Summary

The study focuses on reconstructing historical metal production techniques in the area of present-day Poland, where the earliest evidence of metallurgy dates to the turn of the Common Era. While there are numerous records documenting past metallurgical activities, considerable gaps persist in our understanding of the specific conditions and methods employed in metal smelting. The primary goal of this research was to employ advanced geochemical (ICP-MS/OES, XRF), mineralogical (SEM, EPMA, XRD), and experimental methods to analyze smelting conditions, enabling the reconstruction of historical metallurgical techniques. Key aspects of the research included determining smelting temperatures, melt viscosity, oxygen fugacity, and in some cases cooling rates, sulfur fugacity and reactions occurring in smelting furnaces. The research was conducted based on the slags from Sławków (Pb), Miedziana Góra (Cu), Złoty Stok (Au), Bloomery Fe production (in the Holy Cross Mountains), Polichno (Cu), and Ruda Śląska (Zn).

Metallurgical activities in Sławków took place during the 16th and 17th centuries, using Mississippi Valley types ores, containing Pb and Zn sulfides. Slags from Sławków were composed mainly of SiO_2 (34,58-46,50 wt.%), CaO (11,19-30,39 wt.%), and Fe_2O_3 (9,81-22,83 wt.%) with high concentrations of Pb (>10 wt.%) and Zn (up to 21 wt.%). In terms of phase composition, slags contained mainly glass, augite $(Ca,Mg,Fe)(Mg,Fe)Si_2O_6$), willemite (Zn_2SiO_4), melilite ($Ca_2M(XSiO_7)$)), olivine ($(Mg,Fe)_2SiO_4$), wollastonite ($CaSiO_3$), quartz (SiO_2), wüstite (FeO), K-feldspar ($K(AlSi_3O_8$), lead oxide (PbO), cerussite ($PbCO_3$), galena (PbS), and Zn sulfides. Experimental studies revealed the liquidus temperature of slags was at least 1150°C, with a solidus range of 900-1000°C. Oxygen fugacity (logP O_2) was determined using mineral buffers, indicating values between −4.5 and −12 atm. Viscosity calculations showed a viscosity (logη) ranging from 1.34 to 1.48 Pa·s.

Copper production in Miedziana Góra (Holy Cross Mountains) was conducted from the 16th to the 18th century, utilizing local deposits, including chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4), and tetrahedrite ($[Cu,Fe]_{12}Sb_4S_{13}$). Chemically, the analyzed slags primarily contained SiO_2 (49.81-57.14 wt.%), CaO (11.25-21.64 wt.%), FeO (8.42-11.03 wt.%), and Al_2O_3 (7.54-9.14 wt.%). The slags also contained Pb (0.50-5.91 wt.%) and Cu (0.40-4.98 wt.%). Phase composition analysis showed that slags were mainly composed of glass, SiO_2 polymorphs, wollastonite, anorthite ($Ca(Al_2Si_2O_8)$), metallic Cu, lead oxides (PbO), clinopyroxene, Cu

sulfides/arsenides, The liquidus temperature of the slag was from 1150-1200 °C, while solidus temperature was around 1100 °C. The viscosity of the metallurgical melt (logη) was from 1.19 to 4.42 Pa·s. The smelting process in Miedziana Góra took place under oxygen fugacity conditions (logP O_2) ranging from -4 to -12 atm.

Gold smelting in Złoty Stok occurred during the 16th-17th centuries based on ore mineralization found in pyroxenites, amphibolites, serpentinites, dolomitic marls, and limestone-silica rocks. The most important gold-bearing minerals in the deposit were löllingite ($FeAs_2$) and arsenopyrite (FeAsS). The slags were characterized by a chemical composition dominated by SiO_2 (52.12-56.60 wt.%), MgO (7.43-18.36 wt.%), CaO (10.84-15.19 wt.%), and FeO (9.08-15.36 wt.%). The phase composition of the slags showed the presence of olivine, pyroxene, glass, sulfides, and Fe arsenides. The liquidus temperature was determined to be between 1300-1350 °C, while the solidus temperature was approximately 1200 °C. The cooling rate of slags was from 5 to 300 °C/h. Melt viscosity (logη) at 1350 °C ranged from 0.26 to 0.90 Pa·s. It was found that the smelting process occurred under oxygen fugacity conditions (log P O_2) in the range of −10.5 to −11.5 atm.

