

PYROMETALLURGICAL SLAGS IN UPPER AND LOWER SILESIA  
(POLAND): FROM ENVIRONMENTAL RISKS TO USE  
OF SLAG-BASED PRODUCTS – A REVIEW

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**Abstract:** Slags issued from base metal smelting industry constitute a serious environmental problem in Upper and Lower Silesia (Poland). The waste is located in heavily urbanized areas, covers large surfaces and still may contain large quantities of potentially toxic metallic trace elements. This review paper summarizes all the major problems related to slag storage in Upper and Lower Silesia, including: (i) detailed characteristics of the studied slags, (ii) potential release of toxic elements and (iii) related risks for the surrounding areas and (iv) applications of slags for commercial purposes.

## INTRODUCTION

Mining and smelting activities left large quantities of waste accumulated as dumps covering large surface around former industrial sites of Eastern and Central Europe. Poland used to be the largest producer of industrial wastes in Europe, both in absolute terms and as a function of GDP (Gross Domestic Product; [16]). Since 1992, the accumulation of industrial wastes in Poland has been relatively stable, with average annual production of 120–125 million Mt among which 27% are slags issued from the pyrometallurgical industry (nearly 35 Mt/yr). The largest quantities of industrial wastes have been generated and landfilled in the Upper Silesia and Lower Silesia regions (Southern and South-western Poland; Figure 1; over half of the national total). With 490 Mt of tailings Upper Silesia was described as a region highly polluted by heavy metals and sulphates [18]. Dumps located in Upper and Lower Silesia most often form high and large heaps scattered throughout urban or country landscapes in the surroundings of industrial activities. They consist of a variety of waste materials such as barren rocks, flotation tailings and pyrometallurgical slags. Some of these tailings (e.g. pyrometallurgical slag) are used as cement additives or road ballast. However, the slags still contain up to several percent of trace elements (Zn, Pb, Cd, As, Sb, Cr etc.) which remain hazardous if they join food chain through water or/and soil [17]. In this review paper we will classify all these metal-

lic elements as potentially toxic elements (PTEs) and we define PTEs as all the elements that can be harmful if their concentrations exceed the toxicity thresholds in water and/or soil and/or food. Therefore, assessment of a potential release of PTEs from slags is of interest for environmental and human health purposes.

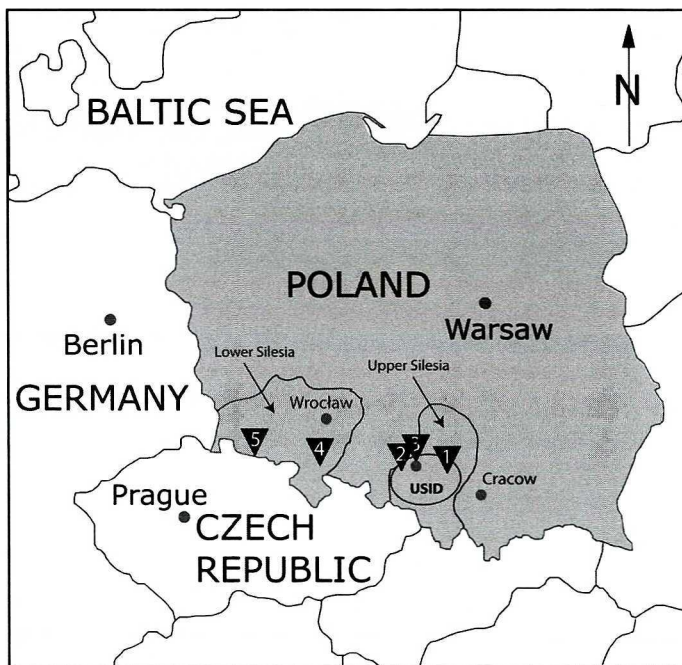


Fig. 1. Map of Poland showing the studied smelting sites in Upper and Lower Silesia: 1 – Bukowno, 2 – Świętochłowice, 3 – Katowice/Wielonowice, 4 – Szklary, 5 – Miedzianka, USID – Upper Silesian Industrial District

This review paper deals with the problem of solid waste derived from metallurgical plants. We propose to review some questions concerning pyrometallurgical slags in Upper Silesia and Lower Silesia where base-metal mining and smelting and coal extraction have been very active until present. The most important questions we attempt to answer are: What are the main specificities of the Silesian slags? How to examine their chemical and mineral composition and PTEs contents? How to forecast potential PTEs release? Are these products really dangerous? How to manage their storage? What about re-use possibilities? To answer these questions, we compare data obtained for several Polish sites, located mainly in Upper Silesia (Fig. 1 and Tab. 1). We present also some data on slags occurring in the Lower Silesia: the Lower Silesia region was the place of intense mining and smelting activity since medieval times, with small sites active until the 20<sup>th</sup> century. Currently the main sources of pyrometallurgical waste are large copper mines and smelters located in the Northern part of the region. The historical sites allow the assessment of long-term environmental effects of pyrometallurgical waste, and studies on more recent sites allow us to discuss broader spectrum of ores treated.

