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The development of the blast furnace metallurgy of the iron in Slovakia

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Abstract
Easily available sources of iron ore, the abundance of hydropower, and wood for charcoal were the prerequisites for the development of iron metallurgy in Slovakia. Since the 16th century, the bloomery process used in iron metallurgy has been gradually replaced by the blast furnace process. This new process was more economical, but it required extremely high investments. The steam engine replaced the unreliable water power in the blowing process, and coke replaced charcoal. Especially due to economic problems, the first blast furnaces in Slovakia started to be built about two hundred years later than in Western Europe. Despite the promising start, the installation of steam engines was lagging. A major drawback was the lack of road and rail networks combined with the absence of local coking coal. The introductory part of the paper compares chronologically the individual stages of the development of blast furnace production in Slovakia and abroad. Next, the paper presents comprehensive results of the analysis of samples of the slag found at 59 sites of extinct ironworks with a blast furnace, localised until now. The samples were analysed by metallographic, chemical, spectral (secondary and trace elements), and X-ray methods. In the past, these data were published with territorial restrictions and mostly in a language other than Slovak. The contents of secondary and trace elements in slag from individual sites using cluster analysis and also metallic iron content in slags categorised according to owners of the blast furnaces and the slag basicity are compared.

Keywords
Slag, blast furnace, 17th – 19th century, Slovakia.

Introduction

The territory of Slovakia was incorporated into Hungary as the Duchy of Nitra after the fall of Great Moravia. Dukes, usual relatives of Hungarian kings, were bearers of power ambitions, sometimes successful (e.g. Duke Andrew, later King Andrew I) and sometimes unsuccessful (Duke Vazul, blinded by King Stephen I). Dukes, backed by strong economic territory (also due to metallurgy of precious metals, copper, and iron) with dynastic contacts with neighbouring states, posed a permanent danger for the monarch. When Bela II the Blind (blinded after a failed uprising against King Coloman I together with his father, Duke Almus) ascended the throne, the post of the Duke of Nitra was not filled. During the 12th century, the territory of the Duchy was administratively included in Hungary (Steinhübel, 1999).

Easily available sources of iron ore, an abundance of hydropower, and wood for charcoal were the prerequisites for developing iron metallurgy in Slovakia. Archaeological evidence of the oldest reduction of iron in pit furnaces is dated to the 6th century BC.

The earliest evidence of the use of water-powered installations for metallurgical purposes comes from written sources mentioning, for instance, hammer mills at Somersetshire (England) in 1086, at Cardedeu (Spain) in 1104, etc. (see, e.g., Lucas 2006, 347; Tylecote 1992, p.76).

The use of water power in metallurgy was also mentioned in Slovakia (Štítnik) in 1243. In Europe, two basic types of bloomery furnaces blown by water-powered bellows were developed. The first one was the hearth furnace. It resembled a smithy hearth but was larger in dimensions. It dominated in the Hispanic peninsula, in southern France, in some parts of Italy, and also in northern Germany, Poland, Sweden (in the form of "osmund" furnace), and since the 14th century in Russia. Since the 16th century, it was used in Portuguese, Brazil, and Spaniels in South America, including Mexico and California. Even the first ironworks in the USA have used hearth furnaces since the early 17th century. This furnace was used only exceptionally in Slovakia. The second type was a 3 to 5 m high shaft furnace (Stückofen, Windisch Ofen in Slovakia). High temperature near tuyeres and longer smelting time (about 18 hours) led to perfect consolidation of the bloom, its saturation with carbon (carburising, up to 2%), and the formation of up to 30% of cast iron (proportion of the produced iron). (Tylecote 1992, p. 45; Pleiner 1958, p. 173)

The use of water power has allowed a larger amount of air to be blown into the furnace at a higher pressure than by manual blowing. The furnace could have a larger volume and height. Improving the efficiency of iron production in the shaft furnace could only be achieved by increasing its height. This led to a decrease in the temperature at the top of the furnace shaft. In the high shaft furnace, the temperature from the throat to the hearth increased more slowly. Longer contact of reduced iron with carbon created the likelihood of high-carbon iron alloy - the cast (pig) iron. In cast iron production, the charcoal/iron – ore ratio was generally higher compared to the batch intended for the bloomery process (Tylecote 1992, p. 48).

If the demand for cast iron increased - especially in the form of artillery ammunition - these furnaces began to work primarily as blast furnaces producing cast iron.

Although the oldest blast furnaces discovered by archaeologists date back to the Han Dynasty of China in the 1st century BCE, the blast-furnace process was not adopted in Europe until the 1100s CE (Lawton, 2019). The earliest European blast furnaces operated in Sweden (Lapphytan and Vinarhyttan or even in Moshyttan (Myrstener, 2019) between 1150 and 1350, in Belgium (Liege, Vennes, Grivenge, Namur) since 1340 (Awty 2007), in England (Rieveulx) since 1496 (or 1491), in France (Pays de Bray, Hodeng, Ardennes) since 1486 (Tylecote 1992, p. 76). The early introduction of the blast furnaces is also indicated by 12th-13th century archaeological finds in southwest Germany (Swabia).

The early blast furnaces were square in plane view; they were built usually of sandstone and blown by two water-powered bellows. Their construction was reinforced with a wooden or iron frame (scaffold). The ore was roasted and charged without flux, and charcoal was used as the fuel. At first, the slag was tapped through a hole in the wall of the furnace hearth which was sealed with clay when the furnace was emptied. Since the middle of the 1550s, the open fore-hearth (or "open hearth", as a siphon) was used. The fore-hearth was closed by a "dam "; the molten iron in it was covered with a layer of slag, and the iron was tapped through a hole in the foot of the dam. Low levels of silicon in the cast iron are typical for the "cold" (the air was not heated) blowing. The cast iron contained about 0.8% Si, 3.7% C, 0.7% Mn, negligible sulfur content, and 0.7% P, depending on smelted ore. In the blast-furnace process, practically all phosphorus from the ore passed into the iron, as the acidic (fayalitic) slag was not able to absorb it. Phosphorus increased the hardness but severely reduced other mechanical properties of the iron. Hard and brittle "white" cast iron was the product of the early blast-furnace process; such iron was easily refined (conversion to wrought iron) compared to "gray" cast iron, produced by "hot" blowing. The occurrence of grey cast iron in the 16th-19th centuries with an unchanged chemical composition (especially with low content of Si) was caused by cooling conditions of the castings (e.g. slow cooling of thick-walled castings) (Tylecote 1992, p. 98, 284). Blast furnaces were used throughout western Europe outside the Hispanic peninsula in the 16th century. From the beginning of the 16th century, the description of the blast furnace by Nicole Bourbon was preserved. Valuable is the image of the Flemish painter Bless, who displayed a blast furnace in the Ardennes between 1511 and 1550 (Pleiner 1984, p. 284).

The first blast furnace in Bohemia was built in Králův Dvůr in 1595 (Pleiner et al. 1984, p. 74, 104). Italian metallurgists built bloomeries that could also produce cast iron in Samsonow (Poland). "Real" blast furnace built there the "Hungarian" in 1679 (Radwan 1963, p. 104, 108). The first blast furnace in Austria (Carinthia) was built in Urtl in 1567. However, they started to build to a greater extent only in the 18th century (Carinthia: Vonderberg, Treybach since 1758, Styria: Eisenherz in 1760) (Klemm, Strobl & Haubner 2013).

As for Scandinavia, the first blast furnace in Norway was built in Larvik in 1767 (Tylecote 1992, p. 137, 144). Due to the iron ore composition, blast furnaces have not been able to compete with the local variants of bloomeries in Sweden for a long time. In Finland, the first ironworks with blast furnaces were founded in the first half of the 17th century in the Pohjan region (Fiskar 2014).

Ironworks in Ireland (Creevele) with blast furnace was founded in 1621. It was destroyed during the Anglo-Irish War in 1641 (Lings 2017).

In Russia, the first blast furnace was built according to the "Dutch pattern" in 1626. Two blast furnaces were mentioned in Tula about 1631. The blast furnace in Nevyansk on the Ural (13 meters high) was built in 1699 (Gladilin 1955, p. 10; Pusztai 1978, p. 62).

In Hungary, the first blast furnaces were built in Mukačevo in 1670 (today in Ukraine), in Ľubietova in 1692 (today in Slovakia), in Sebeshely in 1716, and in Bogsani in 1721 (both last mentioned today in Romania) (Pusztai, 1978, p. 90, 261; Hackenaszt 1991, p. 200).

