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Origin, early history and technology of the blue pigment in azulejos

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SUMMARY: A few years ago I supervised an MSc dissertation on the blue cobalt pigment in Portuguese glazed tiles (azulejos). Looking for sources on the history of the cobalt pigment in Europe, I was directed to two papers published in German and one (unpublished) in Dutch. Those were:

Beiträge zur Geschichte der Kobaltfarbe und ihre Verwendung in der Keramik (Contributions to the history of the cobalt colour and its use in ceramics) by Josef Horschik, an article originally published in Keramos nr. 85, pp. 119-142, 1979;

Das Sächsische Blaufarbenwesen und der Handel mit Kobaltfarben – nach Unterlagen der Bücherei der Bergakademie Freiberg (The Saxony blue pigment and the trade in the cobalt colour - according to documents in the library of the Bergakademie of Freiberg) by Peter Hammer, a communication to the VII Int. Symp. 'Cultural Heritage in Geosciences'. Scripta Geol. Spec. Issue 4, Winkler Prins & Donovan, 2004; and

Zaans Blauw - van zaffer tot smalt naar ultramarijn (Zaan Blue - from zaffre to smalt to ultramarine) by Martin E. de Gruijl (written after 1993 and presumed unpublished).

I translated the relevant parts of the papers for the benefice of the student and, finding in them information that was new to me, kept in mind that I would one day write down an abstract of the contents that might help other researchers to source historic and technical information on the pigment so famously used in Portuguese azulejos.

The present text includes selected information abridged from those valuable texts to tell the whole story with incompatibilities between two of them critically assessed and edited, complemented with other information to encompass the relevant period for the pre-industrial production of azulejos in Portugal. A number of personal comments are added, particularly in the conclusive chapter.

KEY-WORDS: cobalt blue; Portuguese azulejos; history of the cobalt pigment production in Europe

1. AN INTRODUCTION OF SORTS

A few years ago I supervised the MSc dissertation of a young researcher from the University of Bologna, on the cobalt blue pigment in Portuguese tiles [1]. Looking for sources on the cobalt pigment in Europe, I consulted Dr. Johan Kamermans, director of the Dutch Tegelmuseum in Otterlo who kindly sent us two papers published in German and one (unpublished) in Dutch. Those were:

- *Beiträge zur Geschichte der Kobaltfarbe und ihre Verwendung in der Keramik* (Contributions to the history of the cobalt colour and its use in ceramics) by Josef Horschik, an article originally published in Keramos nr. 85, pp. 119-142, 1979;
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I translated the relevant parts of the papers for the benefice of the student and, finding in them information that was new to me, kept in mind that I would one day publish a commented abstract of the contents hoping they might help other researchers. This seemed a good time to do it!

2. FUNDAMENTAL NOTIONS ON COBALT BLUE, ITS ASSOCIATIONS AND SOURCES

The blue in azulejo glazes is obtained from a cobalt oxide refined from ores containing several other metals and metalloids. Cobalt itself, all of its most common ores, and the cobalt oxides directly obtained from them are grey or pink. The blue in glazes is the result of cobalt-oxygen groups formed when a chemical structure is built with silica in the presence of alkali oxides that act as suppliers of oxygen to build the chemical blocks [2].

What must be kept in mind is that the blue colour was not seen in cobalt-rich ores. Also that any pigment coloured blue acquired in the 16th, 17th or 18th centuries to paint azulejos was actually a smalt obtained by firing the cobalt and all its impurities with the components of glass- at least silica and an alkaline oxide. For that reason, cobalt blue could not be recognized in ores until they were calcined with sand and potash and, in fact, the element "cobalt" was unknown until well into the 1700s. Therefore, the fact that cobalt exists in Spain, Portugal, Morocco, France, etc. does not mean that it was recognized long ago as a source of blue.

Cobalt often occurs in nature combined with arsenic, as in cobaltite (CoAsS), safflorite (CoAs2) and skutterudite (CoAs3). Linnaeite (Co3S4) of Sweden and other regions is a cobalt sulphite occurring in a series with polydymite (in which the cobalt is replaced by nickel) none of which contain arsenic.

Most importantly, cobalt-bearing ores often include minerals of nickel, iron, copper, bismuth... The association with other metals and metalloids may be particularly characteristic and could help pinpoint the source of the cobalt used as pigment in some

application. However, before being sold as a pigment, the ores were refined by roasting. When heated, lower-fusing components such as bismuth (270ºC) would melt and be almost wholly extracted. Also the arsenic would partially fume out. And so, the combination we get depends both on the source and on the roasting/refining process. Nickel, iron and copper were difficult to separate [13] and can be expected to be found associated to cobalt in azulejos. However the contents of both Ni and Fe are very variable in the same locations and are not particularly useful on their own to pinpoint a source.

The sources of cobalt are a fascinating subject. Cobalt was found in early Egyptian, Persian, Roman… glass but was rather seldom. Its early sources are not particularly relevant to the study of azulejos but a location for the ore imparting the blue colour to glass was known since ancient times, possibly in Persia, and old blue glass beads could be "recycled" and used as pigment for new glass.

In medieval times one, two or even three sources of cobalt were known in East Asia (one or two in China and, possibly, one in Sumatra) but that pigment, used in Chinese porcelain, did not reach Europe. Until around 1500, pigment from at least one known source in Persia could reach Europe. There might be a second source of cobalt pigment in Iraq, possibly near Samarra, where the earliest tin-glazes (9th – 10th century AD) were found in archaeological contexts.

At least two cobalt pigments with different associations were used in Europe before 1500. Both had little or no arsenic in their compositions but one of them had high nickel content while the other had only traces of Ni. The nickel content is that which is more readily visible in the colour because it darkens the blue [14] in a quite undesirable way - figure 1.

