based type. Besides this rather big family of stains there are also other possibilities to obtain lighter, more rose colour tones like MnAl stains and CrAl stains. Lilac colour stains are normally based on Sn and Cr with a small amount of cobalt to turn the lilac more into the bluish shade. The bigger family of CrSnCa stains has different members but most of them have a maroon, crimson, wine-red or cherry-red like appearance with light and darker members and with reddish or more blue-reddish family members. The final colour depends e.g. on the amount of chromium in the composition, which other components are present, on the processing of the stain but also on the composition of the glaze in which the stain is applied.

Making colourstains by a calcination process (a solid state reaction) is a standard process in ceramics and described in many ceramic books, publications and patents. Through this process it is possible to obtain more temperature stable products also for the highest firing temperatures as applied in ceramics. An important contribution for the development of colours in general and in particular for the family of CrSn pinks was made by Alexandre Brongniart who was leading the still famous Sèvres porcelain factory near Paris. Many new colours were developed under his leadership (1800 – 1847). Something similar happened in England where new developments were made by Josiah Wedgwood in the 2nd half of the 18th century and by his successors. In Germany, they had a famous development centre for porcelain and for colours in Meissen as from the mid 18th century. It is still amazing to see how these people were able to make the most beautiful colours under the conditions and with the limited possibilities of that time. Now, with all our know-how, quality control programmes and extensive possibilities for making analyses it is in many cases not possible to compete with the masters of ceramic painters and paint manufacturers of that time. For a couple of hundred years, these countries, Germany, France and England have been very important for the various colour developments in ceramics later on followed by e.g. USA with the development of ZrSi based colour stains. Nowadays, there is another threat for the handful of ceramic colour manufacturers left in the Western European world as economical reasons seems to dictate that production of stains is cheaper to do in countries as China. The high demand for ceramic stains in China's home market itself is a main reason that production volumes are increasing year by year and the Chinese made stains are therefore also becoming more and more an important factor as export product, especially for the high volume stains. Prices of the Chinese made stains are in general under the price level of European made stains.

For calcination of a given stain one makes a choice for the most suitable raw materials. Purity and fineness are some of the parameters which are important in this respect[(50)]. The raw materials are weight into the right proportion for that particular stain followed by mixing. This mixed raw material batch of a given colour stain is than put into refractory saggers followed by a firing process which is typical for that particular stain. After firing the colour stain is milled to the right fineness, if necessary washed, dried, sieved and packed. This is only a general way to produce a standard basic stain. As every new production firing of a new batch may cause some small deviations from standard, the final colour stain is in most cases build up by a high

percentage of the basic stain and some materials which give the possibility to correct the small deviations from batch to batch production of the basic stain. In this way, the final colour as supplied to the customers is always brought up and corrected to the standard colour values. Making colourstains is a rather specialized job and very much based on empirical know-how and the above mentioned way is only a general way for manufacturing. Many stains have their special parameters, production process, their special mineralisers to be added, etc. Much of this know-how stays within the manufacturing companies and the specialists involved. Compared to roughly some 50 years ago and given the scaling up and concentrating of volumes at only some limited locations resulting in less production types, the number of experienced people for the manufacturing of colourstains has decreased over time. One can state that the major producers of ceramic stains concentrate on high volume – high profitable products and they avoid making small volume stains which in a way is a reduction of the total available ceramic colour pallet. Compared to roughly some 50 to 60 years ago some very interesting ceramic pigments are not available anymore as economical reasons, health issues (hexa valent chromium), relocation and concentration of production sites have stopped production of those (smaller volume) stains. One of the examples meant here is e.g. the so-called Manganese-Rose colour stain.

One of the production processes was as follows[51]:

- 3 kg of manganese nitrate was dissolved in water and mixed with 0.9 kg in water dissolved ammonium phosphate
- the precipitate was dissolved in 1 ltr nitric acid and mixed with 1 kg aluminium hydroxide
- this mass was dried and calcined at 1140 °C – 1160 °C.
- after the calcination the stain was milled, washed and again calcined at 1280 °C.

The resulting rose pink stain was, after bringing to the right fineness of course, used as under glaze colour, as colourstain for glazes and as body stain. Given the very special way of preparation and health aspects of today it is no wonder that these special stains are no longer produced. MnAl colour stains are still available on the market but made according to a complete dry process.

Another example is the production of Aluminium Rose, a CrAl stain:

- 48 kg of aluminium hydroxide and 45 kg of zinc oxide was mixed.
- added to this mix was 6 kg potassium dichromate dissolved in water and well mixed together
- this mixture was than dried and calcined at 1300 °C – 1400 °C.
- after calcination the product was milled and washed and then dried.

Also this type of flamingo rose pink colour stain is not produced in this way anymore.

A very nice flamingo rose pink has been made as follows:

tin oxide	41.16 %
calcium carbonate	27.44 %
fine quartz	22.52 %
lead oxide	8.65 %
potassium dichromate	0.23 %

Mixing and calcining at 1250 °C followed by wet milling and washing, drying and sieving. The result is a nice and clear flamingo rose. Also this stain is not produced anymore for economical and health reasons.

The possibilities for the still widely used wine-red CrSn stains which are worthwhile to mention here are based on the calcination of calcium carbonate, tin oxide, quartz and (green) chromium oxide.

In former days one used to make first a calcium stannate out of calcium carbonate and tin oxide in the ratio 40 : 60. This mixture was wet-milled and calcined at 1150 °C. This calcination product was than wet-milled together with quartz, tin oxide and a chromate, dried and calcined at 1280 °C. This calcined product was wet milled to the right fineness, washed till all soluble chromate salts were removed and then dried.

An example is the following receipt:

calcium carbonate	23.34 %
tin oxide	15.56 %
quartz	38.89 %
tin oxide	19.40 %
lead chromate	2.80 %
	100.00 %

Also following cherry-red lead containing pink was produced in the past by dry mixing the raw materials, calcining, washing and drying:

calcium carbonate	25.70 %
quartz	22.48 %
tin oxide	42.60 %
potassium dichromate	0.72 %
red lead oxide	8.50 %
	100.00 %

Such formulations, having a small percentage of lead (introduced e.g. as lead chromate $PbCrO_4$, lead carbonate $PbCO_3$ or as red lead oxide) show normally a somewhat more bright and clear (wine) red colour compared to lead free compositions.

As the toxicity of lead compounds and also the lead release following DIN EN 1388 became more and more important, the ceramic industry uses now unleaded stains by preference. In this respect one has also looked for replacements of the lead addition while keeping the good properties caused by the lead addition. An example for such a development is given in US patent 4358321 published in 1982[52]. The invention describes the application of bismuth and / or phosphate compounds instead of lead compounds resulting in an intense red colour.

Compositions mentioned are:

tin oxide	40.08 %	40.66 %
calcium carbonate	31.01 %	31.47 %
silica	24.05 %	24.40 %
chromium oxide	1.25 %	1.07 %
potassium nitrate	1.77 %	—
potassium carbonate	—	1.80 %
bismuth oxide	1.84 %	—
bismuth nitrate	—	0.60 %
	100.00 %	100.00 %

Following the patent, the materials were wet-mixed and finely ground, the potassium and the bismuth compounds added, mixed and calcined at 1340 °C for 1 hour, wet-ground and washed and then dried.

Today, only the dry process is utilized by dry mixing calcium carbonate, tin oxide, quartz and chromium oxide. For a better dispersion of the chromium oxide, a pre-mix is often made of chromium oxide and quartz with an intensive mixer. The dry mixed batch is than calcined and the pigment is than dry milled to the right fineness. Special materials acting as a catalyst can be added to achieve darker colours.

Lilac colour stains are composed out of tin oxide and a chromium compound, in most cases potassium dichromate $K_2Cr_2O_7$ now replaced by chromium oxide. Materials as cerium oxide, boric acid and lithium carbonate are added following the development of that particular stain.

Some examples are:

	Dark red lilac	**Bluish lilac**
tin oxide	91.45 %	75.35 %
potassium dichromate	3.45 %	0.65 %
cerium oxide	3.75 %	—
lithium carbonate	1.35 %	—
boric acid	—	22.35 %
cobalt oxide	—	1.65 %
	100.00 %	100.00 %
calcination temperature:	1290 °C	1210 °C

After calcination the stains must be wet-milled to the right fineness, washed and dried. The cobalt oxide is added to turn the lilac colour into a more bluish colour tone (lavender).

With all these examples, however, it is possible to create beautiful wine red, crimson, maroon or cherry-red colours but no clear red colours as possible with CdSe stains or glazes. People with some experience in colour ceramics know that the composition of the glaze is also important for the proper development of CrSn colour shades. Small additions of tin oxide in the glaze formulae help to stabilize the colour. Magnesium must be out of the compositions. No reductions must take place during the glostfiring otherwise the famous white spots will appear in the coloured glaze.

A typical lead containing glaze which shows a good development for CrSn stains is based on following frit:

Na_2O	0.145	Al_2O_3	0.172	SiO_2	2.977
K_2O	0.050	B_2O_3	0.222		
CaO	0.266				
PbO	0.539				

The milling formula for the glaze is 90 parts of the frit together with 10 parts of kaolin. This glaze has a maturing firing range of 1020 °C till 1100 °C and shows normally no lead release after standard DIN EN 1388-1 / –2. Despite this, many of this type of glazes have been replaced by unleaded glazes like glazes based on strontium containing frits[53] like e.g.:

Li_2O	0.062	Al_2O_3	0.134	SiO_2	2.302
K_2O	0.039				
CaO	0.357				
BaO	0.107				
SrO	0.435				

Milling formula of the glaze is 90 parts of frit together with 10 parts of kaolin. Glazes as these are nowadays widely used as unleaded transparent glazes, also as base glaze for CrSn wine red glazes.

As mentioned, the calcination process gives some different possibilities to obtain reddish colours. However, also in this case none of them can compete or even come close to the clear and bright red colour having a dominate wavelength of about 614 nm. Photograph 11 shows an example of a CrSn coloured ceramic vase.



Photograph 11: Ceramic vase with CrSn *wine-red coloured glaze*

7 NICKEL

A purplish red.

Nickel was discovered by the Swedish chemist Axel Fredrik Cronstedt back in 1751 from niccolite (NiAs) see Figure 6. He tried to isolate copper from the mineral but to his surprise at the end he had a silver-like powder what he called nickel. The name comes from the German 'Kupfernickel': German miners could not derive any copper from the ore and believed that a sprite from the German mythology named 'Nickel' did the copper disappear and put the other material instead. The nickel ore was at those times often confused with copper ore. As from 1881 nickel was used for coins and later on it has found many applications in the metallurgy. Most of the nickel today comes from pentlandite ($NiS \cdot 2FeS$), from garnierite or limonite. The main areas producing nickel are in Ontario / Canada, at Norilsk / Russia, at Cuba, Australia and Indonesia.

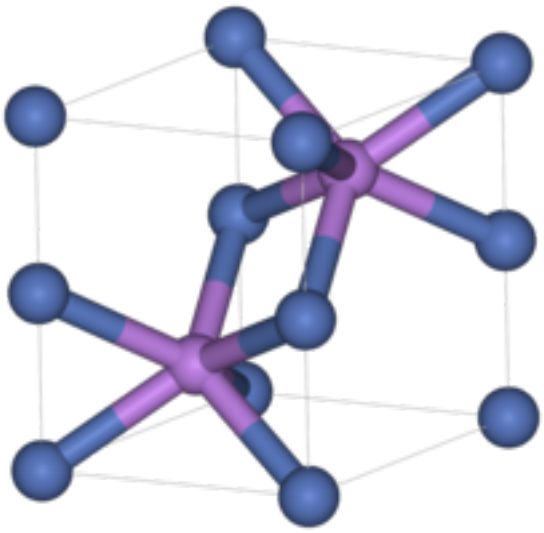


*Figure 6: Molecular model of niccolite (*NiAs*)*

Nickel has been used for long time already although people at those times did not realise that it was the element nickel as we know it today. In the area of what we now know as Syria various metal objects have been found which contain nickel. The oldest known use of nickel goes back till 3500 BC. Also from old Chinese documents appears that nickel-containing minerals as niccolite were already used to give a green colour to glass.

In ceramics nickel is often used as nickel oxide (NiO) as such and as raw material for the production of calcined stains like a black stain (Cr — Fe — Ni or Cr — Fe — Ni — Co), a grey stain (Co — Ni — Si) or brown stains (Fe — Cr — Ni). When used as raw material for the production of a ceramic stain it ends up in a certain structure (periclase or spinel) and has in such cases normally a stable character. When nickel oxide is used as such as direct colouring compound in glazes, the effect is often unpredictable and unstable.

Greenish, grayish and brownish colours may be obtained depending on the glaze components and firing conditions. Especially when it comes to reddish colours the necessarily compositions

are quite narrow and it is only possible to obtain rather stable violet-like colours in a matt glaze composition. No comparison with red colours which can be obtained through chromium oxide or salts, uranium compounds or cadmium selenium stains or glazes.

As a general glaze composition to obtain these violet red nickel coloured glazes counts:

Li_2O, Na_2O, K_2O	0.00 – 0.15	Al_2O_3	0.08 – 0.35	SiO_2	0.80 – 2.10
BaO	0.35 – 0.50				
PbO	0.00 – 0.10				
ZnO	0.40 – 0.50				

In 1921 an investigation was published[54] describing the colouring effects of nickel oxide resulting in green, blue, violet-purple and brown colours. The best compositions for violet-purple-red colours were:

	BaO	0.50	Al_2O_3	0.35	SiO_2	2.10
	ZnO	0.50				
					1. NiO	0.025
and:	K_2O	0.15	Al_2O_3	0.35	SiO_2	2.10
	BaO	0.45				
	ZnO	0.40			1. NiO	0.025

Lehnhäuser[55] gives similar recipes for purple-violet glazes and mentions following composition for a temperature of 1100 °C till 1140 °C:

Na_2O	0.05	Al_2O_3	0.12	SiO_2	1.20
BaO	0.20				
PbO	0.15		1. 1% $NiCO_3$: lilac		
ZnO	0.60		1. 2% $NiCO_3$: violet-red		

In most of the compositions mentioned an amount of 0.10 to 0.15 of NiO in the Seger formula is present. The presence of BaO and ZnO is necessary for a good violet-red colour but the end result is a glaze with a matt finish for temperatures of 1100 °C or higher. A way to decrease the firing temperature and remaining the violet-red colour is to add a low smelting flux. The best result in that case is obtained by adding 10 to 20% of a simple lead mono silicate which makes it possible to decrease the firing temperature to 1040 °C.

In 1964 an investigation was published by Franz Kure[56] describing possibilities for red coloured glazes. Basically, he mentioned similar compositions as described above with the remark that compositions for red-violet colour tones have narrow possibilities and are sensitive for temperature differences.

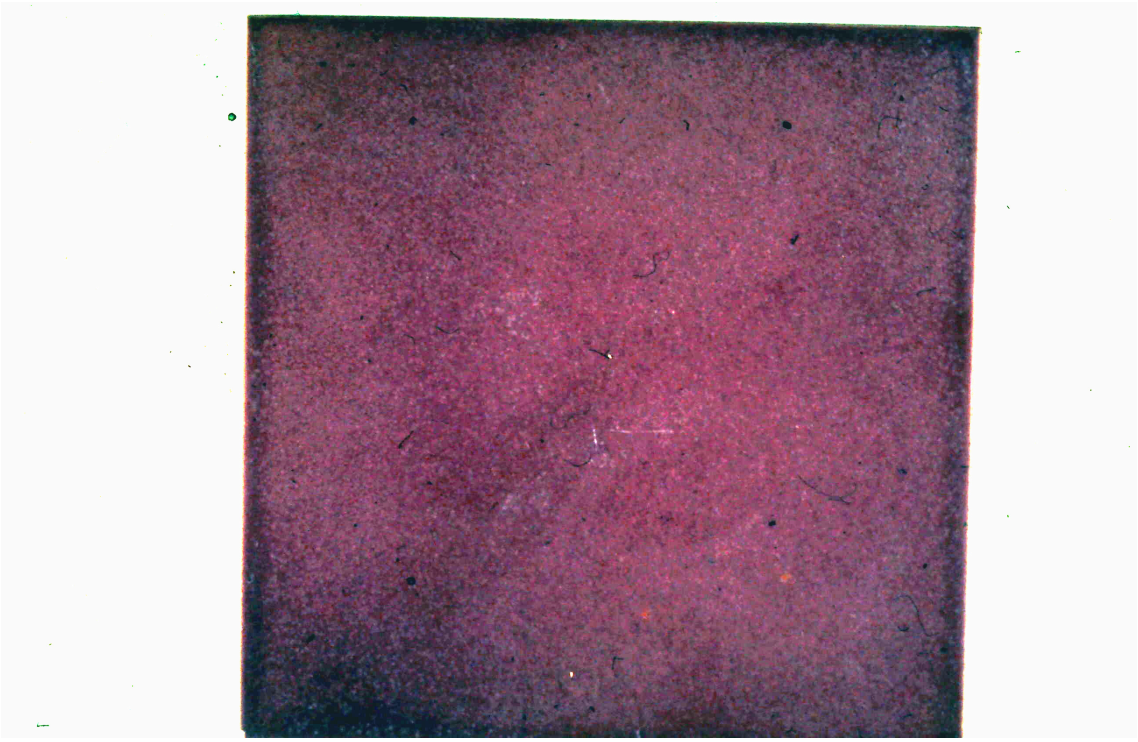
For the possibilities with nickel he mentioned that:

- a low amount of alkali is necessary for the flow properties of the glaze
- too high an amount of Li_2O turns the colour to blue
- a certain amount of BaO and ZnO must be present for a red-violet colour
- the Al_2O_3 content is not that important for the red-violet colour but more for the reactivity of the glaze
- too much CaO turns the colour into violet-blue
- (too much) PbO turns the colour into brownish
- also a too high amount of NiO makes the glaze too refractory and too brownish

An example for this type of violet-purple red coloured nickel glaze is shown by Photograph 12. The following glaze composition was used to obtain this result at a firing temperature of 1040 °C – 1060 °C:

(Ferro) frit 32570	36.00 %	(BaO frit)
(Ferro) frit 35200	54.50 %	(PbO – ZnO frit)
Kaolin	8.00 %	
Nickel oxide	1.50 %	
	100.00 %	

Firing of this glaze was done at 1060 °C in an electrical fired kiln in a traditional cycle. The glaze surface has a matt finish and is rather stable between 1020 °C and 1080 °C.