The first blast furnace built in North America was at Falling Creek, Virginia, in 1622 (evolution, 2016), but the first successful blast furnace operated between 1640 and 1668 in Saugus, and the next in 1702 in Pembroke (both Massachusetts). In South America, the oldest blast furnaces were built in Mexico (Coalcoman, state Michoacan) in 1807, by Andrés Manuel del Rio (Uribe Salas 2006), in Paraguay (Ybycuí - "La Rosada") in the 1860s (Roedl, 2012 p. 141, 171), and in Brasil in 1881 (Roedl, 2007 p. 41).

During the reign of the Ming Dynasty (1313-1637), "blast furnaces" with a height between 1.8 and 2.4 m were opened in China. Such a furnace produced up to 600 kg of cast iron per day. It was fueled by coke; the iron has a high content of sulfur and silicon. This type of furnace was used until the 19th century (Tylecote 1992, p. 99). The Chinese method of cast iron-producing in the hand-powered blast furnaces since 600 BC has also affected other countries in eastern Asia. In Japan, a "Tatara" furnace produced simultaneously malleable iron, steel, and cast iron (De Campos & De Castro, 2020).

The height of the blast furnace increased from 7 m in 1650 to 13.5 m in 1800; the height of about 13 m was the maximum possible height of charcoal-fueled furnaces. In a furnace exceeding this height limit, the charcoal would be crushed by the pressure introduced by the charge, and this would cause subsequent sealing of the shaft. A new fuel – the coke allowed a further increase in height: it reached 15 m in 1850, 20 m in 1860, and 30 m in 1930, *Fig. 1.*

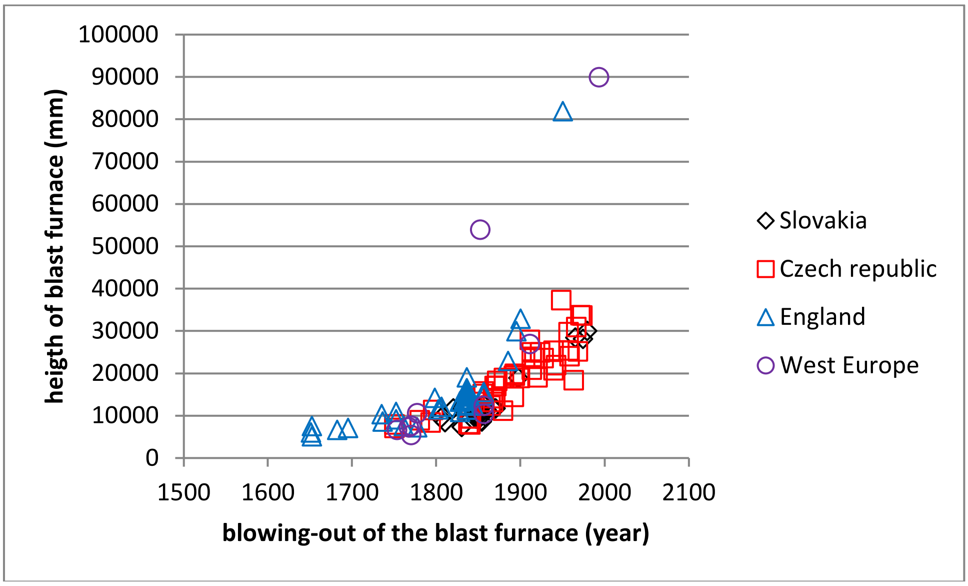

Fig. 1. Change in blast furnace height (Slovakia, Czech Republic, Great Britain, West Europe, "outlier"at the top of the figure refer to blast furnaces in Duisburg and Clay Lane.

J. B. Nielson patented "hot" blowing – the heating of the air in 1828. In addition to increasing the efficiency of the blast furnace process, the content of silicon in cast iron has increased. The result was the formation of grey cast iron, which brought problems in the refining process. The stack gas has been used for pre-heating since 1832. In Bohemia, pre-heated air was firstly used in 1840 (Ostrava - Vítkovice). In terms of efficiency, pre-heating increased production by 10% (New Jersey, USA, 1834) (Pleiner 1984, p. 92; Kruliš 1972, p. 83).

The first patent to use coal in the blast furnace was granted in England in 1611. Abraham Darby has used coke for blast furnaces since 1709 (Coalbrookdale, Shropshire) (Tylecote 1992, p. 123). The last charcoal blast furnace in England was blown out in 1829 (Pleiner 1986, p. 11). To remove the sulfur from coke and phosphorus during the blast-furnace process, the basicity of the slag increased in the 18th and 19th centuries.

The first coke blast furnaces were built in France (La Creusol) in 1785, in Silesia (Glewitz, Hlivice) in 1796, in the USA (George Creek, Maryland) in 1817, in Belgium (Seraing) in 1823, in Bohemia (Ostrava – Vítkovice) in 1836, in Germany (Mühlheim, Rhineland) in 1849), in Russia (Donetsk) in (1871), in Austria (Schwechat and Zeltweg) in 1872 and Spain (Bilbao) in 1880. In 1854, the proportion of charcoal cast iron was still 47% in the USA (Kruliš 1972, p. 83).

Abraham Darby II used a steam engine to blow the blast furnace in 1742 - the "liberation of metallurgy from water". By the end of the 18th century, almost all blast furnaces in Britain had been blown by a steam engine. After 1790, multi-cylinder blowers ensured a uniform flow of air.

The refining process was carried out in the finery – the hearth was similar to a blacksmith hearth; it was blown by bellows powered by a water wheel. The process aimed to convert brittle cast (pig) iron to malleable form by decreasing C, Si, Mn, P, and other impurities. The loss by burning was about 30% overall (Tylecote 1992, p. 102, 126).

The first use of a reverberatory furnace for refining (the "puddling") was designed in 1783. The hearth of the furnace was rammed with a roasted slag. Iron loss by burning was 7 - 18%. Part of the sulfur and up to 80% of the phosphorus passed into the slag. The puddling process started to be used in central Europe in the 1830s; the first reverberatory furnace for "puddling" was built in Bohemia (Ostrava - Vitkovice) in 1830 and in the USA (Boston) in 1835 (Kruliš 1972, p. 84).

Expansion of the water-blown high shaft "Slovak furnace" ("Windisch Ofen") since the 14th century begins the period of furnaces and hammer mills connected to the water. Both the blowing of the furnace and the forging of the yielded product – a large (about 100 kg) bloom required water energy for processing. Slovak furnaces were documented in Jasov, Dobšiná, Spišská Nová Ves and Slavošovce at the beginning of the 14th century, in Gelnica (1435), in Krompachy and Velký Folkmar (1574) (Pleiner, Vozár & Šarudyová, 1976; Hapák, 1962; Šarudyová, 1989, p. 9-21).

"Massa" (maša, derived from "Massel", a piece of iron) appears since the middle of the 16th century (firstly between Štítnik and Dobšiná). It was a water-powered shaft furnace similar to the Slovak-type furnace. The products were rectangular castings of pig iron (sow, "Gans"– the goose) (Paulinyi, 1966, p. 70) (Pleiner 1984, p. 174). The cast-iron stele of P. Kielmann, dated to 1598, witnessed the production of cast iron in Slovakia before the construction of the first blast furnace (Pleiner 1984, p. 174).

The first blast furnace in Slovakia was built in a free mining town of Ľubietová in 1692, a century later than in neighbour countries. The most important cause of the lag was the wars with Turkey. The Turks occupied central and east parts of Hungary in the 16th century. The territory of Slovakia, Croatia, and Transdanubia along the border with Austria constituted the "free" part of Hungary. All the defensive wars ravaged the country, and the army upkeep cost a huge amount of resources. The efforts of the reigning Habsburg dynasty to establish an absolutist government resulted in repeated uprisings. Together with the plague and the famine, they caused an absolute decline in the country. However, the blast furnace required significant capital and stabilised conditions. The army was the main consumer of cast iron, mainly in the form of artillery ammunition. Above mentioned blast furnace in Ľubietová was built by a consortium of citizens of the free mining town of Banská Bystrica, and later it was purchased by the exchequer. In 1722, parts of the first steam engine in Central Europe, constructed by Isaac Potter, were cast here. Another blast furnace was built in the town of Dobšiná during the uprising of Ferenc II Rákóczi in the early 18th century. The expulsion of the Turks and the stabilisation during the 18th century enabled the construction of the other blast furnaces in Dobšiná (the second in 1722), Hronec (1739), Poniky (1729), Píla (1730), Rejdová (Massa or blast furnace?); mainly owned by the exchequer. In 1776 there were 124 "Slovak furnaces" and 5 blast furnaces in Slovakia in 1776. Other blast furnaces were built in Betliar (1781), Osrblie (1795), Revúca (the 1800s), Gombasek (1816) and Drnava (1821) (Pleiner 1984, p. 92; Pleiner, Vozár & Šarudyová, 1976, p. 12-60, 217).