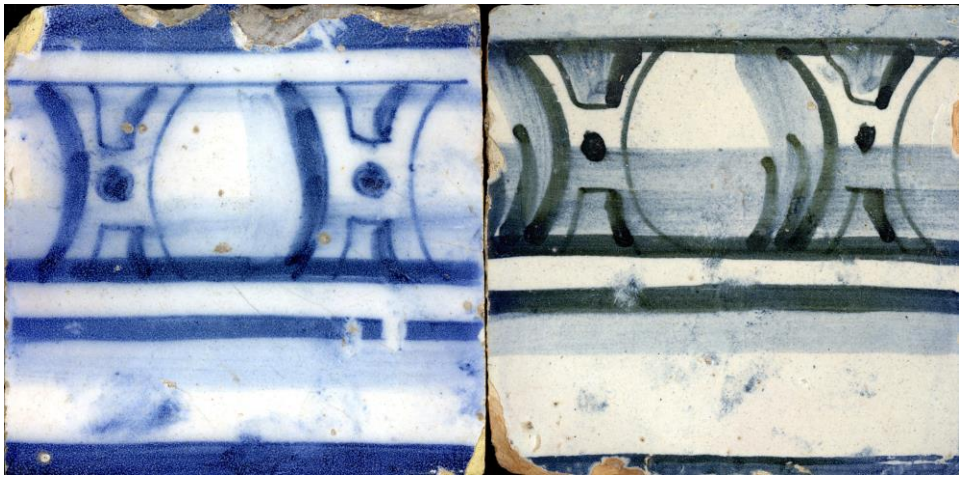

Figure 1. Two Portuguese tiles photographed simultaneously. On the left side, the blue pigment has little nickel; on the right side the pigment differs only on having high nickel content. Image: João Manuel Mimoso

In the 12-13th centuries, the cathedrals in France were being decorated with huge areas of blue and red stained glass windows, certainly using great amounts of blue pigment… its

source is unknown and the fact that tons of cobalt oxide was probably imported and circulated through France without a hint to their source, gives an idea of the problems facing researchers in this field.

3. THE FINDING OF THE COBALT PIGMENT IN EUROPE

We now travel to the Erzgebirge (Ore Mountains) a mountainous region that follows the present border of Germany's Saxony with the Carlsbad District of the Czech Republic (figure 2). In the 16th century this was the border between the kingdoms of Saxony and Bohemia. It has been a region of ore mining since pre-historic times, particularly silver, copper and iron.

In his excellent paper [3] Josef Horschik, with substantial sources, points out that bismuth was discovered in the Erzgebirge during the 15th century, probably before 1450. It was mined, refined and used for several purposes including the lead alloys used to cast printing types. It occurs associated with cobalt, but the presence of a substance that could produce a blue pigment was unknown at the time. Bismuth was extracted by roasting the ores. When the metal separated, cobalt, with a higher point of fusion, remained as part of the slag and was discarded as waste without value. The name "kobold" (a mountain and mine devil) was associated with this slag possibly because of the nefarious fumes rich in arsenic caused by its roasting.

Horschik adds: *cobalt ores and cobalt occurring under different forms and compounds were known to the miners of the Erzgebirge mountains at least since the 15th century. Before the invention of the blue colour, the simple mountain men called all arsenic and sulphur containing rocks and ores "kobold". When they did not contain bismuth, they were cast away as unusable rubble. Usable bismuth ores often contained cobalt, nickel, sulphur and arsenic. Therefore, the miners also spoke of "bismuth-kobold". The bismuth low melting point facilitated its extraction. It was "roasted" outdoors over an open wood fire. This resulted in the bismuth giving away toxic smoke. The slag-like residues were named "bismuth barley" and only at a higher temperature did cobalt melt from them. About the meaning of the word "barley" the "Oeconom Encyclopedia" of JG Krünitz states: "In the mine mills, the coarsest pieces of pounded ore are called grains or barley".*

The discovery that a blue pigment could be obtained from this slag is not well documented, partially because the local authorities later aimed to keep the details of its production secret to try and ensure a monopoly. The kings of Portugal did the same with the sea routes explored in the 15th and 16th centuries and as a result there is now little information about important explorations in the Americas and in the Pacific.

A first reference to cobalt appears in writing in 1499 but no association is made with the blue colour. This suggests that the slag had by then some demand but was not associated locally to any pigment. Several authors suggest that foreigners active in the mountains (possibly Italians) had discovered that the blue pigment could be obtained from the slag and were acquiring it but, obviously, did not make known their purpose. There is no doubt that the blue pigment was available throughout Italy and in Spain before 1500 and some Italian sources connect it with a German origin. But its true origin remains unknown until a scientific study may connect the pigment used e.g. in the Italian *albarellos* of the late 15th century (figure 3) with a specific geographical source.

Figure 2- The Erzgebirge with the border between Germany and Czech Republic. Saxony was north of this border; Bohemia was mostly south of the present day border (image: Alexander Karnstedt, Wikimedia Commons- Deutsch Wikipedia)

Local traditions collected in the 17th century state that a cobalt mill was operated in the Erzgebirge around 1500-1510 by a German called Peter Weidenhammer, who sold the product to the Venetians. If indeed the Italians had discovered the blue pigment in the ores, it was logical to have it partially refined locally so as to transport only a concentrated product. Writing in 1684, more than a century after the death of this man, Christian Meltzer reported in the Chronicle of Schneeberg [16] about the earliest refinement of the cobalt in the bismuth barley: *Peter Weidenhammer, a Frank [17] came here as a poor man [but] has, however, with the colour that he made from bismuth grains and in many portions priced at 25 thaler each, sold to Venice. So he has come to great resources and had a nice house built in the Main Square. His name stands in the Great Church in the lower window with this year: 1520*.