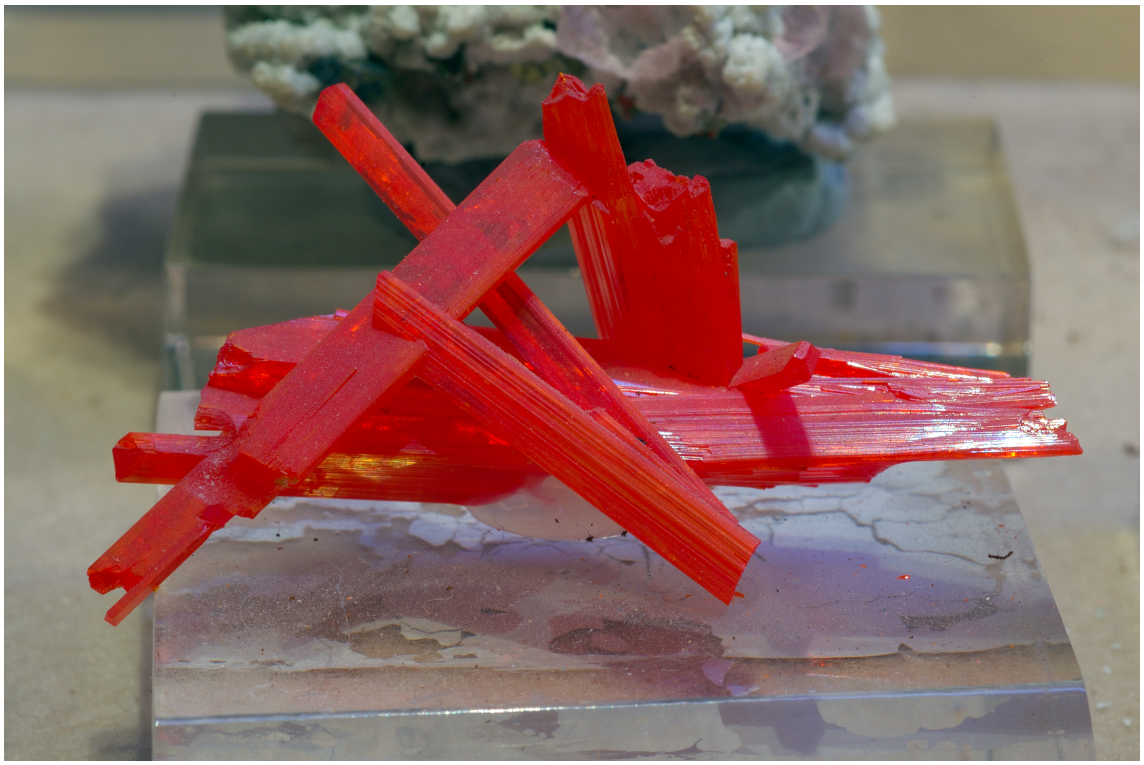
Photograph 12: Violet-purple nickel-coloured glaze

Also in this case counts that this type of nickel red glazes is not applied in the ceramic industry because of its instability, the type of colour which isn't always favourable and the narrow possibilities to create these colour tones, viz. only in BaO, ZnO matt glazes. Some artists / potters may apply those compositions to create some one-off pieces. A further restriction of the application of nickel is the health and environmental regulations which are in place today. Glazes which do contain free nickel oxide are obliged to be labelled accordingly. The use of free nickel oxide is therefore decreased significantly and in most cases replaced by a calcined nickel silicate or a frit where nickel is melted into the frit. For people with some experience in ceramics it is not a surprise that those compounds react different compared to free nickel oxide which makes the realisation of a good and stable red-purple nickel glaze even more complicated.

8 CHROMIUM

Red results with a multi-colouring component.

The element chromium was in fact discovered when Johann Gottlob Lehmann found an orange-red mineral in the Beryozovskoye mines in the Ural Mountains in 1761. He called this mineral 'Siberian red lead' because he thought that it was a lead compound with selenium and iron. Later on, it appeared that he had found the mineral Crocoite which exists as leadchromate ($PbCrO_4$). See also Photograph 13.



Photograph 13: The mineral Crocoite ($PbCrO_4$*), a natural lead chromate*

A few years later Peter Simon Pallas visited the same location again and discovered that this 'Siberian red lead' was very suitable as pigment for paints. The good resistance properties of paints with lead chromate made the application afterwards very common and some examples of the warm and signaling yellow colour are very well known as i.e. the colour of the school busses in the USA and the house colour of Deutsche Post. In more recent times, the lead chromate based paints and colours have been substituted more and more by organic and lead free compounds due to environmental and safety concerns.

It was the French chemist Nicolas-Louis Vauquelin who in 1797 succeeded in isolating chromium oxide out of Crocoite by mixing the mineral with chloric acid. A year later he succeeded in making the metal chromium out of the chromium oxide by heating the material in a kiln. During the 19th century chromium became more and more important as metal in alloys to increase the properties of the alloys.

Very remarkable in this respect is that the application of chromium metal to increase the quality of metal alloy properties has already been applied by the Chinese. The tips of swords and crossbows as found in burial pits dating from the late 3rd century BC - Qin dynasty of the famous Terracotta army near Xi'an have been analysed by archaeologists. The ancient bronze tips showed no sign of corrosion due to the fact that the tips were coated with chromium[57].

The most important source for chromium is the mineral chromite ($FeCr_2O_4$) which is mainly found in South Africa, Kazachstan, Russia, India and Turkey. In 2000 an amount of 15 million tons have been mined which give about 4 million tons of the metal chromium.

The name chromium comes from the Greek word 'chroma' which means colour. For everyone involved in chemistry this may be clear given the numerous and different coloured compounds which are able to create with chromium. Also for people in ceramics it is clear. Chromium compounds and stains are a base for very different colours as green (chromium oxide; chromium silicate; chromium aluminium silicate), yellow (lead chromate), pink colours in chromium tin stains and, of course, chromium red glazes.

Chromium red glazes have been studied and developed from the early beginning of the 20th century. Some important studies and publications in this respect are from A. Berge: 'Rote Chromglasuren'[58] from A. Heubach: 'Chromrote glasuren'[59] from W. A. Weyl and E. Thümen: 'Konstruktion und Farbe der Chromgläser'[60] from K. Grössl: 'Chromrote Glasuren bei SK 1a aus dem Dreistoffsystem $PbO - SiO_2 - ZrO_2$'[61] from W. Wanie: 'Chrom als Farbstoff in Gläsern (Glasuren) und keramischen Farben'[62] from W. Lehnhäuser: 'Glasuren und ihre Farben'[63] and from H. Balduin: 'Rote Chrom-Glasuren für erhöhte Temperaturen'[64]. All these publications describe the various influences of some raw materials, quantities involved, ratios for the various compounds, firing conditions, etc.

Important fact is that the red colour of chromium red glazes is caused by $Cr(VI)$ while $Cr(III)$ is causing the well known green colour. The chemical comparison: $2CrO_3 \longleftrightarrow Cr_2O_3 + \frac{3}{2}\,O_2$ is in this respect important. What happens in wet-chemistry also happens in ceramic glazes: when a solution of a lead salt is being brought into contact with potassium chromate, a precipitation of yellow lead chromate is formed. When this solution is made more alkaline, the lead chromate is going over to a basic salt what is coloured red. This principle can be used to steer the colour of chromium glazes. Normally, the basis for chromium red glazes is a lead alumina silicate or a simple lead silicate.

The above mentioned can be proven when to such a chromium red glaze quartz is added in small steps. The colour of the glaze will go from the bright red into the green caused by Cr_2O_3 . Reason for this is that the more quartz is available, the more lead-silicate is formed leaving not enough lead for the forming of lead chromate and so the green colour of Cr_2O_3 appears. For that reason it is important for the formulations of chromium red glazes that the SiO_2 content is not too high (under or just over 1.00 in the Seger formula), that there is no boron, some alumina and some alkaline. An addition of tin oxide may help to create a more uniform red colour.

Chromium red glazes can approximate the appearance of CdSe colour quite close with regard to colour value. However, they are normally not stable at temperatures over 1000 °C. The best results are achieved therefore at temperatures as high as 900 °C till 980 °C in a normal / traditional firing cycle.

A good and bright shiny chromium red is achieved on basis of a lead alumina silicate frit with composition:

Na_2O	0.03	Al_2O_3	0.07	SiO_2	1.43
K_2O	0.04				
PbO	0.93				

The composition of the glaze is:

frit	62.50 %	
tin oxide	6.25 %	
basic lead chromate	31.25 %	$(2PbO \cdot PbCrO_4)$
	100.00 %	

This glaze has been supplied e.g. to Ceramica SMOV in Italy during the 70ties of last century. They have applied the glaze onto a floor tile with high relief. In such a case one did not scratch the glaze too much because one is walking onto the relief of the tile itself (see also Photograph 14).



Photograph 14: Ceramic floor tile with chromium red glaze, produced by Ceramica SMOV (Italy)

Another very bright red chromium glaze with crystal building on the surface can be obtained in the following way using a lead silicate as basis:

PbO	1.00	SiO_2	1.00

The composition of the glaze is (dry mix formula):

frit (milled)	78.0 %
calcium carbonate	3.2 %
tin oxide	7.8 %
feldspar (Na, K) fine	3.2 %
potassium dichromate	7.8 %
	100.0 %

The glaze can be dry mixed with an intensive mixer, mixed with water and sprayed onto the biscuit fired surface. Firing temperature is 940 °C.

All these type of glazes have been developed and applied during the first half of the last century and partly till the 60ties and the 70ties. Although beautiful red glazes can be achieved, the negative aspects of these types of glazes became more and more important. Of course, the health aspect of using chromates and bi-chromates, the carcinogenic properties of Cr(VI), the necessary application of lead alumina silicates or just simple lead silicates, the vaporization of chromium compounds during the firing which can result in unwanted colour-effects and the very low chemical resistance which made these type of glazes only applicable for ceramic art- and giftware. With the industrial introduction and increasing possibilities of cadmium selenium glazes as from the mid of last century, the chromium red glazes disappeared and are now only applied in some rare cases by artists or some smaller potters.

9 URANIUM

The radioactive red.

The history of uranium based red glazes is as a matter of fact of course a young but also a rather short one. Young because it developed only after the discovery of the element uranium and after the different oxides were put into operation. Short because one distinguished on one hand also the negative and dangerous properties with regard to radiation phenomena when people are exposed to these components and on the other hand governments also blocked the various applications, this in favour of the application for the investigations in the atomic energy area.

Uranium is called after Uranus, in the Greek mythology the father of the goddess Aphrodite. The name for the element was chosen because of the planet which was discovered some years before by the Englishman W. Herschel in 1781.

The German chemist and mineralogist Martin Heinrich Klaproth (1743 – 1817) must be honoured as the discoverer of the new element. He was first a pharmacist and a chemistry master before he became a professor at the University of Berlin. He did much work on the analyses of rocks. As a result of this he found several new elements such as uranium but also zirconium (1789), titanium (1795) and cerium (1803). He also discovered strontium as well and studied tellurium. By that time one called the component as representative in pitchblende uranium, while later on it became clear that it was the oxide form U_3O_8 which was present in pitchblende or uranite.

Although the official discovery of the element took place on the eve of imposing developments in both physics and chemistry, one had already found some pieces of yellow coloured glass containing about 1% of uranium near Naples. These pieces could be dated as from AD 79.[65]

The developments with respect to uranium went very fast after the discovery of its radiation properties. Wilhelm Conrad Röntgen, a German physicist, did an investigation during 1895 about the penetration of cathode-beams when he did his great discovery of the special radiation which is called after him. He proved that such radiation had other properties than the cathode-beams.

The French physicist Henri Bequerel studied this important phenomenon and investigated the possibility of a relation between the origin of the X-rays and fluorescence phenomenae. During this investigation he discovered the radiation of uranium salts. As the successor of his father and grandfather in the position of professor in the Muséum d'histoire naturelle (Paris), he studied the radiation of uranium in a magnetic field, generated by an electromagnet. This studies resulted in the appointment that the radiation was a property of the uranium atom and valid for all the uranium components.

Maria Curie Sklodowska continued in this field and discovered that uranium was not the only element showing radiation properties. Together with her husband and well known French physicist Pierre Curie she established that the radiation was not an exclusive property of uranium and that also thorium showed this radiation. During further investigations of minerals they found that pitchblende showed a much stronger radiation than the quantities of uranium or thorium did presume. This led to the discovery of polonium and finally to radium in 1898.[66]

The importance of these new materials was soon distinguished. The main mineral and source for uranium was and still is pitchblende, also called uranite: U_3O_8. Uranium occurs however also in much other minerals such like carnotite (an uranium potassium vanadate), in autunite

(a calcium uranyl-phosphate), in uranophane (a hydrated uranium calcium silicate), in curite (a hydrated lead urinate), in torbernite (a hydrated copper uranyl phosphate and many others.[67]

Intensive searching programmes showed that the element is not as rare as it was once thought. Because of its importance in the field of the atomic energy one has searched very intensively to uranium containing minerals. Some main and well known uranium deposits are at Sjinkolobwe (Zaire), Jáchymov (Czech Rep.), Cornwall (England), Colorado (USA), near Great Bear Lake and Athabasca Lake (Canada), Witwatersrand (South Africa), Rum Jungle and Isa Mount (Australia), Bihar (India) and Poços de Caldas (Brasil).[68]

All these deposits are mainly explored with regard to the economical value of uranium. One of the most important applications is its use in electrical power plants. It may be clear that this application is out of the scope of this publication. The point however where these two items do come together again is at the developments which mention the use of a glass in a unit for the melting-in of nuclear waste material.[69, 70]

Other than some early findings of uranium containing glass through which an early application is known, a deliberated use of uranium containing minerals was uncommonly limited. The application of several uranium salts in the glass[71] and ceramic industry came slightly into fashion during the first half of the 20th century. There are however not so many publications available as far as the ceramic sphere is concerned. An article of Charles F. Binns and Frobisher Lyttle[72] published in 1920 mention some compositions for uranium red glazes. As uranium source they mentioned sodium uranate ($Na_2U_2O_7$). The glazes, with 20 and 37 % $Na_2U_2O_7$ resp., developed a bright cinnabar red at a temperature of SK 04a (1020 °C). The base glaze was a lead alumina silicate with only an introduction of some potassium and zinc oxide in the R_2O / RO group.

Another article was published by Zimmermann[73]. He started with a simple lead-alumina-silicate with the following composition:

PbO	1.000	Al_2O_3	0.175	SiO_2	0.850

As a recommendation he indicated that the SiO_2 content may not exceed an amount of 1.0 according to the Seger formula. The influence of different compounds in the R_2O / RO group was also studied. For these trials he used 20 parts of $Na_2U_2O_7$ to 100 parts of glaze.

Arnulf Holl[74] studied also the rule of the body composition and found the negative influence of high calcium containing bodies with regard to the development of the red colour. A notable fact to be recorded is that he used an amount of 18 to 21 % of uranium nitrate as colouring compound. Other authors, among them the German Hans Eska, warned against the use of this soluble uranium salt. The preparation of the glaze with this soluble component and the handling of the glazed articles by hand are reasons that a direct contact with this toxic element and the skin is almost unavoidable. The negative influence of calcium oxide on the red colour is in contradiction with the results of other investigators.

One of the most comprehensive and detailed studies was published in 1933 by Hans Eska[75]. In this publication called 'Wetterfeste uranrote Glasuren' ('Weather resistant uranium red glazes') he described the best possible glaze compositions to obtain resistant red uranium glazes. He mentioned the application of uranium nitrate, as soluble salt, very injudicious. He also turned

down the argument that this particular uranium source should be cheaper. In his investigation he indicated the influences of modifications in the R_2O / RO, R_2O_3 and RO_2 groups on the colour, gloss, craze resistance and weather resistance.

As a base glaze composition he used a fritted lead meta silicate, completed with components as BaO, ZnO, CaF_2, MgO, Na_2O (as sodium uranate), K_2O and B_2O_3 also fritted, Al_2O_3 and UO_3 as uranium oxide U_3O_8.

The trials were fired in a brown coal fired muffelkiln at SK 08a (940 °C) and SK 05a (1000 °C). Heating up took 26 hours and the cooling 50 hours.

One of the tests applied after the firing was a test with hydrochloric acid. The results were classified in 7 groups ranging from 'not attacked' to 'completely affected'. Glazes with only a variation in the SiO_2 content according to the formula:

PbO	1.00	Al_2O_3	0.10	SiO_2	0.80 – 1.60
		UO_3	0.20		

showed an improved resistance with an increasing SiO_2 content. The colour of these glazes was red.

