



Auriferous wastes from the abandoned arsenic and gold mine in Złoty Stok (Sudetes Mts., SW Poland)

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Wierchowiec J. and Wojciechowski A. (2009) — Auriferous wastes from the abandoned arsenic and gold mine in Złoty Stok (Sudetes Mts., SW Poland). *Geol. Quart.*, 53 (2): 233–240. Warszawa.

The historical arsenic and gold-ore operation at the Złoty Stok mine generated around 1 500 000 tonnes of wastes. The gold-bearing post-flotation tailing dumps, waste slag heaps, mined rock and arsenic roasting spoils (cinders) from mining of metamorphogenic, hydrothermal As-Au deposits have been examined to evaluate their gold grade. The waste material is dominated by calc-silicate skarn, dolomitic marbles, serpentinites and As-Au ore fragments. Sulfides are mainly loellingite, arsenopyrite and pyrrhotite with some pyrite, chalcopyrite, sphalerite and galena. In oxidized material, sulfides are rare or absent. Over 1000 samples of post-flotation waste muds and three bulk samples of mined rock spoils were analyzed. Only tailings show high concentrations of Au (0.8–20.1 ppm) and As (1.0–2.6 wt.%). An average contents of other metals (in ppm) are: Cu — 177.5; Pb — 212.2; Zn — 127.5; Ag — 0.38; Pt — 0.006; Pd — 0.001. Analytical results indicate that concentrations of these elements are very low along profiles, with no obvious relationship between content and depth. Average gold content of 0.3 ppm in waste slags disqualifies this material as a source of gold. The remaining resources of gold in the flotation tailings and waste heaps are estimated at as high as 2370 kg. The main pollutant is As with contents exceeding 52 100 ppm in the mined rock spoils.

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Key words: Sudetes, Złoty Stok, wastes, auriferous tailings, gold grade, resources of gold.

INTRODUCTION

The Złoty Stok (Reichenstein) region has been one of the most important precious metal producers in the Sudetes since the late Middle Ages. However, some authors believe that the beginning of mining activities can be dated back to the 7–8th centuries (Morávek, 1992).

During the period 1540–1550, the Złoty Stok mines produced large quantities of gold and were considered among the richest in Central Europe. Since the beginning of the 18th century, gold extraction associated with by-production of arsenic took place for two hundred years. At this time, the Złoty Stok mine was the world's largest producer of this metal (Dziekoński, 1972). Mining was carried out in four excavation fields: the Western Field (Góra Haniak), the Biała Góra Field, the Góra Krzyżowa Field and the Góra Sołtysia Field.

According to Bałdys (1954), between 1481 and 1944 about 3 800 000 t of arsenic ores and from 9–13 t of gold were extracted in the region. After the Second World War, economic

gold-bearing arsenic ores had an average arsenic content of up to 6 wt.% and yielded 3.2–3.5 g/t of Au. The mine was closed in autumn 1961, due to the poor quality of the arsenic ores (Dziekoński, 1972).

In the 1990s, extensive exploration in the surroundings of the Kłodzko–Złoty Stok Massif provided new insights into our knowledge of the economic potential and evolution of the Złoty Stok area. Despite the long-lasting operation, this gold-bearing district still has potential for discovery of Au-rich arsenic and other ores (Kanasiewicz, 1992; Muszer, 1992; Mikulski, 1996; Wojciechowski, 1998; Speczik and Mikulski, 2001). Furthermore, gold contents during the medieval and more recent mining operations has been a subject of numerous studies (Wojciechowski, 1990, 1993, 1994; Muszer and Łuszczkiewicz, 1997).

The purpose of this study is to provide data on the gold grade and total metal concentrations in wastes of the Złoty Stok mining district and to estimate the economic potential of these technogenic deposits. Data are compared with background lev-

els of the elements analyzed to estimate the potential risk for releasing metals to the nearby environment.

SAMPLING AND ANALYSIS

Augering was the main method used to collect over 1000 samples from different tailings dumps. 124 auger holes were manually drilled into the ground to depths of up to 15 m. A cochleary-drilling set (4 inch in diameter) was employed to drill through dumps and representative samples were collected at regular 1 m intervals. Surface-to-bedrock tailing cores were chemically analyzed to evaluate Au and As contents variations through the dump. During the drilling, the cores were collected and stored in hermetically sealed bags.