This information checks with the fact that just before 1520 Della Robbia started using a cobalt pigment from some new source with characteristics compatible with the Erzgebirge [22]. Accepting that Weidenhammer might indeed be refining ore at such an early time, it is likely that he was following precise metallurgical instructions from the Venetians and was not aware of the purpose and true value of his production.

Whether at that time the Italians obtained their cobalt pigment from Saxony, from Persia, from Iraq or from several of those sources is not particularly relevant to us, but the fact that they held a monopoly on the cobalt pigment would be relevant if the monopoly did stand. But it was broken when a glassmaker in the Erzgebirge called Christopher Schürer discovered how to turn the bismuth barley into blue glass that could be milled into a usable pigment. In a short time, the origin of the cobalt trade in Europe moved from Italy to North Germany and the Low Lands and was to be dominated for a long period by the Dutch merchants. The same thing happened when Portugal brought spice from India to Europe by

the Cape route, distributing it through Antwerp and breaking the Venetian monopoly that was based on a land route through Egypt.

Figure 3- Italian albarello in the Louvre Museum- Deruta circa 1500. The blue pigment is the dark high-Ni type seen in Italian and Spanish faïence dated from the late 15th and early 16th centuries.
(image: *Sailko*, Wikimedia Commons-"Albarellos")

Again we turn to Horschik's text [3]: *The oldest information about Schürer and his fate are in a written report by Christian Lehmann, a clergyman from Scheibenberg. His small village is near the town of Annaberg, by the Saxony-Bohemia border, in the middle of the silver and cobalt mining area. Lehmann's report was written only a hundred years after what he records and is part of the "Collection of mixed notes on Saxony history" published in 1769. […] He wrote down the following traditions: "The colour mills have been erected here approximately a hundred years ago. Christopher Schürer, a glass-maker moved from the lowlands to Neudeck, where he manufactured glass. When he was once in Schneeberg he saw the beautifully coloured cobalt [4] and took samples. He put them in the glass furnace and saw that it melted. He joined the ashes with the raw materials necessary to make glass*

and made a beautiful blue glass from it. He pondered the matter better afterwards, and made boxes full of blue colour, only for the potters. This colour was taken to Nuremberg, and they were very surprised, and some of them knew the Dutch. They were not able to duplicate his finding and came to Neudeck to learn how to make it from the master, and asked him to go to Magdeburg and to make samples from the Schneeberg cobalt, and said they would make him a rich man. But sent him back up. Afterwards Schürer built a small mill and obtained 50 kg of colour worth here 7.5 thalers and in Holland 50 to 60 florins."

[…] Christoph Schürer came from a family of Saxony glassmakers that spread through the upper Erzgebirge and had also a branch located in Bohemia. [He] established himself in Eulenhütte, between Platten and Neudeck in Bohemia where in 1530 he succeeded in fusing the glass and cobalt to obtain smalt. ln 1540 he built in the Rohlau near Neudeck a water-driven colour mill in which the smalt was crushed to a powder. In the same year he sent a report with a cost estimate "of how much 50 kg of blue glass melted in Schneeberg should cost" to the Elector in Dresden. The letter stated that with 5,000 kg of zaffre by the addition of white quartz 10,000 kg of blue glass could be obtained at a cost of 3 and ¼ florins per 50kg. That letter is still kept in the Dresden state archives but was ignored at the time. ln 1542, after waiting in vain for a response from Dresden, Schürer took the suggestion of some Dutchmen to go to Magdeburg. There he showed them his manufacturing process, but earned for it neither thanks nor the promised reward…

The fact that Schürer's document survives, ascertains the historicity of the most important facts, namely that a production of blue cobalt pigment started in Saxony around 1540 and in Holland some years later, probably before 1550.

4. EARLY TECHNOLOGY OF THE COBALT PIGMENT

In the early 16th century, before Christopher Schürer's discovery of how to turn the bismuth barley into cobalt blue, there was almost certainly at least one mill operating in the Erzgebirge region, supplying a roughly processed material to Venice. The raw ore was roasted to extract bismuth, which was easily melted. The extraction and preparation of a cobalt product started from the slag pellets that remained. This slag was crushed (if needed) and calcined, possibly in an open air fire. Sulfur and arsenic escaped and the cobalt was oxidized. The resulting mass, a sort of slag possibly with a high content in silica, was then thrown into water so that the thermal shock would break it into pieces and then crushed with heavy iron mallets and grinded mechanically as finely as possible. This is the product which, at the time, Italians called "zaffera" and the Germans and English "zaffre". This is seemingly a reference to the safflower (Carthamus tinctorius L.) [5] from the seeds of which a pigment was obtained.

In 1679 Johann Kunkel gave in the "Ars Vitraria Experimentalis" a unique information on the production technology of cobalt blue, much refined by this time. Kunkel obtained his knowledge some years earlier when he worked as a chemist at the plants in Saxony. He published his book in Frankfurt and Leipzig and Horschik gives the opinion that he would not dare do the same in Saxony because the technology was a closely guarded secret [3, pps.136-137].

Kunkel's report, slightly edited, goes as follows: *There is one mined stone in Schneeberg, in Meissen which people dig and mine from the earth and they call cobolt but it is not wholly a*

good metal. Sometimes they get much of it but often almost nothing. This cobolt is initially thrown in a furnace when it starts to glow it smokes a white smoke that comes out of it. Such is collected in a wooden construction and this is the arsenic [...] This fumed and then roasted cobalt is then thrown into a crushing mill. When it goes through it several times the cobolt is the smallest fraction that passes through a narrow sieve and is taken into storage.