If part of the lead content was replaced by barium oxide (0.1 mol and 0.2 mol resp.) the colour changed more towards orange-red colour tones. While the surface became more matt, craze resistance worsened, but the weather resistance should improve.

The introduction of ZnO (0.1 mol and 0.2 mol resp.) resulted in more bright red glazes and even more bright with an increasing SiO_2 content. As best composition is mentioned 0.1 mol ZnO in combination with 1.4 mol SiO_2. Those glazes showed a high gloss but the resistance was bad.

CaO was applied and introduced as CaF_2 because this Ca-compound showed the best results if several Ca containing materials were compared. The calcium fluoride had a positive effect on the red colour development and also on the weather resistance.

A partly replacement of lead by magnesium oxide resulted also in red colours but the properties with regard to craze- and weather resistance worsened.

A partly replacement of lead by potassium resulted in more crazing while it also became more difficult to obtain a reasonable weather resistance. The red colour developed well but in the red appeared yellow spots.

Sodium had in common with potassium that it had a negative influence on the red colour development especially at higher temperatures. A good red colour however was obtained with a Na_2O content of 0.05 mol with at the same time a SiO_2 content of not lower as 1.20 mol. An increased Na_2O content till 0.10 mol required a SiO_2 content 1.20 mol or preferably somewhat lower. The sodium-lead uranium glazes had a strong disposition to crazing and good weather resistant glazes were not obtained.

In summary it was concluded that good resistant uranium red glazes could be obtained with compositions between:

PbO	0.85 – 0.90	Al_2O_3	0.10	SiO_2	1.20 – 1.60
BaO	0.15 – 0.10				
CaF_2	0.15 – 0.10				
K_2O	0.15 – 0.10				

The influence of metal oxides such as CuO, CoO, Mn_2O_3, Fe_2O_3 and Sb_2O_3 on the colour development was also ascertained. The main conclusion was that these oxides destroyed the original uranium orange or red colour, but that sometimes colour effects were created which were impossible to obtain with more conventional (and cheaper) stains.

Another interesting but also rather compendious article was published in 1934 by Karl Kautz[76]. He used $Na_2O \cdot 2UO_3 \cdot 6H_2O$ as colorant and studied the influence of glaze components on the development of specific colours. As a result he mentioned for a variety of colours the best possible glaze compositions.

A 'pleasing red glaze of this type with a crystalline structure' could be obtained with the following glaze composition:

Na_2O	0.10	UO_3	0.20	SiO_2	2.00
PbO	0.90				

The remark that this glaze was only used to produce 'a few small pieces of art ware' is significant in respect of the stability and reproducibility of this red coloured glaze.

Franz Eggert[77] published an article in 1951 about the affecting of the tomato-red uranium glazes. His base glaze was a lead alumina silicate in combination with black UO_3 as colouring component, this to avoid the simultaneously introduction of sodium. He concluded among other things that in general all the glazes showed as a matter of fact different coloured layers. A first layer with a notable influence of the body; a middle layer and the top layer which was in most cases responsible for the final colour tone. Some remarks out of this publication are worthwhile to mention in respect of the realization of red colours.

An addition of 10 % of zinc oxide resulted in a colour shift towards more blood red.

5 % of lithium carbonate resulted in a dark-brown coloured first layer; a yellow-transparent middle layer and a dark blood-red top layer.

However, and as also reported in other publications, an addition of 2 % of beryllium carbonate should create the best possible and brightest tomato red uranium glazes.

F. H. Norton[78] mentioned in 1952 the calcium and sodium uranates as suitable for the development of brilliant red, orange and yellow colours but pointed also out that 'present restrictions make their use in ceramics impossible'.

Two articles of Fritz Jochmann[79, 80] published in 1958 and 1959 respectively are given some more information about the reactions with uranium compounds in glass. Glasses, no matter which composition, coloured with the normal available uranium compounds, resulted in yellowish-greenish fluorescence when melted under oxidizing conditions Reducing conditions resulted in a smoke-like greyish brown. In these cases he drew a parallel between copper-ruby caused by (reduced) copper in a colloidal state. The greyish-brown colour developed under reducing conditions should be created by uranium, also in a colloidal state.

An investigation to the radioactivity of the uranium glasses of his study was subject of the second part of the first publication. Concluded was e.g. that the glass composition as such had absolutely no influence on the radiation. Also the manufacturing procedures of the glasses (melting at rather high temperatures) did not influence the radiation. The only measure for radiation was the amount of uranium in the glass. Measuring the radiation of a glass composition before and after melting showed no noticeable differences if one made a correction for the melting weight factor. This factor must be understand as a difference in weight between a mix of raw materials and the weight of the same mix after melting, not involving the practical looses during melting.

Although the author pointed out the risks for the workers health when applying these compounds, he indicated in his second article that the compounds in question were available again when one had a special allowance and if it were materials without the for fission necessary $^{\{235\}}U$. This point of view can be considered as overtaken. To the more recent regulations in this respect we will revert later on.

Lehnhäuser[81] listed the uranium compounds as colouring compounds for glazes in 1959. Although he indicated that these particular colouring compounds were expensive, he gave no special restrictions for their use. For a good uranium red glaze he recommended a SiO_2 content between 0.4 mol as a minimum and 1.3 mol as a maximum. Other glaze components should be only Al_2O_3 and PbO. As colouring component was applied an addition of 20 % (sodium) urinate. An oversaturation should result in a uranium-aventurine glaze, analogous to the iron-aventurines. The influence of common used alkaline earth components is also mentioned. The remark that the uranium compounds are toxic and must be treated as lead is nowadays a too brief information regarding the important radiation phenomenae for one's health.

Another application of uranium compounds and mentioned by Viehweger[82] is in compositions for lustres. These type of lustres are the resinate salts of metal oxides dissolved in volatile essential oils. The preparation of this type of lustres is a very special one and requires an experience to a high degree.

For a golden yellow luster one made e.g. first a uranium resinate (a mixture of uranium nitrate and soft soap in the ratio 1: 1). This uranium resinate is then applied with colophony, benzene and oil of lavender. In the same book are also mentioned some glaze compositions which have sodium uranate in their composition. These glazes should realize a dark salmon coloured glaze. No special restrictions are given for the application of these compounds in respect of the harmful properties for the human health, except the information that the uranium compounds may not be used anymore in the ceramic industry.

The fact that these compounds are no longer applied in the ceramic sphere is mainly due to the very severe regulations and that those compounds must be registered because of its radioactivity. The radiation consists in fact of three different kinds of radiation. The α parts consists of 2 protons and 2 neutrons. The radiation has only a reach of 5 cm and cannot pass the human

skin. The β parts are in fact a fast moving electron. They have a reach of roughly 1 meter. The third kind of radiation is formed by the γ parts which are comparable with X-rays. This kind of radiation can only be stopped by thick walls of concrete or lead. This radiation is the cause of the so-called radiation disease.

The literature indicates that the characteristics of uranium red glazes are based upon the formation of lead-uranate: $PbO \cdot 2UO_3$. This is the reason that only a lead silicate or lead-alumina-silicate forms a suitable base glaze. The firing stability of these glazes was however rather limited. The available literature mentions in general glazes which develop a red colour at temperatures ranging from roughly 900 °C till 1020 °C. The sensitivity for a not well balanced firing atmosphere was more than normal compared with other glaze systems. Only oxidizing firing conditions resulted in the required results. Also a slightly reducing atmosphere caused already colour deviations, in most cases to more brownish colour tones. Uranium glazes were also sensitive for influence of sulphur. An addition of barium carbonate helped to suppress the sensitiveness.

Another aspect which made the glazes less easy to apply was the fact that in many cases sodium uranate was used as the colouring compound. The high amount necessary for a sufficient colour development (between 15 and 25 %) gave the glazes an alkaline character with sometimes strong leaching phenomenae, resulting in settling-down problems. The use of setting-up agents was in most cases a necessity.

The sometimes varying quality grades of the uranium compounds was also reason for deviating colour shades. Together with the high price of the compounds and the meanwhile distinguished dangerous properties with regard to the radiation made the glazes not suitable for industrial use on a large scale. The restrictions were reasons that these glazes were mainly applied on a limited scale for small pieces of art ware. Various pieces of orange-red to red glazed ceramic pieces could be seen in various factory musea e.g. of the Konakovo Faience Factory in Konakovo (Russia).

For the lower temperatures (900 °C – 960 °C) it was often advised to apply raw, unfritted glazes while for the higher temperatures (960 °C – 1020 °C) some sources in the literature mention that for those cases fritted glazes would render better results.

A not proper glaze application often resulted in an irregular glaze and colour appearance. A cloudy effect with different coloured glaze layers was the result.

One used several salts to reach the required colour shades. The origin of those compounds was not always clear, neither was the measure of radiation. For colouring of the glazes the mainly applied uranium compounds were:

Name	**Formula**
Uranium dioxide	UO_2
Uranium trioxide	UO_3
Uranium oxide	U_3O_8
Sodium uranate	$Na_2O \cdot UO_3$
Sodium diuranate	$Na_2O \cdot 2UO_3$
hydrated sodium diuranate	$Na_2O \cdot 2UO_3 \cdot 6H_2O$
uranium nitrate	$UO_2(NO_3)_2 \cdot 6H_2O$

Although not a red-giving composition but a main one in respect of the application of uranium for the well known greenish-yellowish fluorescence, the following composition is mentioned by Jochmann:

Na_2O	12.80 %
K_2O	4.94 %
CaO	6.03 %
BaO	2.83 %
As_2O_3	0.21 %
UO_3	0.58 %
SiO_2	72.60 %
	99.99 %

The uranium was introduced through sodium uranate. If the glass was melted under the proper oxidizing conditions it resulted in the required yellowish fluorescence.

In those cases the uranium should be present as UO_3.

The early uranium red glazes mentioned by Binns and Lyttle were based on the following compositions:

K_2O	0.12	Al_2O_3	0.12	SiO_2	1.33
PbO	0.80				
ZnO	0.08				

An addition of 20 % of sodium uranate should result in a cinnabar red glaze for SK04a (1020 °C).

The base glaze:

K_2O	0.04	Al_2O_3	0.12	SiO_2	0.79
PbO	0.87				
ZnO	0.09				

together with an addition of 37 % sodium uranate resulted in a matt red glaze for SK 04a (1020 °C).

Zimmermann mentioned the following compositions for orange-red glazes, suitable at SK 07a till SK 03a (960 °C till 1040 °C):

PbO	1.00	Al_2O_3	0.175	SiO_2	0.4 – 0.6
K_2O	0.10	Al_2O_3	0.175	SiO_2	0.85
PbO	0.90				
PbO	0.90	Al_2O_3	0.175	SiO_2	0.60
ZnO	0.10				

For these compositions counted that an addition of 20 parts of sodium uranate to 100 parts of base glaze was applied.

The study of Eska is detailed and built up in a very schematic way. The glazes were fired at SK 08a (940 °C) and SK 05a (1000 °C). The below mentioned glazes gave, according to the author, good red glazes:

PbO	1.00	Al_2O_3	0.10	SiO_2	1.40
		UO_3	0.20		
BaO	0.10 – 0.20	Al_2O_3	0.10	SiO_2	1.20 – 1.40
PbO	0.90 – 0.80	UO_3	0.15		
PbO	0.90 – 0.80	Al_2O_3	0.10	SiO_2	1.20 – 1.40
ZnO	0.10 – 0.20	UO_3	0.20		

The weather resistance was not always sufficient and the glazes were heavily attacked. This as contrasted with glazes where the lead content was partly replaced by fluorspar:

CaF_2	0.10	Al_2O_3	0.10	SiO_2	1.40
PbO	0.90	UO_3	0.15		

This glaze should give an intensive and deep bright red colour. The surface of the glaze was a glossy one and the weather resistance was good.

If part of the lead content was replaced by magnesium the investigator observed an increased tendency for crazing and a matt surface.

The introduction of potassium resulted in bright red glossy glazes with a good resistance. The following examples can be mentioned:

K_2O	0.10 – 0.20	Al_2O_3	0.10	SiO_2	1.60
PbO	0.90 – 0.80	UO_3	0.15		

A too high an amount of sodium had a negative influence on colour, glaze, surface and craze- and weather resistance. The sodium content may not exceed 0.10 mol while as preferable SiO_2 content is mentioned 0.40 mol to a maximum 0.80 mol.

Kautz gives some compositions for respectively green, yellow, ivory, orange and red uranium based glazes. As possibility for a vermillion red glaze he mentioned:

Na_2O	0.10	UO	0.20	SiO_2	2.00
PbO	0.90				

A good tomato red glaze for SK 07a (960 °C) with good processing properties is mentioned by Eggert. As base glaze was used:

PbO	1.00	Al_2O_3	0.10	SiO_2	1.80

The basic red glaze was made with an addition of 16.7 % black uranium oxide UO_3, this to avoid the simultaneous but unwanted sodium introduction. These glaze components were not fritted before, but applied as raw glazes. As components with a negative influence on both the red colour and the glaze appearance are mentioned: calcium carbonate, boric acid and rutile. A more matt surface was supported by the introduction of e.g. tin oxide (8 %), barium carbonate (5 %), tungsten acid (2 %) and molybdenum acid (2 %). Components which radiate a positive influence on the red colour are zinc oxide (8 %), magnesium oxide (5 %), lithium carbonate (5 %) and beryllium carbonate (2 %).

Viehweger mentioned a fire-red, opaque matt glaze with following composition:

ZnO	2.55 %
PbO	64.08 %
Al_2O_3	5.41 %
SiO_2	11.02 %
$Na_2U_2O_7$	16.94 %
	100.00 %

An orange-red opaque glaze for SK 05a – 03a (1000 °C – 1040 °C) had the following composition:

Na_2O	3.81 %
CaO	5.35 %
PbO fritted	24.38 %
Al_2O_3	5.04 %
B_2O_3	5.28 %
SiO_2	36.14 %
UO_3	15.00 %
Kaolin	5.00 %
	100.00 %

Another application of uranium salts is also mentioned, namely in the composition of some coloured lustres. For this purpose one first made a resinate which is than dissolved in a colophony and various essential oils such as oleum rosmarini, oleum lavendular, oleum spicae, oleum foeniculi and others. Uranium nitrate was used to produce brilliant, iridescent lustres of a yellow colour. For the necessary uranium resinate one dissolved the uranium nitrate and soft soap in a separate way. The solutions were then poured together under the forming of a resinate. This resinate must be washed, air-dried and could then be used.

A golden-yellow luster was then prepared using following composition:

uranium resinate	25.0 parts
colophony	25.0
benzene	25.0
oil of lavender	25.0

The colophony was first dissolved in the oil of lavender using moderate heat. Then the uranium resinate was added, followed by the benzene. After cooling the liquid was first filtered before it was stored in bottles.

Apart from that, Viehweger stated that it was no longer allowed to use uranium compounds in the ceramic sphere. The already before mentioned reasons were a cause that the application of these type of glazes felt into abeyance.

Photograph 15 shows the uranium glaze which is in all respect a specific one and therefore difficult to replace by other colouring compounds.

Nowadays we can only wonder that the use of these compounds was rather wide spread. Till the 2nd World War however, when all uranium compounds were claimed for nuclear investigations, it was a way to create orange and red ceramic colours which was impossible to do in another way. Still today, the glazes have a very good, nice and brilliant appearance. There are various examples in factory musea in several countries which I have seen and the tomato red colour was still impressive. An example is shown by Photograph 15. It shows an uranium glaze made by the famous ceramic factory Mobach in Utrecht / The Netherlands. This and other uranium based glazes were made around 1930.



Photograph 15: Uranium red glaze. Courtesy of Mobach B.V., Utrecht, The Netherlands, c. 1930.

Another example is the Homer Laughlin factory in East Liverpool - Ohio / USA. They make the so-called Fiesta ware (dinnerware in earthenware) in various colours ever since 1936. It included at that time a red-orange colour which was made through a uranium red glaze (Photograph 16).



Photograph 16: Uranium red glazes on "Fiesta" dinnerware (Homer Laughlin, USA) and Californian pottery, 1930–1940.

In 2001 a comprehensive article was published by Donna Strahan[83]. The article is a survey of over 400 glass, ceramic and enamel objects from museum and private collections. It is an investigation for the extent of uranium colorants, mainly produced between 1830 till 1940. It shows that uranium colorant was widely used in glass and ceramic and also that little health risk was found from the uranium containing objects.

10 CADMIUM SELENIUM

A ceramic creation of real red colours.

Before describing the ins and outs of producing and application of cadmium selenium red, orange and yellow glazes a short description is given about the colour forming and therefore essential elements selenium, cadmium and sulphur.

10.1 Selenium

In 1818 the Swedish scientists and chemists Jöns Jakob Berzelius and J.G. Gahn discovered and isolated the element selenium which is called after 'Selene', the Greek word for moon. In the Greek mythology Selene was the daughter of Hyperion and sister of Helios. As selenium was found when Berzelius was working with and investigating the element tellurium and because there are similarities between these two elements he choose for the name of selenium. The element tellurium was named after the Latin word Tellus which means earth. In that way the similarities as between Earth and Moon were also expressed in the names of the elements.

Selenium, with atom number 34, has an atomic weight of 78.96. Its melting point is 217 °C; the boiling point is 684.9 °C $\pm$ 1 °C. The specific gravity is 4.79. Some of the natural sources of selenium are the minerals crookesite ($(CuTlAg)_2Se$) and clausthalite ($PbSe$). The main source, however, of industrial Se (and Te) is the anode slib which is formed during the electrolytic purification of copper. Major producers of selenium in the world are Japan, Canada, Belgium, the US, Russia and Germany.