The research on bloomery iron production focused on comparing smelting conditions across different locations (Suchedniów, Skarżysko-Kamienna, and Starachowice) in the Holy Cross Mountains. The analyzed slags primarily consisted of FeO (43.97-75.32 wt.%) and SiO_2 (18.04-47.14 wt.%). The dominant phases in the slags included olivine, wüstite, spinel from the magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$)-hercynite ($Fe^{2+}Al_2O_4$) series, and leucite ($KAlSi_2O_6$). Isotopic dating confirmed the ancient (196 BC–4 AD) age of slags. The liquidus temperature of slags was from 1150 to 1200 °C and the cooling rate was 5-300 °C/h. The viscosity of the melt was from 0.15 to 1.02 Pa·s. The maximum oxygen fugacity (logP O_2) during smelting ranged from -12.53 to -13.20 atm.

The analysis of slags from Polichno (Holy Cross Mountains) were focused on applying a more precise method for determining the oxygen fugacity during smelting. The chemical composition of the analyzed slags mainly consisted of SiO_2 (34.88-49.69 wt.%), FeO (12.62-17.71 wt.%), and CaO (12.57-29.95 wt.%). The most important phases observed in slags were: glass (containing PbO and ZnO), wollastonite, calcite ($CaCO_3$), SiO_2 polymorphs, clinopyroxene, barite ($BaSO_4$), cerussite, metallic Cu and Fe, chalcocite (Cu_2S), Cu arsenides, Pb and Fe oxide, pyrrhotite ($Fe_{1-x}S$), and galena. The liquidus temperature of the slags ranged from 1100 to 1200 °C, while the solidus temperature fell between 800 and 1100 °C. Based on thermodynamic calculations the oxygen and sulfur fugacities during slag formation were determined. The slags from Polichno were formed under an oxygen fugacity range of logP O_2 = −4.30 to −14.08 atm., and the sulfur fugacity during slag formation ranged from logP S_2 = −2.50 to −6.92 atm.

The study of slags from Ruda Śląska were focused on the chemical and phase reactions in the contact between the metallurgical melt and the refractory materials. Analysis showed that the slags consisted mainly of SiO_2 (38.17 wt.%), Fe_2O_3 (22.71 wt%), Al_2O_3 (15.81 wt.%), and CaO (10.56 wt.%). The refractory material was primarily composed of SiO_2 (65.70 wt.%) and Al_2O_3 (29.08 wt.%). Phase analysis of the slags revealed the presence of feldspar, clinopyroxene, melilite, spinel, and zincite (ZnO). The refractory materials were dominated by mullite ($3Al_2O_3 \cdot 2SiO_2$) and SiO_2 polymorphs. Microscopic observations revealed the presence of K-feldspars enriched in Pb and Ba, glass with high As and Pb content, and alumohematite ($(Fe,Al)_2O_3$) in the contact zone. The first type of reactions involved reactions between the gaseous/fluidal phases and the refractory material, where some components of the metallurgical charge (PbO, K, As, Zn, and Na_2O) migrated in the gaseous (or fluid) form into the refractory material. The second type of reaction involved reactions between the liquid melt and the refractory material. In this process, certain components of the charge (primarily PbO_2, As_2O_3, and FeO) moved toward the bottom of the retort. As a result, K-feldspar with Pb substitutions, Fe-rich pyroxene, and glass containing As_2O_3 and PbO formed in the contact zone.

A notable component of the dissertation involved developing methodological approaches for reconstructing historical metallurgical processes. This included creating dedicated software (SLAG) for modeling the basic smelting parameters. The software allows for the determination of liquidus temperature, slag viscosity, and oxygen and sulfur fugacities during smelting. The main goal in developing software was to enable individuals without specialized knowledge in thermodynamics and rheological studies to reconstruct smelting processes.