Table 1. Main smelting sites in Silesia

Site	Smelted ore	Extracted metals	References
Bukowno (Upper Silesia)	Zn-Pb sulfide ore	Zn, Pb	[19, 29]
Świętochłowice (Upper Silesia)	Zn-Pb sulfide ore	Zn, Pb	[2, 36, 47]
Wełnowiec (Upper Silesia)	Zn-Pb sulfide ore	Zn, Pb	[26]
Szklary (Lower Silesia)	Ni laterite	Ni	[23, 25]
Miedzianka (Lower Silesia)	Cu sulfide ore	Cu, Ag, As	[5, 26]

## PYROMETALLURGICAL SLAGS IN UPPER AND LOWER SILESIA

Pyrometallurgical wastes (Fig. 2) are the by-products of base-metal smelting which usually form at high temperatures (over 1000°C) and may still contain elevated levels of PTEs (e.g. Pb, Zn, Cu, Ni, Cr, As). Pyrometallurgical wastes include slags and associated mattes. The latter can be defined as denser material composed of local sulphide or metal concentrations of all sizes, whereas slags have lower density than mattes (ca. 2.5 to 3 g/cm<sup>3</sup>) and mainly consist of siliceous glass, silicates and oxides. Mattes are more abundant in older slags due to the fact that ancient smelting processes were not able to extract as much metals as recently used techniques. Zn, Cu and Ni are known as being the oligo-elements but these elements might also become toxic as demonstrated by very low toxicity thresholds for PTEs such as Zn, Cu and Ni (their admissible concentrations in water or food being of several tens to several hundreds µg/kg). In Silesia, PTEs involved in metallurgical industry come from the treated ores and also from the coal used for smelting processes (Tab. 1), most of them being extracted from Polish mines in the last two centuries. The concerned elements are mainly Zn-Pb. As a result, Upper Silesian slags mainly contain PTEs such as Pb, Zn, the first being known for its high toxicity even at low concentration.

Silesia is a heavily inhabited region (mean density = 377 inhabitants/km<sup>2</sup> for Upper Silesia and 144 inhabitants/km<sup>2</sup> for Lower Silesia). Smelting activity began on industrial scale in the early 1800 near Katowice and has continued until very recently. The economic evolution of the country over the last twenty years resulted in closing up of a major part of the mining and metal-extraction activities and the abandonment of numerous waste materials. The presence of mining and extraction sites within urban zones poses important problems for the affected towns and their future development. Abundant dumps are scattered throughout the entire region and often occur near the hearts of the towns, gathering on a local scale heterogeneous smelting waste (Fig. 2). These dumps include solid waste issued from blast furnaces mixed with coal and other solid waste of various origins [2, 19, 29, 36].

Dumps consisting of slags produced during reworking of silicate (lateritic) Ni-ores occur in the vicinity of the village Szklary (Lower Silesia, Table 1). However, the phase assemblages and chemical composition of the pyrometallurgical slags from Szklary dump are similar to those issued from sulphide ores smelting [25].

The Rudawy Janowickie area (Lower Silesia; Table 1) is also of interest because base metal mining and smelting activities began there in medieval times. Historical sources describe mining activity in the vicinity of the village Miedzianka as early as 1310.



