Miraculous cementation water in Špania Dolina and Smolník - an underappreciated mining heritage

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ABSTRACT
This article is concerned with the occurrence of unusual cementation water in Špania Dolina and Smolník, a Hungarian rarity, that was long an object of attention and curiosity for many domestic and foreign alchemists, chemists, mineralogists and scientists. In particular, the peculiarities of this water allowed the extraction of copper from the cementation water, of interest because of the development of technological processes of copper extraction in the Slovak region of Habsburg Monarchy. Copper has been obtained via precipitation of iron from Špania Doline and Smolník since ancient times.

Key words: cementation water, vitriol waters, copper ore, pyrite, copper, iron, transmutation of elements, mining inheritance, mining tourism

INTRODUCTION

The cementation waters from Špania Dolina originated in extensive deposits of copper, the ores of which occur in two types: a yellow variety (chalcopyrite) containing 8-10% of Cu with a very low silver content and a black one (tetraderite) with copper content varying considerably from 4 to 18% of Cu, 250 -1250g/t of Ag and few grams of Au in one ton. The copper ore was not as concentrated as the silver, but more or less contained a spoil, so that it in some cases contained only 3-4% copper.

The copper from Smolnik differed from that of Špania Dolina in that it contained a considerable amount of pyrite, 6-8% on average. The poorer contained 2-3% and the better 12% or more. The silver content was generally low. (Herčko, 2003a; Herčko, 2003b)

The mysterious, long inexplicable process of copper apparently extracted from iron led alchemists to incorrectly believe that this was clear evidence of the transmutation of a lesser metal - iron, to a superior one - copper (Herčko, 1982). This method had been used to extract copper from water standing in mining tunnels or the runoff from slag heaps.

These mysterious waters contained compounds of copper, mostly copper sulphate, known at the time as bluestone or vitriolum. (Herčko, 2002b). The copper sulphate originated in copper-ore mines by the decomposition of chalcopyrites and tetrahedrites. When a metal item was immersed in a solution of copper sulphate, the iron dissolved and copper precipitated from the solution. This is the process that was incorrectly accepted as transmutation of metals by the alchemists, and the reason for their interest.

THE CEMENTATION WATERS IN SLOVAKIA – AN UNDERAPPRECIATED MINING HERITAGE

The evolution of opinions, primarily those of alchemists, concerning the apparent transmutation of elements (precipitation of copper from iron via the influence of the cementation water) in the Hungarian regions of Slovakia is valuable heritage which might be interesting to both scientists

and the general public. The cases of occurrence and exploitation of cementation waters in Špania Dolina and Smolník are remarkable examples of areas of interest for scientists of an earlier age, in that many scientists from throughout Europe came to study it in order to explain the chemical processes behind this phenomenon. The conception and realization of a center for mining tourism would be a valuable project to pursue. It would attract tourists not only with exhibitions of historical documents and alchemical, chemical and geological laboratories, but also with the opportunity for visitors (with professional supervision) to operate the machines, accessories and methods used for the exploitation of cementation waters in previous centuries. We are sure that appropriate locations for such centers could be found in Špania Dolina, Smolnik or both cities. The authors of this article are willing to assist with such a project.

THE EVOLUTION OF OPINION REGARDING CHANGES IN METAL TO COPPER BY CEMENTATED WATERS

We can find references to the occurrence of cementated waters Špania Dolina and Smolnik in the writings of alchemists, polymaths, doctors and scientists as early as the 16th century (Tibenský, 1966). The royal counsellor of Spiš chamber, Juraj Wehrner, was one of the first to introduce the European scientific public to chalcopyrite stream and the possibility „to change“ a metal to copper in his work *De admirandis Hungariac aquis hyppomnemation*, published in 1542 in Basel. He described a process of copper extraction from the waters of Smolník with the assistance of embedded metal objects. The settled mass contained a copper, called „cement“ by the miners (Stillhammerová, 2003). This settled copper was first melted and then further refined. The copper extracted by this method had the same characteristics as the copper produced from ore using conventional technology.

This apparent transmuting ability of cementated water Wehrrner noted is due to the chemical that he called „markazit“ – a pyrite contained in the cemenated water (Wernher, 1542). The alchemists sought evidence that Nature could extract copper directly from iron, thus producing one metal from another.

The young English doctor Edward Brown (Herčko, 1976) visited Špania Dolina at the behest of the Royal Educational Society in 1672. In his journal from Špania Dolina he described two springs of vitriol water which changed a metal to copper, calling them new and old cement. The springs rose deep in the mines and the metal was generally submerged for 14 days. These waters were extremely valuable as the lowest grade of iron, including scrap could be changed into pure copper, which was even more malleable and easy to melt than most. Doctor Brown also found that this metal could be melted without the addition of other elements, while copper ore required several remeltings to become usable. In one experiment, he immersed an iron ingot in the shape of a heart in the water for about 2 weeks. It retained the original shape, but all iron was replaced by copper.