Country	Se metal in MTons 2003
Belgium	200
Germany	100
Russia	81
Sweden	110
Canada	253
Chile	90
China	65
Japan	734
Other countries	267
World total	**1,900**

Table IX: Estimated world production of selenium metal (MTons) per country for 2003. Source: British Geological Survey.

The price of selenium has long been on a stable and low level but has increased incredibly as from 2003. Reason for this is the enormous demand for selenium from China for application in

the ceramic and glass industry as well as fertilizer for the Chinese soil. A general price level in 2000 was US$ 5.50/kg but in 2009 it was already increased to US$ 88.10/kg and increasing. See also Figure 7 which shows the remarkable price increase shortly after 2003.



Figure 7: Price trend of selenium metal (US$/kg) from 2000 to 2010

Selenium is mainly used in glass manufacturing (50 %), chemicals & pigments (15 %), metallurgy (13 %), electronics (10 %) and others, like agriculture (2 %). It plays also a role in nutrition and is mentioned, together with vitamin A and vitamin E, to have an effect on slowing down the growth of cancer cells.[84]

The electrical properties of the element are important (semi-conductor application in the electronic industry) as well as the photoconductor properties (changes light into electrical energy). The application as photoreceptor in photocopiers was very important for a long period but is nowadays more and more replaced by organic based photoreceptors. Also its role as semi-conductor is taken over by pure silicon.

The application in the glass industry is still important. It is a so-called decolourant: the greenish colour of glass caused by iron impurities can be neutralized by small additions of selenium to make it more colourless. Another application is of course the one as colourant to create rubin-red colours.

Selenium dioxide (SeO_2) is by far the most important oxide of selenium. It is soluble in water and forms seleneous acid H_2SeO_3. By oxidation of seleneous acid e.g. by $HClO_3$, selenic acid H_2SeO_4 arises. Salts of selenic acid like e.g. $BaSeO_3$, $ZnSeO_3$ and Na_2SeO_3 are used as sources of Se. Some of them are in particular of importance at the manufacturing of CdSe glazes. Na_2SeO_3 has the disadvantage that it is highly hygroscopic.

10.2 Cadmium

The element cadmium is called after the Greek word ‘kadmeia’. This is the ancient name for calamine, zinc carbonate.

Cadmium, with atomic number 48, has an atomic weight of 112.41. Its melting point is 320.9 °C and the boiling point is 765 °C. The specific gravity of the element is 8.65.

The element was discovered in 1817. Stromeyer found it as an impurity in zinc carbonate. Cadmium most often occurs in small quantities associated with zinc ores such as sphalerite (ZnS). Greenockite (CdS) is the only mineral of any consequence bearing cadmium.

Almost all cadmium is obtained as a by-product in the treatment of zinc, copper and lead ores. This fact that cadmium is a component in zinc ores hasn't always been distinguished in the past. The way how zinc metal was produced in an industrial way was started in the beginning of the 19th century. Knowing now that the cadmium, present in the zinc ores, was also reduced to the cadmium metal, it escaped during the process. Now, more than a hundred years later, this uncontrolled part of the process is a serious source of environmental contamination.

Calamine mines were already explored for centuries in some European countries for the production of brass. So also those mines near Moresnet in the Altenberg (la Vieille Montagne) in Belgium. On March 24, 1806 the chemist Abbé J. J. D. Dony from Liège was the new owner. In 1808 he started with the production of metallic zinc using horizontal retorts in St. Leonard, a suburb of Liège. Due to a lack of capital and business view, the main part of this company was sold to Dominique Mosselman, a businessman from Brussels. This new alliance was the base for the founding of the 'Société des Mines et fonderies de La Vieille Montagne' in 1837.[85]

The three developed processes for the manufacturing of metallic zinc are all based on the very same principle, viz. the heating of calamine with cokes; a distillation of zinc.

> The 'English method' is called after the method developed by William Champion. A patent was granted to him in 1739. According to this method, the first zinc kilns were built in Warmley near Bristol in 1734.
>
> The 'Liège method' with horizontal retorts started in 1809 but became of any importance only after ± 1840.
>
> The 'Silesian method', using half cylindrical shaped retorts was developed by Johann Christian Ruhberg in 1798.

A fundamental change in processing was the development of the electrolytic manufacturing of zinc. The first patents were granted already in 1880 but it became important for the industry after ± 1920. If one considers that e.g. the zinc factory as the one in Budel (North Brabant - The Netherlands), which was founded in 1892 by Lucien and Emil Dor and started production with only 8 small kilns according to the 'Liège method', switched over to the electrolytic process in 1973, one can imagine how much cadmium is also 'produced' and released through the chimney and the slags. These slags were given to the local farmers and used for elevation of local roads etc. The community is now confronted with the fact that a great number of hectares are contaminated with the toxic dust from this 170,000 tons zinc p/a producing factory.[86]

The world production of cadmium amounts 15,000 to 20,000 tons p/a.[87] More than half of this amount is delivered by the USA, Mexico and Canada. Also Russia is an important producer. A minor amount is delivered now by Belgium, France and Germany.

Cadmium is used in thin metal coatings to prevent it from atmospherical influences. As metallic material it forms the negative pole in nickel-cadmium batteries. Cadmium is also a component in some low-melting eutectic alloys as solders for lead.

The brown coloured cadmium oxide CdO can be obtained by the combustion and oxidizing of the metal. Together with cadmium carbonate ($CdCO_3$, white powder) it is the most important raw material source for the manufacturing of CdSe glazes. The yellow cadmium sulfide (CdS) occurs in nature as greenockite but it is chemically produced by precipitation from solutions of cadmium salts. After precipitation it has a cubic structure but after calcining it has a hexagonal crystal structure which makes it a stable pigment. The cadmium pigments do have very good properties for application in polymers. This has always been by far the most important application of cadmium pigments what is also expressed in Table X showing the use of cadmium pigments in Germany in 1981.[88]

Type of industry	%	Application
Paints and Lacquers	5	Powder coating 3 % Silicon coating 1 % Automotive lacquers 1 %
Ceramics Enamel Glass	10	Ceramics 7 % Enamel 2 % Glass 1 %
Synthetic material	85	Consumer goods, toys 35 % Food packing 35 % Technical articles 10 % Fibres, sanitary parts, Sport equipment 5 %

Table X: Industrial application of cadmium pigments in Germany (1981)

The price of cadmium showed a high peak during the early part of this century (2006) but has come down now and is more or less stable as shown in Figure 8.



Figure 8: Price trend of cadmium metal (US$/lb) from 2000 to 2010

The toxicity of cadmium is already subject of all kind of investigations, regulations, discussions and restrictions for use after the Itai-itai disease in Japan became a world-issue. Mining in the Toyama Prefecture by the Mitsui Mining and Smelting Co. was already done since long times. The Kamioka Mines in Toyama increased the output of the mines due to the wartime demands for zinc, lead and other metals caused by the Russian Japanese war and World War I. The output increased significantly before World War II and so did the cadmium contamination. The waste water contaminated the Jinzu river and all water what was used for preparing food, washing, drinking, fishing and irrigation of the rice fields.

The main cause of the disease was determined in 1955 by Dr. Hagino followed by investigations of the Toyama prefecture in 1961. In 1968 a statement was issued by the Ministry of Health and Welfare mentioning the symptoms of Itai-itai disease caused by cadmium poisoning. The cadmium poisoning is mainly causing weakening of the bones and kidney failure.

Various conferences were held on national, European and a world-wide scale focusing on cadmium with the unavoidable outcome to come to minimizing the application of cadmium with only some minor exceptions. During the 80ties and 90ties of last century the application of cadmium for most applications is forbidden and laid down in laws. Only some exceptions are made were it is technically not possible to substitute the cadmium by other alternatives. Ceramic colour application is e.g. still an exception.

10.3 Sulphur

The element Sulphur (Sanskrit: sulvere; Latin: sulphurium) with symbol S was already known to the ancients; referred to in the book of Genesis as brimstone. It is also a component of gunpowder (together with potassium nitrate and charcoal) which was invented by the Chinese in the 12th century.

Sulphur is also found in meteorites. A dark area near the crater Aristarchus on the moon has been studied by R.W. Wood with UV light. This study suggests strongly that it is a sulphur deposit.

It is widely distributed in nature as iron pyrites, galena (PbS), sphalerite ((Zn, Fe)S), cinnabar (HgS), stibnite, gypsum, Epsom salts, celestine, barite, etc.

The element sulphur has atomic number 16. Its atomic weight is 32.06. The melting point for the rhombic form is 112.8 °C and for the monoclinic form 119.0 °C. The boiling point is 444.7 °C. The specific gravity of the rhombic form is 2.07 and of the monoclinic form 1.96 (20 °C).

It is commercially recovered also from wells sunk into the salt domes along the Gulf Coast of the USA. It is obtained from these wells by the Frasch process which forced heated water into the wells to melt the sulphur that is than brought to the surface.

Sulphur is a pale yellow, odourless, brittle solid which is insoluble in water but soluble in CS_2. In every state, whether gas, liquid or solid, elemental sulphur occurs in more than one allotropic form of modification. They present a confusing multitude of forms whose relations are not yet fully understood.

A finely divided form of sulphur, known as 'flowers of sulphur', is obtained by sublimation.

A main application of sulphur is at the vulcanization of natural and synthetic rubber and as fungicide. A tremendous tonnage is used to produce sulphuric acid, one of the world's most important manufactured chemicals. In 2001 the world production of sulphuric acid was 165 million tons.[89]

For the manufacturing of ceramic red and yellow glazes the more important compounds are cadmium sulphide and zinc sulphide. In old recipes one can still find the introduction of the necessary amount of sulphur by the yellow element as flowers of sulphur. Investigations have, however, proven that this is a less good method of introducing sulphur into the formulation of frits and glazes.

10.4 Development of frits and glazes

The use of cadmium selenium glazes in their actual compositions does not have such a long tradition. The base for the development of these glazes however can be found in the use of Se in glass. The knowledge how to obtain red colours in glass by using Se extended more and more in the second part of the 19th century after Berzelius has isolated the element in 1818.

Although it is clear that selenium based rose till reddish coloured glasses were already known for a longer time, it is generally accepted that the patent granted to the French chemist Théophile Jules Pelouze in 1865 was an important step for the development of the CdSe based glass compositions. As far as known it is the first patent where Se is claimed to be the colouring component for red glasses. T. J. Pelouze (1807 – 1867) did a lot of investigations e.g. in Germany for Liebig. He invented e.g. the preparation of formic acid starting from cyano hydrogen acid.

The next step was a patent of Welz, granted in 1892 for the use of Se or Se compounds for producing rose, red and orange coloured glass.

In 1893 a British patent was granted to H. T. and W. R. von Kralik for the use of Se and its compounds in glass manufacturing.

In 1894 Spitzer obtained a German patent for the use of selenites and selenates.

From this time the ruby coloured glass on a basis of Cd, S and Se was a subject of investigation for various scientists. It was known that the ruby glasses based on colloidal gold developed their real colour after an annealing process. A same kind of behavior was noticed for the ruby glasses based on Se. Therefore, it was generally believed that the particle sizes of the colouring particles were decisive for the final colour. Investigators to these phenomena were e.g. Treadwell, Fenaroli, Kraze, Witt, Frankel, Krak, Granger, Fuwa and Sugie.

An important step for the investigations was made by Rooksby and published in 1932. He investigated the red coloured glasses using the XR-Diffraction method. He stated for the first time that the mixed crystals of the solid solution of CdS and CdSe are responsible for colouring. The final colour, between yellow and dark red, is depending on the ratio CdS : CdSe in the mixed crystal. The more CdSe the darker red the colour.

Bigelow and Silverman[90] confirmed the conclusions as found by Rooksby in an investigation published in 1933. They started with following sodium-zinc-silica glasses:

$$\mathrm{Na_2O : ZnO : 8SiO_2}$$
$$\mathrm{Na_2O : ZnO : 7SiO_2}$$
$$\mathrm{Na_2O : ZnO : 6SiO_2}$$
$$\mathrm{Na_2O : ZnO : 5SiO_2}$$
$$\mathrm{Na_2O : ZnO : 4SiO_2}$$
$$\mathrm{Na_2O : 2ZnO : 4SiO_2}$$
$$\mathrm{2Na_2O : ZnO : 4SiO_2}$$

After a smelt study they took the glass according to the composition $\mathrm{Na_2O : ZnO : 4SiO_2}$ as a foundation glass. After a great number of trial smelts they concluded that the best ruby glass was obtained by adding 2.0 % selenium, 1.0 % cadmium sulphide, 1.0 % arsenic trioxide and 0.5 % carbon to the basic glass batch. The glass made in this way was annealed for 30 hours at 350 °C to 400 °C and further subject for X-ray examinations. For this investigation they prepared solid solutions of CdS and CdSe and compared this with the ruby coloured glasses. As a result they found that the values for the lattice parameters a_o and c_o and the ratio $c_o : a_o$ for both the solid solution and the colouring agent in the glass had such an agreement that one could conclude that the colouring agent in the glass was a solid solution of CdS and CdSe. This was a confirmation of the results as found and published by Rooksby.

In 1934 a patent was granted to E. I. du Pont de Nemours in the USA.[91] In this patent it is claimed that a glass without cadmium sulphide and/or selenium, is added an amount of cadmium sulphoselenide (CdS · CdSe) together with elementary cadmium. Following the patent it was possible to obtain the final colour directly after quenching and it was no longer necessary to make use of an annealing process. It may be noticed that they mentioned exactly the same glass composition as published and used by Bigelow and Silverman, namely $\mathrm{Na_2O : ZnO : 4SiO_2}$. In this patent it is already stated that oxidizing batch components like nitrates must be avoided. On the contrary, one must made use of reducing components such as carbon, sugar or tartaric acid.

The second claim in this patent mentions that the selenium in the cadmium sulpho selenide can be replaced partly by tellurium. Although this is also mentioned in earlier publications it never has found a real great application in the practice of ceramic glaze manufacturing. Besides the reason of a less stable colouring result with tellurium, the price is also very important. An indication for the price, valid per 28.12.2007, for selenium metal is US$ 60/kg and for tellurium US$ 137.50/kg.[92)]

Before WW-II the classical CdSSe pigments were applied for onglaze decoration firing, for colouring porcelain enamels and only to a minor extent as a ceramic stain. These types of products were fired at abt. 800 °C for 15 minutes and the pigments of that time could just stay at those firing temperatures. From there, during the 50ties, the pigments were also started to be applied in low firing glazes which were first based upon the formulation of porcelain enamel frits. As the final results were very attractive, one started to improve the pigments as well as the glazes to make them more suitable for higher firing temperature glazes.

During the 50ties and 60ties of last century there were mainly two ways to produce the yellow and red CdSe glazes viz. a pigmented type and a melted-in type. For the yellow pigmented type one added a CdS to a suitable base glaze resulting in a bright yellow glaze with, however, a limited firing range. The other way was a melted-in method where a S compound, S as flowers of sulphur or as ZnS, was melted-in into a cadmium containing frit composition which was suitable for that. In most cases, these glazes also contained a certain amount of cadmium carbonate (2 or 3 %) as mill addition to support the yellow colour development.

An example for such a pigmented yellow glaze is following composition:

base frit (PbO and CdO containing)	94.50 %
cadmium sulphide	2.50 %
cadmium carbonate	2.00 %
bentonite	1.00 %
	100.00 %

For red glazes there was a similar way: on one hand the method of adding a CdSSe pigment to a suitable base glaze and on the other hand a melted-in method. The latter method rendered better results for firing stability and had also a better firing range.

An example of a very clear, bright and real red pigmented glaze as used during the late 60ties and early 70ties of last century was following:

base frit (PbO and CdO containing)	91.85 %
boric acid	4.50
quartz fine	1.50
calcium phosphate	0.80
red stain CdSSe	1.35
	100.00 %

The base frit was dry milled first. The boric acid, quartz and calcium phosphate were mixed separately first and later added. The complete receipt was dry mixed.

Both methods, the pigmented as well as the melted-in method, however, were not stable enough for the ceramic industry which started to demand for more stable glazes and for CdSe glazes suitable for higher firing temperatures. In the late 50ties and early 60ties of last century the melted-in reds had already a better firing stability compared to the pigmented types. Some sources mention Mondré & Manz as being the first company which brought melted-in CdSe glaze on the market, followed by Reimbold & Strick, Degussa and Ferro (Holland) B.V. There is a brochure dated 20th January 1961 where Ferro (Holland) B.V. announced that they have a stable red cadmium selenium glaze for firing at 980 °C – 1000 °C. This glaze, with reference number 55148, was a pigmented glaze. The melted-in type of glazes followed later. Also in 1961 a patent was turned in by W. Wanie[93] and published in 1969. The patent describes a method (example 1) to obtain a red colour by applying 18 weight percent of a CdSSe pigment and in the other examples it claimed the development of red colours by melting in all relevant components in one frit. The patent has been opposed at the time by Mondré & Manz and Ferro (Holland) BV.

In the 60ties of last century these glazefrit formulations for the melted-in CdSe glazes were basically derived from the red glass compositions. The basic idea was that the red colour was based on the mixed crystal of CdS · CdSe and so the frit compositions had these components in their composition. Some improvements were realised by making other choices for the raw materials like e.g. sodium- or zinc selenites instead of the elements Se as metal and zinc sulphide as sulphur source instead of S as flowers of sulphur.