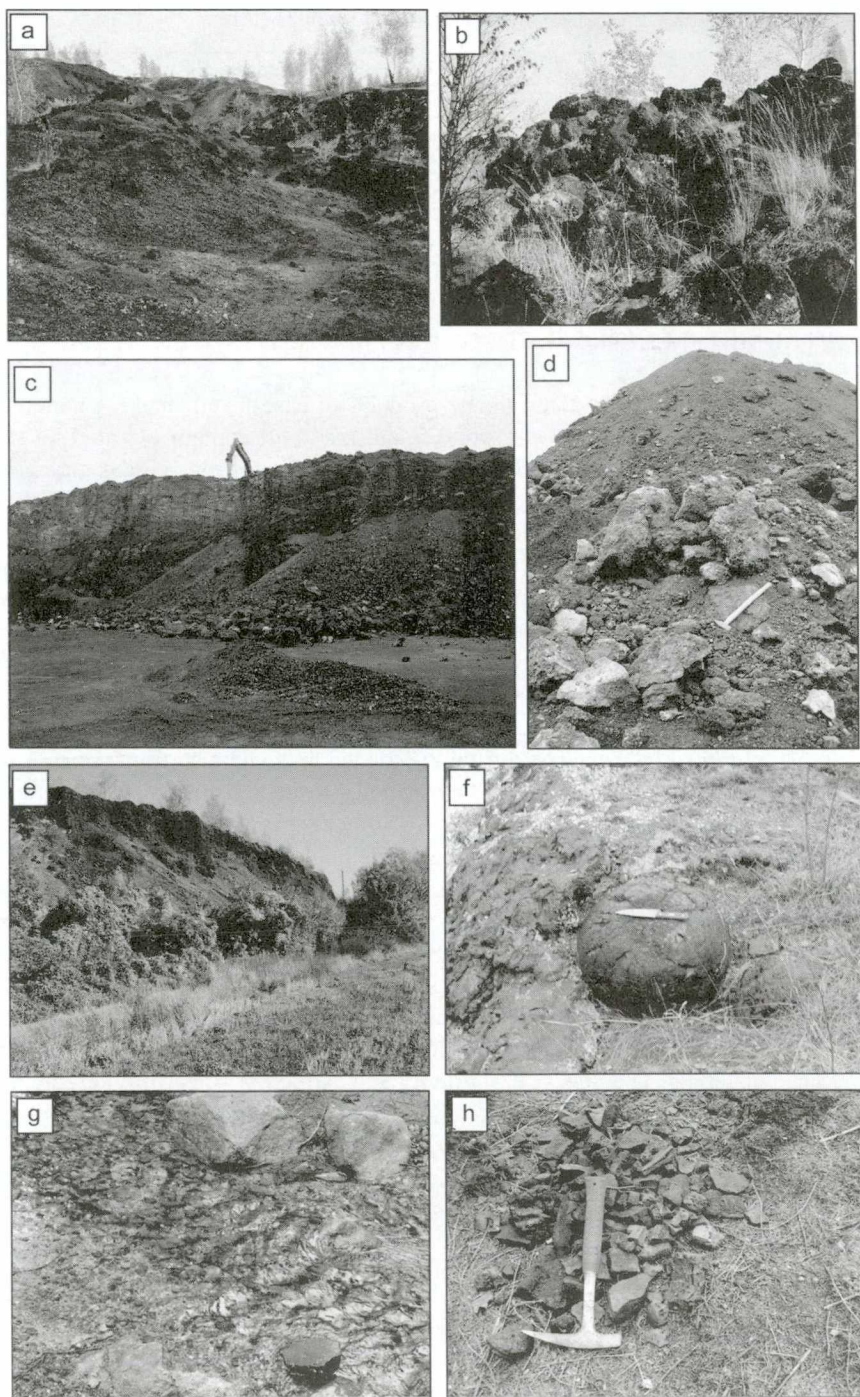


Fig. 2: Photographs of different tailings heaps and material constituting these tailings located in: (a, b) Świętochłowice (Upper Silesia), (c, d) Katowice/Wielowice (Upper Silesia), (e, f) Szklary (Lower Silesia), (g, h) historical slags present in stream in Rudawy Janowickie (Lower Silesia)



During the 14<sup>th</sup> century the Rudawy Janowickie area was the largest center for mining and smelting of metals such as Cu, As and Ag [5]. Since then, mining has closed and started again several times. Exploitation was definitely abandoned in 1925, leaving unattended mine tailings and slags located in the surroundings of the villages Miedzianka and Janowice Wielkie. The area covered by dumps is estimated to be around 35 ha. Some of the medieval dumps were further reprocessed during the 17<sup>th</sup> century by dissolution of secondary Cu sulfates, the method being characterized by particularly cheap and relatively easy application [5].

#### METHODS FOR STUDYING CHEMICAL AND PHASE COMPOSITION OF THE SLAGS

Each step of environmental study includes some amount of uncertainty which contribute to the final results. Sampling is the first step of such studies which deal with heterogeneous material due to the various origins of the concerned ores and to the long time of their extraction and treatment. In order to minimize sources of uncertainty, each collected sample should be representative and properly chosen for further study. Before sampling, it is necessary to prepare a sampling plan that fits to the main aims of the study and that reflects the properties of the whole study area. Sampling locations should be chosen taking into account specific conditions at the studied site (e.g. vegetal cover diversity, topography, hydrology etc). The most important prerequisite for a representative sampling is to explore the whole site area to get a view of the overall material variability. Then, if an attempt focuses on the average composition and if there is no interest for studying the spatial variability of the studied materials heterogeneity, most appropriate procedure consists in randomizing the sampling.

Methods applied for studying slags are those used in classical chemistry, mineralogy and petrology. These methods are nowadays supplemented by very fine techniques: micro focused scanning X-ray fluorescence (SXRF), micro X-ray absorption spectroscopy (XAS) and micro scanning X-ray diffraction (SXRD) in order to obtain data at the atomic scale.

For bulk chemical analyses, slag samples are dried and then prepared by particle size reduction to produce a homogeneous sub-sample which is representative of the original sample. For most analytical methods, this sub-sample will undergo some forms of dissolution and decomposition. Each sample decomposition procedure has its own advantages and limitations. The final technique used for the determination of elements depends on the required detection levels of the elements of interest. Typically two principal means of determination: Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are selected for slags. ICP-AES measures the light-waves and light intensities to determine what elements are present in the solution and the quantities of each. ICP-MS measures the element concentrations by counting the atoms for each element present in the solution. Generally, ICP-MS can determine concentrations that are 1 to 2 orders of magnitude lower compared to ICP-AES.

X-ray powder diffraction patterns provide important information on phase composition of studied slag samples. However, even by using Rietveld refinement, it is impossible to point out the presence of minor and trace phases (< 5% of the bulk sample) using this

method. Optical and Scanning Electron Microscopy (SEM) on polished sections or rough material coupled with Energy Dispersive Spectrometry (EDS) analyses allow to observe relationships between phases present in the studied material. Furthermore, complementary characterization of slags at nanoscale using transmission electron microscopy (TEM) is useful and allows to identify small inclusions which often occur within the glass (Fig. 3) and which generally contain high amounts of PTEs [38, 25].