From this cobolt is taken one portion and mixed well with two or more parts of the finest and smallest crushed gravel pieces (which the miners call quartz) mixed and fired together, put in barrels until it is hard and strong like stone. After a long period finally it is again crushed with iron mallets. Such gravel will be sent away to the Dutch and other nations and used to paint their fine tableware and other things with it. And this is precisely what many mountain people and particularly miners call "zaffera".

The sand is from Meissen and no other material is mixed so that the strength of the blue needed in other countries that the women want (and the painters also call "blue smalt") cannot be imitated or reprocessed at a profit. For it is also known that if this fumed cobolt with a certain part of sand and potash is again mixed and molten the glass then carefully crushed and ground in a good mill between two particularly hard stones, a powder is obtained and then separated in different kinds, there is always one more beautiful than the others and sold in portions by an important trader from which a not small revenue is obtained by His Highness of Saxony. So, they also could sell raw cobold which is very highly forbidden to all factors. If they did so, the blue strength could also be made other and benefit reaped from it making double the product. But if one wants to have a pure cobolt he must look for it in this land and pay the higher price. [6]

From this revealing text we get a view of the technology used to produce zaffre and blue smalt in the 17th century (figure 4) which was a two-stage process not necessarily done at the same plants (figures 5, 6, 7). The composition of zaffre was cautiously controlled so that the product exported from Saxony would have always the same strength for processing as smalt. The sale of raw ore was, as is seen, forbidden. This was part of the local monopoly by the rulers of Saxony and will be again referred in the next chapter.

Figure 4. Left side, unrefined cobalt oxide (*zaffre*); right side the finished product (*smalt*)
Image sources: left side [10], right side Wikimedia Commons, file "Cobalt Blue"- *FK1954*

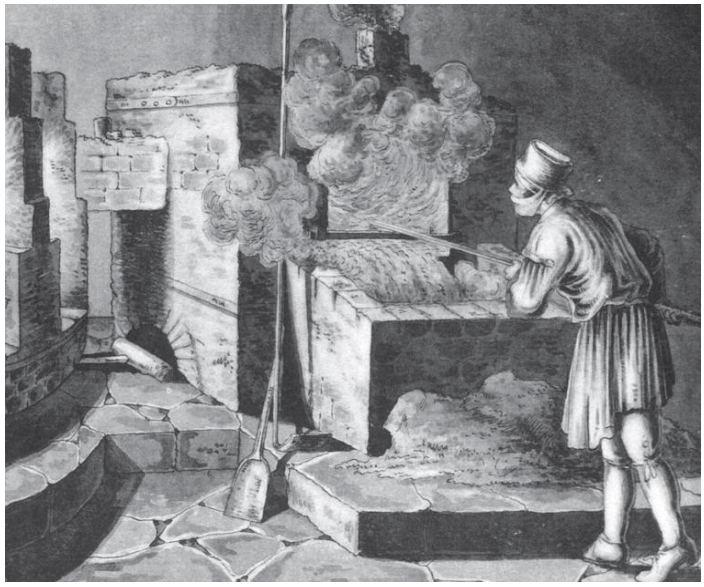

Figure 5- Roasting of the cobalt ore. Most of the unhealthy sulfur and arsenic fumes were channeled and condensed inside constructions called "smoke chambers" however the workers still had to cope with part of them.
Source of the engraving: Winckler, 1790 [12] as reproduced by Hammer [11]

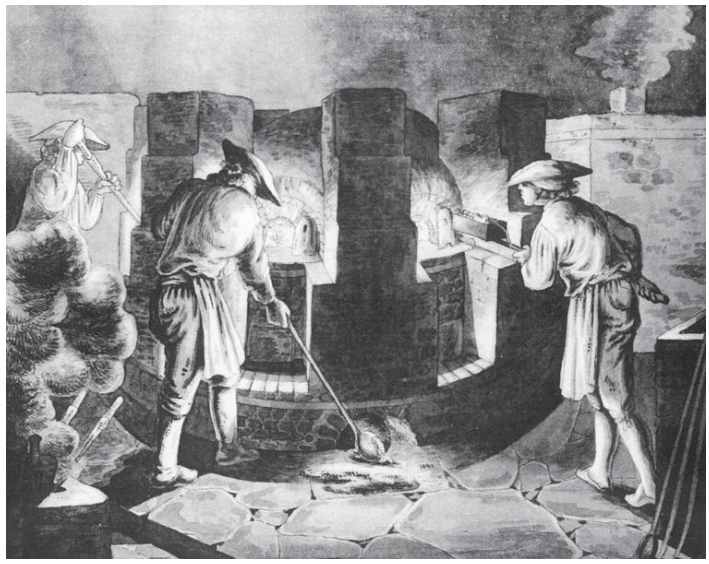

Figure 6- The hard work under the heat of the glass furnace. The melting of smalt was made in pots of clay at 1100 to 1250 ° C. The worker at right feeds the oven while at left the molten smalt is taken.
Source of the engraving: Winckler, 1790 as reproduced by Hammer op. cit.