However, many experts of the time refused to accept that this represented true transmutation, insisting instead that the cementated water contained a „vitriolum Veneris“ (Venus vitriol) which, when meeting a Mars-like body (iron), imparts characteristics of Venus which immediately penetrate and dividere et imperare (divide and rule), until the original material degenerates and is replaced by the copper.

When iron is apparently transformed to copper via this process, many particles are isolated and gather on the bottom in a powder form. This material is not, however, iron but copper. Dr. Brown was able to extract this powder from the water and melt it into excellent copper. If this copper residue had not appeared, Dr. Brown could not have explained its absence.

However, he was able to artificially replicate a process which naturally occurred in the mine, in his opinion successfully.
While Doctor Brown carried out his studies on the cementated waters of Špania Dolina and their interesting effects on metals, the mining administrator presented him with several specimens of the copper metal produced in the waters. From this he produced some high-quality copper plates and bowls.

Rulers as well as professional society took an interest in the cementated waters of Slovakia in the 17th century. Its mysteries were of interest to the eminent scientific autority Isaac Newton, secretary of the Royal Society in London. A letter, written in 1667 to Cambridge Aston and published in 1966 by Tibenský, contained detailed instructions as to what to look for on foreign trips (Tibenský, 1966). Specifically regarding the gold, copper and antimony mines of Kremince and Hungary, he was to determine whether iron was transformed to copper by the vitriol waters found there in the rocks, and whether this copper could then be melted to appear after cooling.

In Špania Dolina´s mines, Dr. Brown observed „two springs with vitriol water" and although he accepted the traditional opinion that this represented a transmutation of a lower metal to the higher one, copper to iron, he was attentive to the changing opinion of other scientists. The latter belived that the springs were composed of a copper sulphate solution (Vitriolum von Kupfer), parts of which are deposited in copper form in immersed iron. This opinion correctly describes the gist of the cementation process. He also addressed the questions put by Isaac Newton to Cambridge Aston regarding the vitriol springs in Špania Dolina.

Earl A. F. Marsigli, (Fig. 1) a member of the Paris, London and Montpelier Royal Societies, visited Špania Dolina in 1696 and also directed his attention to the cementated waters (Duka, Z., N., 1974). In his work concerning the mines of Vindšachta, he included a supplement (No. XI), which describes a split of Špania Dolina mines.

Fig. 1 Luigi Ferdinando Marsigli

On the Fig. 2 there is the split of Smolník mines, fashioned in the same manner as that of the Vindšachta mines, the only difference being a panoramic view at the top. A copper engraving of the slit was produced by Jan Schenck.
Marsigli explained this formation by writing that there were three streams of cementated water which flow from the surface to underground where they collect in pools (Fig. 3).
Iron there is slowly covered by copper powder which is secreted from the cementated water. The origin of the latter was explained as sulfate particles melted into mountain spring water, becoming cementated water, which deposits it copper as a result of iron activity. These copper particles bond with sulphates very easily.
Another notable visitor to Špania Dolina was medical doctor F.E. Bruckmann, in 1724. He was a member of the Imperial Academy of Natural Curiosities as well as the Royal Prussian Academy (Fig. 4).