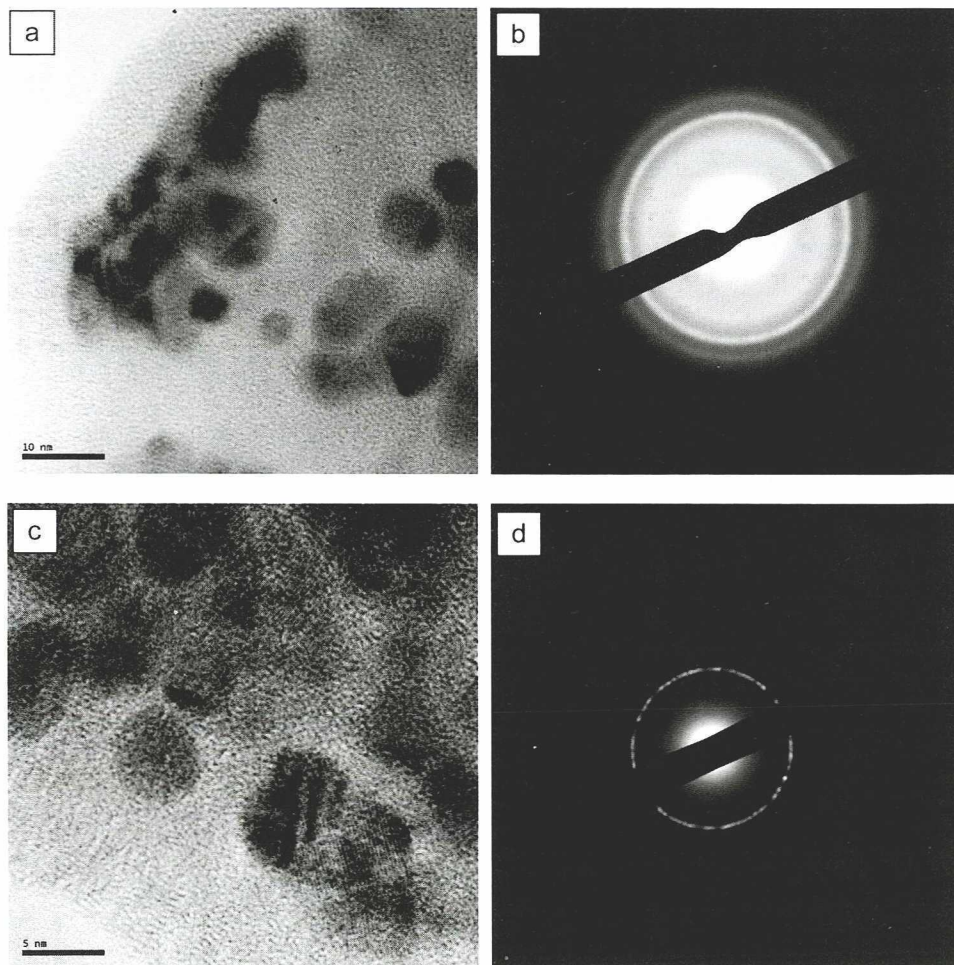


Fig. 3. Transmission electron micrographs of glass containing nanometric inclusions of PTE bearing phases: (a, c) coupled with selected area electron diffraction patterns (b, d)

Microprobe analyses using Wavelength Dispersive Spectrometry (WDS) system provide information concerning the chemical composition of a given phase when its size is larger than the focus of the electron beam. The EDS system can be also used for quantitative analysis. For many combinations of elements, however, the EDS system is less precise than WDS because corrections must be made for overlapping peaks and the background noise is much higher, lowering the detection levels. WDS analyses results in a



spectral resolution and sensitivity an order of magnitude better than is possible with EDS. Changes in window aperture (from 4 nA to 500 nA) and rising in accelerating voltage (from 20 to 35 keV) allow to detect metallic element present at very low levels (several up to dozens of mg/kg) depending on the element [13].

### FORECASTING POTENTIAL PTEs RELEASE FROM SLAGS

Within slags storage, potential risks related to the waste evolution are often estimated only on the basis of the total PTEs contents. Indeed, knowledge of PTEs solid speciation, which corresponds to the identification of the PTEs chemical and structural bonding forms, gives more exhaustive information about their potential mobility, bioavailability and toxicity [41]. The solid speciation of PTEs in slags can be assessed in two ways. The most used way consists of application of several types of chemical extractions. Chemical reagents are supposed to preferentially dissolve specific groups of waste components in a given type of previously defined conditions (e.g. acidic, reduced). On the basis of such chemical extractions, Alter [1] defined a copper slags as non-hazardous using an aggressive test consisting on leaching by buffered acetic acid. However, experimental conditions applied during these chemical procedures do not account for all possible environmental factors.

The second way of studying the PTEs speciation from waste comprises detailed mineralogical and petrological study of slags. Those methods consist in (i) identification of weathering conditions and processes leading to crystallization of secondary phases and ii) determination of chemical and structural (mineralogical) composition of the materials exposed to the meteoric agents. Interpretation of such studies is done according to the known stability conditions of the identified PTEs-bearing phases. Observations of secondary phases crystallizing in cracks or at the periphery of the parent material enable to assess the stability of the primary phases and to provide information about the mobility of the concerned elements. These observations coupled with spectroscopic techniques (e.g. Raman, Mössbauer) are particularly of interest to point out transformation of some primary phases (e.g. willemite –  $Zn_2SiO_4$ ) to secondary phases (e.g. hemimorphite –  $Zn_4Si_2O_7(OH)_2 \cdot (H_2O)$ ) by hydration [43].

Despite their names which sound very good (fraction bounded to carbonates or to oxides, extraction procedure toxicity test etc.), the chemical methods which are often automatically and solely applied, do not correctly reproduce the actual environmental conditions nor the ultimate potential release in a given situation. In spite of approximations they imply (e.g. carbonate fraction is rarely the real and entire carbonate fraction), their reproducibility justify their use in most official national and European norms for regulation. Twardowska and Szczepańska [42] point out the inconsistency of the laboratory leaching tests particularly when equilibrium conditions are imposed by kinetically determined reactions. These authors also underline that such tests reflected entirely wash-out of phases and dissolution that does not comprise delayed PTEs release.