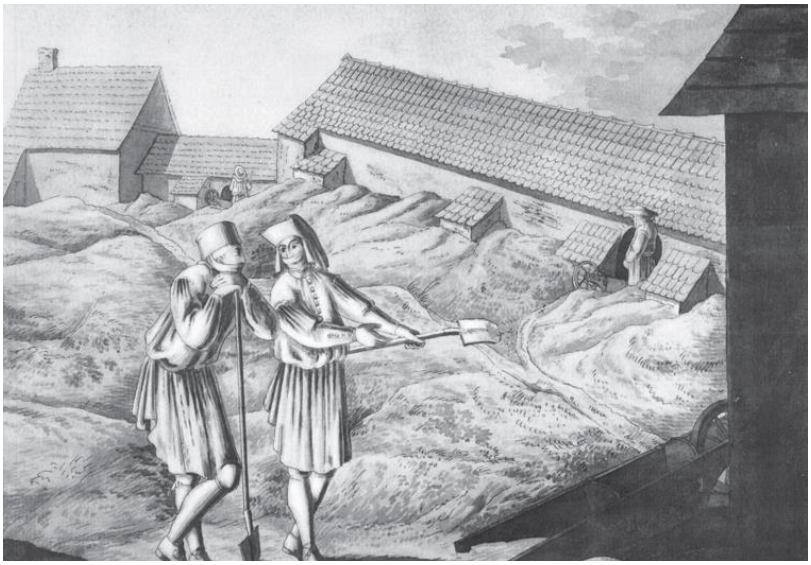

Figure 7. The large amount of accumulated toxic waste (mostly arsenic oxide) that has collected in the smoke chambers is scooped out by workers wearing mouth masks.
Source of the engraving: Winckler, 1790 as reproduced by Hammer op. cit.

A Dutch text written in remembrance of a local cobalt mill [10] provides a full description of the process, this time probably from written sources of the late 18th century because new cobalt mines that became available earlier in the century are already mentioned: *In 1701 was established in Westzaan a company for the grinding of cobalt smalt to a required fineness, but which also needed the availability of cobalt glass. The grinding was done in the mill "Het Blauwe Hengst" (The Blue Stallion) while the cobalt glass was produced in the adjacent glass foundry. Cobalt oxide, the raw material, was obtained from Germany, mostly from Saxony (Erzgebirge) but also from Thuringia and from the Black Forest. The purchase was done through trading houses in Amsterdam which were specialized in this material.*

Cobalt is a metal that is never found pure but always combined with arsenic, sulphur, silver, bismuth, etc... The mining of cobalt ore was carried out by dozens of small mining companies. The ore extracted was crushed to small bits in water mills. This was followed by the so-called "roasting" during which the cobalt oxidized and the sulphur was burned out, while most of the arsenic precipitated in iron pipes connected to the specially built furnace. The roasters were fired with charcoal to a temperature of 950 ºC.

When the cobalt was sufficiently oxidized, the hot mass was poured into water with the result that the thermal shock broke the cobalt oxide into a coarse powder almost black in colour. This product was called "zaffre" and was one of the raw materials used by the Westzaan company for the manufacture of blue smalt. Zaffre consisted of approximately 70% cobalt oxide and also the remains of arsenic and other metals.

The production of cobalt smalt needed first the refining of the raw material so as to remove as completely as possible unwanted substances such as arsenic, silver, etc. Ceramic smelter pipes were filled with one part of potash (called a "flux") so that the melting temperature of the two parts quartz sand (silica) was lowered from 1700 to 1300 ºC. Depending on the desired colour intensity more or less zaffre was added up to about 5%. After some 8-10 hours, the glass mass was molten. The top layer was the cobalt glass, and the sediment consisted of the unwanted metallic compounds. This was called "speiss"[18]. *The glass was gently scooped out with iron implements, taking care that it was not contaminated by the speiss. Again the technique of pouring the glass in water was used, resulting in pulverized blue glass. This was followed by grinding at De Blauwe Hengst.*

So that an optimum colour was obtainable, the cobalt glass had to be grinded to a micro-fine dust while maintained free from iron. This was and is true for all smalts, regardless of colour. Another condition was that the grinding was done wet. Because of the massing together of the glass particles into a hard solid mass the grinding would be impossible if no water was added. Thanks to the wetting, the grinding produced no dust in the mill and therefore virtually no product was lost. The cobalt oxide was an expensive material! Also the wet conditions ensured a longer life of the millstones, which already had to work in difficult abrasive conditions with the hard glass powder.

The end product was "smalt" that one uses in the so-called "frits". Like "zaffre" those are names deriving from other languages, still used today in the industry.

5. PRODUCTION CENTRES OF THE COBALT PIGMENT

We now deal with the production centers of cobalt blue and its trade. We have seen that the first colour mill of which there are historic references was installed by Christopher Schürer in the Saxony side of the Erzgebirge around 1540. The source states that it was a small mill and mentions a production of "50 kg of colour" (e.g. blue smalt) but does not say whether this was just a tentative production or some periodic output.

To understand the early establishment of the blue pigment plants processing the Erzgebirge ores, we take again Christian Lehmann's text [7] after he referred Schürer's mill as being the very first: *The Dutch built in their country eight colour mills, but had no cobalt. So they bought it from here already fired and put into casks that they took with them for processing in their mills. Johann Georg from Churfürst was the first to want to take on the trade by making the colour [in Saxony...] He sent word to Holland to get two colour makers, willing to pay a thousand florins to each one of them, to manufacture the colour in Schneeberg.*

Taking now directly Horschik's sum-up from his carefully listed sources: *After Christoph Schürer had established the first Saxon smalt mill, several small businesses emerged in the second half of the 16th century in the Saxony and the Bohemia side of the Erzgebirge, which dealt with the production of smalt and blue glass. (...)The oldest of those on the Saxony side was founded in 1568 by Christoff Stahl near Mühlberg, west of Schneeberg. In 1571 he expanded it to a complete blue colours workshop. His goal was to produce a "transparent colour" and blue glasses. A flood of the Lindenau destroyed it in the year 1573.*

Subsequently the electoral chamber man Hans Harrer and his companion, the chamber secretary Hans Jenitz, succeeded in obtaining a cobalt-privilege that granted them the sole

manufacturing rights. Both had courtiers tell the Prince that they had "researched through diligent effort and at great cost" to discover the secret of the preparation of the colour. In their presentation they mentioned neither Stahl nor Schürer or Sebastian Preussler, whose glass works manufactured at this time blue blown glass. Because of their false statements Harrer and Jenitz received a ten-year privilege for buying and selling all resulting cobalt [in Saxony] which was extended in 1580 for another nine years. Jenitz lived to the end of the contract but the two did not earn the anticipated income.