As some typical base frit compositions for melted-in yellow glazes at that time can be mentioned:

	Na_2O	0.284	Al_2O_3	0.098	SiO_2	2.380
	K_2O	0.062	B_2O_3	0.122	S	0.083
	BaO	0.283				
	ZnO	0.335				
	CdO	0.036				
or	Na_2O	0.242			SiO_2	1.667
	BaO	0.262			S	0.046
	CdO	0.031				
	ZnO	0.465				

In most cases the cadmium was introduced as cadmium oxide and the sulphur as zinc sulphide. These frits were the basic frits for yellow melted-in cadmium glazes. The milling formulae of the glazes had often 2 % of cadmium carbonate to support and stabilize the colour development.

A typical glaze composition for a melted-in type of yellow glaze was as follows:

basic frit containing Cd and S	60 %
supporting frit containing Pb and Cd	21 %
addition frit lead free	7 %
cadmium carbonate	2 %
kaolin	4 %
ball clay	6 %
	100 %

It was clear that one had to create certain conditions with regard to the compositions of the yellow and red glaze frits to realize a good colour development and to avoid all kinds of ceramic defects such as crater-forming, boiling, burning-away of the colour, etc.

The fact that compositions of yellow and red glazes are restricted in their compositions is also illustrated by the following fact. Table XI shows analyses made in 1972[94] of four cadmium yellow glazes of four different manufacturers. As can be seen, the compositions do not deviate that much. All four glazes are in general comparable after firing although they differ on minor points.

The fact that frit and glaze compositions often have a preferred composition for the best possible development of a given colour is well known in ceramics. This is certain so in case of cadmium yellow and red frits and glazes. What the analyses, however, does not tell is how the different glazes have been manufactured. For sure, each of the glazes is built up from various frits. How these different frit compositions differ and, even more important, how these frits have been manufactured cannot be seen from the analyses neither the milling formulae of the glazes.

Prod. ref.	43276 Degussa	60576 R&S	32901 Mondré&Manz	53451 Ferro Holl.
Li_2O	ca 0.12 %	ca 0.12 %	ca 0.28 %	0.15 %
Na_2O	6.0	6.5	7.4	7.6
K_2O	1.3	4.5	8.0	0.6
CaO	0.5	0.02	0.3	0.1
MgO	traces	0.5	traces	traces
BaO	14.0	15.0	8.6	11.3
PbO	2.5	0.1	0.1	2.9
ZnO	5.3	10.0	12.5	10.7
CdO	3.4	2.7	2.2	2.7
Al_2O_3	5.4	3.8	n.a.	5.4
B_2O_3	4.8	n.a.	traces	5.9
SiO_2	52.0	50.0	52.0	52.0
F				0.3
S				0.4
SrO	traces	traces	traces	traces
c.o.e. (3α)	229×10^{-7}°C	239×10^{-7}°C	252×10^{-7}°C	221×10^{-7}°C

Table XI: Chemical analyses of cadmium yellow glazes from four different manufacturers (1972)

The development for a more stable glaze formulation was soon focused on the splitting up of the basic frits. From many trials it became clear that the optimum melting conditions for one component (S) worked out very negative for the other component (Cd). Investigations at the various frits learned that the loss of cadmium can easily go up to 80 % due to volatilization during the melting of the frit.[95] In case the melting conditions were not optimal the cadmium oxide could rather easily be reduced to cadmium metal which is even more volatile than cadmium oxide.[96] Also the melting temperature had a dramatic effect on the retaining of the cadmium in the frit. Investigations clearly showed that bringing down the melting temperature from 1450 °C to 1350 °C while maintaining the same yield resulted in a 50 % less loss of cadmium oxide in the molten frit. The combination of these two facts and information as e.g. from the German patent 2 023 710 from Hercules Inc. was the start for a study for the development of a new generation of base frits for cadmium yellow and red glazes. The start was made by splitting up the basic (Cd + S) frit for yellow glazes in a frit containing the cadmium and another part containing the sulphur and in such a way that the two frits together matched the same original basic frit again. Next step was to melt the splitted frits under three different melting conditions, viz. oxidizing, neutral and reducing melting conditions. See also Table XII. For the oxidizing conditions the choice was made in the end for the introduction of 2 % sodium nitrate in the raw batch composition. For the reducing conditions a choice was made for melting with less air and with a reducing agent in the batch composition. After testing various possibilities carbon (C) was taken as the reducing agent. Also sugar was tried but was less effective. SiC was also tested with good reducing properties but the disadvantage was that it causes contamination of the frit and later contamination of glazes in the mills resulting in pinholes.

Cd containing frit	S containing frit
Melting conditions	Melting conditions
(i) oxidizing	(iv) oxidizing
(ii) neutral	(v) neutral
(iii) reducing	(vi) reducing

Table XII: Experimental melting conditions for cadmium and sulphur-containing frits

Testing of the application of carbon as reducing agent learned that a quantity of 2 % was the optimum; 1 % was less effective and more than 2 % didn't render better results. These six frits (see Table XII) were tested again in the standard glaze composition by making combinations of resp. the oxidizing melted Cd frit (i) with the three different molten S frits (iv, v and vi); the neutral melted Cd frit (ii) with the three different molten S frits (iv, v and vi) and the reduced melted Cd frit (iii) with the three different molten S frits (iv, v and vi). The results clearly confirmed that the cadmium frit needed different smelting conditions as the sulphur containing frit. By combining the cadmium frit melted under oxidizing conditions (i) and the sulphur containing frit melted under reducing conditions (vi), the final results were significant better compared to the original yellow glaze formula.

Next step was to realize a really low-melting frit for the cadmium component as this had shown that it was the best way to retain as much as possible cadmium in the frit. Normally, an addition of the cadmium frit in the glaze composition was rather high to have a contribution of about 2 till 3 % of cadmium oxide through the frit. As the influence of a high amount of frit with low melting compositions should be too big in the glaze compositions, the choice was made for a cadmium content as high as possible in the low melting frit compositions. Two different low melting compositions were chosen as starting point, viz. a lead silicate and a sodium boron silicate.

In the lead silicate the one mol PbO was partly replaced by CdO:

(a)	PbO	0.50			SiO_2	2.00
	CdO	0.50				

and in the sodium boron silicate the sodium was partly replaced by CdO:

(b)	Na_2O	0.50	B_2O_3	0.25	SiO_2	2.50
	CdO	0.50				

These two frits were tested in combination with the same S-containing frit (vi) to control its effectiveness. From all trials it appeared very clearly that the cadmium frit based on the lead silicate gave a good yellow colour but only till rather low firing temperatures (1040 °C – 1060 °C). The cadmium frit based on the sodium boron silicate, however, showed good and strong yellow colour development also on higher firing temperatures. It was known that about 80 % of the cadmium was evaporating from the basic frits having both cadmium and sulphur in its composition. Therefore, the amount of cadmium in the new trial frits was investigated. The

theoretical amount of CdO in the batch formula of the frit (b) is 24.38 %. After melting the amount was 24.02 % which means a loss of only 2 %. A tremendous improvement was realised with regard to retaining of the cadmium in the frit. One of the reasons was that a choice was made for easy and quick melting raw materials as boric acid and hydrated borax. The idea behind it was that these components start to melt very early. When boric acid is heated it gradually looses water until anhydrous boric acid (B_2O_3) is formed.[97] This boric oxide melts at about 325 °C. Borax ($Na_2B_4O_7 \cdot 10H_2O$), on heating, begins to melt at 62 °C with frothing and five molecules of the crystallisation water have been lost at 100 °C. Four more molecules are lost at 160 °C until it is completely dehydrated at 400 °C. In fritting processes borax pentahydrate ($Na_2B_4O_7 \cdot 5H_2O$) is also often used. Dehydrated borax starts melting at 741 °C and is therefore a preferred material to starts the melting process during fritting. The early start of melting of boric compounds takes care that the cadmium oxide is already enwrapped by the molten boron components before going into solution and cannot evaporate that easy.

The following step was trying to improve the sulphur containing frit. By varying the amount of sulphur and also the source of it, it became clear that an amount of 1 % was the optimum. With 2 % sulphur or more a lot of bubbles appeared in the fired glaze which was even worse with 3 %. The introduction of S through zinc sulphide (ZnS) was shown the best one regarding the retaining and the stability of the frit.

Variations of the components learned following:

aluminium oxide:	makes the compositions too hard at rather low percentage (4 %).
soda:	is not harmful for the yellow colour development very smooth surfaces can be realised, however, the influence on the coefficient of expansion becomes too big.
borax:	an amount between 5 and 15 % is not disadvantageous for the yellow colour. A bigger amount increases the forming of the vein structure of the glaze.
quartz:	not disadvantageous.
zinc oxide:	if more than 10 % is put into the formulae it has a clearly negative influence on the yellow colour development.
barium carbonate:	at quantities varying between 0 and 20 % no negative influence has been noticed.
zinc sulphide:	is needed for the necessary amount of sulphur.
fluorspar:	negative effect: forming of matt spots and craters.
calcium carbonate:	not negative for the yellow colour. Bigger amount makes the glaze too hard.
strontium carbonate:	same as for calcium carbonate.
carbon / norit:	is necessary as reducing agent.

All these testing of different raw materials finally resulted in a stable frit with a strong yellow colour development. Lithium was also tested, replacing part of the sodium content. It resulted in a very smooth surface at temperatures of 980 °C – 1020 °C but the strength of the yellow colour

became less, especially at the sharp rims of darker coloured bodies and at higher temperatures (1080 °C – 1120 °C).

All the investigations resulted in the following basic sulphur containing frit:

Na_2O	0.467	Al_2O_3	0.129	SiO_2	2.346
K_2O	0.052	B_2O_3	0.112	S	0.077
CaO	0.173				
ZnO	0.308				

This sulphur containing frit melted at about 1350 °C under reducing conditions (meaning with less air than normal and including a reducing agent in the batch formula), together with the cadmium containing frit melted at 1250 °C under oxidizing conditions was the base for a new strong cadmium yellow melted-in glaze. Its colour strength was compared to the standard cadmium yellow glazes by mixing 50 parts of the yellow glazes with 50 parts of a standard cadmium red glaze. With this test it was clear that the new frit combination gave a much more yellow-orange colour compared to the 'old' frits which was an indication that the new yellow glaze had more colour strength compared to the old glaze composition.

Now having the best possible cadmium and sulphur base frits, the next step was trying to find the best possible glaze composition which should fit the requirements as covering power and colour strength also on dark manganese bodies, covering power on sharp rims of cups and saucers, firing stability on high firing temperatures as high as 1200 °C, etc. Various addition frits were tested among them high and low lead containing frits, very stable and proven unleaded alkali-calcium frits, high barium containing frits, zinc containing frits, etc. and finally the best composition was found:

basic sulphur containing frit	48 parts
basic cadmium containing frit	7 parts
transparent u/l addition frit	32 parts
sodium boron silicate	8 parts
ball clay	5 parts
	100 parts

This glaze was tested at customers under various firing conditions and production conditions, on various bodies (white, red and manganese brown burning), at both wall- and floor tiles and at vases and dinnerware and showed good colour strength even at 1200 °C. One of the best and very temperature stable cadmium yellow glazes with high colour strength was born.[98] This glaze is still promoted and in the market as can be seen in Ferro's Technical Information GL07.

As can be noticed no addition of cadmium carbonate was necessary anymore to stabilize the yellow colour. This was an improvement regarding the health and safety regulations besides the economical advantage. The glaze powder was tested according to the stomach acid simulation test ($\frac{1}{4}$ N HCl for 1 hour) and the lead- and cadmium release was found below the limits set. Also

a lead- and cadmium release test with 4 % acetic acid for 24 hours (DIN EN 1388-1/-2) showed a release below the limits as set for this test.

The investigations continued with the aim to improve the existing red cadmium selenium glazes in the same way as the yellow glazes. Till the end of the 60ties – early 70ties the basic frits contained cadmium as well as sulphur and selenium. Also here, a split was made in the way that the necessary amount of cadmium was introduced through the new developed and low melting and concentrated cadmium frit. The sulphur was in most cases introduced already through zinc sulphide. The necessary amount of selenium was introduced through an alkaline selenite, mostly sodium selenite (Na_2SeO_3) or zinc selenite ($ZnSeO_3$).

Now a switch is made to the manufacturing of CdSSe red colour stains as the development made in that area had later on a great impact on the cadmium-selenium frit and glaze development. Till the end of the 19th century CdSSe stains were made in a dry way by mixing the materials cadmium sulphide, sulphur and metallic selenium together and heating the mix in a, sometimes rotating, kiln at about 600 °C.

Different manufacturers may have applied somewhat different combinations of raw materials and firing conditions but this was the general basis.

It doesn't ask that much imaginative faculty to realise that this method was very much unhealthy and uneconomical due to the volatibility of the selenium metal and also the cadmium compounds. This method was step by step replaced by the wet-chemical precipitation method which was invented by BASF in 1919. By this process the Se metal was dissolved in Na_2S. This solution was added to a cadmium salt solution. A precipitate of cadmium-sulpho-selenide (CdSSe) was the result and this precipitate was washed and dried at the proper temperature. By changing the amounts of resp. cadmium, sulphide and selenium, but also with additions of e.g., zinc oxide or aluminium oxide, one was able to influence the colour tone of the pigment. This wet method replaced the dry method more and more during the 20th century.

Following this process for the wet preparation of CdSSe stains, a method was found in the early 70ties for a better introduction of these components for the selenium frit production. This method was very similar to the method of the wet preparation of CdSSe stains. Basically, the cadmium was replaced by zinc and the following procedure was followed:

- zinc sulphate was dissolved in water of 50 °C and pumped into a reaction vessel
- sodium carbonate was also dissolved in water of 50 °C and also pumped into the reaction vessel
- sodium sulphide was dissolved in water of 45 °C and a quantity of selenium metal was added, stirred till it was dissolved
- the sodium sulphide + selenium solution was pumped into the reaction vessel resulting in a precipitate
- washing of the precipitate and centrifuging of the washed material
- drying of the material.

The reactions which took place were following:

(i) $ZnSO_4$ solution + Na_2CO_3 solution

$$3H_2O + 5Zn^{2+} + 5CO_3^{2-} \longrightarrow Zn_5(CO_3)_2(OH)_6 \downarrow + 3CO_2 \uparrow$$

(ii) Na_2S + Se solution

$$Na_2S + Se \longrightarrow 2Na^+ + SSe^{2-}$$

(iii) (i) + (ii)

$$Zn_5(CO_3)_2(OH)_6 \downarrow + 3SSe^{2-} \longrightarrow Zn_5(CO_3)_2(SSe)_3 \downarrow + 6OH^-$$

The resulting precipitate of zinc-sulpho-selenide (ZnSSe) was centrifuged, dried and later on mixed with quartz in a ratio 1 : 3 for better handling and weighing of the precipitate.

The precipitate of zinc-sulpho-selenide had the following typical composition:

Se :	33.2 %
Zn :	35.7 %
S :	9.0 %
moisture :	6.2 %
H_2O sol. :	0.7 %

The mixture of quartz and ZnSSe was used as raw material to introduce the necessary S and Se in the basic frits for red glazes.

Also in these cases a significant improvement was realised with regards to a decrease of the volatilization of the component selenium. Most of the systems for making basic red frits of that time contained cadmium as well as selenium and sulphur at the same time. Analyses of production molten frits learned that up to 83 % of the cadmium disappeared after melting. The figure for selenium was abt. 52 % and for the sulphur in these type of frits abt. 91 %.

A typical basic frit for cadmium red glazes was:

quartz	56.77 %
sodium carbonate	20.80 %
zinc oxide	8.87 %
zinc sulphide	2.66 %
alum.oxide	2.80 %
boric acid	4.27 %
cadmium oxide	1.70 %
zinc selenite $ZnSeO_3$	2.13 %
	100.00 %

The knowledge of the new frits as developed for the yellow frits and glazes was transferred for the development for new basic frits for red frits and glazes. Of course, the cadmium was separated from the basic frits in the first place. The raw material zinc selenite as source for Se was changed for the zinc-sulpho-selenide (ZnSSe) and the reduction agent carbon was introduced into the raw batch formula. Some other small adaptations were made in the composition but it is mainly the different way of melting which made these types of frits much better with regard to the red colour development and the colour strength.[99]

An example of such a modified frit is:

quartz	56.73 %
sodium carbonate	20.73 %
zinc oxide	10.50 %
zinc sulphide	0.67 %
alum.oxide	2.80 %
boric acid	4.23 %
norit	2.00 %
zinc-sulpho-selenide	2.33 %
	100.00 %

Through XR-F analyses a comparison was made between the 'traditional' melted frit and the new developed frit. Results are mentioned in Table XIII.[100]

contains		**theoretical**	**amount**	**after**	**melting**	**% volat.**	
old	**new**	**old**	**new**	**old**	**new**	**old**	**new**
CdO	-	1.90 %	-	0.14 %	-	92.6 %	-
Se	Se	0.98 %	0.90 %	0.31 %	.77 %	68.4 %	14.5 %
S	S	0.98 %	0.74 %	0.41 %	0.28 %	58.2 %	62.2 %

Table XIII: Comparison of volatilization losses (Cd, Se, S) between traditional and modified frit melting processes

The important changes in the batch compositions of the sulphur frit for yellow and the suphur/ selenium frits for red were of course very important for the retention of the red colour. However, the way of melting was and is also important. It may be clear that an oxidizing melting atmosphere was and is easier to obtain in a melting kiln (continuous or batch/rotating) than a reducing atmosphere. Although one speaks about a reducing atmosphere it is of course not possible to create a real reducing atmosphere in e.g. a continuous melting kiln of 1.80m by 4.80m with a double feeding system and at melting temperatures of about 1350 °C where a sufficient amount of gas and oxygen is necessary to reach the smelting temperature and to maintain it as well. A reducing atmosphere here means that the oxygen was reduced as far as possible. Also the draught in the melting kiln could not be reduced completely as this had a very negative effect

on the quality of the frit. The experience of how to melt these frits was very important and also difficult to lay down in fixed instructions as it happened quite often that one kiln reacted different than another similar melting kiln. One of the measurements taken was to smelt a high viscosity zircon white frit at temperatures as high as 1400 °C – 1425 °C before smelting a production run of basic frits for red or yellow glazes. In this way the bottom of the melting kiln had a smooth and stable surface when the basic red and yellow frits followed at lower temperatures, e.g. 1350 °C. The zircon frit stayed rather stiff at the bottom of the kiln and experience learned that the basic frits for red and yellow glazes were less contaminated and more stable. As many people involved in classical ceramics know: ceramics is for a major part an empirical science. Trial and error is for ceramic people a way of life. Production of cadmium selenium frits and glazes has therefore always been a job which asked the highest discipline and cooperation between the various people involved from chemical and ceramic laboratories, production (melting, milling, drying) and quality control.