In contrast, mineralogical studies enable the solid speciation of PTEs to be determined and the PTEs-bearing phases in slags to be characterized. As a consequence, mineralogical examinations provide information about the actual rate of PTEs release in the real weathering conditions, whereas the chemical extractions give a view of the potential release in given experimental conditions. Hence, in most recent studies, authors use de-

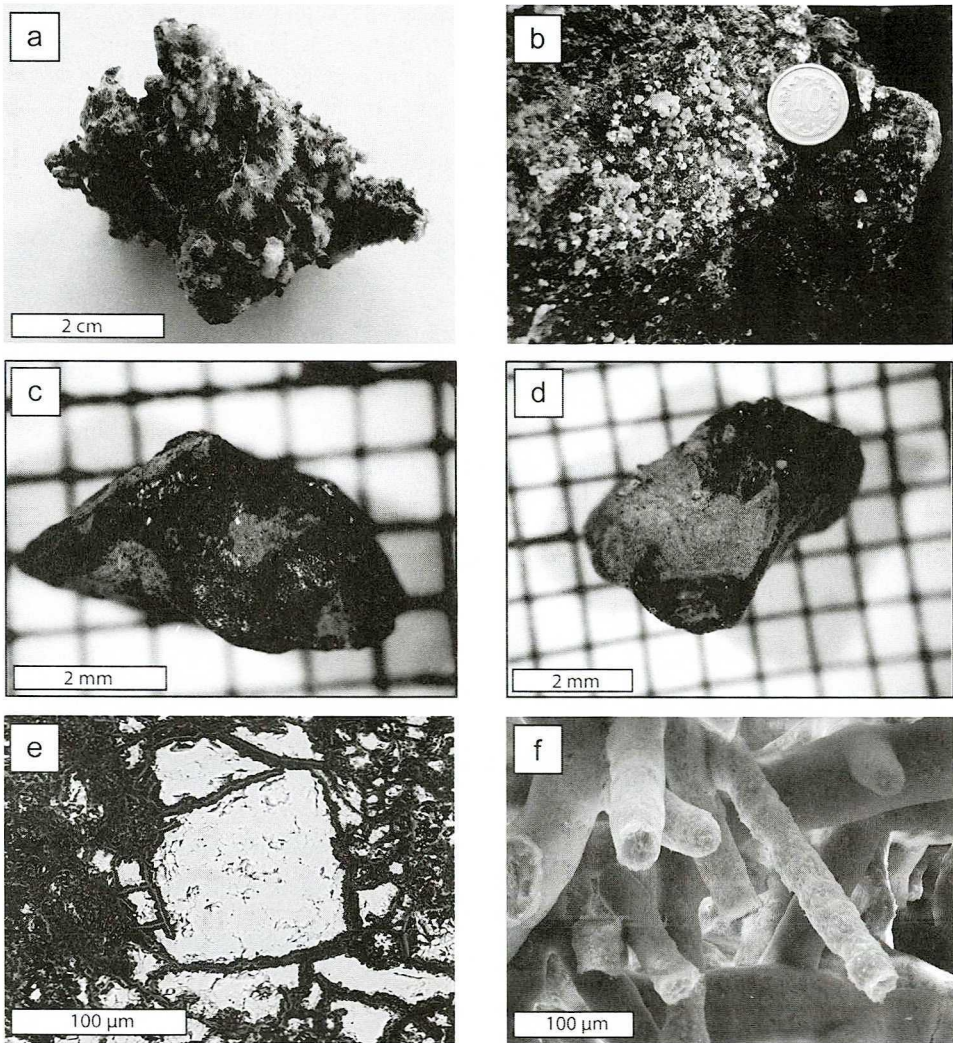


Fig. 4: Photographs of slag weathering products:

(a) small needles of gypsum from Katowice/Wielnowiec slags, (b) aggregates of carbonates (aragonite) on the surface of slag from Katowice/Wielnowiec smelter, (c, d) weathered slag particles from cultivated soil located in the vicinity of the Szklary smelter, (e) secondary Fe oxy-, hydroxides replacing sulphides in historical Cu slag from Rudawy Janowickie, (f) needles of secondary zincite occurring in slags from Katowice/Wielnowiec

tailed mineralogical examinations as a complement of the chemical laboratory experiments. This can be done in equilibrium conditions by examining of the solid residue obtained after specific chemical extractions [24]. Other studies attempt to simulate natural conditions over long periods of time (several months) using mineralogical observations in order to assess the actual slags weathering. These include leaching tests performed on the surfaces of polished sections [9, 30] or crushed samples in batch [34, 35] and in column tests [37]. In most cases, these experiments show that significant amounts of PTEs are released from the slags [34, 35].



## ARE PYROMETALLURGICAL SLAGS REALLY DANGEROUS?

All freshly generated anthropogenic materials are not geochemically stable and not environmentally safe when abandoned on surface climatic conditions. However, waste issued from pyrometallurgy is different than mine tailings waste because it was subjected to industrial treatment of various kinds. They also include numerous solid phases such as silicate glass and silicate and oxides deemed to be more stable because they present lower solubility in water [44] in the most frequent environmental conditions than sulphide or sulphates. Therefore, slags are generally considered as chemically stable. However, numerous studies have shown that PTEs can be mobilized from slags and may contaminate soils and streams and have then deleterious effects on the environment [2, 30, 31, 35, 39].

It is important to point out that potential environmental risk related to PTEs release from slags strictly depends on weathering processes which are very complex. They not only depend on the solid speciation of PTEs in the waste but also on numerous different factors such as: (i) textural characteristics and permeability of the material, (ii) local climatic and environmental conditions, (iii) human activities in the site of the slags storage, and (iv) time of residence of the wastes in a given site. Therefore, risk assessment related with slags, landfilling of such wastes or their possible re-use require a systematic survey of many factors influencing local weathering conditions.