Harrer and Jentz had already complained in 1579 that about twenty people at the Schneeberg region were trading cobalt illegally. After the establishment of the electoral monopoly, the regulations were even stricter. The border area, in particular the almost uncontrollable forest on both sides of the Pechöfener Creek, was ideal for cobalt smuggling. The Bohemian cobalt did not have the quality of that from the Schneeberg and Annaberg deposits. Free trade was permitted there but the colour was poorer.

(...)In the plateau between Johanngeorgenstadt and Neudeck in Bohemia, after Schürer's first colour mill eleven other mills have been built in the late 16th and early 17th century, almost all of which are listed in the old registers (Messtischblättern). Some companies are missing from this list, since they had already shut down in the 17th century because of the export ban to Bohemia, which did a great damage to the local businesses. Among these were the Magdeburg pharmacist Lorentz Bergkau and Ernst Nordhoff from Friesland.

Bergkau had travelled through the Ore Mountains in 1603-1609 and learned very quickly how to produce the blue and recognized the positive economic outlook. His residence was initially in Joachimsthal[8]. From there, he tried to find cobalt deposits in the surrounding area. In 1609 he approached the Elector[9] with the proposal to nationalize the blue trade. He told the rulers his observations that Schneeberg sent annually large amounts of the cobalt colour to Hamburg, Holland and Zeeland from which the Elector only reaped small earnings. Bergkau wanted to produce good colour at half the price established by the traders of Hamburg and the Dutch and said that there would be better-made coloured glass (smalt) as well as raw colour (zaffre) to sell. Together with Ernst Nordhoff he would take over the management of the production and fabricate annually 100,000 – 150,000 kg. The letter was accompanied by a detailed estimate along with demands for his future and Nordhoff's. The letter was never answered, but Bergkaus' proposal was taken by the Elector as his own and in the same year he increased the tax per 50 kg zaffre and the following year nationalized commercial cobalt.

The disappointed Bergkau went to Bohemia and built a colour mill at the border. He later sold the business to Martin Pressler, this left it to Hans Burkhardt, a wealthy Schneeberger. Burkhardt had built after 1644 the large colour mill Schlema and thus was one of the four powerful cobalt-contractors.

(...) After 1640 wealthy entrepreneurs succeeded to get the total cobalt accumulation in their hands. Lengthy negotiations between the Elector's Court and the cobalt mills led to a contract with a cartel made by Hans Veit Schnorr and John Burkhardt from Schneeberg, Sebastian Oeheim from Leipzig and Hans Friese from Hamburg which specified the amounts to produce and the distribution pricing. After the death of Friese, the complete blue colours business was in Saxon hands. The 1649 Cobalt Agreement Contract includes Hans Burkhardt, Sebastian Oeheim, Rosina Schnorr, the widow of Hans Veit, and Erasmus

Schindler. As Burkhardt had no heirs, he bequeathed his operation to the Elector. A large part of the production still went to Holland, where it was again processed to yield many more colour varieties.

In conclusion, after a first largely unsuccessful effort in Saxony around 1540, where the basic technology had been discovered, the first industrial colour mills were set in Holland, probably before or around 1550 and the technology perfected there to an extent that was never duplicated in the Erzgebirge. In Saxony the first permanent colour mill was built in 1568 and a number of other mills were established both in Saxony and in Bohemia, particularly from the early 17th century. The ore on the Saxon side of the border returned a better blue (at least with the technology locally available) but the local ruler established a monopoly over the production, limiting private enterprise. On the Bohemian side there were no such limitations but to obtain a good colour, the ore had to be acquired from Saxony. This was made impossible after the Elector decreed a ban on the sale of unrefined products but still there were some colour mills operating in Bohemia. Those aspects are related with the availability and cost of the colour in Europe and will be reviewed from a Portuguese perspective at the end of this paper.

6. USES AND QUALITIES OF COBALT BLUE

Those in the art and in the heritage fields always think of cobalt blue as a pigment used in paints, ceramics and glasswork. But actually it had other industrial applications that were more relevant in terms of demand than the first group. Part of the success of Dutch entrepreneurs in this and other businesses stemmed from the fact that they could devise new applications for their products which were then kept secret. They found that cobalt oxide in small amounts could correct a yellowish colour, making it look whiter than before. Although the process is not a bleaching but merely a colour correction, they sold cobalt oxide as a bleacher to whiten linen and other fibers, as well as paper. Used on transparent glass in minute amounts it would also render the glass clearer. The demand for bleaching was much higher than the demand as an art pigment but this was not of general knowledge and so, even if the pigment could eventually be produced in Saxony and Bohemia to the same standard as in Holland, they were only aware of a much smaller market for their product.

As for quality of the cobalt pigment produced, as seen above in another context, sources remark that *the Bohemian cobalt did not have the quality of that from Schneeberg and Annaberg deposits* in Saxony [3]. This may be an important remark as far as azulejos are concerned, as we shall see, although there seemingly is no further information on the subject.