New ironworks companies (especially Rimavsko – Muráňska company, Rimamurány Vasmű R.T, RIMA), as well as the investment of aristocratic families, built several other blast furnaces in the early 19th century. The production of the iron smelted in blast furnaces surpassed the production of "Slovak furnaces" in the 1830s; the last "Slovak furnace" was closed down in 1853 in Lúčka. Only 11 of 43 ironworks in Slovakia had two blast furnaces in 1868; the furnace produced an average of 2 000 tonnes of iron per year. The number of blast furnace plants reached 53 in the 1870s; some of them disappeared due to the crisis in the coming years. On the other hand, the crisis resulted in the concentration and modernisation of iron metallurgy. The largest producers of iron in the late 19th century were the exchequer, joint-stock companies such as RIMA, Pohornádska (Hernádvölgy

Magyar vasipar, R. T.), Concordia, and aristocratic families as Andrássy, Csáky, Coburg, and Sztáray. Unlike iron ore resources, Slovakia does not have any coking coal. Therefore, charcoal was used as fuel until the end of the 19th century. The import of mineral fuels started after the completion of the basic railway network in the 80s. The first coke blast furnaces were built in the late 19th century (Hnúšťa, Krompachy). After World War I., in the course of a few years, almost all blast furnaces have disappeared. Only one blast furnace operated in Tisovec. At present, there is only one ironwork in Slovakia - the U.S. Steel in Košice.

The first steam engine mentioned above, used in a mine, was installed in the free mining town of Nová Baňa in 1722 (Tibenský 1986, p. 247; Kisszely, 1978, p. 36). Another steam engine in Slovakia - the cast iron blower for the blast furnace in Drnava, was put into operation only in 1821 (Pleiner 1984, p. 50). Only 13 steam engines operated in Slovakia in metallurgy in 1861 (Pleiner 1986, p. 81). As a rule, the blowers were doubled - mainly water-powered blowers were used, and steam blowers were used as a reserve.

Pre-heated air was used firstly in Slovakia in Hronec (210°C, the first trials began in 1835), and in Stratená, both in 1837 (Pleiner 1984, p. 50; Pleiner 1986, p. 219). The closed hearth of the blast furnace was patented in 1867; in Slovakia, it started to use in the 1860s. The open-hearth (fore-hearth) was used for a long time in ironworks in which they produced castings. The first coke blast furnace in Slovakia was built in Likier in 1885; five coke furnaces operated in 1901 (Likier, Krompachy Tisovec, Chyžnianská Voda). The volume of the biggest furnace (Krompachy) was 372 m^3, and only 24 m^3 of the smallest one (in Henckovce) (Pleiner 1984, p. 92).

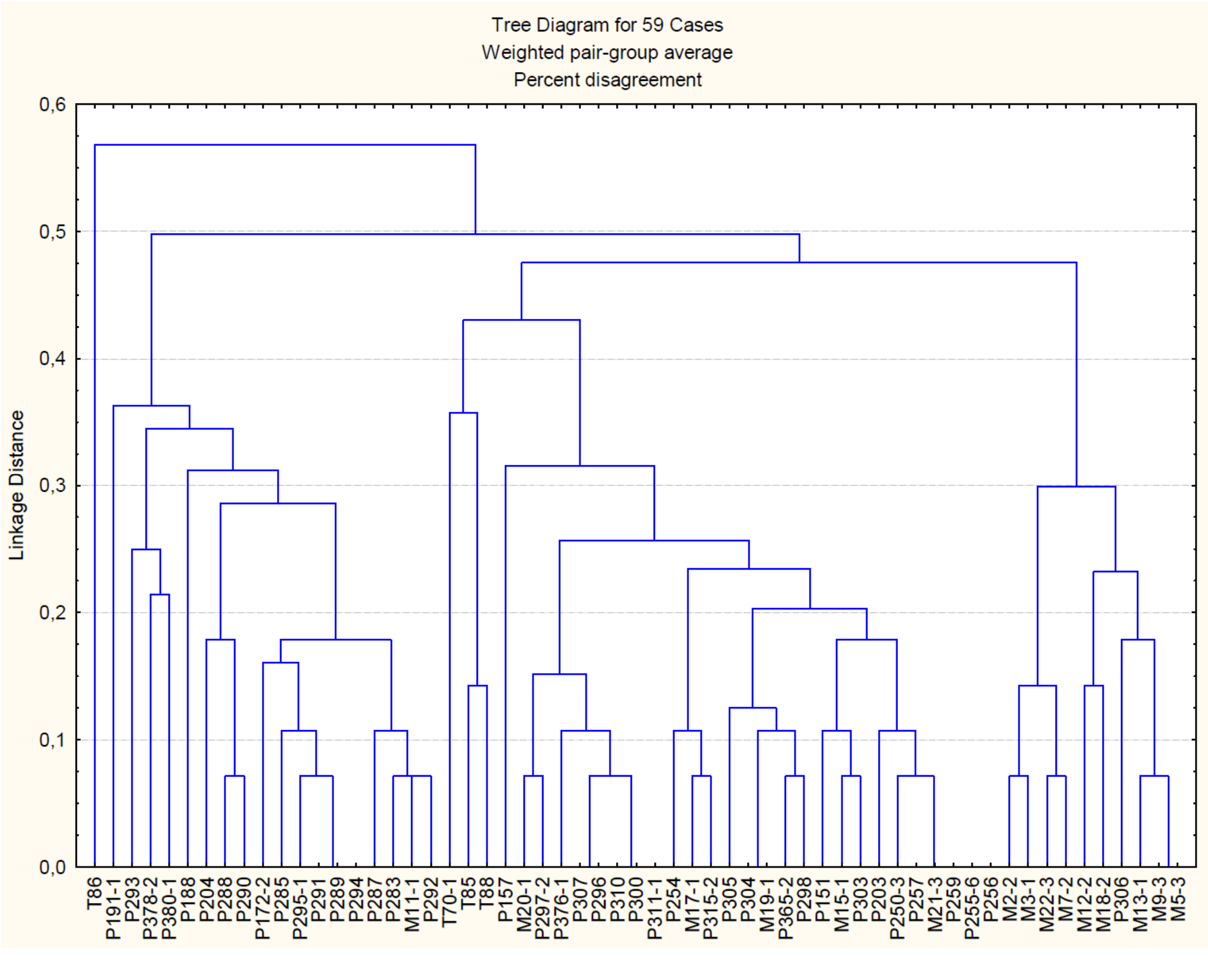

Fig.2. The cluster analysis of the presence of secondary and trace elements.

The refining process was the same in Slovakia and West Europe. Typical finery consisted of a rectangular or square hearth, heated with charcoal and blown with bellows powered by water, and a water-powered hammer mill. Since the 1830s, waste heat has been used for the pre-heating of cast iron. For this purpose, they started to build hearths with the vault. Since 1839, the blown air has been pre-heated. In the 1840s, the Comté-hearths with vault and pre-heat air began to be introduced; the first operated in Stratená. In 1885, the fineries operated in Zvolen, Prakovce, Bujakovo, Vajsková, Hrabušice, Košické Hámre, and Krompachy (Hapák 1962, p. 36; Šarudyová, 1989, p. 23; Pleiner 1984, p. 92).

The "puddling" process has been used in Slovakia since 1839, and the first reverberatory furnace was built in Chvatimech near Hronec. The Champagne method - a combination of the "puddling" and refining in the hearth was also used. Attempts to use gas in the "puddling" process were made in Betliar (also with brown coal in 1845), Drnava, Hnúšťa, and Hronec in the 1840s - 1850s. The double puddling gas-fired furnace was built in Kružlovska Huta in 1852, and it was the first in Hungary. Puddling furnaces operated in Podbrezova, Bujakovo, Zvolen, Piesok, and Vajsková in 1885 (Pleiner, Vozár, & Šarudyová, 1976, p. 56; Hapák 1962, p. 36).

The first Bessemer converters operated in Hronec (1879), Zvolen (1887), Bujakovo (1886) and Pohorelá (1893), Siemens-Martin furnaces in Podbrezová (1879), Zvolen (1889), Pohorelá (1893) and Krompachy (1904). Crucible steel was produced in Prakovce since the 1870s (Pleiner 1984, p. 92; Schmiedl & Weigner et al. 2006, p. 92).

A significant handicap of the iron metallurgy in Slovakia was the above-mentioned absence of local sources of coking coal. Until the year 1872, when the Košice-Bohumín railway was built, only the non-efficient roads connected it with the nearest source - the surroundings of Ostrava. Moreover, the roads leading through the mountainous terrain and their capacity were significantly influenced by the weather. The interconnection of the Central Slovakian region with the source of coke was realised only in the last quarter of the 19th century. The ironworks in Gemer (Muráň and Slaná valley) acquired rail link in 1874, and those in the valley of Hron River between 1884 (Podbrezová) and 1903 (Pohorelá). For comparison, in England, the basic railway network was completed in 1872, and rail links between metallurgical enterprises and ore and coking coal sources have been built since 1848. And we do not take into account a quality system of roads and canals, not to mention a system of quality roads and canals (Morgen, 1999, p. 400).