### ***Solid speciation***

Solid speciation is one of the most important factors controlling potential risk of PTEs release related to the slags. Solid speciation in slags varies according to the processes applied to extract metal from the ore. For example, Ettler *et al.* [7] collected four different types of slags in the same area in Přebram (Czech Republic) where the smelting of Pb-Zn ores has been used since the 6<sup>th</sup> century BC. The oldest period of Zn-Pb ores reworking consisted of smelting at low temperatures, while present technological process involves battery processing and smelting at high temperatures. Total metal content is higher in the oldest slag material from Přebram. Each type of slag was characterized by different proportions of glass and different assemblages of metal bearing phases due to the variation of the efficiency of smelting processes and to temporary procedures that were used for valorizing subordinate elements such as Sb in lead ores. Hence, the knowledge of the smelting history enables to forecast not only main feature of the chemical speciation but also feature of physical speciation such as proportion of glass and textural characteristics.

Metallurgical slags are dominated by silicates, oxides (commonly spinel) and silicate glasses. In silicates, PTE are either concentrated in phases with pure metallic end member (for example willemite or hardystonite for Zn) or as few percentage metals occurring as replacement of other cations such as Mg – Zn substitution in olivine or in pyroxenes [36]. In mattes, numerous types of sulphides or arsenides are still present. Alloys or intermetallic compounds are also frequent because the mutual metal solubility (e.g. Pb in Sb or Sb in Pb) is important at a relatively low temperature [10, 11]. Alterability of these reduced phases when placed in oxic environment is high and as a consequence, in a given sample, they can be considered as weak zones through which the destabilization of all the surrounding material can begin. Conversely, silicates and well crystallized oxides (e.g. spinels) are more resistant to weathering [8, 25]. For example, Soubrand-Colin *et al.*

[40] observed spinels as the only phases unaffected by weathering from topsoils where none of other primary minerals was preserved. Usually glasses are well known to be less resistant to weathering than crystallized material and Goldich's series give a well-known classification of the susceptibility to weathering of the most spread phases. However, this classification is based on standard alteration conditions which are not well defined. In smelter products, proportion of oxides is more important than in natural material. Finally, glasses are not always "true" glasses because PTE found by punctual EMPA analyses are included in glasses as small nanometric inclusions of sulphides and intermetallic compounds. This fact was reported by Seignez [37] and by Kierczak [23] following TEM investigations (Fig. 3).

### ***Textural characteristics and permeability***

Some physical characteristics of waste such as porosity or/and particle size distribution play an important role in PTEs release from slags. For example, a good penetration of water within a porous waste material allows for better exchanges and the renewal of percolating water and as a consequence better release of PTEs. On the contrary, compact and dense slags (Fig. 2) may significantly delay water penetration, progress of weathering and crystallization of secondary phases. Textural characteristics, such as proportion of glass considered as more susceptible to weathering than crystalline phases, are also important to predict the PTEs release. Weathering of glass containing small inclusions of sulfides and intermetallic compounds, generally considered as environmentally hazardous and the most important PTEs carriers, may expose them to atmospheric conditions and increase the rate of PTE release from slags [25].

### ***Local climatic conditions***

The knowledge of the local climatic conditions in the area of the wastes storage is another important factor which has to be considered to predict potential environmental hazard related with the slags. Climatic effects are very often transitory thus sites of slags storage require continuous inspection. For example, abundant secondary phases named evaporative efflorescences usually crystallize during summer after dry periods on Rio Tinto historical smelter site [31]. These phases include ubiquitous more or less hydrated Ca or Mg sulphates but also more or less complex metal sulphates (Zn, Cu, Pb or Fe). España *et al.* [6] show that the most soluble phases disappear during consecutive rainy episodes in autumn when they are not sheltered from falling waters or runoff. On abandoned slag tailings other secondary minerals grow resulting in the formation of metallic oxides or hydroxides, iron oxy-hydroxides, etc. containing PTEs at concentrations as high as several percent [2, 10].

### ***Local environmental conditions***

Local environmental conditions constitute also an important factor controlling weathering and PTEs release from the slags. Thus, it is fundamental to collect as much information as possible about the site of the slags storage. Kierczak *et al.* [25] pointed out that weathering of Szklary slags issued from silicate ores appears to be less advanced than that of the slags issued from sulfide ores processing. It is probably due to both phase assemblage and their composition, but also because the local environmental conditions in Szklary, such as soil pH, are unfavorable for chemical weathering of silicate phases. Furthermore,



Kierczak *et al.* [25] compared secondary products issued from the same Ni slags collected in a heap located at Szklary. Glassy slags exposed to weathering within surface horizons of a cultivated soil were more altered than the same glasses exposed to weathering on the top of the heap poorly colonized by vegetation. The differences in the rate of weathering are probably caused by agricultural treatments and lower pH values for the cultivated soil than those predominating on the waste dump. Alteration phenomena are generally more important in acid environments than in alkaline ones. However, Sobanska *et al.* [39] found that after fifty years, the slags fragments issued from the same lead smelting factory from Northern France were more altered in alkaline soil than in acidic environments. This was explained by the influence of several possible factors, such as organic matter content in the acidic soil which may slow down the slag weathering. Another assumption is the more hydromorphic conditions in the alkaline soil which limit precipitation of iron oxides that currently prevent soluble phases from alteration in the more acidic soil. Hence, there is no general rule giving one effect to one specific factor.

### ***Importance of human activities***

Human activities can act as a favorable or as a limiting factor of the PTEs stability in slags. As mentioned above, soil drainage or re-vegetation of the waste heap can enhance formation of stable secondary PTEs bearing phases and contribute to limitation of the environmental risk of PTEs release. In contrast, smoke emissions cause acidification and further soil pollution. It was pointed out that some compounds dissolved in particulate matter of industrial fumes, have strongly acidified (to pH 3) rainfalls [20]. Worsztynowicz and Mill [45] highlighted that this excessive acidification of precipitation occurs in Upper Silesia region due to hard coal burning. In the authors' opinion, "Leaving this system out of control can result in spontaneous release of heavy metals and their migration into soil, surface and ground waters. This may lead to unforeseen consequences the more dangerous that addressed to one of the most populated areas in Europe".