Once in the laboratory, the dried primary samples from each interval were divided in a Jones type — riffle splitter to sub-samples of about 100 g according to the procedure described by Gerlach *et al.* (2002). The samples were then sieved with a 0.06 mm sieve and oversize particles were ground in a ball-bearing pulverizer.

Additionally, bulk samples of 1000 ±50 kg from slag (one sample) and mined rock spoil (three samples) were collected. Each of the samples was run through a jaw crusher to obtain grains smaller than 1 mm. Then samples were split by coning and quartering to samples of 10 kg. After desiccating, samples were divided in a Jones splitter to 1 kg sub-samples, sieved with the 0.06 mm sieve and oversize particles were ground in the ball-bearing mill. Geochemical samples were prepared for Inductively Coupled Plasma (ICP) analyses using a standard procedure (Van Loon and Barefoot, 1991; Jarvis and Jarvis, 1992).

The gold and PGM contents were determined by fire assay (FA/ICP), and As, Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, U, Th, Sr, Cd, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K and W by Atomic Emission Spectroscopy (ICP-AES) after aqua regia extraction from 100 gram of sample in teflon bombs in the ACME Analytical Laboratories Ltd. in Vancouver. The data derived by analyzing the samples from the wastes were used to calculate the mean weighted Au and As contents as well as the total error in grading and assaying analyses.

GEOLOGICAL SETTING

All auriferous wastes studied (post-flotation tailings, slag, arsenic roasting and mined rock spoil) from the arsenic and gold mine at Złoty Stok were deposited on fractured metamorphic rocks of the Złoty Stok–Skrzynka Tectonic Zone, which is the northernmost unit of the Łądek–Śnieżnik metamorphic structure (Sawicki, 1956; Don, 1964; Cwojdziański, 1975). This dislocation zone, defined by Cymerman (1996) as the Złoty Stok–Trzebieszowice (ZST) regional shear zone, has a NE–SW trend and was developed at the time of the Variscan deformation.

The rock complex of this unit is characterized in the Złoty Stok area by the phenomena of cataclasis and mylonitization of varying intensities. The basic rock complex of the ZST shear zone is composed of mica schists, mica-quartz schists

and quartzite schists, along with gneisses, leptynites, amphibolites, as well as serpentinites and crystalline limestones. In the north, the ZST Tectonic Zone is limited by the Sudetic Marginal Fault of NW–SE trend (Fig. 1) and in the west and the north-west by the granitoid intrusion of Kłodzko–Złoty Stok (Cwojdziański, 1974, 1975).

The late-tectonic Kłodzko–Złoty Stok Massif is an intrusion of mixed granitoids of syntectonic-contamination type origin developed along dislocation planes with NW–SE trend, during late phases of the Variscan orogeny (Smulikowski, 1979). The intruding magma had a high temperature, as shown by reomorphic melting of the Haniak gneisses, by intensive microclinization, and by the appearance of cordierite and formation of migmatites within biotite schist (Cwojdziański, 1975), it was also responsible for ore-forming metasomatic processes on the Złoty Stok As-Au deposit (Kowalski, 1963, 1969; Wierzchołowski, 1976).

The roof of the Kłodzko–Złoty Stok Massif is covered by relics of sedimentary cover, now represented by hornfelses, amphibolites, skarnoids and gneisses. Recently, some of these were recognised as having metallogenic potential (Mikulski, 2000; Speczik and Mikulski, 2001).

ARSENIC AND GOLD-BEARING MINERALIZATION

Three types of mineralization are generally recognized in the Złoty Stok area: 1) loellingite-rich skarns which envelope stocks and lenses of dolomitic marbles; 2) elongated wedges of diopside-tremolite ore with patches and nests of ore minerals; 3) disseminated ore related mainly to dolomitic marbles, with significant serpentinization.