Material and Methods

The slag accumulated around the furnace as waste from the smelting process. In certain cases (for instance, during floods), some slag could have also been swept further away. Such "mixing" of slag of various origins (iron and also non-ferrous metallurgy) is often found on the banks of rivers. Since the 19th century, large plants with several blast furnaces have produced large amounts of slag. It has been placed in heaps, often at a greater distance from the plants. The slag also found several potential uses, for example, the production of slag bricks as filler material in construction work (railway embankments, road bedrocks) and addition to the batch (Bergfest, 1954).

The blast furnace slag contains above all SiO_2, Al_2O_3, MnO, CaO, MgO, P_2O_5, and sulfur. The slag includes iron particles - inclusions, the content of which varies depending on the smelting technology.

Blast furnace slag analysed in this paper (59 samples in total) was obtained by prospecting smelting-plant sites, to a lesser extent from archaeological excavations or museums' collections.

Presented slag samples are typical for individual extinct plants discussed in this paper. Of course, more slag samples were collected and analysed; the reader can find the results of these analyses in the relevant literature, as referred to in references. After documentation, each sample was cut with a diamond saw. A metallographic sample was prepared by grinding with dry SiC sandpaper (220 →3000ANSI/CAMI grit) and polishing with diamond paste (1 μm) moistened with kerosene. The rest of the sample was milled on a vibration mill, and the powder was used for chemical analysis (classic "wet" analysis complemented by analysis with a mobile spectrometer Niton XL3 Goldd), X-ray diffractometer analysis by powder diffractometer DRON 3-M, using the cobalt radiation to identify the phase components. The results of the chemical analyses are in Tab. 1. The presence of secondary (1-0.001%, bold type in Tab. 1) and trace (0.01 - 0.00001%) elements was determined by semi-quantitative spectral analysis with the spectrograph PGS-2. The relationship between the samples of the slag using the content of secondary and trace elements was evaluated using the cluster analysis (by weighted pair-group average and per cent disagreement method, software Statistica), Fig. 2 (Halčinová & Trebuňa 2012; Bu et al., 2020). The fact that the method of cluster analysis is increasingly used in archaeometallurgy is evidenced, for example, by its use in the analysis of medieval militaries in Poland (Imiołczyk et al., 2020).

Analysis of sulfur content helps to refine the dating of slag. Its main source is the mineral fuel, eventually in iron ores accompanied by pyrite. Iron, reduced with charcoal, contains only traces of sulfur. The concentration of sulfur in the metal decreases with increasing slag basicity. European slag containing sulfur usually is not older than 300 (150 in Slovakia) years. (Petrík & Moravčíková, 2006). The softening and the melting points of some samples were evaluated by high - a temperature microscope Leitz – Wetzlar (Petrík & Burdzová 2013).

Results

1. Betliar (48°41'49"N; 20°29'54"E) - the slag is the product of a blast furnace operated between 1842-1903, owned by Counts Andrássy. The iron ores were mined in Volovec, Nadabula, and Rožňava - Turecká. The slag M 5-3-1 is brown glass. The slag bricks, an additional product of the plant, are in *Fig. 3*.

2. Brzotín (48°37′31"N; 20°30′27"E) - the slag is product of the blast furnace working between 1847 and 1890 owned by Schlosser family and later by Counts Andrássy. The ores were mined in Čučma, Betliar, Dobšiná, Rožňava – Kalvária and Rožňava – Turecká. Analyzed sample of the slag P 256 is dark-blue glass.

3. Cinobaňa (48°27'21"N; 19°38'30"E) - the slag is the product of a blast furnace operated between 1847 and 1860. The Kuchinka family was the owner of the plant. The ore was mined in the surroundings: Turíčky and Kalinovo (Šarudyová, 1989). The slag P 311-1 is cobalt-blue glass with a glassy/fayalitic microstructure with particles of metallic iron.

4. Dobšiná, site of Horná Huta (48°49'01"N; 20°18'49"E) - the slag M 7-2 is the product of a blast furnace working between 1790 (1756?) and 1919, owned by the mining town Dobšiná. The ores were mined in Dobšiná (Altenberg, Massorter, Gúgel, Dilngarten), and Mlynky. The analysed slag is pastel-grey; the microstructure consists of glass partly separated into blocks (Fečková et al., 2006).

5. Dobšiná – site of Dobšinská Maša (48°51'29"N; 20°22'33"E) - the slag P 297-2 is the product of a blast furnace working between 1712 and 1919 owned by the town. The ore was mined in Dobšiná, Gelnica, Žakarovce - Klippenberg, Prakovce, Kišovce (with a high content of Mn), Altenberg, Dilgarten, Mossorter, and Gúgeľ. The analysed slag is brown glass. About 80 railway wagons per year of local slag were used in Třinec Ironworks (Czech Republic) between 1936 and 1942 as an addition to the batch (Grecula et al., 1995; Bergfest, 1954).

6. The owner of the ironworks in Drnava (48°38'25"N; 20°29'33"E) operated between 1830 and 1913 were Counts Andrássy. Parts of Szechenyi Lánc Híd (Chain Bridge) in Budapest (Hungary) were cast here. The sources of iron ores were in Krásna Hôrka and Drnava. The slag P 255-6 is black slag, partly separated into blocks. Local slag was used in Třinec between 1937 and 1938 (Bergfest, 1954).

7. Ironworks with a blast furnace, finery, and hammer mill were established by A. Patz in 1810 in the free mining town of Gelnica, the local part of Mária Huta (48°52'09"N; 20°57'44"E). Mansdorfer's family acquired this plant in 1850. A rolling mill was built in 1870. The plant was extinct in 1880. The smelted iron ore was mined in Prakovce. The sample of the slag P292 is grey and glassy; the microstructure consists of the glass with fragmentation into columniform blocks. Local slag (about 140 railway carriages per year) was smelted in Třinec in the 1940s (Petrík et al., 2001; Bergfest, 1954).

8. Gelnica – local part Matilda Huta (48°49'13.79" N; 20°55'11.21"E) - baron O. Jacobs was the owner of the ironwork with a blast furnace, finery, hammer mill, rolling mill, and wire drawing mill built in 1850 and destroyed by the floods in 1878. The sample of the slag P 376-1 is black glass without cracks and metallic inclusions.

9. Gombasek is today a part of village of Slavec (48°34'09"N; 20°27'58"E). The blast furnace was built there in 1842 (or even in 1816, according to (Hapák, 1962) and operated until 1903. The ore was mined in Štítnik and Nižná Slaná or in surroundings (with high copper content). The analysed sample of the slag M 13-1 is pastel blue-grey glass. The microstructure consists of glass with partial fragmentation into blocks.

10. Henckovce (48°42'50"N; 20°25'58"E) - the slag is the product of a blast furnace operated between 1852 and 1903, owned by the company Concordia. The slag M3-1 is brown; the microstructure consists of glass. The ore was mined in Rudná, Ratkovské Bystré, Nadabula, Hrádok and later also in Kobeliarovo.

11. Hnúšťa, the local part of Likier (48°33'38"N; 19°57'39'E) - the blast furnaces operated between 1884 and 1921, owned by RIMA company. Coke was used as a fuel since the end of the 19th century as the first in Slovakia. The ore was mined in Železník and Rákoš. Slag P300 is laminated grey-black glass.

12. Hnúšťa, the local part Maša (48°34'59"N; 19°56'30"E) - the slag is the product of a blast furnace (1805 – 1918), owned by RIMA company, the source of the ore was also Železník and Rákoš. The slag P 250-3 is black glass.

13. Hrlica (48°37'37"N; 20°03'46"E) - the slag is the product of a blast furnace operated between 1844 and 1880, owned by the Hrlicko-tapolcsánska company. The ore was mined in Železník and Rákoš. Analysed sample of the slag P 298 is dark-blue glass.

14. The exchequer was the owner of the ironworks in Hronec (48°47'40"N; 19°34'45"E) since 1548. The slag is the product of blast furnaces (1739 – 1883). The smelted iron ores were mined in Dobšiná or surroundings (Balog, Bystré, Halny). The analysed sample of the slag P290 is grey glass with a hint of crystallisation.

15. Chyžné, site of Chyžnianska Voda (48°39'13"N; 20°11'45"E) - the slag is the product of blast furnace operated between 1846-1903, owned by Heinzelmann family. Sample M 18-2 is the green glass. The ore was mined in Železník, Rákoš, Hrádok, Rožňava – Turecká.