### ***Importance of residence time***

The next important factor which determines potential risk related to PTEs release from slags is time. When permeability of metallurgical tailings is high enough to allow formation of secondary products which are stable at local climatic and environmental conditions, the concerned tailings are considered to be in equilibrium. One can indeed believe that slags dumped for long periods (several centuries) have reached an equilibrium state with the surface conditions depending on the rate of weathering penetration. However, historical mining and smelting activities generally left highly polluted soils and sediments and caused irreversible changes to the environment [15].

## HOW TO MANAGE THE SLAGS STORAGE AND WHAT ABOUT RE-USE POSSIBILITIES?

Regarding the social perception of metallurgical waste, three periods can be distinguished. Until 1980 metallurgical slags were not considered as tailings, thus they were abandoned without any care in the surroundings of mines or factories. Main difference between mine and metallurgical tailings is that the latter are more often abandoned in inhabited areas. This is particularly the case in Silesia where urban tailings are visible until now, for

example in Bukowno, Świętochłowice or Welnowiec in the surroundings of Katowice. However, the good news is that pyrometallurgical slags are not as finely crushed as their mining equivalents and generally form decimetric to metric boulders, which are potentially more resistant to weathering (Fig. 2).

Since 1980 until now, pyrometallurgical slags have been considered as waste. They are either stocked in secure landfill sites or partially used as material for roads or concrete production. Waste stocking is very expensive because it requires: (i) location and preparation of appropriate site and (ii) transfer of huge quantities of polluted material onto several kilometers or more. Recently, due to their composition, stability and mechanical properties [14], slag wastes are used as quarries supplying materials which appear to be the best way to get rid of these harmful products. Hence, pyrometallurgical slags have been often used as road ballast or backfill material, as sandblasting agents, as cement additives, even if they contain high concentrations of potentially toxic metals [35, 45]. Though advantage of addition of granular blast furnace slags in high performance concrete is not so obvious and within some ratio, it can lead to a deleterious decrease of the concrete resistance to freeze-thaw and to compression strength [46]. Furthermore, as shown by numerous studies [12, 30, 31, 32] risks of PTE release are still high because most reuse operations resulted in placing the slags in oxidizing and well drained conditions. The best conditions of PTEs immobilization are obtained for slag inclusions in cements [19] because of their basicity.

Blast furnace slags have also been widely used in wastewater treatment and pollution control technology for the removal of phosphate, heavy metals and organic pollutants. High phosphate sorption capacity of slags has been demonstrated by batch and column experiments as well as field research [21, 22, 28]. Slags are used as filter and adsorbent in on-site wastewater treatment systems, such as constructed wetlands and industrial soil filtration systems [4, 21]. The major advantage of slag is cost effectiveness and abundance, which makes the treatment process economical. On the other hand, in such processes, slags are confined in reductive water saturated conditions that are considered to facilitate the PTEs immobilization. However, within such water treatment system, there is neither regulation nor systematic survey of the actual evolution of the slag speciation.

Very recently, due to the increasing cost of raw materials and ongoing prices of metals, a new technologic goal arises in examination of perspectives of metal extraction by the re-use of slags. In spite of their sharp decrease in 2008, prices of metals have indeed increased in a rate over 200% for the last ten years (266% for Ni, 249% for Cu and 229% for Pb), except for Zn for which the price is 69% of the price of year 1999 (Fig. 5). As for mine tailings [3], due to changes in economic context and to improvement in extraction techniques, waste can be regarded as a profitable resource. In particular, slags can be treated as ore being added to the melts instead of raw materials in metallurgic processes, for example as fluxes or only as metal supplier. Some studies [33] are performed in order (i) to know bulk composition of the slags, (ii) to assess potential stock of heavy metals which can be salvaged, and (iii) to get a precise knowledge of the solid speciation of heavy metals in order to define processes which must be used for their recovery. Upper Silesia and Lower Silesia are surely very good experimentation areas for such studies.