This serpentinization, accompanied by the formation of several varieties of calc-silicate skarn-type rocks, was the critical process for formation of rich arsenide ores (Muszer, 1992; Niczyporuk and Speczik, 1993). The main ores include Au-bearing loellingite, arsenopyrite, pyrrhotite and magnetite with some pyrite, chalcopyrite, sphalerite and galena. The mineralized structures are 1 to 3 m thick (although some reach 10 m) and are 700 to 2000 m long. Mineralization is particularly rich (up to 40% by volume) in samples with increased amounts of organic material (Speczik and Mikulski, 2001). It is dominated by large (2–4 mm) loellingite crystals, which form pinacoids and prisms.

Disseminated low-grade ores were found occasionally in on mined country rocks, mainly in mica schists containing zones of graphite, garnet and As-Au mineralization. Arsenic minerals are common also in aplites, pegmatites, and other spessartite-bearing vein rocks, which occur throughout the area.

Native Au is extremely rare, occurring mostly in carrier minerals as sub-microscopic particles. The chemically determined Au content in rich arsenic ores varies from 15 to 35 ppm, and from 3 to 13 ppm for poor ores (Kowalski, 1961; Budzyńska, 1971). Backscattered electron and X-ray mapping of loellingite crystals suggest that gold is nearly evenly distributed throughout loellingite crystals (Niczyporuk and Speczik, 1993). Gold forms minute inclusions (0.5–5 µm) in loellingite, arsenopyrite, pyrrhotite, magnetite, Ni-Co sulphoarsenides,

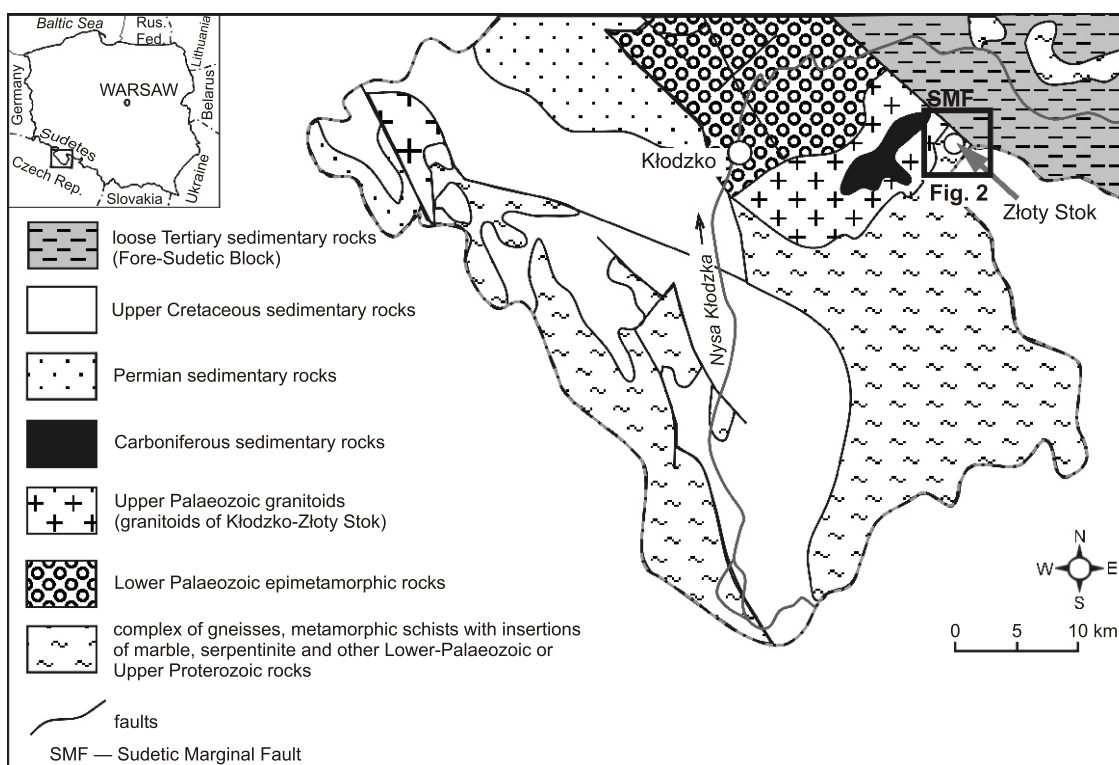


Fig. 1. Location of Złoty Stok mining area on the background of the regional geological structure

quartz, garnet and limonite (Muszer, 1992; Niczyporuk and Speczik 1993; Mikulski, 1996). The most common form for individual Au inclusions in arsenic ore are oval Au grains in quartz which includes healed cataclased grains of loellingite. It is suggested that Au dispersed in loellingite was remobilized and concentrated in microscopic quartz veins during the later metasomatic stages, or as a result of hydrothermal activity within shear zones during post-Variscan time (Speczik and Mikulski, 2001).