With these new basic frits for cadmium selenium red glazes and together with the earlier mentioned concentrated cadmium frit, it was possible to create new and very stable cadmium selenium red glazes for all kind of applications.

Besides the concentrated cadmium frit already mentioned, other concentrated cadmium frits have been developed e.g. with the target to develop CdSe glazes with a lower coefficient of expansion resulting in a composition like:

Na_2O	0.353	Al_2O_3	0.054	SiO_2	3.871
K_2O	0.137	B_2O_3	0.630		
CdO	0.510				

With this handful of basic frits it was very well possible to create an endless range of CdSe glazes. During the 70ties, thousands of tons of cadmium selenium yellow and red glazes were produced per year by the various but only a handful of suppliers and applied onto wall- and floor tiles, giftware, vases, dinnerware, etc. The production of these type of glazes needed attention of people from ceramic development laboratory, quality control, and the various production disciplines like melting and milling department. To produce a given glaze every time to the same colour and same characteristics, first a choice was made for the red and yellow frits of specific batches out of a production run. This was done because it could happen that some molten batches of red frits were more red or less red than others. A small test was then made where the specified frit batches were used in the milling formula of the glaze. In case the result was approved, a production mill (e.g. 5 tons of material) was charged with the specified batch references of the frits involved and the production milling was started. After milling and controlling the glaze slib was mixed with similar prepared glaze slib of the same glaze reference before it was finally pumped to a spray drier. In this way, manufacturers could make a stable glaze for colour and colour strength all the time.

The ‘space’ in the glaze compositions between the sum of the necessary basic selenium and cadmium frits and the total composition allowed applying other frits which could answer certain demands from the market. Especially here, this ‘space’ was utilized by technical ceramic engineers to realize certain targets as set by customers. As there were many customers with

many different kilns and firing cycles, the necessary adjustments were made using this ‘space’ in the glaze composition. The advantage was that fairly quick a solution was found for a given problem but the disadvantage was that there was a kind of unlimited growth of new cadmium selenium glazes. As long as volumes justified this way of working there were no problems but as soon as volumes started to drop down the production had so its difficulties with keeping up the quality, same colour and colour strength for all these, sometimes only slightly, different glazes.

As an example how this space was utilized the various matt glaze compositions can be mentioned. The space in the glaze composition was partly filled up with a suitable matt frit, resulting in a nice and stable matt red, orange or yellow glaze.

To realize the required matt surface structure, different matt frits were used in different quantities and in combination with other transparent basic frits to give e.g. good melting and flow properties to the glaze. The particular choice which matt system should be used was dictated by the kiln and firing conditions at the customer site and, of course, which particular colour and surface structure was required.

Good and stable matt glazes have been developed as this was also a strong demand from the market during the 70ties of last century especially for floor tiles. Different methods to arrive at a satisfying matt result have been investigated. It was tried to modify the basic cadmium and sulphur / selenium frits already to create matt glazes. All these investigations did not render any good results. The basic selenium / sulphur frits are very sensitive for changes and the fired results of modifications were very often a crater-like landscape. All modifications which were made resulted in a worse result as basic red frits. Another way was to take an existing barium matt frit and implement the necessary sulphur / selenium into this frits. Also these trials all failed.

As barium carbonate as powder is rather unhealthy, special frits have been developed based on barium aluminium silicate with compositions like:

	BaO	1.000	Al_2O_3	0.500	SiO_2	2.018

Some other frequently used barium matt frits were e.g. frits with following composition:

	Na_2O	0.032	Al_2O_3	0.324	SiO_2	2.061
	K_2O	0.066	B_2O_3	0.046		
	CaO	0.093				
	BaO	0.256				
	PbO	0.502				
	ZnO	0.051				
and	BaO	0.400			SiO_2	0.700
	PbO	0.100				
	ZnO	0.500				

Together with this type of matt frits some special cadmium selenium glazes for application onto floor tiles have been developed such as:

Matt red glaze through Ba-aluminate for 1080 °C – 18 hrs firing cycle:

basic red frit	28.2 %
basic yellow frit	31.6 %
basic cadmium frit	12.8 %
lead mono silicate	3.5 %
Ba-aluminate	16.2 %
kaolin	4.3 %
alum. oxide fine	3.4 %
	100.0 %

Matt red glaze through Ba-Al-Si frit for 1040 °C – 18 hrs cycle. No crazing after 1 h – 7 bar autoclave test.

basic red frit	14.6 %
basic yellow frit low c.o.e. version	22.6 %
basic cadmium frit low c.o.e. version	15.4 %
Ba-Al-Si frit	43.8 %
kaolin	3.6 %
	100.0 %

Matt red glaze through a Ba-Pb matt frit for a firing cycle of 1020 °C – 18 hrs:

basic red frit	25.0 %
basic yellow frit	17.5 %
basic cadmium frit	7.5 %
Ba-Pb matt frit	21.0 %
Na/K/Ca/Al/B/Si frit	16.5 %
alum.oxide fine	6.7 %
ball clay	5.8 %
	100.0 %

Another method for making matt cadmium selenium glazes was the addition of barium carbonate and aluminium oxide in a certain ratio to existing red and yellow glazes as also described in the German patent ref. 2 006 814 from Baykara.[101]

Also more brilliant and glossy glazes could be made in that way like the glaze which is used for the vase as shown with photo 1. In that particular case a zircon white frit and a lead aluminum silicate frit were used to obtain a very smooth and brilliant surface:

basic red frit	27.2 %
basic yellow frit	21.7 %
basic concentrated cadmium frit (i)	5.1 %
basic concentrated cadmium frit (ii)	14.0 %
zircon white frit	15.0 %
lead alum silicate frit	15.0 %
kaolin	1.7 %
bentonite	0.3 %
	100.0 %

Cadmium selenium glazes for screen print application were specially developed. Next to the basic red, yellow and cadmium frits, these glazes contained frits with e.g. good flow properties. For application of those glazes, in most cases over a zircon white glaze, a screen of 18T was advised and a screen print medium based on e.g. polyethylene glycol.

Glossy red screen print glaze for over zircon white glazes:

basic red frit	27.7 %
basic red frit	21.5 %
basic yellow frit	3.6 %
basic cadmium frit	6.4 %
Na-B silicate	21.4 %
zircon frit	5.7 %
zinkoxide	3.0 %
	100.0 %

The above mentioned glazes are examples of glazes which have been developed and have been in production for a certain period, mainly in the 70ties and 80ties of last century. Besides these glazes many more glazes like these were developed in the same way. The glazes are examples of how a certain surface, colour or effect can be realized by making use of the ‘free space’ in the glaze formulae. This way of working could only be done by the glaze manufacturers as basic red, yellow and cadmium frits have never been free available on the commercial market.

From the basic frits there have been developed various standard cadmium selenium glazes which were directed already into a specific application, e.g. for normal twice firing, for high firing / once firing, suitable for wall- or floor tiles, for vases, giftware, white or coloured bodies, etc.

Next to that the standard glazes were also used as starting points and additions were given to develop a specific colour shade, surface appearance, gloss, a higher abrasion resistance, etc. at customers' site. Some of these additions were:

material	addition	result
corundum	10 to 30 parts	higher abrasion resistance
zirconium silicate	10 to 30 parts	higher abrasion resistance
mixture of wollastonite, al.oxide, kaolin and petalite	20 to 30 parts	higher abrasion resistance
alkaline boron silicate	5 to 10 parts	to smoothen the surface and increase gloss
lead alumina silicate	10 to 20 parts	to increase gloss, less texture, lower thermal expansion
zircon white frit	10 to 30 parts	to decrease texture, lower thermal expansion
barium / lead matt frit	10 to 30 parts	to achieve matt structures
barium / alum. frit	10 to 30 parts	to achieve matt structures
ball clay	5 to 10 parts	improve glaze suspension properties
bentonite	0.3 to 0.5 parts	improve glaze suspension properties
cobalt oxide or silicate	1 part	addition to cadmium yellow gives a nice avocado green
chromium oxide	1 part	addition to cadmium yellow gives a nice light green. Addition to red / yellow glaze combination gives a mustard colour

In this way many standard cadmium selenium glazes have been customized to fit customers' requirements technically and aesthetically. Some examples of such glazes are:

Cadmium selenium red glaze.
Glaze for SITI multi layer roller kiln 1100 °C - 3hrs (Gres de Nules, 1983).

cadmium selenium red glaze	36.19 %
cadmium yellow glaze (93618)	40.95 %
high boron frit u/l milled	22.86 %
	100.00 %

Yellow cadmium glaze for floortiles.
Heimsoth roller kiln 1160 °C – 60 min. (Halis Toprak, 1983).

cadmium yellow glaze (93618)	60.00 %
zircon frit milled	15.00 %
	100.00 %

Yellow cadmium glaze for floortiles.
Heimsoth roller kiln 1160 °C – 60 min. (Halis Toprak, 1983).

high boron frit u/l milled	15.00 %
lead aluminium silicate milled	5.00 %
zircon silicate 5μ	5.00 %
	100.00 %

Red glaze for floor tiles once firing 1130 °C
40min Heimsoth roller (Todagres, 1983).

cadmium red glaze	59.05 %
cadmium yellow glaze	3.25 %
lead boron silicate milled	22.93 %
kaolin	4.92 %
corundum	9.85 %
	100.00 %

Red glazes for floor tiles once firing 1160 °C
60min Heimsoth roller kiln. Glaze application on top of each other by disc. (Philkeram-Johnson, 1986).

	Layer 1	**Layer 2**
cadmium red glaze (i)	32.88 %	–
cadmium red glaze (ii)	–	36.36 %
cadmium red glaze (iii)	19.57 %	18.18 %
cadmium yellow glaze (93618)	14.87 %	–
lead aluminium silicate milled	7.05 %	4.55 %
high boron u/l frit milled	7.05 %	13.64 %
zircon frit milled	–	13.64 %
K-feldspar	3.91 %	–
wollastonite	3.91 %	–
zircosil 5μ	–	4.55 %
zinc oxide	0.78 %	–
bentonite	0.58 %	–
corundum 100	9.40 %	9.08 %
	100.00 %	100.00 %

Cadmium orange glaze for wall tiles firing cycle 1060 °C
16h in a Highgate kiln (H&R Johnson, 1983).

cadmium red glaze	50.0 %
cadmium yellow glaze	39.0 %
	100.00 %

Cadmium orange glaze for wall tiles firing cycle 1060 °C 16h in a Highgate kiln (H&R Johnson, 1983).

alum. oxide fine	8.0 %
zinc oxide	3.0 %
	100.00 %

Red glaze for tableware with surface structure twice firing 1000 °C 12hrs (Ker. Liboje / 1983).

cadmium red glaze	62.0 %
cadmium yellow glaze (93618)	13.0 %
Ba / Pb matt frit milled	10.0 %
lead alum. silicate frit milled	10.0 %
zircon silicate 5μ	2.5 %
talcum	2.0 %
bentonite	0.5 %
	100.00 %

Red glaze for floor tiles once firing 1210 °C 25hrs tunnel kiln (Cerabati, 1983).

cadmium red glaze	61.35 %
cadmium yellow glaze (93618)	12.27 %
Ba / Al / Si matt frit milled	21.47 %
kaolin	4.91 %
	100.00 %

These glazes were also often used in multi-layer application. As an example for a floor tile glaze which has been applied in Italy on a 25 cm × 25 cm floor tile:

Mono-firing 1160 °C – 60min. roller kiln.

1st layer:	red glaze	50 parts	application by disc
	yellow glaze	50	application weight: 55 grs wet
	corundum 150	20	
	colour stain brown	1.5	
2nd layer:	red glaze	10 parts	application by disc
	yellow glaze	100	application weight: 15 grs wet
	corundum 150	20	
3rd layer:	red glaze	20 parts	application by disc
	yellow glaze	100	application weight: 15 grs wet
	corundum 150	20	
4th layer:	coloured frit	99.5 parts	application by disc
	bentonite	0.5	application weight: 10 grs wet

The 4th coloured layer could be changed to achieve different colour effects.

Especially for single firing floor tiles with a dark firing body the application of an engobe as 1st layer was often applied. Such an engobe could have following composition:

Na/K/Ca/Al/B/Si transparent frit	5 %
feldspar (Na/K)	22 %
nepheline syenite	18 %
ball clay	33 %
aluminium oxide fine	11 %
kaolin	11 %
	100 %

Knowing the extensive lines for glaze application for wall- and floor tiles (mainly in Italy, Spain, Germany, Brasil and other countries) the different methods were used to achieve various effects e.g. a 1st thin layer of a dark coloured glaze applied by (double) disc followed by 2 or 3 different layers of different coloured cadmium selenium glazes applied by a mottling technique. These glazes could include different compounds to realize various surface effects or to increase abrasion resistance.

Another example which shows how one could ‘tailor-made’ cadmium selenium glazes is shown by Photograph 17. This ceramic tableau called ‘Walking Orange’ shows an outside of an orange which really looks like the real outside of an orange: a matt grainy surface and a so-called orange

peel effect. The effect is created among other things by adding a course aluminium oxide and other raw materials to a mixture of a red and a yellow glaze. The inside, however, of the orange also looks exactly like the real inside of an orange: this surface is more soft and glossy. This is realised by adding soft lead fluxes the get a more shiny glaze. The ratio red to yellow glaze is also different for the outside and for the inside of the orange. The white veins are made by a stiffer zircon white glaze.



Photograph 17: "Walking Orange" (1978), a ceramic tableau by the author showcasing varied glaze textures

The a.m. glaze combinations show that one could realize many different appearances of cadmium red glazes and made them suitable for each existing firing cycle at that time. Later on in the 80ties of the last century the trend colour changed and the cadmium red, orange and yellow glazes started to disappear from the volume users: wall- and floor tiles. For art- , gift- and tableware the trend continued and the glazes are still applied today for these purposes.

10.5 Defects

Although they are coloured glazes, the group of cadmium selenium melted-in glazes is always prepared by the bigger glaze manufacturers. It is not a coloured glaze in the sense of adding a colour stain to a suitable transparent glaze to achieve the required colour. Only now, with the last generation of strong cadmium selenium stains it is indeed possible to add these (expensive) stains to a transparent glaze to achieve a strong yellow, orange or red colour. But the group of cadmium selenium glazes meant here are the so-called melted-in glazes. The glazes create

their final colour out of the special composed frits which contain the colour-giving components. The glazes are made ready-to-use by the manufacturers which mean that only water needs to be added. They normally contain Westerwalder clay or ball clay, kaolin and / or bentonite to prevent the glaze from settling down. As these glazes have a rather high amount of alkali, it is to be advised to prepare only the amount of glaze necessary for a job to do or an amount which will be finished during a working day. In case some settling should appear the normal setting up agents as calcium chloride or magnesium chloride can be used to keep the glaze in suspension.

The group of cadmium selenium glazes sometimes shows some defects which are more or less typical for these glazes. Especially for the melted-in cadmium selenium glazes counts that they must meet certain requirements with regard to the composition for a good colour development. These requirements results e.g. in a substantial amount of alkali components (mostly sodium) resulting in a rather high thermal coefficient of expansion (c.o.e.) with a typical figure of (3α) 210 to 240 $\times 10^{-7}$ for these glazes. The result is that most of the cadmium selenium glazes show crazing at the normal applied earthenware and stoneware type of bodies. Only during the 70ties and when the demand for red-glazed articles was that high, some manufacturers applied a special body with increased coefficient of expansion resulting in a craze free red glaze. In many other cases the inside of vases was and is glazed in such a way that the inside glaze was not crazing and therefore not leaking when the vase was filled up with water. This procedure is still applied today e.g. for flower vases where a cadmium selenium red glaze is applied on the outside and a transparent semi-matt glaze is applied on the inside. Application of the glazes is done by automatic spraying machines on the pressed and dried body and the articles are subsequently once fired at about 1050 °C.

Extensive investigations have been made during the 70ties for the development of a craze free red glaze starting from the frits. Trials to lower the thermal c.o.e. of the glaze were focused on (i) lowering the c.o.e. of the basic selenium-sulphur frit; (ii) lowering the c.o.e. of the basic cadmium frits and (iii) lowering of the c.o.e. of the low cadmium containing transparent supporting frit. The average thermal c.o.e. (3α) for a cadmium selenium red glaze is 220 $\times 10^{-7}$. Target was a c.o.e. of about 180 $\times 10^{-7}$.