16. The first director of copper smeltery, "Nicolaus" in Slovinky near Krompachy A. Probstner bought originally state ironworks with a blast furnace (since 1776) in Jakubany (49°13'02"N; 20°40'56"E) in 1828. The smelting of the iron was terminated in the 1860s. The blast furnace was reconstructed in the 2010s, *Fig. 4.* The sample of the slag M22-3 is glassy, pastel-green; the microstructure consists of glass with hints of fragmentation into blocks. The ore was mined in Gretla and in surroundings of the mining town of Spišská Nová Ves (Moravčíková et al., 2004).

Fig.3. The slag bricks, Betliar.

Fig.4. The blast furnace in Jakubany (partly reconstructed in 2012).

17. The owners of the village of Javorina (49°16'03.24"N; 20°08'39.73"E), today a part of the village Ždiar, were Counts Horváth-Palocsay. They founded ironwork with a blast furnace and hammers in 1759. The rolling and wire-drawing mills were built in 1837. The finery with hearths and puddling furnaces was here since 1842. The blast furnace was destroyed between 1856 and 1861. The ore was mined in the surroundings or imported from Smižany and Kišovce. The slag P380-1 is blue layered glass (Veselská & Majzlan, 2016).

18. In Myslava, a local part of Košice (48°42'02"N; 21°13'13"E), a company of the burghers of the free town of Košice owned a little blast furnace (1852 -1867). The ore was mined in the surroundings (Holica). The slag P 157 is black glass. The microstructure consists of glass with the sign of crystallisation.

19. The ironworks in Košické Hámre (48°49'56"N; 21°04'33"E) with the Slovak-type furnace was the property of the free town of Košice since 1503. Baron Jacobs bought it in the 1850s. The blast furnace operated between 1852 and 1911. The site lay is flooded with the Ružín dam at present. Smelted ore was mined in the valley Potoky near Vyšný Klátov. The slag P 188 is pastel-green glass. The microstructure consists of glass with the fragmentation into columniform blocks (Heckenast, 1991).

20. Krompachy (48°55'18"N; 20°53'23"E) - the slag is the product of older ironworks in the locality "Maša". The first blast furnace was built there in 1831. Its owner was the noble family Gundelfinger, later Pohornádska Company, and RIMA company since 1900. It built new ironworks with coke blast furnaces and Siemens-Martin steelworks on the new site near the railway station. The plant was demolished after 1921. The copper smeltery was built in its place in the 1930s. The ore was mined in Folkmár, Žakarovce/Klippenberg, and Helcmanovce. Overall, 876 railway carriages, each with about 20 tons of slag, were used as an additive to the charge in Třinec in the 1930s. The slag was also used as a filler for railway embankments in the 1950s. The analysed sample of the slag P 191A is black-brown glass.

21. The slag found in Kružlovská Huta (49°19'02"N; 21°08'03"E) is a product of a blast furnace (1840 – 1868) owned by Counts Forgách. The smelted ore was mined in Žakarovce. The analysed sample of the slag P 294 is pastel-green glass.

22. The site of Hámor (48°35'44"N; 20°23'20"E) situated between the villages of Kunova Teplica and Pašková – black, glassy slag P 306 is the product of blast furnace (1885-1910), owned by the Concordia company in Štítnik. The smelted ore was mined in Rudná, Nadabula, Ratkovské Bystré and Hrádok.

23. The exchequer or members of the Habsburg family were the owners of the blast furnace in Liptovský Hrádok (49°02'03"N; 19°46'07"E). It smelted the iron ore mined in Spišská Nová Ves (Bindt) (Grecula et al., 1995) or surroundings (Važec, Svarín, Hybe, Boca, hillsides of Ďumbier, Malužiná) between 1808 and 1867. Sample M 9-3 is brown-grey and glassy. The microstructure consists of glass with hints of fragmentation into blocks.

24. The slag is the product of a blast furnace (1692 – 1909), built in free mining town of Ľubietová (48°44'55"N; 19°21'29"E) by the company of burghers from free mining town Banská Bystrica. It was the first blast furnace in Slovakia. The widow of Melchior von Smrtník was a member of the company. Her husband, the mayor of Banská Bystrica, was beheaded during the reprisals after the suppression of the Tököly uprising (1678-

1683). The exchequer step-by-step bought shares of the company. The ore was mined in surroundings: Jamesná, Drienina, Staré Hory, Stefansberg, Železník, Hiadeľ, and (since 1878) in Poniky. Finery slag was also added into a burden. The analysed slag P 288 is grey glass.

25. The owners of the blast furnace operated between 1853 and 1903 in Lúčka (48°37'59.00"N; 20°43'06.00"E) were Counts Zichi and Ferreris and Concordia company. The slag M2-2 is grey and glassy; the microstructure consists of glass with hints of fragmentation into blocks. The smelted iron ores were mined in Lúka, Bôrka, Smolník, Štós, Medzev, and Rožňava – Turecká.

26. Medzev, local part Goldseifen (48°42'31"N; 20°53'10"E) the slag is the product of a blast furnace operated between 1868 and 1888, owned by the company of local burghers and later by Ganz company. Smelted iron ore was probably mined in surroundings - Smolník or Poproč. The sample of the slag P 204 is black glass.

27. Medzev, local part Počkaj (48°41'39"N; 20°56'50"E) - the slag is the product of iron works with blast furnace (1790 – 1910) owned by the abbey in Jasov. The ore was mined in Smolník, Štós, Nováčany, and Poproč. Overall, 2180 railway wagons of local slag were used as an additive to the charge in Třinec between 1935 and 1944. The slag was also used as gritting material for the maintenance of roads. The sample of the slag P 203 is green glass. The microstructure consists of glass with the fragmentation into columniform blocks (Bergfest, 1954).

28. The site of the ironworks in the ownership of the exchequer was situated between the villages of Michalová and Pohronská Polhora (48°46'21"N; 19°21'29"E). The blast furnace operated between 1797 and 1885. The ore was mined in Sirk, Dobšiná, Železník and Rákoš. Slag P289 is grey glass. The microstructure consists of glass with hints of fragmentation into blocks.

29. Mlynky, a local part of Palcmanská Maša (48°51'11"N; 20°23'07"E) - the slag is the product of a blast furnace (1799 -1880) owned by the Paltzmann family. The ore was mined in Mlynky-Biele Vody (with high copper content, so they mixed it with ore, minded in Dobšiná), Rudňany and Ďumbier (Nízke Tatry). The slag P 296 is glassy, with layers of different shades of green colour. About 40 wagons of local slag per year were used in Třinec between 1937 and 1942 (Roth, 2004).

30. The glassy, pastel-green slag P 303 is the product of the blast furnace in Mníšek nad Popradom (49°24'56"N; 20°43'00"E), which Karl Heyssel built-in 1856. It terminated during the economic depression in 1867. The microstructure consists of glass with the fragmentation into blocks. The smelted iron ore was mined in central Spiš.

31. The blast furnace in Nálepkovo (48°50'19"N; 20°37'20"E), owned by the Nepko family, was built in 1854 and blown out in 1910. The iron ore was mined in Žakarovce and Gelnica. The slag P 287 is black glass. Overall, 1725 railway carriages of local slag were used in Třinec between 1937 and 1944.

32. Nižná Slaná (48°44'20" N; 20°25'03"E) – the slag is a product of the blast furnace "Etelka" (1867 – 1907), owned by Counts Andrássy. The iron ore was mined in surroundings - Gompel, mine Manó (Nižná Slaná), and mine Ignác (Gočovo). The slag P 259 is pastel-green glass.

33. The company of burghers from Banská Bystrica established their iron works with the blast furnace in Osrblie, the local part of Tri Vody (48°43'33.66"N; 19°30'12.82"E) in 1795. Noble family Prihradny von Brezó bought the plant in the 1850s. The shaft of the blast furnace, blown-out in 1873, was renovated in the 1980s. The turquoise-coloured or grey-blue pebbles of the slag were found in the creek near the furnace. The homogeneous microstructure of analysed slag T88 consists of slag glass with globular iron inclusions. Sources of smelted ore were Dobšiná, Bacúch and Ľubietová.

34. The slag found in Píla (48°30'57.63"N; 18°36'09.96"E) is the product of the blast furnace operated from 1730 (1735?) to about the end of the 18th century (or 1823). Maybe the exchequer (owner of the silver smeltery in near Žarnovická Huta) or Kallosch Hochweisser Eisenhandlung company were the owners of the plant. The information is very short. The ores were mined in the surroundings or maybe in Vyhne. The slag P 378-2 is black glass (Bergfest, 1954).

35. Ploské (48°36'58"N; 20°04'40"E) - the slag is the product of the blast furnace operated between 1830 and 1887, owned by the Latinák family. The ore was mined in Železník and Rákoš. The sample of the slag P293 is blue glass; the microstructure is glass with a hint of crystallisation. The classicist building – the house of the owner dated to 1814 has been preserved.