The polymetallic deposit of Złoty Stok also contains radioactive minerals, chiefly autunite (Przylibski, 2001). The first analyses to explain the weak radioactivity of the rocks mined at Złoty Stok were carried out in the 1950s by the R-1 enterprise from Kowary. In 1960, they resulted in the discovery of a locality in the Biała Góra Field (Fig. 2) with an average uranium content of 0.03 wt.% and a maximum concentration of 0.2 wt.% (Głowacki and Kopeć, 1963). The studies of Muszer (1995) have proved that radioactive minerals occur in the area of the Złoty Stok deposit between the mountains of Haniak (Western Field) and Biała Góra (Biała Góra Field). The occurrence of uranium ore mineralization in the form of a secondary mineral, autunite, has been confirmed in this area, while a primary uranium mineral (uraninite — UO_2) has been found in the ore on the Złoty Stok deposit. Its weathering caused the concentration of autunite around Biała Góra.

CHARACTERIZATION OF THE WASTES: A REVIEW AND NEW DATA

Mining and smelting of Au-rich arsenic ores in the Złoty Stok area have generated 1 500 000 tonnes of wastes, including flotation tailings, mined rock spoil, waste slag and arsenic roasting spoil (cinders) deposited in ponds (flotation tailings) and heaps. Wastes from mining and smelting, of various ages, are spread over a hilly area south and north of the town of Złoty Stok (Fig. 2).

FLOTATION TAILINGS

Tailings produced by a processing facility remain in four embanked deposition sites in the valley of the Trujaća Creek. Near the mine, alongside the Trujaća Creek, 500 000 tonnes of sandy-silt tailings were disposed in the retention ponds (dumps) that have spread with time over site.

Gold-bearing tailing dumps occur in the Trujaća Valley, which is an extension of the Złoty Jar Valley. These tailings are the waste product after flotation of crushed and milled arsenic ore at the treatment plant of the arsenic smelter at Złoty Stok. Flotation enrichment was carried out between 1935–1962 (until the smelter was closed down).