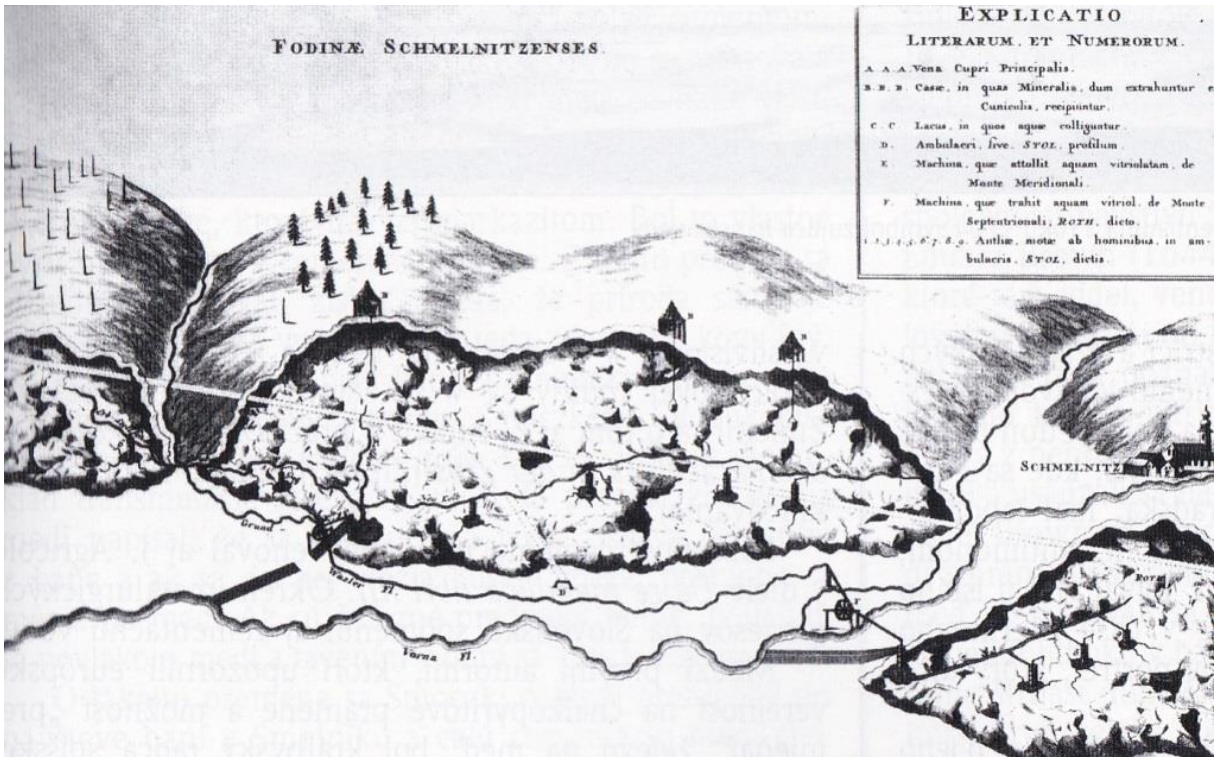

Fig. 2 Capture cementing waters Smolník from 1696 as shown in the work of L.F. Marsiglio