Fig. 5. The blast furnace in Podbiel.

Fig. 6. The headquarters of RIMA, Rimavské Brezovo.

36. The slag P 291 is the product of the blast furnace, a part of the ironworks "Františkova Huta "(1836 - 1862), *Fig. 5*, owned by "Oravský Komposesorát" (árvai uradalom, the consortium of landlords, successors of Count Thurzo) in Podbiel (49°17'58"N; 19°30'02"E). The ore was mined in surroundings (Oravské hámre, Ústie nad Priehradou). The slag is black glass with hints of crystallisation.

37. Pohorelá, local part Nová Maša or Ferdinandova Huta (48°50'04"N; 20°03'10"E) - the slag is the product of the blast furnace (1805 – 1893) owned by Dukes von Coburg. The ore was mined in Spišská Nová Ves (Bindt), Dobšiná or in surroundings (about 10%). The slag P 295 is green glass. The microstructure consists of glass with the fragmentation into columniform blocks (Mihok et al., 2007a).

38. The blast furnace (1729 – 1875) in Poniky (48°41'27"N; 19°18'03"E) was owned by the exchequer. The smelted iron ore was mined in surroundings: Na Hlinke, Dúbravica, Staré Hory, Zolná, Habakuk, Einheimisch. The slag P 310 is dark-green glass.

39. The ironworks ("Huta Ľudmila") were established by Count Csaky in Prakovce (48°48'57"N; 20°53'34"E) in 1808. It consisted of the blast furnace, three fineries, and a hammer mill. The rolling mill was built in 1843. The cupola furnaces, the new rolling – mill, and crucible steelwork were built in the 1880s. The blast furnace was blown-out in the time of World War I (1914-18). The ore was mined in Žakarovce and Gelnica. The slag P315-1 is white glass.

40. The slag M 11-1 is the product of the "Massa" or "Floss Ofen", a transition between "Slovak furnace" and a blast furnace. The furnace (48°47'35"N; 20°17'38"E), operated between 1733 and 1779, was owned by the village of Rejdová. The ore was mined in the surroundings: Radzim, Romolová (mine Šimon - Juraj). The slag is glassy, dark-grey colour.

41. Remetské Hámre (48°50'51.18"N; 22°11'01.70" E) - the blast furnace (about 1780 – 1873) owned by Counts Sztáray. Analysed sample of the slag T86 is glassy, blue-green. The microstructure consists of glass with the skeleton-shaped particles of diopside, determined by X-ray diffraction and with globular iron inclusions. The slag is a typical waste product of a charcoal blast furnace. The smelted iron ore was mined in Trnava, Banské, Veľká Rybnica and Porúbka pod Vihorlatom.

42. The slag M 19-1 found in Revúca, local part Kiešková (48°41'01"N; 20°06'22"E) is the product of the blast furnace blown in about 1808 and extinct in 1892. It is grey and glassy; the microstructure consists of the glass with hints of fragmentation into blocks.

43. Revúca, local part Rudná (48°40'33"N; 20°07'11"E) - the slag M 20-1 is the product of the blast furnace working between 1805 and 1884. It is green-grey and glassy; the microstructure consists of the glass with hints of fragmentation into blocks.

44. Revúca, local part Šramková (48°41'01"N; 20°05'27"E) - the slag M 21-3 is the product of the blast furnace blown-in in 1810 and blown out in 1903. It is grey and glassy; the microstructure consists of glass with hints of fragmentation into blocks. The owner of all blast furnaces in Revúca was RIMA company.

45. The slag is product of blast furnace (1852 – 1877) owned by noble family Czékus in Revúcka Lehota, local part Podhora (48°39'55"N; 20°10'17"E). The ore was mined in Železník and Rákoš. The sample of slag P 304 is dark – green glass.

46. The classicist office building of RIMA company (1808), the owner of the ironworks, has been preserved in Rimavské Brezovo, a local part of Hámor (48°31'57"N; 19°57'20"E), *Fig. 6*. The blast furnace (1794 – the 1830s) stood near the office building. Blue-white laminated glassy slag P305 is the product of a charcoal blast furnace. The iron ores were mined in Železník and Rákoš or the surroundings.

47. The blast furnace owned by Hrlicko – tapolcsánska company in Sirk, local part Červeňany (48°36'15.09"N; 20°06'31.54"E) was in operation between 1871 and 1903. The shaft of the furnace was

renovated in the 1970s. Analysed slag T85 is shiny, black, and glassy. When cut, it is layered with alternating layers of pastel–grey and black colours. The microstructure is homogeneous glass with globular iron inclusions. Sources of smelted ore were in Železník, Sirk, Rákoš, and Nandráž.

Tab.1. The number of analysed slag (1-59), site of the ironworks, secondary and trace elements, the chemical composition of the slag [%], and estimated production of the slag [t].