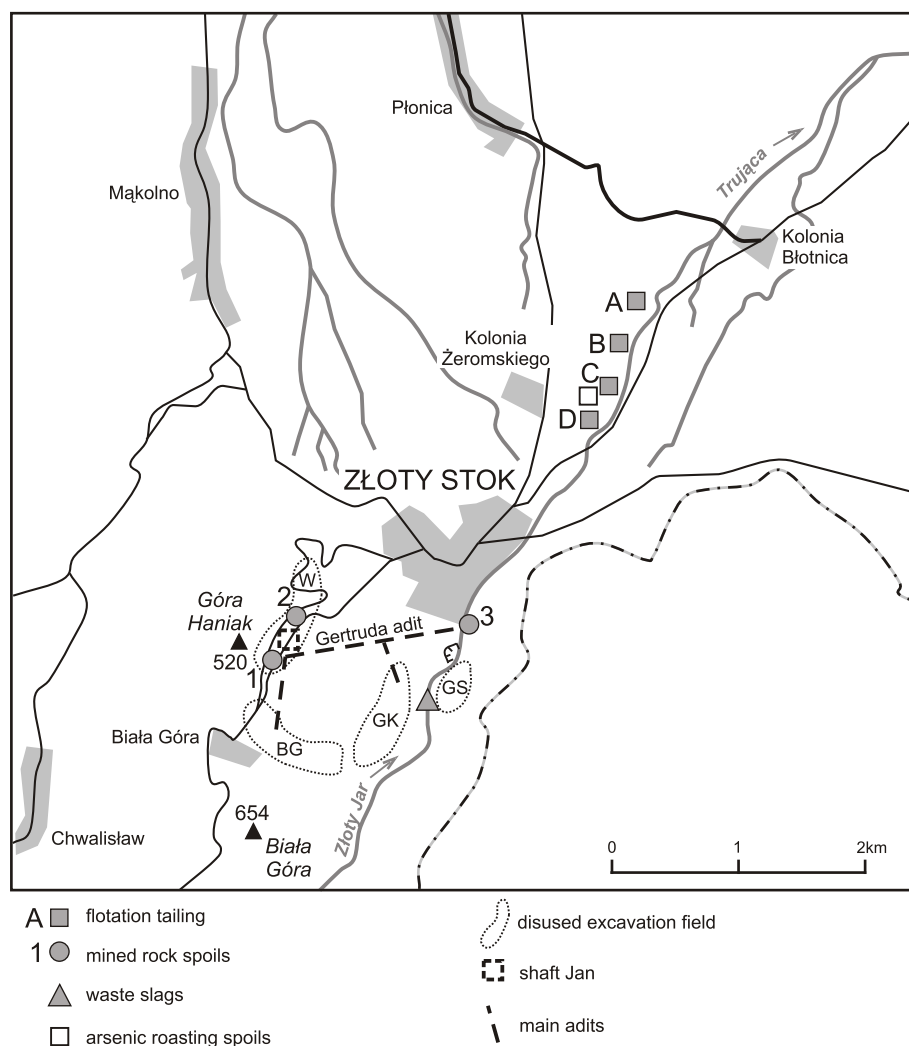


Fig. 2. Locality map showing location of sampled wastes in the disused arsenic and gold mine in Złoty Stok area

Mining fields: W — Western (Góra Haniak), BG — Biała Góra, GK — Góra Krzyżowa, GS — Góra Sołtysia

In all retention ponds, the tailings are to a various degree mixed with other products of the wet enrichment process. Unpublished data of the Arsenic Treatment Laboratory (ATL) from the period 1958–59 show that the main ore components of the flotation concentrate were loellingite, arsenopyrite and scorodite, followed by gangue of serpentine, olivine and quartz.

The arsenic content in the concentrate ranged from 32.15 to 38.85 wt.% (the average of 12 samples was 36.02 wt.%). Arsenic contents in the general wastes (analysed daily) ranged from 0.31–2.50 wt.% (the average of 30 samples was 2.04 wt.%). The average gold concentration in the above concentrate was around 10 mg/kg (10 ppm).

Post-flotation waste muds fill four retention ponds (marked as A–D in Fig. 2), located over a distance of 1.2 km along the Trująca Creek. The topographically highest pond D contains the oldest waste. The average thickness of arsenic and gold-bearing waste muds is 0.8 m in pond A, 5.7 m in pond B, 7.9 m in pond C and 9.9 m in pond D. The width of ponds varies from 100 to 300 m (Wojciechowski, 1990, 1998). After 1962, pond C was used also to retain barite wastes and pond D

as a collector of the waste water from the then factory of paints and varnishes.

Preliminary data indicate that the gold contents in the dump of pond A was — 0.35 ppm, B — 0.52 ppm, C — 1.12 ppm and in dump of pond D — 1.86 ppm; while arsenic ranged from 2.0–2.6 wt.% (Wojciechowski, 1990, 1994). This study indicated that the average gold content in the flotation tailings is higher, while arsenic is lower. Gold contents in these wastes ranged from 0.8 to 20.1 ppm Au. Pond B averaging (arithmetic mean x_a) 0.818 ppm Au, standard deviation $s = 198.83\dots$, $n = 27$; pond C — $x_a = 11.833$ ppm Au, $s = 450.28\dots$, $n = 61$; pond D — $x_a = 20.120$ ppm Au, $s = 551.02\dots$, $n = 36$. Arsenium contents ranged from 0.97–2.57 wt.% As. Pond B averaging (x_a) 0.97 wt.% As, $s = 0.26\dots$, $n = 27$; pond C — $x_a = 1.66$ wt.% As, $s = 0.83\dots$, $n = 61$; pond D — $x_a = 2.57$ wt.% As, $s = 0.85\dots$, $n = 36$ (see Table 1 and Fig. 3).