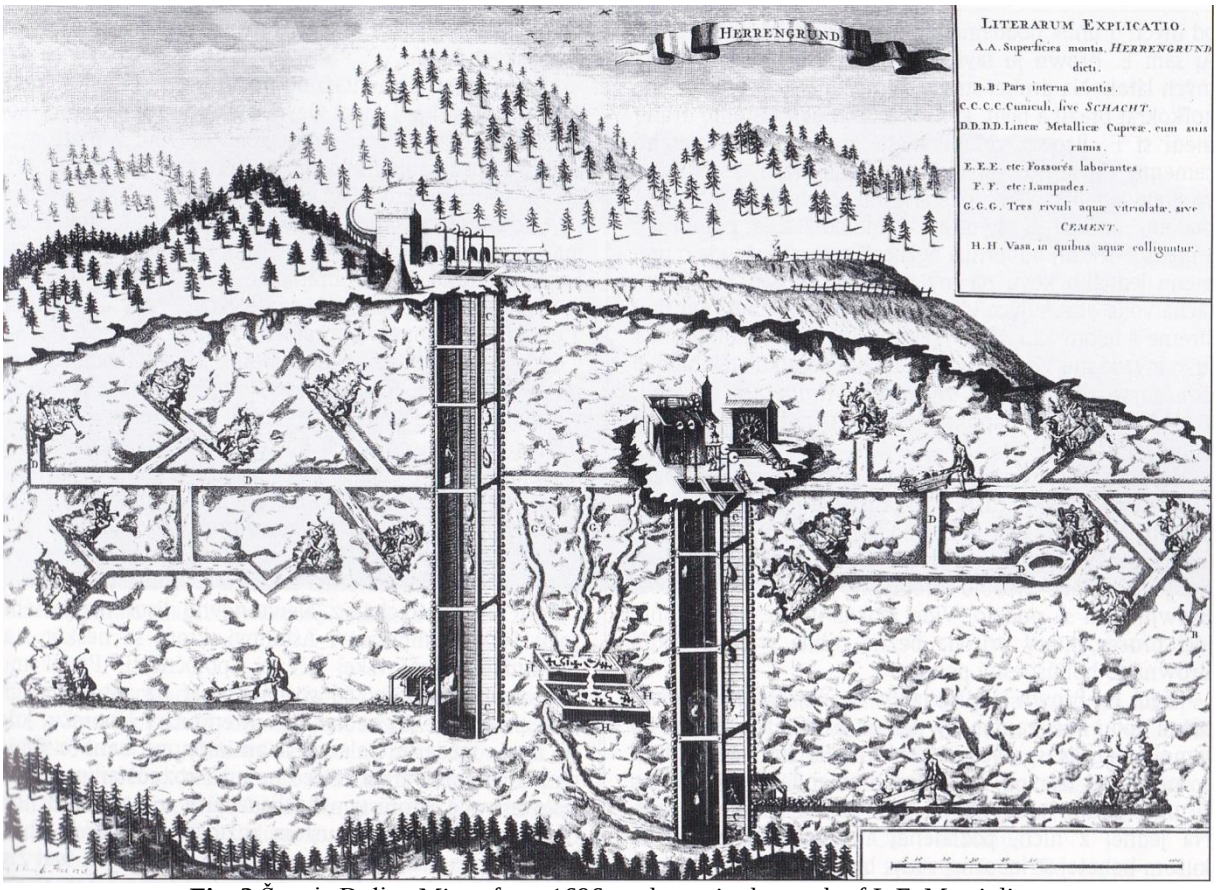

Fig. 3 Špania Dolina Mines frpm 1696 as shown in the work of L.F. Marsiglio

He published extensively about Špania Dolina, but only his observations on base conditions and the cementated waters are of interest to us here. The mines in Špania

Fig. 4 Francis Ernest Bruckmann

Dolina were the biggest and most important in Europe, because here it is possible to tunnel extensively underground and emerge in a different location. Ore extracted here was very valuable: 1 pound (cent) of ore generally contained 20-60 funts of copper. However, most of this ore was tightly bound to the surrounding mineral and was very difficult to separate. In many places, ore and rock were joined in a continuous body (dike). During Dr. Bruckmann's visit to Špania Dolina, approximately 4000 cents of pure copper (1 cent = 54 florens) and 20-24 cents of cementated copper was extracted.

At the depth of 70 *siaha* (in old units) in the mine, the cementated water was collected in a small closed bin. Over the course of a few months, several cents of iron bar was transformed into copper by simple precipitation. The copper particles accumulate in the water in the place of the iron precipitate Crocus Martis and are transformed into a copper usually called cementated copper. This transformation occurs more rapidly in different conditions, often in as little as 30 days. The longer period here of several months is due to suboptimal conditions in one of the springs. The miners would sometimes place iron items like horseshoes or nails in the water to become covered by copper, a practice mentioned by Bruckmann. These were given as gifts to collectors of curiosities and became part of some collections of natural history.

On the surface of the mine, a green soil called Mountain Green or shale copper (Chrysocolla natica, viride montanum) was collected in wooden bins. Bruckmann had never seen this substance before, as it appeared only in association with rich copper veins in Slovakia. Painters used it as a green pigment.

Once an adequate amount of sediment was collected, the bin was cleaned and the soil sorted into three grades. The first was captured in the first bins the water passed through; it was raw, coarse and mixed with sand. The material in the next bin was somewhat smoother, and the third was the finest, captured in the bins at the end of the water's flow (Herčko, 1975).

DISTINGUISHING CHARACTERISTICS OF THE CEMENTATED WATERS IN ŠPANIA DOLINA AND SMOLNÍK

F.E. Bruckmann also pointed out the differences between cementated waters in Špania Dolina and Smolník, where, compared to Špania Dolina, deposits of copper pyrites settled quickly. During intensive mining these cementated waters offered more methods of copper acquisition from iron fragments and waste (Herčko, I., 2003a).

Differences between Smolník´s cementated water and that of Špania Dolina have been enumerated as follows (Fig. 5):

1. While the water from Smolník corroded iron to sludge and dust because of vitriol concentration, the iron immersed in water in Špania Dolina remained intact. This is what allowed such items as crosses and