No.	Site	Secondary and trace elements	SiO_2	Fe_{met}	CaO	MgO	Al_2O_3	MnO	S	P_2O_5	slag
1	Betliar	**Mn Cu** Ni Ag Zn Pb V Cr	32.3	2.8	17.4	26.4	0.6	0.53	0	0.080	432 000
2	Brzotin	**Mn** Cu Ni Ag **Zn V** Cr	73.3	2.2	25.2	13.2	?	4.7	0	?	194 000
3	Cinobaňa	**Mn Cu**Ni Ag **Zn V Cr**	44.1	1.4	22.7	0.99	8.2	3.63	0	?	166 000
4	Dobšiná	Mn Cu Ni Ag Zn V Cr	33.4	2.5	14.0	18.0	5.7	5.4	0	0.135	536 000
5	Dobšiná	**Mn Cu Ag Zn V Cr**	46.5	10.33	9.0	6.0	3.2	1.06	0	0.12	345 000
6	Drnava	**Mn** Cu Ni Ag **ZnV** Cr	38.4	2.8	26.9	23.2	0.4	1.7	yes	?	236 000
7	Gelnica	**Mn Cu** Ni Ag Sn **Zn** Pb Mo **V Cr**	25.7	5.9	29.1	28.5	0.8	1.16	0	0.055	<18 000
8	Gelnica	**Mn Cu** Ag **Zn Mo V Cr**	38.2	7.2	21.0	1.1	4.5	0.19	0.09	0.07	?
9	Gombasek	**Mn Cu** Ni Ag Sn Zn Pb V Cr	35.2	5.6	20.2	11.2	0.4	1.62	0	0.075	480 000
10	Henckovce	**Mn** Cu Ni Ag Sn Zn V Cr	38.8	10.3	26.3	12.8	0.2	1.0	yes	0.05	67 000
11	Hnúšťa - Likier	**Mn Cu** Ni Ag **Zn V Cr**	25.1	1.11	27.4	22.4	1.2	1.54	0	0.11	2 460 000
12	Hnúšťa	**Mn** Cu Ni Ag **Zn** Pb **V** Cr	46.7	2.8	14.6	17.6	6.1	3.1	0	0.119	441 000
13	Hrlica	**Mn** Cu Ag **Zn** Pb **V Cr**	22.6	1.95	31.4	19.6	1.6	4.45	yes	0.121	152 000
14	Hronec	**Mn** Cu **Ni** Co Ag Sn **Zn** Mo **V** Cr	30.5	2.23	24.6	23.2	0.8	1.2	0	0.08	60 000
15	Chyžné	Mn Cu Ni Ag Sn **Zn** Pb **V** Cr	25.8	3.9	23.5	18.8	1.0	4.21	0	0.137	375 000
16	Jakubany	Mn Cu Ni Ag Zn Pb V Cr	48.8	1.7	25.2	[illegible]	1.6	4.1	0	0.06	122 300
17	Javorina	**Mn Cu** Ag **Zn** Pb Mo **V** Cr	36.7	2.0	11.4	2.3	3.5	13.1	0.14	0.07	330 000
18	Košice - Myslava	**Mn Cu** Zn **V Cr** In	36.6	8.37	10.1	17.2	4.7	2.72	0	0.025	38 000
19	Košické Hámre	**Mn Cu** Co Ag Sn **Zn Mo V Cr**	23.0	4.5	23.5	17.6	0.4	5.2	yes	0.1	184 000
20	Krompachy	Mn Cr Co Ag Sn **Zn** Sb Mo **V** Cr	28.5	14.0	21.8	20.8	0.6	1.5	0	0.09	3 251 000
21	Kružlovská Huta	**Mn** Cu Ni Ag Sn **Zn** Mo **V** Cr	72.3	3.9	9.0	4.4	0.0	1.6	0	0.116	48 000
22	Pašková	**Mn Cu** Ag Sn Zn Sb **V** Cr	43.5	12.4	8.3	6.2	4.5	2.3	0	?	242 000
23	Liptovský Hradok	**Mn Cu** Ni Ag Zn Pb V Cr	32.0	2.5	26.9	19.6	2.0	3.8	yes	0.158	155 000
24	Lubietova	**Mn** Cu **Ni** Co Ag Sn **Zn** Pb Mo **V** Cr	38.0	4.5	21.8	16.8	0.4	1.8	0	0.039	555 000
25	Lúčka	**Mn** Cu Ni Ag Zn V Cr	27.2	3.9	23.5	26.0	0.4	4.8	yes	0.04	29 000
26	Medzev-Golds.	**Mn** Cu **Ni** Ag Sn **Zn** Pb Mo **V Cr**	32.2	5.0	25.8	12.8	0.4	0.0	0	0.124	78 000
27	Medzev -Počkaj	**Mn** Cu Ni Ag **Zn** V Cr	22.6	15.1	24.6	12.4	0.4	1.2	yes	0.128	460 000
28	Michalová	**Mn** Cu Ni Ag Sn **Zn** Mo **V** Cr	28.6	2.5	16.2	17.2	1.2	2.4	0	0.115	332 000
29	Mlynky	**Mn Cu** Ag **Zn V Cr**	39.1	0.7	20.2	6.7	3.8	8.9	0.88	0.48	160 000
30	Mníšek	**Mn Cu** Ag **Zn V** Cr	27.6	2.2	19.6	27.2	5.1	8.7	0	?	20 000
31	Nálepkovo	**Mn Cu** Ni Ag Sn **Zn Pb** Mo **V Cr**	39.8	1.7	4.4	28.8	3.1	0.0	0	0.158	226 000
32	Nižná Slaná	**Mn** Cu Ni Ag **Zn V** Cr	31.6	5.6	24.6	27.2	?	4.2	yes	?	392 000
33	Osrblie	**MnCu** Ni Co Ag **V**	58.9	2.2	16.2	8.8	2.7	3.2	0.013	0.00	160 000
34	Píla	**Mn Cu** Ni Co Ag **ZnPb**Mo**V** Cr	34.9	16.0	6.1	1.5	1.9	5.1	0.36	0.1	51 000
35	Ploské	**Mn** Cu Ni Co Ag **Zn** Mo **V** Cr	2.1	2.8	19.0	21.2	0.8	3.1	0	0.078	257 000
36	Podbiel	**Mn** Cu Ni Ag Sn **Zn** Mo **V** Cr	60.2	6.4	3.9	3.2	2.4	1.9	0	0.147	16 000
37	Pohorelá	**Mn Cu** Ni Ag Sn **Zn** Mo **V** Cr	29.1	2.5	20.7	14.8	0.4	8.2	0	0.112	665 000
38	Poniky	**Mn Cu** Ni Ag **Zn V Cr**	26.3	3.9	20.7	19.6	0.2	6.1	0	0.053	181 000
39	Prakovce	**Mn Cu** Ni Ag **Zn** Pb **V Cr**	38.9	1.3	31.3	2.2	9.2	2.0	0.29	0.29	743 000
40	Rejdová	**Mn Cu** Ni Ag Sn **Zn** Mo **V Cr**	29.8	36.3	4.5	3.6	1.0	5.2	0	?	288 000
41	Remetské Hámre	**Mn** Cu Co Ag **Zn Sb PbCr Zr**	67.5	5.6	19.0	5.5	4.1	0.2	0.157	0.07	85 000
42	Revúca – Kiešk.	**Mn** Cu Ni Ag **Zn V Cr**	30.2	1.4	20.2	18	1.2	4.2	0	0.08	?
43	Revúca - Šramk.	**Mn** Cu Ni Ag **Zn V** Cr	39.8	5.3	11.2	13.6	1.6	2.4	0	0.066	605 000
44	Revúca - Rudná	**Mn** Cu Ni Ag **Zn V Cr**	34.1	2.5	18.5	19.6	2.6	3.1	0	0.2	581 000
45	Revúcka Lehota	**Mn Cu** Ni Ag **Zn V Cr**	45.2	5.7	12.1	3.9	6.8	5.3	0.09	0.78	143 000
46	Rimavské Brezovo	**Mn** Cu Ag Sn **Zn V Cr**	32.4	2.2	19.0	17.2	2.0	2.3	0	1.11	32 000
47	Sirk	**Mn** Cu Ni Co **Ag V**	52.5	1.7	28.0	0.0	2.2	3.0	0.02	0.05	155 000
48	Slavošovce	**Mn Cu** Ni Ag Sn **Zn** Pb **V** Cr	49.8	5.6	5.0	8.4	1.6	3.0	[illegible]	0.032	21 600
49	Smižany	**Mn** Cu **Co Ag Zn Sb V**	45.5	3.9	15.6	8.0	1.6	5.3	0.84	0.13	468 000
50	Smolnícka Huta	**Mn Cu** Ni **Co** Ag Sn **Zn** Mo **V Cr**	46.2	7.0	18.5	12.4	1.6	3.7	0	0.041	150 000
51	Stará Voda	**Mn Cu** Ni Ag Sn **Zn Pb** Mo **V Cr**	22.4	2.4	12.3	20.8	1.4	0.3	0	1.2	143 000
52	Stratená	**Mn** Cu Ag **Zn V Cr**	36.7	6.8	10.9	8.4	2.9	11.1	1.0	0.59	668 000
53	Štítnik - Fesmuth	**Mn** Cu Ag **Zn V** Cr	20.3	3.6	26.3	25.6	0.8	2.4	yes	0.133	277 000
54	Štítnik - Ujremeny	**Mn** Cu Ni Ag **Zn** Pb **V Cr**	33.8	4.2	27.4	18.8	1.4	3.5	0	0.05	144 000
55	Šumiac	**Mn** Cu Ni Ag Sn **Zn** Mo **V Cr**	28.3	2.5	20.7	26.0	1.0	7.5	yes	0.038	107 000
56	Tisovec	**Mn Cu** Ag **Zn V Cr**	22.4	2.5	35.3	15.6	3.5	1.0	0	0.144	1 000 000
57	Vidová	**Mn** Cu Ni Ag Zn Pb **V Cr**	60.1	5.6	12.3	14.8	0.4	4	yes	?	252 000
58	Vlachovo	**Mn** Cu Ni Ag **Zn V** Cr	48.6	4.5	14.0	28.8	0.0	1.9	0	?	527 000
59	Zemplínske Hám.	**Mn** Cu **Zn V** Cr	60.5	2.3	3.4	0.0	0.0	1.2	0	0.11	48 000

48. The blast furnace (1825 - 1861) in Slavošovce (48°42'31"N; 20°16'53"E), owned the family Stankovič (Sztankovics). The smelted iron ore was mined in Železník and Rákoš. Analysed slag M 12-2 is glassy, cream coloured.

49. Smižany (48°56'57"N; 20°30'28"E) - the slag is the product of the blast furnace operated between 1850 and 1888. The family of Counts Csaky was the owner of the plant. There is no right information about the sources of smelted ore. Maybe, local sources (Kišovce with high manganese content) were used. Analysed slag T 70-1 is glassy, grey-green; the microstructure consists of glass with the hints of crystallisation, cracks and cavities.

50. The exchequer was the owner of the blast furnace (1863 - 1893), the part of copper and also silver smeltery (1740-1918) in Smolník and Smolnícka Huta (48°44'45"N; 20°46'28"E). The smelted iron ores were mined in the surroundings. The sample of the slag P 172-2 is black glass.

51. The copper and mercury were also smelted in Stará Voda (48°48'00"N; 20°40'30"E). The black, glassy slag P283 is a product of the blast furnace (1870 – 1882) owned by Partl family. The information about the sources of iron ore (maybe locally mined) is absent. About 100 railway wagons of local slag were used in Třinec between 1937 and 1942.

52. The ironworks with the blast furnace founded Count Csaky in 1821 in Stratená (48°52'05.54"N; 20°20'49.45"E) in the place of extinct copper smeltery. The puddling furnace, heated by the wood and later by gas, was built by the new owner, Duke von Coburg, in 1842. The pig iron was also refined in the Comte-hearts (1843-1846) and Hrabušice. The blast furnace was blown-out in 1921. The ore was mined in Dobšiná, Spišská Nová Ves, occasionally in Žakarovce - Klippenberg, Prakovce, Mlynky (because it had a high copper content, it was mixed with the ore mined in Gelnica) and Stratená. The slag P 365-1 is glassy, grey-brown. The microstructure consists of glass with the fragmentation into columniform blocks.