Cross-sections of the tailing dumps show that three bed assemblages could be distinguished, that differ in gold and arsenic content. The bottom beds have 200–500 ppb Au and 1.5–2.0 wt.% As, the middle section contains 1.8 ppm Au and

Table 1

The average gold and arsenic content in the retention ponds (dumps)

Ponds ¹	Concentration	
	Au [ppb]	As [wt.%]
Pond B, <i>n</i> = 27	818 ± 75	0.97 ± 0.10
Pond C, <i>n</i> = 61	11833 ± 113	1.66 ± 0.21
Pond D, <i>n</i> = 36	20120 ± 80	2.57 ± 0.28

¹ — in drill cores from pond A the gold and As contents were not determined

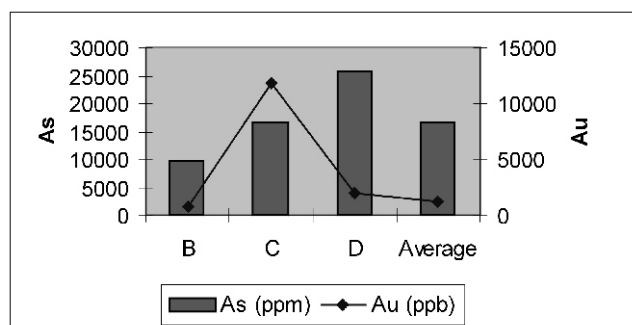


Fig. 3. Gold and arsenic contents in the post-flotation waste muds; retention ponds (dumps) marked as B, C and D

1.5–2.0 wt.% As, and the top part has similar Au and As concentrations to the bottom part. Erratic Au and As concentrations in the middle section (Fig. 4) are probably related to the release of waste pulp with differing concentrations of these elements.

Statistical treatment of the analytical data (*n* = 124) revealed a high correlation between Au and As (coefficient of correlation of a regression analysis $r^2 = 0.9598$) and Au-Cu ($r^2 = 0.7905$). On the other hand, no obvious relationship between metal content and sampling depth was found.

The average metal content in the pulp is low: Cu — 178 ppm, Pb — 212 ppm, Zn — 128 ppm, Ag — 0.38 ppm, Pt — 0.0006 ppm and Pd — 0.001 ppm).

MINED ROCK SPOIL

The main spoil heaps, with an estimated volume of 360 000 m³, are located near the shaft Jan in the Western Field and near the entrance of the Gertruda adit in Złoty Jar (Fig. 2). The waste rocks comprise crushed black and green serpentinites, calc-silicates and other local rocks including massive loellingite-arsenopyrite-pyrite and pyrrhotite ore (Muszer, 1992; Muszer and Łuszczkiewicz, 1997).

According to Muszer and Łuszczkiewicz (*op. cit.*), the average concentration of metals in the waste heap in the Western Field is — 1.76 ppm Au, 0.4 ppm Ag and 16 wt.% As.

Subsequent detailed sampling was carried by Wojciechowski (1998). His results are presented in Table 2.

High Au and As contents in sample 2 of Wojciechowski (1998) result from the fact that about 70 wt.% of waste here consist of mineralized rocks from the ore zone, including massive ore hosted by green serpentinites. Samples 1 and 3 contain

Table 2

Weighted average concentrations of gold and arsenic in the mined rock spoils deposited in the heaps (Wojciechowski, 1998)

Bulk sample number	Location (see Fig. 1)	Metal content [ppm]	
		Au	As
1	S part of the waste heap in the West Field	0.232	3279
2	S part of the waste heap in the West Field	3.804	52120
3	waste heap near the Gertruda adit	0.167	2298

only minor mineralized rock chips and the concentration of gold is reduced to 0.2 ppm. Concentrations of Cu, Pb, Zn, Ag, in the sampled material are low (<45, 25, 70, 0.3 ppm, respectively). Contents of Pt and Pd are below the detection limit.

Apart from these three waste heaps, the Złoty Stok area contains also numerous small mining waste bodies (having an estimated volume of 25 000 m³), which are clearly seen in the local topography. Some rock spoil after medieval gold mining does not have expression in the morphology.