However, it is possible to obtain similar good results for the red glaze characteristics by lowering the c.o.e. of one of the composing frits (i, ii or iii) but as soon as all basic and necessary frits (i, ii and iii) are modified to lower c.o.e. versions, the characteristics of the red glaze changes. In most cases it resulted in glazes which were too hard and/or had a too short a maturing range.[102] This was the reason that one stayed with the standard red glazes which had been accepted by the market knowing that crazing was simply an unavoidable characteristic property of the glazes. What often was done to decrease the c.o.e. of the cadmium selenium red glazes was an addition of a zircon white frit with a c.o.e. of approx. 168 $\times 10^{-7}$ or a suitable lead free transparent frit, also with a c.o.e. of approx. 168 – 170 $\times 10^{-7}$. Also additions of a frit with an extreme low c.o.e. were applied.

Such additions to red glazes (up to 15 parts) helped to decrease the c.o.e. but the glazes were in most cases not craze resistant to a Harkort test.

Another phenomenon which occurred at the production of e.g. red glazed vases but also tiles was blistering; quite an amount of open and closed craters on the glaze surface often together with matt spots or matt areas. The defect appeared very often at only one side of the fired articles and a closer inspection often learned that it was always the place where the gases passed the

articles, in any case places with a less good ventilation. Changing and improving the ventilation in the kiln (more volumes of air) normally improved and prevented those defects. Also a more open setting is helpful although there is a loss of capacity in that case.

A rather open setting and enough ventilation is even more important when more organic compounds are involved e.g. in a decoration firing. In such cases all the organics has to be burned off before the glaze matures. In case of less good ventilation this may cause problems resulting in pinholes and/or small bubbles. The reason can be that for the printing media and the cover coat often poly acrylate resins are used. Most of these components start to decompose at 360 °C at which temperature gases are formed from these organic materials which must be removed from the kiln as soon as possible. If not enough air/oxygen is available to remove these organic gases, the vapour pressure is increasing in the first part of the kiln which may result in pinholes and small bubbles. For a complete burning off of one gram of these polymers one needs about 10 liter of air/oxygen.[103] This makes clear that a good ventilation and a more open setting is very important in firing cadmium selenium red glazes.

A typical defect for cadmium yellow and cadmium selenium red and orange glazes are also the black or brown spots visible in the fired glaze and destroying the nice warm and uniform colour of the article. The root cause of this defect is in almost all cases small metal or metal oxide impurities. A reason can be a contamination of the body by small metal or metal oxide parts (like pyrite). It is also possible that a piece of production equipment e.g. for the glaze preparation (stirrer, sieves, pumps, etc.) shows too much wearing resulting in small metal parts coming into the glaze slip. A magnet can prevent further damage and clean up the glaze. In case of copper metal particles this is, however, not possible. Many of these dark coloured spots have been investigated by making a cross section of the fired piece and investigating the particular spot with the help of XR-F. In the majority of these cases the observations using an optical microscope learned that the contamination was in most cases originated from the body and that it was confirmed by XR-F analyses that Fe in most cases was the reason for the dark coloured spot.

Sometimes transparent colourless rims appeared, especially the rather sharp rims of cups and saucers. As an explanation for these phenomena is given that soluble salts are moving to the rims after application of the glaze and when the glaze is still wet. Drying of the article starts from the rims so the moisture goes from the mid parts of the article to the rim taken the soluble salts with it. The moisture disappears at the rim leaving the salts behind. Those places with higher concentrations of soluble salts will result in a lower surface tension of the glaze and therefore a thinner glaze layer after firing. In this thinner glaze layer the red colour will disintegrate and a colourless layer appears.

Some red and yellow glazes, not all, sometimes showed a white film over the glaze after firing. This white film is also caused by salts like sodium sulphate which have moved to the surface area during drying of the articles while the glaze is still in a wet state. In these cases an addition of a barium salt to the glaze slip helps to prevent the white film.

10.6 Vein structure

Another aspect of the melted-in cadmium selenium glazes versus the pigmented glazes are the so-called veins in the glaze. The melted-in cadmium selenium glazes always have a more or less cloudy appearance while the pigmented red glazes more look like a lacquer red. These veins are

sometimes visible with darker rims. Some glazes have an outspoken vein structure, some less. This has mainly to do how the glaze is built up. The composition of the glaze as well as the firing cycle have an influence on the final appearance of the glaze and the vein-structure. As contrasted with the melted-in glazes, the pigmented type of red glazes never show this phenomenon. If one prepares cross-sections of the fired glaze and have a closer look with an optical microscope one can determine that the veins are in fact transparent 'canyons' formed between the 'clouds' of the red glaze. The darker parts of the veins are in most cases caused by a shadowing effect. These darker coloured striations are generally located on ridges or overhangs of canyons of clear glass between the 'clouds' of the red coloured glaze. It can also be noticed that in many cases the top layer of the glaze is transparent as also the intermediate layer between glaze and body. This effect is more clear and visible if one goes to the high end of the firing range of a given glaze. Investigations using XR-F analyses have been done on the transparent, clear glass parts, the canyons so to speak. The measurements were done for Ba, Cd, Se, Pb and Zn. The first measurements were done on the glaze surface with only a few microns depth. After these first measurements the surface of the glaze was progressively ground off and polished after which the same elements were analysed again. When the measured amounts of the elements were plotted against the depth of the glaze it was clearly shown that the amounts for Ba, Pb, Zn and Cd were the same for all depths but that the amount of Se was increasing with every measured depth till the level of 25 to 30 microns. From that depth the measured amount of Se followed a horizontal line. This meant that the Se clearly had evaporated from the surface.[104]

Literature learns that the loss of Cd, S and Se from glasses is controlled by the chemical potential of oxygen in the glass. Both Zn and S act as redox buffers that help maintain a stable chemical potential. If the chemical potential is too low (glass too reduced), excessive amounts of Cd will be lost, while if too high (glass too oxidized), selenium will be rapidly volatilized.

Cadmium selenium melted-in red, orange and yellow glazes are always multi-fritted glazes. The selenium containing frit is melted under moderate reducing conditions to minimize the volatilization of the selenium and thus fixing the chemical potential on a fairly low level. The cadmium containing frit (or frits), however, are melted under oxidizing conditions using sodium nitrate as one of the frit raw materials. These frits may thus be highly oxidized (high oxygen chemical potential). When the glaze is fired its chemical potential will adjust eventually to the average value of the various frits of the glaze. The fact that Se has been lost from the surface layer and that the Cd is stable suggests that the resulting chemical potential was too high (glaze too oxidizing). The selenium is most probably lost before the glaze has reached its transformation point. A way to reduce the effect of vein structure in red glazes is therefore to reduce the amount of high oxidized melted frits or to introduce frits which are melted in a more neutral way.

With the above mentioned knowledge it is possible to 'adjust' the composition of red, orange and yellow melted-in cadmium selenium glazes in such a way that a less pronounced vein structure is the result. The firing stability at higher firing temperatures and colour strength of the glazes are however more important for a manufacturer than, in most cases, a nice 'cloudy' effect with some vein structure. If one doesn't like this typical structure of melted-in glazes there is now a way to overcome this with the 3rd generation of encapsulated CdSe pigments which are suitable to fire at high temperatures and give a more lacquer appearance.

10.7 Pigmented red

It is already mentioned before how the first classical cadmium selenium red pigments were made by mixing the dry materials selenium metal, cadmium oxide or carbonate and sulphur and burn it in a (rotating) kiln at about 600 °C. Different combinations of these raw materials have been used in the past to achieve the final results. Literature[105] is mentioning e.g. the combinations cadmium sulphide or cadmium carbonate, sulphur and metallic selenium. Also Shaw is mentioning these raw materials for the preparation of the classical cadmium selenium pigments. Table XIV gives compositions for CdSSe pigments as mentioned by T.V. Prasad (Cadmium Seminar, New Delhi, India). Also H. W. Webb gives these compositions.

Colour	**percentage by weight**		
	$CdCO_3$	**Se**	**S**
Orange	81.50	3.40	15.10
Orange Red	78.80	6.62	14.58
Red	76.28	9.62	14.10
Bright Red	75.00	10.00	15.00
Bright Red	71.00	19.00	10.00
Purple Red	69.90	14.00	16.10
Blue Red	69.90	17.50	12.60

Table XIV: Chemical compositions of CdSSe *pigments for varied red and orange shades*

BASF found a way to improve the manufacturing through the wet precipitating process which has been described here earlier already.

Those pigments have been improved all the time by several manufacturers especially during the middle period of the last century. The majority of the volume of these cadmium pigments was applied in plastics mainly (abt. 85 %) and only a minor part was applied in ceramics, see Table X. The reason for this was that among other things the stability of the cadmium pigments was much better compared to the available organic colours of that time.[106] They could easily withstand the higher temperatures at which the plastics must be formed, particle size was good and the necessary percentage for a good strong colour was rather low. Moreover, the organic colours of that time were fading out over time. Well known examples of that time were the plastic yellow, green and red beer and beverage crates of various famous breweries, household packaging, toys, etc. The overall disadvantage, however, of the classical CdSSe pigments was the fact that they couldn't be applied in ceramics at temperatures higher than 1000 °C till 1020 °C maximum without losing too much colour strength or turning into dark / black discolorations. Therefore, the application in ceramics was mainly limited to decoration colours and porcelain enamels. For both counts a firing temperature of about 800 °C.

An UK patent was filed in 1979 by Corning Glass Works[107] for improvement of the CdSSe pigment, especially when applied as screen print decoration colour. Following the patent the classical pigment was mixed with a $CdO - PbO - B_2O_3 - SiO_2$ glass enamel flux, an organic vehicle for printing and also an amount of a potassium borosilicate glass. The composition was

mixed in an ink mill and screened onto silkscreen paper. This layer was then covered by a second layer of the same glass enamel flux as used in the first layer. This principle of applying a second layer as transparent cover flux over a red coloured first layer is still applied on some occasions and also recommended when applying red colours as screen printing colour. It protects the red colour against negative influences from the kiln atmosphere resulting in a better, bright and high glossy red decoration colour.

The improvements realised by the systems of melting-in cadmium, selenium and sulphur into glass (frit) compositions from the sixties and especially during the seventies of last century, resulted in much more stable yellow, orange to red glazes with a good resistance to high firing temperatures as required by the ceramic industry. The melted-in cadmium selenium glazes could therefore overtook the role of the classic pigmented yellow and red glazes (not the red decoration colours for onglaze firing at 800 °C) in the ceramic area during this period as also is shown in Table XV.

Higher firing temperatures were possible and this opened the way for application onto wall tiles, floor tiles, stoneware and earthenware. The glaze character and appearance of a pigmented red is different as from a melted-in red glaze. However, by adapting the glaze composition of a red glaze one could come very close to the appearance of a pigmented glaze with the advantage of higher firing stability. During this period, the melted-in red, yellow and orange glazes were much more important than the pigmented glazes.

Period	CdSSe pigments	CdSSe melted-in glazes
19th century	Production in classical dry way	Application of Se in glass for rubin red glass and as decolourant.
1919	Invention (BASF) of wet precipitation method	
1932		Rooksby: CdS · CdSe mixed crystals
1950	Application as o/g colour and low firing glazes but mainly in plastics.	Start of 1st melted-in ceramic glazes
1960	Improved quality. Application till ± 1000 °C	
1970	1st generation inclusion pigments (Dr. Broll et al.) for glaze application	Improved systems: separation of frit-systems. Optimalisation of production processes.
1980	2nd generation encapsulated pigments (BCRA) for glaze application	Top in production of glazes for wall- and floor tiles, vases, dinnerware, gift-ware, etc.
1990	further improvements of production processes of inclusion pigments	
2000		Continued application on a lower level mainly for giftware, vases, art ware.
2010	3rd generation strong Chinese pigments for glaze application as well as for in-glaze firing.	

Table XV: Short historical review of CdSe *pigments vs.* CdSe *glazes.*

A real breakthrough for the pigments for ceramic glaze application was the invention of the first generation of inclusion pigments by Dr. Broll et al. as also described in US patent 3802900.[3]

The mechanism for including colour-giving components into a crystal structure was already known. An example was the SnZr yellow colour which was encapsulated into the zircon crystal (1932, Stuckert, Degussa), the ZrV blue (1948, Seabright, Harshaw) and the ZrFe rose (1960, Seabright, Harshaw). The inclusion of a red pigment based on CdSSe and $ZrSiO_4$ was studied for years by H. H. Beyer, A. Broll, H. D. de Ahna and E. Meyer-Simon in the early 70ties. It resulted in the first generation of inclusion CdSSe pigments into a zircon crystal.[108–110]

As described by the patent the invention was that the CdS · CdSe mixed crystal stain was formed in a calcinating process and that these mixed crystals were included in the $ZrO_2 \cdot SiO_2$ crystals formed during the same process.

The following compositions are mentioned as examples in the patent:

example reference:	(1)	(2)	(4)
ZrO_2	2381 g	85 g	85 g
SiO_2	1174	42	42
$CdCO_3$	950	34	–
$CdSO_4$	–	–	50
Se	129	4.1	–
S	188	–	–
LiF	178	3	6.3
$NaSiO_3$	–	52	25
Sugar	–	–	3.6
	5000	220.1	211.9

Table XVI: Batch compositions for first-generation CdSSe *inclusion pigments*

These mixtures were mixed with water for 15 minutes, poured into crucibles and fired at resp. 900 °C, 900 °C and 950 °C for 1 hour. After the firing the calcined products were treated with HNO_3 to remove the excess of not included cadmium components. In this way resp. a light red (1), a bright red (2) and a yellow (4) colour was obtained.

In another patent[111] published in 1976 A. Broll et al. describe the forming of colour intensive frits to be applied with transparent basic frits to give stable red and / or yellow glazes. The basic principle, following the patent, is that 'colour-intensive' coloured-frits are made composed out of the colour-giving materials, zircon, quartz, a mineraliser and a basic frit (example 1). The patent includes also tin oxide instead of zircon and quartz (example 2) and other raw materials in the examples 3, 4, 5 and 6. The coloured-frits are mixed with a normal transparent ceramic frit and the standard additions for setting-up the glaze.

As an example the patent gives for the coloured-frit (example 1):

cadmium oxide	8.6 g
selenium	0.8
sodium sulphite	7.3
sugar (reducing agent)	3.3
zirconium oxide	29.5
quartz	14.6
lithiumfluoride (mineraliser)	2.1
transparent frit*	33.6

* Seger formula:

K_2O	0.25	Al_2O_3	0.50	SiO_2	4.00
CaO	0.75	B_2O_3	1.00		

These materials were first dry pre-mixed, than wet mixed, dried and fired at 1100 °C. 10 Parts of this coloured-frit together with 90 parts of a transparent basic ceramic frit and 8 parts of kaolin formed a red coloured stable glaze.

From the end of the 70ties these inclusion pigments found their way into ceramic application. The fact, however, that the colour saturation was rather low meant that these stains of the first generation of inclusion pigments could not be applied e.g. as strong decoration red colour or as glaze stain in case that a real bright red colour was required with a wavelength of about 614 nm and high colour saturation. One of the typical applications was therefore in the sanitary industry. Even with low additions of this stain they gave good stability to make trend colours as Bahama beige, Carneol, Caramel, Sunset, Stella, Magnolia and Anemone.[112]

V. Lambies Lavilla and J. M. Rincón López[113] gave an explanation with regard to the forming of the $ZrSiO_4 \cdot Cd \cdot S \cdot Se$ inclusion pigments, mentioning the reactions which take place for the forming of the pigment. They studied mixtures with ZrO_2, SiO_2, CdS, $CdCO_3$, S, Se and the mineralisers NaF and LiF. See Table XVII for the mixtures. The mixtures were fired at 900 °C in an electrical furnace with a heating rate of 300 °C p/h and 1/2h soaking at top temperature.

Following the article, the authors concluded after investigations with XR-D and SEM analyses that the formation of small crystals of $ZrSiO_4$ takes place between ZrO_2, SiO_2 and the mineralizer according to the reactions as proposed by Eppler. Simultaneously hexagonal crystals of $Cd(S_xSe_{1-x})$ are formed. In the main stage the crystals of $Cd(S_xSe_{1-x})$ are trapped by zircon. This phenomenon can be explained in terms of the theory of sintering in the presence of a liquid phase.