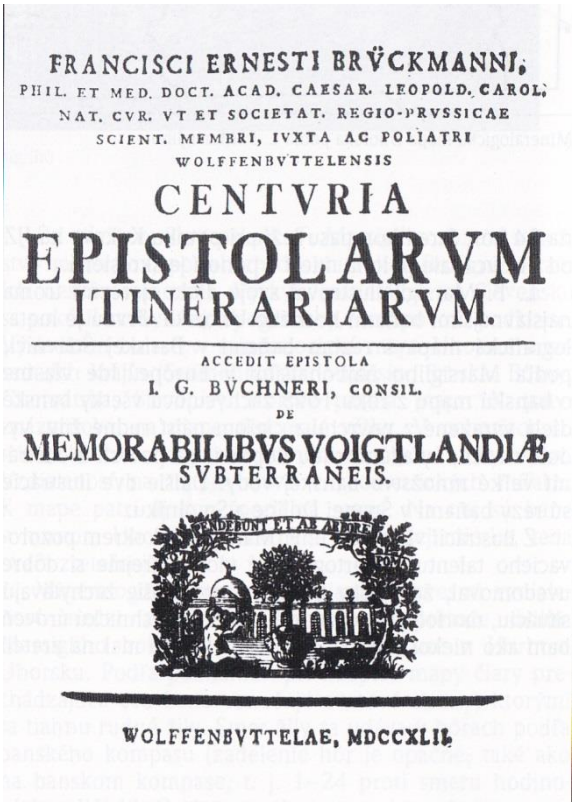
FRANCISCI ERNESTI BRVCKMANNI,
PHIL. ET MED. DOCT. ACAD. CAESAR. LEOPOLD. CAROL.
NAT. CVR. VT ET SOCIETAT. REGIO-PRVSSICAE
SCIENT. MEMBRI, IVXTA AC POLIATRI
WOLFFENBVTTELENSIS
CENTVRIA
EPISTOLARVM
ITINERARIARVM.
ACCEDIT EPISTOLA
I. G. BVCHNERI, CONSIL.
DE
MEMORABILIBVS VOIGTLANDIÆ
SVBTERRANEIS.
WOLFFENBVTTELAE, MDCCXLII.

Fig. 5 The title pages Bruckmann page Centuria Epistolarum Itinerariarum

horseshoes to be placed in the water, to be covered with copper and presented as gifts.

2. The cementated water in Smolník has been maied on the surface by the machines and also it´s percipitation became on the ground . It contained a lot of copper particles which came if were met with iron.The cementated water in Špania Dolina has been used underground. The cementated water in Smolník was pumped to the surface by machines and its precipitates appeared on the ground. It contained many copper particles which appeared upon contact with iron. The cementated water in Špania Dolina was exploited underground.
3. In Smolník 600 cents of iron per year were transformed, while production in Špania Dolina was only 20-24 cents, because water in Špania Dolina did not escape in large amounts and in some cases travelled through a barren vein.
4. In Smolník, the precipitation took only one month, while in Špania Dolina iron must be submerged for a year for the process to complete. Miners drank this water to treat stomach problems; the vitriol in the water often led to severe vomiting followed by a degree of relief (Magula, 1976).

Bruckmann also wrote that the collectors of curiosities often requested souvenirs such as snuffboxes, cups and other decorative items to be plated in this water. Samples of silver ore were also submerged, along with a silver mine model on which Bruckmann saw the following text:

(raw translation)
„My mother bore me completely black,
After a bath I was nicely reddish,
Then the summer clothed me in its vesture
Now everyone enjoys me“

Bruckmann records this text on another object:

„I was iron, now I am copper
There is silver in me and I am covered by gold“

The following rhyme was found on a cup:
What I can everything do ,
It’s a strange thing
I am copper but I was iron
After 30 days sitting in the water
You will find this pure and bright water
In Špania Dolina, and its secret nobody will discover,
But surely it´s a fact.“

CONCLUSION

It was a common belief at the time that the waters of Špania Dolina and Smolník were unique to Hungary. However, F. E. Bruckmann pointed to other localities with cementated water and wrote: „Hungarian gentlemen shouldn’t think that there are no

similar cementated waters in the world; I will mention some facts about the existence of others“ (Herčko, 2002b).

In the second edition of Bruckmann´s oeuvre Magnalia dei in locis subterranies,published in Wolfenbuttel in 1730, there are also facts taken from Probier – Buchlein (exam book, page 175) from an unknown author , who observed the Špania Dolina mine via the drainage tunnel through to the Ferdinand shaft and then eventually to the cementation equipment. There were eight cementation machines which could hold a total of 100 pounds of iron, 50 pounds in the largest one. Iron was placed there indiscriminately, whether pistons, tubes, locks or scrap iron from the mine. The extracted cementated copper was removed after one year or so, depending on the iron content of the pieces. It was then transported to the Chamber palace in Banska Bystrica and thence to the smelter.

This unknown author also mentions a vein containing mostly chalcopyrite without the silver, or sometimes bearing only a small amount. This vein was no wider than a palm width, and was secured by reinforcements, as it was cut into veined rock completely covered in white and green vitriol. The Maximilián tunnel had a depth 132 siah from the surface, and was 56 siah higher than the Ferdinand tunnel. Six hundred people worked there and received weekly compensation (Herčko, I., 2002c).

In these texts, mostly of a descriptive character, authors tried to describe a miraculous cementated water and transformative process of iron into copper. Some of them made no attempt to explain the process; those who tried did so in alchemical terms and accepted it as evidence for the transmutation of metals.

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