WASTE SLAG HEAPS

Slag heaps occur mainly in the Złoty Jar Valley (Fig. 2). These are wastes after gold smelting in the Middle Ages. Auriferous arsenic ore was smelted in primitive furnaces called “dymarki” (Dziekoński, 1972). Then the gold-bearing sulfide melt obtained (“crude stone”) was three times roasted to separate arsenic and sulfur, and to combine the remaining part with lead. The resulting gold-lead alloy was oxidised to litharge, which flew towards the copula of the cupellation furnace, leaving metallic gold on the furnace’s base. Two types of waste slag were produced during this process: a) slag after smelting auriferous arsenic ore and b) slag after oxidation of lead and gold alloy to litharge. Total tonnage of slag around Złoty Stok is estimated at 30 000 t.

The average gold content in smelting slag varies depending on different sources. Muszer (1992) reported values of 0.5, <0.5 and 3.0 ppm (*n* = 3); Wojciechowski (1993) provided values ranging from 0.1 to 0.35 ppm (average 0.19 ± 0.05 ppm, *n* = 9); while Muszer and Łuszczkiewicz (1997) gave values of 2.9 and 0.53 ppm (*n* = 2).

A bulk sample from one of the slag heaps in Złoty Jar Valley returned average values of 0.29 ppm Au and 1159 ppm As. The content of other metals in the heap is low: Cu — <15 ppm, Pb — <20 ppm, Zn — <25 ppm, Ag — <0.3 ppm, and very low: Pt, Pd — <0.001 ppm, except for relatively high (206 ppm) W content (Wojciechowski, 1998).

These results confirm earlier data, which indicated low Au concentrations in smelter slags from the Złoty Stok Mine.

ARSENIC ROASTING SPOIL (CINDERS)

To obtain arsenic oxide and subsequently metallic arsenic the arsenic ores were roasted at temperatures of 740–800°C. Gold contained in the primary ore was concentrated in roasting spoil. The first attempts to extract gold from the roasting spoil