Raw material	**Compositions (weight in g)**			
ZrO_2	119	119	119	119
SiO_2	58.7	58.7	58.7	58.7
CdS	–	–	40.5	40.5
$CdCO_3$	47.5	47.5	–	–
S	13.4	13.4	–	–
Se	10	10	10	10
NaF	–	14.3	–	14.3
LiF	8.9	–	8.9	–

Table XVII: Experimental compositions for CdSSe *inclusion pigments (after Lambies Lavilla and Rincón López)*

An improvement to the system of encapsulated stains was realised by the BCRA (British Ceramic Research Association, now CERAM) during the 80ties of last century and published with UK patent 2 106 530 A.[5] The basic principle of making the encapsulated stain was different as from the 1st generation. Following the BCRA patent the processes were following:

(i) preparation of solutions:
29 grs $CdSO_4$ + 200 ml H_2O

to be mixed with
140 grs solution, cont. ± 35% Zr-acetate

(ii) 3.6 grs Se powder + Na_2S solution (28/1000 H_2O)
+ NH_4OH (to make solution alkaline)

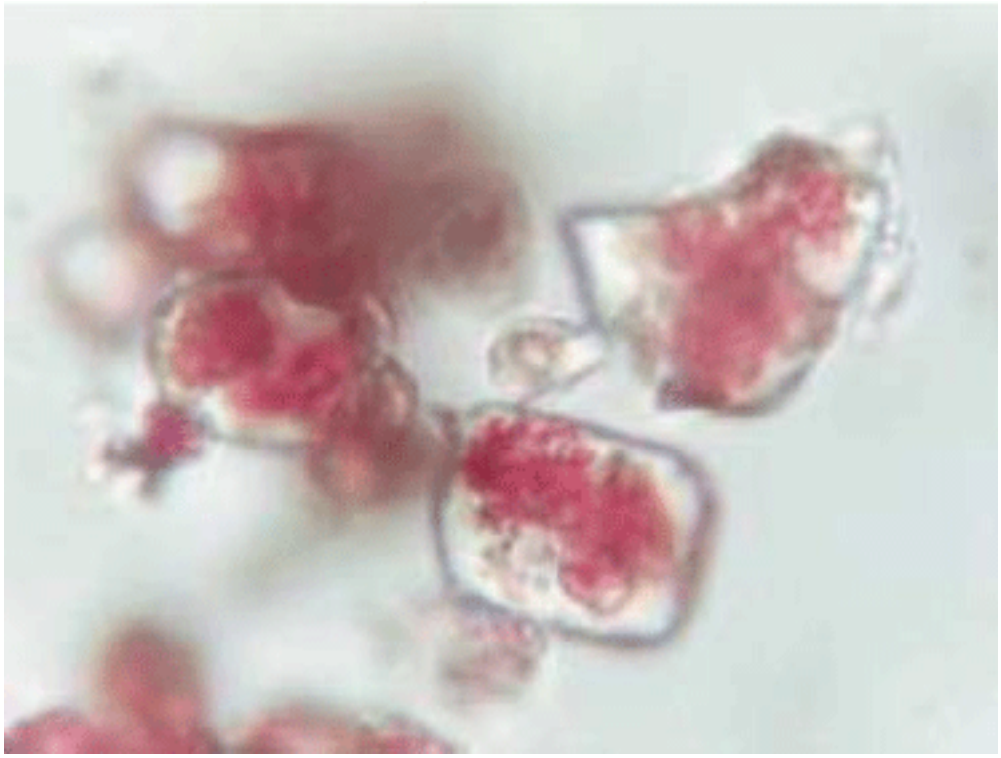
(i) + (ii) precipitate
↓
washing
↓
filtering
↓
drying

mixing the resulting dry powder with 35 ml Na_2SiO_3 solution, dilute to 200 ml with H_2O + acid to neutralize.
↓
gelling
↓
washing
↓
filtering
↓
drying

mixing the resulting powder with 3 weight percent LiF
↓
firing in closed crucibles at 1050°C – 30 minutes
↓
grounding in ball mill
↓
washing with mixture of H_2SO_4 and HNO_3
↓
washing with H_2O
↓
washing with NaOH
↓
washing with H_2O
↓
drying

The result of the process was that the stain had about 4 - 6 times as much pigment encapsulated as the 1st generation resulting in the fact that stronger red colours could be obtained for application as glaze stains as well as (onglaze) decoration colour. See also Photograph 18 for the encapsulated crystals.

The BCRA produced this second generation of CdSSe inclusion stain only on limited scale and the license for production was given to Blythe Colours / Johnson Matthey. The complicated way for production of the stain has always been a drag for making bigger volumes. Together with the health and safety measurements to be taken and the resulting sky-high production costs per kg it meant the end of this development. Dr. Jörg Keyn, however, mentioned in 2004 that with this second generation of CdSSe encapsulated pigments the possibility has been created to make a real red colour.[114]



Photograph 18: Microscopic view of an encapsulated $CdS \cdot CdSe$ *stain within a zircon (*$ZrO_2 \cdot SiO_2$*) crystal*

After the invention of the inclusion pigments and creating the 1st generation of these type of inclusion CdSSe pigments into a zircon silicate crystal, the developments didn't stop and based upon new technologies stronger pigments have been created also by the company Broll Buntpigmente, e.g. red pigment 3033 and others.

Also in the early 80ties some attempts have been made to apply another method to protect the CdSSe stains from an early contact with molten glaze components. This was done with a CVD process (Chemical Vapour Deposition) in cooperation with the Technical University in Eindhoven.[115] In this process a reactor is used where powder material (like a CdSSe stain) can be brought in a vacuum and at higher temperatures and pressure. Various gasses can be led into the reactor to create a coating around the (powder) material. The tests were done to coat the material among other things with the transparent material Si_3N_4. These first attempts did not give enough positive results for continuation.

Because of the threat of a complete ban on cadmium during the 80ties one was looking for different alternatives. The yellow CdS pigment, in the hexagonal crystal lattice, has many proven properties over (organic based) yellow colours. Only a low amount of the pigment is necessary to

give a strong yellow colour in plastics (0.4 – 0.6 %). Also the high temperature resistance during processing of the plastics is a great advantage. The company Colorsil BV in The Netherlands (a joint-venture of Reimbold & Strick and Mr. Ch. Zwart) made attempts in the late 80ties to replace the CdS yellow by zircon silicate 'doped' yellow pigments, viz. zircon-praeseodimium yellow (ZrSiPr) for application in plastics. One of the problems was that the zircon silicate material made the plastic more stiff and had also other negative impacts on the chemical/physical properties. Also the average particle size was too high and had to go down to a D^{50} of 4 μm. In cooperation with the Technical University of Delft they tried to find ways to connect organic 'tails' to the zircon silicate material to make it fit better in the plastic materials.[116] This method was successful and starting from 1994 no cadmium pigments were used anymore e.g. for the famous beer crates of some of the biggest breweries worldwide. Instead, one applied specially prepared and coated zircon-praeseodimium yellow stains for the yellow colour. This continued till about 2001 when other organic green and yellow phthalo pigments came on the market, replacing the zircon-praeseodimium stains for economical reasons.

Besides the inclusion pigments as manufactured by the company Broll Buntpigmente, which soon will likely be the only manufacturer for these type of pigments left in Europe, another and third generation of very strong cadmium stains came on the market after 2000. This generation was developed and made in China and showed a stronger colour compared to the existing and available stains from West European origin. The internal Chinese market is demanding huge amounts of products and also red stains for the ceramic industry which is affecting prices of cadmium and selenium remarkably ever since about 2002. The Chinese manufacturers have found a way to produce the encapsulated CdSSe pigments resulting in much stronger red, orange and yellow pigments than the existing ones.[117–121] On top of that the production volumes are that high that there is also volume available for the export market. An estimation of the actual Chinese production of cadmium stains now (2010) is that the production of the cadmium stains is amounting to about 800 MT / month. An estimated production e.g. at Wanxing company is approximately 60 MT / month; at Jino approximately 80 MT/month and there are at least more than 10 other factories more producing cadmium pigments like Baifu, Hangzhou Hongyan Pigment Chemical Ltd Comp. (hy-pigment) and others. These factories will undoubtedly come to other than the Chinese markets with attractive prices for their strong cadmium selenium encapsulated stains. A company as Wangxing e.g. has already facilities in Turkey, Italy, Spain and Mexico.



Photograph 19: Lead-free transparent glaze coloured with a strong CdSe *red stain (2009). Courtesy of Newland Pottery BV, The Netherlands.*

With these strong stains one can obtain strong and stable red coloured glazes also at rather high firing temperatures up to 1200 °C. The vase as shown on Photograph 19 is an example of a cadmium selenium red glaze made with one of the strong red stains. The glaze is a lead free transparent one with reference ECR10493-P and the glaze is coloured with 10 % of the strong red stain 14P8003.

These very strong red stains have also been applied to develop strong inglaze red decoration colours e.g. for firing at a level of 1180 °C till 1220 °C in about 90 minutes. The strong pigments are used in combinations with suitable flux systems to develop new ranges of red, orange and yellow inglaze colours which now show a colourstrength and colourstability which were not possible some years ago.

It is known that China intends to be in line with international health and safety regulations, despite the actual state of some cadmium selenium stain production sites now and in the past. It is already announced in China that new regulations with regard to health and safety of different materials, also cadmium, will apply in China as from 2012. This will probably affect the production of these stains in the near future.

Now, 2010, the ceramic industry is able to produce very strong red, orange and yellow CdSSe stains which enable manufacturers to produce really laquer-like ceramic products, no matter if it is for wall- or floortiles, vases, giftware or dinnerware and at any temperature which is required by the kiln conditions. An achievement which could be dreamed of only some decades back.

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13 CORRECTIONS

This section lists the specific corrections and adjustments made to the original manuscript during the conversion to PDF. They were made to ensure scientific accuracy, have consistent formatting, and improve readability while maintaining the original tone and intent of the book.

- **Figures:** Captions are now positioned *under* all figures in slightly smaller, italic type.
- **Captions:** Performed a comprehensive audit of all table, figure, and photograph captions. Data from the manuscript's original outline (index) was synthesized with on-page captions to provide more descriptive labels.
- **Tables:** Readability and accessibility were improved by adding semantic structure and headers in bold type.
- **Formulas:** Used centered dot (·) for chemical adducts instead of period (.).
- **Formulas:** The notation for oxidation states was standardized to the IUPAC recommended format (e.g., 'Cr(VI)') instead of the hyphenated form (e.g., 'Cr-VI') found in the manuscript.

13.1 Chapter 1: Introduction

- **Formulas:** The mathematical notation for the CIE chromaticity coordinates was corrected to clarify the order of operations. The formulas now read $x = \frac{X}{X+Y+Z}$ and $y = \frac{Y}{X+Y+Z}$.

13.2 Chapter 2: Historical Aspects

- **Spelling:** Corrected 'profirine' to 'porphyrin'.
- **Spelling:** Corrected 'Caesalpina and Heamatoxylon' to 'Caesalpinia and Haematoxylum'.
- **Spelling:** Corrected 'chlorophyl' to 'chlorophyll'.
- **Spelling:** Corrected 'carotenoides' to 'carotenoids'.
- **Spelling:** Corrected '1, 2-dihydroxyantrachinon' to '1,2-dihydroxyanthraquinone'.
- **Figure:** Figure 2 and Figure 3 were replaced with the high-resolution originals.
- **Figure:** The Seger formula in Table VI was reformatted.
- **Table:** Table VIII was renamed to 'Lapis Lazuli-like blue body composition' to better reflect its purpose and the author's intent.

13.3 Chapter 3: Iron

- **Visualization:** Figure 5 was converted from a spreadsheet-like table to a chart, using data found in the author's sources.

13.4 Chapter 4: Copper

- **Spelling:** Corrected the name of the French chemist 'Ebelman' to 'Ebelmen'.

- **Transliteration:** Updated Dutch phonetic transliterations of Chinese dynasties (e.g., ‘Tsjow’, ‘Tsjin’) to standard Wade-Giles (‘Chou’, ‘Ch’in’) or Pinyin (‘Xia’) where appropriate.
- **Enhancement:** Added Simplified Chinese characters (e.g., ‘Chou (⌧)’) to dynasty names for clarity and modern context.
- **Caption:** Corrected the caption for Photograph 7 to “Guangxu period, Ch’ing dynasty” (was “GuangxuChh”).

13.5 Chapter 5: Gold

- **Spelling:** Corrected the title of the 10th-century manuscript ‘Mappas Clavicula’ to ‘Mappae Clavicula’.
- **Photograph:** Photograph 9 was replaced with the higher resolution original.
- **Photograph:** Photograph 10 was also replaced with the higher resolution original.

13.6 Chapter 6: Chromium Tin Stains

- **Spelling:** Corrected the name ‘Alexandre Brongiart’ to ‘Alexandre Brongniart’.
- **Spelling:** Corrected the name ‘Josiah Wedgewood’ to ‘Josiah Wedgwood’.
- **Spelling:** Added *the* in ‘An example is the following receipt’.

13.7 Chapter 7: Nickel

- **Spelling:** Corrected the name ‘Axel Frederik Cronstedt’ to ‘Axel Fredrik Cronstedt’.
- **Spelling:** Corrected the mineral name ‘garnirite’ to ‘garnierite’.

13.8 Chapter 8: Chromium

- **Spelling:** Corrected the name ‘Nicolas-Louis Vanquilin’ to ‘Nicolas-Louis Vauquelin’.

13.9 Chapter 9: Uranium

- **Spelling:** Corrected the name ‘Frobisher Lyttl’ to ‘Frobisher Lyttle’.
- **Presentation:** Ascii-art in Uranium composition table was replaced with repeating the value $0.15 - 0.1$ three times.

13.10 Chapter 10: Cadmium Selenium

- **Mineralogy:** Corrected the chemical formula for sphalerite from ‘(Zn,Hg)S’ to ‘(Zn,Fe)S’.
- **Spelling:** Corrected the mineral name ‘crooksite’ to ‘crookesite’.

- **Spelling:** Corrected ‘Hyperioon’ to ‘Hyperion’.
- **Spelling:** Corrected ‘nutricity’ to ‘nutrition’.
- **Spelling:** Corrected ‘grow of cancercells’ to ‘growth of cancer cells’.
- **Spelling:** Corrected ‘Greenocktite’ to ‘Greenockite’.
- **Spelling:** Corrected ‘Itai Itai’ to ‘Itai-itai’.
- **Spelling:** Standardised ‘odorless’, ‘celestite’, ‘sulfuric’, ‘sulfide’, ‘sulfo’, ‘sulfite’, ‘color’, ‘laquer’, and ‘flower-of-sulphur’ to British English (‘odourless’, ‘celestine’, ‘sulphuric’, ‘sulphide’, ‘sulpho’, ‘sulphite’, ‘colour’, ‘lacquer’, ‘flowers of sulphur’).
- **Grammar:** Corrected ‘this phenomena’ to ‘this phenomenon’.

13.11 Literature

- **Deduplication:** The following entries were deduplicated, reducing the literature count by 5:
  - Methuen, 1978
  - Römpp, 1962
  - Berendsen, 1975
  - US patent 3802900
  - UK patent 2 106 530 A
- **Enrichment:** Corrected missing or incorrect metadata for books with ISBN.
- **Formatting:** Entries are shown in ISO 690 format.

13.12 Index Differences

The lists of tables, figures, and photographs have diverged from the original manuscript to better reflect the semantic content of the referenced materials. The following structural changes were made:

- **Tables reclassified as Figures:**
  - Manuscript Table IX (price graph of selenium metal) is now Figure 7.
  - Manuscript Table XI (price graph of cadmium metal) is now Figure 8.
- **Figures reclassified as Tables:**
  - Manuscript Figure 5 (composition zukû glass) is now Table VI.
- **New Table:**
  - A new table, Table XV (“Short historical review of CdSe pigments vs. CdSe glazes”), was introduced.
- **Renumbering (Tables):**
  - The reclassifications and addition above shifted the numbering of tables.
  - Manuscript Tables VI–VIII are now Tables VII–IX.
  - Manuscript Table X remains Table X.
  - Manuscript Tables XII–XV are now Tables XI–XIV.
  - Manuscript Tables XVI–XVII remain Tables XVI–XVII.
- **Renumbering (Figures):**
  - Manuscript Figures 6–7 are now Figures 5–6.
- **Photographs reordered:**

- Manuscript Photograph 19 (‘Walking Orange’) was moved to Photograph 17 to match the location of its first mention in the text.
- Consequently, Manuscript Photograph 17 is now Photograph 18, and Manuscript Photograph 18 is now Photograph 19.

13.13 Acknowledgments

The conversion, formatting, and technical validation of this manuscript were assisted by `Gemini-3-Pro-Preview` (Google), an AI Large Language Model. The AI was utilized for:

- Extracting and structuring text from `.odt` source.
- Generating Typst code for layout, tables, and figures.
- Applying specific corrections listed in this chapter.
- Verifying mathematical formulas and chemical syntax.

Human oversight was applied to all AI-generated output to ensure accuracy and alignment with the original work’s intent.

ABOUT THE AUTHOR

After a chemical education he started working at the chemical laboratory of Ferro (Holland) B.V. at Rotterdam. In this way he became familiar with silicate analyses and all common raw materials as used in the ceramic, glass and porcelain enamel industry. After three years he moved to the R&D department of the ceramic laboratory. During another 18 years he was developing a wide range of products for the growing ceramic industry during the 70ties and the 80ties of last century. Especially, he redesigned the formulations for the cadmium selenium frits and glazes to what they are still today. Worked and lived half a year in Italy to support the ceramic business for Ferro (Holland) B.V. Continued as product manager.

Left Ferro (Holland) B.V. in 1987 and was asked to join Drakenfeld Colours to set up a new plant for the European market mainly for the compounding of the black obscuration glass enamels for the automotive industry. Stayed also a period at the Drakenfeld USA plant. Finished studies on Management and courses for 'Statistical Process Control', 'Taguchi Methods', 'Fundamentals of Glass Technology' and 'Organic Additives in Ceramic Processing'.

Returned to ceramics in 1993 when Drakenfeld Colours and Degussa set up the Cerdec joint venture and the unit in The Netherlands was closed.

Joined Johnson Matthey as from 1993 till now with several technical and commercial responsibilities in the ceramic field viz. technical manager ceramic laboratory and Commercial & Technical Manager Special Ceramics.

ABOUT THIS EDITION

Only after I had read, and re-read, every page, table, and formula in this book, and transferred them from a long-lost but suddenly found `thedefiantred final4.doc`, could I appreciate the enormity of its contents. My youthful hubris when I wrote "This book describes all possibilities known to man on how to create red coloured glazes for ceramic application" on the website doesn't even do it justice.

It *does* contain all possibilities known to man on how to create red coloured glazes for ceramic application.

Not only that, but its science was, and is, rock solid. Yes, the newly added chapter with corrections is over two pages, but it's mostly grammar and the fallout of busywork related to the rigid confines of computer code.

This electronic edition fills the need of many a would-be customer who contacted me over the years. I hope the knowledge of my late father continues to educate and inspire ceramists all over the world.

J.L. Baaij
Amsterdam, 2026
The Netherlands



L.W. Baaij (1947–2025)