53. The slag found in Štítnik, site "Fesmuth "(48°40'13"N; 20°21'41"E) is the product of a blast furnace operated between 1833-1910. The Concordia company in Štítnik was the owner of the plant. The smelted iron ore was mined in Rožňava – Kalvária or in the surrounding area (Rudná, Ratkovské Bystré, Nadabula, and Hrádok). Analysed sample of the slag M 15-1 is white-blue and glassy; the microstructure consists of glass with hints of fragmentation into blocks. Overall, about 20 railway wagons, each with 20 tons of slag, were used as an additive to the charge in ironworks in Třinec in 1942 (Grecula et al., 1995).

54. The slag found in Štítnik, site of "Ujremény" (48°37'05"N; 20°23'10"E) is a product of blast furnace (1847 - 1880), owned by Benedikty and Concordia companies. The sample M17-1 is glassy, cobalt-blue. The ore was mined in Rožňavské Bystré, Hrádok, Rožňava, Rudná and Ochtiná.

55. The blast furnace (1750 - 1882) in Šumiac, local part Červená Skala (48°49'12"N; 20°08'06"E) owned by Counts Koháry and later by Dukes von Coburg. The sources of iron ore were Dobšiná, Spišská Nová Ves, Vyšná Slaná, 10% has local origin. The sample of the slag P 285 is green glass. The microstructure consists of glass with fragmentation into columniform blocks.

56. The exchequer was the owner of the ironworks with a single one several-times rebuilt blast furnace in Tisovec (48°41'13"N; 19°56'08"E), operated between 1772 and 1965. The slag P307 is the product of a charcoal blast furnace (the coke was used as a fuel since reconstruction in 1913). The slag is pastel-blue glass, and the microstructure consists of glass with fragmentation into columniform blocks. The smelted iron ore was mined in Železník, Rákoš, Rožňava, Dobšiná, Nadabula (1854: Dobšiná 40%, Železník and Rákoš 52%) or the surroundings.

57. Vidová, today a part of village Slavec (48°32'36"N; 20°26'40"E) - the slag is a product of a blast furnace (1860 – 1888) owned by local nobles, Hámos and widow Radvánszka, and later by Counts Andrássy. The ore was mined in Rožňava-Turecká and Štítnik. The sample P 254 of the slag is green glass. The microstructure consists of glass with partial fragmentation into blocks.

58. The pastel-green glassy slag P257 is the product of a blast furnace in Vlachovo (48°47'48.79"N; 20°23'05"E), owned by Counts Andrássy (1843 – 1907). The furnace shaft still exists. The ore was mined in Dobšiná, Mlynky, Rejdová (Romolová and Radzim - Kupferberg).

59. Noble family Rholl von Udvarnok and Counts Csaky established ironworks with the blast furnace operated between 1815 and 1873 in Zemplínske Hámre (48°56'58.25"N; 22°09'18.89"E). Only the hearth of the original furnace can be seen at present. The model of the furnace was built in conformity with documentation in 2015. Analysed slag P 151 is glassy, grey-green. The microstructure consists of homogeneous glass with globular iron inclusions. The presence of quartz, wollastonite, fayalite, magnetite, and hematite was determined by X-ray diffraction. The product of smelting is "acid" slag, typical for the initial period of the blast furnace process. The ore was mined in Zamutov and Hermanovce.

Discussion

In Slovakia, the blast furnace metallurgy lagged behind comparable European countries. The first furnace was built as late as 1692. The main cause was the war with the Turks and the resulting instability. Many ironworks were closed during the crisis in the 1860s. Local iron ores were employed until the mid-20th century. Coke replaced charcoal as late as the turn of the 20th century. To remove sulphur that entered the produced pig iron from the coke it was necessary to increase the basicity of the slag. Such slag is better separated from iron, which reduces its losses. Subsequently, the number of metallic-iron inclusions trapped in the slag decreased; hence the yield of iron increased. Older, acid fayalitic slag is glassy, coloured by oxides most often in black, blue, or green. A more recent, basic slag is often porous, grey, or brown. Since the beginning of the 20th small ironworks with one or two furnaces and finery hearths for refining pig iron into wrought iron rapidly disappeared. These were replaced by several large ironworks with steelworks equipped with puddling or Siemens-Martin furnaces and, to a lesser extent, Bessemer converters (Bujakovo, Hronec, Pohorelá). The production of slag increased many times compared with the past. Heaps of slag coming from the blast furnace, finery as well as smithy and foundry processes were established at larger distances from blast furnaces.

Cluster analysis is one of the statistical methods and involves calculation procedures that aim to decompose the data set into several relatively homogeneous clusters. The essence of cluster analysis is to create clusters of objects whose mutual similarity will be as small as possible, and at the same time, the similarity of objects within the cluster is as large as possible. As a result of the application of cluster analysis in dealing with the distribution of secondary and trace elements, a more significant territorial distribution of slag was expected. It was assumed that ores mined in the vicinity of the blast furnace were processed. The significance was somewhat reduced by the relatively homogeneous distribution of these elements in the slag (Mn, Cu Ag, V, and Cr almost always) and the mixing of ores from different deposits in the younger period. The isolated slag from Remetské Hámre (T86, No. 41 in *Tab. 1*) is the result of the use of local deposits. Similarly, in the case of Smižany, there is no right information about the sources of smelted ore. In addition to the hypothetical possibility of using local ore (Kišovce), it is also possible to import ores from localities that were used by ironworks in a cluster with Smižany (Sirk and Osrblie).

The content of metallic iron in the slag produced by ironworks in Slovakia and comparison with slag produced in Great Britain and Russia is in *Fig. 7*. It is comparable to abroad at the ironworks belonging to the aristocracy (Andrássy, Csáky) as well as at the exchequer's ironworks. The worst results were achieved by town-owned ironworks. They, as well as small enterprises and companies, are characterised by high dispersion, i. e. parallel existing enterprises with relatively good but also very poor results.

Radioactivity was recovered in the current slag produced in Slovakia, but these values are below the limit allowed by the decree of the Ministry of Health (Slovak Republic) No. 406/92 about the restriction of radiation from radon and other natural radionuclides. Similar results have also brought the analysis of the current slag from iron metallurgy in Romania. In this sense, it would be appropriate to analyse also the heaps of old iron slag (Michalíková et al., 2005; Legemza & Majerčák, 2001; Ene & Pantelică, 2011). In this context, it would be useful to confirm or rebut speculation about the possible radioactivity of older blast furnace slag (for example, Stratená, Smolnícka Huta).

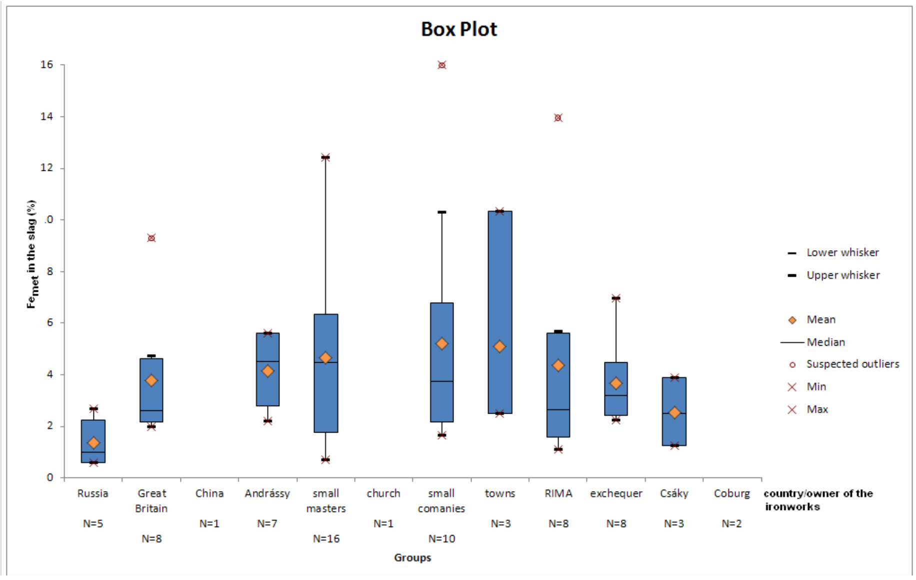

Fig. 7. The content of metallic iron in the slags according to owners of ironworks

The approximate amount of slag produced by the ironworks is shown in the last column of *Tab. 1*. It was calculated based on the amount of iron produced. Heaps of old iron slag are usually not the environmental burden as to the potential toxicity (Veselská & Majzlan, 2016). However, they create unstable subsoil with the possibility of landslide or cave-in of excavated trench or cavity.

Conclusions

- The iron metallurgy in a blast furnace in Slovakia lagged behind comparable European countries.
- The first furnace was built only in 1692.
- Coke replaced charcoal as fuel as late as the 20th century.
- Since the beginning of the 20th century, small ironworks were gradually replaced by several large ironworks with coke blast furnaces and steelworks equipped with puddling or Siemens-Martin furnaces and, to a lesser extent, with Bessemer converters.

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