On the extraction of arsenic from the pigment, Hammer [11] states that *arsenic may remain at a low content because it then has a favourable effect to the colour*. Sourcing a 1761 book by D.J. Lehmann (Cadmiologia oder Geschichte des Farben-Kobolds, Teile 1-2. Königsberg) he lists four shades of cobalt blue available at the time: Flemish Blue; Dutch Blue; Prussian Blue; and Saxony Blue.

He also lists a number of quality levels of which there seemingly were at least eight of smalt and zaffre counted together, including: Ordinary High = OH; Medium High = MH; Fine High = FH; Ordinary Mixed = VE and Finest Zaffre = FS.

On quality control Martin De Gruijl says: *It commands respect how simple means could exercise effective quality control, resulting in a good product to satisfy requirements. For instance, they did a sinking test with a tall glass filled with water into which glass powder was emptied to settle. Large particles would drop faster than smaller, constituting a good indicator to the grain of the dust and its homogeneity. Furthermore, smear on a black wooden board to appreciate the grain. And especially a broad experience in the manufacturing process was the key to making a reliable and successful product* [10].

An engraving in Winkler's book [12] shows the appraisal of the colour of different outputs. This was compared with standard samples and mixing ratios were decided to produce the several shades of blue (figure 8).

Figure 8. The Board advises on the selection of the best mixing ratios on the basis of samples from the furnace.
Source of the engraving: Winckler, 1790 as reproduced by Hammer op. cit.

7. SOME NOTES ON THE MARKET FOR COBALT BLUE IN THE LATE 18TH AND EARLY 19TH CENTURIES

Cobalt trade in the Erzgebirge suffered heavily from the discovery of new sources of cobalt. During the first half of the 18th century cobalt was found elsewhere in Germany (most importantly at the time, in the Black Forest region) and in Spain. Subsequently it was found in Austria, Sweden and Norway.

Of these the most important find was in Modum, Norway, in 1772. A plant to process the ore (called *Blaafarveværket* [19]) was started under royal patronage in 1776 and by the 1820s it supplied 80% of all the world needs in cobalt pigment.

It was the fact that most of the uses of cobalt blue did not call for a stability at high temperatures that led to its demise: when a French chemist invented ultramarine blue in the 1828, the artificial pigment, much cheaper to produce, replaced cobalt blue in most all applications except those that called for stability at temperatures over its own 350ºC limit. During the 1840s cobalt plants started closing. In 1848 Blaafarveværket, once the second most important industrial plant in Norway, was bankrupt and after changing hands several times it closed in 1898. In the Erzgebirge the production fell to almost nil and some of its colour plants closed, some went on using Norwegian ore (in 1855 Blaafarveværket had been acquired by the Saxon Sächsischer Blaufarbenwerkverein), some converted to the manufacture of ultramarine.

Cobalt blue was the only reliable pigment for firing at any temperature, including the 1400ºC attained when firing fine porcelain but, as I stated before, the market was minimal compared to the remaining industrial fields, most of which were lost.

8. CONCLUDING REMARKS

A few years ago we analyzed blue pigments in 50 different azulejos for the MSc research mentioned before [1]. The oldest of those was a hispano-moresque fragment done by the cuerda-seca technique, datable from the late 15th to the early 16th century. This sample was analyzed by both ED-XRF and WD-XRF and the results have shown conclusively that the pigment did not contain arsenic. On the other side it had a high content in copper [15]. This has been noticed by other authors [e.g. 20, 21] who decided that it represented a different location based on the association Co-Cu. I agree this represents a pre-Erzgebirge pigment, possibly obtained from Persia, but I base this opinion on the total absence of arsenic. We have found copper in the blue of other (more recent) hispano-moresque tiles that had arsenic in their composition and since the blue-coloured glass in hispano-moresque tiles also included the addition of tin oxide, I cannot state conclusively that the copper was not added purposefully e.g. to alter the shade of blue.

During the whole classic period of pre-industrial azulejo production in Portugal, which I will (quite arbitrarily) set for the two centuries from the earliest manufacture of faïence tiles, during the third quarter of the 16th century, until the first azulejo productions by Fábrica do Rato, the blue pigment was almost certainly originary from the cobalt ores of the Erzgebirge and their analysis returns a characteristic association Co+As+Fe+Ni in which the content in nickel may be important, or then only residual, but the presence of arsenic is constant and well defined. Eventually it may also contain sizeable amounts of bismuth [1].

After ca.1750 a few samples of Coimbra production show only minute contents in arsenic. The blue is different, somewhat greyish (and it brings to mind the remark that a low content in arsenic had a favourable effect on the colour [11]. I cannot ascertain at present whether that pigment represents a new source of cobalt or merely a choice between available blue shades, some of which were processed at higher temperatures and lost most of the arsenides. During the 19th century another pigment is used, without As, Ni or Fe [1].