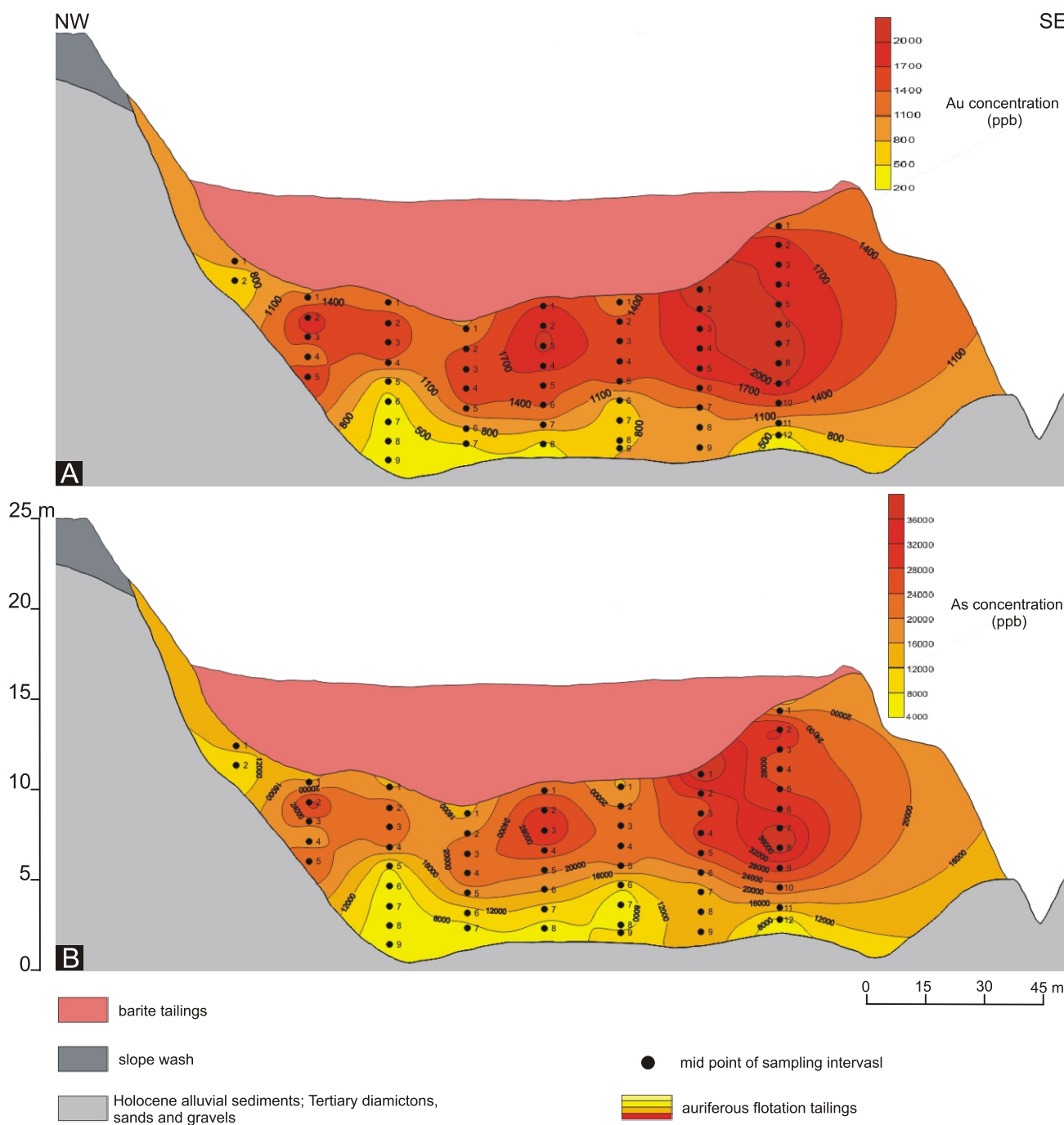


Fig. 4. Schematic cross-section through the flotation dump C showing the location of core samples studied and concentrations of Au (A) and As (B) in the section

The location of the dump is shown in [Figure 2](#)

by amalgamation, carried out in the first half of the 19th century, were unsuccessful. The platner method was used to extract gold from 1850. This method, with modifications, was used until the 1950s. According to ATL data, gold contents in roasting spoil untreated for this metal ranged 19.2 to 34.8 ppm Au, averaging (arithmetic mean) 27.6 ppm Au, standard deviation $s = 3.68$ ($n = 36$). Gold contents in roasting spoil previously treated for gold ranged from 2.0–12.0 ppm, averaging 3.9 ppm Au, standard deviation $s = 2.36$ ($n = 36$). Maximum gold concentration in “post-sulfide” water (liquid waste after

chlorination of roasts in the Platter method) was 0.46 mg/l. Chemically, roasting spoil is dominated by iron oxides (~60 wt.%) and silica, along with an average of 1.0 wt.% As. The samples were analysed for Au and As only.

After closure of the smelter in 1962, several tons of roasting spoil previously treated for gold were covered by a range of other waste materials and are currently a part of younger building embankments. The main arsenic roasting spoil heap is located in the Trująca Valley, near the post-flotation tailing dump C ([Fig. 2](#)). This type of waste was not analyzed in this study.

CONCLUSIONS

The higher gold content in the flotation tailings compared with a previous estimate (Wojciechowski, 1998) increases their gold content from 1200 to 1380 kg.

Results of the current sampling of mined rock spoil indicate close correlation between Au, As and the presence of ore and mineralized rocks from the ore zone.

The sampling also confirms erratic gold and arsenic concentration in the analyzed material. Nevertheless a gold content ranging from 0.16 to 3.80 ppm Au, averaging 1.4 ppm Au ($n = 3$), is somewhat higher than previously estimated at around 1.3 ppm (Muszer and Łuszczkiewicz, 1997). This allows increase of the remaining resource of the mining waste heaps to about 990 kg Au.

Chemical analyses of smelter slag indicated low Au concentrations with contents ranging from 0.2 to 0.4 ppm.

As expected, the highest As concentration (52 100 ppm) was found in the mined rock spoils (waste heaps). Slag material and tailings also had high concentrations of As, in the range of 9 650–25 700 ppm.

A relatively high gravity-recoverable gold value during gravity enrichment of the flotation tailings and mined rock spoil (Muszer and Łuszczkiewicz, *op. cit.*) indicates good gravity amenability and may encourage further attempts at gold extraction. Extraction of gold through this process may be profitable under the prevailing economic conditions.

Acknowledgements. We are very grateful to S. Speczik and an anonymous reviewer for critical revision of the manuscript and for very valuable comments.

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