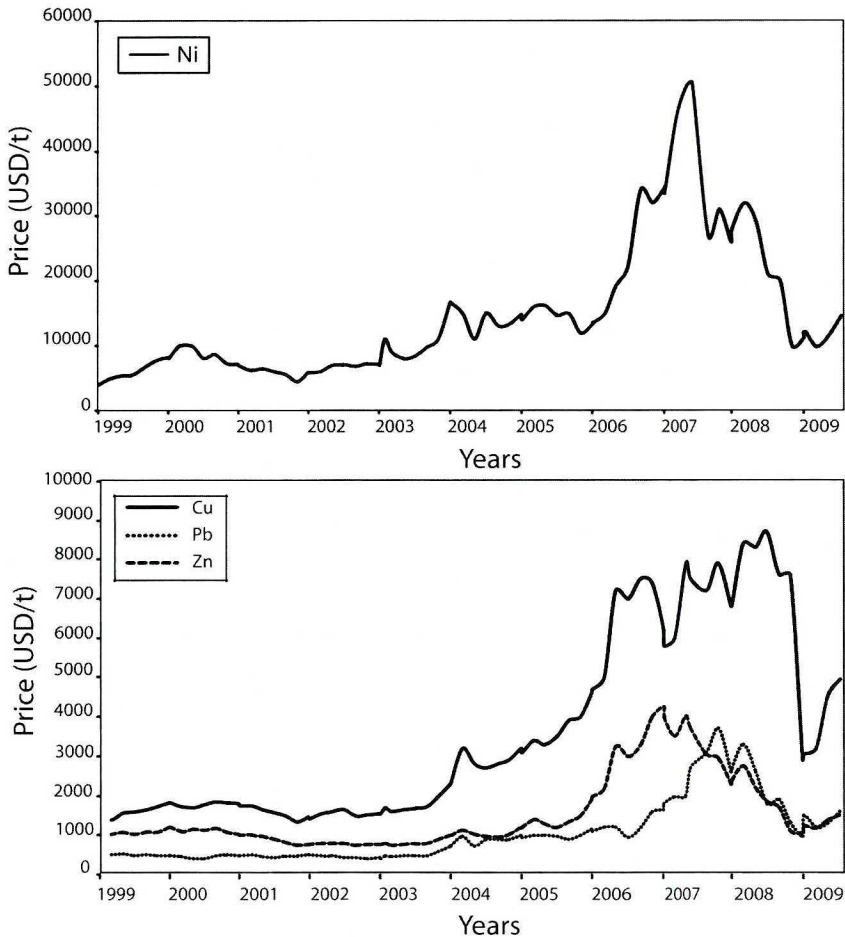


Fig. 5. Evolution of the course of Ni, Cu, Pb and Zn from 1999 to present

## CONCLUSION

Poland is one of the UE countries which is the most affected by the storage of slags derived from smelting industry. The main part of pyrometallurgical waste dumps occurs in Upper and Lower Silesia. Even if the present review mainly focused on four sites, it is representative for the case diversity that can be found in Silesia. Studied sites include various types of technological processes, diverse ore origins implying different metals (Zn, Pb, Cu, Ni). Moreover, slags from studied areas have been stored for a long period of time.

Pyrometallurgical slags in Poland constitute a real and serious hazard for the environment. In order to answer the question: "What could we do to protect us against consequences of PTEs release from slags?", we should define first the current stage of the slags weathering and stability, and secondly the final aim consisting of possible re-use or landfilling of such waste. A variety of experiments coupled with in situ monitoring should

be applied in order to estimate the real risk related with the pyrometallurgical slags. Interest of detailed mineralogical examinations has been underlined. These methods should be used as a complement to the chemical methods which are the only ones generally required by the legislation. If the slag material is too hazardous to be re-used as additive, it should be stored in secure landfills. However, it was shown that factors determining the slags weathering are complex and quite impossible to forecast. The areas of the hazardous slag dumping have thus to be constantly controlled.

Pyrometallurgical wastes are not safe for the environment when exposed to atmospheric conditions, either at the disposal site, or in the case of its bulk use for construction purposes or water treatment. Although slags constitute potentially reusable materials, as highlighted by Twardowska and Szczepańska [42], it does not provide the best possible solution, either from an economic or environmental point of view, to consider them from the category of 'waste' as 'secondary raw materials' or 'by-products', or just 'materials'.

Due to increasing prices of metals some slags (e.g. Ni-rich) would better be reused as new ore, rather than being only "hidden" somewhere or landfilled. However, it requires a detailed study which responds what technological process should be used to extract the metal content remaining in the waste. In the case of slags where metal content is too low to make the extraction profitable, its reuse rather as a construction material is the best way for environmental preservation.

Finally, it is important to point out that slags do not constitute the only problem related to mining and smelting industry in Silesia. There are also huge quantities of mine tailings, fly ashes and smoke emissions which contaminate the whole area.

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#### ŻUŻLE METALURGICZNE NA GÓRNYM I DOLNYM ŚLĄSKU (POLSKA): OD RYZYKA ŚRODOWISKOWEGO DO WYKORZYSTANIA ODPADÓW HUTNICZYCH – PRZEGLĄD

Żużle powstałe w wyniku przetopu i obróbki rud metali stanowią poważne zagrożenie dla środowiska na Górnym i Dolnym Śląsku. Odpady te często zajmują duże obszary znajdujące się na terenach miejskich bądź w bezpośrednim ich sąsiedztwie. Dodatkowo, żużle metalurgiczne mogą zawierać znaczące ilości (nawet do kilkunastu procent wagowych) toksycznych dla środowiska pierwiastków metalicznych.

Prezentowany artykuł porusza główne problemy związane ze składowaniem żużli metalurgicznych na terenie Górnego i Dolnego Śląska. Podstawowe pytania, na które autorzy próbują odpowiedzieć w niniejszej pracy to: (1) jakie są charakterystyczne cechy żużli zdeponowanych na Śląsku (2) jak należy badać tego rodzaju odpady aby przewidzieć ich potencjalny wpływ na środowisko (3) czy wszystkie żużle metalurgiczne są niebezpieczne dla środowiska (4) jak planować składowanie tych odpadów oraz (5) czy i jak można powtórnie je wykorzystywać. W celu uzyskania odpowiedzi na postawione pytania autorzy dokonują porównania wyników uzyskanych w czasie badań różnych typów żużli metalurgicznych zdeponowanych na Górnym i Dolnym Śląsku.

Z przeprowadzonych badań wynika, że większość żużli metalurgicznych zdeponowanych na Górnym i Dolnym Śląsku stanowi poważny problem dla środowiska. W celu dokładnej oceny ryzyka jakie niesie za sobą składowanie tego rodzaju odpadów należy prowadzić dokładny monitoring składowisk połączony z różnego rodzaju badaniami. Na podkreślenie zasługuje użyteczność badań mineralogicznych do oceny mobilności pierwiastków metalicznych, które powinny być używane w celu uzupełnienia analiz chemicznych wymaganych przez normy prawne.