The following important points must be born in mind:

i) the pigment used by painters in other media was of a much better quality than that normally needed for painting on azulejo glazes. Cobalt for azulejos could be acquired as zaffre or smalt, the former being considerably less expensive. Painting could be done directly with zaffre suitably milled. But it seems likely that, if a workshop acquired zaffre it would then produce smalt from it, to be used by its painters. This is clearly seen in 17th century Portuguese tiles in those cases where a section of the glaze shows it to contain many small aggregated inclusions, such as grains of sand and feldspars. However, in the very same sections, in the blue areas the glaze is devoid of inclusions showing that the glass in those areas was introduced with the pigment, and thus meaning that the pigment was used as smalt. (figure 9)

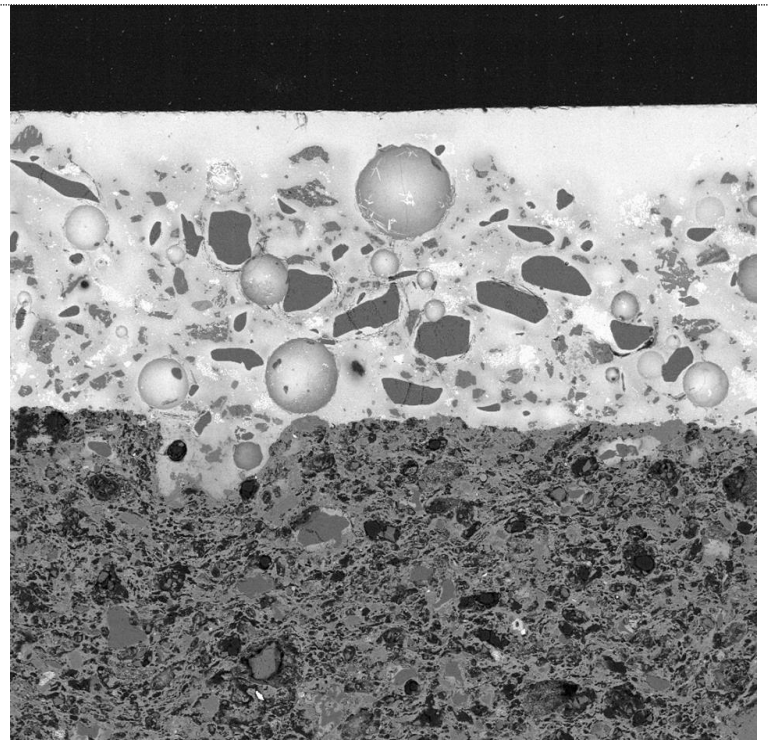

Figure 9. Section on a 17th century azulejo glaze and biscuit with many inclusions in the glaze. The areas devoid of inclusions on top are those painted in blue – the pigment was mixed with glass without aggregates.

ii) once the technology was known, there was a margin of profit to be gained by acquiring zaffre and processing it to smalt. The fact that cobalt furnaces operated in Portugal does not necessarily imply a local source of cobalt, but may simply mean that someone was trying to manufacture smalt from zaffre acquired in the market.

iii) variations seen in the quality of the blue in Portuguese azulejos may be related with the suppliers available and the economic situation, because - as was seen - there were several qualities available at different prices. The very pure blue found in some azulejos from

around 1600 may derive from the fact that Portugal was then under the Spanish Crown and Spain had possessions in the Low Lands and direct access to the best colour producers.

iv) considering figure 1, it is evident that the colour of the Ni-poor blue is much better than that of the Ni-rich blue. This brings to mind the remark that the colour obtained from the Bohemian cobalt did not have the quality of that from Saxony [3] and I wonder whether this duality stems from those two origins. As pointed in another publication by my colleagues and I [15] the "ugly" nickel blue seems to have appeared in Portugal only around 1630 or 1640, when Portugal was living a difficult economic situation, first while under the Spanish Crown, then in war with Spain (the 28-year long War of Restitution lasted from 1640 to 1668). When azulejos were displaced and rearranged elsewhere, as in Beja, they are often re-set according to pattern and not colour and it is sometimes possible to see, side by side, azulejos painted with both pigments (figure 10).

Figure 10-. Side-by-side 17th century azulejos painted in the nickel-poor and nickel-rich cobalt blue. (left to right: Ducal Palace of Vila Viçosa; Cloister of the former Convento da Conceição in Beja; Loggia of the Igreja da Misericórdia in Beja). All pictures: J-M Mimoso

By the end of the century and for most of the 18th century, when the country was fattened by the gold influx from Brazil, the "nickel blue" seems to have rightfully fallen from grace but reappeared in Lisbon around 1800 at the time of another economic crisis and yet another war: the Peninsular War. It does not seem to have been used after the situation stabilized during the second quarter of the 19th century.

v) the matter of the availability of cobalt blue for azulejos may be connected with more than the situation in Portugal. The confusing Thirty Years War started in 1618, precisely with a revolt in Bohemia, lasting until 1648, with surges of battling in the region, after which territories changed hands (and religion) causing large movements of populations and a high death toll. It is quite likely that during this time productions were halted for months or years, stocks exhausted, prices changed… which may have caused a shift towards lesser cobalt pigments.

Créditos

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4- The "beautifully coloured cobalt" is not a blue mineral but a pink or reddish mineral such as erythrite which is a hydrated cobalt arsenate mineral formed at the surface and which prospectors call "cobalt bloom".

5- The plant is a species of a spice group usually called "saffron" in English and in Portuguese "açafrão".

6- Translated from Horschik's transcription of the text in "Ars Vitriaria Experimentalis" by Johann von Löwenstern-Kunckel, first published in Frankfurt a.M. in 1689.

7- LEHMANN, C, Historischer Schauplatz der natürlichen Merkwürdigkeiten in dem Meissnischen Oberertzgebürge, Freiberg 1699 (as reproduced by J. Horschik op. cit.).

8- This is a small town formerly in Saxony and now in the Czech Republic, called "Jáchymov" in Czech.

9- The Elector was the ruler of Saxony.

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17- "Frank" meant a German (from beyond Saxony), not a Frenchman. Also "Frieslander" referred someone from Friesland in Lower Saxony, not Holland.

18- "Speiss" is a metallurgical denomination used for metallic arsenides

19- The plant "Blaafarveværket" (literally "The Factory of the Blue Colour") is now a museum. Its history may be read in the Norwegian Wikipedia: http://no.wikipedia.org/wiki/ Blaafarveværket

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